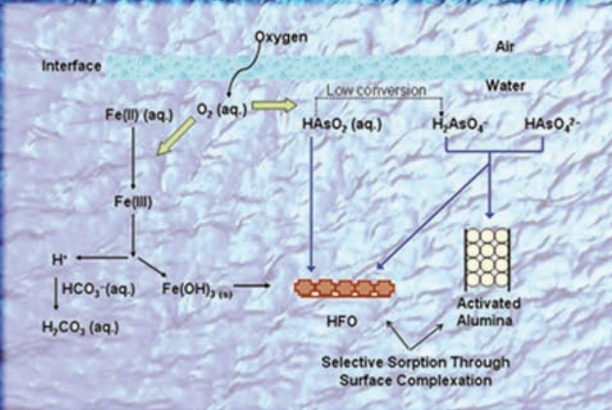

ARSENIC CONTAMINATION OF GROUNDWATER

Mechanism, Analysis, and Remediation

Edited by
SATINDER AHUJA

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Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

Library of Congress Cataloging-in-Publication Data:

Ahuja, Satinder, 1933–
Arsenic contamination of groundwater : mechanism, analysis, and remediation / Satinder Ahuja.
p. cm.
Includes index.
ISBN 978-0-470-14447-3 (cloth)
1. Groundwater pollution. 2. Arsenic—Environmental aspects. I. Title.
TD427.A77A48 2008
628.1′6—dc22

2008021429

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

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PREFACE

Arsenic contamination has been found in regional water supplies in Argentina, Bangladesh, Cambodia, Canada, Chile, China, Ghana, Hungary, India, Laos, Mexico, Mongolia, Nepal, Pakistan, Poland, Taiwan, Thailand, the UK, the United States, and Vietnam. Even in advanced countries such as the United States, nearly 10% of groundwater resources exceed arsenic levels of 10 ppb. Recognizing the fact that inorganic arsenic is a documented human carcinogen, the World Health Organization (WHO) set a standard at no more than 10 μg/L (or 10 parts per billion) of arsenic (As) in drinking water in 1993. This standard was finally adopted by the United States in 2006; however, 50 μg/L (50 ppb or 0.05 mg/L) is the maximum contamination level (MCL) considered acceptable in Bangladesh. The population at risk approaches 100 million in Bangladesh at the MCL set by the WHO. Some experts estimate that as many as 500 million people could be affected by this problem worldwide.

Groundwater can be contaminated with arsenic from a variety of sources, such as pesticides, wood preservatives, glass manufacture, and other miscellaneous uses of arsenic. These sources can be monitored and controlled. However, the contamination from naturally occurring arsenic in the ground is difficult to control. The worst case of this problem was discovered in Bangladesh, where a large number of shallow (10 to 40 m) tube wells installed in the 1970s were found in the 1980s to be contaminated with arsenic. It is estimated that as many as 100 million people in Bangladesh may be exposed to high levels of arsenic, exceeding the WHO guidelines. It should be noted that these guidelines do not consider different species of arsenic, even though it is already well established that the toxicity of arsenic can vary enormously with its speciation. The effects of the oxidation state on chronic toxicity are confounded by the redox conversion of As(III) and As(V) within human cells and tissues. Clinical symptoms of arsenicosis may take about six months to two years or more to appear, depending on the quantity of arsenic ingested and also on the nutritional status and immunity level of the individual. Arsenic ingestion causes various effects on the skin, such as dark spots on the chest, back, and limbs; and enlargement of the liver, kidneys, and spleen. Later, patients may develop nephropathy, hepatopathy, gangrene, or cancers of the skin, lung, or bladder.

The book has been planned to improve our understanding of the horrific problem of groundwater contamination with arsenic and offers some meaningful solutions. The focus is primarily on groundwater pollution from natural sources, and the nature and scope of the problem is discussed in the first two chapters. Chapter 1 provides a broad overview of the problem. Accumulation of arsenic in various crops that are irrigated with arsenic-rich water and its consequences on dietary intake are covered in Chapter 2. Various remedial measures to combat arsenic accumulation in soils and crops are also discussed.

In West Bengal, India and in Bangladesh, aquifer sediments containing arsenic are derived from weathered materials from the Himalayas. Arsenic typically occurs at concentrations of 2 to 100 ppm in these sediments, much of it sorbed onto a variety of mineralogical hosts, including hydrated ferric oxides, phyllosilicates, and sulfides. The mechanism of arsenic release from these sediments has been a topic of intense debate, and both microbial and chemical processes have been invoked. The oxidation of arsenic-rich pyrite has been proposed as one possible mechanism. Other studies have suggested that reductive dissolution of arsenic-rich Fe(III) oxyhydroxides deeper in the aquifer may lead to the release of arsenic into the groundwater. A large number of studies that have been conducted in Asia, the United States, and the United Kingdom to improve our understanding of the mechanism of groundwater contamination, covered in Chapters 3 to 6, favor the microbial processes.

Detection and quantification limits for arsenic down to ultratrace levels (below 1 ppm) are possible with inductively coupled plasma mass spectrometry (ICP-MS). However, the speciation of arsenic requires separations based on solvent extraction, chromatography, and selective hydride generation. High-performance liquid chromatography coupled with ICP-MS is currently the best technique available for determination of inorganic and organic species of arsenic; however, the cost of the instrumentation is prohibitive. For underdeveloped countries confronting this problem, reliable, low-cost instrumentation and reliable field test kits are desperately needed. To address this issue, various low-cost analytical methods and kits that can be used to monitor arsenic contamination in water are described in Chapters 7 and 8.

A large number of approaches have been investigated for removing arsenic from drinking water. The basic chemistry for these processes is discussed in Chapters 9 to 14. A number of remediation methods that utilize natural or relatively inexpensive materials to purify the water have been discussed. The devices that earned the first and second Grainger Challenge Prizes of $1 million and $200,000, respectively, from the National Academy of Engineering, Washington, DC, are described in this volume.

Finally, potential solutions to this devastating problem are provided in Chapter 15. Piped potable surface water should be given the desired priority; this will require total commitment from local governments and funding agencies. Other surface water options, such as rainwater harvesting, sand water filters, and dug wells, should be tapped as much as is reasonably possible. The next best option is deep tube wells. They should be installed properly such that surface contaminants cannot get into them. Furthermore, the water should be tested properly to assure that they do not contain other harmful contaminants. Arsenic removal systems can work for a family or for small communities; however, their reliability initially and over a period of time remains an issue. Other contaminants in water can affect their performance. The education and training of local scientists should be encouraged in the underdeveloped countries so that they can address these problems.

It is believed that this book will be of interest to numerous scientists working in the field of geochemistry, hydrology, analytical chemistry, environmental chemistry and engineering, and separation science and technology. Academic and regulatory personnel working in these fields, along with aid agencies (WHO, World Bank, UNICEF, etc.) and nongovernmental organizations are also likely to find a lot of significant information of interest to them. Furthermore, it is anticipated that this book will encourage scientists, environmentalists, engineers, and other well-wishers to rise to the occasion and explore the interesting science involved in the mechanism of arsenic contamination, develop low-priced instrumentation for analysis, and find suitable methods for remediation of the problem.

Satinder Ahuja

January 5, 2008

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THE PROBLEM OF ARSENIC CONTAMINATION OF GROUNDWATER

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INTRODUCTION

Nature and Scope of the Problem

Groundwater contamination by arsenic (As) can occur from a variety of sources, such as pesticides, wood preservatives, glass manufacture, and miscellaneous other arsenic uses. These sources can be monitored and controlled. However, this is not the case with naturally occurring arsenic. The natural content of As in soil is mostly in a range below 10 mg/kg; however, it can cause major havoc when it gets into groundwater. The worst case of this problem was discovered in Bangladesh, where a large number of shallow tube wells (10 to 40 m) installed in the 1970s were found in the 1980s to be contaminated with arsenic [1]. Arsenic screening of 4.73 million tube wells showed 1.29 million wells to be above the 50-μg/L level, the acceptable limit in Bangladesh. Since the estimated total number of tube wells in Bangladesh is 8.6 million, it may be concluded that more than 2 million wells in Bangladesh are likely to be contaminated. It has been estimated that as many as 100 million people in Bangladesh are exposed to high levels of arsenic, exceeding the World Health Organization (WHO) standard of 10 μg/L, or 10 ppb. The maximum contaminant level (MCL) of 10 μg/L for drinking water has been approved by many countries in the world and has been enforced since the beginning of 2006 in the United States. It should be mentioned that the guidelines do not consider different arsenic species, even though it is

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already well established that the toxicity of arsenic can vary enormously with its speciation (see the discussion below).

Skin lesions and cancers related to arsenic were rare and ignored until new evidence emerged from Taiwan in 1977. The serious health effects of arsenic exposure, including lung, liver, and bladder cancer, were confirmed shortly thereafter by studies of exposed populations in Argentina, Chile, and China. In 1984, K. C. Saha and colleagues at the School of Tropical Medicine in Kolkata, India, first attributed lesions observed on the skin of villagers in the state of West Bengal in India to the elevated arsenic content of groundwater drawn from shallow tube wells. As noted in the Preface, the countries affected by elevated arsenic concentrations in groundwater include Argentina, Bangladesh, Cambodia, Canada, Chile, China, Ghana, Hungary, India, Laos, Mexico, Mongolia, Nepal, Pakistan, Poland, Taiwan, Thailand, the UK, the United States, and Vietnam. Figure 1 shows groundwater contamination in the United States; over 31,000 samples analyzed over an almost 30-year period revealed that a large number of states are affected by it. Of various countries affected by this contamination, Bangladesh (see Figure 1 in Chapter 2) and West Bengal are experiencing the most serious groundwater arsenic problem, and the situation in Bangladesh has been described as "the worst mass poisoning in human history." In addition to consumption through drinking water, arsenic can also be taken up via the food chain. Direct consumption of rice irrigated with arsenic-rich waters is a significant source of arsenic exposure in areas such as Bangladesh and other countries where rice is the staple food and provides the main caloric intake.

Arsenic is a semimetal or metalloid that is stable in several oxidation states (−III, 0, +III, +V), but the +III and +V states are the most common in natural systems. Arsenic is a natural constituent of the Earth's crust and ranks twentieth in abundance in relation to other elements. Table 1 shows arsenic concentrations in various environmental media. Arsine(−III), a compound with extremely high toxicity, can be formed under high reducing conditions, but its occurrence in gases emanating from anaerobic environments is relatively rare. Arsenic is a well-known poison with a lethal dose in humans of about 125 mg. Most ingested arsenic is excreted from the body through urine, feces, skin, hair, nails, and breath. In cases of excessive intake, some arsenic is deposited in tissues, causing the inhibition of cellular enzyme activities. The relative toxicity of arsenic depends mainly on its chemical form and is dictated in part by the valence state. Trivalent arsenic has a high affinity for thiol groups, as it readily forms kinetically stable bonds to sulfur. Thus, reaction with As(III) induces enzyme inactivation, as thiol groups are important to the functions of many enzymes. Arsenic affects the respiratory system by binding to the vicinal thiols in pyruvate dehydrogenase and 2-oxoglutarate dehydrogenase, and it has also been found to affect the function of glucocorticoid receptors. Pentavalent arsenic has a poor affinity toward thiol groups, resulting in more rapid excretion from the body. However, it is a molecular analog of phosphate and can uncouple mitochondrial oxidative phosphorylation, resulting in failure of the energy metabolism system. The effects

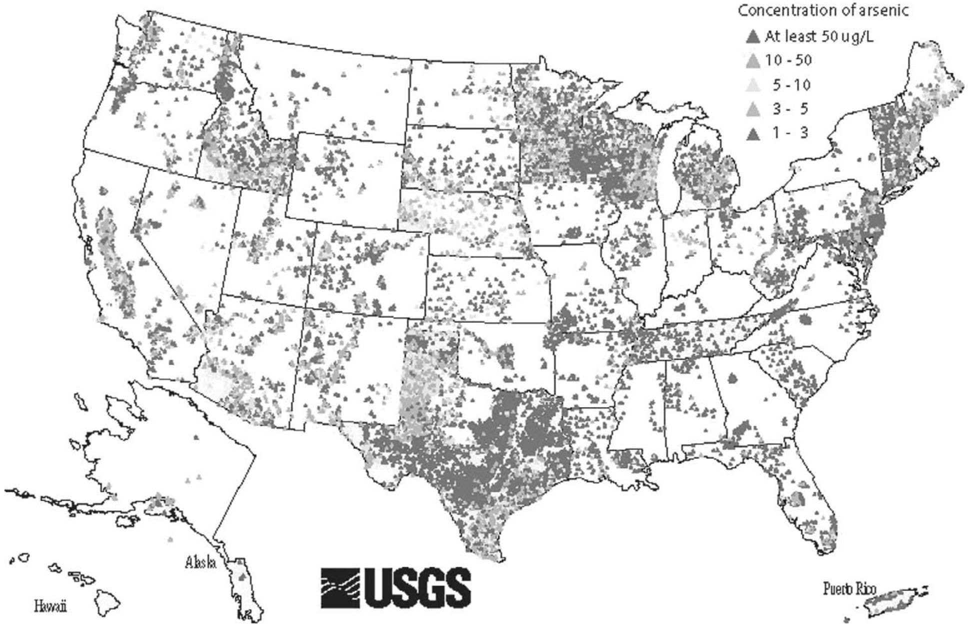

Figure 1 Arsenic concentration in groundwater in the United States. (*See insert for color representation of figure.*)

TABLE 1 Arsenic Concentrations in Environmental Media

Environmental Medium	Arsenic Concentration Range
Air (ng/m^3)	1.5–53
Rain from unpolluted ocean air [μg/L (ppb)]	0.019
Rain from terrestrial air (μg/L)	0.46
Rivers (μg/L)	0.20–264
Lakes (μg/L)	0.38–1000
Groundwater (well) (μg/L)	1.0–1000
Seawater (μg/L)	0.15–6.0
Soil (mg/kg)	0.1–1000
Stream/river sediment (mg/kg)	5.0–4000
Lake sediment (mg/kg)	2.0–300
Igneous rock (mg/kg)	0.3–113
Metamorphic rock (mg/kg)	0.0–143
Sedimentary rock (mg/kg)	0.1–490

Source: Ref. 2.

of the oxidation state on chronic toxicity are confounded by the redox conversion of As(III) and As(V) within human cells and tissues. Methylated arsenicals such as monomethylarsonic acid (MMAA) and dimethyl arsenic (DMAA) are less harmful than inorganic arsenic compounds. Clinical symptoms of arsenicosis may take about six months to two years or more to appear, depending on the quantity of arsenic ingested and the nutritional status and immunity level of the person. Untreated arsenic poisoning results in several stages: for example, various effects on the skin with melanosis and keratosis; dark spots on the chest, back, limbs, and gums; and enlargement of the liver, kidneys, and spleen. Later, patients may develop nephropathy, hepatopathy, gangrene, or cancers of the skin, lung, or bladder.

Arsenicosis now seriously affects the health of many people in Bangladesh, India, China, Nepal, and a number of other countries worldwide. In the United States, nearly 10% of groundwater resources exceed the MCL. Arsenic toxicity has no known effective treatment, but drinking arsenic-free water can help arsenic-affected people at the preliminary stage of their illness rid themselves of the symptoms of arsenic toxicity. Hence, provision of arsenic-free water is urgently needed for mitigation of arsenic toxicity and the protection of the health and well-being of people living in acute arsenic problem areas in these countries.

A national policy and implementation plan for arsenic mitigation was developed in Bangladesh in 2004, along with protocols for installation of alternative water supply options, disposal of arsenic-rich sludge, diagnosis of arsenicosis cases, and water management. However, provision of alternative arsenic-safe water supplies has thus far reached approximately 4 million citizens, only 2.9% of the population of Bangladesh.

In this book we focus primarily on groundwater pollution resulting from natural sources. Until recently it was generally believed that arsenic is released in the soil as a result of weathering of arsenopyrite or other primary sulfide minerals. Currently, it is believed that arsenic pollution of groundwater is a by-product of the microbes that metabolize organic matter, a process that releases arsenic, iron, phosphate, bicarbonate, and other species to groundwater. The precise microbial ecology responsible for arsenic release is still not fully understood and is the subject of further investigation. In an attempt to improve our understanding of this horrific problem, this book has been planned to improve our understanding and to offer some meaningful solutions:

- Nature and scope of the problem (Chapters 1 and 2)
- Mechanism of groundwater contamination (Chapters 3 to 6)
- Low-cost analytical methods and testing kits (Chapters 7 and 8)
- Remediation methods (Chapters 9 to 14)
- Workable solutions (Chapter 15)

Fate of Arsenic in Irrigation Water and Its Potential Impact on the Food Chain

The observation that arsenic poisoning in the world's population is not consistent with the level of water intake has raised questions regarding possible pathways of arsenic transfer from groundwater to the human system. Even if an arsenic-safe drinking water supply could be ensured, the same groundwater will continue to be used for irrigation purposes, leaving a risk of soil accumulation of this toxic element and eventual exposure to the food chain through plant uptake and animal consumption. Studies on arsenic uptake by crops indicate that there is great potential for the transfer of groundwater arsenic to crops. Chapter 2 deals with the fate of arsenic in irrigation water and its potential impact on the food chain, particularly as it occurs in Bangladesh and similar environments. Contamination of the irrigation water by arsenic; the retention, release, distribution, and buildup of arsenic in soil, accumulation in various crops that are irrigated with arsenic-rich water, the result of arsenic accumulation in crops and its consequence on dietary intake, and possible remedial measures to combat arsenic accumulation in soils and crops are discussed.

Of the various crops and vegetables analyzed, green leafy vegetables were found to act as arsenic accumulators, with arum (kochu), gourd leaf, *Amaranthus*, and *ipomoea* (kalmi) topping the list. Arum, a green vegetable commonly grown and used in almost every part of Bangladesh, seems to be unique in that the concentration of arsenic can be high in every part of the plant. Arsenic in rice seems to vary widely. Speciation of arsenic in Bangladesh rice shows the presence of As(III), DMAV, and As(V); more than 80% of the arsenic recovered is in the inorganic form. It has been reported that more than 85% of the arsenic in rice is bioavailable, compared to only about 28% of arsenic in leafy vegetables. It is thus pertinent to assess the dietary load of arsenic from various food materials otherwise contaminated with arsenic. A person consuming 100 g [dry weight (DW)] of arum daily with an average arsenic content of 2.2 mg/kg, 600 g (DW) rice with an average arsenic content of 0.1 mg/kg, and 3 L of water with an average arsenic content of 0.1 mg/L would ingest 0.56 mg/day, which exceeds the threshold value calculated based on the U.S. Environmental Protection Agency (EPA) model.

MECHANISM OF ARSENIC CONTAMINATION OF WATER

Until recently it was generally believed that arsenic is released in the soil as a result of weathering of the arsenopyrite or other primary sulfide minerals. Important factors controlling this phenomenon are:

- Moisture (hydrolysis)
- pH
- Temperature
- Solubility
- Redox characteristics of the species
- Reactivity of the species with CO_2/H_2O

It has been reported that weathering of arsenopyrite in the presence of oxygen and water involves oxidation of S to $SO_4{}^{2-}$ and As(III) to As(V):

$$4FeAsS + 13O_2 + 6H_2O \leftrightarrow 4SO_4{}^{2-} + 4AsO_4{}^{3-} + 4Fe^{3+} + 12H^+ \qquad (1)$$

Although there are both natural and anthropogenic inputs of arsenic to the environment, elevated arsenic concentrations in groundwater are often due to naturally occurring arsenic deposits. Whereas the average abundance of arsenic in the Earth's crust is between 2 and 5 mg/kg, enrichment in igneous and sedimentary rocks, such as shale and coal deposits, is not uncommon. Arsenic-containing pyrite (FeS) is probably the most common mineral source of arsenic, although it is often found associated with more weathered phases. Mine tailings can contain substantial amounts of arsenic, and the weathering of these deposits can liberate arsenic into the surface water or groundwater, where numerous chemical and biological transformations can take place. Arsenic can also be released directly into the aquatic environment through geothermal water, such as hot springs. Anthropogenic sources of arsenic include pesticide application, coal fly ash, smelting slag, feed additives, semiconductor chips, and arsenic-treated wood, which can cause local water contamination.

In Bangladesh and West Bengal, India, where the problem has received the most attention, the aquifer sediments are derived from weathered materials from the Himalayas. Arsenic typically occurs at concentrations of 2 to 100 ppm in these sediments, much of it sorbed onto a variety of mineralogical hosts, including hydrated ferric oxides, phyllosilicates, and sulfides. The mechanism of arsenic release from these sediments has been a topic of intense debate, and both microbial and chemical processes have been invoked. The oxidation of arsenic-rich pyrite has been proposed as one possible mechanism. Other studies have suggested that reductive dissolution of arsenic-rich Fe(III) oxyhydroxides deeper in the aquifer may lead to the release of arsenic into the groundwater. Additional factors that may add further complications to potential arsenic-release mechanisms from sediments include the predicted mobilization of sorbed arsenic by phosphate generated from the intensive use of fertilizers, by carbonate produced via microbial metabolism, or by changes in the sorptive capacity of ferric oxyhydroxides.

A large number of experts from various countries, including Bangladesh and India, who participated in a workshop in Dhaka and in symposia in Atlanta, Georgia [3–5], generally agreed that sedimentary arsenic is being carried downstream to Bangladesh by the Ganges–Padma–Meghna river system. Bacteria have been implicated in the desorption and dissolution of arsenic in the anaerobic, reducing environment in the subsoil. The results from a study conducted in Araihazar, Bangladesh indicate that the accumulation of arsenic in groundwater and sediment release rate in the uppermost 20 m of the Holocene aquifer appear to be fairly constant within a range of favorable geochemical conditions. This suggests that the groundwater flow regime controls much of the spatial variability of dissolved arsenic concentrations in shallow aquifers; however, this needs to be tested elsewhere in Bangladesh.

Role of Microbes in the Geochemical Behavior of Arsenic in Groundwater Systems

In Chapter 3 a brief review of high arsenic concentrations in the groundwater and proposed mechanisms for the release of arsenic into groundwater systems is provided, with particular significance to the possible role of metal-reducing bacteria in arsenic mobilization into the shallow aquifers of the Ganges delta. The bacterial effects on arsenic behavior in anoxic sediments and the various interactions between mineral, microbes, and arsenic, which have a significant impact on arsenic mobilization in groundwater systems, are also discussed.

Throughout evolution, microorganisms have developed the ability to survive in almost every environmental condition on Earth. Their metabolism depends on the availability of metal ions to catalyze energy-yielding reactions and synthetic reactions and on their aptitude to protect themselves from toxic amounts of metals by detoxification processes. Furthermore, microorganisms are capable of transforming a variety of elements as a result of (1) assimilatory processes in which an element is taken up into cell biomass, and (2) dissimilatory processes in which transformation results in energy generation or detoxification. Arsenic is called an "essential toxin" because it is required in trace amounts for growth and metabolism of certain microbes but is toxic at high concentrations. However, it is now evident that various types of microorganisms gain energy from this toxic element, and subsequently, these reactions have important environmental implications.

Bacterial reduction of As(V) has been recorded in anoxic sediments, where it proceeds via a dissimilatory process. Dedicated bacteria achieve anaerobic growth using arsenate as a respiratory electron acceptor for the oxidation of organic substrates or H_2, forming arsenite quantitatively as the reduction product. The reaction is energetically favorable when coupled with the oxidation of organic matter, because arsenate is electrochemically positive; the As(V)/As(III) oxidation–reduction potential is +135 mV. To date, at least 19 species of organisms are known to respire arsenate anaerobically, and these have been isolated from freshwater sediments, estuaries, hot springs, soda lakes, and gold mines. They are not confined to any particular group of prokaryotes, and they are distributed throughout the bacterial domain. These microbes are collectively referred to as *dissimilatory arsenate-reducing prokaryotes* (DARPs), and there are other electron acceptors used by these organisms which are strain-specific, including elemental sulfur, selenate, nitrate, nitrite, fumarate, Fe(III), dimethyl sulfoxide, thiosulfate, and trimethyamine oxide. For example, *Sulfurospirillum barnesii* (formerly strain SES-3), a vibrio-shaped gram-negative bacterium isolated from a selenate-contaminated freshwater marsh in western Nevada, is capable of growing anaerobically using As(V) as the electron acceptor, and it can also support growth from the reduction of a variety of electron acceptors, including selenate, Fe(III), nitrate, fumarate, and thiosulfate. The gram-positive sulfate-reducing bacterium *Desulfotomaculum auripigmentum*, isolated from surface lake sediments in eastern Massachusetts, has been found to reduce both As(V) and sulfate. DARPs can oxidize a variety of organic and inorganic electron donors, including acetate, citrate, lactate, formate, pyruvate, butyrate, fumarate, malate, succinate, glucose, aromatic hydrogen, and sulfide. Two gram-positive anaerobic bacteria, *Bacillus arsenicoselenatis* and *B. selenitireducens* were also isolated from the anoxic, muds of Mono Lake, California. Both grew by dissimilatory reduction of As(V) to As(III), coupled with oxidation of lactate to acetate plus CO_2.

Detection of Dissimilatory Arsenate-Respiring Bacteria in North Carolina Groundwater

Dissimilatory arsenate-reducing bacteria (DARB) are considered to be highly involved in arsenic mobilization in anoxic environments. To determine their contribution to arsenic levels found in underground aquifers, DARB communities in two drinking water wells (labeled D and R) located in western North Carolina were examined by molecular detection methods and enrichment culture techniques (Chapter 4). The genes encoding arsenate respiratory reductase (*arrA*) were amplified with newly developed polymerase chain reaction (PCR) primers from the DNA extracted from groundwater samples and were used to examine the diversity of DARB communities. The enrichment cultures with groundwater samples were established to measure arsenate reduction activities. The *arrA* genes detected from both well waters were closely related to the gene found in *Geobacter uraniumreducens*. A higher diversity of the *arrA* genes was found in well R, where a higher amount of arsenic was found. In addition, higher arsenate-reducing activities were measured in the R well water. This might imply that more diverse DARB communities have higher reduction activities, which lead to higher levels of dissolved arsenic found in groundwater. Using molecular and microbial tools, this study demonstrates the significance of DARB in arsenic contamination in the North Carolina underground aquifers.

Biogeochemical Mechanisms of Arsenic Mobilization and Sequestration

Sediment diagenetic processes are the biogenic and abiotic changes that occur to alter the sediment during and after deposition (see Chapter 5). Sediment diagenesis involves chemical, physical, and biological processes, including (1) deposition, (2) diffusion, (3) reductive dissolution (and other redox changes), and (4) secondary mineral precipitation. Diagenesis is driven primarily by the mineralization of organic carbon and the subsequent changes in redox potential with depth. As the sediments become more reducing, the redox equilibrium of various chemical species in the sediment shifts. However, it is important to recognize that the kinetics of these reactions is variable and sensitive to environmental parameters such as microbial activity. Thus, it is common to observe As(III) and As(V) or Fe(III) and Fe(II) co-occurring under a variety of redox conditions because of kinetic factors.

Reductive Fe(III) oxide dissolution is controlled by a complex interplay of many different parameters, such as pH, redox state, mineralogy, biological activity, and solution chemistry. Biologically mediated reduction depends strongly on the bacterial consortia present in the sediments, as well as substrate availability (e.g., organic carbon) and Fe oxide crystallinity. The rate of dissolution can, in turn, affect the mineral transformation products, which have the potential to sequester arsenic in more crystalline lattice structures, or the release of arsenic to pore waters as surface binding sites are lost.

A case study illustrates how arsenic partitioning between the solid and dissolved phases can be affected simultaneously by arsenic redox cycling, sediment diagenesis, and pore water composition. Ultimately, the mobility of arsenic in surface and groundwater systems is determined by (1) the arsenic redox state, (2) associations with the solid phase, (3) transformation of the solid phase during diagenesis, and (4) pore water composition, which can also change as a result of diagenetic processes. Many of these parameters are driven by microbial processes. This interplay of biogeochemical mechanisms makes understanding the processes responsible for arsenic mobilization in the environment inevitably complex.

Geomicrobiology of Iron and Arsenic in Anoxic Sediments

Microbially mediated reduction of assemblages comprising arsenic sorbed to ferric oxyhydroxides is gaining consensus as the dominant mechanism for the mobilization of arsenic into groundwater. For example, a recent microcosm-based study provided the first direct evidence for the role of indigenous metal-reducing bacteria in the formation of toxic mobile As(III) in sediments from the Ganges delta (see Chapter 6). This study showed that the addition of acetate to anaerobic sediments, as a proxy for organic matter and a potential electron donor for metal reduction, resulted in stimulation of microbial reduction of Fe(III), followed by As(V) reduction and the release of As(III). Microbial communities responsible for metal reduction and As(III) mobilization in the stimulated anaerobic sediment were analyzed using molecular (PCR) and cultivation-dependent techniques. Both approaches confirmed an increase in numbers of metal-reducing bacteria, principally *Geobacter* species. However, subsequent studies have suggested that most *Geobacter* strains in culture do not possess the *arrA* genes required to support the reduction of sorbed As(V) and mobilization of As(III). Indeed, in strains lacking the biochemical machinery for As(V) reduction, Fe(II) minerals formed during respiration on Fe(III) have proved to be potent sorbants for arsenic present in the microbial cultures, preventing mobilization of arsenic during active iron reduction. However, the genomes of at least two *Geobacter* species (*G. unraniumreducens* and *G. lovleyi*) do contain *arrA genes*, and interestingly, genes affiliated with the *G. unraniumreducens* and *G. lovleyi arrA* gene sequences have been identified recently in Cambodian sediments stimulated for iron and arsenate reduction by heavy (^{13}C–labeled) acetate using a stable isotope-probing technique. Indeed, the type strain of *G. unraniumreducens* has recently been shown to reduce soluble and sorbed As(V), resulting in mobilization of As(III) in the latter case. Thus, some *Geobacter* species may play a role in arsenate release from sediments. However, other well-known arsenate-reducing bacteria, including *Sulfurospirillum* species, have also been detected in ^{13}C–amended Cambodian sediments and hot spots associated with arsenic release in sediments from West Bengal. Although the precise mechanism of arsenic mobilization in Southeast Asian aquifers remains to be identified, the role of As(V)-respiring bacteria in the process is gaining support. Indeed, recent studies with *Shewanella* sp. ANA-3 and sediment collected from the Haiwee Reservoir (Olancha, California) have suggested that such processes could be widespread, but not necessarily driven by As(V) reduction, following exhaustion of all bioavailable Fe(III). In this study, arsenate reduction started before Fe(III) reduction and ceased after 40 to 60 hours. During part of the experiment, arsenate and Fe(III) were reduced simultaneously.

ANALYTICAL METHODS

It is not difficult to determine arsenic at 10 ppb or an even lower level in water. A number of methods can be used for determining arsenic in water at the ppb level:

- Flame atomic absorption spectrometry
- Graphite furnace atomic absorption spectrometry

- Inductively coupled plasma-mass spectrometry
- Atomic fluorescence spectrometry
- Neutron activation analysis
- Differential pulse polarography

Very low detection limits for arsenic down to 0.0006 μg/L can be obtained with inductively coupled plasma mass spectrometry (ICP-MS). The speciation of arsenic requires separations based on solvent extraction, chromatography, and selective hydride generation. High-performance liquid chromatography (HPLC) coupled with ICP-MS is currently the best technique available for the determination of inorganic and organic species of arsenic; however, the cost of the instrumentation is prohibitive. For underdeveloped countries confronting this problem, the development of reliable, low-cost instrumentation and reliable field test kits would be very desirable (see the discussion below).

Development of Low-Cost Measurement Technologies for On-Site Arsenic Determination

Hydride generation (HG) has been known for many decades and has the advantage that arsenic may be determined by a relatively inexpensive atomic absorption spectrometer or an even cheaper atomic fluorescence spectrometer (AFS) at single-digit μg/L concentrations (see Chapter 7). Its generation is prone to inference from other matrix components, so every "new" matrix can represent a new analytical problem. In this technique, arsenic compounds are converted to volatile derivatives by reaction with a hydride transfer reagent, usually tetrahydroborate III (also known as borohydride), whose sodium and potassium salts are relatively stable in aqueous alkalis. HG can be quite effective as an interface between high-performance liquid chromatographic separation and element-specific detection. In fact, it is possible to get the same performance from HG-AFS as from ICP-MS. Therefore, as the former detector represents a significant saving in both capital and operational costs over the latter, there is considerable interest in this "niche" use of AFS. The disadvantage of any method in which an atomic spectrometry instrument is involved is that the procedure has to be carried out in a laboratory setting in which appropriate supplies of electricity, gas, power, and sometimes cooling water are available.

Accurate, fast measurement of arsenic in the field remains a technical challenge. Even though the technological advances in a variety of instruments have met with varying success, the central goal of developing field assays that reliably and reproducibly quantify arsenic has not yet been achieved. The exquisite selectivity of the hydride generation process is very tempting as an integral pretreatment stage, but always comes with the associated issues of safety unless all of the arsine generated ends up bound to a solid surface somewhere in the apparatus. However, it will be quite some time before the Gutzeit method is obsolete.

There are clearly many prospects for the further development of chemical measurement technologies for the determination of arsenic in environmental waters down to single-digit μg/L concentrations. In this scenario, techniques such as atomic fluorescence spectrometry are good candidates for such a "lab" facility. The quartz crystal microbalance, a device whose interface is more robust than an electrode for stripping voltammetry, also holds promise, especially as the measurement incorporates an inherent preconcentration step (the accumulation of arsenic at the surface of the oscillating crystal).

Reliability of Test Kits

In a comprehensive study (see Chapter 8) using three field kits (Merckoquant, NIPSOM, and GPL), more than 290 wells were tested against reference methods. At arsenic concentrations below 50 μg/L, the false positive results were acceptably low: 9.2% (NIPSOM) and 6.5% (GPL). In the range between 50 and 100 μg/L, false positives increased to 35% and 18%, respectively. As a result, using the NIPSOM kit, 33% of the unsafe tube wells were colored green (i.e., safe). The false negative results reported between 50 and 100 μg/L were 57% and 68%, which means that up to two-thirds of the wells painted red were safe. Above 100 μg/L, the percentage of false negatives was still considerable (26% for NIPSOM and 17% for GPL). The mislabeling of 45% of the wells is unacceptable but cannot be explained easily by possible variability of arsenic concentration, a lack of quality assurance/quality control, or operator error. This study clearly demonstrates the need for a stringent testing procedure to generate reliable data and the need to develop more reliable analytical systems that would make costly retesting unnecessary. Emphasis should be given to new developments of electrochemical methods and their potential to form the basis of a "new generation" of field kits that satisfy all requirements for reliable arsenic detection in the field.

Two main approaches are used at present for the on-site analysis of arsenic. By far, the most widely used systems are those based on a colorimetric principle. These systems require few reagents, are supposedly easy to use, and give results that should be straightforward. The second approach is based on electroanalysis and on the possibility of reducing or oxidizing arsenic species. Although more difficult to operate, the detection limits obtained with such devices can be much lower than those obtained by colorimetry. The EPA supports an environmental technology verification (ETV) program to facilitate the implementation of innovative new technologies for environmental monitoring. The ETV works in partnership with recognized standards and testing organizations, with vendors and developers, and with stakeholders for potential buyers. The ETV tested several commercially available kits in July 2002 and added four more in August 2003 under field conditions with trained and untrained operators [6]. An assessment of the new generation of field testing kits is provided in Table 2 of Chapter 8.

In contrast to colorimetric field tests kits, which are selective for arsenic only, voltammetric systems can be tuned to detect other metals simultaneously. For example, at a gold electrode, metals such as Cu, Hg, Zn, Mn, or Sb can be detected along with arsenic. For instance, antimony has been shown to modulate the toxicity of arsenic [7] and was found in samples containing high levels of arsenic [8]; 35% of the arsenic-contaminated groundwater samples from Bangladesh also contained levels of manganese above the WHO value of 500 ppb [9]. Knowledge of the concentrations of other metals brings insights into the toxicity of the sample and is the basis for efficient removal technologies. Field systems should therefore be as selective as possible.

The performance of field testing kits for arsenic is unsatisfactory overall, although the new generation of kits have become much more reliable. The report of false negative and false positive results of over 30% is not unusual, although the latest seem encouraging, and more reliable measurements can be done in the field. However, these studies were using a water standard of 50 μg/L as a decisive concentration. If the new WHO guideline of 10 μg/L is adopted as a decision-making criterion, the sensitivity of most arsenic testing kits based on colorimetric methods will not be sufficient. This is particularly the case for kits that are battery powered and also for electronic systems. Although some reports surprisingly suggest that in some cases untrained operators produce more reliable results, the training aspect of the operator should not be underestimated. Voltammetric sensors should be ideally suited for on-site analysis of arsenic. However, the need for a chemical reduction step seems to be the major problem, limiting potential applications both in the field and in sample throughput. Systems using voltammetric reduction of arsenate are probably easier to implement for on-site analysis, although the SafeGuard system developed by TraceDetect Inc. has remarkable performance rates. Potential problems in the voltammetric determination of arsenic are numerous because of the sample matrix effect. To be highly efficient for on-site analysis with unqualified operators, these voltammetric systems should therefore be as sensitive as possible to allow dilution of the original sample. For such purposes, the use of microelectrodes is preferred. In addition, specifically designed software and hardware are required to guide the user through the simple actions required to make the analytical system more accessible to unqualified operators. Although promising results have been obtained using voltammetric systems, more work is needed to develop methods toward these arsenic species. The most promising development in direct arsenic speciation is by electrochemical detectors, but they still have to be tested in the field.

REMEDIATION OF ARSENIC-CONTAMINATED WATER

A large number of approaches have been investigated for removing arsenic from drinking water. Several useful reviews of the techniques for removing arsenic from water supplies have been published [10–13]. Existing and emerging arsenic removal technologies include:

- Coagulation with ferric chloride or alum
- Sorption on activated alumina

- Sorption on iron oxide–coated sand particles
- Granulated iron oxide particles
- Polymeric ligand exchange
- Nanomagnetite particles
- Sand with zero-valent iron
- Hybrid cation-exchange resins
- Hybrid anion-exchange resins
- Polymeric anion exchange
- Reverse osmosis

Reverse osmosis is essentially a nonselective physical process for excluding ions with a semipermeable membrane The basic chemistry for the rest of the processes includes either or both of the following interactions: (1) As(V) oxyanions are negatively charged in the near-neutral pH range and therefore can undergo coulombic or ion-exchange types of interactions; and (2) As(V) and As(III) species, being fairly strong ligands or Lewis bases, are capable of donating lone pairs of electrons. They participate in Lewis acid–base interactions and often show high sorption affinity toward solid surfaces that have Lewis acid properties.

Flocculation of Arsenic with the Mucilage of *Opuntia ficus-indica*

The design of a benign and sustainable water purification technology based on natural products is gaining interest because of the inherently renewable character, low cost, and nontoxicity. The use of mucilage, derived from nopal cactus, *Opuntia ficus-indica*, provides a reliable technology to treat drinking water supplies that have been contaminated with particulates and toxic metals (Chapter 9). The long-term goal is to deploy the optimized design in rural and underdeveloped communities in Mexico, where drinking water supplies are contaminated with toxic metals, the nopal cactus is readily available and amenable to sustainable agriculture, and where access to conventional technologies is limited. This work shows how cactus mucilage is extracted from the nopal cactus and used as a flocculant to remove particulates and heavy metals from drinking water. Mucilage efficiency to reduce arsenic and particulates from drinking water has been determined by light scattering, jar tests, atomic absorption, and hydride generation–atomic fluorescence spectroscopy. Comparisons against a synthetic flocculant [i.e., aluminum sulfate, alum, $Al_2(SO_4)_3$] show the high efficiency of that cactus mucilage to separate particulates and arsenic from drinking water. These flocculation studies prove that mucilage is a much faster flocculating agent than alum, with the efficiency increasing with mucilage concentration. Jar tests reveal that lower concentrations of mucilage provide the optimal effectiveness for supernatant clarity, an important factor in determining the potability of water. This work has established a systematic approach for providing clean water that can be expanded to communities of other underdeveloped or even developed countries with similar pollution problems. This natural material has shown the potential for development of a worldwide technology that is innovative, environmentally benign, and cost-effective. The mucilage from *O. ficus-indica* is a better flocculant than aluminum sulfate in all three of its extracted forms (GE, NE, and CE) and could be used by low-income Latin American communities for settling suspended solids in turbid drinking water–storage containers. The use of mucilage is also appropriate for removal of total arsenic in contaminated drinking water and owes its flocculation abilities to its chemical structure, consisting of C–O functionality. Further investigation is required to review the mucilage-selective removal of arsenic based on speciation as well as the feasibility of implementing this technology in a distributable or easy-to-assemble filter form for small-scale household removal. The possibility of introducing an indigenous material as an improver of quality of life and health to concerned residents is attractive from a cultural sensitivity and sustainability standpoint.

Arsenic Removal by Adsorptive Media

Rapid, inexpensive tests are needed to predict the arsenic adsorption capacity of adsorptive media to help communities select the most appropriate technology for meeting compliance with the new arsenic MCL, 10 μg/L. A main goal of this project is to evaluate alternative methods to predict pilot- and full-scale performance from laboratory studies. Prediction of arsenic removal from a packed column is very challenging (Chapter 10). Three innovative adsorptive media that have the potential to reduce the costs of arsenic removal from drinking water were selected. The arsenic removal performance of these different adsorptive media under constant ambient flow conditions was compared using a combination of static (batch) and dynamic flow tests. These included batch sorption isotherm and kinetic sorption studies, rapid small-scale column tests (RSSCTs), and a pilot test at a domestic water supply well. The media studied included a granular ferric oxyhyroxide (E33), a granular titanium oxyhydroxide (MetSorb), and an ion-exchange resin impregnated with iron oxide nanoparticles (ArsenX). They exhibited contrasting physical and chemical properties. The E33 media gave the best performance, based on volume of water treated until breakthrough at the arsenic MCL (10 ppb) and full capacity at media exhaustion. The relative arsenic sorption capacity of the three media could be predicted from batch sorption studies and RSSCT column results. The Klinkenberg analytical solution gave good semiquantitative descriptions of arsenic breakthrough curves and pore water profiles in the pilot tests, based on parameters obtained in the RSSCT studies. The model is potentially useful for scaling up adsorptive media performance to any reasonable size from the data obtained in laboratory studies.

Arsenic is removed in fixed-bed filtration via adsorption, the physical and chemical attachment of the adsorbate (arsenic) to the surface of the adsorbent media grains. The removal capacity and effectiveness of the arsenic removal media are dependent on a number of physical and chemical factors. Chemical factors include the strength of the chemical bond between the arsenic and the adsorbent, the kinetics of the adsorption reaction, the concentrations of ions competing for sorption sites, the concentration of arsenic in the feed water, and the pH of the feed water. Physical (transport) factors include the effective surface area, which is a function of the accessibility of the porosity of the media grains; steric factors affecting the accessibility of the pore sites by arsenic ions; and the time available for arsenic ions to migrate to pore sites. The latter property is related to the flow rate of the feed water that conveys the arsenic into the bed of adsorbent media. In this study the consistency among capacity estimates made by batch and dynamic methods are compared, and their relevance to full-scale performance is evaluated.

Remediation of Bangladesh Drinking Water Using Iron Oxide–Coated Coal Ash

In Chapter 11 a process is described for removing arsenic from water based on using fine particles of coal bottom ash that have been coated with iron oxide. This technique is called *ARUBA* (arsenic removal using bottom ash). The bottom ash is the ash left at the bottom of a coal-fired boiler after the combustible matter in coal has been burned off. A study successfully demonstrated the ability of this technique to reduce arsenic concentrations to below the Bangladesh standard of 50 ppb in six of the eight samples of Bangladesh groundwater collected. The water was collected from two geographically distinct areas of Bangladesh and across six different villages. For water samples from the two remaining wells, numbers 2 and 8, where the final concentration measured with ICP-MS was above 50 ppb, a larger dose of coal bottom ash coated with iron oxide would have certainly lowered the concentration to below 50 ppb. The study also demonstrated the feasibility in some samples of reducing arsenic concentrations in the water to below the WHO standard of 10 ppb.

Development of a Simple Arsenic Filter for Groundwater in Bangladesh

Chapter 12 covers the development and deployment of a water filter called SONO filter based on especially made composite iron matrix for the purification of groundwater to safe potable water. The filtered water meets WHO and Bangladesh standards, has no breakthrough, and works without any chemical treatment (before or after), without regeneration, and without producing toxic waste. It costs about $40, lasts for five years, and produces 20 to 30 L/h for the daily drinking and cooking needs of one to two families. Approved by the Bangladesh government, about 35,000 SONO filters are deployed all over Bangladesh and continue to provide more than 1 billion liters of safe drinking water. This innovation was also recognized by the National Academy of Engineering's Grainger Challenge Prize for Sustainability, with the highest award for its affordability, reliability, ease of maintenance, social acceptability, and environmental friendliness. The device meets or exceeds the local government's guidelines for arsenic removal. The filter is designed with Bangladesh village people in mind. It does not require any special maintenance other than replacement of the upper sand layers when the apparent flow rate decreases. Experiments show that the flow rate may decrease 20 to 30% per year if groundwater has a high iron content (>5 mg/L) because of the formation and deposition of natural HFO in sand layers. The sand layers (about an inch thick) can be removed, washed, and reused, or replaced with new sand. The presence of soluble iron and the formation of HFO (hydrous ferric oxide) precipitate are also common problems with other filtration technologies.

The use of tube wells to extract groundwater was initiated to provide drinking surface water that is not contaminated with pathogenic bacteria. However, pathogenic bacteria can still be found in drinking water because of unhygienic handling practices, and also in many shallow tube wells, possibly located near unsanitary latrines and ponds. To investigate the issue of bacterial growth in these filters, a Bangladesh nongovernmental organization called the Village Education Resource Center (VERC) recently tested 193 SONO filters at 61 locations in one of the remotest fields, Sitakundu in Bangladesh. The report shows that of the 264 tests, 248 were found to have 0 ttc (thermotolerance coliforms)/100 mL and 16 had 2 ttc/100 mL. Pouring 5 L of hot water in each bucket every month has been shown to kill pathogenic bacteria and eliminate coliform bacteria. This protocol can be followed once a week in areas where coliform counts are high. There are no records of diarrhea or waterborne diseases from drinking SONO-filtered water, and it appears that the filtration system does not foster pathogenic bacteria on its own.

Except for basic training in hygiene, no special skill is required to maintain the filter. The maintenance process requires about 20 to 30 minutes. Because this filter has no breakthrough, the active medium does not require any processing, such as backwashing or chemical regeneration. The filter will produce potable water for at least five years (the time span of our continuing test results). The actual filter life span was determined by the life span of the six experimental filters running in the field. Except for manufacturing defects, mechanical damage due to mishandling, transportation, and natural disasters (flooding), none of the filters have shown MCL breakthrough to date. Presently, at $35 to $40 for five years (equivalent to one month's income of a village laborer in Bangladesh), SONO is one of the most affordable water filters in Bangladesh.

Community-Based Wellhead Arsenic Removal Units

In many remote villages in West Bengal, arsenic-contaminated groundwater remains the only feasible source of drinking water. Cost-effective arsenic removal technology is a minimum necessity to provide safe drinking water. The groundwater is otherwise free of other contaminants and safe for drinking. Over 150 wellhead arsenic removal units, containing activated alumina as the adsorbent, are currently being operated by local villagers in this state in India, which borders Bangladesh. The units are maintained and run by the beneficiaries. In regular operation the units require no chemical addition, pH adjustment, or electricity (Chapter 13). Each unit serves approximately 250 to 350 families living within a short distance of the unit, and the flow rate is modest, approximately 10 L/min.

Arsenite [As(III)] and arsenate [As(V)] from the groundwater are effectively removed to render it safe for drinking and cooking. Regenerability and durability of the adsorbent allows a low-cost, sustainable solution for the widespread arsenic poisoning in this area. After regeneration, the spent regenerants, containing high concentrations of arsenic, are converted to a small-volume sludge that is stored under oxidizing conditions, to prevent future arsenic leaching. This process offers a superior economic advantage with regard to treatment and management of dangerous treatment residuals compared to conventional adsorbent-based processes where regeneration and reuse are not practiced. With conventional processes, disposal of huge amounts of media in landfills leach out dangerous concentrations of arsenic. A global scheme for the overall process of arsenic removal, including the management of treatment residues, has been provided. Input to the process is groundwater contaminated with arsenic and caustic soda and acid for regeneration, whereas the outputs are only treated drinking water and neutralized brine solution. Thus, besides being most appropriate for rural sections of the affected area in terms of ease of use and economics, the technology also offers considerable ecological sustainability.

From the data for 150 running units, it is estimated that the total volume of water treated by a unit in one year, on average, is about 8000 bed volumes (i.e., 800,000 L), so the cost of water per 1000 L is equal to $0.85. The estimated amount of arsenic-safe water used for a family of six for drinking and cooking purposes in a month at the rate of 5 L per capita per day is 900 L. The water tariff for a family of six for one month is around $0.75, or 30 Indian rupees at the time of this writing. While regeneration helps reduce the volume of the sludge about 150-fold, reusability of the sorbent media helps decrease the cost of the treated water significantly.

Water Supply Technologies for Arsenic Mitigation

Development of water supply systems to avoid arsenic-contaminated water sources, and the removal of arsenic to acceptable levels, are two options for a safe water supply (Chapter 14). Totally arsenic-free water is not available in nature; hence the only workable option to avoid arsenic is to develop water supply systems based on sources that have very low rates of dissolved arsenic. Rainwater, well-aerated surface water, and groundwater in very shallow as well as deep aquifers are well-known arsenic-safe sources of water. Rainwater has very low arsenic levels, often undetectable by conventional detection methods and measurement techniques. The arsenic content of most surface water sources ranges from less than 1 μg/L to 2 μg/L. Very shallow groundwater replenished by rainwater or surface water and relatively old deep aquifers have arsenic contents within acceptable levels.

The technologies for producing drinking water using sources known to have a low arsenic content include:

- Treatment of surface water by slow sand filtration, conventional coagulation–sedimentation–filtration, and disinfection. Rivers, lakes, and ponds are the main sources of surface water, and the degree of treatment required varies with the level and type of impurities present in water.

- Dug wells/ring wells or very shallow tube wells to abstract low-arsenic groundwater from very shallow aquifers.
- Deep tube wells to collect arsenic-safe water from deep protected aquifers.
- A rainwater harvesting system (RWHS) to collect, store, and use rainwater before it joins the surface water and groundwater.

A wide range of technologies based on arsenic-safe water sources is available for the water supply at low cost, but the performance of the technologies varies widely, depending on the quality of raw water. Community participation in the operation and maintenance of small surface water–based technologies and RWHS is not encouraging. The performance of medium-size to large systems that can support a full-time operator is comparatively better. Tube well technologies are the preferred option for people in arsenic-affected areas, but tube wells are not always successful in producing arsenic-safe water at all locations.

Arsenic removal technologies have improved significantly during the last few years, but reliable, cost-effective, and sustainable treatment technologies are yet to be identified and developed further to meet requirements. All treatment technologies concentrate arsenic at some stage of treatment in different media. Large-scale use of an arsenic removal system may generate significant quantities of arsenic-rich treatment wastes, and indiscriminate disposal of these wastes may lead to environmental pollution. Safe disposal of arsenic-rich media is a concern that needs to be addressed.

Solutions Available for Providing Arsenic-Free Water

Regarding the mechanism of arsenic contamination, there is reasonable agreement within the scientific community that research should continue (Chapter 15). Economical and reliable analytical methods, including field kits, need to be developed to help solve this problem. The Implementation Plan for Arsenic Mitigation of Bangladesh issued in 2004 states that while the research to devise appropriate options continues, the arsenic mitigation programs must promote the following options: improved dug wells; surface water treatment, including pond sand filters and large-scale surface water treatment; deep hand tube wells, rainwater harvesting, arsenic removal technology, and piped water supply systems. In the implementation plan, preference is given to pond sand filters and improved dug wells while government's role in rainwater harvesting will be limited to promotional activities only. In case of arsenic removal technologies, the implementation plan recommends waiting until the issues relating to the safety of these technologies, in terms of chemical and biological water quality, along with issues relating to the disposal of liquid and solid wastes, are better understood.

Based on input from various participants in the Dhaka workshop [3] and the Atlanta symposia [5], the following recommendations appear to be logical for Bangladesh and the other Southeast Asian countries that are most severely affected by this problem. Piped surface water should be intermediate to long-term goals and should be given the desired priority. This will require total commitment from the local government and the funding agencies that deem this a desirable option. Along these lines, other surface water options, such as rainwater harvesting, sand water filters, and dug wells, should be tapped as much as is reasonably possible. The next best option is safe tube wells. More than likely they would be deep tube wells. It is important to assure that they are located properly and do not contain other contaminants that can add to the arsenic problem. Furthermore, they should be installed properly such that surface contaminants cannot get into them. The arsenic removal filtration systems can work on a small scale; however, their reliability initially or over a period of time remains an issue. Other contaminants in water can affect the systems' performance. Low-price reliable test kits are needed that can address this issue. There is a need to identify reliable filters that can be scaled up for larger communities. In this way, both maintenance and reliability issues can be addressed. The education and training of local scientists and technicians need to be encouraged so that the local people can address these problems themselves. There is a need for more analytical scientists, instrumentation, and testing laboratories. Consumers of contaminated water need to be better educated so they do not continue to drink contaminated water because of their reluctance to switch wells or to take other steps to purify water.

The use of some of these options depends on local conditions. It is important to remember that local scientists and others are the final arbiters as to what is best for a given area.

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FATE OF ARSENIC IN IRRIGATION WATER AND ITS POTENTIAL IMPACT ON THE FOOD CHAIN

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INTRODUCTION

Arsenic (As) is a potent killing agent not only through incidences of homicide but also through its invasion into human systems either through drinking water or through the food chain. Although the importance of arsenic as a slow killing agent is still recognized, its role in crippling a large population at a time has, surfaced during the last decade and a half when groundwater contamination by this element was identified in the deltaic region of Bengal, particularly in the Gangetic alluvium, including Bangladesh and West Bengal in India. It has been termed the world's biggest natural calamity in known human history. More than 35 million people in Bangladesh are exposed to arsenic contamination in drinking water exceeding the national standard of 50 μg/L, and an estimated 57 million people are at the risk of exposure to arsenic contamination exceeding the World Health Organization (WHO) guideline of 10 μg/L (BGS/DPHE, 2001). Similarly, about 44% of the total population in West Bengal is suffering from arsenic poisoning (Chandrashekharam, 2005). Arsenic contamination in the groundwater was reported in Bangladesh during the early 1990s. Extensive contamination there was confirmed in 1995, when, an additional survey showed the contamination of mostly shallow tube wells (STWs) across much of southern and central Bangladesh (Imamul Huq et al., 2006a). However, a few

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Edited by Satinder Ahuja

instances of deep tube well (DTW) contamination have also been reported. Data from Jessore showed that 87% of irrigation DTWs contained more than 0.05 mg As per liter (JAICA/AAN, 2004). On the other hand, surveys conducted with more than 6000 DTW samples of the six divisions of Bangladesh showed that all the samples comply with the Bangladesh standard, whereas, in terms of compliance with the WHO standard (0.01 mg/L), there are variations among the six divisions. About 20% of samples have been found to exceed the WHO limit in Chittagong, 8% in Dhaka and Khulna, and 3% in Barisal. No sample in Sylhet exceeded the limit (APSU/JAICA, 2006). Approximately 27% of STWs and 1% of DTWs in 270 upazillas (subdistricts) of the country are contaminated with arsenic by Bangladesh standards whereas about 46% of STWs are contaminated by WHO standards. So far, 38,000 persons have been diagnosed, with an additional of 30 million people at risk of arsenic exposure (APSU, 2005). Concentrations of arsenic exceeding 1000 μg/L in STWs were reported from 17 districts in Bangladesh (Ahmed et al., 2006). High levels of arsenic in groundwater occur in the districts of Chandpur, Comilla, Noakhali, Munshiganj, Brahmanbaria, Faridpur, Madaripur, Gopalganj, Shariatpur, and Satkhira. High levels of arsenic have also been found in isolated "hot spots" in the southwestern, northwestern, northeastern, and north-central regions of the country (Ahmed et al., 2006).

The problem of arsenic is now apparent because it is only during the last 30 to 40 years that groundwater has been used extensively for drinking purposes in rural areas (BGS/DPHE, 1999). It is now well recognized that ingestion of arsenic-contaminated groundwater is the major cause of arsenic poisoning in arsenic-affected areas of the world, including Bangladesh. Groundwater contamination by arsenic has been reported in 20 countries of the world, encompassing all the continents (Rahman et al., 2006), but the extent of groundwater contamination in Bangladesh is by far the most severe, as it covers almost 80% of the country.

It has been proved beyond doubt that the origin of arsenic in groundwater in Bangladesh is geogenic. Although several hypotheses regarding its release mechanism have been postulated, the iron oxyhydroxide hypothesis has more scientific evidence (Nickson et al., 1998; 2000; Bhattacharya et al., 2002; Burges and Ahmed, 2006). Involvement of anaerobic bacteria in the dissolution of arsenic in groundwater has also been reported (Khan et al., 2003; Islam et al., 2004, Oremland and Stolz, 2005).

The observation that arsenic poisoning among the population is not consistent with the level of water intake (Imamul Huq et al., 2001a) has raised questions as to the possible pathways of arsenic transfer from groundwater to human systems. There is also significant variation in the manifestation of arsenicosis in the country. These regional variations in arsenicosis cast significant doubt on the original hypothesis that arsenic-contaminated drinking water is the sole cause of arsenicosis (Correll et al., 2000).

Efforts are being directed toward ensuring safe drinking water through either mitigation techniques or by finding alternative sources. Even if an arsenic-safe drinking water supply could be ensured, the same groundwater will continue to be used for irrigation purposes, leaving a risk of soil accumulation of this toxic element and eventual exposure to the food chain through plant uptake and animal consumption. Given the studies on arsenic uptake by crops (Imamul Huq et al., 2001b;. Abedin et al., 2002; Meharg et al., 2002; Ali et al., 2003; Farid et al., 2003; Islam et al., 2005), there is much potential for the transfer of arsenic present in groundwater to crops. The use of groundwater for irrigation has increased steeply over the last several decades. About 86% of the total groundwater withdrawn is utilized in the agricultural sector (Imamul Huq et al., 2005a). There has been a gradual increase in the use of groundwater for irrigation over the last two decades. In the *boro* (dry) season of 2004, 75% of the irrigation water was from groundwater (BADC, 2005), which was 41% of the total in 1982–1983. About 40% of total arable land of Bangladesh is now under irrigation, and more than 60% of this irrigation need is met by groundwater extracted from DTWs, STWs or hand tube wells, (BBS, 1998). Of the total area of 4 million hectares under irrigation, 2.4 million hectares is covered via STWs and 0.6 million hectares is covered via 23,000 DTWs. In the dry season, 3.5 million hectares is used for boro rice, 0.23 million hectares for wheat, and 0.27 million hectares for other crops (FAO, 2006). Numerous greenhouse and field studies have revealed that an increase in arsenic in cultivated soils leads to an increase in the levels of arsenic in edible vegetables (Burló et al., 1999, Carbonell-Barrachina in et al., 1999, Helgensen and Larsen, 1998, Chakravarty et al., 2003, Farid et al., 2003), with many factors affecting bioavailability, uptake, and phytotoxicity of As (Carbonell-Barrachina et al., 1999).

The most severely contaminated districts lie in the north-central, southeastern, and southwestern regions of the country, where up to 90% of the wells tested are contaminated (Figure 1). In general, the southern half of the country is more contaminated than the northern half. In terms of the concentration of arsenic in water, there are very wide variations. However, there is general pattern to this variation: It is wide in the northwest and southwest, whereas it is uniform in the southeast. The distribution of arsenic concentration in the groundwater has been reported to range from below the detection level to more than 1 mg/L. The distributions are controlled by geology and hydrogeochemical processes active in the aquifers. There are also marked spatial and depth variations in the arsenic concentration patterns. In general, the maximum arsenic concentrations are found 20 to 40 m below the ground surface. Very shallow wells (about 10 m) and deep wells (>150 m) are mostly arsenic-safe. In a study in five villages in Sonargaon, Munshiganj, and Comilla covering 30 wells, it was observed that with exceptions of a few, aquifers of depths ranging from 20 to 200 ft contained the maximum amount of total arsenic. The form of arsenic in the groundwater is mostly As(III). In more than 90% of cases, arsenic in groundwater is in this form (Imamul Huq and Naidu, 2003). Of the major aquifers, only the Holocene alluvial aquifers are contaminated; the Pliocene Dupi Tila aquifers are not. Among the geomorphologic units of the country, the Chandina deltaic plain in southeastern Bangladesh is the most severely contaminated, whereas the Pleistocene tracts

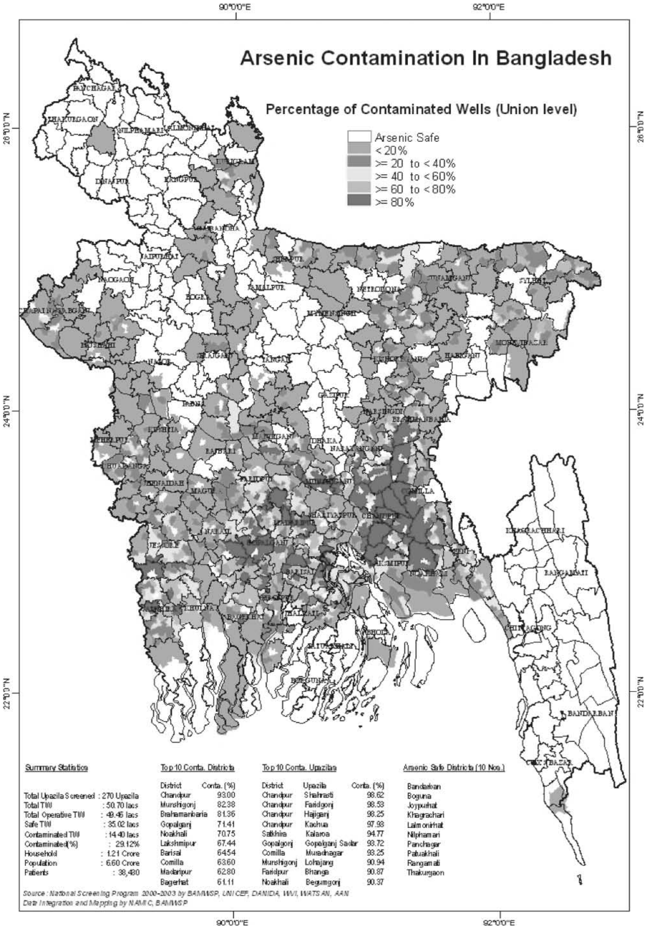

Figure 1 Arsenic-affected areas of Bangladesh. (From www.bwspp.org.) (*See insert for color representation of figure*.)

are not contaminated at all. Most of the Ganges delta is also contaminated. The Teesta fan in the northwest is either not contaminated or very lightly contaminated (Harvey et al., 2005; Imamul Huq et al., 2006a). Next, the findings of the author from various experiments are described.

ARSENIC ACCUMULATION IN THE SOIL

More than 2500 soil, water, and plant samples were collected from over 160 sampling sites covering 15 districts and analyzed for arsenic (Figure 2). The locations selected represented areas affected by arsenic as well as unaffected areas. The

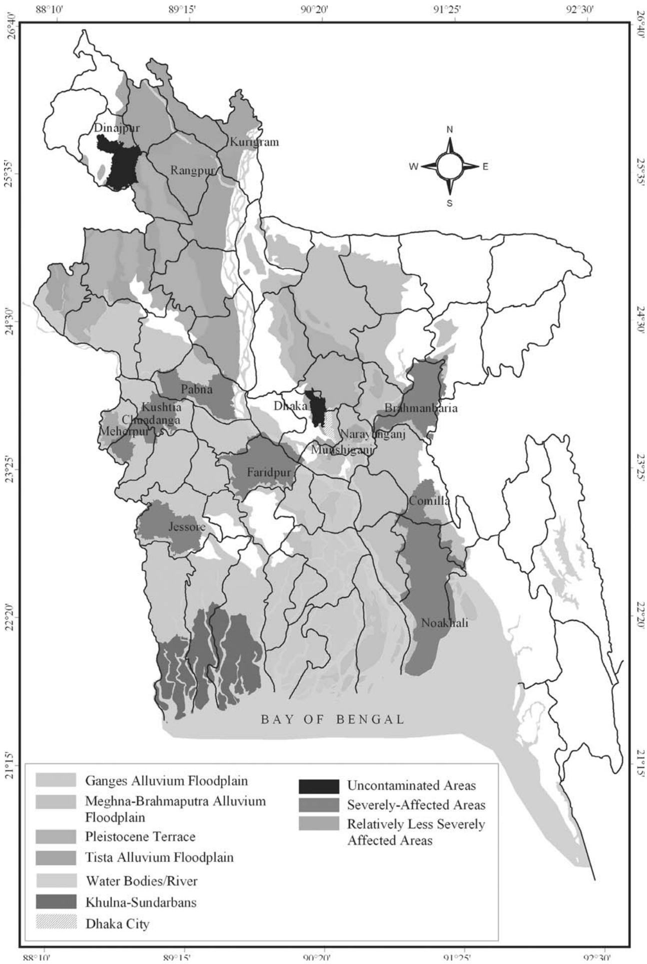

Figure 2 Location of sampling sites. (*See insert for color representation of figure*.)

details of sample collection and analytical procedures are described in Imamul Huq et al. (2006b). The arsenic contents in different depths of soils collected from affected and unaffected areas showed that with a few exceptions, the top 0 to 150 mm contained more arsenic than did the bottom 150 to 300 mm. Arsenic in the aquifer seems to have a bearing on the distribution and loading of arsenic in soils. For uncontaminated soil, the arsenic content is usually less than 10 mg/kg, with an average of 7.2 mg/kg. When a soil is contaminated due to anthropogenic activities such as mining and smelting, the value could range up to 42 mg/kg, and when contaminated due to pesticide application it could be as high as 60 mg/kg (Walsh et al., 1977). In general, most soils were found to contain <10 mg/kg As, and as such meet the guidelines for residential soils of 100 mg/kg required by Australian Health and 20 mg/kg required by the Environmental Guidelines (Imamul Huq and Naidu, 2003). In contrast, the regulatory limit established by the UK is set at 10 mg/kg for domestic gardens and at 40 mg/kg for parks, playing fields, and open spaces (O'Neil, 1990). Much tighter guidelines (0.80 mg/kg for residential and 3.7 mg/kg for nonresidential) have been established in Florida (Tonner-Navarro et al., 1988). Similar variations exist in other countries, although in Bangladesh such a guideline does not exist. It is, however, worth noting that in some soils, *aqua regia*–extractable arsenic exceeded >50 mg/kg, with the highest concentration being 81 mg/kg. The highest concentration was recorded for soil receiving irrigation from an STW (0.077 mg/L). At this site (Faridpur, see Figure 2), the subsurface soil contained about 3 mg/kg. Saha and Ali (2006) have reported that where the irrigation water contained elevated arsenic(79 to 436 μg/L), the concentrations of soils were much higher compared to those in the unaffected areas and varied significantly with both depth and sampling time. Arsenic concentration in the topsoil of a paddy field has been reported by Dittmar et al. (2005) to approach 100 mg/kg. These indicate that the arsenic added to the soil through irrigation is concentrated primarily in the top 0- to 150-mm layer. This layer corresponds to the main root zone depth for most cultivated crops.

Usually, in soils contaminated through anthropogenic activity the arsenic content may exceed 50 mg/kg. Ali et al. (2003) reported that arsenic accumulates in the soil of rice fields, where higher levels are found in the top 75 to 150 mm. The concentration of arsenic in irrigated soils varied from 3.2 to 27.5 mg/kg. On the other hand, in areas where irrigation water does not contain arsenic, the soil arsenic varied from 0.10 to 2.75 mg/kg. According to this study, arsenic concentrations in soil decreases with depth. Alam and Rahman (2003) have also reported that the average arsenic content in soil is well below 10 mg/kg. Soils from uncontaminated areas have been found to contain less than 1 mg/kg As on average. Meharg and Rahman (2003) working with 71 soil samples observed that the highest measured soil concentration was 46 mg/kg, while less than 10 mg/kg was observed in areas with low arsenic contents in irrigation water. In another study, Islam et al. (2005) reported an average soil arsenic concentration of 12.3 (range: 0.3 to 49 mg/kg). Soils in the western and southwestern parts of the country contain the highest concentration, the irrigated soils containing more than the nonirrigated soils, and the top 0 to 150 mm having the highest levels (FAO, 2006). Nevertheless, either negative or no significant correlation between the arsenic content of irrigation water and surface soil arsenic loading has been observed by the author in his investigations. Table 1 shows the results from three of the areas studied.

On the other hand, with many arsenic values in irrigation water higher than those noted above, the soil arsenic content remained within the average value. Laboratory-based column studies showed that between 60 and 70% of the arsenic applied in influent water containing arsenic similar in concentration to the soils being irrigated leached out of the column. However, the proportion of arsenic retained varied with soil texture and pH: high-pH soils showing low retention

TABLE 1 Soil and Water Arsenic (mg/kg) Content of Three Sampling Areas

Munshiganj				Sonargaon				Comilla			
		Soil	Water			Soil	Water			Soil	Water
23°N40.013,	90°E35.083	4.228	0.286	23°N38.675,	90°E35.926	5.085	0.006	23°N30.101,	90°E58.130	5.475	0.419
23°N40.014,	90°E35.084	2.409	0.026	23°N38.713,	90°E35.933	5.966	0.011	23°N30.101,	90°E58.130	5.659	0.382
23°N40.015,	90°E35.085	3.249	0.176	23°N38.713,	90°E35.933	5.916	0.424	23°N29.459,	90°E59.903	6.749	0.210
23°N40.013,	90°E35.083	15.013	0.050	23°N38.713,	90°E35.933	6.862	0.451	23°N30.101,	90°E58.130	7.638	0.453
23°N34.678,	90°E22.273	5.398	0.032	23°N39.543,	90°E34.616	7.867	0.602	23°N30.132,	90°E58.094	5.005	0.441
23°N34.626,	90°E22.415	1.437	0.209	23°N39.550,	90°E34.644	6.775	0.693	23°N30.132,	90°E58.094	6.060	0.447
23°N40.043,	90°E35.063	8.837	0.250	23°N39.501,	90°E34.614	8.245	0.052	23°N30.132,	90°E58.094	6.293	0.280
23°N40.053,	90°E35.083	5.512	0.369	23°N40.128,	90°E35.206	5.661	0.032	23°N30.063,	90°E58.165	4.032	0.359
23°N40.054,	90°E35.084	9.834	0.581	23°N40.011,	90°E35.093	4.880	0.112	23°N30.036,	90°E58.157	3.466	0.368
23°N40.053,	90°E35.083	3.166	0.052	23°N40.011,	90°E35.093	6.694	0.052	23°N29.459,	90°E59.903	7.047	0.353
23°N40.054,	90°E35.084	3.226	0.103					23°N30.182,	90°E58.090	7.489	0.524
								23°N30.204,	90°E58.080	5.831	0.374
								23°N30.219,	90°E58.096	8.634	0.481
$r = -0.409$,	$p = 0.059$,	$n = 22$		$r = -0.798$,	$p = 0.000$,	$n = 20$		$r = -0.842$,	$p = 0.000$,	$n = 26$	

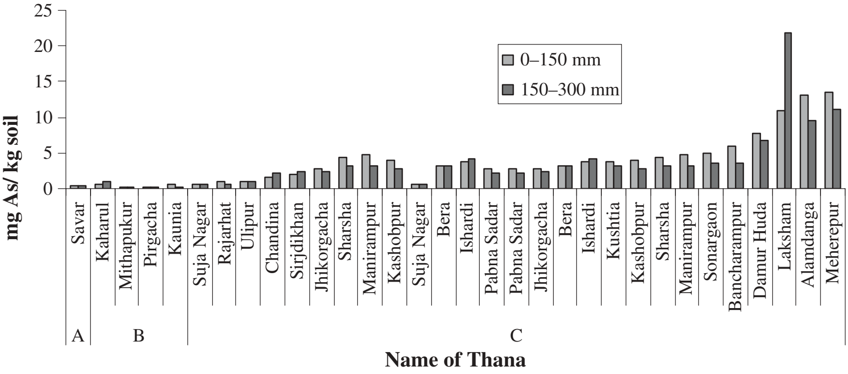

Figure 3 Soil arsenic at two depths in Pleistocene (A), Teesta (B), and Gangetic (C) alluviums. (From Imamul Huq and Naidu, 2003.)

(Imamul Huq et al., 2006c). In a laboratory batch experiment with three soils, one being calcareous, the retention of arsenic by soil has also been found to be governed by soil properties such as nature and clay contents and pH (Joardar et al., 2005; Imamul Huq et al., 2006a). The adsorption characteristics of soil colloids are one of the main mechanisms controlling the mobility of arsenic in the water–soil system. Further, the affected soils of the Teesta alluvium showed relatively less arsenic than that in the affected soils of the Gangetic and Meghna alluvium (Figure 3). From the information on soil arsenic thus gathered, it is becoming apparent that there is a slow buildup of arsenic in many arsenic-affected areas, particularly where arsenic-contaminated groundwater is used for irrigation (Imamul Huq and Naidu, 2003).

Arsenic loading from irrigation is also taking place in Bangladesh soils. With arsenic concentrations in irrigation water varying between 0.136 and 0.55 mg/L, Imamul Huq and Naidu (2003) calculated the arsenic loading in irrigated soils for a boro rice requiring 1000 mm of water per season to be between 1.36 and 5.5 kg/ha per year. Similarly, for winter wheat requiring 150 mm of irrigation water per season, arsenic loading from irrigation water has been calculated in the range 0.12 to 0.82 kg/ha per year. They also calculated the loading for other crops that require irrigation and have estimated the buildup of arsenic in surface soil through irrigation. It was found that the buildup would be greatest for arum (*Colocassia antiquorum*), followed by boro rice, which requires supplemental irrigation; the values ranged from 1.5 to about 6 kg/ha per year. The authors concluded however, that soil buildup of arsenic from groundwater irrigation is likely be a soil-dependent phenomenon, not a generalized one. According to Meharg and Rahman (2003), with irrigation water containing 0.1 mg/L As and the top 100 mm of soil retaining the arsenic, the yearly input could cause a yearly increase of 1 mg/kg. Duxbury and Zavala (2005) have estimated that 10 years of irrigating paddy fields with arsenic-contaminated water would cause an addition of 5 to 10 mg/kg soil to 41% of the 456 study sites they investigated. Yet in another study, Islam et al. (2005) have calculated that for boro rice the level of soil arsenic would increase by 0.50 μg/g per year.

To assess the fate of arsenic in the soil profile, the author conducted a field study on a soil catena where both ground water irrigation with arsenic-contaminated water as well as nonirrigated agriculture are practiced. Simultaneously, monoliths collected from the field were used with simulated irrigation water. A noticeable accumulation of arsenic after irrigation was evident in all soil horizons of highland and medium highland. But in irrigated medium lowland, arsenic accumulated in surface horizons (Ap1g and Ap2g) and the deeper C2 horizon (below 0.9 m). Rainfall intensity during the dry season and soil physical properties, particularly the compact plough pan (Ap2g horizon), seemed to govern the arsenic movement and accumulation in subsoil horizons. On the other hand, capillary rise of arsenic in all nonirrigated lands was evident in the dry season, indicating that arsenic could act as a soluble salt. Variation in the duration and depth of submergence of soil in the same land type by irrigation or by natural water, which control soil properties such as clay, iron, and organic matter contents, might play an important role in determining the fate of arsenic in soils (Imamul Huq et al., 2006d). Saha and Ali (2006) reported that average arsenic concentrations in the top 0- to 150-mm layer of paddy fields increase significantly at the end of irrigation compared to levels at the beginning of the irrigation season. However, after the rainy season and before the start of the next irrigation season, the arsenic in the topsoil decreases significantly, returning to levels comparable to those found at the start of the irrigation season. The monolith study revealed that a fraction of the arsenic added through irrigation water does end up in the groundwater.

ARSENIC ACCUMULATION IN PLANTS

Field samples of vegetables, rice, and wheat were collected from both arsenic-affected and arsenic-nonaffected areas of the country, representing different geological formations—the Gangetic alluvium, the Meghna–Brahmaputra alluvium, the Teesta alluvium, and the Pleistocene tract—to assess the accumulation of arsenic in crops receiving irrigation or watering with arsenic-contaminated water (Imamul Huq et al., 2006b). The first three formations represent arsenic-affected areas, and the last represents the control or arsenic-unaffected area. Pot experiments in spiked and nonspiked soils with rice, leguminous crops, and vegetables have also been conducted to assess the accumulation of arsenic into these crops (Imamul Huq et al., 2006e, 2007a, 2008; Parvin et al., 2006; Rabbi et al., 2007). Samples of rice and other food materials cooked with arsenic-contaminated water collected in situ have also been analyzed for their arsenic content (Imamul Huq and Naidu, 2003). Different varieties of rice have been cooked with arsenic-contaminated water by two different methods in the laboratory to assess the retention of arsenic (Imamul Huq et al., 2006b). Questionnaire surveys were conducted among the inhabitants of arsenic-affected areas to assess the dietary load of arsenic (Correll et al., 2006).

All plant samples were analyzed for total arsenic by hydride-generation atomic absorption spectrometry (HG-AAS). The arsenic from the plant samples was extracted with HNO_3 (Portman and Riley, 1964). Certified reference materials were used throughout the digestion and analyzed as part of the quality assurance/quality control (QA/QC) protocol. Reagent blanks and internal standards were used, where appropriate, to ensure accuracy and precision in the analysis of arsenic. Each batch of 10 samples was accompanied by reference standard samples to ensure strict QA/QC procedures.

Plant arsenic content was found to vary considerably with plant types, nature of soil type, and the irrigation water arsenic content. The arsenic content of most plant samples from contaminated areas was found to be elevated, and often exceeded that of samples from uncontaminated areas (Table 2), suggesting phytoaccumulation of soil arsenic in plants grown in contaminated areas (Imamul Huq et al., 2006a). Chakravarty et al. (2003) reported similar observations from West Bengal. These authors indicated that vegetables grown in the garden and receiving irrigation with arsenic-contaminated water had significantly higher levels than those grown in unaffected areas. Green papaya, red amaranth, bottle gourd leaf, potato, ripe tomato, green chili, and so on, were among the vegetables. Farid et al. (2003) reported from 9 to around 300% increased accumulation of arsenic in vegetables grown with arsenic-contaminated water over those grown with arsenic-uncontaminated water. Williams et al. (2006) analyzed total arsenic in vegetables, roots and tubers, pulses, and spices and found values up to 1.59 mg/kg dry weight (DW) in fruit vegetables and 0.79 mg/kg DW in leafy vegetables.

A marked difference in the arsenic content of vegetables was found and was related to the arsenic content of the groundwater. The groundwater arsenic data revealed elevated arsenic in water draining the Gangetic or Meghna–Brahmaputra alluvium compared to the Teesta alluvium. Comparison of arsenic in similar

TABLE 2 Arsenic in Common Plants from Uncontaminated and Contaminated Areas

		As (mg/kg)	
Common Name	Botanical Name	Uncontaminated Areas	Contaminated Areas
Green papaya	*Carica papaya*	0.212–0.46	0.04–2.22
Arum	*Colocassia antiqourum*	0.077–0.387	0.13–153.2
Bean	*Dolicos lablab*	0.092	0.13–1.16
Indian spinach (Pui)	*Brasilia alba*	0.102–0.146	0.07–1.00
Long bean	*Vicia faba*	0.3	0.37–2.83
Potato	*Solanum tuberosum*	0.62	0.71–2.43
Bitter gourd	*Momordicum charantia*	1.56	2.12
Aubergine	*Solanum melongena*	0.23	2.3
Chili	*Capsicum* spp.	0.41	1.52

Source: Imamul Huq et al. (2006a).

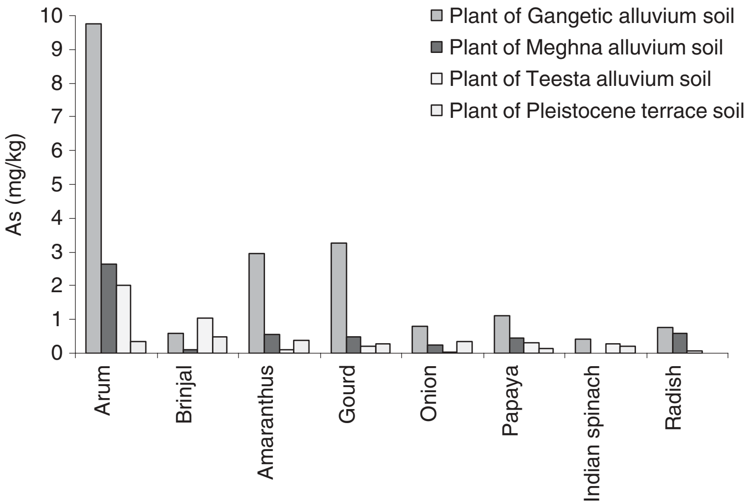

Figure 4 Comparison of the arsenic content in similar food sources from different geological origins. (From Imamul Huq et al., 2006a.)

plants from Gangetic alluvium, Teesta alluvium, Meghna–Brahmaputra alluvium, and Pleistocene tracts confirms the role that groundwater arsenic plays in the arsenic content of crops (Figure 4). A similar effect of parent geology on groundwater and plant arsenic content was observed in plants growing in Gangetic/ Meghna–Brahmaputra and Teesta alluviums. The highest arsenic concentration, recorded for arum, ranged from <10 to >100 mg/kg in the peeled-root samples. To further substantiate the hyperaccumulative capacity of arum for arsenic, an experiment was conducted with one variety, Bilasi, and two germplasms, Mukhi-029 and Mukhi-140, of arum to compare their responses to different levels of arsenic. All these materials showed severe symptoms of arsenic toxicity—reduced vegetative growth—at an arsenic application of 100 mg/L. Arsenic treatments had a significant ($p = 0.002$) negative effect on dry matter production of the individual material as well as arsenic accumulation ($p < 0.001$). Mukhi-029 accumulated the maximum amount of arsenic (334.33 mg/kg) followed by Mukhi-140 (209.73 mg/kg) and Bilasi (195.88 mg/kg). The arsenic accumulation followed the order Mukhi-029 > Mukhi-140 > Bilasi, while the individual plant parts followed the order root > stem > leaf irrespective of the variety or germplasm (Parvin et al., 2006).

Comparison of soil arsenic content with the arsenic content of arum did not reveal any significant relationship ($p = 0.234$), indicating that soil arsenic levels do not dictate the arsenic uptake capacity of arum plants; the very high concentration indicates the capacity of this plant to bioaccumulate arsenic. However, when the analyses were conducted at the district level, there was a nonsignificant positive correlation ($r = 0.162$) between plant arsenic content and soil arsenic.

A log-log relationship between arsenic concentration in arum and arsenic concentration in the irrigation water ($r = 0.78$) was obtained. On the other hand, the coefficient for soil arsenic was negative. A possible explanation for this is that the plant takes up the arsenic in the irrigation water or the part of soil arsenic soluble in water. Similar observations have also been made with pot experiments (Imamul Huq and Naidu, 2003). Generally, the highest arsenic concentration was recorded in plant roots, and this may be attributed to contamination from fine colloidal particles. Peeled vegetable samples also showed concentrations of arsenic higher than the permissible Australian levels [1 mg/kg fresh weight (FW)], indicating significant accumulation in plant tissues.

Of the various crops and vegetables analyzed, green leafy vegetables were found to act as arsenic accumulators with arum (kochu), gourd leaf, *Amaranthus* (shak, both data shak and lal shak), and *ipomoea* (kalmi) topping the list. The arsenic content in these crops ranged from 8 in gourd to 158 mg/kg in arum (DW) or 6 to 125 mg/kg (FW) (Imamul Huq et al., 2006b). Arum seems to be unique in that the concentration of arsenic can be high in every part of the plant. Arum is a green vegetable commonly grown and used almost everywhere of the country. It is a very rich source of vitamins A and C. It is worth noting that arum is usually grown in wet zones adjacent to tube wells. Analyses of arsenic in the wet soils collected adjacent to tube wells generally had higher phytoavailability of arsenic than that of soils from dry regions. It is thus advisable that arum cultivation be relocated to regions away from tube wells where wetting and drying cycles might have an impact on arsenic phytoavailability.

A comparison of the average values for arsenic in different plant samples collected from the Ganga–Meghna–Brahmaputra (GMB) and Teesta alluviums revealed that similar plants growing on contaminated soils of Teesta alluvium had much less arsenic than did those growing on GMB alluvium (Imamul Huq et al., 2006b). The marked difference in the arsenic content of vegetables could be related to the arsenic content of groundwater. The groundwater arsenic data revealed elevated arsenic in water draining the Gangetic or Meghna–Brahmaputra alluvium compared to the Teesta alluvium. This confirms the role of groundwater in the arsenic content of crops. Farid et al. (2003) also found that the accumulation of arsenic was greater in similar vegetables grown on soils belonging to Gangetic alluvium compared to those growing on soils of Teesta alluvium.

The concentration of arsenic in plants seldom exceeds 1 μg/g (Merkert, 1992). However, the concentration of arsenic in arum, amaranthus, gourd leaf, tomato, and certain weeds exceeds the WHO food arsenic content of 2 μg/g FW. Farago and Mehra (1992) have postulated that when the transfer factor (plant/soil ratios) for any particular element is 0.1, the plant can be considered as excluding the element from its tissues. In the present case, most plants have shown this phenomenon, although a few [e.g., arum (*Colocassia antiquorum*) and several leafy vegetables] have shown the reverse phenomenon, indicating their affinity for arsenic accumulation. Experiments on arsenic-spiked soil with different arums have shown that the transfer factors ranged from 0.57 to 6.57, meaning that arums in general have a great affinity to accumulate arsenic from the growth

TABLE 3 Arsenic in Arum Collected from Various Districts

	As (mg/kg)		
District	Average	Minimum	Maximum
Brahmanbaria	23.55	0.83	138.33
Comilla	2.03	0.03	4.66
Dhaka	0.4	0.05	0.96
Dinajpur	0.15	0.09	0.21
Jessore	5.27	0.92	11.37
Meherepur	0.71	0.15	1.52
Munsiganj	0.78	0.18	3.05
Narayanganj	3.08	0.02	20.5
Pabna	24.65	1.05	115.32
Rangpur	1.1	0.14	3.82

Source: Imamul Huq et al. (2006a).

medium and that arsenic extraction by arums is quite significant (Parvin et al., 2006). Arsenic content in arum has been found to vary depending on the source and extent of contamination of groundwater by arsenic (Table 3).

Arsenic accumulation in plants grown under experimental conditions has been found to depend on the type of plant, plant part (root vs. shoot), concentration, the nature of arsenic in solution, the amount of iron oxide in the soil, and the amount of phosphorus added to the soil (Onken and Hossner, 1995; Cox et al. 1996; Burló et al., 1999; Carbonell-Barrachina et al., 1999; Pickering et al., 2000). This is consistent with work by Thornton (1994), who studied plant uptake of arsenic in vegetables grown in arsenic-contaminated garden soils from southwestern England. He found that the uptake of arsenic (mg/kg DW) by lettuce, onion, beetroot, carrot, pea, and bean was species-dependent, with the highest amount in lettuce (average = 0.85, range 0.15 to 3.9) and the lowest in beans (average = 0.04, range 0.02 to 0.09). In lettuce, the uptake increased with increasing phosphorus in the soil and decreased with increasing iron. On the other hand, Queirolo et al. (2000) reported that in various plants, arsenic exceeded the UK statutory limit of 1 mg/kg FW. They found that the average value for arsenic in maize was 1.8 mg/kg and in potatoes was 0.86 mg/kg. Both values exceeded the Chilean limit of 0.5 mg/kg for food. The elevated concentration in vegetables was attributed to soil and water contamination by arsenic.

ARSENIC ACCUMULATION IN CEREALS

The main cereals receiving irrigation are boro (dry season) rice and wheat. The arsenic content of rice grain samples collected from various districts varied from below the detection limit to more than 1 mg/kg. The concentration ranged in root from less than 1 to as high as 267 mg/kg; in straw the range was between less than 1 to 30 mg/kg. In wheat grain the values ranged between 0.5 and 1 mg/kg; in straw, between 0.2 and 30 mg/kg; and in root, between 1.5 and 3 mg/kg. Other investigators have reported similar results (Abedin et al., 2002; Alam and Rahman, 2003; Hironaka and Ahmed, 2003; Meharg and Rahman, 2003). Das et al. (2004) reported that the arsenic content of rice grains was 0.14 mg/kg. It was also observed that the arsenic content in rice varied with the variety as well as with the area where grown (Imamul Huq et al., 2006b). In a recent study, Williams et al. (2006) observed that the districts with the highest mean arsenic rice grain levels were in southwestern Bangladesh: Faridpur (boro) 0.51 > Sathkhira (boro) 0.38 > Chuadanga (boro) 0.32 > Meherpur (boro) 0.29 μg/g. They also reported substantial amounts of arsenic in the aman (rain-fed) variety of rice. The author conducted a survey of rice arsenic collected during the two seasons from the same locality and observed that the arsenic left in the soil after boro irrigation is taken up by the following aman crop, and the same variety of rice cultivated in the boro and aman season was found to accumulate less arsenic in the aman than in the boro season (Imamul Huq et al., 2007b).

Arsenic was found to be concentrated primarily in the roots and straws of rice and other cereal crops. The uptake of arsenic is passive (Streit and Stumm, 1993) and is translocated to most parts of the plants. Comparing the arsenic in rice from Bangladesh and Japan, Hironaka and Ahmad (2003) have confirmed that the contents are very similar. However, they mentioned that the rice being produced in arsenic-contaminated areas of Bangladesh contained two to three times more arsenic than that in rice grown in uncontaminated areas. Similar observations were made in another study (Alam and Rahman, 2003) on rice collected from 21 field locations situated in areas of Meghna alluvium. These authors have shown that the grain arsenic-concentration was below the detection limit. Meharg and co-workers (Meharg and Rahman 2003; Meharg et al., 2001) reported similar results from their experimental study involving rice. Data on rice arsenic pooled from the findings of these authors are summarized in Table 4.

Arsenic in rice seems to vary widely. Table 5 summarizes the values of arsenic in rice samples of Bangladesh obtained by the author and by others. The same variety appears to accumulate differently depending on the soil–water arsenic ratio. Islam et al. (2005) have shown that the arsenic contents in boro rice grain

TABLE 4 Distribution of Arsenic in Rice Plant Parts

	As (mg/kg)			
Plant Part	Average	Minimum	Maximum	*n* (Number of Data)
Grain	0.29	0.02	2.81	108
Leaf	1.21	0.06	3.32	13
Stem	4.29	0.35	25	18
Root	29.1	9.06	73.38	6
Husk	0.07	0.02	0.15	9

TABLE 5 Total Arsenic in Rice from Various Locations

Location	Total As in Rice[a] (mg/kg)	Rice Type
Gazipur	0.092 (0.043–0.206)[1]	11 cultivars
Bogra	0.058 – 0.104[1]	Four cultivars
Dinajpur	0.203[1]	BR11
Naogaon	1.835[1]	BR11
Nawabganj	1.747[1]	BR11
Mymensingh	0.078[1]	BR8
Rangpur	0.185[1]	BR11
Rajshahi	0.075 – 0.117[1]	Three cultivars
Kachua, Hajiganj	0.14[2] (0.04 – 0.27)[2]	
Sharishabari	0.173[3]	
Northwest	0.759 (0.241–1.298)[4]	
Chapai Nawabganj	0.13 (0.03— 0.3)[5]	
Market	0.183 (0.108–0.331)[6]	Various aman cultivars
Various	0.117 (0.072–0.170)[6]	Raw boro rice
Various	0.125[6]	Raw aman rice
Jessore	0.612[7]	Processed rice
Brahmanbaria	0.507[7]	BINA6
	0.775 (0.34–1.11)[8]	BR36
Teesta alluvium	0.81(0.05–1.65)[8]	Boro rice
	0.31[8]	BR28
	0.29[8]	BR14
	0.11[8]	IRRI532
	0.05[8]	BR76
Manikganj	—	BR33 T, aman

[a]Obtained by: 1, Meharg and Rahman (2003); 2, Das et al. (2004); 3, Watanabe et al. (2004); 4, FAO (2006); 5, Williams et al. (2005); 6, Duxbury et al. (2003); 7, Farid et al. (2005); 8, the author.

were 0.08 to 0.93 μg/kg in Brahmanbaria, 0.10 to 1.08 in Faridpur, 0 to 0.53 in Paba, 0.13 to 0.92 in Senbag, and 0.09 to 1.01 in Tala.

In pot experiments with arsenic-spiked soil, Imamul Huq et al. (2006e, 2008) observed that arsenic accumulation in rice is dependent on variety and soil. Not all varieties accumulate arsenic to the same extent. For example, under similar experimental conditions, BRRI dhan 28 was found to accumulate more arsenic than BRRI dhan 29. As usual, in either variety, arsenic accumulation was more from As(III) than from As(V), and root accumulated the maximum. While working with a salt-tolerant local variety, *Sraboni*, and a nontolerant HYV, BRRI dhan 26, in spiked soil with 10 mg/L As irrigation, Rabbi et al. (2007) observed that the HYV accumulated more arsenic than the local variety accumulated. These authors also reported that calcareousness of soil accentuated the arsenic accumulation, irrespective of variety. In the HYV the average arsenic accumulation was more than 3.5 mg/kg dry grain in calcareous soil compared to less than 1.0 mg/kg dry grain in noncalcareous soil. With wheat, the author observed a phenomenon similar to that for rice: more arsenic in root and straw than in grain. In wheat, the grain arsenic has been found to be almost similar to rice (i.e., an average of below 1.0 mg/kg dry grain), but the root and straw contained comparatively less arsenic than is usually found in rice (Imamul Huq and Naidu, 2003). The lower arsenic level could be attributed to the lower water requirement for wheat. Wheat samples from Faridpur had 0.62; from Pabna, between 0.63 and 0.96; and from Jessore, 0.51 mg/kg DW.

Most arsenic data in rice relate to total arsenic. Williams et al. (2005, 2006) have presented data on various arsenic species of Bangladeshi rice samples. According to these authors, Bangladesh rice contains more than 80% inorganic arsenic, followed by a small fraction of organic arsenic and a sizable portion that could not be accounted for. The principal species identified were As(III), DMA(V), and As(V).

ARSENIC ACCUMULATION IN THE SYMBIOTIC SYSTEM

Very little information is at hand about the response of the symbiotic system to arsenic contamination. Grain legumes occupy an important part of dietary protein in Bangladesh. As such, the response of leguminous plants to arsenic contamination is of importance. In our field survey we have found that different beans collected from arsenic contaminated areas contained appreciable amount of arsenic (see Table 1). Our field samples of different beans have shown them to contain 0.885 mg/kg DW on average (range 0.04 to 5.08); the higher values were, primarily for cowpea. The response of cowpea (*Vigna sinensis* L.) to different levels of spiked arsenic in pot soil was investigated (Imamul Huq et al., 2008). The experiment was conducted with two soils (i.e., Sonargaon and Dhamrai) to see the effect of spiked arsenic on the growth performance, symbiotic association, mineral nutrition, and accumulation of arsenic in cowpea. The pot experiments were done with three levels of arsenic treatments (i.e., 20, 30, and 50 mg/L in irrigation water) along with a control. Arsenic content in plants increased with increasing arsenic application to soil. Arsenic-treated cowpea plants were shorter in height, and at 50 mg/L treatment, all leaves were shed after 60 days of growth. A striking difference was observed in the nodulation of cowpea. In treated plants, the number and size of nodules showed gradual decrease with increasing arsenic application. The nitrogen and phosphorus nutrition was modified by arsenic treatment. The plant nitrogen decreased while phosphorus increased. The nodule nitrogen content showed a decreasing tendency with increasing arsenic accumulation in the plants, thus demonstrating a negative impact on rhizobium–legume symbiotic association.

Fodders

Limited investigations conducted on fodder crops show a wide variation in the uptake of arsenic, which ranged from 0.75 to >330 mg/kg DW (Imamul Huq and Naidu, 2003). One interesting thing to note here is that in the samples collected from the Teesta alluvium, the arsenic content is relatively less than that in samples collected from the GMB alluvium. But in the former case also, samples collected from affected areas usually contained more arsenic than did those collected from unaffected areas. A more detailed study is needed to assess the potential role in the transfer of arsenic from fodder to humans via animals. Recognizing the potential for significant transfer of arsenic via animals to human, the Austrian authorities have established a threshold value for arsenic in fodder as 2 mg/kg DW (Brandstetter et al., 2000).

Dietary Intake

Bangladesh rice has been reported to accumulate less arsenic than is accumulated by American rice (Williams et al., 2005). These authors have, however, reported that the main species detected in Bangladesh rice were As(III), DMAV, and As(V), of which more than 80% of the recovered arsenic was in inorganic form. Yet in another study it has been found that more than 85% of the arsenic in rice is bioavailable compared to only about 28% in leafy vegetables (Imamul Huq and Naidu, 2005). It is thus pertinent to assess the dietary load of arsenic from various food materials otherwise contaminated with arsenic.

A Bangladeshi consumes, on average, about 500 g of rice per day. The maximum allowable daily limit (MADL) of arsenic ingestion without injury is 0.22 mg/day. Assuming that 3 L/day of drinking water with an arsenic content of 0.05 mg/L and nothing but rice is to have been consumed with an average arsenic content of 0.437 mg/kg, it has been simulated that the mean load is 304 μg/day, and effectively, all cases will exceed the 0.22-mg/day limit. Rice here is found to contribute 144 μg/day, approximately 65% of the 220 μg/day limit (Correll et al., 2006). It has also been observed that even if a rice sample does not contain any detectable amount of arsenic, the cooked rice (*bhat*) contains a substantial amount of the element when it is cooked in arsenic-contaminated water. The amount of arsenic in *bhat*, plus an average consumption of 4 L of the same source of water as drinking water that has the Bangladesh standard of 50 μg/L arsenic along with arsenic-rich vegetables, is sufficient to bring the value of daily ingestion of arsenic above the maximum allowable daily level (MADL) of 0.22 mg/day (Imamul Huq et al., 2006b). It needs to be mentioned further here that cooked rice collected from households during the field survey showed arsenic concentrations from 0.11 to 0.36 mg/kg (Imamul Huq and Naidu, 2003). Chakravarty et al. (2003) estimated that the content of arsenic ingested by a person from *bhat* is 0.124 mg from 460 g of rice. Williams et al. (2006) have calculated that daily consumption of rice with a total arsenic level of 0.08 μg/g would be equivalent to ingesting a drinking water arsenic level of 10 μg/L, and that vegetables, pulses, and spices are less important than water and rice to total arsenic intake.

A person consuming daily 100 g DW of arum with an average arsenic content of 2.2 mg/kg, 600 g DW of rice with an average arsenic content of 0.1 mg/kg, and 3 L of water with an average arsenic content of 0.1 mg/L would

TABLE 6 Maximum Arsenic (mg/kg DW) of Various Plant Materials, and Amount of Material[a–c] That Will Exceed an MADL of 0.2 mg/day When Ingested

	District[d]									
Plant Type	Dha	Din	Jes	Kur	Meh	Mun	Nar	Pab	Ran	Overall
Amaranthus	—	0.0	1.0[a]	—	—	1.7[a]	1.1[a]	18.7[b]	0.3	18.7[b]
Arum	1.0[a]	0.2	11.4[b]	0.9	0.5	0.6	19.8[b]	9.0[b]	5.5[b]	19.8[b]
Arum root	0.4	—	—	—	1.5[a]	2.6[a]	—	115.3[c]	—	115.3[c]
Bean	0.4	—	0.4	—	0.2	0.3	—	5.1[b]	—	5.1[b]
Gourd leaf	—	—	1.0[a]	—	—	0.3	2.4[a]	20.1[c]	—	20.1[c]

Source: Imamul Huq et al. (2006a).
[a] >200 g/day.
[b] >40 g/day.
[c] >10 g/day.
[d] Dha, Dhaka; Din, Dinajpur; Jes, Jessore; Kur, Kurigram; Meh, Meherpur; Mun, Munshiganj; Nar, Naryanganj; Pab, Pabna; Ran, Rangpur.

ingest 0.56 mg/day, which exceeds the threshold value calculated using the U.S. Environmental Protection Agency model (Imamul Huq et al., 2006a). Table 6 indicates the maximum arsenic content (dry weight) of various plant materials that will exceed MADL of 0.2 mg/day when ingested.

On the basis of the arsenic content in rice, the dietary load estimation—the possibility of a certain proportion of the population risking the exposure to excess of MADL—has been calculated for Jessore (representing Gangetic alluvium) to be 32%, for Rangpur (representing Teesta alluvium) to be only 2%, and for the entire country to be 19% (Imamul Huq et al., 2006a). Correll et al., (2006) have concluded that food can contribute more than a third of the total daily intake of arsenic. In a separate study, with a different model, it has been calculated that in Jessore, the daily ingestion of arsenic in adult is more than 4 mg and in children it is more than 2 mg (Monica Das, personal communication, 2004).

These observations assert that arsenic ingestion in the human body is through the food chain, as well as through drinking water. Crops receiving arsenic-contaminated irrigation water take up this toxic element and accumulate it in different degrees, depending on the species and variety. However, the portion of this arsenic that goes directly to the various metabolic pathways and causes the problem of arsenic toxicity needs to be evaluated. The bioavailability of the arsenic in various food materials needs to be assessed further, and the vegetables, including the varieties of rice that have been found to contain exceptionally high levels of arsenic, need to be screened.

REMEDIAL POSSIBILITIES

Ensuring arsenic-safe drinking water is the first and foremost priority. A number of alternatives have been evolved in this regard. In the agricultural sector, remedial measures are, however, imminent. Several remedial approaches have been tried by the author, some of which have produced promising results. In pot experiments using two vegetables crops [i.e., arum (*Colocassia antiquorum*) and kangkong (*Ipomoea aquatica*)] it has been observed that mixing surface water with irrigation water (groundwater) could reduce about 50% of arsenic accumulation in both crops. In practice, this would not be practical, as the scarcity of surface water during the dry season makes it necessary to opt for groundwater irrigation. Amending arsenic-contaminated (natural or spiked) soils with various types of organic matter, including cow dung, poultry litter, sewage sludge, or compost, could reduce the accumulation of arsenic in plants; however, the effectiveness was found to depend on the source of organic matter. Using high levels of phosphatic fertilizers produced variable results. With low soil arsenic, phosphatic fertilizers could alleviate arsenic accumulation in red amaranth, kangkong, or arum, but at high soil arsenic levels, phosphorus-fertilizer applied even at one and a half times the rate used in the country side was not sufficient to alleviate arsenic accumulation in the plants.

Two different indigenous ferns, *Pteris vittata* and *Nephrodium molle*, were grown in pots with spiked arsenic concentrations ranging from 0 to 100 mg/kg to find their abilities as phytoremediators for the element. The results showed that *P. vittata* could remove more than 95% of the soil arsenic, whereas the removal by *N. molle* was little over 68% (Hossain et al., 2006). The wide distribution with easy adaptation to different conditions, *P. vittata* demonstrated a favorable prospect for its application in the phytoremediation of arsenic-contaminated soils. Commercial cultivation of *P. vittata*, particularly along agricultural fields receiving arsenic contaminated groundwater irrigation, could be a prospective remedial measure.

In yet another experiment, marigold (*Tagetes patula*) and ornamental arum (*Syngonia* sp.) were grown on arsenic-spiked soils to assess their properties as phytoremediators. The arsenic-accumulating property of the *Tagetes patula* and *Syngonia* sp. appeared to make them good sources to be exploited to phytoremediate arsenic-contaminated soil (Imamul Huq et al., 2005a). From observations with the two plants (Figure 5) it could be concluded that they have the characteristics to hyperaccumulate arsenic from soil and could be used as possible phytoremediators. Ornamental arum is, however, a better phytoremediator than marigold in extracting arsenic from soil.

Green and blue-green algae were found to hyperaccumulate arsenic from soil (Imamul Huq et al., 2005b; Shamsuddoha et al., 2005; Gunaratna et al., 2006). Historically, the growth of algae in rice fields has been considered a natural fertilization process, as decomposition of algae in rice fields adds nitrogen and other nutrients to the soil. The algae growing in rice fields are supposed to take up, among other content, the arsenic present in the water. This hyperaccumulation characteristic of algae could be used to remediate rice grown with arsenic-contaminated irrigation water. A study was made based on this rationale to access the possibility of the extent of bioremediation of arsenic in rice culture through algae by growing a boro rice with or without the presence of algae in

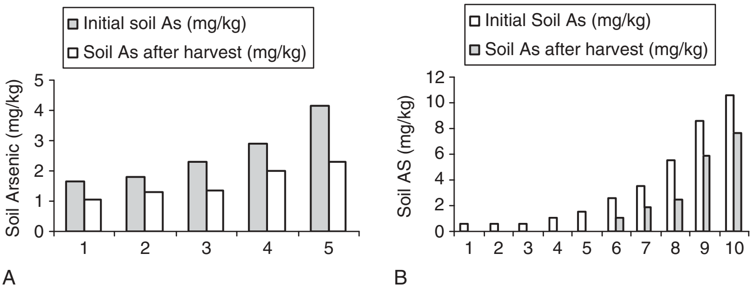

Figure 5 Phytoremediation of soil arsenic by (A) marigold and (B) ornamental arum. (From Imamul Huq et al., 2005a.)

spiked pot soils and was found to have decreased the arsenic accumulation in rice plants (BRRI dhan-28) by about 72% (Imamul Huq et al., 2007a).

Management strategies to reduce As uptake by rice are very pertinent and urgent. In another study, Imamul Huq et al., (2006e) attempted to devise remedial measures to minimize arsenic toxicity by oxidizing arsenite as well as to reduce the entry of arsenic into the growing rice. An experiment was undertaken to observe the impact of manipulation of water regimes to make a more oxidized rice rhizosphere, and at the same time, using two oxidation states of arsenic on the response of two varieties of rice [i.e., BRRI dhan-28 (BR-28) and BRRI dhan-29 (BR-29)], compare the uptake of arsenic under the prevailing conditions by the two varieties. Reducing the water requirement by 25% of the field capacity was found to have alleviated arsenic accumulation significantly in two varieties of rice (BRRI dhan 28 and BRRI dhan 29) without any significant decrease in their yields (Imamul Huq et al., 2006e). It was evident from the study that reducing the moisture level could substantially abate arsenic accumulation in rice plants, thereby helping to some extent to remediate its entry into the food chain.

CONCLUSIONS

Our studies, and studies of others, reveal that crops receiving irrigation through arsenic-contaminated groundwater accumulate the toxic element in them. The extent of arsenic accumulation is, however, generally soil and species dependent. Although the average soil arsenic is well below 10 mg/kg, there is evidence that this value may exceed 80 mg/kg in places where arsenic-contaminated groundwater is used for irrigation. As such, there has been a slow buildup of arsenic in the irrigated soils. Plant arsenic is more correlated with water arsenic than with soil arsenic. Of the many vegetables, arum has been found to be a hyperaccumulator for arsenic. Some other leafy vegetables also accumule arsenic at an accelerated rate. The Ganges–Meghna floodplain aquifers are more contaminated, and so are the crops growing on soils of these floodplains compared to the

Teesta alluvium and Pleistocene lands. The groundwater arsenic is dominated by As(III), and as a result, the crop arsenic is also dominated by this species. The staple cereal rice, particularly the dry season (boro) rice, is the major recipient of groundwater irrigation, and in most cases where the irrigation water is contaminated with arsenic there is an elevated level of arsenic in the rice grain. Rice and other food materials cooked with arsenic-contaminated water have also been found to contain substantial amounts of arsenic. The amount of rice consumed per person per day (450 g uncooked), along with arsenic-contaminated drinking water (4 L/day), including vegetables with a high arsenic content, is sufficient to cross the MADL limit of 220 μg/day. Food alone can contribute more than a third of the total arsenic intake. Although much work still needs to be done to get a better picture of exposure to arsenic of humans in Bangladesh, the information available demands further detailed study and also the need for development of strategies that minimize the water–soil–plant transfer of arsenic. It can be concluded that the largest contributor to arsenic intake by Bangladesh villagers in affected regions is contaminated drinking water, and the second-largest contributor is food, notably rice, followed by vegetables. Dietary loads of arsenic in Bangladesh need to be considered a public health problem. Steps to reduce this load, on the farm and in the kitchen, are recommended as a matter of urgency.

Such a situation demands remedial measures. Reversal of groundwater irrigation is not an immediate solution, as surface water sources are ever increasing, particularly during the dry season, when irrigation is most demanding. Chemical methods have resulted in doubtful or unsatisfactory results. Moreover, although some amendment approaches appear promising, their field verification and carryover effects on other soil characteristics remain to be ascertained. Several possibilities that can keep the food sources arsenic-safe are selection of arsenic-nonaccumulating plants, mixing fresh water with arsenic-contaminated irrigation water for soil cleanup, phytoremediation with indigenous plant species, use of green algae as a bioremediator for rice, and manipulating the water regime in rice culture. Further detailed study and need to develop strategies that minimize the water–soil–plant transfer of arsenic are proposed.

Acknowledgments

The author thanks J. C. Joardar of BACER-DU for his help during the preparation of the manuscript, and A. F. M. Manzurul Haque, for preparing the map on sampling location.

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3

MICROBIAL CONTROLS ON THE GEOCHEMICAL BEHAVIOR OF ARSENIC IN GROUNDWATER SYSTEMS

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INTRODUCTION

Arsenic is a chemical element that is present in air, soil, and water. It is commonly found in weathered volcanic and marine sedimentary rocks, fossilfuels, and a number of arsenic-containing minerals (e.g., scorodite, arsenopyrite, realger, orpiment) (Newman et al., 1998). In the Earth's crust, it is present at levels from 0.1 to several hundred ppm (Bhumbla and Keefer, 1994). In nature, rocks typically contain 1.5 to 2.0 mg/kg of arsenic, but concentrations of arsenic may be up to 500 mg/kg in contaminated soil. Arsenic can also be emitted to the atmosphere by industrial processes, causing higher arsenic levels, up to thousands of parts per million near many centers of human activity (Bhumbla and Keefer, 1994).

Localized groundwater arsenic problems have been identified at concentrations above 50 μg/L (even up to 3200 μg/L for West Bengal, India, and Bangladesh) from various parts of the world (Smedley and Kinniburgh, 2002). Incidences of high arsenic concentrations in groundwaters from alluvial aquifers in the Bengal delta plains in West Bengal and Bangladesh and their poisonous effects on millions of people in these areas have received significant attention during the last

Arsenic Contamination of Groundwater: Mechanism, Analysis, and Remediation,
Edited by Satinder Ahuja

decade. This issue has become a worldwide problem and therefore a challenge for scientists to determine the significant sources and causes of such elevated arsenic concentrations in groundwater systems. In this chapter we review briefly high arsenic concentrations in groundwater and propose mechanisms for the release of arsenic into groundwater systems, with particular focus on the possible role of metal-reducing bacteria in arsenic mobilization into the shallow aquifers of the Ganges delta. The bacterial effects on arsenic behavior in anoxic sediments, and the various interactions among minerals, microbes, and arsenic that affect arsenic mobilization in groundwater systems significantly are also discussed.

CHEMICAL NATURE AND TOXICITY OF ARSENIC

Arsenic is a semimetal or metalloid with four oxidation states—As(V), As(III), As(0), and As(−III)—corresponding to the inorganic compounds arsenate, arsenite, arsenic metal, and arsine gas, respectively. Arsenic metal occurs rarely, but traces of toxic arsines can be detected in gases emanating from anaerobic environments (Cullen and Reimer, 1989), and As(0) is stable under reducing conditions. Chemically, arsenic is always present in compounds containing oxygen, chlorine, carbon, or hydrogen, and can also be associated with lead, copper, gold, or iron (Nriagu, 2002).

Arsenic is a poison. It offers a very good example of the significance of speciation in relation to toxicity. The relative toxicity of arsenic depends mainly on its chemical form and is dictated in part by the valence state. Trivalent arsenic has a high affinity for thiol groups, as it readily forms kinetically stable bonds to sulfur. Thus, reaction with As(III) induces enzyme inactivation, as thiol groups are important to the functioning of many enzymes (Knowles and Benson, 1983). It affects the respiration system by binding to the vicinal thiols in pyruvate dehydrogenase and 2-oxoglutarate dehydrogenase (NRC, 1999) and has also been found to affect the functioning of the glucocorticoid receptor (Kaltreider et al., 2001). Pentavalent arsenic has a poor affinity toward thiol groups, resulting in its more rapid excretion from the body. However, it is a molecular analog of phosphate and can uncouple mitochondrial oxidative phosphorylation, resulting in failure of the energy metabolism system (Andreae, 1986). Methylated arsenicals such as monomethylarsonic acid (MMAA) and dimethyl arsenic (DMAA) are less harmful than inorganic arsenic compounds.

The lethal dose of arsenic for humans is about 125 mg. Most of the arsenic ingested is excreted from the body through urine, feces, skin, hair, nails, and breath. Some arsenic is deposited in tissues, which causes the inhibition of cellular enzyme activities in cases of excessive intake. Clinical symptoms of arsenicosis may take about six months to two years or more to appear, depending on the quantity of arsenic ingested and the person's nutritional status and immunity level. Untreated arsenic poisoning results in several stages; for example, various effects can be seen on the skin with melanosis and keratosis, dark spots on chest, back, limbs, and gums; and enlargement of the liver, kidneys, and spleen, with which conjunctivitis, bronchitis, and diabetes may also be linked. Later, affected persons may develop nephropathy, hepatopathy, gangrene, or skin, lung, or bladder cancer.

ARSENIC IN GROUNDWATER

Poisoning of drinking water extracted from shallow sedimentary aquifers contaminated with arsenic threatens the health of millions worldwide (Smith et al., 2000). Areas affected by elevated groundwater arsenic concentrations include Argentina, Bangladesh, Cambodia, Canada, Chile, China, Ghana, Hungary, Mexico, Mongolia, Nepal, Pakistan, Poland, Taiwan, Thailand, Vietnam and West Bengal, India (Nickson, 1998, 2000; Jain and Ali, 2000; Berg et al., 2001; Smedley and Kinniburgh, 2002; Polya et al., 2003; Ahmed et al., 2006). Among these areas, Bangladesh and West Bengal have the most serious groundwater arsenic problem in the world, which has been described as "the worst mass poisoning in human history" (Smith et al., 2000; Smedley and Kinniburgh, 2002). In addition to consumption through drinking water, arsenic can be taken up via the food chain. Direct consumption of rice (*Oryza sativa* L.) irrigated with arsenic-rich waters is another significant source of arsenic exposure in areas such as Bangladesh, where rice is the staple food and provides the main caloric intake (Meharg and Rahman, 2003; Williams et al., 2005).

Arsenic is generally present in groundwater as an oxyanion [i.e., arsenite (H_3AsO_3) or arsenate (H_3AsO_4) or both]. Several studies of arsenic speciation have shown a wide range in the relative proportions of dissolved arsenate and arsenite present in groundwater (Das et al., 1995; Acharyya, 1997; Gault et al., 2003). The usual proportion of arsenite appears to be between 50 and 60% of the total arsenic, especially in the Bengal delta aquifer, reported by BGS and DPHE (2001). Various geological and geochemical conditions can control the concentrations of arsenic in groundwater. These factors include leaching of geological material; factors such as pH, Eh, solution composition, sediment chemistry/mineralogy, grain size distribution of aquifer sediment, competing and complexing ions, aquifer mineralogy, reaction kinetics, and hydraulics of the groundwater system (Smedley and Kinniburgh, 2002; Gault et al., 2005a); and the extent of microbiological activity and associated biogeochemical reactions.

The depth of the Bengal aquifers affected is generally less than 150 m, and they are composed of micaceous sands, silts, and clays laid down during the Holocene age (Smedley and Kinniburgh, 2002). High-arsenic groundwaters are characterized by high Fe (>0.2 mg/L) and HCO_3^- (>500 mg/L) concentrations and low levels of SO_4 (<1 mg/L) and NO_3 (<1 mg/L), with low Eh and pH values, close to or greater than 7 (Smedley and Kinniburgh, 2002). The associated sediments have arsenic concentrations in the range <2 to 20 μg/g, close to the baseline level of 5 to 10 μg/g (Smedley and Kinniburgh, 2002). The regional distribution of high-arsenic-content waters in West Bengal and Bangladesh is known to be extremely inconsistent (PHED, 1991; CSME, 1997; BGS/DPHE, 2001), and it is presumed that the great variation in sedimentary characteristics and variations in abstraction depth are the most probable reasons for these features.

POTENTIAL CAUSES OF ELEVATED GROUNDWATER ARSENIC CONCENTRATIONS IN WEST BENGAL AND BANGLADESH

The source of arsenic in groundwater is still under dispute in the academic world. It is thought that sedimentation of arsenic-laden soils in the West Bengal/Bangladesh region began about 25,000 to 80,000 years ago during the Quaternary era, known as the Younger Deltaic Deposition (YDD) (MIG, 1998). Continued sedimentation has concentrated arsenic in specific zones of these countries. Bangladesh is situated at the lower end of the three great river systems: the Ganges, Brahmaputra, and Meghna, which have a total catchment area of 1.5 million km^2. The catchment area, which includes the Himalayan mountain system, the Indian shield, the Shilong plateau, and the great Gangetic plains, produces huge amounts of sediments each year. Approximately 2.4 billion tons of sediment is currently transported through Bangladesh and West Bengal (Goodbred and Kuehl, 2000) by these river systems. Depending on the sediment type, arsenic typically occurs at concentrations of 2 to 100 ppm and is found in, and adsorbed onto, a variety of mineralogical hosts. Hydrated ferric oxides, phyllosilicates, and sulfide minerals are most commonly cited as the dominant hosts for solid-phase arsenic (Battey, 1990; Nickson et al., 1998, 2000; BGS/DPHE, 2001; Smedley and Kinniburgh, 2002), and the immediate source of arsenic in the groundwaters in Bengal is widely considered to be the host sediments.

A number of mechanisms have been proposed for the release of arsenic from these minerals into the groundwater in shallow alluvial sedimentary aquifers in Bengal (Das et al., 1995, 1996; Nickson et al., 1998, 2000; Acharyya et al., 1999; Chowdhury et al., 1999; Harvey et al., 2002; Smedley and Kinniburgh, 2002; Oremland and Stolz, 2003; Akai et al., 2004; Islam et al., 2004). One of these processes is via *pyrite oxidation*, in which reduced arsenic-bearing minerals such as arsenopyrite present in Ganges delta sediments may experience oxidizing conditions due to exposure to the atmosphere. This might happen as a result of natural processes and anthropogenic interventions. The excessive withdrawal of water for pumping lowers the water table and may also allow atmospheric oxygen to enter the aquifer. This causes the oxidation of arsenic-bearing pyrite and the release of arsenic, iron, and sulfate into the surrounding water (Das et al., 1995, 1996; Chowdhury et al., 1999). However, this drawdown is typically limited to 3 to 5 m, whereas maximum groundwater arsenic concentrations are found much deeper. Also, the rate of arsenopyrite dissolution is dependent on the availability of oxygen as well as the rate of oxidation of sulfide (Loeppert, 1997), and the arsenic could flush into the underlying aquifer, due to recharge during subsequent monsoon periods.

A second mechanism of arsenic release is via *oxyhydroxide reduction*. This hypothesis, proposed by Nickson et al. (1998, 2000) and McArthur et al., (2001) suggests the possibility that in Late Pleistocene–Recent times, iron- and arsenic-bearing sulfidic minerals in upper reaches of the Ganges river system may have been exposed to the atmosphere due to erosion, and then oxidized. This caused the mobilization of iron and arsenic into the surrounding environment, ultimately leading to dispersion downstream by the Ganges river system (Nickson et al., 1998). The iron released was precipitated as iron oxyhydroxide, and the arsenic was adsorbed and/or coprecipitated with this iron mineral phase. Arsenic-bearing precipitates were then deposited as iron oxyhydroxide coatings on aquifer soil particles in the Gangetic delta region. Following deposition of this fine arsenic-bearing sediment, arsenic is mobilized into the associated groundwater, due to the reductive dissolution of arsenic-rich iron oxyhydroxides (Nickson et al., 1998, 2000), driven by microbial consumption of sedimentary organic matter, which causes strongly reducing groundwater conditions, resulting in the release of Fe(II) and of the As(III) and As(V) present on such coatings. Thus, microorganisms play an important role in oxidizing the organic matter and maintaining reducing conditions in the water system.

Both of these hypotheses were presented in international journals where the origin of the arsenic was the main concern, but field and laboratory research (Ahmed et al., 1998; Nickson et al., 1998) supported the oxyhydroxide reduction hypothesis, suggesting that it is the leading mechanism of arsenic release in the Bengal basin. Several issues should be raised in this regard. First, the release of arsenic by oxidation is very unlikely where the chemistry of the affected water is strongly reducing. A good correlation between iron and arsenic, but not between sulfur and arsenic, is found from the arsenic-affected aquifers through chemical analyses of groundwaters (Smedley and Kinniburgh, 2002, and references therein). Geological studies (Umisto, 1987) based on Bangladeshi and Indian sites failed to show any evidence of arsenic-rich sulfidic mineral deposition either on the surface or in the subsurface in the affected region. Moreover, oxidation of arsenic-bearing sulfidic minerals that causes mobilization of arsenic from these minerals is highly unlikely in the relative oxygen-poor subsurface environment (Von Bromssen, 1999). It has been reported by Ahmed et al., (1998) that evidence for reducing conditions includes direct measurement of redox potential, very low concentrations of dissolved oxygen, nitrate and sulfate combined with high concentrations of iron, manganese, and bicarbonate, plus occurrence of dissolved gases such as carbon dioxide and methane. Furthermore, it has been reported by Nickson et al. (1998) that pyrite is present in a stable diagenetic (framboidal) form, indicating that it has formed after deposition and could be a sink instead of being a source of arsenic.

Notwithstanding these various models, there is a general consensus that microorganisms play a key role in the genesis of arsenic-rich groundwaters. For example, (1) we mentioned above that in oxyhydroxide reduction, there are redox changes induced by microbially driven oxidation of organic matter within the aquifer which cause dissolution of arsenic-bearing Fe(III) oxides and subsequent arsenic release (Nickson et al., 1998, 2000; Bhattacharya et al., 2001; McArthur et al., 2001, 2004; Ravenscroft et al., 2001; Akai et al., 2004; Zheng et al., 2004;

Harvey et al., 2005; Klump et al., 2006), or (2) not only microbes can use Fe(III) directly, within arsenic-bearing Fe(III) oxides, as an electron acceptor causing replacement by Fe(II) phases and/or dissolution with subsequent arsenic release (Cummings et al., 1999; van Geen et al., 2004), (3) but also once released into the groundwater, direct utilization of arsenic as an electron acceptor by them either sequentially after, or in the absence of, Fe(III) reduction (Zobrist et al., 2000; Oremland and Stolz, 2003, 2005; Islam et al., 2004, 2005b; Lloyd and Oremland, 2006) can occur. We explore these possibilities in the next sections with potential examples, including direct DNA-based evidence for this phenomenon for sediments from Bengal (Islam et al., 2004, 2005b).

Microbial reduction of hydrous iron oxides requires a source of degradable organic carbon. This has variously been proposed to be peat layers within sediments (McArthur et al., 2001), other organic carbon within the sediments (McArthur et al., 2004; Gault et al., 2005a), or can be sourced from surface-derived waters carrying modern organic matter that can percolate into the aquifer (Harvey et al., 2002). Harvey et al., (2002) have shown that pumping of tube wells can serve to enhance the arsenic concentrations of the groundwater that they abstract. They reported that young organic matter, flushed into the aquifer due to pumping, was used for microbial respiration, leading to the onset of anaerobic conditions conducive to reductive dissolution of HFOs (hydrous ferric oxides).

In addition to dissolution of the host phase, desorption of arsenic by competing anions such as bicarbonate has also been suggested to account for the presence of arsenic-rich groundwaters in the Bengal delta (Appelo et al., 2002). Nonetheless, the intensive use of phosphate fertilizers can contribute to releasing arsenic into groundwater (Acharyya et al., 1999). Where phosphate concentrations are abnormally high (more than 0.5 mg/L as phosphate), they can cause mobilization of arsenic competing for sorption sites on the iron oxyhydroxides. Furthermore, anthropogenic activities and combustion of fossil fuels can cause the release of arsenic to soil and groundwater systems via precipitation from the atmosphere (Ferguson and Gavis, 1972). Additionally, the reader is referred to the following extensive literature on the distribution, behavior, and origin of arsenic in shallow groundwaters in Bangladesh and West Bengal (BGS/DPHE, 2001; Chakraborti, 2001; Bandyopadhyay, 2002; Smedley and Kinniburgh, 2002; Harvey et al., 2005).

MICROBIAL INTERACTIONS WITH ARSENIC

Throughout evolution, microorganisms have developed the ability to survive in almost every environmental condition on Earth. Their metabolism depends on the availability of metal ions to catalyze energy-yielding and synthetic reactions and on their aptitude to protect themselves from toxic amounts of metals by detoxification processes. Furthermore, microorganisms are capable of transforming a variety of elements as a result of (1) assimilatory processes in which an element is taken up into cell biomass, and (2) dissimilatory processes in which transformation results in energy generation or detoxification (Stolz and Oremland, 1999). Arsenic is called as “essential toxin” because it is required in trace amounts for growth and metabolism of certain microbes but is toxic at high concentrations (Stolz et al., 2002). However, it is now evident that various types of microorganism gain energy from this toxic element, and these reactions have important environmental implications.

Microbial Arsenate Respiration

Bacterial reduction of As(V) has been recorded in anoxic sediments (Ahmann et al., 1994; Dowdle et al., 1996; Newman et al., 1997b; Stolz and Oremland, 1999; Oremland et al., 2000; Oremland and Stolz, 2003), where it proceeds via a dissimilatory process (Dowdle et al., 1996). Specialist bacteria achieve anaerobic growth using arsenate as a respiratory electron acceptor for the oxidation of organic substrates or H_2, quantitatively forming arsenite as the reduction product (Newman et al., 1997b; Stolz and Oremland, 1999; Oremland et al., 2000). The reaction is energetically favorable when coupled with the oxidation of organic matter because arsenate is electrochemically positive; the As(V)/As(III) oxidation/reduction potential is +135 mV (Oremland and Stolz, 2003).

To date, at least 19 species of organisms are known to respire arsenate anaerobically (Ahmann et al., 1994; Macy et al., 1996; Newman et al., 1997b; Stolz and Oremland, 1999; Oremland et al., 2000; Oremland and Stolz, 2003; Hoeft et al., 2004; Oremland et al., 2005) and these have been isolated from freshwater sediments, estuaries, hot springs, soda lakes, and gold mines (Oremland and Stolz, 2003, and references therein; Oremland et al., 2005; Lloyd and Oremland, 2006). They are not confined to any particular group of prokaryotes and are distributed throughout the bacterial domain (Oremland and Stolz, 2003). These microbes are referred to collectively as *dissimilatory arsenate-reducing prokaryotes* (DARPs), and there are other electron acceptors used by these organisms which are strain specific, including elemental sulfur, selenate, nitrate, nitrite, fumarate, Fe(III), dimethyl sulfoxide, thiosulfate, and trimethyamine oxide. For example, *Sulfurospirillum barnesii* (formerly strain SES-3), a vibrio-shaped gram-negative bacterium isolated from a selenate-contaminated freshwater marsh in western Nevada (Oremland et al., 1989, 1994), is capable of growing anaerobically using As(V) as the electron acceptor and can also support growth from the reduction of a variety of electron acceptors, including selenate, Fe(III), nitrate, fumarate, and thiosulfate (Oremland et al., 1994; Laverman et al., 1995). The gram-positive sulfate-reducing bacterium *Desulfotomaculum auripigmentum*, isolated from surface lake sediments in eastern Massachusetts, has been found to reduce both As(V) and sulfate (Newman et al., 1997a,b). DARPs can oxidize a variety of organic and inorganic electron donors, including acetate, citrate, lactate, formate, pyruvate, butyrate, fumarate, malate, succinate, glucose, aromatic hydrogen, and sulfide (Niggemyer et al., 2001). *Chrysiogenes arsenatis*, a dissimilatory arsenate-reducing prokaryote isolated from gold mine wastewater (Macy et al., 1996), can reduce As(V) to As(III) using acetate as the electron donor. The reduction is catalyzed by a terminal arsenate reductase (Arr). Krafft and Macy (1998) described the purification and characterization of this enzyme. Arr from *C. arsenatis* is a heterodimer $\alpha_1\beta_1$, consisting of a major subunit of 87 kDa (ArrA) and a minor subunit of 29 kDa (ArrB) (Krafft and Macy, 1998). The enzyme is located in the periplasm of the cell and contains molybdenum, iron, acid-labile sulfur, and zinc as cofactor constituents and is specific for arsenate. Two gram-positive anaerobic bacteria, *Bacillus arsenicoselenatis* and *B. selenitireducens*, were also isolated from the anoxic muds of Mono Lake, California (Switzer Blum et al., 1998; Oremland et al., 2000). Both grew by dissimilatory reduction of As(V) to As(III) coupled with oxidation of lactate to acetate plus CO_2. Afkar et al., (2003) reported the characteristics of the purified respiratory arsenate reductase of *B. selenitireducens*. It is a membrane-bound heterodimer (150 kDa) composed of two subunits, ArrA (110 kDa) and ArrB (34 kDa). N-Terminal sequence data suggest a 50% sequence identity and 85% similarity of ArrA and ArrB subunits of *C. arsenatis* (Afkar et al., 2003). It should be noted that until now, one obligate arsenate-reducing prokaryote, strain MLMS-1, an anaerobic chemoautotroph isolated from Mono Lake, California, has been identified (Hoeft et al., 2004).

Microbial Arsenite Oxidation

Oxidation of As(III) to As(V) is also known to occur in a range of microorganisms. Over 30 strains representing at least nine genera of arsenite-oxidizing prokaryotes have been identified, including α-, β-, and γ-Proteobacteria, Deinocci (i.e., *Thermus*), and Crenarchaeota (Oremland and Stolz, 2003). These organisms are physiologically diverse and metabolically versatile, and include chemolithoautotrophic arsenite-oxidizing bacteria (CAOs) and heterotrophic arsenite-oxidizing bacteria (HAOs) (Oremland and Stolz, 2003). CAOs gain energy from coupling the oxidation of As(III) to the reduction of oxygen (Ilyaletdinov and Abdrashitova, 1981; Santini et al., 2000) or nitrate to fix CO_2 into cell material and achieve growth (Oremland et al., 2002; Senn and Hemond, 2002). HAOs need organic carbon as their source of energy and cell material. Not all As(III)-oxidizing bacteria conserve energy from As(III) oxidation; several As(III)-oxidizing heterotrophs do not appear to use As(III) as an electron donor for respiration (Anderson et al., 1992), suggesting that microbial oxidation of arsenite to arsenate can be used both for detoxification and for energy generation. The physiological role of arsenite oxidation is best studied in *Alcaligenes faecalis* (Anderson et al., 1992), and an outstanding update of the genetic basis of arsenite oxidation by this soil bacterium has been given in a recent review based on its genome sequence (Silver and Phung, 2005). A novel species of the *Ectothiorhodospira* clade of Eubacteria, designated strain MLHE-1 and isolated from Mono Lake, California, oxidizes arsenite under anoxic conditions using nitrate as the terminal electron acceptor, while it cannot grow on or oxidize As(III) under oxic conditions (Oremland et al., 2002). Recently, nitrate-linked microbial oxidation of As(III) and subsequent immobilization of As(V) have been reported in an arsenic-rich freshwater lake (Senn and Hemond, 2002) and a subsurface aquifer system (Harvey et al., 2002).

Microbial Arsenic Detoxification

Microorganisms sometimes reduce As(V) to As(III) as a means of resistance so that they can cope with high arsenic concentrations in their environments. These microorganisms, called *arsenate-resistant microbes* (ARMs) do not gain energy from this reduction process. Several different mechanisms for arsenic detoxification or resistance have been described. The common themes for the detoxification system are uptake of arsenate by phosphate transporters (Rosenberg et al., 1977), uptake of arsenite by aquaglyceroporins (Sanders et al., 1997; Liu et al., 2002), reduction of the arsenate to arsenite by arsenate reductases (Ji and Silver; 1992; Oden et al., 1994), and export of arsenite from the cells (Ghosh et al., 1999). In addition, arsenic can be methylated for detoxification (Andreae, 1986), although the high toxicity of trivalent methylated arsenicals suggests that this process may increase toxicity rather than contributing toward detoxification (Styblo et al., 2000).

The best studied mechanism of detoxification and resistance, which has been found in bacteria, yeast, and some lower eukaryotes, is the ArsC system (Chen et al., 1986; Mukhopadhyay et al., 2000). When arsenate is taken up, it is reduced to As(III) prior to extrusion or sequestration. ArsC is a small-molecular-mass protein (13 to 16 kDa) that mediates the reduction of As(V) to As(III) in the cytoplasm, and then toxic As(III) can be excreted via an As(III)-specific transporter ArsB. At least three independently evolved families of arsenate reductase enzymes have been recognized (as reviewed in Mukhopadhyay et al., 2002; Rosen, 2002). One family is typified by the arsenate reductase (ArsC) encoded by the *ars* operon of *Escherichia coli* plasmid R773 (Chen et al., 1986). A second family of arsenate reductases is represented by the *ars*C gene product of *Staphylococcus aureus* plasmid pI258 (Ji and Silver, 1992; Ji et al., 1994). The third family of arsenate reductases belongs to the superfamily of protein phosphatases (Hofmann et al., 1998), and is represented by Acr2p from *Saccharomyces cerevisiae* (Mukhopadhyay and Rosen, 1998). The nonrespiratory detoxifying ArsC reductase system differs both functionally and structurally from the respiratory reductase enzyme (Arr). However, recently, *Shewanella* strain ANA-3 has been found to have both respiratory and detoxifying arsenate reductases (Saltikov and Newman, 2003; Saltikov et al., 2003). ANA-3 couples the oxidation of lactate to acetate with the reduction of As(V) to As(III) during its growth.

MINERAL–MICROBE INTERACTIONS: EFFECT ON ARSENIC MOBILIZATION

A number of investigators have hypothesized that microbial Fe(III) reduction is responsible for As solubilization and may be the predominant mechanism by which As is released into solution. Iron can exist in two oxidation states: insoluble ferric (Fe^{3+}) iron, which can be reduced to the more soluble ferrous (Fe^{2+}) iron by a variety of specialist microorganisms. Indeed, Fe(III) reduction is the dominant terminal electron acceptor (TEA) in a range of subsurface environments. A large number of microorganisms are capable of conserving energy for their growth via Fe(III) reduction. The best known group of Fe(III)-reducing bacteria is the family Geobacteraceae, and members of this family have been recovered from a variety of aquatic sediments and subsurface environments using acetate as the electron donor and Fe(III) oxide or the humic acid analog anthraquinone-2,6-disulfonate (AQDS) as the electron acceptor (Lovley et al., 1996, 1998). Binding of As(V) to hydrous manganese, aluminum, and especially, Fe(III) present in sediments has made interpretation of the mechanism of arsenic release complicated. However, the ability of certain bacterial species to reduce Fe(III) to Fe(II) may increase the solubility and mobility of arsenic. Through this process, As(V) could become available for further chemical or biological reduction (Lovley, 1993), leading to the eventual release of any bound arsenic. It is assumed that the reducing conditions occur because of general microbial respiration or fermentation, or a specific role contributed by Fe(III)- or As(V)-reducing bacteria. It has been established by Cummings et al., (1999) that *Shewanella alga* strain BRY, an Fe(III)-reducing bacterium, causes liberation of As(V) from the mineral scorodite ($FeAsO_4{\cdot}2H_2O$) and lake sediments as a result of dissimilatory reduction of Fe(III) to Fe(II).

The biological mechanisms of bacterial reduction of As(V) via a dissimilatory process in anoxic sediments (Ahmann et al., 1994; Dowdle et al., 1996; Newman et al., 1997b) was discussed earlier. It has been proposed that this dissimilatory arsenate reduction (DAsR) activity can increase the mobility of arsenic and hence has a great impact on the speciation and toxicity of arsenic in the environment (Ahmann et al., 1994; Newman et al., 1997b). For example, reduction of As(V) to As(III), catalyzed by *Sulfurospirillum arsenophilum* (Ahmann et al., 1997), released As(III) from sterile sediment containing ferric arsenate. It has now been reported in several studies that DARPs can reduce either aqueous or solid-phase As(V) (Ahmann et al., 1997; Newman et al., 1997b; Nagorski and Moore, 1999), although a fermentative ARM, designated as CN8, has been found capable of reducing only aqueous As(V) and incapable of attacking solid-phase Fe(III) or any As(V) sorbed onto Fe(III) (Langner and Inskeep, 2000). Although not using aquifer sediments, several analogous studies have suggested that in addition to arsenic release via the reductive dissolution of host Fe(III) oxyhydroxides, direct enzymatic reduction of As(V) sorbed to minerals can result in mobilization of soluble As(III). For example, the dissimilatory As(V)-reducing microorganism *Sulfurospirillum barnesii*, capable of growing anaerobically using Fe(III) or As(V) as electron acceptors, reduced and mobilized As(V) that was coprecipitated on ferrihydrite or alumina phases (Zobrist et al., 2000). To date, however, dissimilatory As(V)-reducing bacteria have not been characterized in detail in sediments from West Bengal or Bangladesh, since many As(V)-reducing bacteria are able to respire using other electron acceptors (Oremland and Stolz, 2003), so it seems likely that a subpopulation of Fe(III)-reducing bacteria in Ganges delta sediments could also mobilize arsenic via As(V) respiration. Indeed, microcosm-based studies would support this hypothesis, with (1) the sequential reduction of Fe(III) followed by mobilization of As(III) noted recently in aquifer sediments (Islam et al., 2004; van Geen et al., 2004), and (2) the mobilization of As(III) from sterile sediments by an Fe(III)-reducing enrichment culture (Islam et al., 2004; see below).

ROLE OF INDIGENOUS METAL-REDUCING BACTERIA IN ARSENIC RELEASE FROM BENGAL DELTA SEDIMENTS

Despite the calamitous human health impacts arising from the extensive use of arsenic-enriched groundwaters in these regions, the mechanisms of arsenic release from sediments remain poorly characterized and yet are a topic of intense international debate (Das et al., 1995, 1996; Nickson et al., 1998, 2000; Acharyya et al., 1999; Chowdhury et al., 1999; Harvey et al., 2002; Smedley and Kinniburgh, 2002; Oremland and Stolz, 2003; Akai et al., 2004; Islam et al., 2004). Although the biotic and abiotic processes described earlier may all play a role in arsenic mobilization, it has been concluded that microorganisms play the defining role in catalyzing the redox transformations that ultimately control the mobility of the metalloid (Oremland and Stolz, 2003), and more recently, microcosm-based studies have added further support to the hypothesis that the reduction of As(V)-bearing Fe(III) oxyhydroxides is the dominant mechanism for arsenic release from sediments (Akai et al., 2004; Horneman et al., 2004; Islam et al., 2004; van Geen et al., 2004).

In a recent microcosm-based study, we provided the first direct evidence of the role of indigenous metal-reducing bacteria in the formation of toxic, mobile As(III) in sediments from the Ganges delta using the techniques of microbiology and molecular ecology in combination with aqueous and solid-phase speciation analysis of arsenic (Islam et al., 2004). In this study, sediment samples were collected at a depth of 13 m from a site in the Nadia district, West Bengal, known to have relatively high concentrations of arsenic in the groundwater (Bandyopadhyay, 2002; Chatterjee et al., 2003, Gault et al., 2003). The samples were mixed with artificial groundwater and exposed to a range of biogeochemical conditions to identify the conditions that promote maximal arsenic release from contaminated aquifers in the Ganges delta. As Fe(III) is a significant electron acceptor in these sediments, and the reduction of Fe(III) can support the growth of organisms capable of respiring using sediment-bound As(V) (Zorbist et al., 2000), we focused initially on the speciation of arsenic in the pore water and on the reduction of Fe(III). Our study showed that addition of acetate to anaerobic sediments, as a potential electron donor for metal reduction and a proxy for organic matter, resulted in marked stimulation in the rate of Fe(III) reduction followed by As(V) reduction and release of As(III) (Figure 1C), clearly indicating microbial involvement as well as a function of organic matter as an electron donor driving microbial

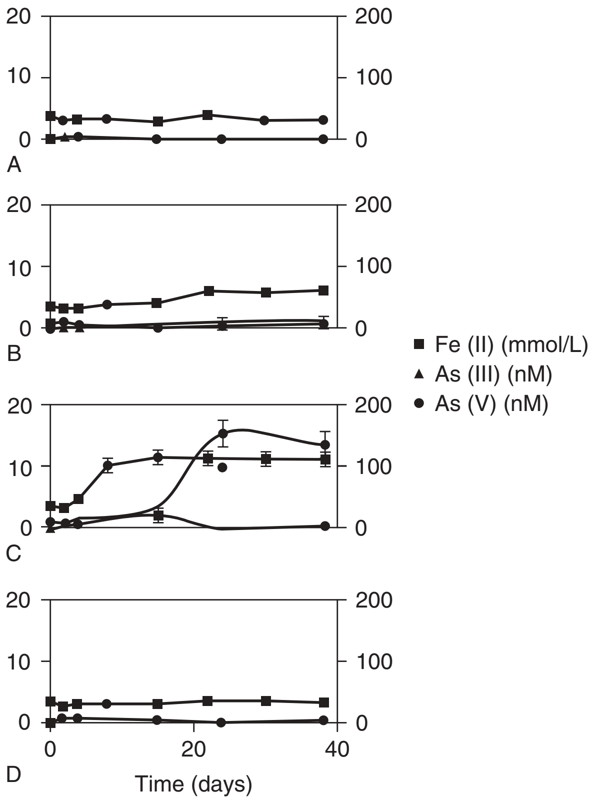

Figure 1 Reduction of Fe(III), and mobilization of arsenic in microcosms incubated under a range of biogeochemical regimes: (A) aerobically; (B) anaerobically; (C) anaerobically with 4 g/L sodium acetate as a proxy for organic matter; and (D) abiotic control sediments with added acetate autoclaved prior to incubation. Each point and error bar represents the mean and standard deviation of three replicate experiments.

respiration in the arsenic cycling of this system. Sediments incubated under aerobic conditions showed very negligible reduction of Fe(III) with time, or release of arsenic from the sediments (Figure 1A), while incubation under anaerobic conditions resulted in Fe(III) reduction concomitant with optimal arsenic mobilization (Figure 1B). Finally, control sediments were autoclaved and then incubated in the presence of acetate, and concentrations of Fe(II), As(V), and As(III) did not increase in these control sediments (Figure 1D), confirming a role for microorganisms in the reduction of Fe(III) and subsequent mobilization of arsenic (Islam et al., 2004). Fe(II) concentration was quantified spectrophotometrically after reaction with ferrozine (Lovley and Phillips, 1986, 1988), total arsenic in solution was assayed by inductively coupled plasma–atomic emission spectrometry

(ICP-AES), and arsenic speciation was analyzed by ion chromatography inductively coupled plasma–mass spectrometry (IC-ICP-MS) using a method adapted from that of Polya et al., (2003) and Gault et al. (2005a). The oxidation state and coordination environment of arsenic associated with the precipitates that had been formed in the reduction experiments was probed using x-ray absorption spectroscopy (XAS). X-ray absorption spectra at the arsenic K-edge were collected at Station 16.5 of the UK CLRC Daresbury Synchrotron Radiation Source operating at 2 GeV with a beam current between 130 and 240 mA. Our ability to exploit different geochemical, mineralogical, and microbiological (both culture-dependent and polymerase chain reaction (PCR)-based molecular techniques) analysis effectively has increased our understanding of the mechanisms involved in microbe–arsenic release interactions. It is a wonder, and the results are extraordinary!

Microbial communities responsible for metal reduction and arsenic mobilization in the stimulated anaerobic sediments were analyzed using both cultivation-dependent and molecular (PCR) techniques. Both approaches confirmed an increase in numbers of Fe(III)-reducing bacteria and therefore suggested a vital role for metal-reducing bacteria in mediating arsenic release. Indeed, sequencing of 16S rRNA gene clone libraries amplified by PCR showed a marked shift in the microbial community present in acetate-amended sediments with a predominance of δ-Proteobacteria, belonging to the Geobacteraceae family, the recognized group of Fe(III)-reducing bacteria known to predominate in Fe(III)-reducing zones of aquifers. Similar DNA-based results have recently been observed by Rowland et al., (2004) for sediments from Cambodia. We found that for the sediments in this study, arsenic release took place, not simultaneously, but subsequent to Fe(III) reduction. Nevertheless, it remains highly probable that the Fe(III)-reducing bacteria, maintained on the relatively high concentrations of Fe(III) in the sediments, played a major role in the subsequent reduction and release of arsenic from sediments once the bioavailable Fe(III) had been utilized as an electron acceptor. However, using both PCR-based molecular techniques and culture-dependent techniques, no previously characterized As(V)-reducing bacteria were detected in any of the acetate-amended sediment samples used in the study. These results suggest that either direct enzymatic microbial reduction of As(V) by Fe(III)-reducing bacteria or indirect mechanisms associated with the reduction of Fe(III) oxides [e.g., reductive dissolution of host Fe(III) oxyhydroxides or reduction of As(V) via microbially generated Fe(II)] could be important mechanisms for arsenic release in these sediments, with the involvement of *Geobacter* species implicated in these transformations. Our results also suggest that the capacity for arsenic release was limited severely by the availability of electron donors in the sediments from our test site. This lends support to theories that the delivery of surface-derived organic carbon into subsurface communities driven, for example, by changes in hydrology due to irrigation pumping (Harvey et al., 2002) may have a dramatic role in enhancing arsenic mobility in shallow groundwaters in the Ganges delta.

POTENTIAL ROLE OF Fe(III)-REDUCING BACTERIA *Geobacter* AND *Geothrix* SPECIES IN CONTROLLING ARSENIC SOLUBILITY AND MOBILITY IN BENGAL DELTA SEDIMENTS

Multiple studies have shown that members of the family Geobacteraceae predominate in subsurface anoxic environments where Fe(III) reduction is a significant terminal electron-accepting process (Coates et al., 1996). Indeed, research has shown that when sediments are amended with acetate to stimulate iron reduction, the numbers of Geobacteraceae bacteria increase by several orders of magnitude (Snoeyenbos-West et al., 2000; Holmes et al., 2002; Islam et al., 2004; Rowland et al., 2004). In these environments they play a dominant role in the degradation of organic matter. Their metabolism involves redox transformations of metal(loids), which lead to the precipitation, transformation, or dissolution of minerals, thus controlling the mobility of toxic metals and radionuclides (Lloyd, 2003). Given the environmental importance of this group of bacteria, considerable research activity has focused on the physiology and biochemistry of *Geobacter* species (Lovley, 2003). Although *Geobacter* species have not been reported to reduce As(V), these organisms do have the physiological capacity to reduce a wide range of metals and metalloids (Caccavo et al., 1994; Lloyd et al., 2003) via a battery of *c*-type cytochromes (Methe et al., 2003). We therefore conducted a detailed analysis of the potential of a model *Geobacter, G. sulfurreducens*, a well-characterized Fe(III)-reducing bacterium, to reduce and mobilize arsenic (Islam et al., 2005a). *Geobacter sulfurreducens*, which commonly serves as the model organism for the Geobacteraceae in the subsurface environments, has all the important metabolic features of the *Geobacter* species. More important, the full genome sequence of this organism was accessible, which showed the presence of a putative arsenic resistance operon potentially catalyzing the enzymatic reduction of As(V) to As(III) (Methe et al., 2003).

Investigations using *G. sulfurreducens* showed that despite the presence of a putative arsenic resistance operon, and the abundance of *c*-type cytochromes potentially involved in metal reduction identified in the genome (Methe et al., 2003), this organism does not have the potential to reduce arsenic enzymatically both in culture and in As(V)-bearing sediments, therefore supporting the hypothesis that *G. sulfurreducens* cannot respire through the dissimilatory reduction of As(V). However, when the cells were grown using soluble chelated Fe(III) and insoluble ferrihydrite as electron acceptors in the presence of As(V), microbial Fe(III) reduction resulted in the precipitation/and formation of the Fe(II)-bearing minerals vivianite and magnetite, respectively, studied by x-ray diffraction (XRD). This was accompanied by the removal/sorption of As, predominantly as As(V), from solution (Islam et al., 2005a). Environmental scanning electron microscopy (ESEM) with energy dispersive spectroscopy (EDS) confirmed the presence of iron, arsenic, and/or phosphorus in biominerals obtained from the cultures (Figure 2). The formation of phosphate minerals has frequently been observed in sedimentary environments under high biological productivity (Konhauser, 1997), where organic matter serves as a source of phosphate

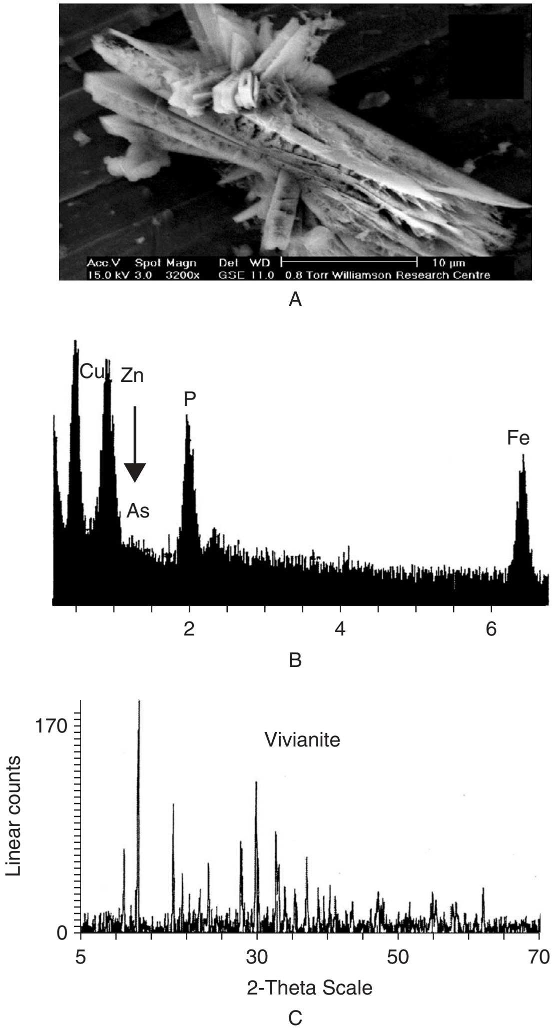

Figure 2 Removal of arsenic by biogenic vivianite formed by *G. sulfurreducens*: (A) ESEM image of biogenic vivianite; (B) EDS spectrum of vivianite; (C) identification of vivianite by XRD.

to sediment pore water through bacterial degradation (Beveridge et al., 1983). In our experiments the phosphate was present as a constituent of the growth medium, which reacted with biogenic ferrous iron, leading to the formation of a new mineral phase with the potential to sorb arsenic. The microbial precipitation of ferrihydrite is widespread in nature. It has been found associated with bacteria growing in marine sediments (Konhauser, 1996), acid mine drainage environments (Ferris et al., 1989a), rivers (Konhauser et al., 1993), and deep groundwater (Sawicki et al., 1995); around deep-sea vents (Juniper and Fouquet, 1988); and on exposed rock surfaces (Konhauser et al., 1994). Iron mineralization has commonly been divided into two modes: biologically controlled mineralization and biologically facilitated mineralization (Konhauser, 1997): as, for example, magnetite formation by magnetotactic bacteria, representing biologically controlled mineralization in which the particles are formed inside bacterial cells templated by a specific internal membrane (Blakemore, 1991). Conversely, magnetite formation by Fe(III)-reducing bacteria, *Thermoanerobacter ethanolicus*, TOR-39 (Zhang et al., 1998), or *Geobacter metallireducens*, GS-15 (Lovley et al., 1987), represents biologically induced mineralization in which the particles are formed extracellularly as a by-product of microbial Fe(III) respiration. In addition to vivianite and magnetite, a range of alternative Fe(II) biominerals are produced by Fe(III)-reducing bacteria, depending on geochemical and mineralogical constraints (Postma, 1981; Zhang et al., 1997, 1998; Fredrickson et al., 1998). For example, siderite ($FeCO_3$) is frequently observed as a diagenic precipitate in aquatic sediments (Pye et al., 1990; Mortimer and Coleman, 1997), where its formation is generally associated with the bacterial respiration of organic matter or hydrogen coupled to dissimilatory Fe(III) reduction in a reducing environment with CO_2 production and high alkalinity (Suess, 1979; Fredrickson et al., 1998; Roh et al., 2003): conditions encountered in sediments in the Ganges delta (Shanker et al., 2001; Pal et al., 2002;). The conversion of Fe(III) oxyhydroxides to secondary Fe(II) phases such as vivianite, magnetite, siderite, or green rust under reducing conditions, is a possibility (Horneman et al., 2004); these phases can be either authigenic or biogenic (Horneman et al., 2004; Smedley and Kinniburgh, 2002; Shanker et al., 2001; Pal et al., 2002). The interaction between biotic and abiotic factors involved in mineralization is poorly understood (Lovley, 1991a, 1993; Zhang et al., 1998), but it is well recognized that microbial metal reduction and mineral formation not only play an important role in cycling of metals, carbon, nitrogen, phosphate, and sulfur in natural and contaminated subsurface environments (Lovley, 1991; Nealson and Saffarini, 1994), but also affect the speciation and fate of a variety of trace metals and nutrients in anoxic subsurface environments (Lovley, 1995; Fredrickson et al., 2001; Roh et al., 2001). We also studied the interactions of biogenic siderite (ferrous carbonate) with As(V), which was also able to remove arsenic from solution (Figure 3). It should be noted that biogenic siderite was obtained from a stable Fe(III)-reducing consortium enriched from brackish waters where siderite was implicated as a dominant iron biomineral (Adams, L. K. personal commmunication). The low concentrations of arsenic remaining in solution were analyzed by IC-ICP-MS and were approximately 3% As(V) and 98% As(III) at both starting concentrations. XAS analysis showed that the arsenic associated with the biomineral phase was a mix of 50% As(V) and 50% As(III), suggesting abiotic reduction of the pentavalent arsenic by Fe(II) and retention of the reduced As(III) by the siderite (Islam et al., 2005a). These results demonstrate that the Fe(II)-bearing mineral siderite is also able to sorb As(V) and As(III) effectively, suggesting that some Fe(II)-bearing minerals can abiotically reduce As(V), but this is probably not an important

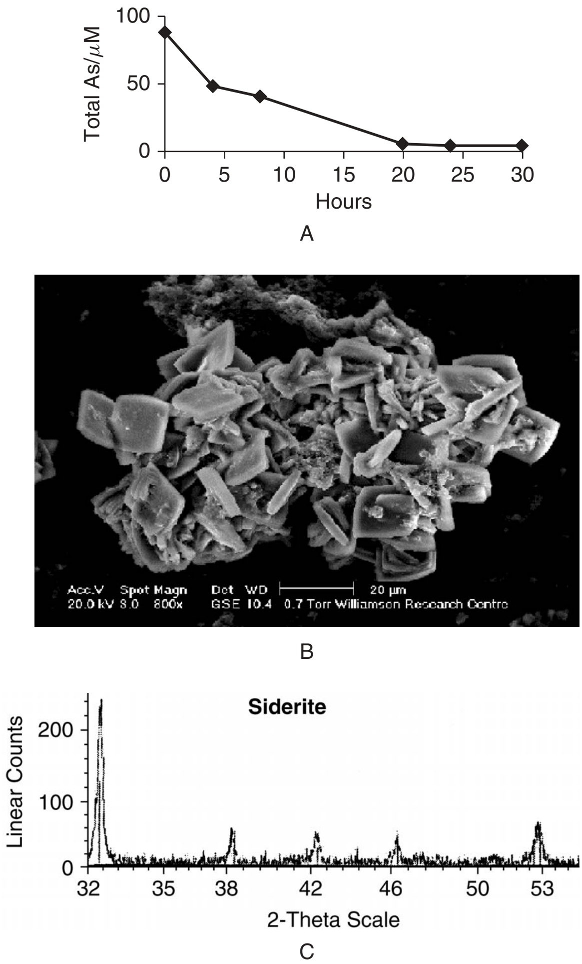

Figure 3 Removal of arsenic (as arsenate) by biogenic siderite: (A) arsenic removal by preprepared siderite; (B) ESEM image of biogenic siderite; (C) identification of siderite by XRD.

mechanism for As(III) mobilization. Instead, other mechanisms are implicated, including the involvement of other specialist As(V)-reducing prokaryotes, possibly sustained initially through respiration using the more abundant bioavailable Fe(III) oxides in the sediments (Islam et al., 2004). The identification of these organisms remains a crucial step in understanding the biogeochemical basis of As(V) reduction and mobilization of As(III) in "at risk" aquifers.

Previous studies from our laboratory have also shown that a stable enrichment culture of Fe(III)-reducing bacteria was able to mobilize arsenic [as As(III)] from sediments collected from West Bengal (Islam et al., 2004). We made a detailed molecular analysis of this enrichment culture to identify the Fe(III)-reducing bacteria that may play a role in the reduction of As(V) and mobilization of As(III) (Islam et al., 2005). A 500-base pair (approx.) region of the 16S rRNA gene was amplified by PCR using broad-specificity bacterial primers, cloned and typed using RFLP analysis. The sequences showed that more than 60% of DNA fragments in the clone library were derived from a close relative of *Geothrix fermentans* (97% sequence homology over 489 to 504 base pairs), which are Fe(III)-reducing bacteria associated with metal-reducing subsurface communities (Nevin and Lovley, 2000). However, while working with the type strain of this organism, it was found to be unable to conserve energy for growth via the dissimilatory reduction of As(V) or to reduce As(V) present in a defined medium containing fumarate as the electron acceptor. Despite this, when the cells were grown using soluble Fe(III)-citrate as an electron acceptor in the presence of As(V), bacterial Fe(III) reduction further resulted in the precipitation of the Fe(II)-bearing mineral vivianite, which was once again accompanied by the efficient removal of arsenic from solution. These results demonstrate that *G. fermentans*, in common with other key Fe(III)-reducing bacteria, such as *G. sulfurreducens*, does not reduce As(V) enzymatically but can capture arsenic in Fe(II) minerals formed during respiration using Fe(III) as an electron acceptor (Islam et al., 2005b). These results also demonstrate that the reduction of As(V)-bearing Fe(III) oxides may not be sufficient to mobilize As(V) in aquifer sediments, as hypothesized previously (van Geen et al., 2004), but they do add weight to the view that biogenic Fe(II)-bearing minerals can act as a sink for the metalloid. It has been reported that vivianite [$Fe_3(PO_4)_2$] and siderite ($FeCO_3$) are present in groundwaters of the Bengal basin because of elevated concentrations of phosphate and carbonate (BGS/DPHE, 2001). Several studies showed that some other components, such as siderite concretions, biotite, chlorite, and coated iron oxyhydroxides with residual magnetite and ilmenite, store arsenic and are identified as arsenic pollutants for groundwater in areas of the Bengal basin (Shanker et al., 2001; Pal et al., 2002). These pollutants are considered to have arsenic adsorbed onto their surfaces. The growth of authigenic siderite concretions is believed to be biogenic and controlled by the activity of microbes (Shanker et al., 2001) present in the subsurface sediments. Therefore, the mobility and adsorption of As in the environment depend not only on As(III)/As(V) speciation but also on the mineralogy of the soil, sediment, or groundwater material. Adsorption of dissolved arsenic on mineral surfaces regulates pore water arsenic concentrations in soils and sediments (Holm et al., 1980; Belzile and Tessier, 1990). These mineral surfaces provide a ubiquitous arsenic-trapping process in environments [e.g., ferrihydrite is considered as one of the most reactive soil components in regard to arsenic sorption and can take up hundreds of mg/kg arsenic, as either As(III) or As(V)] (Goldberg, 2002, and references therein). Indeed, numerous studies have been made of arsenic sorption reactions on mineral surfaces, especially on amorphous aluminum and iron oxides (Pierce and Moore, 1980, 1982; Raven et al., 1998; Goldberg and Johnston, 2001; Dixit and Hering, 2003, and references therein) and goethite (Matis et al., 1997, 1999;

Manning et al., 1998; Lenoble et al., 2002; Lin and Puls, 2003; Sherman and Randall, 2003) in addition to siderite (Pal et al., 2002) and greenrust (Lin and Puls, 2003). The reader is referred to these comprehensive reviews on this issue.

CONCLUSIONS

The microbially mediated release of sediment-hosted arsenic into shallow groundwaters used as drinking and irrigation water, especially in West Bengal and Bangladesh, is having a massive impact on human health. The principal aim of this chapter was to discuss the microbial processes that affect the solubility and mobility of arsenic in West Bengal sediments as well as to characterize As(III) release mechanisms in detail. Previously, some researchers predicted the possibility of a limited role for microorganisms in the mechanism of the release of arsenic into groundwater (McArthur et al., 2001, 2004; Oremland and Stolz, 2003), However, the evidence that we received from our microcosm-based study was just breathtaking! It provided the first direct confirmation that the model can explain the importance of the role of indigenous metal-reducing bacteria in arsenic mobilization from Bengal delta sediments (Islam et al., 2004). Research has also shown that during the experimental periods, the rate and extent of Fe(III) and As(V) reduction remained relatively low unless a supply of organic matter (acetate) was introduced into the sediment samples. This suggests that migration of surface-derived organic carbon into the subsurface environment (possibly because of irrigation practices) may have a role in enhancing arsenic levels. The importance of these results gives us the opportunity to work more to assess the control of organic matter on arsenic release and the behavior of the associated microbial communities with the relevant organic matter. Certainly, there is much more to be deciphered: for example, characterizing the nature and extent of the organic matter present in the aqueous and solid phases in arsenic-contaminated subsurface aquifers and identifying the types and components of organic matter utilized by organisms into these environments. For example, in a recent study, Rowland et al., (2006), characterized sediment samples collected from a range of depths (8 to 29.7 m) from a similar study site in the Nadia district, of West Bengal, and determined the composition of organic matter present in the aquifer and found within these sediments petroleum that appeared to be undergoing biodegradation, suggesting that these sediments had been utilized in situ by the microbial community. Determining the precise roles of each species within the microbial community would be beneficial in drawing possible conclusions about bacterial interactions leading to elevated concentrations of arsenic in the shallow aquifers. For example, which species are responsible for breaking down complex organic matter: Fe(III) reduction, As(V) reduction, or even As(III) oxidation? Together with all of this information, it would be possible to come up with a conceptual model for microbially mediated release of arsenic into shallow groundwaters, and this might help to develop models to control groundwater pumping practices on the occurrence of arsenic in drinking water.

We found that neither *G. sulfurreducens* nor *G. fermentans* is capable of reducing As(V) either by direct enzymatic reduction in axenic culture or by indirect reduction via microbially generated Fe(II) and mobilizing arsenic in autoclaved sediment microcosms. However, when provided with soluble chelated Fe(III)/insoluble ferrihydrate in the growth medium in the presence of added As(V), the microbial reduction of Fe(III) led to the formation of various Fe(II)-bearing phases (vivianite, magnetite) that are able to capture arsenic species (Islam et al., 2005a). The secondary mineral phases produced by these two Fe(III)-reducing bacteria could play an important role as potential sinks for arsenic species in shallow aquifers exploited for groundwater in the Bengal delta. Therefore, the complex interplay between Fe(III)-reducing bacteria and their mineral substrates requires further investigation, both on a fundamental level and in relation to the impact on arsenic solubility. For example, it was noted that a range of Fe(II)-bearing biominerals (e.g., vivianite, siderite, magnetite) that could act as host mineral phases for arsenic were produced under specific conditions, but the underlying causes of these differences remain to be investigated. This emphasizes the significance of understanding the bacterial controls on the formation of different mineral precipitates (e.g., the involvement of specific bacteria or mixed microflora), or are other geochemical factors involved (e.g., pH or different concentrations of phosphate and carbonate ions)? Previous studies showed that microbial formation of carbonate minerals and iron oxides may play a crucial role in the immobilization of trace metals (Co, Cr, Ni) which are readily incorporated into the magnetite and siderite crystal structures formed by Fe(III)-reducing bacteria (Fredrickson et al., 2001; Roh et al., 2001). Given the abundance of iron in arsenic-contaminated subsurface environments, iron biomineralization could have a significant impact on controlling arsenic concentration in the contaminated aquifer systems.

It has been implicit in our studies (Islam et al., 2004, 2005a) and in some other studies (Rowland et al., 2004) that *Geobacter* species may play a significant role in arsenic reduction and mobilization in subsurface aquifers and that *Geothrix* species that were dominant in a stable consortium of Fe(III)-reducing bacteria was also able to reduce and mobilize sediment-bound arsenic from West Bengal sediments. Since our model organisms (*Geobacter sulfurreducens* and *Geothrix fermentans*) did not reduce As(V) or mobilize sorbed arsenic in sterilized sediments, the question remains whether there are other *Geobacter* or *Geothrix* species that function as dissimilatory As(V)-reducing prokaryotes and play a direct role in arsenic reduction and mobilization, and which specific microbial community or microbial mechanisms are involved in arsenic dissolution and mobilization. It would seem sensible to obtain *Geothrix* species from Southeast Asian aquifer sediments and to define their roles in arsenic mobilization. It is clear that microbial reduction of As(V)-bearing Fe(III) oxyhydroxides alone is not sufficient to mobilize significant quantities of arsenic from sediments collected from the Ganges delta, and direct microbial reduction of As(V) may therefore be required for the mobilization of this metalloid. Alternatively, other As(V)-respiring organisms, such as *Bacillus* sp., *Shewanella* sp., and *Sulfurospirillum* sp., could also play a role in this activity but be present in the sediments at concentrations below those detectable using our PCR-based techniques. While working with arsenic-contaminated sediments obtained from a range of depths (8 to 45 m), Gault et al., (2005b) found that the composition of the microbiological community in the 24-m sediment exhibiting the maximum arsenic release showed the relative abundance of *Acinetobacter* species, which was found in some other studies as arsenic-resistant isolates in arsenic-contaminated environments (Clausen, 2000; Anderson and Cook, 2004; Turpeinen et al., 2004). Nonetheless, isolation of arsenate-respiring bacteria from the contaminated sites is an important issue given the probable role of these organisms in mobilizing arsenic to groundwaters used for drinking and irrigation.

Molecular techniques are available that could help clarify the role of key organisms and genes in arsenic mobilization (e.g., PCR-based techniques using functional gene probes). However, we still have much to learn about the precise mechanisms for microbial arsenic dissolution in sediments, but molecular tools can be used broadly to identify the microbial agents of arsenic mobilization in subsurface materials. For example, Malasarn et al., (2004) have developed a set of degenerate primers based on the *arrA* (arsenate respiratory reductase) gene to detect the presence and/or expression of this gene in environmental samples. The PCR primer is specific to a portion of the *arrA* gene of the dissimilatory arsenate reductase and was used to amplify and sequence the DNA of a diverse group of isolated As(V) reducers as well as uncultured As(V)-respiring organisms recovered from arsenic-rich sediments. In addition, *arrA*-specific mRNA transcripts appeared to be expressed in arsenic-contaminated sediments where As(V) reduction was thought to occur. The use of primers for amplification of the arsenite oxidase of chemoautotrophic arsenite oxidizers (Santini and vanden Hoven, 2004) would also be of great benefit to investigate the reversal of As(V) reduction and mobilization. For example, nitrate-stimulated microbial oxidation of As(III) and subsequent immobilization has been reported in groundwater environments (Harvey et al., 2002), and the microbes responsible for this transformation remain to be identified. Thus, a better understanding of what stimulates As(III) oxidation and/or limits As(V) reduction would provide a model for bioremediation of contaminated sites.

Once the genes and gene products that catalyze these relevant reactions are understood, as well as the conditions that trigger their expression, it would be possible to predict which organisms are involved, how these organisms operate, and how their metabolisms influence arsenic cycles in these contaminated shallow aquifer systems in Ganges delta. The dynamic behavior of microorganisms and the possibility of combining a range of interdisciplinary fields with advance techniques that are required for meticulous study of arsenic release mechanisms in groundwater systems make this investigation exciting and challenging!

Acknowledgments

The work presented here is a part of F.S.I.'s Ph.D. research, which was conducted at the University of Manchester under the supervision of Jonathan R. Lloyd and David A. Polya. These investigations had been published in several international peer-reviewed journals. The work was supported by grants from EPSRC, the Bangladesh Ministry of Science and Technology (Bangabandhu Fellowship to FSI), the University of Manchester (the Vice Chancellor's Fund to F.S.I.), CVCP (the ORS award to F.S.I.), The Royal Society, GV Instruments, and NERC. XAS work was supported by beamtime awards at Daresbury SRS by CCLRC. Many thanks to Satinder Ahuja for the invitation to contribute to this book.

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4

MOLECULAR DETECTION OF DISSIMILATORY ARSENATE-RESPIRING BACTERIA IN NORTH CAROLINA GROUNDWATER

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INTRODUCTION

Arsenic is a naturally occurring metalloid that is widely distributed in the environment. In its inorganic form, it occurs in four major oxidation states: As^{5+}, As^{3+}, As^0, and As^{3-}. The most predominant of the inorganic forms are arsenate [As(V)] and arsenite [As(III)], which are the forms of most concern for human exposure [11]. Arsenic comes from various natural sources, including the weathering of rocks, fossil fuels, marine sedimentary rocks, various minerals, and volcanic activities in igneous rock [8,11,19]. Along with natural sources, anthropogenic sources also contribute to the amount of arsenic in the environment. Some of these sources include acid mine drainage, coal combustion, pigment production, treated lumber, and farm-raised animals that are fed food enriched with arsenic to prevent bacterial diseases [11].

Arsenic Contamination of Groundwater: Mechanism, Analysis, and Remediation,
Edited by Satinder Ahuja

Regardless of the source, arsenic is being detected at high concentrations in many drinking water wells around the world. The best known place for arsenic contamination in drinking water is Bangladesh, where people are being slowly poisoned by arsenic on a daily basis. This poisoning causes arsenicosis, which is the name for a set of symptoms caused by arsenic exposure. These symptoms include changes in the color of a person's skin, keratosis of the palms and soles of the feet, and many types of cancer [20]. In addition, many people in Taiwan have developed a condition known as black foot disease in which the blood vessels in the extremities become diseased and gangrene sets in [11]. Arsenic in drinking water is also a serious concern in the United States. The criteria for arsenic in drinking water in the United States, as set by the U.S. Environmental Protection Agency (EPA) in 2002, is 10 parts per billion (ppb) [3]. However, many residential wells are not tested and therefore are not maintained to meet this standard.

North Carolina is a place affected by high arsenic concentrations. In the western part of the state, in the Piedmont region, arsenic is detected at levels far surpassing the 10-ppb limit, with concentrations ranging from 1 ppb upward to 110 ppb. In Stanly, Union, and Chatham counties, for example, the probability that the arsenic concentration in a well will be greater than 1 ppb is 62%, 51%, and 38%, respectively [15]. The main reason for these high arsenic levels is not fully understood, but the geology of the region could be a contributing factor since the area known as the Carolina Slate Belt has basins filled with river and volcanic deposits, has a complex geothermal system, and contains many uranium- and gold-mining areas [21]. Thus, high arsenic levels in North Carolina groundwater could be related to geological and environmental factors [4,5].

Microbial activities involved in the reduction of arsenate to arsenite also control the mobility and toxicity of arsenic in aquatic environments [11]. The reduction of arsenate to arsenite causes less adsorption of arsenic to other mineral surfaces, which leads to arsenic mobilization in aquatic systems. Microbial reduction of arsenic has been found as a part of various defensive mechanisms for microorganisms to survive in arsenic-contaminated environments [18]. A wide range of microorganisms were identified as performing arsenate reduction as a strategy for detoxification. Arsenic-resistant microorganisms have enzymes that reduce arsenate to arsenite coupled to an arsenite efflux system (ARS) [18]. Alternatively, other arsenate-reducing microorganisms can utilize arsenate as a terminal electron acceptor in dissimilatory arsenate reduction (DAR).

Dissimilatory arsenate-respiring bacteria (DARB) have a significant impact on the mobilization of sorbed arsenic into aquatic environments under anoxic conditions. *Sulfurospirillum arsenophilum*, a DARB isolate, is able to release arsenite from an initial solid phase consisting of ferrous arsenate as well as from arsenate-adsorbed alumina after the reduction of arsenate to arsenite [2]. Furthermore, some DARB are capable of iron reduction as one of their alternative respiratory systems and are able to reduce Fe(III) and arsenate to Fe(II) and arsenite, respectively [13], which leads to an increase in the levels of arsenic contamination in anoxic aquifers.

Microbial communities consisting of iron reducers and DARB are also capable of increasing the arsenic contamination in groundwater systems. Arsenate, instead of arsenite, can be released from Fe(III) by iron-reducing bacteria, which reduce Fe(III) to Fe(II). The arsenate released can be reduced to arsenite by DARB, which prevent readsorption onto other mineral surfaces and increase the arsenic concentration in aquatic systems. Therefore, the abundance and activities of DARB could determine the fate and transport of arsenic in groundwater and could lead to human arsenicosis when arsenic-contaminated groundwater is consumed.

DARB have been studied extensively to understand their physiology and activities involved in arsenic mobilization in anoxic environments. Diverse DARB were isolated from various environmental samples, and the taxonomic diversity of these isolates was revealed by phylogenetic analyses [12]. Biochemical studies of the DARB isolates showed the presence of a periplasmic enzyme that is capable of reducing dissolved or adsorbed arsenate under anoxic conditions [13]. The periplasmic enzymes were recently purified from *Chrysiogenes arsenatis* and *Bacillus selenitireducens* [1,6] and the functional genes encoding arsenate respiratory reducutases (*arr*AB) were identified in several DARB isolates belonging to Proteobacteria and gram-positive bacteria [10,14,16]. The expression of *arr*A genes in *Shewanella* sp. ANA-3 corresponded to the release of arsenite from arsenate-saturated $Fe(OH)_3$ following arsenate reduction [10]. Most studies were based on the DARB isolates obtained from arsenic-contaminated environments. However, uncultured DARB present in arsenic-contaminated sites could be far more significant and may carry out an actual reduction of arsenate instead of the isolates obtained from these environments, since isolation biases select the best-adapted bacteria to be cultivated from total DARB communities. To understand the significance of DARB in arsenic contamination, we conducted this study with two different water samples collected from drinking water wells located in western North Carolina, where high levels of arsenic were detected due to the desorption of arsenic from natural sources. We examined the diversity of uncultured DARB with molecular methods and monitored arsenate-reducing activities in well water using enrichment culture techniques to determine the involvement of DARB in the arsenic contamination in North Carolina groundwater aquifers.

MATERIALS AND METHODS

Sample Collection

Water samples were collected from two contaminated wells (D and R) in the western part of North Carolina (Figure 1). Water was pumped directly out of the wells into 5-L jugs at each site and placed in a cooler until filtered in our laboratory. The levels of arsenic in both wells were reported from the NCDENR monitoring program. Well R is located in Wingate, North Carolina and has 150 ppb of dissolved arsenic. Well D is located in Monroe, North Carolina and has

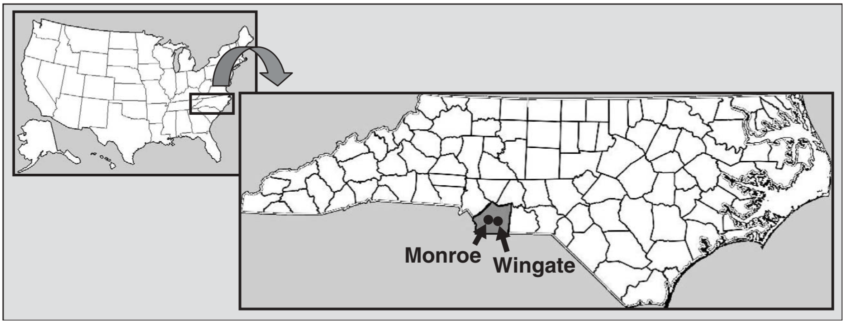

Figure 1 Well water sampling sites in western North Carolina. (*See insert for color representation of figure.*)

TABLE 1 Levels of Arsenic and Other Metals in Two Drinking Water Wells in North Carolina

Metal	Well R (μg/L)	Well D (μg/L)
Aluminum	<50	<50
Arsenic	150	73
Cadmium	<2	<2
Chromium	<25	<25
Copper	17	3.8
Iron	<50	<50
Lead	<10	<10
Magnesium	6100	8800
Manganese	150	<10
Nickel	<10	<10
Selenium	19	14
Zinc	46	<10

73 ppb of arsenic. Concentrations of other metals are also reported from the monitoring program (Table 1).

DNA Extraction from Filters

Water samples (1 L) from both wells D and R were filtered onto 0.22-μm Millipore Sterivex filter units (Millipore Corporation, Billerica, Massachusetts). Genomic DNA was extracted from the filters using Gentra's Puregene Genomic DNA Purification Kit (Gentra Systems, Inc., Minneapolis, Minnesota) with a modified protocol. One end of the filter was sealed with parafilm, and 900 μL of cell lysis solution was pipetted into the filter. The other end of the filter was then sealed with parafilm and incubated at 80°C for 10 minutes. Using a

1-mL syringe, the lysate was taken from the filter and placed into two 1.5-mL tubes. RNAse A solution (1.5 μL) was added to each tube and the tubes were then inverted 25 times. Both tubes were placed in a 37°C incubator for 1 hour. The tubes were removed and placed on ice for 1 minute. Protein precipitation solution (100 μL) was added to each tube and the samples were vortexed for 20 seconds. The samples were then centrifuged for 3 minutes at 14,000 rpm. Avoiding the protein pellet, the supernatant from each sample was pipetted into two 1.5-mL tubes containing 300 μL of 100% isopropanol. The tubes were inverted gently 50 times and centrifuged at 14,000 rpm for 1 minute. While watching the pellet, the supernatant was aspirated off, and 300 μL of 70% ethanol was added to both tubes and inverted several times to wash the DNA. The tubes were centrifuged for 1 minute at 14,000 rpm and the supernatant was again aspirated. The tubes were drained on absorbent paper for 15 minutes and then 30 μL of the DNA hydration solution was added. The tubes were vortexed for 5 seconds and incubated at 65°C for 1 hour or at room temperature overnight. The DNA extracted was quantified using the Quant-iT dsDNA HS Assay Kit according to the manufacturer's protocol (Invitrogen, Eugene, Oregon).

PCR Detection of *arr*A Genes

Nested PCR (polymerase chain reaction) was performed to amplify *arr*A genes from the environmental DNA with the modified method of Lear et al. [7]. DNA from *Desulfitobacterium hafniense* DCB-2 was used as the positive control. An initial PCR was set up in 0.6-mL PCR tubes, with 2.5 μL of 10x Advantage 2 PCR buffer, 0.4 μM of primers As1F and ArrA1R (Table 2), 20 μM of dNTPs, 0.5 μL of 50x Advantage 2 polymerase, and 1 μL of DNA template. The PCR cycle began with an initial denaturation step of 95°C for 5 minutes and 35 cycles of a 95°C denaturation for 1 minute, a 55°C annealing step for 30 seconds, and a 72°C elongation for 2 minutes. A second PCR was set up using 2.5 μL of 10x PCR buffer [500 mM KCl, 200 mM Tris-HCl (pH 8.4)], 1.5 mM of a 25-mM $MgCl_2$, 0.4 μM of both As2F and As1R primers (Table 2), 20 μM dNTP, and 1 U of Taq polymerase. The first reaction (1 μL) was used as a template for the second PCR. The nested PCR cycle began with a 2-minute denaturation at 95°C, followed by 30 cycles of a 95°C denaturation for 30 seconds, a primer annealing at 55°C for 30 seconds, and a 1-minute extension at 72°C. The amplified products were

TABLE 2 Primer Sequences Used to Amplify *arr*A Genes

Primer	Primer Sequence
ArrA1R	5′-ATANGCCCARTGNCCYTGNG-3′
As2F	5′-CTCCCNATBASNTGGGANRARGCNMT-3′
As1F	5′-GAAGTTCGTCCCGATHACNHGG-3′
As1R	5′-GGGGTGCGGTCYTTNARYTC-3′

examined on a 1.0% agarose gel by electrophoresis and then were purified using a Perfectprep Gel Cleanup Kit (Eppendorf AG, Hamburg, Germany) according to the manufacturer's instructions.

Cloning and Sequencing

The cleaned PCR products were used for direct cloning with the TOPO-TA cloning system (Invitrogen, Carlsbad, California) following the manufacturer's instructions. The ligated plasmids were transformed in high-transforming-efficiency *Escherichia coli* TOP10 cells (Invitrogen) following the manufacturer's instructions. The transformed cells were plated on Luria agar plates containing 50 μg/mL kanamycin with X-gal. At least 30 clones from each cloning reaction were selected for sequencing on an ABI 3100 automated DNA sequencer (Applied Biosystems, Foster City, California) using Big-Dye terminator chemistry (Applied Biosystems).

Phylogenetic and DOTUR Analyses of *arr*A Genes

The sequences obtained were BLAST searched using NCBI's BLAST-X search engine (www.ncbi.nih.gov). Putative *arr*A gene sequences were assembled using the DNASTAR Lasergene SeqMan Program (DNASTAR, Inc., Madison, Wisconsin). A sequence alignment and phylogenetic analysis were conducted using the MEGA 3.1 (Molecular Evolutionary Genetics Analysis) program. The *arr*A gene sequences in *Shewanella* sp. ANA-3 (AY271310), *Shewanella* sp. HAR-4 (AY660886), *Shewanella* sp. W3-18-1 (NC_008750), *Chrysiogenes arsenatis* (AY 660883), *Geobacter uraniumreducens* Rf4 (NC_009483), *Bacillus arseniciselenatis* (AY660885), *Bacillus selenitireducens* (AY283639), *Sulfurospirillum barnesii* (AY660884), *Wolinella succinogenes* (NC_005090), *Desulfosporosinus* sp. Y5 (DQ220794), *Desulfitobacterium hafniense* Y51 (NC_007907), *D. hafniense* DCB-2 (NZ_AAAW04000004), *Alksliphilus metalliredigenes* QYMF (NC_009 633), Delta Proteobacterium MLMS-1 (NZ_AAQF01000046), and *Clostridium* sp. OhiLAs (NZ_AAQV01000002) were obtained from the GenBank database to use as references for phylogenetic analysis.

The DOTUR (distance-based OTU and richness) program was utilized to compare the diversity of the *arr*A gene sequences from each sampling site [17]. A 2% difference in nucleotide sequences was used to define the OTUs (operational taxonomic units), which was determined in DOTUR by the furthest-neighbor algorithm comparison. Diversity analyses including the Chao1 and Shannon index numbers were determined for each sampling site using the DOTUR program.

Establishment of Arsenate-Reducing Enrichment Cultures

Water samples from wells R and D were used to establish enrichment cultures to measure arsenate-reducing activities. The site water (150 mL) was used to fill 150-mL serum bottles, which were bubbled with argon gas and sealed with a butyl rubber stopper. Two different conditions of substrates were added to each set in triplicate: (1) 0.1x Y.S.T. (50 mg/L of yeast extract, 30 mg/L of succinate, and 50 mg/L of tryptone peptone) plus 1 mM arsenate; and (2) 1 mM arsenate only. A sterile control of enrichment cultures were autoclaved twice and then 1 mM arsenate and 0.1x Y.S.T. were added. The cultures were incubated at room temperature for a month. The enrichment cultures were monitored by sampling 1 mL of water per week.

High-Performance Liquid Chromatography Analysis of Arsenite

Arsenate reduction in the enrichment cultures was measured by monitoring the increase of As(III) concentration during the incubation. As(III) was separated by high-performance liquid chromatography (HPLC) (Waters, Milford, Massachusetts) with a Hamilton PRP-X100 anion-exchange column as described by Liu et al. [8]. An isocratic 30-mM monobasic sodium phosphate buffer, adjusted to pH 6 with NaOH, was used as the mobile phase. The As(III) was detected at 1.5 minutes using a flow rate of 1.5 mL/min with a wavelength of 200 nm.

RESULTS

PCR Detection of *arr*A Genes from Groundwater Samples

The initial PCR with the primers As1F and ArrA1R did not yield any products. A nested PCR with the primers As2F and As1R generated fragments of 627-base pair size, which were the same size as the amplicon of *D. hafniense* DCB-2.

Diversity of DARB Based on *arr*A Genes

A total of 20 clones from well R and 16 clones from well D were fully sequenced and translated to amino acid sequences for phylogenetic analysis. A phylogenetic tree of *arr*A genes showed that both wells had two groups of DARB populations (R1 and R2 vs. D1 and D2) (Figure 2). The *arr*A sequences in the R1 group shared 95% amino acid sequence identity with each other and 74% with *G. uraniumreducens* Rf4. They also shared 64% amino acid sequence identity with *Desulfosporosinus* Y5, while the R2 sequences shared 76% with *G. uraniumreducens* Rf4 and 63% with *Desulfosporosinus* Y5. The D1 group was 100% identical and shared 78% sequence identity with *G. uraniumreducens* Rf4 and 65% with *Desulfosporosinus* Y5. The sequences in the D2 cluster shared a 99% identity to each other and a 63% sequence identity with *Clostridium* sp. OhILAs (Figure 2).

The DOTUR (distance-based OTU and richness) program was employed to examine diversity as a measure of species richness based on the nucleotide sequences from wells R and D. At a 2% sequence difference, well R had more diverse DARB than well D, based on the *arr*A gene sequences. The well R sequences had eight OTUs, while well D had two OTUs, which are both shown

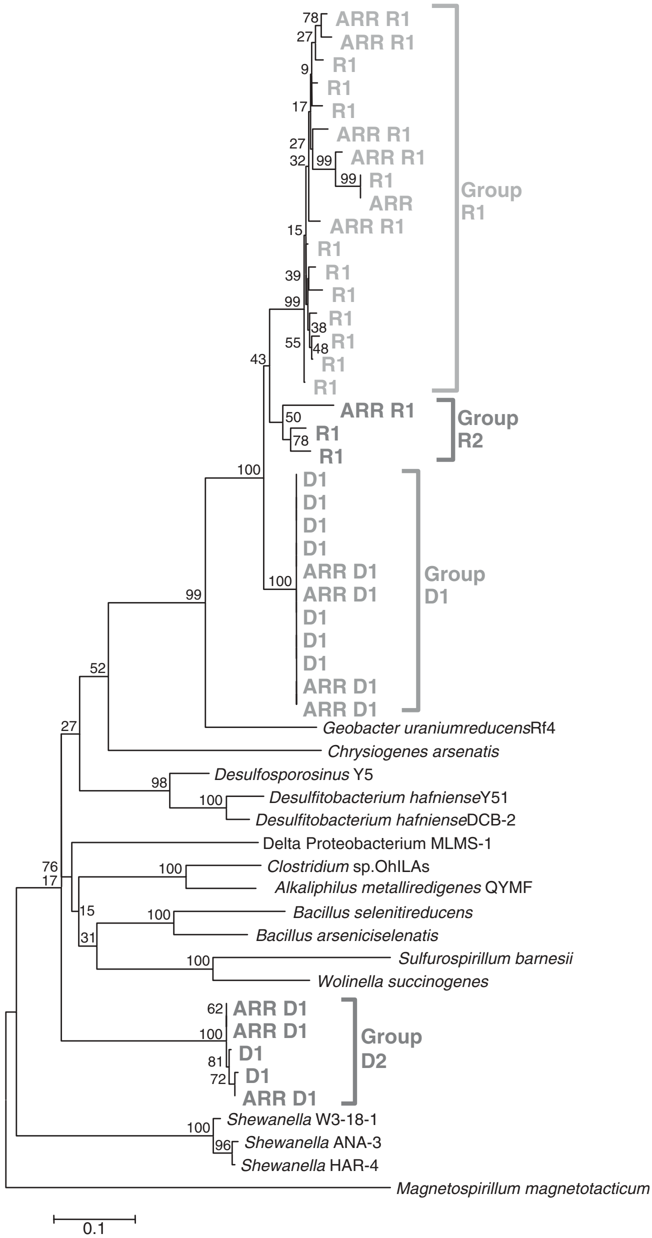

Figure 2 Phylogenetic tree of *arr*A genes from wells R and D. (*See insert for color representation of figure.*)

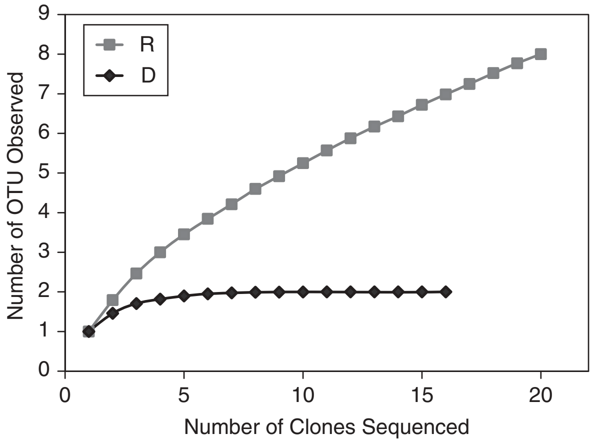

Figure 3 Rarefaction analysis of *arr*A genes detected from wells R and D.

in rarefaction analysis of *arr*A genes (Figure 3). The Chao1 estimate showed the predicted level of phylotype richness. The Chao1 estimates for wells R and D were 13 and 2, respectively. Shannon index numbers also indicated higher diversity of *arr*A genes in well R (1.69) than in well D (0.62).

Arsenate-Reducing Activities in Groundwater

Arsenate-reducing activities in both R and D well water were measured by monitoring the concentration of arsenite in the enrichment cultures. An increase in arsenite concentration was observed in the enrichment cultures amended with Y.S.T. plus arsenate. No measurable reduction occurred in the enrichment cultures amended with arsenate alone and in the sterile controls. The concentrations of arsenite for the D and R enrichment cultures were plotted with standard errors (Figure 4). The enrichment cultures with water from well D yielded up to 0.34 mM of arsenite, while the R enrichment cultures produced 0.62 mM of arsenite during a month of incubation. The D enrichment culture had an arsenite increase at a rate of 38.9 μM/day, while the R enrichment culture had a rate of 62.2 μM/day. All of the rates were measured over an 8-day period since most of the reduction occurred within 8 days.

DISCUSSION

Molecular detection of *arr*A genes in groundwater samples became promising to represent uncultured DARB in underground aquifers. Sequence analysis of *arr*A genes showed the presence of similar DARB communities in both well systems, which were closely related to the *arr*A gene found in *G. uraniumreducens* Rf4.

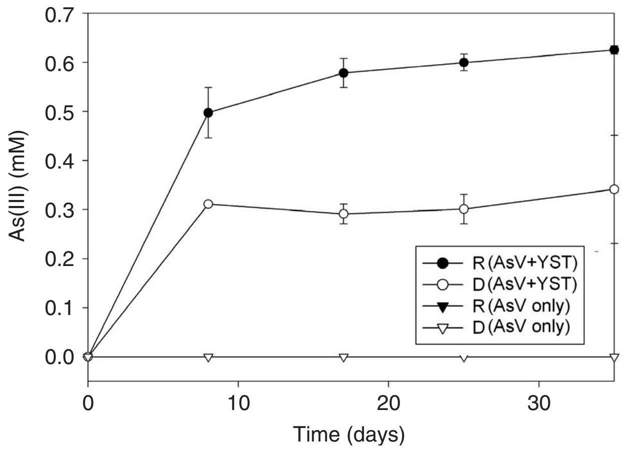

Figure 4 Arsenate reduction in anaerobic enrichment cultures established with R and D well water. Arsenite in the enrichment cultures amended with As(V) only was below the detection limit in both well waters. The data points for wells R and D are overlapped.

The genus *Geobacter* is known for its iron reducing capabilities [9]. The DARB carrying the detected *arr*A gene from both wells might be capable of reducing iron and arsenate simultaneously once sufficient carbon substrates are provided. In addition, well D contained a different group of DARB not found in well R. This shows that the two underground aquifers have unique DARB populations, corresponding to arsenic mobilization.

Based on the rarefaction analysis, well R has a sixfold-higher number of OTUs than well D: 13 and 2, respectively. This number was based on a 2% difference in phylotypes. If the sequences had less than a 2% difference based on DNA sequences, they were assigned as one OTU. Although wells D and R both had two distinct groups based on the phylogenetic analysis, the sequences within groups D1 and D2 shared more than 99% sequence similarities. The R-well sequences, however, had a 95% similarity within each group, making them more diverse than those of well D. Therefore, the molecular analysis showed that well R has a more diverse arsenate-reducing bacterial communities than does well D.

Enrichment culture studies showed that arsenate reduction rates were very different for wells D and R. The rate of arsenate reduction for well D was 38.9 μM/day, while well R had a rate of 62.2 μM/day for the Y.S.T. plus arsenate enrichment culture. Due to the fact that both cultures had the same amendment, the question remains as to what causes these variations in reduction rate. In addition, the R enrichment cultures amended with Y.S.T. plus arsenate yielded a final concentration of arsenite of 0.62 mM, but the D enrichment cultures only had 0.34 mM of arsenite at the end of incubations. The reason for the higher rate and concentration in well R might be related directly to the diversity of DARB present in both wells. Well R has a more diverse group of DARB, which might lead to the higher activity in the enrichments, while the DARB in well D are less diverse and have a lower activity in the enrichments. The lower activity in well D might also be related to the competition for organic carbon substrates from other bacteria, such as denitrifiers and sulfate reducers, which limit the reduction of arsenate by DARB communities. Overall, the findings in this study provide a microbial explanation for the different levels of arsenic found in both wells. Well R had 150 ppb of total dissolved arsenic, while well D had 73 ppb. The higher diversity and activity of DARB in well R could lead to the presence of higher arsenic concentrations than in well D. Since the presence of these bacteria is indicative of high arsenic levels, occasional sterilization of the wells with chlorine might eliminate the DARB and hence reduce the levels of arsenic released into the well water.

In conclusion, as the molecular data reveals, there are clearly arsenate-reducing bacterial communities present in wells containing high arsenic levels. The DARB at both wells actively reduce arsenate to arsenite once organic carbon substrates are provided. Based on the reduction rates and the amount of arsenite measured in the enrichment cultures, the DARB have significant impacts on the levels of arsenic in groundwater systems.

Acknowledgments

This research was supported by an NSF starter grant. We thank Charles Pippin and Joju Abraham at the North Carolina Department of Environment and Natural Resources for their help to gain groundwater samples and providing water chemistry data of the study wells.

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5

BIOGEOCHEMICAL MECHANISMS OF ARSENIC MOBILIZATION AND SEQUESTRATION

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INTRODUCTION

One of the most challenging environmental problems today is arsenic (As)-contaminated drinking water, which currently affects millions of people worldwide. The greatest exposure to arsenic occurs through ingestion, which can lead to acute or chronic arsenic poisoning. Chronic arsenic exposure can result in skin lesions, melanosis (skin discoloration), keratosis, cancer, and possible reproductive effects (Bhattacharyya et al., 2003; Ng et al., 2003). An estimated 41 to 57 million people are potentially exposed to elevated levels of arsenic, from 10 to 10,000 μg/L, especially in the Bengal Delta (Bangladesh and West Bengal, India), Taiwan, China, and parts of South America and Southeast Asia (Nordstrom, 2002; Smedley and Kinniburgh, 2002). The current drinking water standard in the United States is 10 μg/L, decreased from 50 μg/L in 2002 by the U.S. Environmental Protection Agency (EPA). However, there is a greater challenge to find acceptable treatment options in less developed regions where the affected population is primarily rural and large-scale treatment is prohibitively expensive.

Although there are some anthropogenic sources of arsenic in the environment through mining, pesticide application, wood preservation, and combustion

Arsenic Contamination of Groundwater: Mechanism, Analysis, and Remediation,
Edited by Satinder Ahuja

of some coal deposits, elevated concentrations of arsenic are often derived from natural sources. Arsenic occurs naturally in alluvial and deltaic sediments as well as volcanic rocks and thermal springs (Welch et al., 2000; Nordstrom, 2002; Smedley and Kinniburgh, 2002; Ng et al., 2003), and the weathering of such deposits can lead to mobilization of arsenic. The situation in Bangladesh is an example of arsenic occurring naturally in alluvial sediments that is being mobilized into the groundwater. A significant rural population relies on this groundwater for its drinking water supply, and consequently, exhibits extreme health effects of chronic arsenic exposure (Bhattacharyya et al., 2003).

The causes of arsenic mobilization are complex and not well understood. To identify and treat the problem of elevated arsenic concentrations in groundwater, it is necessary to understand the specific biogeochemical controls of arsenic mobility in subsurface environments. By understanding the processes that govern mobilization, it may be possible to predict future problems of arsenic contamination and design effective treatment methods.

SOURCES OF ARSENIC IN THE ENVIRONMENT

With the relatively recent discovery that millions of people worldwide are affected by arsenic-contaminated drinking water, there has been a renewed interest in arsenic sources and biogeochemical processes that lead to arsenic mobilization. Although there are both natural and anthropogenic inputs of arsenic to the environment, elevated arsenic concentrations in groundwater are often due to naturally occurring arsenic deposits. While the average abundance of arsenic in the Earth's crust is between 2 and 5 mg/kg, enrichment in igneous and sedimentary rocks, such as shale and coal deposits, is not uncommon (Cullen and Reimer, 1989; Smedley and Kinniburgh, 2002). Arsenic can cooccur with nickel, cobalt, copper, and iron, as well as precious metals such as silver and gold, especially in sulfidic ores (Tamaki and Frankenberger, 1992). Arsenic-containing pyrite (FeS) is probably the most common mineral source of arsenic, although arsenic is often found associated with more weathered phases (Nordstrom, 2002). Mine tailings can contain substantial amounts of arsenic, and the weathering of these deposits can liberate arsenic into the surfacewater or groundwater, where numerous chemical and biological transformations can take place (Harrington et al., 1998; Cummings et al., 2000). Arsenic can also be released directly into the aquatic environment through geothermal water, such as the hot springs in Hot Creek (Willets et al., 1967; Wilkie and Hering, 1998). Anthropogenic sources of arsenic include pesticide application, coal fly ash, smelting slag, feed additives, semiconductor chips, and arsenic-treated wood, which can cause local water contamination.

High arsenic concentrations in groundwater are not necessarily linked directly to geologic materials with high arsenic content. Hering and Kneebone (2001) calculated that in sediment with an arsenic concentration of 1.8 mg/kg (crustal abundance), only a small fraction of the total arsenic in the solid phase would be needed to account for a dissolved arsenic concentration of 10 μg/L. Therefore, arsenic mobility is related not only to the amount of arsenic in the geological source material, but also to the environmental conditions that control chemical and biological transformation of the material.

Iron-, aluminum-, and manganese-rich minerals are an important sink for arsenic in sediments, particularly through adsorption to mineral surfaces. Arsenic associated with Fe(III) oxide coatings on weathered alluvial sediments has been hypothesized to be an important source of arsenic in the Bengal delta aquifer, and release to groundwater occurs upon reductive dissolution of the Fe(III) oxide coating (Nickson et al., 1998; 2000; Acharyya, 2002; McArthur et al., 2004). Sedimentary biogeochemical processes are the focus of this chapter, with particular emphasis on iron and arsenic transformations.

Arsenic Speciation

Arsenic is stable in several oxidation states (−III, 0, +III, +V), but the +III and +V states are the most common in natural systems. Arsine (−III), a compound with extremely high toxicity, can be formed under very reducing conditions, but its occurrence in nature is relatively rare. Both inorganic and organic species of arsenic are present in the environment, although inorganic forms are typically more abundant in freshwater systems. Mobility and toxicity strongly depend on the oxidation state and structure. The inorganic species are more acutely toxic than organic species, and inorganic As(III) has a higher acute mammalian toxicity than that of As(V) (Ng et al., 2003). The effects of oxidation state on chronic toxicity are confounded by the redox conversion of As(III) and As(V) within human cells and tissues.

Inorganic Arsenic Arsenite [As(III); $H_xAsO_3^{x-3}$, $x = 0$ to 3] and arsenate [As(V); $H_xAsO_4^{x-3}$, $x = 0$ to 3] are the two most environmentally relevant inorganic forms of arsenic in freshwater systems. Arsenate is an anion at the pH of most natural waters ($H_2AsO_4^-$ and $HAsO_4^{2-}$), while arsenite is a neutral species. The structure and chemistry of arsenate are similar to those of phosphate ($H_xPO_4^{x-3}$, $x = 0$ to 3); this similarity has significant implications for sorption behavior and microbial metabolism. The toxicity of As(V) is due to its interference with oxidative phosphorylation in cells, by substituting for phosphorus in adenosine triphosphate (ATP) synthesis, essentially deactivating intracellular energy storage. As(III) toxicity is caused by a strong affinity for sulfhydryl groups, such as thiol groups in enzymes (NRC, 1999; NRC 2001).

As(V) is thermodynamically stable under oxic conditions, while As(III) is stable under more reducing conditions. However, As(V) and As(III) are often found to cooccur in both oxic and anoxic waters and sediments (Anderson and Bruland, 1991), due to kinetic limitations. For example, the oxidation of As(III) by oxygen is slow (on the order of several weeks), while bacterially mediated redox reactions can be much faster (Cullen and Reimer, 1989; Dowdle et al., 1996). The speciation of arsenic observed in natural water depends on local environmental conditions, such as bacterial activity, sediment mineralogy, pH, and redox potential.

Organic Arsenic Although there are many forms of organic arsenic, the most common organic species are monomethylated and dimethylated As(III) and As(V). Organic arsenic is less acutely toxic than the inorganic species, and methylation of inorganic arsenic is one type of detoxification mechanism for some bacteria, fungi, phytoplankton, and higher-level organisms such as humans. Methylation can also occur when organisms are stressed from nutrient limitation (Cullen and Reimer, 1989; Anderson and Bruland, 1991; Ng et al., 2003). Organoarsenicals are typically direct metabolic products and should be clearly distinguished from inorganic As complexed with natural organic matter.

Both inorganic and organic arsenic can be adsorbed onto mineral surfaces, a reaction that is strongly dependent on pH. In adsorption studies with monomethyl arsonic acid (MMAA) and dimethyl arsinic acid (DMAA), the affinity of the organoarsenic species for iron oxides was observed to be less than that of As(V) and greater than that of As(III) below pH 7, but less than that of both inorganic forms of arsenic above pH 7 (Xu et al., 1991; Bowell, 1994). In sediment environments at circumneutral pH, organoarsenicals may be more mobile than inorganic forms.

Significant levels of organoarsenicals can be found seasonally in surface waters, but organoarsenicals generally contribute less than 10% of the total arsenic in interstitial water except in isolated instances (Cullen and Reimer, 1989; Anderson and Bruland, 1991; Azcue and Nriagu, 1994; NRC, 1999; Newman, 2000). Thus, inorganic arsenic will be the focus of further discussion in this chapter.

REDOX CYCLING OF ARSENIC

Redox Cycling of Microbes

Bacteria may be one of the most important agents in arsenic cycling in sediments. Both As(V) reduction and As(III) oxidation can be mediated microbially, and have been observed in the environment (Ahmann et al., 1997; Oremland et al., 2002; Oremland and Stolz, 2003; Malasarn et al., 2004; Macur et al., 2004; Campbell et al., 2006). A complete discussion of bacterial redox cycling of arsenic may be found in Chapter 3.

Abiotic Arsenic Redox Chemistry

Oxygen can oxidize As(III), although the kinetics of this reaction are slow except at high pH (>10) (Manning and Goldberg, 1997; Swedlund and Webster, 1999). Manganese oxides can quickly oxidize adsorbed As(III), and this has been shown to be an active pathway for several synthetic manganese oxides (manganite and birnessite) (Scott and Morgan, 1995; Chiu and Hering, 2000; Manning et al., 2002) and in natural sediments and clays (Manning and Goldberg, 1997; Amirbahman et al., 2006). Green rust may also catalyze As(III) oxidation, although the importance of this reaction in biogenically formed green rust in sediment is unclear (Su and Puls, 2004; Su and Wilkin, 2005). As(V) reduction by green rust has not been observed (Randall et al., 2001; Ruby et al., 2006).

EFFECT OF ORGANIC CARBON ON ARSENIC CYCLING

Source of Organic Carbon

Sedimentary organic matter is derived from decaying phytoplankton and other plant or animal material. As proteins, lipids, and other components decay, compounds such as melanins, humic acids, and fulvic acids are formed and are commonly found in natural sediments (Stumm and Morgan, 1996). Natural organic matter (NOM) is a mixture of many types of functional groups, including phenols, fatty acids, carbohydrates, sugars, and amino acids. NOM can also contain significant amounts of inorganic impurities, such as iron, manganese, and aluminium. The organic carbon pool is a substrate for a range of microbial processes, including but not limited to As(V) and Fe(III) reduction.

Effect on Arsenic Chemistry

There is some evidence that NOM has redox properties and can catalyze the reduction of As(V) or the oxidation of As(III), particularly in the presence of a mineral surface such as hematite (Redman et al., 2002; Ko et al., 2004; Bauer and Blodau, 2006). However, the redox activity of NOM is highly variable; Bauer et al. found that NOM extracted from peat promoted As(V) reduction, while NOM extracted from wetland sediment-catalyzed As(III) oxidation (Bauer and Blodau, 2006). It is therefore difficult to generalize the effect of organic matter on arsenic redox chemistry, although it may be important in some sediment systems.

Organic carbon has been shown to promote arsenic mobilization in laboratory studies, due either to sorption effects or aqueous complexation (Redman et al., 2002; Bauer and Blodau, 2006). Humic and fulvic acids are capable of inhibiting As(III) and As(V) adsorption to Fe(III) oxide surfaces due to steric and/or electrostatic effects (Xu et al., 1991; Grafe et al., 2001, 2002; Redman et al., 2002; Ko et al., 2004). Natural organic matter can adsorb onto iron oxide surfaces through functional groups such as carboxylic acids, phenols, and amines or as outer-sphere complexes (Kaiser et al., 1997; Grafe et al., 2002; Buschmann et al., 2006). Organic carbon has also been shown to complex arsenic in solution, although the mechanism is most likely through inorganic impurities such as Fe(III) and Mn(III,IV). Fe(III) stabilized in NOM [dissolved Fe(III) or colloidal Fe(III) oxide particles] can form bridging complexes with arsenic, for the same reasons that arsenic adsorbs to the surface of Fe(III) minerals (Ko et al., 2004; Lin et al., 2004; Ritter et al., 2006). As(V) tends to form stronger complexes than As(III) on a variety of Fe(III)-containing organic substrates (Thanabalasingam and Pickering, 1986; Warwick et al., 2005; Buschmann et al. 2006). Phosphate competes with arsenic for NOM complexation, supporting the Fe(III) bridging mechanism (Thanabalasingam and Pickering, 1986).

ARSENIC SEQUESTRATION: PRECIPITATION AND ADSORPTION

Authigenic Arsenic Mineral Phases

The partitioning of arsenic between dissolved and solid phases can be controlled by arsenic mineral precipitation as well as adsorption. Arsenite forms insoluble precipitates with sulfide, such as orpiment ($As_2 S_3$), realgar (AsS), and arsenopyrite (FeAsS) in reducing environments (Cullen and Reimer, 1989; Nordstrom and Archer, 2003); precipitation can be mediated microbially (Newman et al., 1997; Nordstrom and Archer, 2003). Sulfide phases are generally unstable in the presence of dissolved oxygen and are subject oxidative dissolution. Authigenic mineral precipitation of arsenate is unlikely at most circumneutral environmental conditions. Scorodite ($FeAsO_4 \cdot 2H_2O$) precipitates only in very acidic environments, such as acid mine drainage (Langmuir et al., 2006). Jia et al. (2006) observed a ferric arsenate precipitate that formed on the surface of hydrous ferric oxide (HFO), an amorphous iron oxyhydroxide, at low pH (3 to 4), but sorption dominated the arsenic–iron association at circumneutral pH. It is important to note that actual concentrations of dissolved arsenic may not reflect equilibrium conditions, due to dissolution or precipitation kinetics.

Adsorption of Arsenic onto Iron Surfaces

Arsenic adsorption onto metal oxide minerals, especially iron oxides, has been observed as an important and widespread mechanism of controlling dissolved arsenic concentrations in a variety of environments (Aggett and O'Brien, 1985; Fuller and Davis, 1989; Azcue and Nriagu, 1994; Nickson et al., 1998, 2000; Hering and Kneebone, 2001). Although there are conditions where authigenic arsenic mineral precipitation controls dissolved arsenic concentrations, a more detailed discussion of adsorption to mineral surfaces is warranted because of its environmental relevance.

As(V) and As(III) Adsorption onto Iron Oxides Sorption reactions at equilibrium satisfy a mass law equation, similar to aqueous equilibrium reactions. For surface reactions, the equilibrium constant is a product of an intrinsic term, corresponding to the chemical free energy of binding, and a coulombic term, which describes the effect of electrostatic charge at the surface.

Surface sites exhibit acid–base chemistry. Positive, negative, and neutral surface groups can be present, depending on the extent of protonation, and can be described by equations (1) and (2), where the symbol "=" denotes a surface site and "$\rightleftharpoons$" signifies chemical equilibrium (Dzombak and Morel, 1990).

$$=\mathrm{FeOH} \rightleftharpoons =\mathrm{FeO}^- + \mathrm{H}^+ \tag{1}$$

$$=\mathrm{FeOH_2}^+ \rightleftharpoons =\mathrm{FeOH} + \mathrm{H}^+ \tag{2}$$

Adsorption of As(V) and As(III) occurs via ligand-exchange reactions with hydroxyl surface groups, also known as inner-sphere complexation (Dzombak and Morel, 1990). Neither the adsorption of As(III) nor As(V) is strongly affected by changes in ionic strength, which is indicative of inner-sphere complexation (Pierce and Moore, 1982; Hsia et al., 1994; Jain et al., 1999; Goldberg and Johnston, 2001). Further evidence of specific adsorption has been obtained by spectroscopic data.

Adsorbed arsenic species are weak acids and can affect the surface charge due to proton-exchange reactions. Whether arsenic adsorbs as a mononuclear or binuclear complex has implications for the level of protonation of the surface species, illustrated in equations (3) and (4) with adsorbed As(III) species as an example. Binuclear complexes have fewer acidic protons due to the binding with the iron oxide surface.

$$=\mathrm{FeOH} + \mathrm{H_3AsO_3} \rightleftharpoons \mathrm{FeH}_x\mathrm{AsO_3}^{x-2} + \mathrm{H_2O} + (2-x)\mathrm{H}^+ \quad \text{where } x = 0\text{–}2 \tag{3}$$

$$(=\mathrm{FeOH})_2 + \mathrm{H_3AsO_3} \rightleftharpoons (=\mathrm{Fe})_2\mathrm{H}_y\mathrm{AsO_3}^{y-1} + 2\mathrm{H_2O} + (1-y)\mathrm{H}^+ \quad \text{where } y = 0, 1 \tag{4}$$

Adsorption isotherms (adsorbed arsenic vs. dissolved arsenic) and envelopes (adsorbed arsenic vs. pH) have shown that As(V) and As(III) adsorption onto HFO depends strongly on pH and As concentration. It is, however, important to note that the structure of surface complexes (e.g., the formation of mono- vs. binuclear complexes) is only poorly constrained by macroscopic sorption data (Hering and Dixit, 2005). Arsenate adsorption decreases with increasing pH, particularly above pH 7 to 8, and maximum sorption occurs at low pH values (3 to 7) (Pierce and Moore, 1982; Raven et al., 1998; Goldberg, 2002; Dixit and Hering, 2003). Arsenite has a broad maximum adsorption at circumneutral pH, and decreasing sorption at high and low pH values (Pierce and Moore, 1982; Dixit and Hering, 2003). Arsenite is often considered to be more mobile than As(V), but this generalization is not always true; the relative affinity for HFO depends strongly on pH as well as the presence of other adsorbed ions (Dixit and Hering, 2003).

The initial rate of arsenic adsorption is fast (about 90% within 2 hours) onto preformed HFO, followed by a period of slower uptake ($>$ 100 hours) (Pierce and Moore, 1982; Fuller et al., 1993; Raven et al., 1998). Fuller et al. (1993) accurately modeled this observation with As(V) diffusion into a sphere, with a subset of adsorption sites located in the interior requiring longer diffusion times than were required by exterior surface sites. Physically, this spherical model could correspond to an aggregate of HFO particles with surface sites in the interior requiring molecular diffusion of arsenic into the aggregate. After aging the HFO for six days before arsenic adsorption, the total amount of adsorbed arsenic decreased by 20%, but the rates were unchanged. Co-precipitated As(V) and HFO had significantly higher arsenic adsorption initially, but the arsenic slowly desorbed as aggregation and aging occurred. The coprecipitated As(V) and HFO approached a steady-state concentration similar to As(V) adsorbed onto presynthesized HFO after >400 hours, indicating that the rate of arsenic adorption/desorption onto HFO may be diffusion controlled (Fuller et al., 1993). As(III) may have slightly faster adsorption kinetics, although this appears to be highly dependent on experimental conditions (Raven et al., 1998).

Many spectroscopic studies have been performed on As(III) and As(V) adsorbed onto HFO, and all confirm that inner-sphere complexation is dominant. Local bonding environments of As(III) and As(V) have been determined by analyzing x-ray absorption (XAS) spectra. There are several possible molecular configurations of arsenic adsorption: mononuclear monodentate, mononuclear bidentate (edge-shared), and binuclear bidentate (corner-shared). Extended x-ray absorption fine structure (EXAFS) studies have shown that As(V) is adsorbed primarily as binuclear bidentate complexes, with average As-Fe bond lengths between 3.26 and 3.3 Å (Waychunas et al., 1993; Sherman and Randall, 2003). Waychunas and co-workers proposed a monodentate mononuclear complex that became increasingly abundant as arsenic surface coverage decreased (Waychunas et al., 1993). However, this surface species has been challenged on the basis of thermodynamic instability and crystal growth poisoning effects (Manceau, 1995; Sherman and Randall, 2003). A mononuclear bidentate complex has been hypothesized by Manceau (1995), but this structure has also been questioned due to calculated thermodynamic instability (Waychunas et al., 1995; Sherman and Randall, 2003). Arsenite is adsorbed predominantly as binuclear bidentate complexes with an average As–Fe bond length of 3.3 Å, although there is evidence for less-important mononuclear bidentate complexes (Manning et al., 1998; Ona-Nguema et al., 2005). No mononuclear monodentate complex has been observed for As(III). Binuclear bonding for both As(III) and As(V) has been supported by FTIR studies (Sun and Doner, 1996).

Competitive Effects on Arsenic Adsorption The presence of other adsorbing ions can significantly affect the adsorption of arsenic onto ironoxides. Arsenic adsorption can be affected by electrostatic, steric, or competitive effects. Phosphate has the greatest effect on sorption of arsenic, due to similarities in molecular structure and surface complexation chemistry. Phosphate competes directly with arsenic for surface sites and effectively inhibits both As(III) and As(V) sorption (Manning and Goldberg, 1996; Liu et al., 2001; Dixit and Hering, 2003). Phosphate sorption is more pH dependent than As(V) sorption, and As(V) may be slightly more strongly adsorbed than phosphate (Jain and Loeppert, 2000; Hongshao and Stanforth, 2001; Liu et al., 2001; Violante and Pigna, 2002; Antelo et al., 2005). Kinetic effects are also important in competitive sorption, as evidenced by the effect of sorbate addition on the extent of sorption, particularly in the case of phosphate and arsenic. The sorbate added first will adsorb to a greater extent than the competing sorbate (Hongshao and Stanforth, 2001; Liu et al., 2001).

Sulfate (H_2SO_4) appears to adsorb to different HFO surface sites than arsenic and may not compete directly for surface sites in the same way as phosphate (Jain and Loeppert, 2000). Sulfate has a very slight effect on As(V) adsorption but can decrease As(III) adsorption below pH 7.5 (Wilkie and Hering, 1996; Jain and Loeppert, 2000; Meng et al., 2000).

The adsorption edge of silicate (H_4SiO_4) is qualitatively similar to that of As(III), with broad maximum adsorption between pH 8 and 10 (Swedlund and Webster, 1999). Silicate decreases As(III) and As(V) adsorption, with a greater effect on As(III) at high silicate concentrations and at pH > 8. Silicate forms a polymer on the surface of HFO at high concentrations, resulting in large Si : Fe ratios (>0.1) (Swedlund and Webster, 1999; Holm, 2002). This surface polymer may inhibit As sorption through steric and/or electrostatic effects. In an experiment by Meng et al. (2000), Ca^{2+} or Mg^{2+} counteracted the effect of silicate on arsenic sorption, indicating that a change in surface potential may be at least partially responsible for the inhibition of arsenic adsorption by silicate. In another study by Wilkie and Hering (1996), Ca^{2+} increased As(V) adsorption onto HFO, probably due to electrostatic effects. High concentrations of silicate can also form colloidal Si–Fe(III) polymers that can increase the Fe(III) mobility at high pH (Meng et al. 2000), but the relevance of this effect in natural systems in probably minimal.

The concentrations of carbonate (dissolved CO_2 as H_2CO_3 and its acid dissociation products) in groundwater can be elevated due to microbial respiration and carbonate mineral dissolution. The effect on arsenic adsorption of carbonate concentrations due to atmospheric equilibration ($\sim$0.07 mM) is minimal (Fuller et al., 1993; Meng et al., 2000; Arai et al., 2004; Radu et al., 2005). However, higher concentrations [10% $CO_2(g) = 22$ mM dissolved inorganic C] suppressed As(V) adsorption and caused significant amounts of As(III) to desorb in column studies with As(III) preequilibrated onto goethite-coated sand (Radu et al., 2005). High concentrations of carbonate affected As(III) sorption more than As(V) (Radu et al., 2005), even though As(V) was hypothesized to be more affected based on surface charge effects (Appelo et al., 2002). Leaching of arsenic from solids by the addition of bicarbonate salts was found to be dependent on both pH and carbonate concentration, with the greatest leaching at high carbonate concentrations and at very low or very high pH values (Kim et al., 2000; Anawar et al., 2004). When compared directly to phosphate, carbonate was a much weaker inhibitor of arsenic adsorption (Radu et al., 2005), although it may still be important in groundwater with high carbonate concentrations. Carbonate forms only a very weak complex with As(III) in solution, and arsenic sorption inhibition is probably due to surface effects (Neuberger and Helz, 2005).

Carbonate adsorption onto Fe(III) oxide surfaces is probably a combination of inner and outer sphere complexes (van Geen et al., 1994; Su and Suarez, 1997; Villalobos and Leckie, 2000, 2001; Bargar et al., 2005). Arsenic adsorption inhibition is probably due to electrostatic effects from specifically adsorbed carbonate. Carbonate adsorption is highly dependent on pH with maximum sorption on goethite at pH 6 (van Geen et al., 1994). Bicarbonate ($HCO_3{}^-$) appears to have a greater affinity for surface complexation than $H_2\ CO_3{}^*$ or $CO_3{}^{2-}$. Ternary complexation with adsorbed carbonate may also be possible and can affect surface electrostatics (e.g., Na–CO_3–Fe oxide) (Villalobos and Leckie, 2001).

ARSENIC MOBILIZATION: SEDIMENT DIAGENESIS AND REDUCTIVE DISSOLUTION

Early Diagenesis in Sediments

Sediment diagenetic processes are the biogenic and abiotic changes that occur to alter sediment during and after deposition (Stumm and Morgan, 1996). Sediment diagenesis involves chemical, physical, and biological processes, including (1) deposition, (2) diffusion, (3) reductive dissolution (and other redox changes), and (4) secondary mineral precipitation. Diagenesis is driven primarily by the mineralization of organic carbon and the subsequent changes in redox potential with depth. As the sediments become more reducing, the redox equilibrium of various chemical species in the sediment shifts. However, it is important to recognize that the kinetics of these reactions are variable and sensitive to environmental parameters such as microbial activity (Hering and Kneebone, 2001). Thus, it is common to observe As(III) and As(V) or Fe(III) and Fe(II) cooccurring under a variety of redox conditions, due to kinetic factors.

Oxygen is the most favorable electron acceptor, and the diffusion of O_2 into sediments from the overlying water is balanced by microbial consumption. In many freshwater sediments, the transition from oxic or suboxic to anoxic can occur within a depth interval of millimeters to centimeters (Song and Muller, 1999). In suboxic zones, manganese oxides and nitrate are reduced, releasing Mn(II) and reduced nitrogen compounds, including nitrite, N_2, and ammonia. Reductive dissolution of iron oxides and sulfate reduction occur in the more reducing anoxic zones. Deeper in the sediment column, methane fermentation may occur under very reducing conditions. Trace elements such as arsenic may also undergo redox transformations during this process, such as As(V) reduction.

As the reductive dissolution of Fe(III) oxides releases Fe(II) and trace elements into the pore water, several chemical processes are possible. Dissolved organic carbon may form aqueous iron and/or arsenic complexes, or inhibit sorption onto mineral surfaces. Competitively sorbing compounds such as phosphate can be released from the dissolving solid phase or from mineralization of organic matter and affect the partitioning of arsenic on the solid phase. Fe(II) may catalyze the formation of secondary minerals such as green rust, magnetite, and goethite, which can either sequester or mobilize arsenic.

Dissolved Fe(II) and arsenic are subject to molecular diffusion. If Fe(II) diffuses into the suboxic zone, it could be reprecipitated by reaction with oxygen or with manganese oxides, resulting in fresh surface sites for arsenic to be readsorbed.

Reductive Dissolution of Iron phases

There are four general pathways for Fe(III) dissolution: proton-assisted (acid), ligand-promoted, reductive, and ligand-promoted reductive dissolution (Afonso et al., 1990). Ligands such as oxalate can promote the dissolution (either reductive or nonreductive) of Fe(III) oxides. However, reductive dissolution is the most important pathway in the natural environment (Cornell and Schwertmann, 1996). Reductive dissolution is driven by the reduction of Fe(III) in the solid phase to the more soluble Fe(II). Dissolution of the solid Fe(III) oxide can potentially release adsorbed trace elements into the pore waters. Reductive dissolution has been observed to release arsenic into aquifers in Bangladesh (Nickson et al., 1998, 2000; Acharyya, 2002; Bose and Sharma, 2002; Swartz et al., 2004) and the United States (Peterson and Carpenter, 1986; Welch and Lico, 1998; Cummings et al., 2000; Welch et al., 2000; Kneebone et al., 2002), as well as into lake sediment pore waters in New Zealand (Aggett and O'Brien, 1985) and Switzerland (Azcue and Nriagu, 1994). The coincident increase in dissolved arsenic and iron concentrations is a strong indicator that reductive dissolution of Fe(III) phases is a likely mechanism of arsenic mobilization. Arsenic mobilization is controlled by the ability of Fe(III) oxides in the subsurface to readsorb arsenic as reductive dissolution proceeds (Welch et al., 2000; Swartz et al., 2004; Pedersen et al., 2006) and by the presence of competing ions.

There are both abiotic and biotic pathways for the reductive dissolution of Fe(III). Lovley and co-workers compared the reduction of HFO by three strains of bacteria (a sediment isolate GS-15, *Clostridium pasteurianum*, and *Escherichia coli*) to chemical reduction by a number of different organic compounds, some of which are likely to be found in a natural sedimentary environment. Microbial reduction was faster and more extensive than chemical reduction at neutral pH, suggesting that microorganisms are primarily responsible for Fe(III) reduction in nonsulfidogenic sediments (Lovley et al., 1991). Roden noted that chemical reduction rates vary by three orders of magnitude, while bacterial rates are more constant even between different strains, and extrapolation of laboratory chemical rates of compounds such as ascorbate to environmental conditions should be done with caution (Roden, 2003, 2004). However, it is useful to compare the differences in mechanisms between chemical and biological reductive dissolution, noting that both pathways could be important under a variety of environmental conditions.

Chemical Mechanisms Chemical reductants include H_2S and various organic compounds, such as ascorbate and humic acids (Hering and Stumm, 1990; Schwertmann, 1991; Rochette et al., 2000; Thamdrup, 2000). Reductive dissolution is thought to occur through a series of reaction steps: adsorption of the reductant, electron transfer to the Fe(III), and release of Fe(II) from the lattice (usually the rate-limiting step). Fe(II) is more readily released from the crystal lattice because the binding energy is less for Fe(II) than for Fe(III). In addition, surface protonation near the sorption site of the reductant can accelerate dissolution (Suter et al., 1991). Organic compounds that are not involved in electron transfer can either accelerate or inhibit reduction. If sorption of the organic compound polarizes the iron bonds, making the Fe(II) bond easier to break, reduction will occur at a faster rate. On the other hand, large organic compounds on the Fe(III) oxide surface may sterically hinder adsorption of the reductant, thus decreasing the reduction rate (Schwertmann, 1991). The reaction pathway can be additionally complicated by catalysis of the dissolution and subsequent mineralogical transformations of the parent Fe(III) phase by Fe(II) (Zinder et al., 1986; Schwertmann, 1991; Suter et al., 1991; Benner et al., 2002; Hansel et al., 2005; Pedersen et al., 2005, 2006). Photoreduction has been observed for Fe(III) oxides but is unlikely to be important in many lacaustrine sediments and aquifers.

Adsorbed oxyanions such as As(V) have been shown to inhibit the reductive dissolution in laboratory studies with ascorbic acid as a reductant and in ligand-promoted dissolution. This could be due to a decrease in surface protonation and/or reductant sorption because of steric or electrostatic effects at the oxide surface (Bondietti et al., 1993; Biber et al., 1994; Kraemer et al., 1998; Eick et al., 1999; Pedersen et al., 2006). However, the importance of these effects in the field is not yet known.

Biological Mechanisms Bacterial Fe(III) reduction can be carried out by a genetically and metabolically diverse group of microorganisms. Bacteria can generally utilize many electron acceptors, usually coupled to organic carbon or H_2 oxidation. The sequence of electron acceptors follows decreasing in the order O_2, nitrate, manganese oxides, Fe(III) oxides, sulfate, and methane (fermentation) (Stumm and Morgan, 1996). Fe(III) oxide reduction may be responsible for a significant fraction of total organic carbon mineralization in sediments (Thamdrup, 2000).

The mechanism of enzymatic reduction is not well known. Some organisms require direct contact with an Fe(III) oxide surface, while others may synthesize electron shuttle compounds or use naturally occurring humic acids to transfer electrons between the cell and the Fe(III) oxide surface (Thamdrup 2000). Some cells may produce reactive oxygen species such as superoxide to mediate Fe(III) dissolution (Fujii et al., 2006). Natural Fe(III) chelators may also accelerate microbial iron reduction without requiring direct cellular contact with the solid phase (Jones et al., 2000; Royer et al., 2002). Rates of bacterial Fe(III) oxide reduction are highest with a poorly crystalline Fe(III) oxide phase and decrease with increasing crystallinity (Roden and Zachara, 1996), confirming the observation that amorphous Fe(III) oxides are the most bioavailable. More detailed information on microbial iron reduction may be found in Chapter 3.

Secondary Mineral Transformation Fe(II) adsorption onto Fe(III) oxides is unique in that electron transfer into the Fe(III) oxide results in migration of the electron, and effectively the Fe(II), into the bulk mineral. This migration was observed by Mössbauer spectroscopy and isotopic exchange experiments (Williams and Scherer, 2004; Pedersen et al., 2005). Fe(II) can destabilize the bulk mineral, allowing mineral transformations to take place more readily.

In the presence of Fe(II), HFO can transform to numerous other Fe(III) oxides, such as goethite (α-FeOOH), lepidocrocite (γ-FeOOH), and hematite (Fe_2O_3), as well as other Fe(II) or mixed Fe(II)–Fe(III) minerals, such as magnetite (Fe_3O_4), siderite ($FeCO_3$), vivianite [$Fe_3(PO_4)_2 \cdot 8H_2O$), and green rusts. The rate of transformation increases with increasing Fe(II) concentrations (Hansel et al. 2005; Pedersen et al., 2006). At low Fe(II) concentrations, goethite and lepidocrocite formation is catalyzed by increased local dissolution of the Fe(III) oxide because of Fe(II) destabilization of the Fe(III) oxide surface. Magnetite formation is more favorable at higher Fe(II) concentrations and proceeds through solid-state conversion or surface nucleation. At high rates of Fe(II) production, siderite can form if there is an adequate concentration of carbonate and vivianite with high concentrations of phosphate (Figure 1).

The mineralization process is complicated by the presence of anions such as chloride, sulfate or carbonate (Figure 1). Phosphate, silicate, carbonate, nickel, cobalt, and calcium can favor the formation of green rusts and vivianite. While there are several forms of green rust, formation of carbonate green rust ($[Fe^{II}_4 Fe^{III}_2(OH)_{12}]^{2+} \cdot [CO_3, nH_2O]$) is more favorable than formation of the sulfate analog (Ona-Nguema et al., 2004). The structure has layers of Fe(II) and Fe(III) octahedra, with water and anions such as carbonate intercalated in the interlayers. Green rusts have been observed as a microbially induced biomineralization product of HFO in laboratory incubations (Fredrickson et al., 1998). Just as HFO is metastable with respect to the formation of goethite and hematite, green rusts are metastable with respect to magnetite and siderite. Green rusts are formed in an early stage of biomineralization. Phosphate, As(V), silicate, and Co stabilize

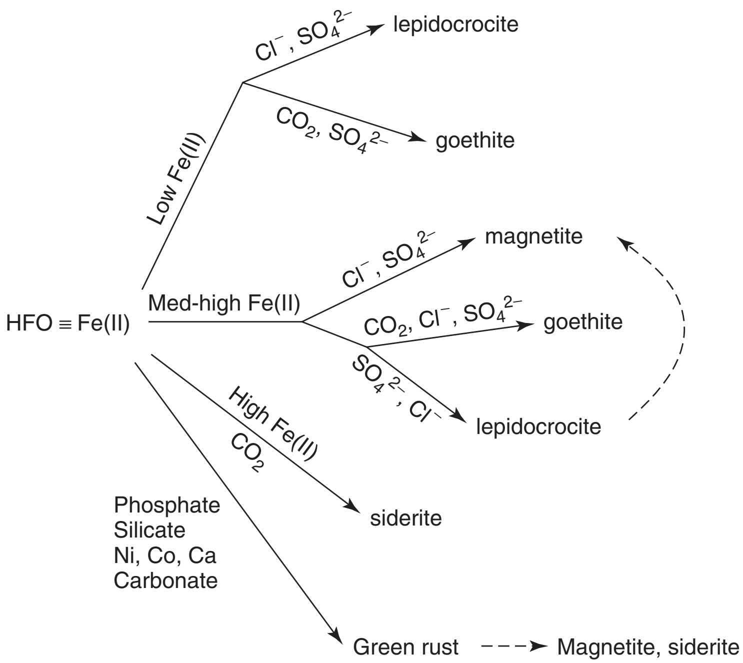

Figure 1 Secondary mineral transformations of HFO due to adsorbed Fe(II). Adapted from references: Fredrickson et al. 1998; Benner et al. 2002; Zachara et al. 2002; Hansel et al. 2003; Hansel et al. 2005; Pedersen et al. 2005; Pedersen et al. 2006. The dashed lines indicate further mineral transformation that can occur spontaneously.

green rusts by preventing recrystallization into goethite, siderite, and magnetite (Zachara et al., 2002; Bocher et al., 2004).

While Fe(II) can be produced by microbial processes, the role of bacteria in secondary mineral transformation is unclear. Many of the same secondary minerals are observed when Fe(II) is added abiotically. However, larger particles are formed in the abiotic Fe(II) reactions than in biogenically produced Fe(II) transformation products (Hansel et al., 2003). In addition, complete conversion of Fe(III) in Fe(III) oxides to Fe(II) is rarely observed in biological experiments. Secondary mineral precipitation and Fe(II) adsorption may make the Fe(III) oxide less bioavailable for reduction (Urrutia et al., 1999; Hansel et al., 2004; Royer et al., 2002). While mineral transformation is primarily an abiotic reaction involving Fe(II), the rate and extent of Fe(II) production can be controlled biologically.

Adsorbed arsenic may be released into solution as minerals transform during sediment digenesis if surface sites are lost (i.e., the secondary mineral has fewer available surface sites for binding arsenic than the parent mineral). It is also possible for arsenic to be sequestered in the mineral structure of the secondary mineral, making arsenic less mobile. High concentrations of arsenic may also affect the stability of the transformation products, such as green rust, in a mechanism similar to phosphate. Thus, the impact of secondary mineral formation on arsenic mobility depends strongly on the biogeochemical conditions and the transformation product. There are many opportunities for further research in the field of secondary mineral transformation and arsenic mobility.

Implications for Arsenic Mobility

Reductive Fe(III) oxide dissolution is controlled by a complex interplay of many different parameters, such as pH, redox state, mineralogy, biological activity, and solution chemistry. Biologically mediated reduction depends strongly on the bacterial consortia present in the sediments, as well as substrate availability (e.g., organic carbon) and iron oxide crystallinity. The rate of dissolution can, in turn, affect the mineral transformation products, which have the potential to sequester arsenic in more crystalline lattice structures or release arsenic to the pore waters as surface binding sites are lost.

CASE STUDY: HAIWEE RESERVOIR

The City of Los Angeles imports water from several different sources, including the Sierra Nevada Mountains in northern California. Approximately 70% of drinking water in the Los Angeles is delivered via the Los Angeles aqueduct (LAA). Natural geothermal springs in Hot Creek, California, contribute large arsenic loads to the LAA source waters, resulting in a long-term average arsenic concentration in the LAA of 22 μg/L. Although the hot springs contribute <5% of the total water flow, they contribute >60% of the total arsenic load to the

LAA. The arsenic flux from the hot springs is relatively constant throughout the year but changes in flow from snowmelt, and aqueduct operations create seasonal fluctuations of arsenic concentrations in the LAA (Willets et al., 1967; Stolarik and Christie, 1999).

The LA Department of Water and Power (LADWP) developed an interim management plan to remove arsenic from the LAA at the Haiwee reservoir (Stolarik and Christie, 1999). An existing treatment plant in the Owens Valley, the Cottonwood treatment plant, was modified to inject ferric chloride ($FeCl_3$) as a coagulant directly into the LAA about 27 km upstream of the Haiwee reservoir (Figure 2). The ferric chloride forms an amorphous iron oxyhydroxide floc in the aqueduct channel. Dissolved arsenic readily adsorbs and/or coprecipitates

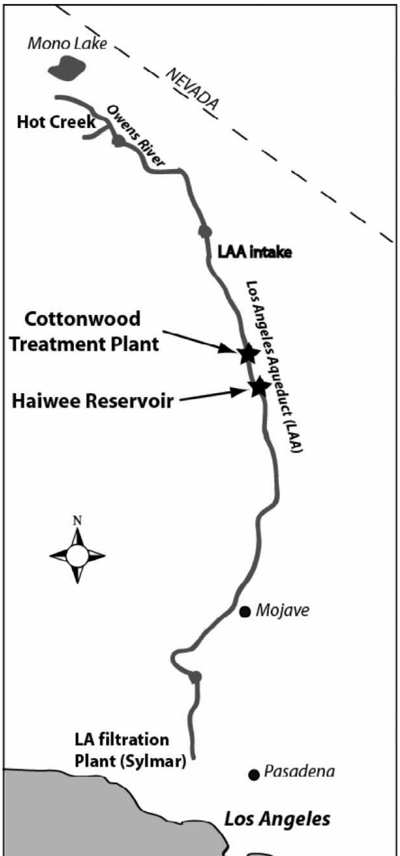

Figure 2 Map of the Los Angeles Aqueduct (LAA) system. Ferric chloride injections at Cottonwood Treatment plant result in Fe- and As- enriched sediment deposition at Haiwee Reservoir, the research site for this study.

with the iron floc and is subsequently deposited in the inlet channel to the Haiwee reservoir. The result of this treatment is substantial deposition of iron- and arsenic-rich sediments in the Haiwee reservoir. The processes governing arsenic mobilization and sequestration are a complex combination of biological, chemical, and physical parameters. The sediment deposited at the Haiwee reservoir provides a unique setting to study the biogenic and chemical diagenetic processes that control arsenic partitioning between the solid and dissolved phases in the environment.

Field studies were conducted in October 2004 and August 2005 to measure the effect of sediment diagenesis on arsenic mobilization. Gel probe equilibrium samplers were used to measure pore water composition and adsorption behavior in situ. The gels were composed of a polyacrylamide polymer matrix cut into slabs $0.2 \times 0.5 \times 2$ cm. The gels were 92% water when fully hydrated. The gels were placed into slots etched into vertical columns of a plastic probe, covered with a 0.45-μm membrane, and deoxygenated before deployment in sediments. The water inside the gel exchanged with the pore water during deployment. The gels were reequilibrated in acid for analysis. Two types of gels were used in this study. The first type of gel was an undoped (clear) gel to measure pore water composition. The second type of gel was doped with HFO, a synthetic Fe(III) oxyhydroxide similar to the floc precipitated in the aqueduct. The HFO-doped gels were used to measure the amount of arsenic and other elements adsorbed onto the HFO embedded in the gel. The probes were configured with two columns of parallel gels so that pore water composition (clear gels) and sorption chemistry (HFO-doped gels) were measured simultaneously. Complete details of gel probe construction, laboratory validation, and field deployment may be found in work by Campbell (2007) and Campbell et al. (2008a, b).

Pore water concentrations of manganese and iron were consistent with reductive dissolution of manganese and iron oxides at depth (Figure 3), as the sediments become more reducing. The pore water concentrations are indicative of the terminal electron acceptors shifting from dissolved oxygen to manganese and iron oxides as diagenesis progresses. There is a strong correlation between dissolved arsenic and iron, suggesting that arsenic is released into the pore waters as the iron oxides are reductively dissolved.

The pore water and sorption profiles are shown in Figure 4 and are divided into three regions. A negligible amount of dissolved arsenic, phosphorus, and iron was observed in the surfical sediment (region 1), where oxygen diffusing from the overlying water was consumed and manganese oxide reduction was occurring. The onset of reductive dissolution of Fe(III) oxides released arsenic and phosphorus to the pore waters at about 10 cm below the sediment–water interface (region 2). Adsorption of arsenic onto the HFO-doped gels did not follow the pore water profile, and did not peak until about 20 cm (region 3). This results in a region between 10 and 20 cm where arsenic was inhibited from adsorbing onto the HFO-doped gels (region 2). Region 3 correlates to the depth where a gray sediment layer was observed, indicating a secondary mineralogical change in the sediments. A carbonate green rust-type phase was detected

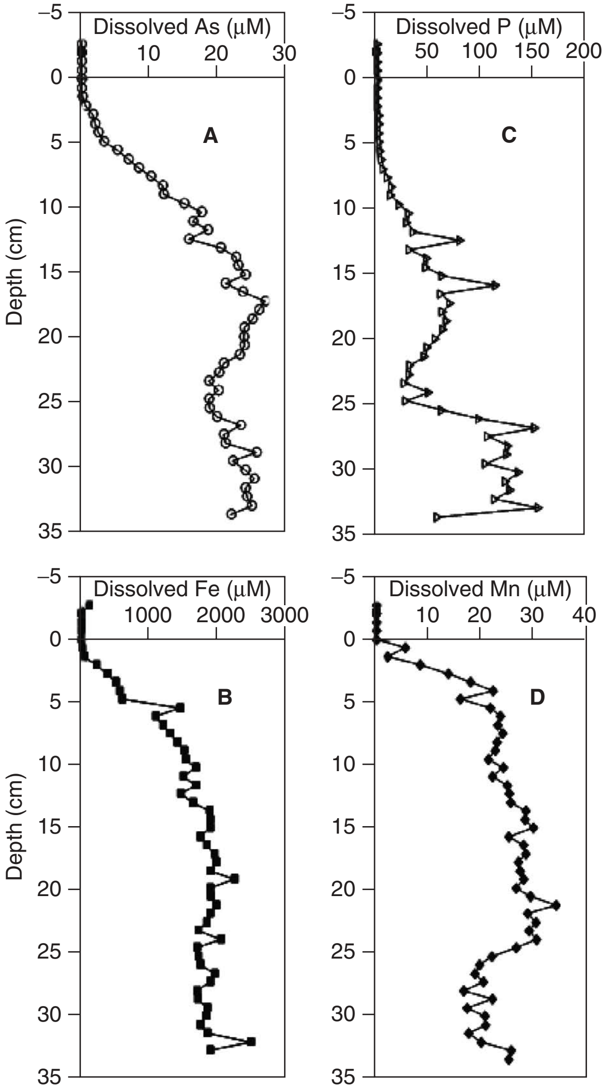

Figure 3 Pore water concentrations of As (A), Fe (B), P (C), and Mn (D) from a gel probe deployed in October 2004. The probe was equilibrated for 24 hours in the sediment.

in a previous study (Root et al., 2007). In this region, arsenic and phosphorus adsorption onto the HFO-doped gels increased, suggesting that a change in the pore water composition affected the amount of arsenic adsorbed. The amount of arsenic adsorbed in this region is probably controlled by the competition with phosphorus (Campbell, 2007; Campbell et al., 2008b). Elevated concentrations

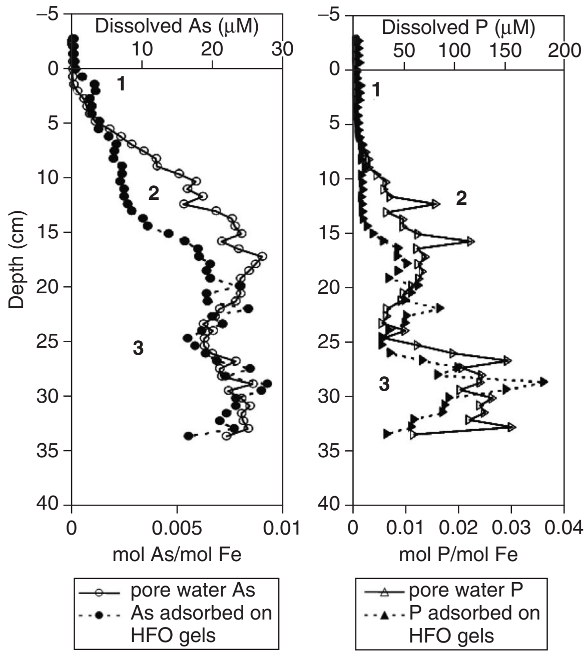

Figure 4 Porewater and adsorption profiles for As and P from a double probe deployed in October 2004. Region 1 denotes the low porewater concentrations of As and P. Region 2 denotes the region of sorption inhibition onto the HFO-doped gels. Region 3 denotes the region where As and P adsorption on HFO-doped gels increase at depth.

of dissolved carbonate from organic carbon mineralization may inhibit the readsorption of arsenic and phosphorus onto the HFO-doped gels in region 2. Deeper in the sediment column, the formation of carbonate green rust may sequester enough of the dissolved carbonate to allow arsenic and phosphorus to adsorb to the HFO-doped gels (region 3), although further evidence is needed to support this hypothesis.

This study illustrates that the processes controlling arsenic mobilization at the Haiwee reservoir are a complex balance between reductive dissolution of the parent Fe(III) oxides; mineralogical change, possibly resulting in a loss of adsorption sites, and sorption inhibition by competitively sorbing ions.

CONCLUSIONS

The case study illustrates how arsenic partitioning between the solid and dissolved phases can be simultaneously affected by arsenic redox cycling, sediment diagenesis, and pore water composition. Ultimately, the mobility of arsenic in surface and groundwater systems is determined by (1) the arsenic redox state,

(2) associations with the solid phase, (3) transformation of the solid phase during diagenesis, and (4) pore water composition, which can also be changed as a result of diagenetic processes. Many of these parameters are driven by microbial processes. This interplay of biogeochemical mechanisms makes understanding the processes responsible for arsenic mobilization in the environment necessarily complex.

Acknowledgments

This work was supported by funding from NSF BES-0 201 888 and EAR-0 525 387. We thank the Los Angeles Department of Water and Power (LADWP), particularly Gary Stolarik, Stanley Richardson, and Fred Richardson, for access to the Haiwee reservoir. We also thank Nathan Dalleska for analytical support, Mike Vondrus for gel probe construction, and Sutinder Ahuja for the invitation to contribute to this book.

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6

GEOMICROBIOLOGY OF IRON AND ARSENIC IN ANOXIC SEDIMENTS

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THE IRON AND ARSENIC REDOX CYCLES: A MICROBIAL PERSPECTIVE

As with other metals, the geochemical cycling of arsenic is complex, involving reduction and oxidation reactions, physical and chemical parameters, and biological factors. The impact of metal-transforming prokaryotes on the arsenic cycle can promote or inhibit the release of arsenic from sediment material. Indeed, reductive dissolution of iron–arsenic minerals is commonly cited as the predominant mechanism promoting arsenic release from sediments, with bacteria able to respire through the enzymatic reduction of sorbed arsenate recently implicated in this process, alongside those able to gain their energy through the reduction of the host Fe(III) minerals (Aurilio et al., 1994; Dowdle et al., 1996; Ahmann et al., 1997;

Arsenic Contamination of Groundwater: Mechanism, Analysis, and Remediation,
Edited by Satinder Ahuja

Islam et al., 2004; Campbell et al., 2006; Kocar et al., 2006). Oremland and Stolz (2005) gave an elegant explanation of the several possibilities regarding the role of metal-reducing prokaryotes on arsenic mobilization, including (Figure 1) (A) reduction of Fe(III) minerals and the subsequent release of arsenate into solution, (B) direct reduction of arsenate by arsenate-reducing microbes and the release of arsenite (which is generally more mobile than arsenate) into solution, or (C) simultaneous reduction of iron and arsenate leading to the release of arsenite. A number of other biological and abiotic factors will influence arsenic mobilization, including the types and genetic capacity of the metal reducers present in the environment; the availability of electron donors and carbon sources; and the physical/chemical conditions in the subsurface environment. Understanding microbe–mineral interactions will be essential to determining which metabolic pathway has the greatest influence on arsenic mobilization, and this is particularly challenging given the complex microbial communities in the subsurface and the ability of metal-reducing bacteria to switch between Fe(III) and As(V) as electron acceptors. However, the dominant control over arsenic mobilization is probably the fine-scale mineralogy of subsurface sediments and the presence of organic matter to drive redox transformations of the mineral assemblages present. Our aim in this chapter is to describe what is known about the mechanisms of

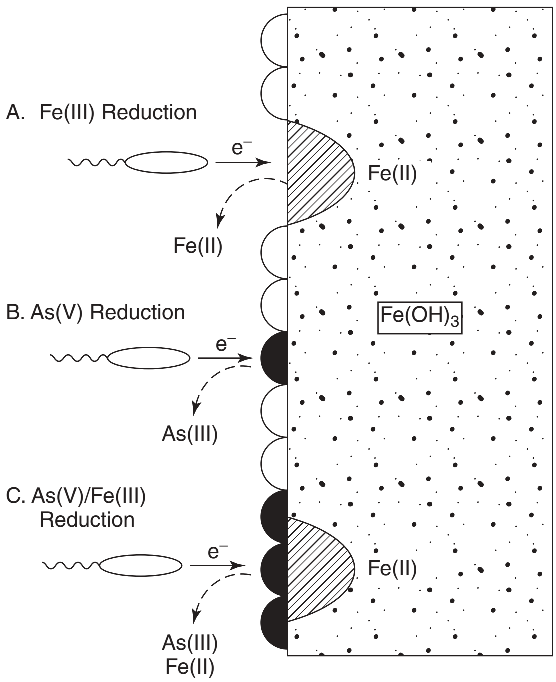

Figure 1 Scheme for arsenate and Fe(III) reduction linked to arsenite production and arsenic mobilization.

microbial release of arsenic from anoxic sediments, focusing on reductive transformations of sorbed As(V) and host Fe(III) minerals, with a particular emphasis on the enzymology and physiology of the process.

MICROBIAL DIVERSITY OF IRON AND ARSENIC REDUCERS

Arsenate-Respiring Prokaryotes

The diversity of arsenate-respiring prokaryotes spans the epsilon, delta, and gamma groups of Proteobacteria, gram-positive bacteria, and Archaea. The study of arsenic-contaminated sites and the exploration of life in extreme environments have led to the isolation of a number of arsenate-respiring prokaryotes, including haloalkaliphilic arsenate-respiring bacteria that require extreme pH and salinities. While the mechanism for utilizing arsenate as a terminal electron acceptor seems to be conserved among a number of prokaryotes, potential electron donors and alternative electron acceptors used by these strains vary widely. Various published strains are summarized in Table 1. A subset of these strains is highlighted below.

The first arsenate-respiring bacterium was reported in 1994 (Ahmann et al., 1994), isolated from sediments with unusually high pore water concentrations of arsenite. Using microcosm experiments containing sediments amended with solid Fe(III) oxides, arsenate, and fermentation end products, dissolved arsenite was shown to increase rapidly within a few days. The accumulation of arsenite was dependent on available electron donors, anaerobic conditions, and microbial activity. From these enrichments an arsenate-respiring bacterium, designated MIT-13, was isolated (Ahmann et al., 1994). Another report focusing on the selenium geochemical cycle described the isolation of a selenate-respiring bacterium, designated SES-3 (Oremland et al., 1994). It was shown that this strain could also use arsenate and other diverse electron acceptors, including fumarate, oxygen, FeOOH, and nitrate. Later, in follow-up papers, SES-3 and MIT-13 were renamed *Sulfurospirillum barnesii* and *S. arsenophilum*, respectively (Stolz et al., 1999). Following the isolation of MIT-13 and SES-3, several geomicrobiology studies confirmed that arsenate-respiring microbes could enhance arsenic release from contaminated sediments, presumably through the reduction of sorbed As(V) (Dowdle et al., 1996; Ahmann et al., 1997).

Many of the known arsenate-respiring bacteria are heterotrophic and capable of using lactate as a carbon source and electron donor (Newman et al., 1997; Macy et al., 2000; Niggemyer et al., 2001; Santini et al., 2002). Other forms of carbon on which arsenate respirers can grow include pyruvate, formate, fumarate, butyrate, succinate, malate, glycerol, ethanol, and acetate, the last of which was used to isolate *Chrysiogenes arsenatis* (Macy et al., 1996). One bacterium, *Desulfosporosinus* strain Y5, isolated from Onondaga Lake, Syracuse, New York is capable of coupling the oxidation of aromatic compounds such as syringic acid, ferulic acid, phenol, and toluene to arsenate respiration (Liu et al., 2004). Y5 is phylogenetically similar to *Desulfosporosinus auripigmenti* (Newman et al., 1997),

TABLE 1 Many of the Known Arsenate-Respiring Strains and Their Origins of Isolation

Strain	Origin	Reference
Bacillus sp. str. HT-1	Hamster feces	Herbel et al. (2002)
B. arsenicoselenatis str. E1H	Bottom mud, Mono Lake, California	Blum et al. (1998)
B. macyae str. JMM-4	Australian gold mine	Santini et al. (2002, 2004)
B. selenitireducens str. MLS10	Mono Lake bottom mud, California	Switzer Blum et al. (1998), Afkar et al. (2003)
Chrysiogenes arsenatis str. BAL-1	Australian gold mine	Macy et al. (1996), Krafft and Macy (1998)
Citrobacter sp. str. TSA-1	Termite hind gut	Herbel et al. (2002)
Clostridium sp. str. OhILAs	Ohio river sediments	J. Stolz, pers. comm.
Desulfitobacterium sp. str. GBFH	As contaminated sediments from a freshwater lake, Idaho	(Niggemyer et al. (2001)
D. frappieri		Bouchard et al. (1996), Niggemyer et al. (2001)
D. hafniense		Niggemyer et al. (2001)
Desulfomicrobium sp. str. Ben-RB	Reed bed mud from Australia	Macy et al. (2000)
Desulfosporosinus auripigmenti (formerly *Desulfotomaculum auripigmentum* str. OREX-4)	Upper Mystic Lake, Massachusetts	Newman et al. (1997)
Desulfosporosinus sp. Y5	Superfund site, Onondaga Lake, Syracuse, New York)	Liu et al. (2004), Perez-Jimenez et al. (2005)

MLMS-1	Anoxic bottom water from Mono Lake, California	Hoeft et al. (2004)
Pyrobaculum aerophilum str. IM2	Boiling marine water hole at Maronti beach, Ischia, Italy	Volkl et al. (1993), Huber et al. (2000)
P. arsenaticum str. PZ6*	Pisciarelli Solfatara, Naples, Italy	Huber et al. (2000)
SLAS-1	Salt-saturated brine, Searles Lake, California	Oremland et al. (2005b)
Sulfurospirillum arsenophilum str. MIT-13 (formerly named *Geospirillum*)	As-contaminated sediments, Aberjona watershed, Massachusetts	Ahmann et al. (1994)
S. barnesii str. SES-3 (formerly named *Geospirillum*)	Selenate-contaminated freshwater marsh, western Nevada	Oremland et al. (1994), Stolz et al. (1999)
Shewanella sp. str. ANA-3	Wooden pier piling in an estuary, Massachusetts	Saltikov et al. (2003)
Shewanella sp. str. HAR-4	Fe-As-rich sediments, Haiwee reservoir, California	Malasarn et al. (2004)
Shewanella putrefaciens str. CN-32	Anaerobic subsurface core, New Mexico, California	Fredrickson et al. (1998), Murphy and Saltikov (2007)
Shewanella sp. W3-18-1	630-m deep marine sediments, Pacific Ocean	Murray et al. (2001), Murphy and Saltikov (2007)
Thermus sp. str. HR13	As-contaminated geothermal spring, Growler Hot Spring, California	Gihring and Banfield (2001)
Wolinella sp. str. BRA-1	Bovine rumen fluid	Herbel et al. (2002)

yet metabolically unique in its ability to utilize organic contaminants. This strain could potentially fulfill an ecologically important niche in arsenic cycling in environments contaminated with industrial pollutants (Liu et al., 2004).

Some arsenate-respiring prokaryotes can also use inorganic electron donors. For example, chemoautotrophic arsenate respiration using H_2 and CO_2 has been reported in some strains of bacteria (Newman et al., 1997; Liu et al., 2004). Also, *Halanaerobacteriales* strain SLAS-1 was recently discovered and was shown to couple sulfide oxidation to arsenate respiration (Oremland et al., 2005b). Because subsurface environments may contain low total organic carbon, various forms of chemoautotrophic arsenate respiration could be significant.

Arsenate respiration is not limited to the bacterial domain of life. There are several known arsenate-respiring archaea: hyperthermophilic Crenarchayotes. The freshwater archaeon *Pyrobaculum arsenaticum* and the marine archaeon *P. aerophilum*, and possibly *P. islandicum* (Huber et al., 2000) can grow either heterotrophically or autotrophically by respiring arsenate and other electron acceptors. All grow optimally near 100°C. The continued investigation for arsenate-respiring microbes in extreme environments should uncover additional novel archaea.

The well-known metal-reducing genus *Shewanella* contains at least four species that are capable of respiring arsenate. Saltikov et al. (2003) reported on the first isolation of an arsenate-respiring *Shewanella* species. This bacterium was originally called *S. trabarsenatis* strain ANA-3; however, it is commonly referred to as *Shewanella* sp. strain ANA-3. This strain was developed into the first genetic system for investigating arsenate respiration pathways. Several other *Shewanellas* have also been shown to respire arsenate: *S. putrefacians* strain CN-32 and *Shewanella* sp. W3-18-1 (Murphy and Saltikov, 2007) and HAR-4 (Malasarn et al., 2004). Strain CN-32 respires arsenate by an identical mechanism, as shown originally in ANA-3. There are no other known genetic systems for arsenate respiration in non- *Shewanella* species.

All of the currently isolated arsenate-respiring prokaryotes are capable of using various alternative electron acceptors, including oxygen, iron, manganese, sulfate, nitrate, and selenate. Using alternative electron acceptors would be advantageous because in many environments, arsenic is found adsorbed onto surfaces of iron and manganese oxides; therefore, the capability of using both a metal oxide and arsenic might promote full exploitation of these sediments. Also, in the case of sulfate reduction, precipitation of arsenic-bearing sulfide minerals could help to remove any soluble toxic components from the microbe's local environment.

Iron-Reducing Prokaryotes

The diversity of Fe(III)-respiring prokaryotes includes the delta and gamma subdivisions of Proteobacteria, gram-negative bacteria, and Archaea. Most of the iron reduction that occurs in sediments is due to the oxidation of fermentative end products, such as lactate and acetate, and only a small percentage is attributed to fermentative bacteria (Luu, 2003). The largest group of characterized iron-reducing prokaryotes belongs to the delta Proteobacteria family of

Gebacteraceae, which can oxidize acetate or other organic acids to carbon dioxide (Lovley, 2000). Members of the *Geobacter* genus are the only iron-reducing prokaryotes known to oxidize aromatic compounds, including aromatic hydrocarbons (Lovley, 2000). For example, *G. metallireducens* and *G. sulfurreducens* can oxidize monoaromatic compounds such as toluene. Other members of this genus that can conserve energy through Fe(III) reduction include members of the genera *Desulfuromonas* (Roden and Lovley, 1993; Coates et., 1995), *Pelobacter* (Coates et al., 1995), and *Desulfuromusa* (Fredrickson and Gorby, 1996).

The first Fe(III)-reducing bacterium shown to link its respiratory growth to the reduction of iron oxide was a *Pseudomonas* species reported by Balashova and Zavarzin (1980) and later reclassified as a strain of *Shewanella putrefaciens* (Nealson, 1994). This bacterium could grow via hydrogen oxidation coupled to Fe(III) reduction. In contrast to the delta Proteobacteria, the gamma Proteobacteria subclass of bacteria, including *Shewanella* species, can use oxygen as an electron acceptor. Members of this subclass include organisms such as *S. putrefaciens, S. alga*, and *Ferrimonas balearica*, which can all generate energy for growth from the reduction of Fe(III) with H_2 or organic acids serving as the electron donor (Lovley, 2000; Luu and Ramsay, 2003). For example, *S. alga* BrY was shown to release arsenate from the mineral scorodite as a result of respiratory reduction of Fe(III) to Fe(II) (Cummings et al., 1999). Many *Shewanella* species, such as *S. oneidensis* strain MR-1 isolated from the anaerobic sediments of Lake Oneida, New York, are capable of reducing Fe(III) and have been used as model organisms to study the mechanism of Fe(III) reduction. The genus *Shewanella* is made up of more than 20 species (and rising) inhabiting diverse environments, including spoiled food, oil field wastes, and redox interfaces in marine and freshwater sediments (Nealson et al., 1991).

Fe(III) reducers outside the Proteobacteria include *Geovibrio ferrireducens* isolated from contaminated soil, which can oxidize fatty acids and acetate but not hydrocarbons (Caccavo et al., 1996), and *Geothrix fermentans* isolated from a contaminated aquifer (Coates et al., 1999). These two bacteria are not closely related to each other or to any other bacteria described previously. Thermophilic and hyperthermophilic iron reducers are expected to be the most important Fe(III) reducers in environments with elevated temperature (e.g. hydrothermal vents, deep subsurface) (Lovley, 2000). *Bacillus infernus* was among the first iron-reducing thermophiles recovered in pure culture and has a temperature optimum of 60°C (Boone et al., 1995). Subsequently, *Deferribacter thermophilus* was isolated at 65°C from production waters of a petroleum reservoir while *Thermoterrabacterium ferrireducens* was isolated from hot springs (Green, 1918; Slobodkin et al., 1997). Thus far, all hyperthermophilic microorganisms recovered from a variety of hot environments can reduce Fe(III) and most fall under the domain of Archaea. Other Archaea that can reduce Fe(III) include some mesophilic and thermophilic methanogens (Lovley, 2000). Thermophiles examined in more detail include *Pyrobaculum islandicum* and *Thermatoga maritime*, which conserve energy to support growth from hydrogen oxidation coupled to Fe(III) reduction (Kashefi and Lovley, 2000). The thermophiles are considered to represent the last common ancestor between Bacteria and Archaea (Pace, 1991; Vargas et al., 1998). For this reason, in combination with geological evidence, iron reduction could be considered an ancient form of respiration (Vargas et al., 1998).

Ecology of Metal-Reducing Prokaryotes

Studies have shown that microbial Fe(III) reduction is likely to be more important than abiotic reduction of Fe(III), especially in conditions where sulfate reduction, leading to sulfide-mediated reduction of Fe(III), is minimal (Lovley, 2000). Indeed, iron reducers are able to outcompete sulfate-reducing or methanogenic microorganisms for electron donors such as H_2 in sediments containing bioavailable Fe(III) (Lovley, 1987). Uncertainty does exist, however, over which types of Fe(III) oxides are available for microbial reduction. Fe(III) is virtually insoluble at neutral pH, and many sediments and soils may contain ferric iron minerals in the range 50 to 200 mmol/kg dry matter (Kappler and Straub, 2005). In aquatic sediments, for example, poorly crystalline Fe(III) (hydr)oxides, which typically exist as coatings on clays and other surfaces, are available for microbial reduction, although more crystalline phases such as hematite may not be (Lovley, 2000).

GENETICS OF ARSENIC GEOCHEMISTRY

Mechanisms of Arsenate Reduction

In the last decade, significant progress has been made toward understanding the biochemical and molecular biological basis for arsenate reduction (reviewed by Silver and Phung, 2005). It is now recognized that at least two mechanisms for arsenate reduction exist, and both have the potential to affect the biogeochemical cycling of arsenic. In addition, there are enzymes that can oxidize arsenite in organisms that use nitrate or oxygen as the electron acceptor (Santini and vanden Hoven, 2004), but these are not discussed in detail here, as reductive and not oxidative transformations have been implicated in arsenic mobilization in sediments. Prior to the first identification of a gene encoding an arsenate reductase, there have been numerous early reports of As(V)-reducing mixed heterotrophic microbial communities (Johnson, 1972; Myers et al., 1973) and pure cultures (Green, 1918; Woolfolk and Whiteley, 1962; Myers et al., 1973; Vidal and Vidal, 1980; Jones et al., 1984). Arsenate reduction would later be found in association with resistance to high levels of arsenite [$\sim$1 to 10 mM As(III)]. Others have referred to these as arsenic-resistant microbes (ARM) (Oremland et al., 2005a). The first genetic studies showed that arsenic resistance was plasmid-associated and encoded by a specific cluster of genes known as the *ars* operon (Hedges and Baumberg, 1973). The proteins encoded by *ars* genes have been investigated thoroughly at the biochemical level and mediate the intracellular reduction of arsenate [which can enter the cell as a phosphate analog (Figure 2A)], and its subsequent efflux as arsenite in an energy-utilizing detoxification pathway.

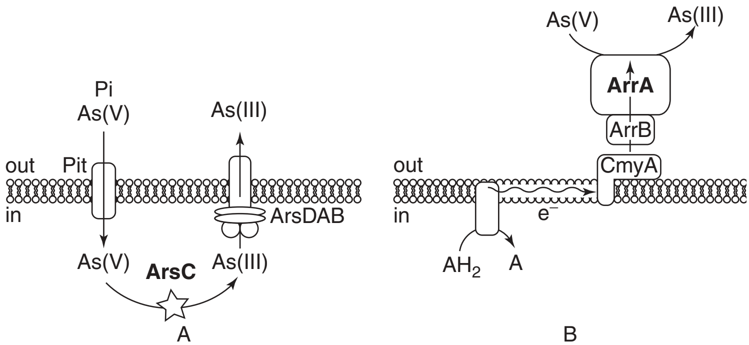

Figure 2 Biochemical models for arsenate reduction in bacteria. (A) Detoxification-based arsenate reduction is mediated by a cytoplasmic arsenate reductase called ArsC. Arsenate enters the cell through a phosphate uptake channel, Pit. Once in the cytoplasm, arsenate is reduced by ArsC and arsenite is chaperoned (by ArsD) to an ATPase-activated (ArsA) pump (ArsB). (B) Arsenate respiratory reduction is mediated by a periplasmic reductase specific for arsenate. AH_2 represents a substrate that is oxidized by a dehydrogenase. The electrons are transferred via an electron transport chain to ArrA, the catalytic subunit for arsenate reduction.

Almost all prokaryotes have *ars*-like genes in their genomes. A second As(V) reduction pathway involved in energy conservation was subsequently discovered by geomicrobiologists investigating the arsenic geochemical cycle. This other As(V)-reduction pathway was shown to be physiologically and biochemically distinct from As(V) reduction carried out by ARMs (Ahmann et al., 1994; Oremland et al., 1994; Krafft and Macy, 1998). This metabolism is conferred by *arr* (arsenate respiratory reduction) genes. Arsenate reduction via respiration allows prokaryotes to use arsenate as a terminal electron acceptor in the absence of oxygen. Arsenate-respiring prokaryotes couple the oxidation of an electron donor to the reduction of arsenate to arsenite. Cells conserve the energy released in the coupled reactions to fuel their growth and other cellular processes.

ars Operon

Resistance to arsenic salts has been known for quite some time. In the late 1970s, resistance to As(V), As(III), and Sb(III) were shown to be associated with a cluster of genes called the *ars* operon (Silver et al., 1981). This discovery came from early biomedical studies of phosphate transport in *Escherichia coli* and *Staphylococcus aureus* (Rosenberg et al., 1977; Willsky and Malamy, 1980b; Silver et al., 1981; Rosenberg et al., 1982). The *ars* operon confers an arsenic resistance phenotype and is distinct from the *arr* operon, which is required for arsenate respiration. Numerous bacteria and archaea have *ars* operon homologs (Mukhopadhyay et al., 2002). For example, the *arsRDABC* operon in *E. coli* has been extensively studied at the biochemical and genetic levels (reviewed by Mukhopadhyay et al., 2002). Figure 2A depicts a model for *ars*-dependent reduction of arsenate. A cytoplasmic 12 to 14-kDa arsenate reductase catalyzes arsenate reduction, which is then pumped out the cell via ArsB, a transmembrane cytoplasmic membrane efflux pump specific for arsenite and antimonite. An arsenite chaperone, ArsD, and an ATPase, ArsA, interact with ArsB to provide high-level arsenite resistance through the hydrolysis of ATP. The DNA binding protein, ArsR, which becomes de-repressed in the presence of arsenite or antimonite, carries out regulation of *ars* transcription.

arr Operon

Although much is known about the biochemistry of Ars proteins and the regulation of the *ars* operon, little is known about the *arr* operon. Studies have reported on the biochemical identification of the ArrA and ArrB proteins in two other bacteria (Krafft and Macy, 1998; Afkar et al., 2003) and the genes required for arsenate respiration have been identified (Saltikov and Newman, 2003). From these studies a putative model for arsenate respiratory reduction is beginning to emerge (Figure 2B). The arsenate respiratory reductase catalytic subunit, ArrA, is a 90 to 95-kDa molybdenum-containing protein and is most likely localized to the bacterial membranes. ArrA receives electrons from ArrB, a 26-kDa (approx.) iron–sulfur-containing subunit. The As(V) K_m values for the ArrAs of *Chrysiogenes arsenatis* and *Bacillus selenitireducens* MLS-10 are 34 and 300 μM, respectively, which are considerably lower than the detoxification reductase, ArsC (~1 mM). Arsenate therefore has a stronger affinity toward ArrA than toward the detoxifying arsenate reductase ArsC. This could have important environmental consequences about the type of reductase involved in reducing arsenate strongly sorbed on surfaces of minerals.

Shewanella sp. ANA-3 has been used as a model organism to study arsenate respiration at the genetic level (Saltikov and Newman, 2003; Saltikov et al., 2003; Murphy and Saltikov, 2007). The *arr* operon of ANA-3 is composed of two genes: *arrAB*, which encodes a ~95-kDa molybdenum-containing subunit, ArrA, and a ~26-kDa FeS-containing subunit, ArrB, similar to those of *C. arsenatis* and *B. selenitireducens*. Strains of ANA-3 without the *arrA* or *arrB* genes neither grow on nor reduce arsenate under anaerobic conditions. However, the *arr* gene deletion strains grow similarly to wild type when other electrons acceptors, such as nitrate, TMAO, and fumarate, are provided. Growth on arsenate can also be restored by complementation with either *arrA* or *arrB* on a plasmid. Recent work identified a third gene, *cymA*, that is essential to arsenate respiration (Murphy and Saltikov, 2007). The *cymA* gene encodes a *c*-type tetraheme cytochrome. Not only is *cymA* essential for arsenate respiration, but it is also required for the use of other terminal electron acceptors [e.g., oxides of Fe(III) and Mn(IV] (Schwalb et al., 2002). Recent gene expression studies showed that *arr* and *ars* transcription patterns are different (Saltikov et al., 2005). The transcription of *arsC* was dependent on arsenite in cultures respiring oxygen and a variety of alternative terminal electron acceptors. On the other hand, *arrA* gene expression was inhibited by oxygen and nitrate, but surprisingly, induced by arsenite and arsenate to a lesser extent. The lowest amount of arsenite required to induce an increase in *arrA* gene expression (compared to no arsenic controls) occurred around 100 nM (~7.5 ppb). This concentration is well within the MCL (maximum contaminant level) for arsenic (10 ppb). In contrast, a detectable increase in *arsC* gene expression occurred around 100 μM (7.5 ppm). Using an arsenate reduction–deficient ANA-3 strain (an *arsC* and *arrA* double deletion mutant) it was shown that arsenate induced *arr* gene expression but not the *ars* operon. The arsenate-dependent gene expression was about 10-fold less than arsenite, suggesting that arsenite had a more potent affect on *arr* gene expression.

Although ArrA is a different type of arsenate reductase than ArsC, ArrA shares several similarities with enzymes of the DMSO reductase family of molybdenum-containing enzymes (Figure 3A); ArrA contains a molybdenum cofactor and iron–sulfur clusters. DNA sequences for several arsenate-respiring prokaryotes have also been determined (Malasarn et al., 2004), and Figure 3 illustrates a phylogenetic comparison of the predicted ArrA proteins to other dimethyl sulfoxide (DMSO) family proteins, including formate dehydrogenase (Fdh), arsenite oxidase (AroA), and various reductases for nitrate (Nap/Nar), selenate (SerA), DMSO (Dms), trimethyl-N-amine oxide (Tor), biotin sulfoxide (BisC), and polysulfide (Psr). The ArrB protein follows similar phylogenetic conservation as that observed with ArrA. The existence of additional subunits and regulatory proteins may be present based on the analysis of the genomic sequence of *Desulfitobacterium hafniense*, which contains a cluster of genes that appear to encode homologous Arr proteins (Figure 3B). The genomic arrangement in *D. hafniense* for the *arr* operon is *arrTSRCABD*, which is structurally different from *arrAB* of *Shewanella* sp. ANA-3 (Figure 3). There are five additional open reading frames that are predicted to encode a membrane protein ArrC that serves as an anchor for ArrAB, a TorD-like chaperone protein, ArrD, which may be involved in cofactor insertion into ArrA, and three regulatory proteins, ArrR, ArrS, and ArrT, which resemble a two-component sensor and response regulators of the histidine kinase family and a periplasmic phosphonate-binding protein (ArrT). Additional evidence for an ArrC membrane anchor for ArrAB is also found in the *arr* genomic region for *Wolinella succinogenes* (Figure 3). In *Shewanella* sp. ANA-3, the membrane anchoring subunit is probably encoded by *cymA*, a membrane-bound *c*-type tetraheme cytochrome (Murphy and Saltikov, 2007). Finally, the *Shewanella arrAB* operon is unique in its close proximity to an *arsDABC* gene cluster. This observation suggests that arsenic resistance and arsenate respiration are encoded on an “arsenic island” either as a transposable element or plasmid (although no plasmids less than 50 kilobase pairs have been observed in DNA preparations from ANA-3). Genome sequences of other arsenate-respiring bacteria should reveal more insight into the origins of arsenate respiratory reduction.

Detoxification Versus Respiration of Arsenate

It is clear that the detoxification and respiratory-based arsenate reduction processes are biochemically distinct and have very different effects on cellular

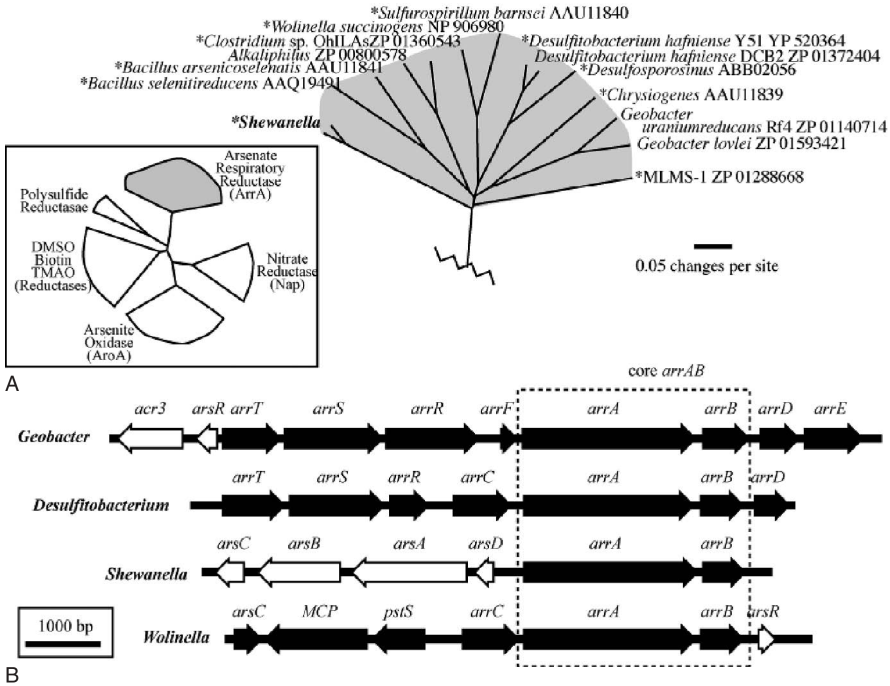

Figure 3 Phylogenetic and genomic locations of the arsenate respiratory reductase gene, *arrA*. (A) The ArrA enzyme is part of the DMSO family of molybdenum-containing oxidoreductases (phylogentic tree in the box). Detailed phylogenetic analysis of ArrA from various known arsenate-respiring bacteria (noted by *) and bacteria with homologous sequences in their genomes. (B) A comparison of four genomes of bacteria with *arrAB* genes shows the structural diversity and composition of *arr* genes. Genes with white fills are associated with arsenic-resistance operons similar to *ars*. The box with the dashed lines indicates the core set of genes for *arr* operons. In *Geobacter lovleyi, arrE* encodes a putative iron–sulfur protein similar to ArrB. The *arrF* gene encodes a predicted small multiheme *c*-type cytochrome.

metabolism. First, the arsenate-detoxifying reductase depletes the cell of intracellular reductant (e.g., glutathione), whereas the respiratory process, when coupled to oxidation of an electron donor, allows the cells to conserve energy for growth and metabolism. Second, because respiring and detoxifying arsenate involves a reductase, the end product, arsenite, can become quite toxic, requiring an additional detoxification step. Pumping arsenite out of the cytoplasm requires energy derived either from the proton gradient, which can be enhanced through ATPase activity of ArsA and its interactions with ArsB. Because of the toxicity of arsenite, it may seem that arsenate-respiring prokaryotes would require a similar system for detoxifying the cytoplasm of the arsenite generated. In *Shewanella* sp. ANA-3, when the *arsB* gene was interrupted by a transposon, the cells became sensitive to >1 mM arsenite. However, the mutant strain still respired arsenate, albeit at a lower capacity than the parent strain with an intact *arsB* (Saltikov et al., 2003). Third, the enzymology of ArsC compared to ArrA is strikingly different. Several reviews have been published summarizing the extensive biochemical characterization of various ArsCs (Mukhopadhyay and Rosen, 2002). However, much less is known about the biochemistry of the respiratory enzyme ArrA. The most obvious distinguishing feature of ArsC is its size; ArsCs are much smaller than ArrA, about 135 versus about 850 amino acids, respectively.

In contrast to ArsC, ArrA is predicted to contain a molybdenum diguanine nucleotide cofactor and iron-sulfur clusters (Krafft and Macy, 1998; Afkar et al., 2003). The mechanism of reducing arsenate by a molybdenum-containing enzyme such as ArrA probably involves the exchange of two electrons and one oxygen atom, which is typical of most molybdenum cofactor–containing enzymes (McEwan et al., 2002). Electron transfer to arsenate by ArsC involves an entirely different mechanism, requiring coordination of thiols from the first cysteine residue of the enzyme (Liu and Rosen, 1997; Martin et al., 2001; Mukhopadhyay and Rosen, 2002). The source of electron donors to the two reductases is also different. Reductant is supplied to ArrA from membrane components of the electron transport chain. In contrast, ArsC obtains its reducing power from intracellular reduced glutathione or ferrodoxin (Mukhopadhyay and Rosen, 2002). Last, ArrA in *Shewanella* sp. ANA-3 contains a signal peptide similar to the twin arginine translocation pathway, which targets secretion or localization to the inner membrane. In contrast, ArsC is located and active in the cytoplasm. Although the properties of ArrA and ArsC are quite distinct in many aspects, they both catalyze the same chemical reaction and may potentially leave the same biogeochemical "footprint." This presents a unique challenge in understanding the fundamental biological mechanism(s) underlying arsenate reduction in the environment.

Phylogenetics of ArrA

The arsenate respiratory reductase ArrA and the arsenite oxidase (AroA) that has been identified in specialist organisms capable of respiration via the oxidation of As(III) (Silver and Phung, 2005) are very similar to each other, sharing on average 35 to 40% amino acid sequence similarities. Each contains a molybdopterin cofactor, both have an iron-sulfur cluster domain, both interact with an Fe–S subunit, and their molecular weights are similar (over 80 kDa). These features also apply to a number of other molybdopterin-containing DMSO reductase family proteins (reviewed by McEwan et al., 2002). However, ArrA is as different from AroA at the amino acid sequence level as it is to the nitrate reductase, NapA, or formate dehydrogenase, Fdh. Phylogenetic analysis of other molybdopterin-containing proteins places ArrA and AroA into two distinct clusters (Figure 3). The polysulfide reductase cluster, Psr, is the nearest neighbor to

ArrA, suggesting that they share features of an ancestral molybdenum-containing enzyme. The amino acid conservation among ArrAs allowed the development of a consensus PCR primer set that was useful for the detection of *arrA* gene in 12 of 14 previously identified arsenate respiring strains and also in environmental samples (Malasarn et al., 2004).

GENETICS OF IRON REDUCTION

The mechanism(s) responsible for microbial-mediated iron reduction has remained elusive. However, multiple studies have shown that iron reducers can cope with the difficulty of transferring electrons from the cell to the surface of the iron mineral by at least three mechanisms: (1) having physical contact between the surface of the cell and the surface of the mineral; (2) secreting iron chelators, which increases the solubility and hence bioavailability of Fe(III); or (3) secreting electron shuttling compounds, which transfer electrons from the cell to the insoluble Fe(III) mineral without direct physical contact. Species of the genus *Geobacter* appear to need physical contact to reduce ferric iron oxides (Nevin and Lovley, 2000; Lovley et al., 2004). These can include low-potential multiheme cytochromes localized on the surface of the outer membrane (Methe et al., 2003) and special conductive cell appendages called *pili* or *nanowires*, which have been shown to be produced when the cell is grown on insoluble Fe(III) but not with soluble Fe(III)-citrate (Reguera et al., 2005). The genome of *Geobacter sulfurreducens* encodes over 100 cytochromes (Methe et al., 2003), possibly to provide the opportunity to form multiple routes for electron transfer to Fe(III) and thus better maximize rates of Fe(III) reduction and/or provide a high degree of flexibility to adapt to disruptions in electron transfer pathways (Leang et al., 2005).

Several detailed reviews on the molecular and biochemical mechanisms for iron reduction have been published (Hernandez and Newman, 2001; Luu and Ramsay, 2003). In summary, the mechanism of Fe(III) reduction in *Shewanella* species shares the basic characteristics of direct electron transfer to mineral surfaces with *Geobacter* species, but these organisms are also able to secrete a yet to be identified electron shuttle to mediate extracellular electron transfer (Newman and Kolter, 2000). Direct electron transfer to Fe(III) oxides can include nanowire structures (Gorby et al., 2006) and also a network of *c*-type cytochromes and accessory proteins traversing the cytoplasmic membrane and periplasm and terminating on the outer membrane. *Shewanella oneidensis* strain MR-1 has been used as the model organism in these studies, and its genome encodes ~40 cytochromes, many of which are predicted to be multiheme in character. Multiple studies have shown that the following cytochromes are known to be involved in the reduction of Fe(III) oxides: CymA, MtrD, MtrF, MtrA, OmcA, and MtrC (also called OmcB). Additionally, there are other non-cytochrome proteins, such as MtrB and MtrE, that are thought to interact with the cytochromes and are required for efficient Fe(III) reduction.

Current models for Fe(III) reduction by *Shewanella* species start with the reduction of a meniquinone pool by a dehydrogenase in the cytoplasmic membrane. Oxidation of the meniquinones may lead to the reduction of CymA, which either directly or indirectly transfers electrons to MtrA in the periplasm, possible via another electron transfer protein. Once electrons are passed to MtrA, this cytochrome may transfer electrons to MtrC in the outer membrane. Finally, MtrC, by itself or as part of an enzyme complex, may reduce Fe(III). It has also been suggested that CymA may function as a terminal reductase for soluble Fe(III) chelates (Pitts et al., 2003). Finally, an alternative hypothesis suggests that MtrB is a protein scaffold that permits the transient association between reduced periplasmic proteins and an OmcA–MtrC protein complex (Shi et al., 2006) (Figure 4). Depending on the metabolic needs of the organism, different redox partners may possibly couple with either OmcA or MtrC as a means to maintain critical metabolic pathways important to the energy metabolism of the organism (Shi et al., 2006).

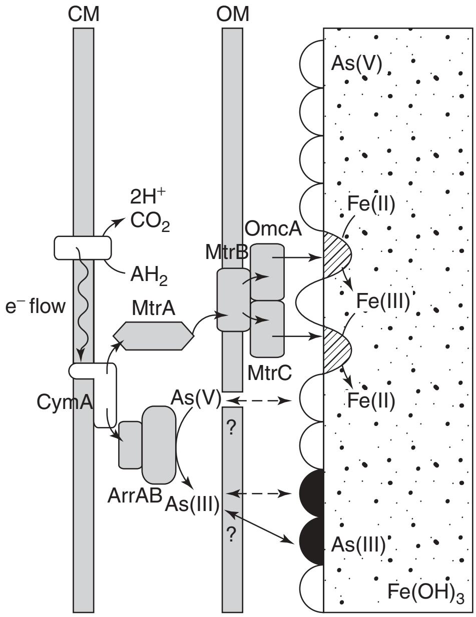

Figure 4 Scheme based on *Shewanella*, showing the molecular details of microbe–mineral interactions with hydrous ferric oxide [HFO or $Fe(OH)_3$] sorbed with arsenate (white half circles) and arsenite (black half circles). Gray vertical bars are the outer membrane (OM) and cytoplasmic membrane (CM) of the bacterium; "e – flow" represents electrons flowing into the quinone pool and to CymA, the tetraheme *c*-type cytochrome. The solid arrows indicated direction of electron flow. The hatched areas in the HFO represents zones of Fe(III) reduction. Dashed arrows indicate desorption/adsorption of arsenate or arsenite. Transport of As(V) or As(III) across the OM is not well understood and is indicated by "?".

IRON REDUCTION AND ARSENIC MOBILIZATION: A MOLECULAR PERSPECTIVE

The biochemical and molecular mechanisms for iron reduction are clearly complex and include a subtle interplay between the electron transfer chains in iron-reducing bacteria, released and exogenous electron mediators [e.g., humics (Lovley et al., 1996)], geochemical constraints, and the structure of the Fe(III) minerals present. With respect to arsenic, microbes are known to reduce solid-phase arsenate [e.g., associated with (hydr)oxides of aluminum and iron]; however, the detailed mechanism of the surface chemistry that makes arsenate available for bacterial reduction is not known. Is arsenate locally desorbed prior to its reduction, or does reduction occur directly on the solid phase? If the latter is true, which arsenate reductase is most likely to be used to reduce solid-phase arsenate, ArrA or ArsC? There are several reports that support ArrA-mediated reduction of surface-associated arsenate. Recent work with *Shewanella* sp. ANA-3 has shown that *arrA* gene expression is increased when it is grown on solid-phase arsenate [adsorbed onto hydrous ferric oxide (HFO)]. In addition, *arrA* is also required by ANA-3 to reduce arsenate adsorbed onto HFO (Malasarn et al., 2004). Strains lacking the *arrA* gene no longer respire arsenate in liquid phase or when it is associated with mineral phases of iron. Moreover, *arrA* gene expression has been detected in anaerobic sediments contaminated with arsenic. *Shewanella* sp. CN-8, which is a detoxifying arsenate reducer and not an arsenate-respiring prokaryote, can reduce aqueous-phase arsenate but not arsenate sorbed onto Fe(III) oxides (Langner and Inskeep, 2000). Because ArrA is located in the periplasmic space of the bacterium compared to the cyotplasmic location of ArsC, it is possible that electrons are more efficiently transferred to surface-associated As(V) by an ArrA-mediated mechanism instead of one involving ArsC directly. It is interesting that most prokaryotes have ArsC, which is an adaptation for detoxifying the cytoplasm of arsenate. On the other hand, *arrA* is not commonly found in the genomes of most sequenced microbes. Under anaerobic conditions where ArrA seems to be active, it is possible that ArsC-dependent reduction could occur when other electron acceptors are available (e.g., nitrate, DMSO, fumarate), and the organism is, therefore not respiring on arsenate. However, evidence is mounting that ArrA is mediating the reduction and release of surface-associated arsenic in subsurface anoxic sediments (Afkar et al., 2003; Oremland et al., 2005b).

MICROBIOLOGICAL MECHANISMS UNDERPINNING ARSENIC MOBILIZATION IN SEDIMENTS

Contamination of groundwater from arsenic in Earth's crust poses a public health crisis in areas such as Mexico, China, Hungary, Argentina, Chile, Cambodia, West Bengal, India, and Bangladesh (Smith et al., 2000). For example, 28 to 62% of the 125 million inhabitants of Bangladesh are at risk of arsenic poisoning from drinking water. Long-term exposure to arsenic can lead to scaling of the skin, circulatory and nervous system disorders, and skin, lung, and bladder cancers (Smedley and Kinniburgh, 2002). In West Bengal and Bangladesh, where the problem has received most attention, the aquifer sediments are derived from weathered materials from the Himalayas. Arsenic typically occurs at concentrations of 2 to 100 ppm in these sediments, much of it sorbed onto a variety of mineralogical hosts, including hydrated ferric oxides, phyllosilicates, and sulfides (Nickson et al., 2000; Smedley and Kinniburgh, 2002). The mechanism of arsenic release from these sediments has been a topic of intense debate, and both microbial and chemical processes have been invoked (Das et al., 1996; Nickson et al., 1998; Chowdhury et al., 1999; Oremland and Stolz, 2003; Akai et al., 2004). The oxidation of arsenic-rich pyrite has been proposed as one possible mechanism (Das et al., 1996; Chowdhury et al., 1999). Other studies have suggested that reductive dissolution of arsenic-rich Fe(III) oxyhydroxides deeper in the aquifer may lead to the release of arsenic into the groundwater (Nickson et al., 1998, 2000; Harvey et al., 2002; Smedley and Kinniburgh, 2002). Additional factors that may add further complication to potential arsenic-release mechanisms from sediments include the predicted mobilization of sorbed arsenic by phosphate generated from the intensive use of fertilizers (Acharyya et al., 1999), by carbonate (Appelo et al., 2002) produced via microbial metabolism (Harvey et al., 2002), or by changes in the sorptive capacity of ferric oxyhydroxides (Smedley and Kinniburgh, 2002).

However, microbially mediated reduction of assemblages comprising arsenic sorbed to ferric oxyhydroxides is gaining consensus as the dominant mechanism for the mobilization of arsenic into these groundwater (Nickson et al., 2000; Smedley and Kinniburgh, 2002; Akai et al., 2004; Islam et al., 2004; van Geen et al., 2004). For example, a recent microcosm-based study provided the first direct evidence for the role of indigenous metal-reducing bacteria in the formation of toxic, mobile As(III) in sediments from the Ganges delta (Islam et al., 2004). This study showed that the addition of acetate to anaerobic sediments, as a proxy for organic matter and a potential electron donor for metal reduction, resulted in stimulation of microbial reduction of Fe(III) followed by As(V) reduction and release of As(III). Microbial communities responsible for metal reduction and As(III) mobilization in the stimulated anaerobic sediment were analyzed using molecular (polymerase chain reaction) and cultivation-dependent techniques. Both approaches confirmed an increase in numbers of metal-reducing bacteria, principally *Geobacter* species. However, subsequent studies have suggested that most *Geobacter* strains in culture do not possess the *arrA* genes required to support the reduction of sorbed As(V) and mobilization of As(III). Indeed, in strains lacking the biochemical machinery for As(V) reduction, Fe(II) minerals formed during respiration on Fe(III) have proved potent sorbants for arsenic present in the microbial cultures, preventing mobilization of arsenic during active iron reduction (Islam et al., 2005). However, the genomes of at least two *Geobacter* species (*G. unraniumreducens* and *G. lovleyi*) do contain *arrA* genes (Figure 3), and interestingly genes affiliated with the *G. unraniumreducens* and *G. lovleyi arrA* gene sequences have been identified in Cambodian sediments stimulated for iron and arsenate reduction by heavy ^{13}C-labeled acetate using a stable isotope probing technique (Lear et al., 2007). Indeed the type strain of *G. unraniumreducens* has recently been shown to reduce soluble and sorbed As(V), resulting in mobilization of As(III) in the latter case (Gault et al., unpublished). Thus, some *Geobacter* species may play a role in arsenate release from sediments. However, other well-known arsenate-reducing bacteria, including *Sulfurospirillum* species, have also been detected in ^{13}C-amended Cambodian sediments (Lear, 2007) and hot spots associated with arsenic release in sediments from West Bengal (Rowland, Ph.D. thesis, University of Manchester, 2006).

Although the precise mechanism of arsenic mobilization in Southeast Asian aquifers remains to be identified, the role of As(V)-respiring bacteria in the process is gaining support. Indeed, recent studies with *Shewanella* sp. ANA-3 and sediment collected from the Haiwee reservoir (Olancha, California) have suggested that such processes could be widespread but not necessarily driven by As(V) reduction, following exhaustion of all bioavailable Fe(III). In this study, arsenate reduction started before Fe(III) reduction and ceased after 40 to 60 hours. During part of the experiment, arsenate and Fe(III) were reduced simultaneously (Campbell et al., 2006).

FUTURE PERSPECTIVES

Several recent studies have suggested a role for arsenate-reducing bacteria in the mobilization of arsenic in aquifer sediments. However, the precise mechanism of arsenic release, especially from Fe(III) minerals, remains to be identified, and mitigation approaches are yet to be implemented in many regions affected by high concentrations of arsenic in groundwater. Current research activities will continue to focus on the nanoscale interactions of sediment bacteria and host mineral assemblages, and the underpinning biochemistry, in an attempt to understand the molecular basis of this devastating process. It is hoped that by gaining a better understanding of the microbial basis of this process and the precise geochemical and mineralogical controls, improved mitigation processes can be developed.

Acknowledgments

J.R.L. acknowledges the financial support of UK NERC (grant NE/D013291/1). C.W.S. acknowledges the National Science Foundation for financial support (grant EAR-0535392).

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7

DEVELOPMENT OF MEASUREMENT TECHNOLOGIES FOR LOW-COST, RELIABLE, RAPID, ON-SITE DETERMINATION OF ARSENIC COMPOUNDS IN WATER

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ANALYTICAL CHEMISTRY

What analytical chemists do is provide information about the chemical composition of relevant materials that is useful within the context of the problem being studied. Typically, this information is needed so that a decision can be taken about some bulk material or system, and therefore the information provided has to come with a statement about its reliability. For quantitative data, the statement about reliability often takes the form of a ± term, where the ± term is some well-understood summary measure of the spread of the results that can be interpreted in terms of how likely the true value is to fall within this interval. The 95% confidence interval based on $ts/\sqrt{n}$ is often quoted. In this expression, t is Student's t-value (found from tables), s is the sample standard deviation, and n is the number of replicate measurements made.

What is acceptable as a ± term is a decision that the end user of the information has to make, again within the context of the problem. In specifying a ± term, it must be borne in mind that the narrower the interval, the more costly the analysis. There are two reasons for this: One is that measurements that have an inherent narrow interval are made at concentrations well above the detection limit (a

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Edited by Satinder Ahuja

concept discussed in more detail later), and procedures that have low detection limits usually involve measurements with expensive instruments; the second is that the ± term can be narrowed by increasing n, which in turn increases the amount of work and time needed to complete the analysis.

However, it should also be borne in mind that the ± term says nothing about the accuracy of the result. It is quite possible to be precisely wrong. To make a statement about accuracy, the true value must be known. It is possible to purchase, from reputable suppliers, standard reference materials whose chemical composition, established by repeated analyses (possibly by different laboratories), is described in the accompanying certificate. It is common practice when validating an analytical method to consider the method accurate if the range of values represented by the mean ± the 95% confidence includes the certificate value. Thus, a relatively large ± term (large, that is, in relation to the mean value) may mean that the method is "accurate," as the interval about the mean contains the true value, but this interval may be so large that the information is not useful. Context is everything in this situation. If the goal of the measurements is to decide whether the total arsenic concentration in a ground water sample is greater or lower than 50 μg/L, then a result of 20 μg/L with a relatively large ± term, even ± 20 μg/L, is still useful, whereas a measurement of 40 ± 20 μg/L is clearly not useful. On the other hand, 40 ± 5 μg/L is a useful result.

Developments in analytical chemistry methodology are often driven by the need to provide end users with information that is not only useful within the context of the problem, but also comes with an affordable price tag and within a useful time scale. That is, the pragmatic issues surrounding the cost-effectiveness of chemical measurement support for a project are often paramount. Such developments can be tracked in the analytical chemistry literature, as the majority of published articles are about the determination of *X,* a more or less well-defined analyte species, in *Y,* a more or less well-characterized matrix, by *Z,* a method that includes as the measurement stage a more or less well-known instrumental technique. Many published reports contain information that is useful to the practicing community, and therefore the methodology described will represent some improvement in the existing measurement performance. Such an improvement may be judged against a variety of performance characteristics, including accuracy, precision, speed, cost, robustness, and portability.

Analytical Chemistry Literature Examining the numbers of publications on a given topic in the original analytical chemistry research literature can be instructive. If there is "one" publication and it dates from the early part of the twentieth century or even earlier, there is a good chance that the method works. The determination of nitrogen by the Kjehldahl method is a good example. On the other hand, if there are hundreds or even thousands of publications, this probably means that the methods don't work quite right, so there is a continued effort by the community to "get it right." The determination of arsenic in water probably falls into the latter category, as the Web of Science database shows about 2500 publications relating to the determination of arsenic species in water.

This number approximately quadruples if the restriction of the sample matrix to water is removed. If the key word search is restricted to the title only, there are well over 3000 publications in the database relating to the determination of arsenic. In recent years, papers have been appearing at the rate of 100 per year.

The majority of these publications are concerned with some aspect of the determination of arsenic, in which the analyses have been performed in a laboratory setting with state-of-the-art instrumentation. It is clear that the need for information about the distribution of the total arsenic among various possible chemical forms, or species, is driving many analytical method development studies. The community would seem to be converging on the combination of some high-performance separation technique coupled with some element-specific detector, of which options the coupling of high-performance liquid chromatography (HPLC) with inductively coupled plasma (ICP) mass spectrometry (MS) would appear to be the most powerful. For the determination of total arsenic, the most popular of the several possible candidate techniques are all atomic optical spectrometries [absorption spectrometry (AAS), atomic emission spectrometry (AES), or atomic fluorescence spectrometry (AFS)] or atomic mass spectrometry. The issues that drive the research and development are the problems of sample preparation and pretreatment, so that the subsequent measurement produces information that is useful within the context of the problem being studied. In turn, this places restrictions on the accuracy and precision of the information. Speciation studies are particularly difficult in that for many sample materials the key step is the mobilization of all relevant species into solution, without changing relative concentrations. There are also issues related to the (non- or limited) availability of standards (such as arsenocholine or arsenosugars) and reference materials certified for species content.

CURRENT STATUS OF ARSENIC DETERMINATION

It is not difficult to determine arsenic in slightly contaminated distilled water at concentrations down to single-digit μg/L values or even much lower, so it is relevant to ask why 100 publications per year are still appearing in the analytical chemistry literature. The answer is related to (1) the increasing interest in obtaining information about how arsenic is distributed among a variety of chemical species, and as discussed above, this analysis is difficult, and (2) to the use of hydride generation. In this technique, arsenic compounds are converted to volatile derivatives by reaction with a hydride transfer reagent, usually tetrahydroborate(III) (also known as borohydride) whose sodium and potassium salts are relatively stable in aqueous alkali. Although hydride generation (HG) has been known for many decades, and has the advantage that arsenic may be determined by a relatively inexpensive atomic absorption spectrometer or an even cheaper atomic fluorescence spectrometer, at single-digit μg/L concentrations, its generation is prone to inference from other matrix components, so every “new” matrix represents a new analytical problem, whose solution merits publication in the analytical literature.

The two topics are linked in that HG can be quite effective as an interface between HPLC separation and element specific detection. In fact, it is possible to get the same performance from HG-AFS as from ICP-MS, and therefore, as the former detector represents a significant saving in both capital and operational costs compared with the latter, there is considerable interest in this "niche" use of AFS. Developments in the analytical chemistry of arsenic (and every other element in the periodic table that can be determined by atomic spectrometry) can be followed in the annual Atomic Spectrometry Update (ASU) reviews in the *Journal of Analytical Atomic Spectrometry*. The ASU Web site should be consulted for further information, but the June ASU issue entitled "Advances in Atomic Emission, Absorption and Fluorescence Spectrometry, and Related Techniques" [1] and the February issue entitled "Environmental Analysis" [2] should be consulted for a full picture of relevant recent developments. For both speciation and total arsenic determinations, there is also the issue of the lowest concentration that can be measured reliably.

Limits of Detection

The detection limit concentration is the subject of ongoing, albeit somewhat low-level discussion in the chemical measurement community [3]. Whatever the basis for the definition, the reality is that for concentrations at the detection limit, the associated $\pm$ term is rather large, perhaps several tens of percent in relative terms. This means that a procedure whose detection limit is close to a critical action threshold, such as 10 or 50 µg/L for arsenic in drinking water, is not much use. As a reasonable guideline, if the detection limit is defined according to the International Union of Pure and Applied Chemistry as the concentration producing a signal equal to three times the standard deviation of a series of measurements of the blank, this value should be at least 10-fold lower than the critical threshold value of concern. For example, if the goal is to make reliable measurements of arsenic at concentrations of 10 µg/L, the detection limit of the procedure used should be 1 µg/L.

It is also worth noting that when the concentration of the analyte is present at the detection limit concentration, if the probability distribution function for the measurement errors is symmetrical about the central value, 50% of the measurements will be above the detection limit and 50% will be below. It is therefore quite likely that for this concentration, the measured value will be below the detection limit and should be reported as the concentration obtained rather than as "not determined" (ND).

To some extent, it is the need expressed by the community of users of quantitative chemical information that drives the research and development effort in chemical analysis to achieve lower and lower detection limits. Already, instrumental detection limits are spectacularly low. With ICP-MS it is possible to detect concentrations at ng/L concentrations and lower, and this would include the measurement of arsenic. For real samples the limit is not set by the signal-to-noise ratio of the instrument, but by the contamination of the reagents needed for pretreatment and preparation with the analyte, thereby creating a measurable blank signal with associated noise. For some instrumental techniques, such as ICP optical emission spectrometry, there is a significant blank signal due to the basic function of the instrument even when the analyte is absent. In the case of ICP emission, the temperature of the plasma is sufficient to generate substantial blackbody radiation at the analyte wavelength. Such a signal, generated in the genuine absence of the analyte, would normally be designated as the "background," and the total signal in the presence of the analyte would be subject to some sort of background correction or background subtraction. It is the magnitude of the noise associated with this background signal that is largely responsible for the relatively high detection limits of ICP-OES compared with other atomic spectrometry techniques. It is the extremely low background signal, and hence extremely low noise, that is responsible for the much lower detection limits of ICP-MS.

At the time of writing, instrumental detection limits in μg/L for arsenic in solution by the major commercially available atomic spectrometry techniques are as follows: FAAS, 150; HG-FAFS, 0.01; HG-AAS, 0.03; ETAAS, 0.05; ICP-OES, 2; ICP-MS, 0.0006. Other variations are possible. It is possible to increase the sensitivity of ETAAS, ICP-OES, and ICP-MS by introducing the analyte as the hydride. For the first two techniques, this will decrease the limit of detection by about an order of magnitude, but for ICP-MS, contamination of the reagents (acid and borohydride) with traces of arsenic means that the improvement in detection limit is less obvious for this technique, which already has extremely impressive detection capabilities.

ON-SITE MEASUREMENTS

The disadvantage of any method in which an atomic spectrometry instrument is involved is that the procedure has to be carried out in some sort of laboratory setting in which appropriate supplies of electricity, gases, power, and for some instruments, cooling water are available. The instrumentation is not very rugged, and although systems have been used onboard ships and put in trailers and driven to remote locations, these are exceptions rather than the norm. The circumstances surrounding the need for on-site analyses often mean that the expense of the creation of a mobile laboratory is not a workable option. In the particular case of the measurement of arsenic in groundwater for drinking purposes, the large numbers of samples and the limited financial resources of the communities or individuals concerned, wherever they are located, mean that some alternative approach to making the measurement is needed.

The people concerned are not necessarily the inhabitants of remote villages. The outreach program that I started under the aegis of the National Science Foundation's Graduate Student Fellows in K-12 Education (GK-12) program, which, among other activities, involved several classes of middle school students in projects concerned with the distribution of arsenic in the local environment, is also underpinned by the provision of information about the chemical composition of relevant materials, and thus I have identified another community of users (a class of middle school students) who need on-site measurement capability. In some ways, the needs of this community place even stricter demands on the measurement technology performance than does the monitoring of private wells in some remote rural community, as the classes are operating on a restricted time scale. This need can be summarized as the requirement for a class of 30 students to make 30 measurements in 30 minutes (or less). Meeting this need has proved to be just as challenging as meeting the needs of villagers in Bangladesh, and although the circumstances of middle school students in Springfield, Massachusetts are in no way as dire as those of Bangladeshi villagers drinking arsenic-contaminated water, they are linked in more ways than just the need to determine arsenic. As soon as school students start investigating some of the broader issues of "arsenic in environment," they quickly find that not only is their own community full of timber structures pressure-treated with chromated copper arsenate, but also that millions of people all over the world (including the United States) are at risk from the consumption, either directly or indirectly, of arsenic in contaminated groundwater. Many students choose to investigate ways of remediating contaminated water or soil as their own small group project in the second half of the program. More information about this middle school activity and the associated programs involving undergraduates and elementary/middle school students in after-school programs may be found at the Arsenic Project Web site [4].

ON-SITE MEASUREMENT OF ARSENIC IN GROUNDWATER

To a large extent it is the plight of the inhabitants of village communities in Bangladesh and West Bengal, India, that has drawn researchers' attention. There is now no doubt that millions of people are drinking, and for many years may have been drinking, groundwater containing arsenic concentrations that will eventually cause a significant fraction (perhaps 10%) to die of arsenic-induced internal cancers, while a much higher percentage may suffer from a whole range of debilitating conditions, including skin lesions, neuropathies, diabetes mellitus, and skin cancer. While there may be debate over what courses of action to take to alleviate this suffering, everyone agrees that an integral part of whatever range of strategies are implemented is that reliable chemical analysis is needed. The most important material to be analyzed is the groundwater used for drinking, but eventually other measurement needs will become important, such as the determination of the extent to which agricultural land (e.g., paddy fields) has become contaminated and the extent to which rice grown in such fields becomes contaminated with arsenic. If communities return to drinking suitably treated surface water, this will need to be monitored in due course.

The crucial nature of the ability to make these measurements was stressed by Caldwell et al., who wrote in their 2003 paper "Searching for an optimum solution to the Bangladesh arsenic crisis" [5], "the most urgent need is not changing the source of water but comprehensive national water testing providing essential information to households about which wells are safe and which are not. . .all progress depends on nationwide testing and retesting of all tubewells, a process that has hardly started."

In 2005, Melamed reviewed [6] "science and technologies with the potential for field measurements" in support of "monitoring arsenic in the environment." His review covers colorimetric procedures, anodic stripping voltammetry, x-ray fluorescence, electrophoresis, laser-induced breakdown spectrometry, microcantilever sensors, and surface-enhanced Raman spectrometry. The latter two techniques are classified under the heading "analytical technologies with possible applications for arsenic analysis." He concluded: "Accurate, fast measurement of arsenic in the field remains a technical challenge. Technological advances in a variety of instruments have met with varying success. However, the central goal of developing field assays that reliably and reproducibly quantify arsenic has not been achieved."

As mentioned briefly earlier, the cost-effectiveness of any candidate technology for on-site or "field" deployment is an issue, but this is not just a matter of dividing the total of the capital and running costs of the technology by the number of samples that might be analyzed in a given period. For the sorts of situations being considered here, capital and running costs have to be almost nonexistent. In 2002, the journal *Talanta* devoted an entire issue to the determination of arsenic in the context of the plight of the inhabitants of the affected areas in the Indian subcontinent. This issue contains many individual contributions that provide a wealth of information and commentary on the relevant issues (of arsenic contamination), much of which is accessible to readers with no specialist knowledge of analytical chemistry.

Kinniburgh and Kosmus [7] provide a thoughtful evaluation of the particular situation of the groundwater in Bangladesh and conclude that with regard to the plan to analyze each of the (maybe 10 million) tube wells as rapidly as possible, "the only feasible approach is through the use of field-test kits," by which they mean test kits based on the production of a colored stain on an indicator paper impregnated with mercuric bromide when exposed to the headspace of a reaction vessel in which the arsenic in a known volume of sample has been derivatized to volatile arsine gas.

The Gutzeit Method

The test just described is known as the *Gutzeit test*, after the inventor of the original test, in which the arsine generated reacted with crystals of silver nitrate [8]. In its modern form, in which a mercuric bromide test strip has replaced the silver nitrate crystals, quantitative information is obtained by comparing the color of the stain with colors on a preprinted chart prepared by the manufacturer of the

Figure 1 Reaction vessel with test strip in place. The graduated mark indicates the level corresponding to 50 mL of sample solution. (From ref. 9.)

kit. The reaction vessel with a test strip in place and the preprinted chart provided by the Hach company [9] are shown in Figures 1 and 2. This test has been known for over 130 years, but despite the possible similarity to the Kjehldahl method alluded to earlier, the user community has been critical of the performance of the test.

In “Arsenic contamination in Bangladesh: an overview,” Hossain [10] writes of the progress in testing the water delivered from the country’s 2.5 million tube wells in the following terms: “field kits used to measure As in the region’s groundwater are unreliable and that many wells in Bangladesh have been labeled incorrectly.” He is alluding to the current practice of painting the well green if the water contains less than 50 μg/L and red if it contains more than 50 μg/L. In his review, Hossain cites an earlier study by Rahman et al. [11], who concluded in answer to the question posed in the title of their paper, “Effectiveness and reliability of arsenic field testing kits: Are the million dollar screening projects effective or not?”, that “millions of dollars are being spent without scientific validation of the field kit method. Facts and figures demand improved, environmentally friendly laboratory techniques to produce reliable data.” Despite the word “laboratory,” the last sentence is probably a reference to the fact that (1) the Gutzeit test generates arsine gas, probably the most toxic form of the element, and (2) the mercuric bromide in the test strips is toxic also.

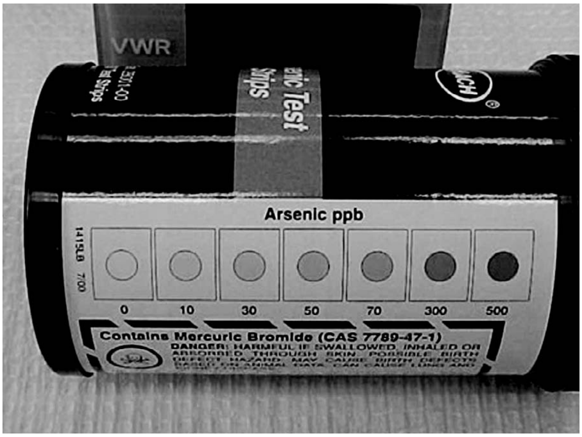

Figure 2 Container for bromide strips showing printed color chart corresponding to solutions containing 0, 10, 30, 50, 70, 300, and 500 μg/L of arsenic. (From ref. 9.) (*See insert for color representation of figure.*)

In the last five years or so, a number of reports concerning the evaluation of field test kits based on this version of the Gutzeit reaction have appeared. In addition, the U.S. Environmental Protection Agency (EPA) has, through the Environmental Technology Verification (ETV) Program [12], been arranging for the evaluation of arsenic test kits according to a standard protocol. The ETV program has also included some test kits based on the Gutzeit reaction, for which a small spectrometer is used to measure the color of the stain produced, and has also looked at other techniques entirely, such as anodic stripping voltammetry (ASV), which will be discussed later. At the time of writing, the ETV program appears to have evaluated six versions of this test kit (see Table 1).

The first comparison of the performance of test kits to appear in the refereed literature was made by Pande et al. of the National Environmental Engineering Research Institute Nehru Marg in Nagpur, India [13]. Their manuscript, submitted in July 1998, described a comparison of five versions of the test manufactured by Merck, the Asia Arsenic Network (AAN), the Aqua Consortium Calcutta, the National Institute of Preventive and Social Medicine (NIPSOM), and the All India Institute of Hygiene and Public Health (AIIH&PH). Although it is of interest to read the protocol chosen as the basis of the evaluation, the results are out of date in the sense that in the intervening years many improvements have been made to the kits supplied by these, and other, manufacturers. Some of the problems with the early versions of the test were (1) arsenic impurities in the reagents (in addition to the zinc and hydrochloric acid needed to generate the arsine, each of these "early" versions of the kit involved the addition of potassium iodide and stannous chloride); (2) some versions of the kit had no means of removing the interference from sulfide, which produces a positive interference due to the formation of hydrogen sulfide, which also gives a stain with mercuric bromide;

TABLE 1 Gutzeit Tests Commercially Available Around the World

Manufacturer	Location	Web Site	Name of Kit	References for Evaluation Information
Industrial Test Systems, Inc.	Rockhill, South Carolina	www.sensafe.com	Quick	12
			Quick Low Range	12
			Quick II	12, 17
			Quick Ultra Low II	12
			Quick Low Range II	12
Peters Engineering	Graz, Austria	www.pe-ag.de/index_en.htm	AS 75	7, 12
National Institute of Preventive and Social Medicine (NIPSOM)	Dhaka, Bangladesh	www.nipsom.org www.asia-arsenic.net/akhtarhp/	NIPSOM	11, 13
Merck	Darmstadt, Germany	www.merck.de/servlet/PB/menu/1168840/168840.html www.merck.de/servlet/PB/menu/1001723/	Arsenic Test	11
			Arsenic Test (Sensitive)	17
			Arsenic Test (Highly Sensitive)	
General Pharmaceuticals Ltd.	Gazipur, Bangladesh	www.generalpharma.com/	GPL-Kit	11
Hach	Loveland, Colorado	www.hach.com	EZ	15, 16
			Regular	7, 17, 20
All India Institute of Hygiene and Public Health	—	—	AIIH&PH	13
Wagtech	Thatcham, UK	www.wagtech.co.uk/	Arsenator	23
Asia Arsenic Network	Fukuoka, Japan	www.asia-arsenic.jp/en/	BVC-100	13, 17
			ECO-W100	17
LaMotte	Chestertown, Maryland	www.lamotle.com	—	17
National Chemical Lab.	Pune, India	www.ncl-india.org/	—	20
M/s Aqua	Calcutta, India	—	—	13
Envitop	Oulu, Finland	www.envitop.com/products.php	As-TOP	12

and (3) the mercuric bromide strips were rather variable in quality and had limited shelf life in hot and humid conditions. In addition, the kits did just not have the detection power or the ability to distinguish between different concentrations. For example, the concentration corresponding to the lightest color on the scale of the Merck kit was 100 μg/L, and only six colors were provided, corresponding to 0, 0.1, 0.5, 1.0, 1.7, and 3 mg/L. Currently, Merck offers two additional versions of the test.

The next study to appear in the reviewed literature was that of Rahman et al. [11] alluded to above. The manuscript submitted from the School of Environmental Studies at Jadavpur University, Calcutta, India in February 2002 by Chakraborti contained results from studies dating back to 1998. It is not easy to decipher which kits of those involved in the studies are to be included in the rather unflattering conclusions about their performance. Most of the criticism appears to be leveled at three of the kits already evaluated by Pande but whose study is not cited by Rahman et al.: the original Merck, AAN, and NIPSOM kits. In addition, results are presented for two other kits: a newer version of the Merck kit, referred to as the "Merck (doubling method)," and the AIIH&PH kit (already evaluated by Pande). Probably the most serious deficiency found was that of 1723 wells previously identified as unsafe based on field testing, 862 were subsequently found to be safe on the basis of analysis by flow injection hydride generation AAS (FI-HG-AAS). The contents of the paper were part of an A-page article by Erickson [14] in the following issue of *Environmental Science and Technology*, from which we learn that the "preferred kit for both UNICEF. . .and the Bangladesh Arsenic Mitigation Water Supply Project (BAMWSP) is now a field kit produced by the U.S.-based instrument company Hach." The article also indicates that there is some disagreement between the UNICEF approach to the analyses (field testing) and that of Chakraborti, who thinks that laboratory-based analyses are cheaper in the long run.

Information about the Hach kit is included in a study by Kinniburgh and Kosmus [7], who show the percentage probability of misclassification as a function of the true concentration for various scenarios. They use values for the standard deviation at zero concentration, s_0, and for the k factor in the equation that relates the standard deviation and concentration (i.e., $s_c = s_0 + kC$, obtained from previous reports (for the PeCo 75 and AAN kits) or, in the case of the Hach kit, from a representative of the company. They show results both for field test kits and for a composite of laboratory instrumental methods, pointing out that in either case some misclassification is inevitable (but predictable). They conclude that "providing care is taken to avoid sources of bias during testing, modern field-test kits should be able to reduce this misclassification to under 5% overall." One of the sources of bias is the interference from sulfide: Kinnibrugh and Kosmus state that "it should be routinely removed to ensure reliable As analyses." They also discuss the issue of particulate material and the pros and cons of filtration. Currently, most field tests are performed on unfiltered samples, and therefore there is a risk that arsenic in particles will be measured under the acid conditions of the test. This is a well-written report and should be read carefully by anyone contemplating the testing of groundwater for the arsenic (or any other contaminant) with field test kits or with laboratory-based procedures.

There are now two versions of the Hach kit, and further information about the Hach EZ version was supplied by van Geen et al. [15], who on evaluating the kit report that "the most widely used field kit correctly determined the status of 88% of 799 wells relative to the local standard of 50 μg/L." They did suggest, though, a minor modification of the recommended protocol: increase the reaction time to 40 minutes. They raised the issue that perhaps some of the problems previously reported for field testing were due to field workers who, pressed for time to complete a certain number of analyses in a day, were not allowing the prescribed 20 minutes (or whatever time was appropriate) to elapse before reading the strip.

Most of the evaluations described so far have been in the context of the 50 μg/L action level (although Kinniburgh and Kosmus did include 10 μg/L as one of the scenarios simulated). Steinmaus et al. evaluated [16] the Quick Arsenic kit and the Hach EZ kit in the context of the 10 μg/L standard by the analysis of 136 water sources in western Nevada. The laboratory reference method involved HG-AFS. They increased the time to 40 minutes for the Hach kit as suggested by van Geen et al., although (at the time at least) this was contrary to the manufacturer's instructions. The sulfide removal step was omitted for all but a few samples. They report that for all samples (109 out of the 136) that contained more than 15 μg/L, both kits correctly identified the concentration as being above the EPA/WHO limit of 10 μg/L. For the 27 samples that contained less than 10 μg/L, the Quick Arsenic kit recorded four false positives, and the Hach EZ kit registered two false positives, numbers that are in agreement with the percentage predicted by Kinniburgh and Kosmus [7]. They conclude that "as a whole the results of this study suggest that the Quick Arsenic and the Hach EZ kits may provide reliable and convenient tools for public health arsenic surveillance and remediation progams."

However, only a few months later, Spear et al. conclude from their "evaluation of [seven] arsenic field test kits for drinking water analysis" [17] that "water professionals should be cautious in choosing field test kits for noncompliance analyses." The basis of their test was (1) to make repeated measurements of a standard containing about 0 μg/L of either arsenite, arsenate or a $1 + 1$ mixture of the two species, and (2) to analyze of a series of real water samples spiked at concentrations of 5, 10, 25, 50, and 75 μg/L with the test kits and by a reference method in which graphite furnace AAS was the instrumental technique. Not surprisingly, the kits with the least number of color increments on the scales performed poorly on the first test. The kits tested included six that were based on the Guzeit reaction: the BVC-100 and ECO-W100 from the AAN, the Hach kit (not the EZ version), the LaMotte kit, and the Quick II and Merck kits (it is not clear which version was used). The seventh test kit was a portable anodic stripping voltammetry instrument (see later).

PROGRESS AND PROSPECTS

This, I am sure, is not the last word of the story with regard to methods based on the Gutzeit reaction, and it seems likely that evaluations of these and other, as yet to be developed, versions of the kits will appear in the literature for some time to come. There are at least two other kits that have not been subject to "independent" evaluation in any of the reports published in the reviewed literature, about which little is known. One is the kit developed for UNICEF by the National Chemical Laboratory in Pune, India (available in the United States from Alpha Environmental). The other is the kit developed by Deshpande and Pande of the National Environmental Engineering Research Institute Nehru Marg in Nagpur, India [18]. Although the report was published in 2005, their manuscript was submitted in May 2003. Both of these kits may have been overtaken in performance, but probably not in cost, by recent developments in the production of arsenic test kits by Merck, Hach, LaMotte, and Industrial Test Systems. The As-Top kit, whose use does not appear to have been described in any analytical research journals, was evaluated by the ETV program in 2002. As recently as Februrary 2007, a report appeared of the performance of a modified Gutzeit method devised by Baghel et al. [19]. In their procedure, the zinc powder was replaced by magnesium turnings and they used oxalic acid. The Hg(II) bromide was replaced by Au(III) chloride (one drop of 1% auric chloride on filter paper), which in the presence of arsine was reduced to metallic gold, imparting a pink-violet color to the test paper whose intensity was proportional to the arsenic concentration. With this chemistry they were able to detect 10 μg/L in a 100-mL sample after 10 minutes.

In anticipation of such future evaluation studies, the following suggestions are offered. In the report it should be quite clear what test kit is being used; thus both the name and the manufacturer's catalog number should be provided. It should also be made clear whether the kit is being used according to the manufacturer's instructions or whether some modification was made (such as omitting the sulfide removal stages or increasing the length of time for a reaction), it should also be clear how the operators are assigning numbers when comparing the resulting color on the test strip with the colors on the preprinted chart (e.g., does the value correspond to the closest color taken, or is some interpolation made, or is the number below/above the color taken?).

Studies in my research group [20, 21], with the two versions of the Hach kit indicate that the reliability of the test at values of 10 and 50 can be improved by the simple expedient of allowing longer time to elapse before removing and "reading" the strip. We have even gone as far as investigating the 24-hour version of the test, which makes it possible to measure at concentrations below 10. Of course, the original manufacturer's color chart is no longer valid, and a new one has to be created by the analysis of standards. This may be a rather extreme case of increasing the time, but it is one that has some merit for our classes of school students, who can return the following day to take the reading. This suggests to us that it should be possible to create several versions of the preprinted strip based on several different exposure times. As the design of the vessel cap makes it particularly easy to remove the strip, examine it, and put it back without losing any arsine, one might imagine a strategy for the determination of low concentrations in which the strip is removed at various time intervals, examined, and replaced until a "measurable" color had developed.

Some concerns have been expressed about the safety issues arising from the generation of toxic arsine gas, which may escape into the atmosphere in the immediate vicinity of the operator [22]. This investigation by Hussam et al., submitted for publication in February 1999, was based on an examination of the Merck kit and did find that concentrations of arsenic in the air immediately above the kit exceeded the threshold limit value of 50 ppbv during testing of a solution containing 100 μg/L. Since then, most major suppliers of kits have addressed this issue and taken steps to design vessels that do not leak during the testing stage and from which the strips can be removed with minimum release of arsine. Of course, the operator has to be aware of the possible hazards of venting and cleaning the vessels for reuse, and this operation certainly needs to be performed in a well-ventilated area if the kit has no provision for adsorption of the excess arsine. It would be useful to know how much of the arsenic released from solution is eventually trapped on the test strip. Two other interesting features of this study were: (1) the researchers measured the arsine generation efficiency to be about 90% on average, and (2) they measured the arsine release with a device that passes a known volume of air at 350 mL/min through/over a paper tape impregnated with a reagent containing silver nitrate, which is subsequently interrogated by reflectance spectrometry. This device was manufactured by Zellweger Analytics, a Swiss company that was recently bought by Honeywell.

The reagent formulation is another potential issue. The community involved in the application of HG for the introduction of analytes for atomic spectrometry quantification uses borohydride as the generating reagent, typically added as a solution in dilute aqueous alkali to the acidified sample solution. The reaction is often performed in a flow injection or continuous flow manifold. Generation of arsine from arsenite is rapid and quantitative. During the residence time in a typical flow system, the generation from arsenate is much less efficient, and this necessitates the inclusion of an additional stage in the analysis, the reduction of As(V) to As(III), for which a variety of reducing agents have been proposed, including potassium iodide, ascorbic acid, and L-cysteine. However, in the batch generation system adopted by the manufacturers of the test kits, this is not an issue, as both As(III) and As(V) will react over a period of several minutes to produce arsine, As(V) first being reduced to As(III). Borohydride solutions are rapidly decomposed in acid to release hydrogen gas, and there are some kinetic limitations associated with the reduction of As(V) to As(III) with borohydride which mean that a borohydride solution is not a good choice for a field test kit reagent. Solid reagents, prepackaged into unit doses, are preferable for field test kits, a consideration that favors the use of zinc and sulfamic (or other solid) acid over borohydride and hydrochloric acid solutions. However, sodium borohydride is a solid and it is possible to create borohydride "tablets" that react sufficiently slowly so that (1) the reaction vessel can be sealed before any arsine is released, and (2) the release of hydrogen is controlled sufficiently that the test strip is not wetted by droplets of water that are produced when borohydride reacts rapidly in aqueous acid.

Spectrophotometric Detection

One of the criticisms that has been leveled at the test kits based on the Gutzeit reaction is that the response scale is discrete, and the reading involves the exercise of some judgment by the operator. One way in which this problem may be overcome is to use a reflectance spectrometer to read the color on the strip. Both the Arsenator test kit and the PeCo AS 75 kit have this option. The purchase price is now in the range \$500 to \$1,000, perhaps more, as both of these devices are manufactured in Europe, where at the time of writing, exchange rates are not very favorable to a purchaser in the United States. However, there is a significant improvement in performance. Some results of a comparison between the results obtained by an early version of the Arsenator and by ICP-AES are provided by Kinniburgh and Kosmus [7]. The most recent version of the device, manufactured by Wagtech [23] in the UK, has been evaluated by the Shiram Institute for Industrial Research, Delhi, India (March 2006), and the report, which is very favorable, may be downloaded from the Wagtech Web site (see Table 1). The device is designed to cover the range 0 to 100 μg/L, with higher concentrations being handled by comparison with a color chart or by dilution and reanalysis. We can confirm that the arsenator performs well in the concentration range 5 to 55 μg/L [24]. A crucial feature, however, is the inclusion of a sulfide removal filter. Much more erratic results were obtained when the filter was omitted. The device also traps excess arsine and hydrogen sulfide. The Peters Engineering device has been evaluated by the EPA's ETV program [12].

For some years now, we have been experimenting with the use of digital images of the strips as a means of quantifying the extent of the color formation [20]. Our initial experiments were based on those of Mathews et al. [25], who described a procedure for the quantification of the starch iodine reaction that involved obtaining images with a flatbed scanner. We have used the software they created to extract values of the red (R), blue (B), and green (G) color intensity from the digital image. More recently we have used the commercial product Adobe Photoshop for the same purpose [21]. It is relatively straightforward to average the color in a large number of pixels and then to extract the R, G, B values (each of which ranges from 0 to 255). Results for the Hach EZ kit (catalog number 2822800) used according to the manufacturer's instructions, except that the sulfide removal step was omitted, are shown in Figure 3. It can be seen that the blue color intensity is most responsive to the arsenic concentration. The possibilities afforded by increasing the time of reaction to 24 hours are shown in Figure 4, from which the increased sensitivity in the range 0 to 20 μg/L can be readily seen. Our experiments also indicate that not all flatbed scanners give the same sensitivity. We also find that similar data treatment can be applied to the

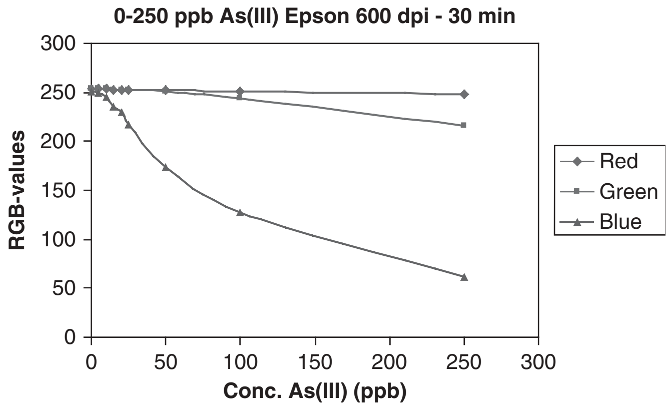

Figure 3 Plot of R, G, and B values obtained from images produced with an Epson scanner as a funtion of the concentration of arsenic in the test solution. The Hach EZ kit was used according to the manufacturer's instructions, except that the sulfide removal steps were omitted.

images produced by digital cameras, and as these devices are widely available at prices that benefit from the mass production of consumer electronics, we propose that similar analyses of a digital camera images could be used as a means of improving the reliability of the field test kit measurement. At present, the image has to be processed by a computer and appropriate software, which is not necessarily a major drawback if hundreds of images can be stored and then

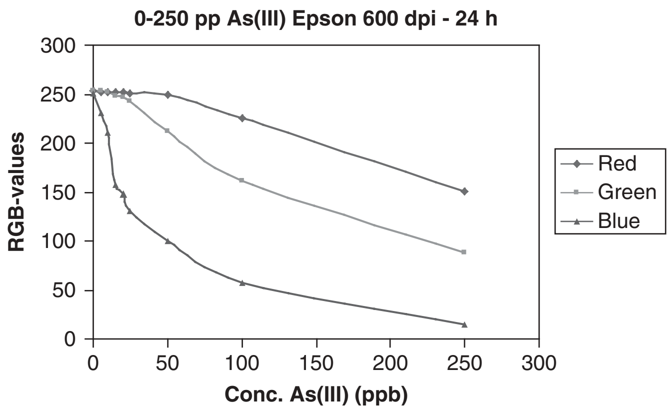

Figure 4 Plot of R, G, and B values obtained from images produced with an Epson scanner as a funtion of the concentration of arsenic in the test solution. The Hach EZ kit was used according to the manufacturer's instructions, except that the sulfide removal steps were omitted and the strips were left in the vessels for 24 hours.

processed back at "base camp"; on the other hand, if immediate action is needed (such as painting the well red or green), either the field operator has to carry the computer or, possibly, if cell phone coverage is available, the image (taken by the camera in the phone) is transmitted to a central location, where it is analyzed and the result communicated to the field operative.

Ideas of this kind have occurred to other researchers: Shiskin et al. [26] measured the color intensities of complexes adsorbed on polyurethane foam by analysis of the images (with Adobe Photoshop) and showed that an exponential first-order decay function was a good model for the relationship between R, G, or B color value and analyte concentration. Paciornik et al. [27] determined mercury by scanning the exposed copper(I) iodide papers and processing of the digital image with Digital Micrograph software from Gatan Inc. They found that the RGB model was not a suitable basis for quantification and that better results were obtained with the (1) cyan, magenta, yellow and (2) hue, saturation, lightness models.

Rahman et al. [28] have measured the intensity of the colored stain produced by the reaction of arsine with mercury(II) bromide (the paper was also impregnated with rosaniline chloride, which stabilized the color) by tristimulus colorimetry. In this approach a tristimulus colorimeter is needed together with the image-processing capability to assign a numerical value to the location of the image's color in color space. In their approach they measured lightness (L^*) and chromaticity in the red/green (a^*) and yellow/blue (b^*) directions. They calculated the distance between the image color and a reference color as the square root of the sum of the squares of the individual ΔL^*, Δa^*, and Δb^* values. Although this approach may appear to be moving in the direction of the need for complicated instrumentation, it has recently been shown by Suzuki et al. [29] and by Martinez-Verdu et al. [30] that a digital still camera can function as a tristimulus colorimeter, although in this application [29] it was the colors of solutions measured in absorption or reflection (the image of the frosted side of the cuvette was taken) that formed the basis of the quantification. This required that a special light box be constructed, although this did not appear to involve major expense. The white LEDs could be run from 4 AA dry cell batteries.

Absorbance in Solution

As many companies make low-cost field-portable absorption spectrometers, a possible approach to the determination of arsenic in groundwater is to add the appropriate reagents to a known volume of water, wait for the color to develop, and measure the absorbance. Both Melamed [6] and Kinniburgh and Kosmus [7] examined the possibilities of this approach, but neither was particularly enthusiastic about the prospects. There are probably two well-established laboratory-based procedures that have the detection capability to make them serious contenders for a field-based version: the silver dithethyldithiocarbamate method and the molybdenum blue method. The first of these is already available as part of Merck's Spectroquant methods (catalog number 1.01747.0001); it is based on the generation of arsine, which is passed through an absorbing solution of silver dithethyldithiocarbamate in an organic solvent in the presence of an organic base. Such solvents are difficult to pack and transport, and the procedure is much more time consuming, taking 2 hours for completion of the color-forming reaction, during which time the flask needs to be swirled or stirred. The problems of reagent disposal are probably even more severe than those of dealing with the Hg(II) bromide test strips. On the other hand, the procedure is capable of measuring concentrations down to 1 μg/L. Currently, there seems little interest (as shown by activity in the recent analytical chemistry literature) in any further developments in this chemistry.

The other laboratory method is based on the formation of heteropolymolybdate by reaction with molybate in the presence of acid and, possibly, another heteropolymolybdate-forming element, such as antimony or bismuth. When the yellow isopolymolybdate is reduced, a compound with an intense blue color forms, known almost universally as molybdenum blue. Almost every known oxoanion can participate in this reaction and is therefore a potential interferent (problem 1). The particular problem of phosphate has exercised the analytical community from the late 1930s, and although the work of Johnson and co-workers in the early 1970s [31, 32] resulted in a procedure that was able to measure arsenite, arsenate, and phosphate in the same samples, the lowest concentration that could be measured was on the order of 40 μg/L, i.e., about 0.5 μmol/L (problem 2). The formation of the arsenic complex is slow; in the Johnson and Pilson method, 4 hours is needed (problem 3).

Despite these apparently rather formidable obstacles, several researchers have described further modifications to the method. Dhar et al. [33] revisited the reagent formulation and found that provided that the sample contained at least 2 to 3 μmol/L of phosphorus (as phosphate), full color was formed in 8 minutes. They also reported the ability to measure down to 2 μg/L. All this sounds very promising, but undergraduate students in my group have so far been unable to replicate this performance. Dasgupta et al. [34] devised a procedure in which the phosphate and arsenate (and silicate) were retained on an anion exchanger and the unretained arsenite was injected into a flow injection manifold, where it was first oxidized to arsenate and then merged with an acidified ammonium molydate solution and then with ascorbic acid in 30% glycerol. After passing through a heater at 70°C, the absorbance was measured by an LED-source spectrophotometer. The detection limit was 8 μg/L. The researchers indicate that a number of possible improvements are under investigation.

The alternative approach to the problem of the phosphate interference is to separate the anions. Although chromatographic and solid-phase extraction methods have been described, these (particularly the chromatographic procedures) are difficult to implement in the field. However, hydride generation is a particularly good way to achieve this separation since there is no reaction by phosphate to form the analogous phosphine. Rupasinghe et al. devised a pervaporation procedure [35] to do this in which the arsine generated in the donor chamber diffused across a Teflon membrane into an acceptor chamber filled with iodine solution to absorb the arsine with conversion to arsenate, which was then merged in a flow injection manifold with a reagent containing all the components necessary to form molybdenum blue. The procedure had a detection limit of 15 μg/L. It was also necessary to heat the reaction mixture and then to remove bubbles, so the resulting apparatus did not look particularly field portable. They later showed that even better performance could be obtained by substituting permanganate as the colorimetric reagent [36], whose decrease in color due to oxidation of the As(III) was monitored, thereby avoiding all the problems of molybdenum blue chemistry. We can confirm [20] the validity of this approach. With the pervaporation chamber shown (in an exploded view in Figure 5. we have determined arsenic down to 0.5 μg/L. The procedure is still not genuinely field portable, but has possibilities for use in our partner middle school classrooms, where reliable electrical power is available.

Probably the most impressive exploitation of molybdenum blue chemisty has been by Toda and Ohba [37], who also incorporated separation by HG into their scheme. The apparatus is shown in Figure 6. Air was dragged through the gas generator (GG) by the pump (AP) and the evolved arsine was transported to the diffusion scrubber (DS) and exhausted via a mist trap (MT) and flow meter (FM) following merging with a makeup flow from the ballast tube (BT). The diffusion scrubber was a porous polypropylene tube containing alkaline permanganate as

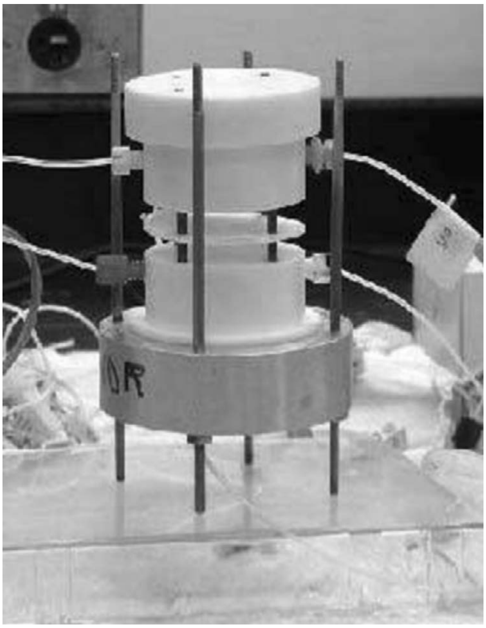

Figure 5 Pervaporation vessel showing the Teflon membrane that separates the lower (donor) chamber from the upper (acceptor) chamber. (*See insert for color representation of figure.*)

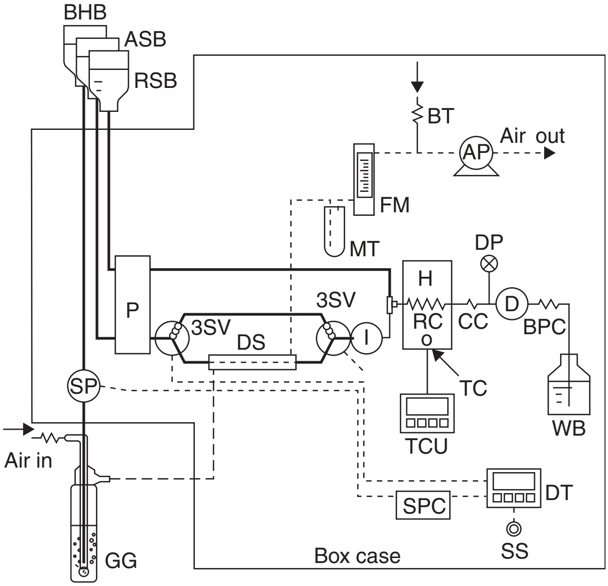

Figure 6 Schematic diagram of a flow manifold for the determination of arsenic based on hydride generation followed by adsorption in an acceptor solution by diffusion through a porous tubular membrane. For a full explanation of the manifold components and operation, see the text.

the absorbing solution delivered by a pump (P) from a reservoir (ASB). After 5 minutes of HG, during which time the generating reagent (alkaline borohydride solution) was delivered by the solenoid pump (SP) at a flow of 2 mL/min, the three-way solenoid valves (3*SV*) were switched so that the arsenate collected passed through the loop of a six-port injection valve (I) and a subsample was merged with the color-forming reagent (ammonium molybdate, ascorbic acid, and sulfuric acid) and passed through a reaction coil (RC) in a heating block (H), whose temperature was monitored by a thermistor (TC) and controlled (TCU), then through a cooling coil (CC) and debubbler (DP) to the detector (D). The detector was a homemade spectrometer with a near-infrared LED light source and a photodiode detector. Finally, the solution was delivered to the waste bottle (WB) via a backpressure coil (BPC). Some of the operations were under the control of a digital timer (DT) and were initiated by a smart switch (SS). The solenoid pump operated on pluses from a pulse generator (SPC).

The results are shown in Figure 7, from which it is clear that the detection limit is less than 1 μg/L and that while each analysis takes about 15 minutes, a faster throughput could be achieved if the samples could be loaded into the generation cell faster. The signal for 4 mg/L of As(V) injected directly at I (the six-port valve) shows that the system has preconcentrated the arsenic by a factor of about 200. As the volume ratio of solutions involved is 20,000 : 85 (i.e., 235 : 1), this

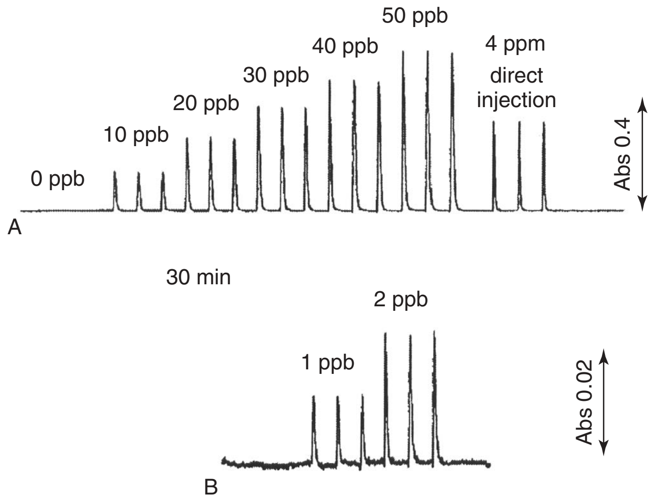

Figure 7 Results for replicate measurements of arsenic standards following hydride generation, adsorption through a tubular membrane, and formation of molybdenum blue.

indicates that the processes of generation, stripping, and collection of the arsine were at least 85% efficient. A field version has been developed and evaluated [38].

In an effort to exploit the cost advantage of the test-strip approach, Matsunaga et al. [39] devised a “naked-eye” detection method for the determination of arsenic based on the formation of molybdenum blue by reaction of a molybdenum-loaded chelating resin with arsenate and a reducing agent in acid solution. The color developed fully after heating for 4 hours at 40°C, whereas the 20-minute (45% of the maximum color) detection limit was 75 μg/L, indicating that further improvements are needed if this approach is to rival that of the latest versions of the Gutzeit test. A procedure with greater detection power was described by Morita and Kaneko [40], who exploited the formation of nanoparticles by the reaction of ethyl violet with molybdate and iodine tetrachloride in acid solution. In the absence of arsenic, the purple color fades due to conversion to a colorless carbinol species, but in the presence of arsenic the color decays much more slowly and allows a visual detection limit of about 1 μg/L, with an instrumental detection limit of 0.5 μg/L. Interference from phosphate was removed by passage through a weak base anion-exchange resin (Dowex Marathon WBA) in the chloride form and from silicate by the addition of fluoride. The separation from phosphate would appear to be a particularly useful finding, as at the pH of 7, shown to be the upper limit at which arsenate is not retained by the column, arsenic is still very much an anionic species, although As(III) is neutral. The facile separation of phosphate and arsenate, without resorting to hydride generation, could be exploited in a number of molybdenum-based procedures.

Of course, if the goal is to determine both phosphate and arsenate, the Johnson and Pilson [32] approach may be the better option. In this method two measurements are made, one following the addition of an oxidant, to ensure that all the arsenic is present as As(V), and the second following the addition of a reducing agent, to ensure that all the arsenic is present as As(III), which does not react to form a heteropolymolybdate. In the first case, both arsenate and phosphate are measured and in the second only phosphate, so that the arsenate can be determined by difference. Of course, if a third measurement is made in which neither oxidant nor reductant is added, the arsenic speciation in the original sample may be deduced. Tsang et al. [41] reexamined the Johnson reducing reagent [a mixture of sodium metabisulfite ($Na_2S_2O_5$) and sodium thiosulfate ($Na_2S_2O_3$)], which they said released SO_2, resulting in the formation of colloidal sulfur. They replaced this reagent with sodium dithionite ($Na_2S_2O_4$) and reoptimized the composition of the reagent (ammonium molybdate, potassium antimonyl tartrate, and sulfuric acid). No investigation was made of the reducing agent, ascorbic acid, needed to produce the blue color. The detection limit was about 1 μg/L, but it was a little difficult to calculate the overall time of analysis. The procedure would be difficult to implement in the field, as the reduction step requires heating at 80°C for 20 minutes, and the color development stage also involves heating. They did not appear to add an oxidant, and no validation of the method was presented.

FUTURE PERSPECTIVES

Luminescence

To date, no feasible photoluminescence (fluorescence) procedure for the determination of low concentrations of arsenic has been described. In principle, chemiluminescence (CL) measurements are simpler than those for absorbance, as no light source is needed. In practice, to get good performance, a high-quality detector is needed and the procedure requires a lighttight reaction chamber. But again, no workable batch CL methods for arsenic have been reported, although the element has been determined in a mixture separated by ion chromatography by a post-column reaction scheme is which heteropolymolybdates were formed which then reacted with luminol in alkaline solution. Fujiwara et al. [42] were able to find a reagent formulation (involving vanadate) that was suitable for As(V), Ge(V) and P(V) following reaction in a flowing stream at 80°C. The detection limit for arsenic was 10 μg/L. On the other hand, gas-phase CL appears to hold some promise. Idowu et al. described [43] a procedure based on a sequential injection system in which arsine was generated and reacted with ozone in a reaction vessel positioned immediately in front of the window of the photomultiplier housing. The detection limits were between 0.05 and 0.09 μg/L. Despite the apparent complexity of the system, the researchers concerned are very focused on the potential of the device for field-based analyses, and in addition to making available a complete parts list in the supporting information (available free at the ACS Web site), they offer to "provide reasonable advisory assistance to those interested in building such instruments for nonprofit purposes."

Bioluminescence and Other Biosensing

Several research groups are developing bacterial biosensors. The basic strategy is that when exposed to arsenic, a genetically modified organism produces a protein that can be sensed by an appropriate transducer. This can be as simple as naked-eye detection if, for example, the protein is an enzyme that can catalyze a reaction that produces a colored product. However, more sensitive detection is possible if the protein is luminescent, as would be the case for green fluorescent protein, or if it catalyzes a luminescent reaction, as would be the case for luciferase. Sensors based on all three of these concepts were described by Stocker et al. [44] in a 2003 report. Although the sensors can detect single-digit μg/L concentrations, the response is relatively slow, as the bacteria need to be incubated with the sample for at least 30 minutes (preferably longer) and then the reaction catalyzed may need an additional 30 minutes (in the case of a colored product) for the color to develop. Incubation temperatures are typically 30°C, and some protocols required centrifugation and/or agitation with a mechanical shaker. There are also some issues associated with attaching the cells to the test strips and the long-term viability of the cells [45]. The system based on the expression of luciferase has been tested in Vietnam on 194 real groundwater samples [46]. Interference from iron was encountered but overcome by acidification of the sample with nitric acid to pH 2, then the addition of the bacterial cells in Luria broth solution, which raised the pH to about 5.5, followed by the addition of sodium pyrophosphate to raise the pH to about 7.0. At this point the mixture was incubated for 30 minutes at 30°C with continuous shaking. The substrate for the expressed luciferase was *n*-decanal, which was added as an 18-mmol/L solution, and the luminescence was measured after 3 minutes. The results were compared with those obtained by a method employing AAS, and comparable results were obtained for concentrations between 10 and 100 μg/L.

Electrochemistry

There does not appear to be any direct potentiometric sensor (ion-sensitive electrode) for any arsenic species. Although it would undoubtedly be possible to make such a device, the performance of others, whether based on liquid-supported membranes or insoluble salts, suggests that the desired detection capability of around 1 to 10 nmol/L is beyond the capability of such devices. Reports of the electrochemical determination of arsenic date back almost 40 years, and the relevant literature with emphasis on the analysis of environmental, food, and industrial materials was reviewed by Cavicchioli et al. in 2004 [47]. They identified various stripping techniques as the most promising, of which anodic stripping voltammetry (ASV) has probably been researched most extensively.

As all stripping procedures include a preconcentration step in which a derivative of the analyte is collected on the working electrode, in principle, detection limits can be decreased by the simple expedient of increasing the accumulation time. In practice, as with all preconcentation procedures, there is a limit set by the concentration of analyte in any reagents needed (or by noise on the background signal). However, in the case of ASV, Huang and Dasgupta [48] showed that for the relatively modest accumulation time of 80 seconds, a limit of detection of 0.5 μg/L was obtained. They deposited the arsenic on a gold film electrode and were able to distinguish between As(III) and As(V) by the simple expedient of controlling the deposition potential. At the lower potential, only As(III) was measured, and then following oxidation to As(V), total arsenic was determined, from which the As(V) content could be calculated by difference. The goal of their efforts was to produce a field-deployable instrument for the measurement and speciation of arsenic in potable water, and for field use the entire instrument could be packaged into a wheeled, padded carrying case (60 × 24 × 42 cm external dimensions) weighing 6.5 kg that had an average power consumption of 3.5 W and could be run from a laptop computer. Such an instrument (the NanoBand Explorer II) is commercially available [49] from a company that also makes a number of products for the determination of arsenic (and other elements) by ASV, including fully automated instruments for use in water treatment plants.

There do seem to be some concerns regarding the reliability of electrode performance, as no solid electrode has been devised that has performance comparably to that of the dropping mercury (or hanging mercury drop) electrode. Feeney and Kounaves described [50] voltammetric detection at a Nafion-coated microfabricated gold array electrode with a field-portable potentiostat. They reported sub-μg/L detection, which seems to be readily achievable, and were able to work for 30 days before the electrode deteriorated due to irreversible oxidation. They also investigated another potential problem with electrochemical detection: the response, or lack thereof, to As(V). They were unsuccessful with electrochemical reduction and resorted to chemical reduction with sodium sulfite. About 100 minutes were needed to get compete reduction, although useful measurements could be made after about 30 minutes. They found that copper was a severe interferent: 50 μg/L of copper decreased the signal for 100 μg/L As by about 50%. Quantification of the real samples was by the standard additions method. More recently, Dai and co-workers reported [51] on a portable, handheld square-wave ASV device. They applied low-frequency sound (250 Hz) during the deposition step and obtained both an increase in sensitivity (50-fold) and a decrease in limit of detection (100-fold). Copper was again reported to be a serious interference. They also evaluated silver and platinum as possible electrode material [52] and showed that it was possible to obtain ultrasound-assisted limits of detection of 1 μg/L at silver in the presence of nitric acid rather than hydrochloric acid. They also showed [53] that gold nanoparticle-modified glassy carbon electrode decreased the copper interference. The answer to the copper problem may be to switch to cathodic stripping voltammetry (CSV). Piech and Kubiak [54] determined arsenic by CSV down to 0.006 μg/L in the presence of copper and sodium diethyldithiocarbamate (DDTC-Na) with a deposition time of 50 seconds. At the time of writing, the last word on ASV comes from Salaun et al. [55], who determined As(III), As(V) and copper contents in water and seawater at a gold microwire electrode. The As(V) could be determined at pH 1, and for all elements, better detection limits could be obtained with stripping chronopotentiometry (SC).

One constraint for the field deployment of such electrochemical procedures appears to be the fragile nature of the electrodes. As a rationale for studying photometric procedures, Idowu et al. wrote [43] that "having had the disappointing experience of discovering that our electrochemical method is less robust than we had thought, we sought altogether different alternatives." Kinniburgh and Kosmus commented [7] that "while arsenic species can be detected using various electrochemical methods, it is unlikely that such methods could ever be made robust enough for incorporation into routine field-test kits. Electrodes are notoriously fickle, and usually expensive and difficult to replace."

Other Prospects

The ideal field test kit is one in which a few drops of test solution are applied to a strip coated with suitably inexpensive and nontoxic chemicals, whereupon digits appear indicating the concentration in μg/L. But as we are some way from this device, there is still a considerable driving force for further developments. As the numbers of samples is very high, it is quite reasonable to speculate about the possibilities for instrumentation with modest to high capital cost. It is probably also reasonable to speculate about the creation of "temporary field laboratories" to which samples are brought, and thus some atomic spectrometry techniques are possible contenders. Simeonsson et al. [56] speculated that an instrument for laser-induced fluorescence detection of atoms produced by a tungsten coil atomizer could, if developed, be deployed for field-based applications. There is even evidence that atomic emission generated by tungsten coils [57] may be the basis of useful analytical determinations. As neither hollow cathode lamps nor hydrogen diffusion flames are particularly difficult to operate in the field, one could imagine that "regular" atomic fluorescence, based on HCL excitation of atoms produced by hydride generation introduction to a hydrogen diffusion flame, is also convertible to field portability. If the measurement is combined with a preconcentration step in which the arsenic in a large volume of water is retained in a relatively small volume of solid-phase extractant, the techniques of x-ray fluorescence [58] and laser-induced breakdown spectrometry [59] may be applied. Both of these techniques are already available in field-portable versions.

Preconcentration procedures in which the retained arsenic is eluted back into a smaller volume can be used with existing spectrophotometric procedures, which currently do not have the detection capability for monitoring at the 10 μg/L level. The time needed could be an issue. To produce a 10-fold increase in concentration with a final volume of 50 mL for testing, 500 mL has to be processed. If the maximum flow that the preconcentration media can handle is 20 mL min^{-1}, then it takes 25 minutes just to load the sample solution.

Melamed suggests [6] that sensors based on (1) microcantilevers, and (2) surface-enhanced Raman spectrometry may have some possibilities, to which might be added (3) total internal reflectance infrared spectroscopy [60] and a quartz crystal microbalance, which has been used for the determination of trace anions, including phosphate [61, 62].

There are still some mysteries to be sorted out regarding the molybdenum blue chemistry. For example, there are several reports [63–65] of the reaction being used in a post-column mode for the detection of anions, including arsenate, separated by ion chromatography. In some of these procedures [64, 65] the color is formed at room temperature. As most of the other reports of the procedure indicate that the reaction is so slow that it has to be heated to form color on a reasonable time scale, it is intriguing that some formulations of the reagent apparently allow good color formation at room temperature in the time it takes the HPLC eluant to flow from the merging point to the detector.

It is perfectly possible that there is some as yet undiscovered reaction involving arsenate or arsenite that produces a color change of 10^5 L/mol per centimeter equivalent molar absorptivity that can be detected at a good signal-to-noise ratio by a simple spectrophotometer at absorbance values of 10^{-3}, thereby providing sub-μg/L detection capability. New methods are, in fact, reported from time to time [66–69].

CONCLUSIONS

There are clearly many prospects for the further development of chemical measurement technologies for the determination of arsenic in environmental waters down to single-digit μg/L concentrations. It seems unlikely that the full possibilities for naked-eye detection have been realized and that further refinements in existing reaction chemistry and the conversion of other colorimetric methods to this mode will give rise to improved method performance. Inexpensive color-measuring instruments, such as those based on digital cameras (still or video) or flatbed scanners, whose price reflects large-scale manufacturing for the general consumer market, are widely distributed, so robust field-portable, hand-held, spectroscopic instrumentation may be available in the very near future. In terms of scientific instruments, simple reflectance photometers are already available, as are portable x-ray fluorescence (XRF) spectrometers and electrochemical analyzers. At present, the XRF instruments cannot measure arsenic directly in water, and the latter do not yet feature reliable and robust working electrodes, so that the prospects for widespread use seem remote unless samples are brought to a localized central site for analysis. Under this scenario, techniques such as atomic fluorescence spectrometry are candidates for such a “lab” facility. The quartz crystal microbalance, a device whose interface is more robust than an electrode for stripping voltammetry, also holds promise, especially as the measurement incorporates an inherent preconcentration step (the accumulation of arsenic at the surface of the oscillating crystal) and the instrumentation is simple and robust. The challenge is to find some chemistry that will selectively bind arsenic to the crystal surface in the presence of other components in the sample. The exquisite selectivity of the hydride generation process is very tempting as an integral pretreatment stage but always comes with associated issues of safety unless all of the arsine generated ends up bound to a solid surface somewhere in the apparatus. However, it will be quite some time before the Gutzeit method is obsolete. Sensing based on genetically modified organisms, such as bacteria seems a remote possibility at present because of the lengthy response time of the systems currently available, but may have the selectivity to rival that of hydride generation. The target range of nanomolar concentrations may also be difficult for biosensors. There seems little interest in kinetic methods at present, but the low analyte concentrations may be better reached through an enzyme (or other catalyst)-linked process than by direct sensing of the analyte activity. The consumer electronics industry has ensured that precise and accurate timing devices (such as those in digital watches) are extremely inexpensive, so instruments for following the course of a reaction, especially if the species followed is colored, will be cheap.

Acknowledgments

Some of the work described in this chapter was funded, in part, by NSF grant CHE-0316181.

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8

FIELD TEST KITS FOR ARSENIC: EVALUATION IN TERMS OF SENSITIVITY, RELIABILITY, APPLICABILITY, AND COST

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INTRODUCTION

Arsenic is a relatively common but toxic and carcinogenic element. As outlined in Chapter 1, it can occur naturally in relatively high concentrations in soils and sediments and consequently also in freshwater and biota. Additionally, anthropogenic influences from the mining, leather, and glass industries, or the use of pesticides, wood preservatives, food additives, or nerve gas waste, can add to naturally occurring arsenic.

Sources of arsenic are varied. Its behavior in the environment is complex, due to its continuous transformation to different species, each of them behaving differently in terms of mobility, bioavailability, and toxicity. Arsenic shows highly diverse distribution patterns throughout the environment which are dependent on the pH, concentration of sorbents, redox potential, ionic strength, and biological activity [1]. The lack of uniformity in the element's environmental distribution, coupled with the lack of understanding of its biogeochemistry, make its

Arsenic Contamination of Groundwater: Mechanism, Analysis, and Remediation,
Edited by Satinder Ahuja

occurrence unpredictable in respect to time and location. Therefore, high spatial and temporal resolutions are both required to monitor effectively the arsenic levels and apply efficient remediation technologies. On-site analysis is the only cost-effective solution to deal rapidly and effectively with the resulting high number of samples.

The main focus of arsenic monitoring over the past few years has been on drinking water, but monitoring of arsenic concentration in soil and staple foods is necessary to predict the effective arsenic burden of people living in the areas affected (see Chapter 2). Furthermore, solids produced by water remediation techniques also need to be monitored on site. To assure that a correct assessment of the environmental risk can be made, on-site measurements of water, soil, sludge, and foodstuffs should comply with the criteria listed below.

CRITERIA FOR FIELD MONITORING

The focus of this chapter is on water analysis, but a few comments are also made about the analysis of solids and gases. The major decision-making criteria for drinking water is the maximum contaminant level (MCL). For total arsenic in groundwater or potable water, the MCL is 50 μg/L (50 ppb) in many countries. Recently, the guideline value of 10 μg/L (10 ppb) for drinking water recommended by the World Health Organization (WHO) has been approved by many countries in the world, and has been enforced since the beginning of 2006 in the United States. It should be mentioned that the guidelines do not consider different arsenic species, even though it is already well established that the toxicity of arsenic can vary enormously with its speciation.

For soil, sludge, and foodstuffs the situation is not as straightforward. Although a few guidelines exist, they are not strictly regulated. In the UK there are environmental quality criteria for soils that depend on soil use; for instance, domestic gardens, allotments, and play areas have a critical value of 10 mg/kg, whereas landscapes and building hardcovers have a threshold of 40 mg/kg. However, assessment criteria of soils for contaminated areas start at 12 mg/kg in Canada, [2], and remediation criteria are again usage dependent. For example, 20 mg/kg is the upper limit for agriculture use, 30 mg/kg for residential parkland, and 50 mg/kg for commercial and industrial land. Recommended guidelines for arsenic in foodstuffs are the subject of contentious discussions [3]. Currently, only Australia has established a guideline value of 1 mg/kg for total arsenic in foodstuffs. Again, no speciation information has been incorporated into this upper limit, although some countries, including China, have introduced import guidelines based on inorganic arsenic (e.g., for rice, as some rice may contain large amounts of dimethyl arsenic) [4].

Since it has been recognized that arsenic intake from drinking water has been linked to an increased risk of contracting cancer, enormous efforts have been made to develop arsenic field kits for water samples, and today a range of these kits are commercially produced. Additionally, online analytical devices have also been built to operate in the field. Those devices are used primarily to monitor arsenic concentration in water which is subject to a cleanup procedure so that potential problems occurring during this process can be detected at an early stage. In this chapter, emphasis is given to new developments of electrochemical methods and their potential to form the basis of a "new generation" of field kits which satisfy all requirements for reliable arsenic detection in the field.

In contrast to water detection, very few field-based methods are used for direct arsenic measurements in solids. Only the handheld x-ray fluorescence (XRF) probe enjoys reasonable success, and alternative instruments are not yet commercially available.

For gas analysis, field kits have been developed for the detection of arsine, mainly for the purpose of assessing occupational environments [5]. These methods are noted later in the chapter.

In judging the performance of an analytical field kit, the performance parameters have to be set and are different for different situations. In general, field kits are used for two different cases: to identify and quantify most reliably unstable compounds in the field and for the semiquantitative determination of an analyte in an environmental medium. The latter is often used in surveys to make a decision as to whether an analyte is below or above a certain level. This is also the rationale for the use field kits to detect arsenic in drinking water where a decision has to be made as to whether the arsenic concentration is below or above a threshold value of 10 or 50 μg/L. Detection is probabilistic with four different outcomes when a threshold value has been established:

1. Correct safe water detection
2. False safe water detection (false positive)
3. Correct unsafe water detection
4. False unsafe water detection (false negative)

Case 4 is a false alarm. As a consequence, a well might be closed due to the analysis, even though it offers a safe water supply. This might lead to the use of unsafe water in the vicinity, but it does not create a toxicological problem directly. In contrast, however, case 2 declares a water supply as safe while it is above the threshold level and is, by definition, unsafe. It creates false hope and is toxicologically and ethically a problem. These decision criteria and the proportion of occurrences of cases 2 and 4 is more important for field kits than is the overall ability of the analytical method to give information about the actual concentration of the analyte. The performance of field kits will be judged in terms of their false positive and negative determination ratios.

Summarizing, field data used for surveys can be used effectively only if commercial instruments:

- Are sensitive, accurate, and precise enough for decision making
- Are highly reliable, so that little further backup or retesting is necessary
- Have high-throughput samples (low response time)
- Are cost-effective
- Are easy to use

ANALYTICAL METHODS FOR WATER SAMPLES

Laboratory-Based Reference Methods

Methods Based on Atomic Spectrometry The standard laboratory-based methods for total arsenic are based on atomic spectrometric detection, such as atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma atomic emission spectrometry (ICP-AES), or inductively coupled plasma mass spectrometry (ICP-MS). All of these methods are expensive, require skilled operators, and require such laboratory services such as cooling water, mains electricity, stable power supplies, and controlled laboratory environments. Thus, these methods cannot be used in field-based measurements.

On their own, all of the methods mentioned are only able to detect elemental concentrations and are incapable of providing information about the speciation of arsenic. However, the techniques may be coupled on- or off-line with species-selective processes, which might be certain pretreatments, such as the use of hydride generation methodologies to separate those arsenic species that can form volatile arsines at the chosen conditions, or coupling to chromatography such as high-performance liquid chromatography (HPLC) or gas chromatography (GC). Finally, it should be mentioned that when hydride generation methodologies are used, arsenic should be in a form that forms arsines readily and quantitatively. When used under a strict quality assurance/quality control (QA/QC) regime, these methods can determine arsenic in water samples in sub-μg/L concentrations with an accuracy of ±10%. However, they are relatively expensive, timeconsuming, have a low sample throughput, and thus are not suited for field applications.

Methods Based on Electrochemical Sensing Arsenic detection by electroanalytical techniques is made by stripping analysis [6–10]. A potential called the deposition potential (E_{dep}) is first applied to reduce the arsenic ions present in the solution into a form that accumulates at the surface of the working electrode (WE). At the end of this deposition step, the arsenic accumulated is stripped from the surface either by imposing an anodic/cathodic current (potentiometry) or by sweeping the potential accordingly (voltammetry). The response (current in voltammetry or time in potentiometry) is directly proportional to the arsenic concentration in the sample. Due to the accumulation step, this technique is highly sensitive; concentrations in the sub-ppb range can be determined.

In the laboratory environment, cathodic stripping voltammetry (CSV) at a hanging mercury drop electrode (HMDE) is probably the most popular technique for arsenic detection [6,7 11–14]. Arsenic is usually codeposited with copper and/or selenium and forms intermetallic compounds at the surface of the mercury:

$$2\mathrm{As}^{3+} + 3\mathrm{MHg} + 6\mathrm{e}^{-} \longrightarrow \mathrm{M}_3\mathrm{As}_2 + 3\mathrm{Hg} \qquad (1)$$

The arsenic is then reduced to arsine during the stripping step by sweeping the potential cathodically:

$$M_3As_2 + 12H^+ + 12e^- + 3Hg \longrightarrow 2AsH_3 + H_2 + 3MHg \quad (2)$$

The ability to renew the mercury drop between successive measurements easily avoids any interfering memory effects but leads to high mercury consumption. Although very sensitive, the relative complexity of the mercury drop system is not well adapted for field measurements.

Field Testing Kits for Water Samples

At present, two main approaches are utilized for the on-site analysis of arsenic. By far the most widely used are systems based on a colorimetric principle. These systems require few reagents, are supposedly easy to use, and the results should be straightforward. The second approach is based on electroanalysis and on the possibility to reduce/oxidize arsenic species. Although more difficult to operate, the detection limits obtained using such devices can be much lower than those obtained by colorimetry.

Colorimetric Methods

Principles of Colorimetric Methods for Arsenic Determination A variety of colorimetric field kits for the determination of arsenic are commercially available, all based on the 100-year-old Gutzeit reaction [15], discussed further in Chapter 7. This reaction generates arsine (AsH_3) gas by reduction of arsenite [equation (3)] or arsenate [equation (4)] under acidic conditions with addition of zinc powder.

$$As(OH)_3 + 3Zn + 6HCl \rightarrow AsH_3 + 3ZnCl_2 + 3H_2O \quad (3)$$

$$H_3AsO_4 + 4Zn + 8HCl \rightarrow AsH_3 + 4ZnCl_2 + 4H_2O \quad (4)$$

The arsine generated is chemotrapped by various reagents to form a colored complex. The intensity of the color has been used for quantification, while arsine generation coupled to complex formation gives a degree of selectivity. The color is commonly determined by comparison with a color chart (Figure 1) mainly for semiquantitative measurements, or by using a simple spectrophotometer, especially when colored complexes are formed.

Impregnated Hg(II) bromide paper is probably the most commonly used reagent. The Gutzeit type of field kit uses a test paper that produces a yellow stain as the result of the reaction with arsine. When more arsine is formed, a darker color appears, suggesting the formation of a different complex, although its structure is unknown [16]. The coloring developed is roughly proportional to the amount of arsine produced and therefore the concentration of the solution

Figure 1 Colorimetric field test kits with corresponding colored scale chart. (*See insert for color representation of figure*.)

being tested. The resulting color is compared visually with the test sheet (compare Figure 1 and Chapter 7). The method is easy to use and is capable of detecting arsenic concentrations down to 1 μg/L. However, the results are only semiquantitative. Interferences are usually caused by sulfides and higher levels of antimony.

Two other methods are commonly used for arsenic, although less so in the field, due to the use of absorption solution, and are not covered here in detail. Briefly, the first detection method is based on the reaction between gaseous arsine and silver diethyldithiocarbamate (DEDTC) [17]. The resulting product produces an intense-red color in pyridine for which the molecular structure is still unknown. Photometric measurement of the purplish-red color produced by the colloidally dispersed silver at the maximum of the absorption curve at a wavelength of about 535 to 540 nm is related to the concentration of arsenic in solution. A second detection method is also on arsine generation, but the chemotrapping reaction is different. Arsine forms a hetropolymolybdate blue complex that can be detected spectrophotometrically at 840 nm. However, the gaseous arsine does not react directly; it first has to be oxidized, usually by a reaction with hypobromite, to arsenate. The resulting arsenate reacts with ammonium molybdate in the presence of hydrazine sulfate to form this complex.

Aspects of Arsenic Speciation Capabilities When they are used according to the instructions, the colorimetric field kits, are not able to differentiate between species. The field kits respond to arsenite and arsenate but under normal field conditions are not capable of detecting organoarsenicals such as DMA(V) and MA(V), although they can be volatilized as their respective methylarsines. One manufacturer (Hach), however, suggests boiling the sample for 30 minutes with monopersulfate to decompose the organoarsenicals, which would make the organoarsenicals detectable. This procedure is, however cumbersome and not realistic under field conditions. Sometimes in small concentrations, methylated arsenic species can be common in freshwater samples, in particular in wastewaters

TABLE 1 Summary of Some Colorimetric Field Kits for Arsenic in Water

Name	Method	MDL (μg/L)	Time	Capital Cost per 100 Tests (dollars)
Merck (various kits)	Gutzeit $HgBr_2$	1–20	30 min–120 h	50
	Test chart	5–500		
Hach EZ arsenic test kit	—	10–500	20–40 min	80–150
GPL test kit	Bromide strips	10–2500	20 min	43
Ditital Arsenator (Wagtech Int.)	Gutzeit method with photometric readout	2–100	30 min	
Visual as detection kit (200 Wagtech)	Gutzeit test chart or photometry	10–500	30 min	
NIPSOM field kit	Gutzeit test chart	10–700	10 min	18

that have microbial activity. Besides their natural occurrence, methylated arsenics in groundwater can originate from anthropogenic products such as pesticides or fungicides. It is therefore anticipated that field testing kits should be prone to a negative bias. The most commercially available field kits based on colorimetric measurements are listed in Table 1, together with other details.

Analytical Performance in the Field The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the implementation of innovative new technologies for environmental monitoring. The ETV program works in partnership with recognized standards and testing organizations and with vendors and developers as well as stakeholders for potential buyers. The program tested several commercially available kits in July 2002 and added four in August 2003 under field conditions with trained and untrained operators [18]. An assessment of the "new generation" of field testing kits is provided in Table 2.

Most new-generation colorimetric methods have detection limits below 10 μg/L, which is sufficient to decide whether a water sample contains more or less than 50 μg/L. The older test kits, such as Merckoquant, are not suitable for making decisions about the 50-μg/L criterion, and their reliability is not satisfactory. For the new generation of colorimetric kits the assessment for making a decision about the 10-μg/L threshold reveals that large numbers of false results are made, although most of them are false negatives, which means that waters of lower concentrations have been reported to be above 10 μg/L. The test kits show reasonably good unit reproducibility. The influence of operators gave

TABLE 2 ETV Joint Verification Statement (U.S. EPA and Batelle) for Arsenic Field Methods, June 2002 and August 2003

Product	Accuracy (%)	Precision[b] (%)	Linearity[c], r^2	MDL (μg/L	Matrix Effects Interferences[d]	Interunit Reproducibility (ub), Operator Bias (ob)	Rate (%) of False Positive (fp) and False Negative (fn) to 10 μg/L	Cost and Time
PeCo (Peters Engineering) with visual testing	For 10 μg/L, ±2 to 17 For 23–93 μg/L, ±1 to 113	0–40 (NTO) 0–26 (TO)	0.977 (NTO)	15–50 (NTO) 20–40 (TO) (given for 25 μg/L)	No significant effects	No performance differences for operators	Fp: 0 (NTO), 3 (TO); Fn: all 0	100 samples for $200
As 75 (Peters Engineering) with electronic testing	For 10 μg/L, ±1 to 157 For >10 μg/L, ±6 to 310	11–38 (NTO) 12–71 (TO)	0.990	33 (NTO) 28 (TO)	No significant effects	No performance differences for ob	Fp: 2 (NTO), 13 (TO); Fn: all 0	Cost of tester $330, additional 100 cost $60
Quick Low Range II color chart	−92 to −8 (TO) −74 to 74 (NTO)	0–55	0.99 (NTO) 0.90 (TO)	1.2–1.5	No significant effects	Better performance of NTO	Fp: 0; Fn: 62 (TO), 33 (NTO)	15-min analysis; 50 samples for $350, 15-min analysis; 50 samples for $350, additional to $1600
Quick Low Range II arsenic scan	−98 to −27 (TO) −76 to 9 (NTO)	0–84	0.96 (NTO) 0.98 (TO)	0.7–2.1	No significant effects	Better performance of NTO Unit differences are not significant	Fp: 0; Fn: 62 (TO), 38 (NTO)	
Quick Low Range II Compu-scan	−93 to 104 (TO) −67 to 81 (NTO)	7–91	0.98 (NTO) 0.98 (TO)	0.5–3.9	No significant effects	Better performance of NTO Unit differences are smaller but significant	Fp: 0–3; Fn: 52–67 (TO), 9 (NTO)	15-min analysis; 50 samples for $350, additional to $1600

Quick II color chart	−61 to 10 (TO) −77 to 96 (NTO)	16–24 (TO) 0–38 (NTO)	0.98 (NTO) 0.96 (TO)	3.6–7	No significant effects	Better performance of NTO	Fp: 0; Fn: 19 (TO), 24 (NTO)	15-min analysis; 50 samples for \$220
Quick II arsenic scan	−78 to −4 (TO) −85 to −22 (NTO)	11–44 (TO) 13–38 (NTO)	0.93 (NTO) 0.92–0.93 (TO)	4.5–6.1	No significant effects	Better performance of NTO No ub	Fp: 0; Fn: 19–33 (TO), 29 (NTO)	15-min analysis; 50 samples for \$220, additional to \$1600
Quick II Compu-scan	−71 to 96 (TO) −82 to 108 (NTO)	10–58 (TO)	0.91 (NTO) 16–108 (NTO)	3.7–18.2 0.92 (TO)	No significant effects	No significant differences (ob), significant unit biased (ub)	Fp: 3–9 (TO), 0 (TO); Fn: 38–10 (TO), 14 (NTO)	15-min analysis; 50 samples for \$220, additional to \$1600
Quick Low Range color chart	−38 to 239 (TO) −81 to 579 (NTO)	0–10 (TO) 0–23 (NTO)	0.98 (NTO) 1.00 (TO)	3.1–6.7	Positive bias when higher levels of sodium chloride, sulfide, and iron	Better performance of NTO	Fp: 3 (TO), 12.5 (NTO); Fn: 0 (TO), 14 (NTO)	15-min analysis; 50 samples for \$180
Quick Low Range arsenic scan	−93 to 99 (TO) −86 to 66 (NTO)	5–23 (TO) 0–42 (NTO)	0.966 (NTO) 0.997 (TO)	4.0–7.2	Positive bias when higher levels of sodium chloride, sulfide, and iron	No significant difference (ob), no ub	Fp: 0–3; Fn: 14–19 (TO), 10 (NTO)	15-min analysis; 50 samples for \$220, additional to \$1600

Source: Ref. 18.

[a]NTO, nontechnical operator; TO, technical operator.
[b]Relative standard deviation.
[c]Linearity = slope × reference value + offset.
[d]Tested for high levels of sodium sulfate, iron, or acidity.

reports [18]) suggests that nontechnical operators generate better results with a series of kits, although the reason for this is not known.

There are some issues raised both about the toxic waste produced with some of the testing sets ($HgBr_2$) and about the safety of the operators (high levels of toxic arsine are generated). The overall costs cover mainly the consumables and vary between $2 and $7 per sample. The extra cost of about $1600 for photometric readouts and a computer does not improve the performance of the colorimetric kits and does not seem to be justified.

Field Studies in the Literature In recent years a few papers have been published that report arsenic concentrations from field measurements and their evaluation with reference laboratory-based values from affected areas. Most of these studies were done on contaminated water samples from Bangladesh and West Bengal [19–29]. In addition, two excellent reviews on field kits and on-site monitoring have been published [30,31].

Since 1997 the World Bank, UNICEF, the World Health Organization (WHO), and other organizations have pressed for testing tube wells in Bangladesh and West Bengal. The various field kits described are currently used in the affected areas, and in Bangladesh alone more than 1.3 million tube wells have been tested and decisions on use made instantaneously: tube wells containing water with arsenic concentrations higher than 50 μg/L were painted red and "safe" wells (below 50 μg/L) were painted green [32]. Most of the decisions made before 2001 were based on the results from field kits which had only a specified minimum detection limit of 100 μg/L (Merck, Merckoquant, 1.10026.0001). The Bangladesh Arsenic Mitigation Water Supply Project [33] and UNICEF [34] tested more than 1 million wells, while the other organizations tested a smaller cohort of wells [35–37]. However, a very poor correlation between the values obtained with field test kits (Merck) and values obtained with laboratory-based reference methods was reported ($r^2 = 0.2$ to 0.5) [19], which triggered a series of investigations. Using HG-AAS as a reference method, Rahman et al. [21] found that 45% of 2866 wells had been mislabeled in the range below 50 μg/L. Since 2001, two more sensitive colorimetric methods have been developed by Merck and Hach. Both kits present a MDL of 10 μg/L, which is better suited for use in field surveys.

In a comprehensive study using three field kits (Merckoquant, NIPSOM, and GPL), more than 290 wells were tested against reference methods [16]. At arsenic concentrations below 50 μg/L, the false positive results were acceptably low [i.e., 9.2% (NIPSOM) and 6.5% (GPL)], whereas in the range 50 to 100 μg/L, it increased to 35% and 18%, respectively. As a result, using the NIPSOM kit, 33% of the unsafe tube wells were colored green (i.e., safe). The false negative results reported between 50 and 100 μg/L were 57% and 68%, which means that up to two-thirds of the wells painted red were safe. Above 100 μg/L the percentage of false negative was still considerable (26% for NIPSOM and 17% for GPL). The mislabeling of 45% of the wells is unacceptable but cannot be explained easily by possible variability of arsenic concentration and a lack of QA/QC or operator error. This study clearly demonstrates the need for a stringent testing procedure to generate reliable data and the need to develop more reliable analytical systems, which should make costly retesting unnecessary.

In addition to these results, it has been revealed that most kits based on the Gutzeit method generate a hazardous amount of arsine during testing, which may exceed the threshold limiting value in occupational air by a factor of 30. The poor performance of the tests created a strong incentive for field test kit developers to improve test kit performance by several low-cost manipulations. The mixing chamber was optimized and errors in visual inspections were eliminated by using spectrophotometers [31].

Using the new generation of field kits (Hach EZ arsenic kit, 2822800) seemed to improve the accuracy of field methods. Van Geen et al. [22] reported recently that 88% of 800 tested in one district of Bangladesh were assigned correctly according to the 50 μg/L drinking water standard. Retesting wells from a previous BAMWSP study which classified more than 66% of the wells incorrectly by changing the protocol (increasing the reaction time from 20 minutes to 40 minutes) reduced this to 34%.

These encouraging results show an improvement in data generated from field-kits when the wells are classified according to the local standard. However, it should not be forgotten that even 12% mislabeled wells in Bangladesh would itself mean that approximately 6.8 million people would drink water from as wells classified safe which contain arsenic concentrations higher then 50 μg/L. This calculation, which was presented in a comment from Mukherjee and co-workers [38], is based on 2.36 million tube wells tested by the Hach EZ kit, each well serving an average of 24 persons. Encouraging, however, is the study recently published by Steinmaus and co-workers [29] in which 136 water sources were tested with the Hach kit and the Quick arsenic field kit and compared with AFS results. All samples above 15 μg/L were identified as not safe. If, however, the WHO guideline of 10 μg/L has to be considered, new challenges appear. Although some new-generation arsenic field kits are able to detect one-tenth of the WHO guideline value, the measuring time of 40 minutes is unacceptable. Furthermore, no arsenic field kit has been shown to be capable of determining arsenic species, including the water-soluble organoarsenicals DMA(V) and MA(V) in ground- and wastewater under field conditions.

Electrochemical Sensors In contrast with spectrometric techniques, electrochemical systems are ideally suited to field determination of arsenic in aqueous media. They combine sensitivity, selectivity, low-cost portable instrumentation with low power consumption and feature a unique ability to detect a variety of oxidation states. Voltammetric systems for field measurement include a portable system for on-site analysis (i.e., directly at the sampling point), an off-line analyzer for high-throughput samples [a benchtop or in-house system that can be installed in remote areas (i.e., transportable but not portable)], and an online analyzer that performs sampling and analysis for continuous monitoring automatically (e.g., real-time measurement of a wastewater effluent). However, in contrast to colorimetric tests kits, very few studies have been done on the reliability of electrochemical field systems for arsenic analysis.

Principles of Electrochemical Methods for Arsenic Determination Although very popular in a laboratory environment, use of the mercury drop electrode system is not well adapted for field studies, although it has been used recently. For such purposes, electrodes such as solid electrodes are much better suited. In that case, arsenic detection is usually made by anodic stripping voltammetry (ASV) or by potentiometric stripping analysis [10] (PSA). In both cases, arsenic is deposited on metallic arsenic As ^{0} at a negative potential [equation (5)] and stripped back into solution [equation (6)] either by sweeping the potential anodically (ASV) or by imposing a constant anodic current (CCPSA):

$$\mathrm{As(III)/As(V)} + 3/5\mathrm{e}^- \longrightarrow \mathrm{As}^{\mathrm{o}} \tag{5}$$

$$\mathrm{As}^{\mathrm{o}} \longrightarrow \mathrm{As(III)} + 3\mathrm{e}^- \tag{6}$$

The deposition and stripping step usually occurs under acidic conditions, hydrochloric acid being the most popular electrolyte (see, e.g., refs. 8, 39, and 40). Optimum concentrations of HCl range between 0.1 and about 6 M. Although very common, the use of high acidic concentrations present major drawbacks: deterioration of the electrode [8], formation of gold–chloride complexes that might passivate the surface [41], strong hydrogen generation [41] or formation of chlorine [42] that modifies the arsenic distribution in the sample. These factors affect the stability of the measurements and can result in a complete loss of signal. Few studies report the detection of arsenic under neutral or alkaline conditions [42–44] by using a relatively low deposition potential, E_{dep}. For instance, detection of arsenite in seawater at natural pH ($\sim$8.4) was reported recently [42] using $E_{\mathrm{dep}} = -1.1$ V. Arsenate detection, however, has only been reported in acidic conditions.

Various electrode materials have been tested, but gold and platinum appear to be the best suited. Different types of electrodes are used: solid electrodes [42,43,45] (rotating disk or fiber), films (formed by electrolysis on a carbon [8], platinum [40] or diamond substrate [46]), microelectrodes (fabricated by photolithographic techniques) [39] and recently, nanoparticles [46–48] (formed by electrolysis or precipitation). At macroelectrodes (size greater than about 100 μm), the mass transport (i.e., the flux of arsenic ion to the electrode) during the deposition step is increased by either stirring the solution or rotating the electrode. When using sufficiently small electrodes (μm/nm range) the mass transport is enhanced by spherical diffusion. Measurement can then be done in unstirred solutions [47,49], which would simplify the analytical system for field analysis. In any case, the nonconductive As^0 accumulated at the surface during the deposition step decreases the linear range by preventing further deposition of arsenic [8,42]. However, by decreasing the deposition time, this linear range can be extended [42]. The detection limit is usually under the ppb level and can reach the ppt range when using microelectrodes. A single measurement time generally does not exceed 5 minutes.

The main interferences affecting the analysis of arsenic in natural samples are metal ions, surfactants, and organic acids. Metals such as Bi, Fe, Ni, Se, Sb, Cu, Hg, and Zn have all been reported to interfere (see ref. 13 and references therein) either by competing for the same reductive sites on the WE surface, by having a redox potential in close proximity to that of arsenic, and/or by formation of intermetallic compounds. Dissolved organic matter (such as fulvic and humic acids) or surfactants can also strongly interfere by adsorbing on the surface of the electrode and blocking the electron transfer reaction [8,40]. Although the electrode can be modified to limit such effects [41,49], the addition calibration procedure is required to take into account any matrix effects. If the level of interferences is too high, adapting the measuring conditions (e.g., deposition potential [40]), diluting the sample [9], using a medium exchange [39], protecting the electrode against adsorption [39,47] and/or destroying the organic matter by ultraviolet (UV) digestion (if only total arsenic determination is of interest) might be needed for accurate analysis. In such cases, an experienced operator might be required.

Aspects of Arsenic Speciation Capabilities Most electrochemical systems are sensitive to arsenite. Arsenate is usually not considered as electroactive. Therefore, most inorganic speciation studies include the chemical reduction of arsenate to arsenite prior to the determination of total inorganic arsenic analysis. Different chemical reagents have been used, such as sodium sulfite [9], gaseous SO_2 [8,50], potassium iodide [12] or more recently L-cysteine [51]. The reducing step is not straightforward. It commonly takes between 5 minutes and 1 hour, includes conditions such as heating and purging, and might interfere with the voltammetric measurement [6]. Not only does the chemical reduction step increase the contamination risk but it reduces the sample throughput strongly and increases reagent consumption. This reduction step is the main limitation to the application of electroanalytical system for on-site analysis.

However, inorganic speciation of arsenite and arsenate has been reported without any chemical reduction (see, e.g., refs. 39,42 and 52). Using an adapted deposition potential, arsenite and total inorganic arsenic can be detected selectively by sole electrochemical means. Although arsenite is the only species detected at a deposition potential higher than about −0.4 V (vs·Ag/AgCl), both arsenite and arsenate are measured at a lower deposition potential (−0.7 to −1.8 V). Although the same sensitivities for arsenite and arsenate were found [53], As(III) is usually oxidized to As(V) prior to the measurement of total inorganic arsenic. Additions of permanganate or bromine water [39] or in-situ generation of chlorine [42] have been used to avoid problems of different sensitivities. In contrary to the chemical reduction, this oxidation step is very fast and well adapted for on-site applications.

Although much simpler than using a chemical reduction step, only a few papers report on this speciation method. Indeed, the detection of arsenate requires both a

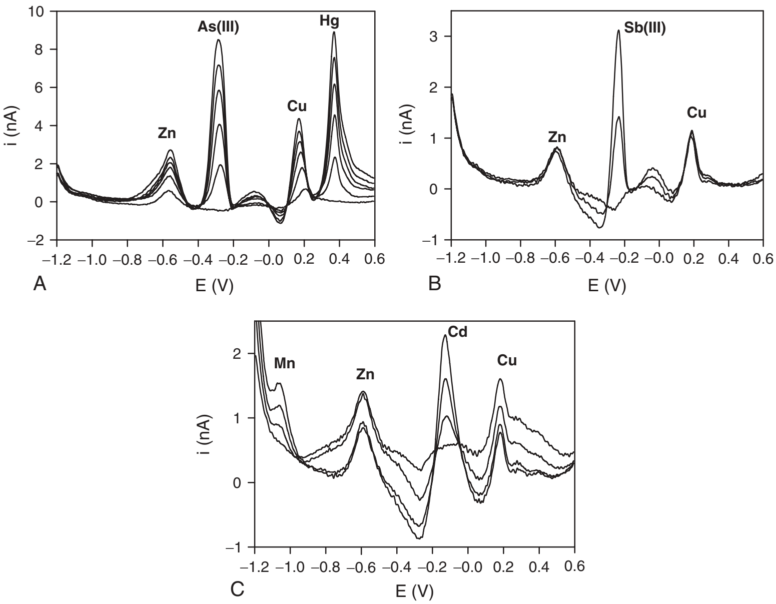


Figure 2 Standard additions of 10 nM (~0.75 ppb) of (A) Zn, As(III), Cu, Hg; (B) Sb(III); and (C) Mn and Cd in purged seawater solution −pH = 8.4. $E_{dep} = -1.2$ V−$t_{dep} = 30$ s−background subtraction. Electrode: gold microwire 5 μm in diameter and about 0.4 mm in length.

low deposition potential and acidic media. In these conditions, hydrogen is generated at the surface of the electrode, which may strongly hamper the measurement reproducibility [41]. In addition, the amount of current generated can be very high and might prohibit the use of macroelectrodes. Microwire electrodes seem the best suited configuration for such purposes [39,42], but macrodisc electrodes have also been used [54].

Finally, in contrast to colorimetric field tests kits, which are selective to arsenic only, voltammetric systems can be tuned to detect other metals simultaneously. For instance, at a gold electrode, metals such as Cu, Hg, Zn, Mn, or Sb can be detected along with arsenic (Figure 2). For instance, antimony has been shown to modulate toxicity of arsenic [55] and was found in samples containing high levels of arsenic [56]; 35% of the arsenic-contaminated groundwater samples from Bangladesh also contained levels of manganese above its WHO value of 500 ppb [57]. Knowledge of the concentrations of other metals brings insights into the toxicity of the sample and is the basis for efficient removal technologies. Field systems should therefore be as selective as possible.

Analytical Performance in the Field Few studies report the study of voltammetric test kit performance. Within the last five years, the Environmental Technology Verification (ETV) department of the EPA tested three voltammetric arsenic test kits [58–60] : the PDV6000, the NanoBand Explorer, and the SafeGuard system. The ETV tests of the PDV6000 and NanoBand Explorer were done in 2003 and have been improved since. A description of these systems is given below and a summary of performances is given in Table 3.

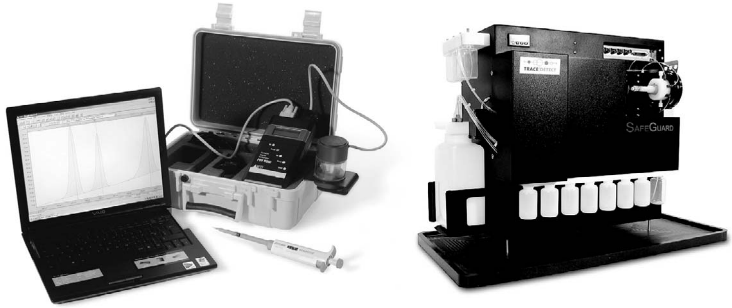
PDV6000 The PDV6000 [61] is a portable system (Figure 3) for field screening of heavy metals. It comprises a small analytical cell (electrodes + stirrer) and a handheld potentiostat. It can be powered from a main power supply, a portable battery pack, or internal 9-V batteries. When used in conjunction with a laptop and specifically developed software (VAS), more accurate analysis is achieved. The sensor is a gold film deposited on a carbon disk electrode 3 mm in diameter. The detection is done by linear scan ASV.

In an ETV test, two units were tested for arsenic detection, with unit 2 showing significantly higher values than unit 1 (paired t-tests at a 5% difference level). The accuracy (expressed as the percent difference between measurement results from the reference method) ranged from −74 to 31%. However, accuracy was always less than 25% except for high- and low-level interference (iron and/or sulfide). The linearity plotted against the reference method is very good ($r^2 > 0.99$), with a slope of 0.91 for unit 2. The LOD at unit 2 was 5.8 ppb. None of the units gave false positive results in any of the samples tested. The false negative rates were 42% for unit 1 and 38% for unit 2. The instrument setup and average calibration time was about 30 minutes. Only 5 minutes is then required per sample. The PDV6000 was found reliable with few exceptions, even though it was used as a stand-alone (i.e., without the laptop). Although easy to use, professional experience was sometimes required for optimum results. It was readily transported in a storage shed where water samples were analyzed. Hardware and software improvements were recently made on the PDV6000. A lower signal-to-noise ratio is obtained, resulting in lower detection limits. Techniques such as square wave and differential pulse are also available. The analyzer and associated equipment are easily stored in a waterproof carrying case. The current price of the PDV6000 is $6000 without the laptop.

NANOBAND EXPLORER The NanoBand Explorer [62] system consists of a WE (array of 100 band electrodes less than 0.5 μm thick), a voltammetric cell, a temperature sensor, an electrode cleaning kit, and a laptop computer. The NanoBand Explorer was tested by the ETV department in 2003 [59] but the system has since been optimized in terms of methods and protocols and in terms of hardware and software to make the system more user friendly. Spear et al. [63] studied the performance of this optimized version together with other colorimetric field tests kits. Recoveries of 30 ppb arsenic close to 100% were obtained for As(III) or As(V) or for a 1 : 1 combination of both. Interference levels as high as 5 ppm antimony or 10 ppm sulfide did not affect the measurement. A linear relation (As: 0 to 75 ppb) in a natural groundwater sample matrix was obtained and compared with results obtained by a standard method (GFAA). A correlation coefficient of 0.9 was obtained, indicating the high reliability of the

TABLE 3 Summary of Voltammetric Analytical System Reported for On-Site Arsenic Analysis

Electrode	Electrolyte	Detection Method	E_d (vs. Ag/AgCl)	LOD, t_d, RSD	Speciation	Comments	Refs.
HMDE	1 M HCl + 4.6 ppm Cu(II) + 3.7 ppb Se(IV)	DPCSV	−0.44 V	0.5 ppb, 60s 4.2% at 5 ppb	Addition of sodium metabisulfite + sodium thiosulfate; 420 s of purging required	Procedure difficult to implement in an on-site system; requires qualified operator; high mercury waste	11
Au film on Pt wire (50 μm in diameter)	0.01 − 0.1M HCl	LSASV	−0.2 V [As(III)] −1.6 V [As(V)]	0.5 ppb, 60 s, 0.2 ppb with 25-μm-diameter wire	Deposition potential + addition of $KMnO_4$ or bromine-water	Flow cell with medium exchange and standard addition; very acidic stripping medium (4 M HCl); Au film renewed for each determination; adsorption of organics/surfactant	39
Au film on GC (3.0 mm in diameter)	4.5 M HCl	LSASV	−0.15 V	1.2 ppb, 120 s, 1–10% ($N = 3$)	Na_2SO_3 + heating near boiling to remove SO_2(g)	Accuracy of chemical reduction ~5–20%; 20–30 samples a day for As(III); 10–20 samples per day for As(III) and total arsenic	9
Au-side RDE (oval shape: 4 × 2 mm)	0.25 N HCl + 20–30 ppb Cu(II)	DPASV	−1.1 V	2 ppb, 60 s, 15% at 10 ppb	Only total arsenic measured but can be adapted for As(III) measurement	No information about stability; Au disk is placed on the side; same sensitivities between As(III) and As(V) is assumed	54
Au microwire (5 μm in diameter)	Natural pH 0.1 M HCl	PSAASV	−1.1 V −1.2 V	15 ppt 22 ppt	As(III) As(III) + As(V)	Electrode very stable; H_2 generation does not affect arsenate detection; chlorine generated at the counter electrode oxidizes arsenite into arsenate	42
Au disk microelectrode array (12 μm in diameter)	2 M HCl	SWASV	−0.4 V	0.013 ppb, 300 s; 0.1 ppb, 80 s; 1.3–3.2%	Sodium sulfite, Na_2SO_3: 30 mn required for ~90% of the reduction process to occur	Portable system for As(III) detection; modified electrode with Nafion layer to prevent adsorption of surfactant; As(V) analysis more difficult to implement on-site; excellent stability of the electrode (60 days)	41,49



A B

Figure 3 Example of voltammetric field tests kits: (A) PDV6000 with laptop; (B) benchtop analysis system SafeGuard. (With permission from MTI Diagnostics.) (*See insert for color representation of figure*.)

voltammetric measurement. Successive measurement ($n = 7$) always showed a low standard deviation (<5%), resulting in a low detection limit (2.1 ppb). The reduction step is made at room temperature in less than 5 minutes and no longer requires air-sensitive compounds or the use of a burner. A further improved version (NanoBand Explorer II) combines the three electrodes (WE, AE, RE) into a single unit (Tritrode electrode), integrates automated stirring, and comes with a sturdy carrying case. The price of the Explorer II is $8750 without the laptop.

TRACEDETECT SAFEGUARD The TraceDetect SafeGuard [62] is a benchtop flow-through system (Figure 3) that can be transported to remote areas. It consists of a fluidic (pumps, valves, tubings) system, potentiostat, laptop, and voltammetric cell. The sensor consists of an interconnected array of 100 carbon band microelectrodes that are batch-printed on a quartz substrate. A gold film is deposited automatically by electrolysis of a gold solution. This film remains stable between 3 and 7 days, depending on use. If a decrease in sensor sensitivity or nonlinear behavior is detected, the operator will be alerted to clean the sensor manually (for 3 minutes) before depositing a new gold film. Measurements are performed without purging or stirring. The SafeGuard system is designed to measure total arsenic concentrations automatically from 1 to 100 ppb. All calibrations, dilutions, reductions, standard additions, and measurements are performed by the SafeGuard with the results displayed and logged in a data file. The system detects possible defaults automatically and requests specific simple actions by the operator. Measurement is done using ASV and the method of standard addition to make metal measurements. Accuracy ranges between −28 and +11% for both technical and nontechnical operators but excluding residential well waters, which could not be measured reliably (a difference of 600%). Similar precision (2 to 44%) was obtained for technical and nontechnical operators. Linearity was always found to be very good ($r^2 > 0.99$), with a slope ranging between 80 and 100% compared to the reference value. LODs of 2.0 and 3.8 ppb were obtained at two different units but can be decreased by increasing the deposition time. The presence of interferences (up to 10 ppm Fe, 30 ppm NaCl, and 1.0 ppm Na_2S) did not affect the detection of arsenic. No significant operator bias was detected. Results show an interunit bias with technical operators but minimal bias with nontechnical operators. Once again, the rates of false positives were negligible, whereas the rates of false negatives range between 4 and 22%. The SafeGuard system was found to be very easy to use, even for a nontechnical operator. The manual and software programs were both clear and easy to follow. No solution or sample preparation is necessary.

Another study [64] reported excellent stability for the SafeGuard (RSD $\sim$ $5\% - n = 60 - [\mathrm{As}] = 50$ ppb). A set of samples with arsenic concentrations ranging between 1 and 100 ppb were measured ($n = 118$) by both the SafeGuard and standard laboratory techniques (GFAA and ICP-MS). A correlation factor of 1.00 was found, indicating a perfect accord between the two methods. For samples below 10 ppb ($n = 30$), no significant differences (95% CI) were observed. Using a deposition time of 4 minutes, increments of 1 ppb were well resolved.

The SafeGuard system can be used both as an autosampler and for single analysis. The analysis time per sample ranges between 30 and 50 minutes. The base of the SafeGuard is 38 by 71 cm and it is 56 cm high. In 2006, the listed price of the SafeGuard was $35,000 and the cost for a 45-sample reagent kit was $80.

Field Studies in the Literature Different systems have been developed for field measurement or were described as potentially applicable for field measurement. Table 4 lists some of the systems that are described below. Using a field-portable potentiostat, Feeney et al. [41,49] achieved the on-site detection of arsenite using a gold microelectrode array produced by lithography techniques. To limit the adsorption of surfactants, the sensor was covered with a thin layer of Nafion (Nafion is a perfluorinated polymer that blocks anionic species from adsorbing on a gold surface). Results obtained on-site for As(III) were within the 95% confidence interval compared to ICP-AES measurement (EPA method 200.7). The excellent stability of the sensitivity was obtained over 30 days before being limited by the growth of an oxide layer at the surface of the gold. Interference studies on 100 ppb As(III) indicated a major effect of Cu (50% loss for 50 ppb and 90% loss for 500 ppb) and a lesser effect for lead and mercury. Iron and Zinc were found not to interfere (<500 ppb). Electrochemical detection of arsenate was attempted but yielded no satisfactory results. Excessive evolution of hydrogen gas at the working electrode surface prevented reproducible data. KI, $N_2H_4 \cdot 2HCl$, Na_2SO_3, and ascorbic acid were tested for the chemical reduction of As(V). Only addition of sodium sulfite followed by heating gave reliable analytical results. The chemical reduction takes approximately 30 minutes but was not performed on-site.

TABLE 4 Summary of Performance of Commercial Voltammetric Field Tests Kits Tested by Independent Operators

Name, Company	WE Technique	Slope vs. Reference Method	r^2	RSD (%)	LOD (ppb)	Accuracy[a]	False Positive/ False Negative Errors[b] (%)	Speciation	Comments	Ref.
PDV6000, Lab21-MTI	Gold disk/ ASV	$0.77 - 0.91$[c]	>0.99	6–16, 3–15	5,[d] ~7[e]	(−74, +31)	0/(38–42)	As(III), As(V): low deposition potential	Portable system in box case; professional judgment sometimes required; 30 min setup, then 5 min per sample; 20 mL waste of dilute HCl per sample; updated system exists; price: £6000	58
NanoBand Explorer, TraceDetect	Gold microbands/ ASV	0.9[f]	>0.9	~5	2.1	n.d.	n.d.	As(III), As(V): chemical reduction	Portable system in box case; detection not affected by the presence of 5 ppm Sb or 10 ppm S; chemical reduction at room temperature (<5 min); improved version exists: NanoBand Explorer II; price: $8750	60
SafeGuard, TraceDetect	Gold microbands/ ASV	$\sim 0.8 - 1.0$[c]	>0.99	$3 - 44$[g] $2 - 38$[h]	1,[d] ~3[e]	(−28, +7)[g] (−28, +11)[h]	(0–2)/(4–22)	As(III), As(V): chemical reduction	Benchtop system; very easy to use; 30–50 min/analysis; ~30- to 40-mL sample required due to standard addition procedure; price: $35,000 + $1.80 per sample (reagents)	63

[a] Percent of samples where the detected arsenic concentration is within 25% of the reference method. n.d., not determined.
[b] Relative to the 10-ppb threshold value. n.d., not determined.
[c] Versus EPA method 200.8, "Determination of Trace Elements in Water and Wastes by ICP-MS," Revision 5.5, October 1999.
[d] Given by the vendor.
[e] Determined by the ETV department.
[f] Versus EPA method 7060A, "Arsenic (Atomic Absorption, Furnace Technique)—Test Methods for Evaluating Solid Waste: Physical/Chemical Methods," 1994.
[g] Technical operator.
[h] Nontechnical operator.

Van Geen et al. [65] used a method developed by He et al. [11] to determine As(III) on-site. The technique is based on the cathodic stripping voltammetry of intermetallic compounds formed between arsenic, copper, and selenium at the HMDE. Addition of 4.6 ppm copper and 3.7 ppb selenium gave an optimum signal for reduction of the $Cu_xSe_yAs_z$ species formed at the surface of the mercury during the deposition step. Due to the formation of different intermetallic species, the peak shape varies as a function of arsenic and of the deposition time. Only dissolved As(III) was determined on-site with this method. Indeed, the chemical reduction procedure is complex and suited neither for on-site speciation nor for high-throughput sample analysis. It involves the addition of sodium bisulfite with sodium thiosulfate to reduce As(III) into As(V) and purging for 420 seconds to remove gaseous SO_2. In addition, the use of a mercury drop system requires an experienced operator and does not seem to be suited for field analysis, although it has the advantage of removing any memory effects by renewing the mercury drop. Recently, He et al. [51] developed a more rapid reduction method using L-cysteine for arsenate determination, which takes only 6 minutes at 70°C. Thirty samples were analyzed in a two-day field expedition, showing the suitability of the technique for field analysis. In addition, using peroxydisulfate combined with ultraviolet photooxidation, determination of organoarsenic species was also achieved.

Huang and Dasgupta [39] developed the first portable device for the field electrochemical speciation of As(III) and As(V). The instrument is compact, lightweight (6.5 kg), and of low power consumption (3.5W). It consists of a laptop, four solenoid valves, a flow cell, and a potentiostat. To reduce power consumption, flow occurs under gravity. The working electrode is a gold film deposited on a platinum wire. The reference electrode is a chloridized 250-μm silver wire. The deposition is done in 0.01 to 0.1 M HCl and the stripping in 4 M HCl. As(III) is measured at $E_d = -0.2$ V, while As(V) is determined at -1.6 V. The first derivative of the current was used to quantify the arsenic concentration to minimize interferences from metals with close peak potentials. The LOD is 0.5 ppb for both As(III) and As(V), with a very low standard deviation (2.2% at 10 ppb). A lower LOD value could be obtained by using a smaller Pt wire and/or by using CCPSA instead of LSASV. Linear calibration ($r^2 > 0.998$) for both As(III) and As(V) was obtained up to 350 ppb with a 5-second deposition time. With a deposition time of 60 seconds, the signal is linear up to 60 ppb. To measure total arsenic, $KMnO_4$ or bromine water is added to the sample to convert all As(III) into As(V). The system seemed well adapted for arsenic speciation. However, continuous experience showed that measured concentrations of arsenic were sometimes much lower than those obtained with reference methods, although the reasons for this are not fully understood [66]. This system is no longer available commercially.

In 2002, Rasul et al. [9] found As(III) in 960 samples and total inorganic arsenic in 238 of them. Although used in laboratory conditions, the system can easily be transported to decentralized areas. It consists of a computer, a potentiostat, and a voltammetric cell. The WE is a thin gold film on a GC electrode. If the signal of the sample was within the analytical range, a standard addition was achieved by the addition of two known amounts of arsenic. If not, the sample was diluted. Speciation was achieved through reducing As(V) by adding sodium sulfite and heating until all excess SO_2 fumes were cleared. The detection limit is 1.2 ppb for a 120-second deposition, a precision ranging between 1 and 10% ($n = 3$), and an accuracy of 10%. The system throughput was 20 to 30 samples per day for As(III) or As(V) and 10 to 20 samples for both species in the same solution. This low sample throughput is due to the standard addition technique and the chemical reduction procedure.

To avoid problems related to the chemical reduction step, Prakash et al. [54] developed a gold side rotating disk electrode. In measurements in a low-acidic electrolyte (0.25 M HCl) together with a side rotating disk electrode which removes the hydrogen bubbles mechanically, speciation was achieved simply by varying the deposition potential. Trace amounts (20 to 30 ppb) of Cu were added to improve the peak shape. The system was tested by measuring groundwater samples. A relatively high detection limit of 2 ppb is obtained, due to the use of a macroelectrode (gold disk with oval shape of 4 by 2 mm). In addition, the electrode needs to be cleaned after only 10 measurements, which strongly limits its potential application for field analysis.

Using a gold microwire electrode 5 μm in diameter, Salaün et al. [42] developed a simplified procedure for the speciation of inorganic arsenic species in seawater. Arsenite is first determined at natural pH ($\sim$8.4) using a low deposition potential ($E_{\text{dep}} = -1.1$ V). The total inorganic arsenic is then determined after acidification to 0.1 M HCl using $E_{\text{dep}} = -1.2$ V. Indeed, during the deposition step at such a low deposition potential, it was shown that chlorine is generated at the counter electrode, and the resulting hypochlorous acid oxidizes arsenite into arsenate. Arsenate is then determined simply by subtraction. The electrode was found to be very stable ($\sim$4000 measurements) and ideally suited for the direct determination of arsenate. It is thought that the mechanical shape of the wire, together with the low roughness value of the gold surface [67], facilitates the removal of hydrogen bubbles generated during the deposition step and thus allows direct measurement of arsenate. Under optimized conditions (background subtraction, deaerated sample), detection limits of 15 ppt in seawater and 22 ppt in 0.1 M HCl were obtained for As(III) and As(III) + As(V), respectively. As well as being highly sensitive, the main advantage is the speciation procedure, which does not involve a time-consuming chemical reduction step. Use of this procedure for field analysis of groundwater is currently under investigation.

Online Analyzer for Real-Time Arsenic Monitoring There is an urgent need for on-site continuous monitoring of arsenic levels, for either water treatment or quality control purposes. Electroanalytical systems are the only ones that can be fully automated for such purposes. A fully automated online analyzer can be found from Lab21-MTI (OVA5000) [61] or TraceDetect Inc. (ArsenicGuard) [62]. Advantages of such systems are numerous and include quasi-instantaneous knowledge of arsenic concentrations, a short response time when facing a contamination problem, and the application of optimized removal procedures (e.g., concentration of coagulant). These systems are still in their infancy and few examples can be found where automated online electroanalytical systems provide real-time measurements of arsenic levels in a water of interest. For instance, the OVA5000 from Lab21-MTI is currently used at a contaminated site in Vineland, New Jersey [68,69]. The Vineland Chemical Company caused a large-scale arsenic contamination of 54 acres by improper raw material storage and depositing waste herbicide material over a period of 44 years. Treatment of the contaminated area consists of a soil fraction separation and washing process. The contaminated ground- and wastewater from the soil washing process are treated through a chemical precipitation process, and the treated wastewater is discharged to a local river when the arsenic concentration is below the 10-ppb limit. The OVA5000 provides real-time continuous monitoring (24 hours a day, 7 days a week) of the arsenic wastewater concentration and communicates the results of analysis to an external location. When the arsenic concentration is higher than the threshold value, the effluent is rerouted back through the process for further arsenic removal before release. In 2006 the OVA5000 had been used continuously for 175 days and performed 4000 measurements. Each measurement takes about 1 hour.

In each case the entire measurement procedure is automated. Sampling, filtration, dilution, ultraviolet digestion, and voltammetric procedures are all controlled by the software. Routine servicing includes verifying pump calibration, cleaning the sample line and analysis cells, and polishing the working electrode, typically a 30-minute task per week. Alarms can be set to indicate if any parameter is out of specification. In this situation, interactive troubleshooting help files guide the user through the steps needed to rectify the problem. All raw and summary data are accessible and can be archived from the instrument through an intranet or the Internet.

Future Methods and Technological Developments

A few reports on the development of new techniques are available. The most promising is probably the method developed by Idowu and co-workers [70]. Arsenic is reduced to arsine by borohydride reduction and reacts with ozone generated from ambient air. The resulting chemiluminescent signal is proportional to the amount of arsine. Speciation of As(III) and As(V) is done by selective reduction at different pH values. The method is very sensitive [50 ppt As(V) and 90 ppt total inorganic arsenic], free from interferences of major ions such as sulfide, nitrate, chloride, or sulfate, and is also sensitive to MA(V) and DMA(V). The measurement time is 4 minutes [no more than 6 minutes for both As(III) ad As(V)], the sample volume is low, and no solid waste is generated. The system is portable, costs $2300 to build (without the laptop), and can be used for thousands of analyses [71]. Current work is in progress to develop a field system.

Another method based on the selective adsorption of arsenic has recently been developed [72]. The surface of a 50-nm-thick gold film is divided in two: the reference and sensing areas. The latter is coated with an arsenic recognition element (e.g., glutathione), while the reference area coating is inert toward arsenic (e.g., dodecanethiol). When a laser beam is reflected from the gold film, the presence of arsenic complexed at the sensing area modifies the absorbance. Although sensitive, the method suffers from interferences of other metal ions.

Other approaches include bacterial fluorescent biosensors [73] or amperometric detection with enzymatic inhibition [74]. One is exploring microlever technology for arsenic, which has been shown to work for phosphate or chromate [75]; the other direction is using molecular recognition coupled to an ELISA (enzymatic linked immunoassay) type of assay. However, these technologies are in the development phase, and it is not anticipated that these field kits will be available and established on the market for the next five years. More information on new developments can be retrieved from Chapter 7.

ANALYTICAL METHODS FOR SLUDGE AND PLANTS

Laboratory-Based Methods for Arsenic in Sludge and Biota

X-ray fluorescence has been developed as a routine method for soil and sediments. Plants are usually easy to digest, which makes solution-based methods more applicable. Thus, digests can easily be determined by the laboratory-based methods mentioned earlier.

Arsenic Field Kits for Solids and Biota

A large range of field kits is not available, although the field testing kits for arsenic in water may be used for assessing the arsenic concentration in solid samples after they have undergone acidic dissolution. One stipulation here, however, is that arsenic might be bound strongly to the matrix or occurs as organoarsenicals, which would not necessarily form volatile species which can then be detected by field kits (this effect is, of course, dependent on the molecular form of arsenic).

The only reliable technology on the market is a portable x-ray fluorescence (XRF) instrument. Samples are irradiated with x-rays or gamma rays. For arsenic a sealed radioactive source (^{109}Cd) is often used. Due to the photoelectric effect, x-rays of characteristic wavelength or energy for the element are generated and detected using an energy-dispersive detection system. Portable spectrometers are commercially available.

Analytical Performance in the Field

A number of XRF units were tested in 1997 [76,77]; each instrument was portable and weighed less than 10 kg. Each device was able to measure 100 mg/kg in soil with a drift of 15%. This level is, however, much too high to screen for contaminated soils which are of environmental or human health concern.

Field Study in the Literature

Reports available about the reliability of these instruments are limited. On-site analyses of abandoned buildings in England were compared with laboratory results, and an arsenic concentration of 60 mg/kg in the solid could be positively identified [77]. However, there is no wealth of information about systematic studies which compare results of laboratory- and field-based XRF methods. Potentially, sensitivity could be increased by on-site digestion of solid samples and preconcentration of the arsenic species on a resin, which can then be determined directly. Another study showed that speciation might be possible when species fractionation is combined with XRF detection [76].

ANALYTICAL METHODS FOR VOLATILE ARSENIC IN GAS SAMPLES

This is a domain that has not been studied extensively but will be of importance in areas affected with arsenic. Indeed, volatilization might take place from a water course or directly from sludge or contaminated soil. As a result of these limited studies, no fully established laboratory method is available. Gas samples can be taken by absorption in wash solution, which can then be analyzed by the spectrometric methods mentioned under water analysis. A field testing method exists for volatile arsine in a gas sample [5,78]. The gas is pumped through a column filled with a gold solution–impregnated support material. The AsH_3 reduces the Au^{3+} to colloidal gold, which can be detected visually within 6 minutes. A concentration of 0.05 to 3 ppm of AsH_3 in the atmosphere can be measured. Phosphine and stibines interfere with this method, which is commercially available.

CONCLUSIONS

The performance of field testing kits for arsenic is overall not satisfactory, although the new-generation kits become much more reliable. The report of false negative and positive results of over 30% is not unusual, although the latest seems encouraging, and more reliable measurements can be done in the field. However, these studies used a water standard of 50 μg/L as a decisive concentration. If the new WHO guideline of 10 μg/L is adopted as a decision-making criterion, the sensitivity of most arsenic testing kits based on colorimetric methods will not be sufficient. This is particularly the case for kits that are battery-powered and electronic systems. Although surprisingly, some reports suggest that in some cases nontrained operators produce more reliable results, the training aspect of the operator should not be underestimated.

Voltammetric sensors should be ideally suited for on-site analysis of arsenic. However, the need for the chemical reduction step seems to be the major problem, limiting both a potential application in the field and sample throughput. Systems using a voltammetric reduction of arsenate are probably easier to implement for on-site analysis, although the SafeGuard system developed by TraceDetect Inc.

shows a remarkable performance. Potential problems in the voltammetric determination of arsenic are numerous due to the sample matrix effect. To be highly efficient for on-site analysis with a nonqualified operator, these voltammetric systems should therefore be as sensitive as possible to allow dilution of the original sample. For such a purpose, the use of microelectrodes should be preferred. In addition, specifically designed software and hardware are required to guide the user through the simple actions that should be undertaken and to make the analytical system more accessible to nonqualified operators.

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9

MUCILAGE OF *OPUNTIA FICUS-INDICA* FOR USE AS A FLOCCULANT OF SUSPENDED PARTICULATES AND ARSENIC

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INTRODUCTION

The source of contaminants in drinking water can run the gamut from chemical to biological to geological in such forms as human-made pollution, stagnation or bacterial contamination, or natural sources of harmful minerals. There are a myriad of guidelines outlining requirements for drinking water contaminant concentrations, and two of them are addressed in this work: particle and arsenic removal.

The turbidity in any water source is due to solids suspended in the water column. These solids result from a variety of sources, including resuspended sediments, inadequate filtration, inorganic particles, or biological sources. All sources of turbidity will decrease the effectiveness of the disinfection process because particles promote the growth of microorganisms and protect them from disinfecting agents. Microbial contamination in drinking water can cause many

Arsenic Contamination of Groundwater: Mechanism, Analysis, and Remediation,
Edited by Satinder Ahuja

hygiene-related illnesses, such as diarrhea and infectious diseases [1]. Drinking water turbidity, or cloudiness, affects a community's opinion of the safety of certain water sources. The visual aspect of cloudy water is enough to discourage any consumer from drinking water from a faucet, well, spring, or any other source. Turbidities below 5 NTU (nephelometer turbidity units) are considered to be "safe" by most consumers, but the World Health Organization (WHO) unofficially considers 0.1 NTU to be the maximum turbidity allowed for disinfection [2].

Some of the indicators to determine the acceptability of water quality include fecal indicator bacteria, turbidity, pH, and free residual chlorine for drinking waters and intestinal helminth counts and trematode eggs for wastewater reuse [3]. Therefore, turbidity reduction can vastly improve the effectiveness of disinfection methods [2].

The WHO currently recognizes four different categories of turbidity-reduction mechanisms for particulates and bacteria as potential areas for investigation [4]: settling or plain sedimentation; filtering with fibers, cloth, or membranes; filtering with granular media; and slow sand and biosand filters. The first process has the advantage of being a low-cost way to reduce suspended solids and some microbes, and is generally recommended as pretreatment before disinfection. Unfortunately, sedimentation will not remove clays and smaller solid particles, nor will it remove smaller microbes [1]. Also, the settling length for some solids can be as long as two days [1]. The use of membrane filters, granular media, and slow sand and biosand filters include filters made of compressed or cast fibers such as cellulose papers or synthetic polymer filters, spun threads, or woven fabrics. Generally, filters are placed over a water source and are used widely for point-of-use water supply systems. These filters do not always remove all suspended solids or all microbial contamination or may require fabrication by user, initial education and training in fabrication, and frequent backwashing [4]. Another process to treat biological contamination of turbid water in the home may use inactivation mechanisms such as ultraviolet radiation from lamps or sunlight. However, it is considered a challenge, due to the effect of turbidity in decreasing access to microbes [1].

The prevalence of arsenic in drinking water is variable, depending on water source and location. Arsenic can be found in rainwater, surface waters, and groundwaters [5]. The latter poses the greatest health risk to humans, due to direct ingestion of arsenic-contaminated well waters [5]. The WHO recognized the risks of ingesting arsenic-contaminated groundwater in 1958, and in 1993 they reduced the recommended guidelines from 0.05 mg/L (50 μg/L) to 0.01 mg/L (10 μg/L). The WHO based this guideline on current detection limits based on equipment diagnostic abilities [6]. The WHO also recognizes a need for investigations into new low-cost physical and physical–chemical techniques.

This study seeks to uncover an innovative new technology that can be implemented for turbidity reduction and arsenic removal in areas of contamination where citizens are economically unable to invest in the established, accepted, and costly methods of drinking water treatment. In doing so, people exposed to arsenic contamination through ingested groundwater will benefit from an inexpensive, easy-to-implement, and natural technology that will be a socially, culturally, environmentally, and scientifically appropriate way to improve their quality of life and health.

Natural arsenic sources include minerals, rocks, soils, sediments, and the atmosphere where arsenic is transported due to industrial effluents, fossil fuel, combustion products, and natural volcanic emissions. Arsenic is not considered a natural constituent of water, so when it is found it is due to several mobilization mechanisms, such as physical, chemical, or biological interactions. Mineral–water interactions are often enough to mobilize arsenic through a solid–solution interaction such as precipitation–dissolution, adsorption–desorption, or coprecipitation interactions [5].

Adsorption–desorption is the primary arsenic mobilizing interaction in many environments. The As adsorption–desorption potential is a function of many different variables, including pH, redox potential, As concentration, the concentration of competing and complexing ions, aquifer mineralogy, reaction kinetics, and biological activity [8]. The mechanism relies on a surface adsorption phenomenon, implying the presence of suspended solids in the groundwater source. Adsorption–desorption contributing aquifer solids include iron oxides, aluminum oxides, oxyhydroxides, manganese oxides, silica oxides, aluminosilicate clay minerals, carbonate minerals, aquifer solids covered with an adsorbed layer of humic acids, and soil and sediment particles [8]. This dependence on the presence of solids in groundwater for the occurrence of adsorption–desorption arsenic mobilization supports a need for the simultaneous reduction of turbidity and mobilized arsenic.

Health effects resulting from exposure to inorganic arsenic depend on the exposure amount and exposure duration. Months of exposure to arsenic concentrations of 0.04 mg/kg per day (considered high) can result in health effects that are usually reversible, including diarrhea and cramping, anemia, leukopenia, and peripheral neuropathy; chronic exposure to high doses for 0.5 to 3 years can result in skin effects such as hyperpigmentation [9].

Mucilage extracted from the nopal cactus has been demonstrated as a flocculant to remove turbidity, metals, and microbes from drinking water [10–14]. *Opuntia ficus-indica* (OFI; commonly referred to as nopal or prickly pear), a well-known cactus found naturally in arid and semiarid regions in many countries, including Mexico and the United States, owes its extensive ability to store large amounts of water to the mucilage stored in its cladode or cactus pad (Figure 1) [15]. This mucilage swells when in contact with water and has been extracted and evaluated for uses including dietary fiber [15], medicinal [16–20], digestive [21,22], lime mortar additive [23], and emulsifying agents [24]. Diced nopal cladodes have been used for centuries in Latin America as a natural technology for the rapid

Figure 1 Opuntia ficus-indica (OFI; prickly pear or nopal) mucilage is a thick substance comprised of proteins, monosaccharides, and polysaccharides [10]. The nopal grows abundantly and is very inexpensive and edible. Nopal pads are formed of complex carbohydrates that have the ability to store and retain water, allowing these plants to survive in extremely arid environments. Nopal mucilage is a neutral mixture of approximately 55 high-molecular-weight sugar residues composed basically of arabinose (67.3%), galactose (6.3%), rhamnose (5.4%), and xylose (20.4%) [13,14]. It also contains several ionic species. In fact, its composition gives the OFI the capacity to interact with metals, cations, and biological substances [11]. Cactus mucilage swells but does not dissolve in water [12]. Natural gums have unique surface activity characteristics, which make them ideal candidates for enhancing dispersion properties, creating emulsifications, and reducing the surface tension of high-polarity liquids. (*See insert for color representation of figure.*)

flocculation of turbid natural spring waters [25], but a scientific baseline was never provided for this phenomenon.

In our work, a scientific explanation of a naturally observed phenomenon will be provided: that is, the ability of OFI to reduce turbidity when added to cloudy or muddy waters. Also, investigations into the ability of OFI extracts to remove heavy metals from water will uncover new scientific pathways for research into natural arsenic removal methods. Data indicate that it is the mucilage of the nopal cactus that provides this outstanding flocculation capacity. The mucilage extract increased particulate settling rates 330% compared to a commonly used flocculant, aluminum sulfate [$Al_2(SO_4)_3$], at dosage concentrations of 3 mg/L. Mucilage flocculation performance is equivalent to $Al_2(SO_4)_3$ at doses 0.3% of the required $Al_2(SO_4)_3$ concentration. Additionally, our results show that nopal mucilage has great potential for the removal of heavy metals: specifically, arsenic. From 35 to 50% of total arsenic content was removed in a 3- and a 36-hour period, respectively. If the water contains around 100 mg/L of arsenic, 50% removal is enough to bring the arsenic levels down to standards set in underdeveloped countries, which consider that 50 mg/L of arsenic is normal. It is expected that our results will be used to implement a low-cost technology in Latin American communities exposed to arsenic and particulates in their drinking water in the near future.

EQUIPMENT, MATERIALS, AND METHODS

Flocculation Experiments

The following were used in the jar and cylinder tests: aluminum silicate (hydrated), also known as kaolin (Fisher Scientific S71954); sodium hydroxide (Acros Organics 206060010); and aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$ (Fisher Scientific S70495). Equipment includes Minimix Laboratory mixer/jar test apparatus, manufactured by ECE Engineering (ECE MLM4), and a Micro 100 Turbidimeter (HF Scientific), able to measure 0 to 1000 NTU (accuracy: ±2% and reading + 0.01 NTU). Any other chemical used in this work is laboratory grade. Kaolin suspensions were produced using milli Q water and allowed to sit for 24 hours before use. The pH of the suspensions was adjusted to 7 by adding the required amount of NaOH. A control sample was run in every experiment without mucilage dosage and a sample with aluminum sulfate, which is a commercial flocculant, for comparison [26,27].

For the cylinder tests, neutral, 50 g/L kaolin solutions were added to 100-mL graduated cylinders fitted with a glass stopper [28–37]. High concentrations of kaolin were chosen since they mimic mud conditions and make the interface visible. The cylinders were then capped and inverted 10 times to ensure uniform suspensions with the desired dose of flocculant [either $Al_2(SO_4)_3$, or mucilage]. Each cylinder was placed on a level surface, and flocs began to form and settle immediately. The height of the visible solid–liquid interface was then recorded with time until the flocs were fully settled. For the jar tests, 0.5 g/L kaolin suspensions were produced. Initially, identical volumes of control solutions and flocculant-free suspensions were quickly filled in each compartment. The experimental error for the cylinder tests is ±2 cm/min.

Residual turbidity tests were carried out according to standard jar test procedures [34,35,38,39]. Mixing was started at 100 rpm, while the desired flocculant dose was added to the jars. Stirring continued for a determinant amount of time (usually, 2 to 5 minutes), depending on the experiment, and then the speed was reduced to 20 rpm for 5 minutes. Stirring was then stopped, the flocs formed were allowed to settle for 30 minutes, and 30-mL samples of the supernatant were collected from each compartment and poured into previously acid-cleaned turbidimeter cuvettes. Supernatant turbidity measurements were recorded in triplicates.

Mucilage Cactus Extraction

Three types of mucilage were extracted. Cactus plants were purchased from Living Stones Nursery, Tucson, Arizona. Following a modified version of the method by Goycoolea and Cárdenas, a gelling extract (GE) and a nongelling extract (NE) were obtained [40]. A combined version (CE) consisting of GE and

NE was obtained using the method of Medina-Torres et al. [41]. All mucilage types extracted were stored dry and at room temperature. Changes were made in the procedures to maximize mucilage extraction and chemical consumption as follows: For the extraction of NE and GE, cactus pads were cleaned and boiled in Milli-Q water until they became tender (ca. 20 minutes). The soft pads were then liquefied in a blender. The pH of the resulting suspension was then neutralized and the solids and liquid supernatant were separated in a centrifuge at 4000 rpm. The supernatant was collected, mixed with 1 M NaCl solution (10 : 1 ratio), filtered, and precipitated with a 1 : 2 ratio of pulp to acetone to produce the NE extract. The acetone was then decanted and the precipitate washed with a 1 : 1 volume ratio of precipitate to isopropanol. The resulting NE precipitate was air dried on a watch glass at room temperature. To separate the gelling portion, the centrifuged precipitates were mixed with 50 mL of 50 mM NaOH. The suspension was stirred for 10 minutes and the pH adjusted to 2 with HCl. The suspension was centrifuged and the solids again resuspended in water while the pH was adjusted to 8 with NaOH. The suspension was then filtered and the solids were washed following the same procedure as for the NE extract. For the combined extract, the initial blend was centrifuged and the supernatant was separated and pH-adjusted to 8 with NaOH, washed with acetone and isopropanol as described above, and finally, was air-dried. On average, for each pad that weighs around 300 g wet weight, a 1.5- to 2-g dry powder is obtained.

Arsenic Removal Experiments

Reagents include arsenic(III) and arsenic(V) (Acros Organics, R45 28 34 50/53 and R45 23/25 50/53, respectively), arsenic standard ($As_2O_3 \cdot 18H_2O$, Hach Company, 14571-42), sodium hydroxide (Acros Organics, 106060010), aluminum sulfate (Fisher Scientific S70495), and nickel nitrate (Fisher Scientific N62-500).

Total arsenic content for what is described as single-dose methods were determined by hydride generation–atomic fluorescence spectrometry (HG-AFS), a 60 PSAnalytical 10.055 Millennium Excalibur instrument. Then 10 mL of each 20-mL sample was combined with 15 mL of concentrated hydrochloric acid, 1 mL of saturated potassium iodide, and 24 mL of deionized water to make the final volume 50 mL [42]. The hydrochloric acid produces an excess of H^+ for HG-AFS, and the saturated potassium iodide converts arsenic species to arsenite for analysis. Tetraborohydride is added to form arsenic hydride (AsH_3), which is then atomized in a hydrogen flame. Fluorescence spectrometry is utilized to establish the arsenic concentration in the sample. Arsenic calibration curves are determined through the use of standards prepared with arsenic reference solutions [42]. HG-AFS is a particularly useful technique, due to the minimal presence of interference from matrix interactions [43]. The equipment used for the other arsenic experiments is an atomic absorption spectrometer (AAS) by Varian, Inc. (Zeeman 240Z) with a detection limit of 10 μg/L. The graphite furnace (GF) technique was chosen because it is the most widely used, and as a result, the best understood. In a graphite tube atomizer, there is a combination of an inert gas atmosphere and reducing conditions produced by incandescent graphite that makes this technique perfect for analyzing pure analytes. Also, GF technique provides a longer residence time (two to three times greater than flame atomic absorption spectroscopy), leading to less interference [44].

The GE performed best to separate suspended solids. Therefore, all the arsenic tests were carried out using this extract only. For single-dosage experiments, acidified arsenic samples (0.4% HNO_3) were diluted fivefold with 5% nitric acid, filtered with 0.22-μm mixed cellulose ester syringe filters, and analyzed with the AAS. Then 1000 mg/L As standard was diluted to 10, 20, and 30 μg/L and used to form the calibration curve using a new rational method for fitting [45]. Finally, 20-μL samples consisting of 15 μL of diluted arsenic samples and 5 μL of a nickel nitrate modifier were injected into the graphite furnace of the AAS. The contents were atomized and analyzed with the concentrations taken from the respective absorption peak heights.

Initial experiments were performed to determine the mucilage–arsenic complex distribution in the water column, since there was no apparent formation of flocs once the mucilage was added. First, 500-mL beakers containing a port at the bottom (i.e., in the 20-mL level) were outfitted with a 2-mm nylon tube at the 250-mL level so that samples could be taken not only from the top of the solution, but also from the bottom and the middle of the column. Different systems were dosed with GE solutions (various concentrations ranging from 0.1 to 100 mg/L), stirred for 10 seconds, and then placed on a level surface. Samples were taken at certain time intervals and examined with AAS. In all these experiments, the highest concentration of arsenic was found at the top of the column. Therefore, it is believed that the mucilage–arsenic complex floats to the air–water interface.

Experiments with a taller water column (300 mL of As standard prepared from a 1000 mg/L stock diluted to about 80 μg/L in a 1000-mL graduated cylinder) were designed to determine more precisely the arsenic concentrations at the air–water interface. This series of experiments was performed at three different mucilage pH values held constant: 7, 8, and 9. In each case the columns were dosed with 5 mg/L GE and inverted 10 times and tested for total arsenic content using AAS.

To optimize the separation of arsenic in the water, other arsenic tests were performed using makeup methods designed to replace spent mucilage removed from the top of the column. GE mucilage solutions of pH 8 were chosen due to its apparent superior performance in creating the highest arsenic concentration differential. Then 300-mL water columns were used with identical arsenic stock solution and initially dosed with 2.5 mg/L GE and inverted 10 times. After 0.5 hour, 5-mL samples were taken at the air–water interface and analyzed as described previously. The 5-mL samples were then replaced with 5 mL of GE at a concentration of 2.5 mg/L at the top of the column. The procedure was performed at 0.5-hour intervals for four hours. The samples were also examined using AAS.

Mucilage Characterization

Raman spectroscopy (RS) is adept at determining functionalization of chemical structures, especially those of organic compounds, from their vibrational spectra. Samples analyzed with RS can exist in either the solid, liquid, or gas states [46]. The samples of GE, NE, and CE analyzed were in the solid phase (powder form), a condition that RS is particularly well suited for since conventional infrared spectroscopy (IR) provides water band interference [46]. The mucilage samples were loaded in a capillary tube, inserted in the Raman spectrometer, and their vibrational spectra were analyzed. The system was purged with nitrogen to reduce interference from ambient contaminants.

RESULTS AND ANALYSIS

A presentation and discussion of results for particulate, arsenic, and bacteria removal are followed by the study of the chemical composition of the mucilage. An evaluation of the cultural sensitivity of the project is presented briefly at the end of the chapter.

Mucilage Flocculation Efficiency

Three different extracts of mucilage from OFI have been investigated for use as a flocculant to remove suspended solids and heavy metals (specifically, arsenic) in the drinking waters of low-income communities in Mexico. It has been determined that some regions of Mexico may have arsenic concentrations as high as about 0.500 μg/L [47–52]. The gelling extract (GE) was found to be the best performer with respect to suspended solids removal, as determined by standard settling tests with 5 g/L kaolin slurry at a pH of 7 dosed with concentrations from 0.01 to 10 mg/L. The fall in liquid–solid interface was recorded with time, and rates were taken from the linear decay portion of settling at flocculant doses of 3 mg/L (Figure 2). GE outperformed NE, CE, and $Al_2(SO_4)_3$, a widely used chemical flocculant and benchmark for this study, whose use could cause contamination and an extra separation step in drinking water treatment [53,54]. The slope of each curve gives the rate of settling. The control (no flocculant dose) settled at rates ranging from −0.53 to −0.57 cm/min. NE and CE settled at rates of −0.70 and −1.10 cm/min, respectively. GE performed at a rate of about −2.20 cm/min, whereas the alum performed close to −0.67 cm/min. This means that the GE performed 3.3 times faster than alum.

The effectiveness of flocculant is related directly to the size of the flocs formed. Larger flocs fall faster under the influence of gravity, leading to a faster settling rate. Larger flocs require more restructuring of the settled solids in the graduated cylinders, leading to a shorter linear settling portion. As the large flocs pile up, they begin to rearrange, leading to earlier removal from the linear settling scheme. Examining the data in Figure 2 it is obvious that GE performs as a faster flocculant, due to its ability to form larger flocs than NE, CE, and alum, as

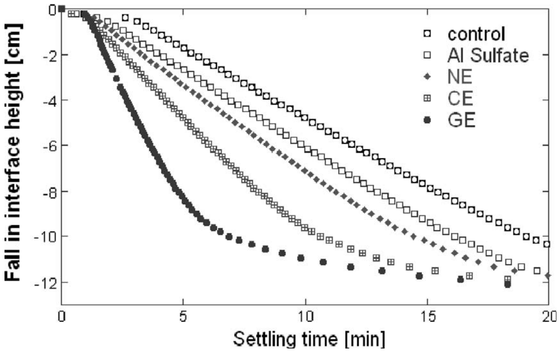

Figure 2 Flocculation rates comparison at 3 mg/L flocculant dosages. The concentration of the kaolin solution is 5 g/L. Kaolin was used to mimic contaminated water containing a high concentration of particulates. The control refers to the settling of a solution without flocculant. A commercial flocculant was used to establish a baseline [$Al_2(SO_4)_3$] and to compare the efficiencies of the three mucilage extracts: NE, CE, and GE. GE performed best. (*See insert for color representation of figure*.)

is evidenced by its relatively early departure from the linear scheme (5 minutes compared to the control's 21 minutes).

Figure 3 shows the effect on the settling rates of a GE dose from 0.01 to 4 g/L. The rates vary from −0.66 at a low dose to −2.64 cm/min. That is, a GE dose of 0.01 mg/L performed at a rate equivalent to $Al_2(SO_4)_3$ dosed at 300 times that concentration (3 mg/L), proving that the GE is a more effective flocculant

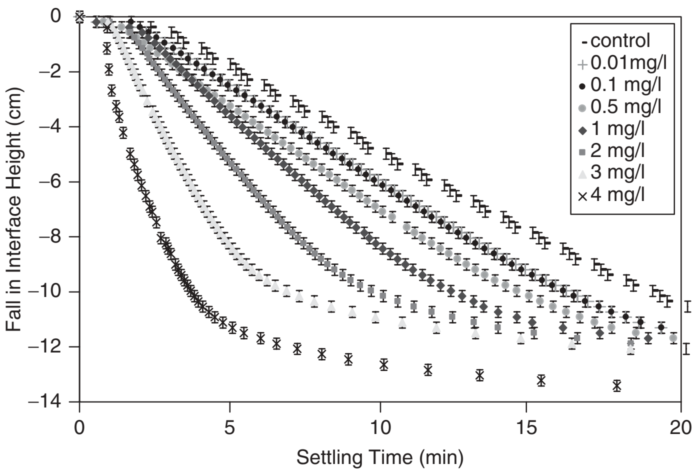

Figure 3 Effect of dose on the settling rates of GE. The concentrations range from 0.01 to 4 mg/L. Kaolin is used to determine the performance of this flocculant against particulates. The control is the first curve on the right. The initial kaolin concentration is 5 g/L. (*See insert for color representation of figure*.)

than the popular alum with respect to settling rate and requires less material to obtain the same results. Another advantage of using GE as a flocculant compared to alum, is the fact that it is a renewable source and its disposal involves simple organic degradation, which requires a chemical or mechanical recovery process to avoid further pollution problems [27,54]. The flocculation effectiveness of all three types of mucilage when the dosage concentration is increased has been reported elsewhere [55].

Residual turbidity measurements of jar tests also showed that GE, CE, and NE improved the settling rates of particulates. In addition, higher mucilage doses also increased the settling rates, as attested in the cylinder tests from above. The turbidity values were similar to alum at low doses (0.01 to 0.1 mg/L) ranging from 30 to 45 NTU. However, at higher doses, the turbidity of the supernatants also increased (up to 250 NTU for concentrations of 10 mg/L of mucilage). In such cases we found that the turbidity in the supernatants could be reduced to standards values by a coarse filter, since the mucilage forms much larger flocs that are easily caught by inexpensive secondary filtration devices such as cloths or colanders.

Arsenic Removal with GE

Arsenic removal tests were carried out using GE due to its convincing effectiveness as a flocculent of suspended solids. In addition, single dose experiments with CE and NE showed little or no removal, so these extracts were abandoned for the rest of the arsenic study and the focus shifted to eliciting the mechanism and performance of GE in removing arsenic. Initial tests were performed by preparing standard arsenic solutions in triplicate from As(III) and As(V) stocks in 50-mL centrifuge vials. Prior to addition of the GE, 20 mL of the arsenic solution was collected to verify the initial arsenic concentration. The remaining 30 mL of arsenic solution was dosed with GE to provide final flocculant concentrations of 0.10, 1.0, and 10 mg/L GE and inverted 10 times to ensure mixing. After 1 hour, 20 mL of the solution was removed from the tops of the vials. Arsenic concentrations in both samples, the before and after, were determined by HG-AFS, and the results are presented in Table 1. The data show removal in some cases, including the 0.10- and 1.0-mg/L doses for the As(V) tests, leading to the possibility that GE removes arsenate more efficiently than it removes arsenite. The initial concentration of arsenic in the solutions was 290 μg/L. These data indicate that in some instances, the removal of arsenic is as high as 37%. The differences in final arsenic concentrations indicate the presence of a specific distribution of arsenic in the mucilage-treated water column, leading to the possibility that the mucilage–arsenic complex is transported by density differences to the air–water interface at the top of the water column instead of by gravity to the bottom of the water column.

To determine the action of the mucilage and, more precisely, the arsenic concentrations at the air–water interface, experiments were performed with a taller water column (300 mL of arsenic standard prepared from a 1000-mg/L stock, equilibrated with atmospheric oxygen, and diluted to about 80 μg/L). Three

TABLE 1 Experiment Results Showing the Variability in Mucilage Performance for Removing Arsenate and Arsenite

	GE (mg/L)	Δ[As] (µg/L)
As(III)	0.10	12.80
	1.0	0.00
	10	34.90
As(V)	0.10	97.30
	1.0	86.10
	10	107.20

columns were dosed with 5 mg/L GE and inverted 10 times. After 1 hour, 5 mL of sample was collected from the top of each column, filtered, acidified, and tested for total arsenic content using AAS. These experiments were performed at three different mucilage pHs: 7, 8, and 9. Table 2 presents the data collected.

Experiments designed to determine the arsenic concentration at the top of the water column when dosed at different GE pH values revealed the action of the mucilage–arsenic complex in the water column and exposed the optimal pH for GE arsenic-removal efficiency. The average changes in arsenic concentrations all showed increases in arsenic at the air–water interface, leading to the conclusion that the GE creates an arsenic concentration differential in the water column, transporting arsenic to the air–water interface instead of the bottom of the water column. The results also showed that at a pH of 8, the top arsenic concentration

TABLE 2 Water Column Tests: Arsenic Concentration at the Air–Water Interface with Mucilage pH

	Total [As]		
pH	Initial (µg/L)	Final (µg/L)	Average Δ [As] (µg/L)
7	82.55	95.15	7.15 ± 9.61
	82.55	96.00	
	82.55	78.95	
8	82.55	90.75	11.28 ± 2.71
	82.55	94.90	
	82.55	95.85	
9	82.55	93.75	9.65 ± 7.50
	82.55	84.05	
	82.55	98.80	

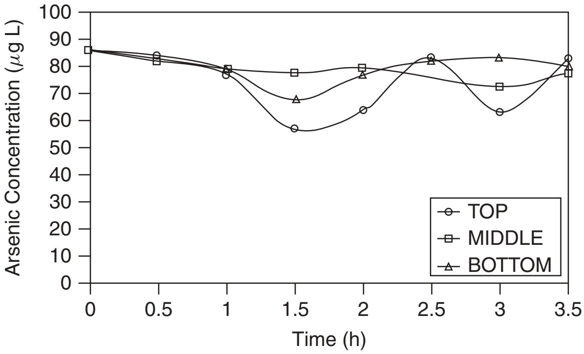

Figure 4 Results of trilevel arsenic distribution experiments in the water column. The open circles represent final concentrations of As taken at the top of the column. The open squares and open triangles represent the middle and bottom concentrations of the column, respectively. After the 1.5-hour sampling, the columns were slightly mixed and initial conditions were established. After another 1.5 hours the highest separation occurs again for top samples (3 hours total time).

was increased by 11 μg/L. This does not agree with the action the GE distributed in flocculating suspended solids, since a neutral pH worked better in these tests. We believe that it is due to density differences between the loaded mucilage and contaminated water. It was found during the GE extraction technique that unlike the NE and CE, the GE mucilage floated. The flocs that formed when turbid water was treated with mucilage are denser than water and were transported to the bottom of the water column due to gravity. The arsenic–mucilage complex formed, however, was less dense than the water and thus ascended to the air–water interface, as does the raw mucilage in water. The maximum As removal was found after 36 hours of mixing and corresponded to 50% removal.

To determine the action of the GE adequately, a trilevel experiment was designed, with the results presented in Figure 4. It is important to note that in this experiment, the samples were filtered to remove the entire mucilage–arsenic complex. As a result of this procedural difference, a decrease in arsenic concentration represents the samples containing mucilage–arsenic complexes. The data suggest that GE does, in fact, transport the As to the top of the water column. At 1.5 hours, the top concentration is at 57 μg/L, reflecting 33% removal. The data reflect a restructuring of the As concentration profile due to intentional mixing of the system between 1.5 and 2.5 hours. However, at 3 hours (after 1.5 hours again), the top concentration is 63.5 μg/L, or 26% removal. This means that even if the system is perturbed, the mucilage–arsenic complex still floats to the top.

Optimization of Arsenic Removal

To optimize arsenic removal, experiments were performed using a newly developed method designed to replace spent mucilage removed from the top of the column. Results have been presented elsewhere [55]. Brieftly, the same 300-mL water column setup was used with identical As stock solution and GE dosage at pH 8. The column was initially dosed with 2.5 mg/L GE and inverted 10 times. A 5-mL sample was taken at the air–water interface after 0.5 hour and treated the same as in the previous experiments. The 5-mL sample was then replaced with 5 mL of GE at a concentration of 2.5 mg/L at the top of the column. This procedure was performed at 0.5-hour intervals for 4 hours. The samples were examined using AAS. A variation of this method was also performed in which the system was mixed between doses. The data from the experiment without shaking showed a lag time of 2 hours before a decrease in concentration, while the shaking perturbed the transport of mucilage to the top of the water column. It also shows an initial concentration increase of 4.4 μg/L above the 86.00 μg/L control before the first recorded decrease at 2 hours. Removal of 35% was reached after 3 hours. This lag and initial increase were a result of the GE–arsenic compound ascending to the air–water interface.

The mucilage was more efficient than aluminum sulfate in settling particulates in drinking water and in addition can be used to remove arsenic from contaminated water. The optimization of this technology is continuing and will be field-tested in a low-income Mexican community that experiences the dual problem of suspended solids and arsenic contamination in drinking water.

Bacterial Removal

Preliminary experiments with pure cultures of bacteria (both gram-positive and gram-negative species) have suggested that mucilage may also be effective at removal of bacteria from water (data not shown). However, results were not reliably reproducible, and further examination of the phenomenon is necessary before any conclusion can be drawn about effectiveness. If this process of bacterial removal can be validated, it suggests an additional potential for a countermeasure to combat human disease from waterborne pathogens [56,57].

Mucilage Composition

Insight into the chemical structure of the GE mucilage was obtained using Raman infrared (IR) spectroscopy (Figure 5). The results show the presence of a glycosidic linkage as well as $C{-}NH_2$ bonds in aliphatic amines. This corroborates past characterization research which found the presence of glycoproteins in the *Opuntia* mucilage [58,59]. Chemicals with similar structures have been characterized as viscous thickening agents, like GE. The IR data also highlight the differences and similarities between the three cactus derivatives. The spectrum for the CE is believed to be a combination of GE and NE. However, significant differences were found between GE and the other two extracts. The NE spectrum shows a broad peak in the isolated OH region (3600 to 3200 cm^{-1}) and peaks in the region suggesting a liberation mode of residual water molecules (about 800 cm^{-1}). They are both split in the GE spectrum, suggesting two types of O–H stretching: isolated OH species and residual water

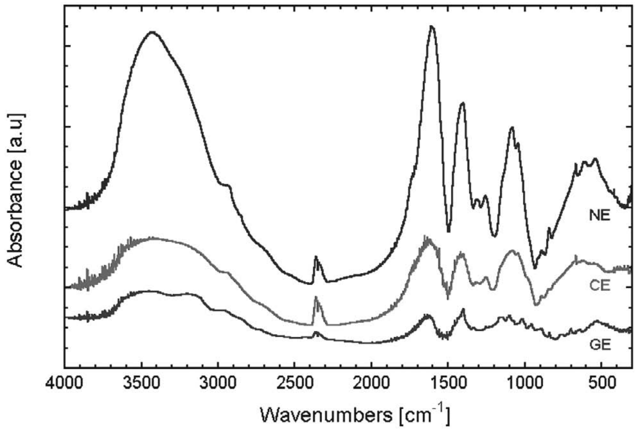

Figure 5 Raman spectra for NE, CE, and GE mucilage extracts, showing different structures. The lower curve corresponds to GE extract, the upper curve corresponds to NE, and the intermediate curve corresponds to CE. (*See insert for color representation of figure*.)

molecules attached to the complex structure of the mucilage with a combination of polyethers. However, the real differences occur in areas relating to ester bounding since small bands are observed in the absorptions at 890, 960, and 1100 cm^{-1} (ν_{C-O-C}) in the spectrum for GE. These bands, which probably explain GE's water-treating properties, are assigned to vibrations of the glycosidic linkage [60]. The broad band in all the spectra at 1414 cm^{-1} (with maximums at 1402 and 1450 cm^{-1}) is due to $\delta_{\mathrm{CH_2}}$ vibrations. An intense band in NE at 1630 and 1610 cm^{-1}, with a shoulder at 1730 cm^{-1}, is attributed to $\delta_{\mathrm{H-O-H}}$ and $\delta_{\mathrm{C=C}}$ vibrations, respectively. These bands correspond to carbohydrates [61].

The cylinder test results suggest that the ability of GE to form a gel, much like polyacrylamide, provides it with excellent floc-forming properties. The ability of GE to perform at the same efficiencies of $Al_2(SO_4)_3$ at doses 300 times smaller is a testament to its attractiveness as a flocculant alternative when the settling rate is a critical variable. Adding this to the fact that it is derived from a renewable resource and is a green technology supports GE, CE, or NE as possible flocculant alternatives.

Environmental Sensitivity

The WHO recognizes a need for investigations into new low-cost physical and physical–chemical techniques to remove turbidity from household water [2]. This study seeks to uncover an innovative new technology that can be implemented for turbidity reduction and arsenic removal in areas of contamination where citizens are economically unable to invest in established, accepted, and costly methods of drinking water treatment. In doing so, people exposed to arsenic contamination through ingested groundwater will benefit from an inexpensive, easy-to-implement, and natural technology that will be a socially, culturally, environmentally, and scientifically appropriate way to improve their quality of life and health. In the process, a naturally observed phenomenon has been reproduced: the ability of the cactus OFI to reduce turbidity when added to cloudy waters. Also, investigations into the ability of OFI extracts to remove heavy metals from water will uncover new scientific pathways for research into natural arsenic removal methods. The WHO recognizes the social applicability of drinking water treatment methods as an essential component in their effectiveness [1]. To be culturally sensitive with respect to low-income indigenous communities, the project must provide a technology that is simple, easily produced, and inexpensive, and must employ indigenous or easily recommended guidelines for social applicability of water remediation projects. This research's long term goal is to provide a case study in the use of sociocultural impact assessment for the shaping of project methods and goals.

CONCLUSIONS

Mucilage from *Opuntia ficus-indica* is a better flocculant than aluminum sulfate in all three of its extracted forms (GE, NE, and CE) and could be used by low-income Latin American communities for settling suspended solids in turbid drinking water storage containers. The use of mucilage is also appropriate for removal of total arsenic in contaminated drinking water and owes its flocculation abilities to its chemical structure, consisting of C–O functionality. Further investigation is required to review the mucilage-selective removal of arsenic based on speciation as well as the feasibility of implementing this technology in a distributable or easy-to-assemble filter form for small-scale household removal. The implications of this project are exciting. The possibility of introducing an indigenous material as an improver of quality of life and health to concerned residents is attractive from a cultural sensitivity and sustainability standpoint.

Acknowledgments

The authors would like to thank Drs. Peter Stroot, Joyce Stroot, and Daniel Lim for providing the materials and workforce to determine preliminary data on the effectiveness of OFI mucilage for bacterial removal. Funding for this project was provided by NSF MUSES grant BES-0442977 and fellowship funding by USF STARS (Students, Teachers, and Resources in the Sciences) NSF Grant DGE-0139348. Also, the authors would like to acknowledge Maya Trotz and her students, Douglas Oti and Joniqua Howard, for their help in the water analysis.

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10

PREDICTION OF ARSENIC REMOVAL BY ADSORPTIVE MEDIA: COMPARISON OF FIELD AND LABORATORY STUDIES

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INTRODUCTION

The Arsenic Water Technology Partnership (AWTP) was a collaborative program involving the American Water Works Association (AWWA) Research Foundation, Sandia National Laboratories (SNL), and WERC (A Consortium for Environmental Education and Technology Development) (Siegel et al., 2005). As a member of the AWTP, SNL conducted pilot-scale evaluations of the performance and cost of innovative drinking water treatment technologies aimed at meeting the

Arsenic Contamination of Groundwater: Mechanism, Analysis, and Remediation,
Edited by Satinder Ahuja

new arsenic maximum contaminant level (MCL) of 10 μg/L (effective January 2006). The costs of the new drinking water standard will be borne disproportionately by small communities in the rural southwestern United States that lack the technical and financial resources to carry out the pilot tests needed to choose the best technology for their water systems. The communities will be further challenged to pay for the costs of construction and maintenance of the water treatment systems and must choose the most cost-effective technology. One of the objectives of this study is to determine the most efficient way to predict the absolute and relative sorption capacities of different candidate adsorptive media so that the most appropriate technology can be selected for community water systems.

Arsenic is removed in fixed-bed filtration via adsorption, the physical and chemical attachment of the adsorbate (arsenic) to the surface of the adsorbent media grains. The removal capacity and effectiveness of the arsenic removal media are dependent on a number of physical and chemical factors. Chemical factors include the strength of the chemical bond between the arsenic and the adsorbent, the kinetics of the adsorption reaction, the concentrations of ions competing for sorption sites, the concentration of arsenic in the feed water, and the pH of the feed water. Physical (transport) factors include the effective surface area, which is a function of the accessibility of the porosity of the media grains; steric factors affecting the accessibility of the pore sites by arsenic ions; and the time available for arsenic ions to migrate to pore sites. This last property is related to the flow rate of the feed water that conveys the arsenic into the bed of adsorbent media.

Prediction of arsenic removal from a packed column is very challenging, for the following reasons:

1. The extremely long breakthrough time for "good" adsorbents with high arsenic capacity
2. A lack of accurate adsorption equilibrium and kinetics data at low As concentration
3. Fluctuations of influent arsenic concentration and other water chemistry during breakthrough tests
4. Fluctuation and scattering of arsenic analysis results
5. Variation of adsorbent properties during the prolonged breakthrough test
6. Variation of the arsenic concentration front inside the column with time

In this study, the arsenic removal performance of three different adsorptive media under constant ambient flow conditions was compared using a combination of static (batch) and dynamic flow tests. These included batch sorption isotherm and kinetic sorption studies, rapid small-scale column tests (RSSCTs), and a pilot test at a community groundwater supply source. The media studied exhibited contrasting physical and chemical properties and included a granular ferric oxide (E33), a titanium oxide (MetSorb), and an ion-exchange resin impregnated with iron oxide nanoparticles (ArsenX^{np}). To understand and potentially predict the transport of arsenic through the media at laboratory and pilot test scales, some basic mineralogical and surface chemical analyses were carried out. These included XRD (x-ray diffraction), SEM/EDS (scanning electron microscopy/energy dispersive spectroscopy), and surface area analysis by the Brunauer–Emmett–Teller (BET) measurement technique. In addition, physical properties that might affect the hydraulic performance of the media during the test were examined. Post-test data were obtained from the pilot test of granular ferric oxides (E33) media, including arsenic concentration profiles in the pore water.

A main goal of this project is to develop an effective but simple modeling tool to predict pilot- and full-scale performance from laboratory studies and to provide guidance for arsenic removal process development, scale-up, and design. Data were collected to compare the abilities of experimental methods and a theoretical analytical solution to describe the arsenic removal and transport. The analytical solution (Klinkenberg analytical solution) could be programmed on a simple spreadsheet to compare to arsenic breakthrough curves and the pore water profiles in pilot tests.

MATERIALS AND METHODS

Water Composition

Socorro Springs in Socorro, New Mexico, was the first demonstration site to be selected in a multiyear pilot demonstration sponsored by the Arsenic Water Technology Partnership. The sources of the water supply are Socorro and Sedillo Springs, located in the foothills west of the city of Socorro. Water from both springs is mixed slightly downgradient of the spring boxes, followed by a shutoff valve. Below the shutoff valve, an 8-inch subsurface carbon steel line delivers approximately 540 gpm water via gravity to the chlorination building, where the water is disinfected and oxidized using chlorine gas injection just prior to storage in the Springs site storage tank. During this pilot, a portion of the chlorinated Springs site water was diverted to the arsenic adsorption media filters, which were located inside the Springs site chlorination building. The treated water and backwash wastewater from the arsenic adsorption media filters were discharged to an on-site subterranean infiltration gallery via a 2-inch polyethylene pipe. The total discharge was limited to 3 gpm or less; none of the treated water was returned to the drinking water distribution system.

A representative analysis of the Springs site raw water quality is presented on Table 1. The water has moderate levels of silica, sulfate, and hardness and is nearly neutral in pH. The arsenic level ranges from four to five times the January 2006 MCL of 10 μg/L (10 ppb).

Adsorptive Media

The three adsorptive media were part of a larger set of five adsorptive media tested at Socorro Springs between January and July 2005 in phase I of the Socorro

TABLE 1 Nominal Socorro Springs Site Water Quality

Parameter[a]	Chlorinated Feed Water
Conductivity (μS)	356–360
Temperature (°C)	30.1–30.5
Free chlorine (mg/L as Cl_2)	0.5–0.8
pH	7.9
Iron (ppb)	38.2
Total arsenic (ppb)	42.9
Speciated arsenic	
Particulate (ppb)	1.9
As(III) (ppb)	2.1
As(V) (ppb)	40.9
Titanium (ppb)	(0.38)[b]
Zirconium (ppb)	(0.22)[b]
Alkalinity (ppm)	NA[c]
Nitrate (ppm)	0.4
Calcium (ppm)	17.4
Magnesium (ppm)	4.1
Sodium (ppm)	57.1
Silica (ppm)	24.9
Aluminum (ppb)	23.2
Vanadium (ppb)	11.3
Gross alpha/beta (pCi/L)	Alpha-6.50, beta-3.52
Chloride (ppm)	12.1
Fluoride (ppm)	0.5
Phosphate (ppm as PO_4)	0.034
Sulfate (ppm)	28.4
Total organic carbon (TOC)	0.5

[a]ppb, parts per billion; ppm, parts per million.
[b]Not detected above method detection limit (the MDL is given).
[c]NA, not available.

Springs pilot test. Technologies were considered based primarily on the results of the 2003 and 2004 Vendor Forums held in October of each year at the New Mexico Environmental Health Conference (Siegel et al., 2006b). The selection process is described at the Forum Web site: www.sandia.gov/water/arsenic.htm. The ArsenX^{np} hybrid resin was supplied by the Purolite Company. Graver Industries (formerly HydroGlobe) supplied the granular TiO_2 MetSorb media, and Adedge supplied the E33 media, a granular ferric oxide. The companies were responsible for providing quality-controlled media and information regarding suggested pilot system design and operational parameters. The pilot test is described in a later section. Purolite, Adedge, and HydroGlobe indicated that no pretreatment was required for their arsenic adsorption media.

Note that the use of the media in the tests does not imply any endorsement of the product by Sandia National Laboratories. In addition, it is important to

TABLE 2 Bulk Properties of Media

Parameter	MetSorb	ArsenX^{np}	E33
Chemical constituents	Nanocrystalline titanium dioxide	Nanoparticle selective resin with iron oxide as the functional group	Iron oxide/hydroxide
Physical appearance	White granular beads	Reddish-orange resin beads	Amber granules
Bulk density (lb/ft^3)	50	49–52	30
Sieve sizes, U.S. standard	16 × 60	16 × 50	10 × 35
Particle size (mm)	1.18 × 0.25	1.18 × 0.3	0.5 × 2.0
Attrition loss (%)	0.8	0.8	13
Uniformity coefficient C_u	1.97	1.64	2.44

recognize that the performance of the media in the tests in 2005 may not be indicative of the performance of other media manufactured by the companies at later dates.

Bulk Physical Properties

Figure 1 shows scanning electron micrographs of the media; Table 2 describes their bulk physical properties. The E33 and MetSorb media were delivered dry; the ArsenX^{np} beads were delivered wet. All media were ready to load into SNL adsorption columns upon receipt. The volume, weight, and height of each medium loaded into adsorption columns were recorded at several points in time: initial, after transport to the Socorro Springs site, after backwashing (BW), after additional media was added, and at the start of the pilot. This information is summarized in Siegel et al. (2007).

An indirect measure of the physical durability of the media was obtained by examining the change in size distribution resulting from shipping and handling prior to loading of the media into the columns. The percentage of media smaller than the smallest particle size fraction declared by the vendor was calculated. The resulting percentage is the attrition loss; percentages for these three media ranged from 0.8 to 13% (see North, 2006). For example, 13% of the E33 medium was smaller than 35 mesh, whereas the vendor-declared range of sizes was 10 × 35; therefore, a 13% attrition loss was determined for the E33. However, some error resulted from the use of a No. 40 sieve instead of a No. 35 or No. 32 sieve (0.425 mm instead of 0.500 to 0.600 mm), which is the size specified by the vendor (Adedge). By comparison, attrition losses for other media examined in the more comprehensive study (North, 2006) ranged from 0.8 to 32.2%.

The uniformity coefficient is $C_u = D_{60}/D_{10}$, where D_{60} is the weight of the grain size that is 60% finer and D_{10} is the weight 10% finer on the grain size distribution curve. Lower values of C_u indicate well-sorted media. Such material will have favorable hydraulic properties because there will be few fine grain particles mixed with larger particles to clog the system. The ArsenX^{np} had the lowest uniformity coefficient, consistent with visual observation of the uniform nature of the resin beads (Figure 1A).

All of the media experienced minor compaction (less than 2% difference from initial height) during transport to the site and required additional media to meet design height requirements. Most of the media swelled after water was added and the columns were backwashed. During operation it was observed that media compacted as much as 2 to 5 inches in some columns. It is somewhat unexpected to see no increase in pressure drop across each of the columns. As discussed in Siegel et al. (2007), this may have been due to poor column design or that the pressure gauges could have been inaccurate and/or malfunctioning when in use.

Mineralogical and Chemical Studies

Methods XRD analyses were performed on a Bruker D8 advance x-ray diffractometer using CuKa radiation, a step size of 0.05°, and a step time of 1 second, operated at 40 kV and 30 mA. The samples were ground to fine particles and dispersed using deionized water on a glass slide and dried at room temperature before analysis. SEM/EDS data were collected on a JEOL JSM-6300V scanning microscope with energy-dispersive capabilities operated at 20 kV. Powder samples were mounted directly on carbon conductive tabs and sputter-coated with gold (or carbon) before analysis.

BET surface area and pore size distribution were measured using a QuantaChrome Autosorb-6B analyzer (QuantaChrome Corporation). The samples were degassed at 120°C for about 12 hours (or 30°C, about 24 hours for ArsenX^{np}). Surface areas were determined using the BET equation on five-point N_2 gas adsorption isotherms, and the pore size distributions were obtained from the desorption branches using the standard Barrett–Joyner–Halenda (BJH) method without further correction (Barrett et al., 1951).

Results Table 3 summarizes the results of SEM/EDS, BET, and XRD studies. E33 and ArsenX^{np} have the lowest BET surface areas and largest average pore diameters. Figures 2 and 3 compare the differential pore size and cumulative pore volume distributions of the various media. The pore size distribution curves show the range of pore sizes, and the peaks indicate the dominant pore size. In the differential pore size distribution curve (Figure 3) the y-axis, Dv (log D), is the derivative pore volume divided by the derivative of the log value of pore diameter. The majority of the pore volumes of E33 arise from pores with diameters of 400 to 700 Å (mode about 600 Å). MetSorb has a higher-diameter dominant pore

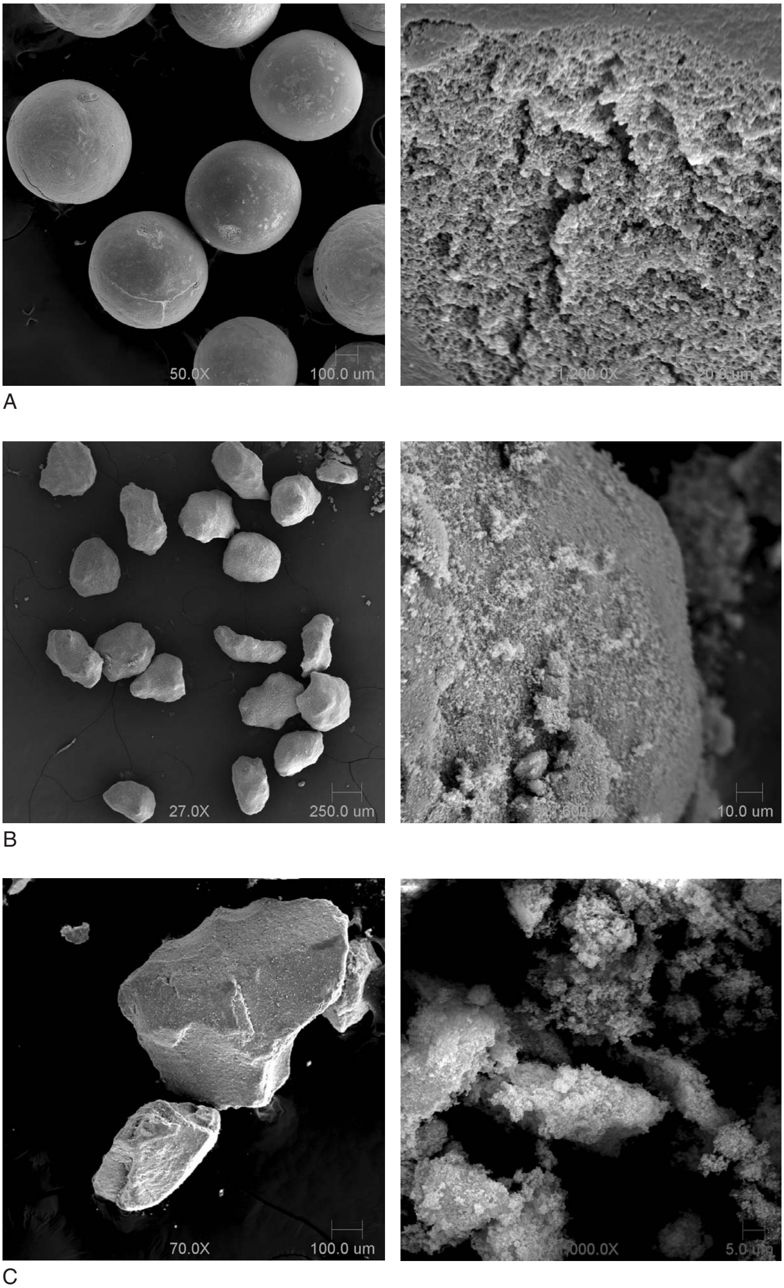

Figure 1 SEM photos of (A) ArsenX^{np} media (50x and 1200x magnification), (B) MetSorb media (27x and 600x magnification), and (C) E33 media (70x and 1000x magnification).

TABLE 3 Summary of Analyses of Arsenic Adsorption Media

Medium	BET Surface Area (m^2/g)	Average Pore Diameter (Å)	Total Pore Volume (cm^3/g)	Constituents (XRD)	Dominant Elements (EDS)
MetSorb	211	64	0.34	Crystalline TiO_2 (anatase)	Ti, O
ArsenX^{np}	120	174	0.05	Amorphous iron oxide/hydroxide	Fe, O, C
E33/AD33	147	245	0.90	Iron oxide/hydroxide (goethite)	Fe, O

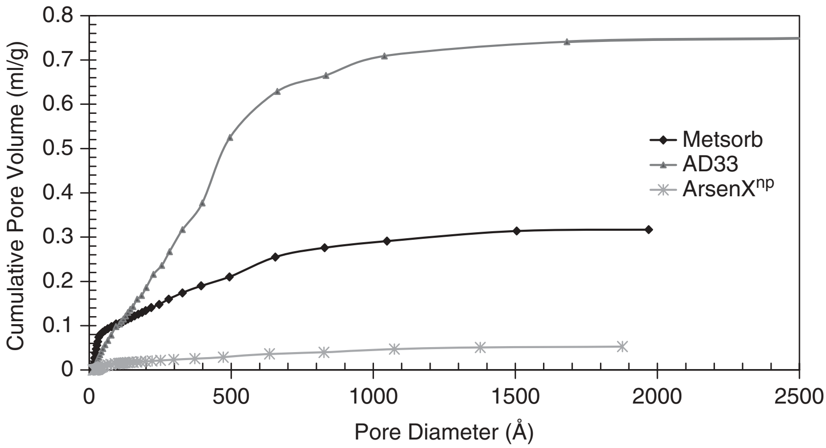

Figure 2 Cumulative pore volume distributions for three adsorbent media. Note AD33 and E33 are similar media.

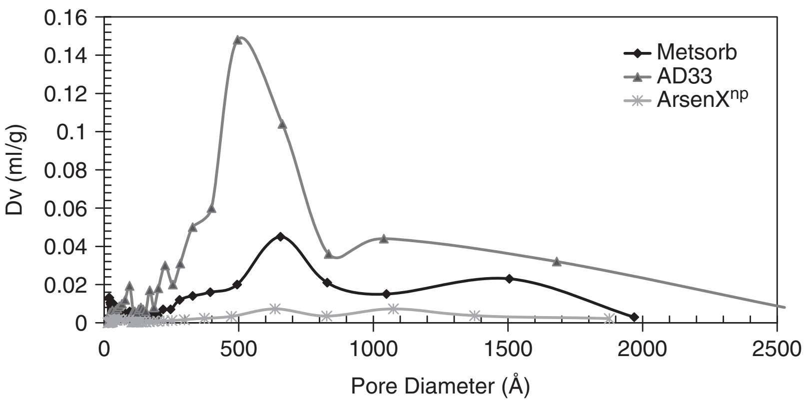

Figure 3 Pore size distributions for three adsorbent media.

size range of about 500 to 800 Å (mode about 700 Å). Possible shrinkage of the resin during the degassing process as well as the presence of volatile compounds may contribute to the characteristics of ArsenX^{np} that were observed.

SORPTION STUDIES

Adsorption Kinetics in Socorro Springs Water

Batch kinetic sorption studies were carried out to determine an appropriate reaction time for establishing equilibrium conditions in the development of sorption isotherms, to measure chemisorption rates, and to extract effective diffusivities for mass transfer. Another objective was to determine if sorption rates at room temperature (about 15°C) differed appreciably from those at the water temperature expected in the pilot test (about 40°C).

Materials and Methods The E33 and MetSorb media were ground and washed with deionized water to obtain a 325 × 400 mesh; the ArsenX^{np} resin was used as received. Adsorption kinetic studies were carried out using 0.20- or 0.01-g samples (0.20 g for ArsenX^{np}) in 1000 mL of arsenic-doped Socorro groundwater at 15°C or 40°C using a temperature-controllable water bath. The doped Socorro waters were prepared by mixing 10 L of the Socorro groundwater (nominal arsenic concentration of 44 μg/L) with 660 μL of a 1000-ppm arsenic stock solution to produce a solution with a nominal arsenic concentration of 110 μg/L. The water sample was put in a 1500-mL double-layered glass jar with the water from water batch flowing through the spacing between the layers. The temperature of the water was monitored to reach 15°C or 40°C before adding the sorbents. Aliquots of the sample (~5 mL) were collected at around 2, 5, 15, 30, 60, 120, 240, 480, 600, 1440, 1680, and 1920 minutes using a 10-mL syringe and filtered through GHP Acrodisc 0.2-μm syringe filters. The water samples were then assayed for arsenic concentration using inductively coupled plasma mass spectrometry (ICP-MS).

Results Figures 4 through 6 show the kinetics of arsenic adsorption on the media tested in Socorro groundwater. The results suggest that arsenic adsorption in Socorro groundwater under the selected experimental conditions was rapid. The results show that a 24-hour equilibration period (1440 minutes) should be sufficient to establish steady state or equilibrium for sorption experiments using similar particle sizes and initial arsenic concentrations. This information was used in designing the sorption isotherm experiments described in the next section.

Data Analysis to Obtain Chemisorption Rate Constants For many adsorption processes occurring on heterogeneous materials, it has been found that chemisorption is the rate-controlling step (Ho and McKay, 1998, 2000; Reddad et al., 2002). Such processes can be described with a pseudo-second-order kinetic equation in which the reaction rate is dependent on the concentration of sorbed species and

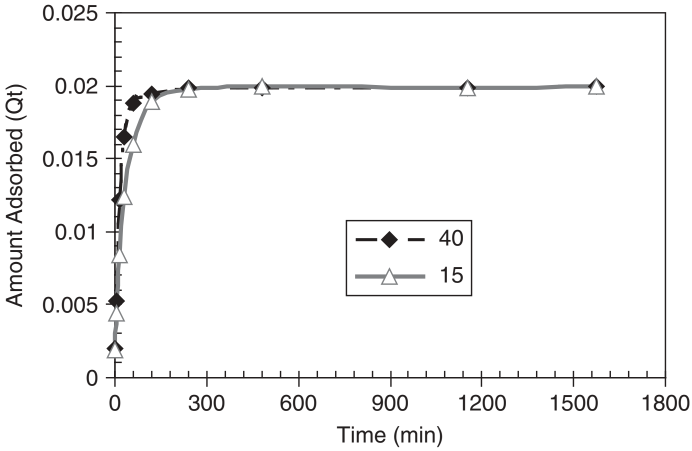

Figure 4 Arsenic adsorption kinetic data for E33 (Q_t as mmol As/g) at 15 and 40°C.

the equilibrium concentration of the sorbed species. The pseudo-second-order kinetic rate equation can be expressed as (Ho and McKay, 1998, 2000; Reddad et al., 2002)

$$\frac{dQ_t}{dt} = k(Q_{\mathrm{eq}} - Q_t)^2 \tag{1}$$

where Q_{eq} (mmol As/g media) is the sorption capacity at equilibrium; Q_t (mmol As/g media) is the solid-phase loading of arsenic at time t, and t is time (min).

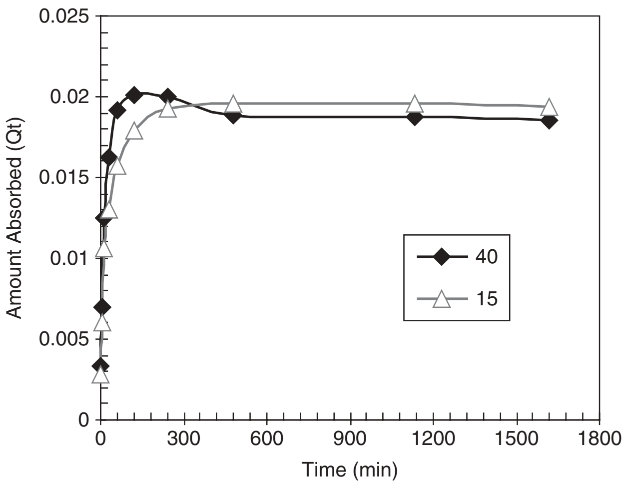

Figure 5 Arsenic adsorption kinetic data for MetSorb (Q_t as mmol As/g) at 15 and 40°C.

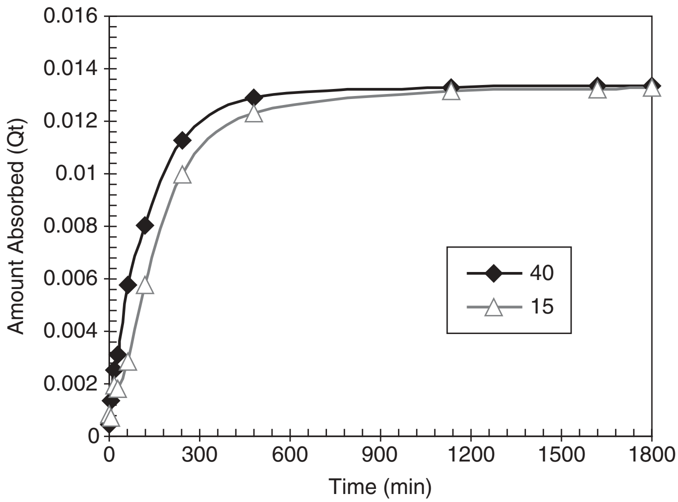

Figure 6 Arsenic adsorption kinetic data for ArsenX^{np} (Q_t as mmol As/g) at 15 and 40°C.

The k (g/mmol · min) is the pseudo-second-order rate constant for the kinetic model. Considering the boundary conditions of $Q_t = 0$ (at $t = 0$) and $Q_t = Q_{eq}$ (at $t = t_{large}$), the following linear equations can be obtained:

$$\frac{t}{Q_t} = \frac{1}{v_0} + \frac{t}{Q_{eq}} \tag{2}$$

$$v_0 = kQ_{eq}^2 \tag{3}$$

where v_0 (mmol/g · min) is the initial adsorption rate. Therefore, by plotting t versus t/Q_t, the v_0 and Q_{eq} values can be determined.

The results were fitted using the pseudo-second-order kinetic model [equation (2)] to estimate the rate constants, initial sorption rates, and adsorption capacities for arsenate. Relevant parameters are summarized in Table 4. The high fitting coefficients ($R^2 \sim 0.999$) indicated that the adsorption of arsenic on the media tested could be well described using the pseudo-second-order kinetic model. Figures 4 to 6 show that approximately 75 to 95% of the initial arsenic in solution (about 110 ppb) was removed by the end of the 24-hour equilibration period. Rate constants and initial adsorption rates decrease in the order MetSorb > E33 ≫ ArsenX^{np}. E33 showed the highest equilibrium sorption capacity in the kinetic tests. Rate constants were considerably higher at 40°C than at 15°C. These differences are potentially attributable to differences in the physical and chemical properties of the media (i.e., composition, pore size, surface area, surface charge, arsenic affinity, etc.). The initial rate appears to be related to the mode of the pore size distribution curve rather than the surface area or average pore diameter

TABLE 4 Kinetic Parameters for Arsenic Adsorption in Socorro Groundwater Using a Pseudo-Second-Order Kinetic Model[a]

Medium	Temperature (°C)	R^2	k	v_0 ($\times 10^{-3}$)	Q_{eq} (mmol/g)	Q_{eq} (mg/g)
E33	40	0.999	6.08	2.43	0.020	1.50
	15	0.998	3.45	1.38	0.020	1.50
MetSorb	40	0.999	20.54	7.42	0.019	1.42
	15	0.999	5.30	1.91	0.019	1.42
ArsenX^{np}	40	0.992	1.03	0.201	0.014	1.05
	15	0.992	0.57	0.111	0.014	1.05

[a] R^2, model-fitting coefficient; k, pseudo-second-order rate constant for the kinetic model (g/mmol · min); v_0, Initial adsorption rate (mmol/g · min); Q_{eq}, sorption capacity at equilibrium (mmol$_{As}$/g) or mg/g.

[MetSorb has the highest mode (~700 Å) in the differential pore size distribution curve in Figure 3 but relatively lower values of the other parameters].

Data Analysis to Obtain Diffusion Coefficients To extract the effective diffusivity of arsenic in the macropores of adsorbent media, a diffusion equation for a macropore-controlled system can be obtained from a differential mass balance on a spherical shell element of the adsorbent particle (Ruthven, 1984):

$$(1-\varepsilon_p)\frac{\partial q}{\partial t} + \varepsilon_p \frac{\partial c}{\partial t} = \varepsilon_p D_p \left(\frac{\partial^2 c}{\partial R^2} + \frac{2}{R}\frac{\partial c}{\partial R} \right) \tag{4}$$

where ε_p is the adsorbent particle porosity, $q(R,t)$ the adsorbed phase concentration (μg/L of adsorbent), t (s) the time, c (μg/L) the adsorbate concentration in the supernate, D_p (cm^2/s) the macropore diffusivity of adsorbate in the adsorbent, and R (cm) the radial distance from the center of the adsorbent particle. The macropore diffusivity (D_p) is assumed to be independent of concentration in the equation.

Solution of this equation based on that of Crank (1976) and Ruthven (1984) is derived in the Appendix. For fractional adsorption uptake $M_t/M_{\max}$ above 70%, the solution with a 2% error is given by

$$\frac{M_t}{M_{\max}} \cong 1 - \frac{6}{\pi^2} \exp\left(\frac{\pi^2 D_e t}{R_p^2} \right) \tag{5}$$

where M_t (μg/L) is the mass gain of adsorbent at time t, $M_{\max}$ (μg/L) the mass gain of adsorbent at infinite time, and D_e (cm^2/s) the effective diffusivity defined by

$$D_e = \frac{\varepsilon_p D_p}{\varepsilon_p + (1-\varepsilon_p)K} \tag{6}$$

TABLE 5 Effective Arsenic Diffusivity for Adsorptive Media at 15°C

Medium	D_e (cm^2/s)	r^2	Range $M_t/M_{\max}$
E33	2.48×10^{-10}	0.975	0.62–1.00
MetSorb	3.72×10^{-10}	0.998	0.54–0.99
ArsenX$^{\text{np}}$	8.69×10^{-11}	0.994	0.43–0.99

where K is the Henry's Law equilibrium adsorption constant. K is equal to $K_d\rho$, where K_d is the linear adsorption distribution constant (mL/g) and ρ is the bulk density (g/mL). A plot of $\ln[1-(M_t/M_{\max})]$ versus time should generate a straight line with a slope of $-\pi^2 D_e/R_p^2$ and an intercept of $\ln\left(6/\pi^2\right)$, from which the effective diffusivity D_e for arsenic diffusion in the macropores of the media can be calculated. D_e/R_p^2 is the diffusion time constant (s^{-1}), which measures the diffusion rate of an adsorbate in porous media. A large diffusion time constant suggests a slow diffusion rate of adsorbate molecules in porous media.

This solution for the fractional adsorption uptake was used to correlate the adsorption kinetics data described above. The values for effective diffusivity D_e are shown in Table 5 and are calculated based on data points with $M_t/M_{\max}$ above 40%, assuming an average particle size of 0.035 mm. The diffusivity values ($\sim 10^{-10}$ cm^2/s) are consistent with the literature value of 2.64×10^{-9} cm^2/s for the GFH adsorbent reported by Sperlich et al. (2005).

Isotherm Studies

Batch sorption studies were carried out to obtain isotherm parameters to estimate the capacity of the media at different influent concentrations. In general, the media were ground into smaller particles than were used in the pilot test, to minimize the effects of mass transfer within the grains and thereby reduce the time required to reach steady state. The equilibration times were based on the kinetic studies described above.

Media Preparation and Sorption Measurements Raw metal oxide media were ground with a mortar and pestle, placed in a sieve shaker, and separated by particle size. Sieve fractions were rinsed with distilled water and except for ArsenX$^{\text{np}}$ were dried at 105°C overnight in an oven; 325 × 400 mesh particles were used for sorption experiments. Titrations with a strong base (1 N KOH) were performed to minimize potential pH drops during the equilibration, due to acid residuals present on media surfaces from manufacturing. Five grams of each media sample were placed into a container and enough water was added to create slurry. Initial pH readings of the slurries were typically below pH 7, and incremental doses of 0.3 mL of potassium hydroxide were added to solution to bring the slurries to a pH between 7 and 8 (bracketing the ambient pH of

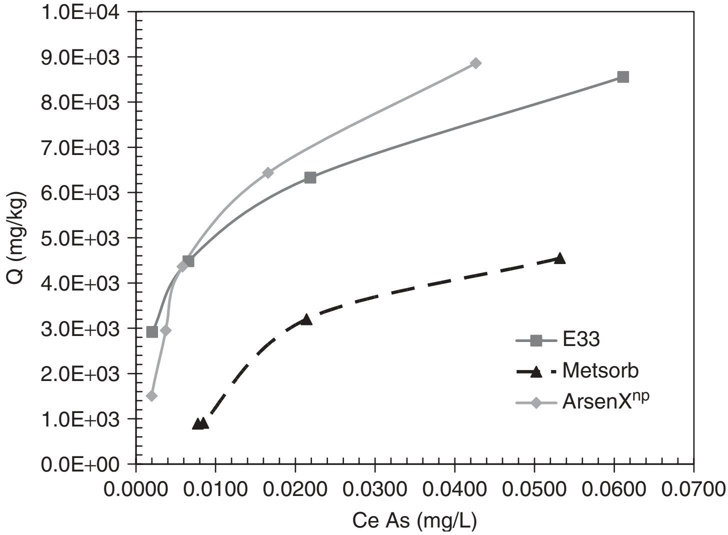

Figure 7 Sorption isotherm plots for E33, MetSorb, and ArsenX$^{\mathrm{np}}$.

the utility water). Samples were agitated overnight; if the pH dropped during this equilibration, the titration procedure was repeated. The fully titrated slurries were placed in weighing trays and were air-dried under a fume hood for a period of more than two days.

Ten 1-L stock solutions with initial arsenic concentrations ranging from ambient concentration [about 44 ppb (44 μg/L) to 12 ppm (12 mg/L)] were prepared from chlorinated water taken from the Socorro Springs water utility (Table 1). For each medium, a set of 10 bottles was filled with approximately 50 mg of media and 40 mL of a specified initial concentration stock solution. Bottles were set in a rotary agitator and sampled approximately 24 hours after the beginning of agitation. The solution from each bottle was placed into a centrifuge for separation of the solids from the supernatant. The final pH in each bottle was recorded. Final arsenic concentrations were measured by ICP-MS analysis.

Data Analysis Figure 7 shows sorption isotherms with Q, the amount of arsenic sorbed (mg/kg), on the y-axis and C_{eq}, equilibrium (final) arsenic concentrations (mg/L), on the x-axis. Two types of isotherm equations were calculated for each medium. An equation for a linear isotherm was calculated from a linear regression of Q and C_{eq}:

$$Q = K_d C_{\mathrm{eq}} \tag{7}$$

where C_{eq} is proportional to Q by a factor K_d (mL/g). A dimensionless K_d value (also known as the Henry's Law constant) was calculated as $K = K_d \rho$. Values of the bulk density ρ are given in Table 2. Results and goodness-of-fit R^2

TABLE 6 Results of Isotherm Experiments[a]

	K_d Model			Freundlich $Q = K_F C^{nF}$				
Medium	Fitted $K_d \rho$	R^2	$K_d \rho$ range	K_F	n_F	R^2	$Q_{10\text{ppb}}$	$Q_{40\text{ppb}}$
E33	78,400	0.578	67,200–690,000	21,000	0.31	0.997	4,970	7,670
ArsenX[np]	203,000	0.347	173,000–655,000	57,000	0.55	0.925	4,630	9,860
MetSorb	95,100	0.831	9,930–120,000	75,800	0.90	0.937	1,180	4,130

[a] Q = mg/kg; $Q_{10\text{ppb}}$ and $Q_{40\text{ppb}}$ refer to sorbed concentration at 10 and 40 ppb arsenic effluent in solution, respectively, and were calculated from the isotherm equations; $K_d \rho$ (dimensionless) is also known as the Henry's Law constant; K_F = L/kg or mL/g.

values are shown in Table 6. A range of dimensionless K_d's was also calculated as $K = K_d \rho = Q/C_{\text{eq}}$ from each measurement over the concentration range studied.

For each medium, an equation for a Freundlich isotherm was calculated from the linear regression of the logarithmic plot of Q and C_{eq}:

$$Q = K_F C_{\text{eq}}^{nF} \tag{8}$$

where the slope and the y-intercept of the logarithmic linear regression are equal to n_F and K_F (mL/g), respectively. Results are shown in Table 6.

DYNAMIC STUDIES

Pilot Tests

Design The design of the pilot system and intended standard operating procedures are described in detail in the pilot test specific test plan (PTSTP) for the Socorro Springs pilot (Siegel et al., 2006a). The pilot test skid contained 10 columns, each designed as an independent arsenic adsorption media filter operating in parallel. Each column is modular in design, consisting of the following components: rotameter, three-way valve (for service or backwash mode), up-gradient pressure gauge, column with adsorptive media, down-gradient pressure gauge, another three-way valve (service or backwash mode), sample tap, totalizing flow meter, check valve, and all associated piping. During the pilot test, the flow rate, cumulative flow, pressure drop across the media, and the corresponding backwash requirements (frequency and volume) were measured (Table 7). The arsenic adsorptive columns were designed based on information on particle size, desired hydraulic loading rate, and optimum empty bed contact times (EBCTs) supplied by the vendors (Siegel et al., 2006a).

The arsenic adsorption media filters operated continuously during the test with the exception of the potential for occasional backwash (as required by unacceptable head loss across a filter bed). Water samples were taken daily for the first

TABLE 7 Summary of Final Pilot Design

Parameter	MetSorb		E33		ArsenX^{np}
Number of pilot-scale columns	1		3		1
Hydraulic loading rate (gpm/ft^2)	8		6		8.2
Column number	SC-6	SC-8	SC-9	SC-10	SC-5
EBCT (min)	2	2	4	5	3
Column height (in.)	39	39	60	60	60
Column diameter (in.)	3	3	3	3	3
Media depth (in.)	25.7	19.3	38.5	48.1	39.2
Media volume (L)	2.97	2.23	4.50	5.57	4.74
Water flow rate (gpm)	0.4	0.3	0.3	0.3	0.4
Face velocity (ft/min)	1.07		0.80		1.09
Backwash flow rate (gpm)	0.3		0.3		0.2

two weeks of the test and twice weekly for the remainder of the test. Field operation, maintenance procedures, sample collection, and sample management are described in the PTSTP (Siegel et al., 2006a) and the pilot test report (Siegel et al., 2007). At the conclusion of the test, pore water samples were taken at regular intervals from several of the columns. The media were removed from each column and returned to SNL for posttest characterization. The Toxicity Characteristic Leaching Procedure (TCLP) (U.S. EPA, 1992) and California Wet Extraction Test (CA WET) (State of California, 2005) analyses were performed for each medium prior to final disposal.

Pilot Test Results Breakthrough curves for arsenic in the pilot test columns are shown in Figures 8 to 10. In Figure 8 the arsenic concentration in the chlorinated influent is compared to the arsenic concentrations for each sampling event. Note that changes in the arsenic concentration of the influent are often correlated with changes in the effluent. In some cases, concentration spikes in the effluent bring the arsenic levels in the effluent above the MCL for short periods of time. Figure 9 compares the arsenic concentrations at equivalent numbers of bed volumes of flow through the columns for three media run at the EBCT recommended by the media vendors through July 19, 2005.

Figures 8 to 10 show that initially, arsenic [as As(V)] was removed completely from the chlorinated water in all of the columns and that as the capacity of the medium for arsenic was exhausted over the course of several months, arsenic concentrations in the effluent rose. Figure 8 shows that the influent arsenic concentration was variable over the course of the test period, ranging from 35 to 55 ppb. This variability may result from nonuniform mixing of water from the two sources of water that feed the Socorro Springs well site. Detailed information, including the breakthrough curves for other solutes, interlaboratory calibration studies, operational data, and results of TCLP and CA WET are given in Siegel et al. (2007). Figure 10 shows breakthrough curves for E33 run at three different

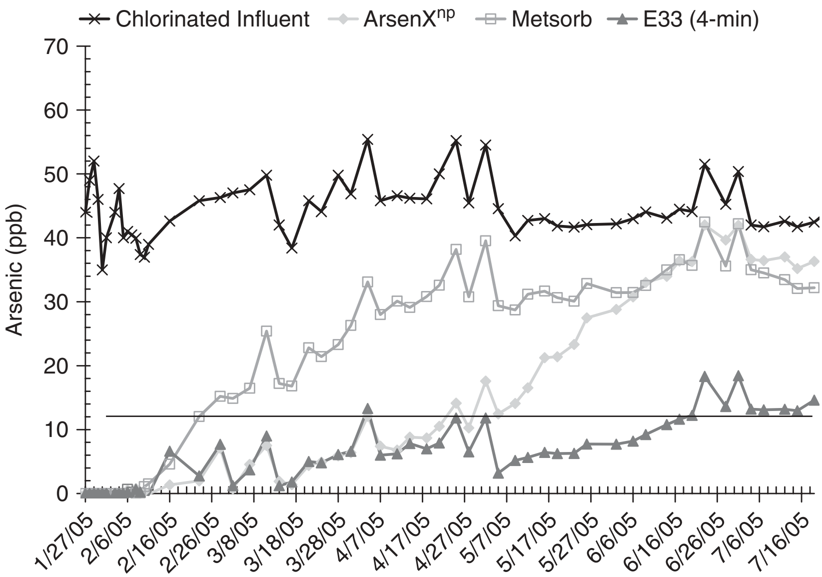

Figure 8 Arsenic breakthrough and influent arsenic concentrations for adsorbent media columns at Socorro Springs.

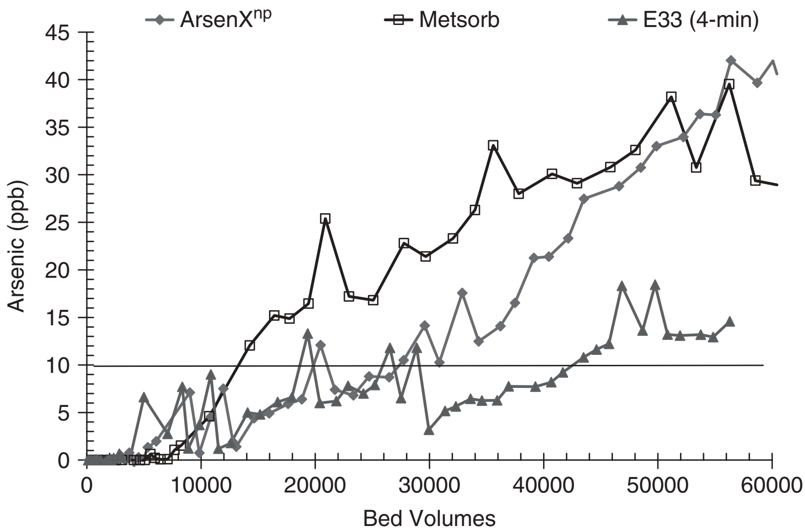

Figure 9 Arsenic concentrations in column effluent as a function of cumulative bed volumes. (*See insert for color representation of figure*.)

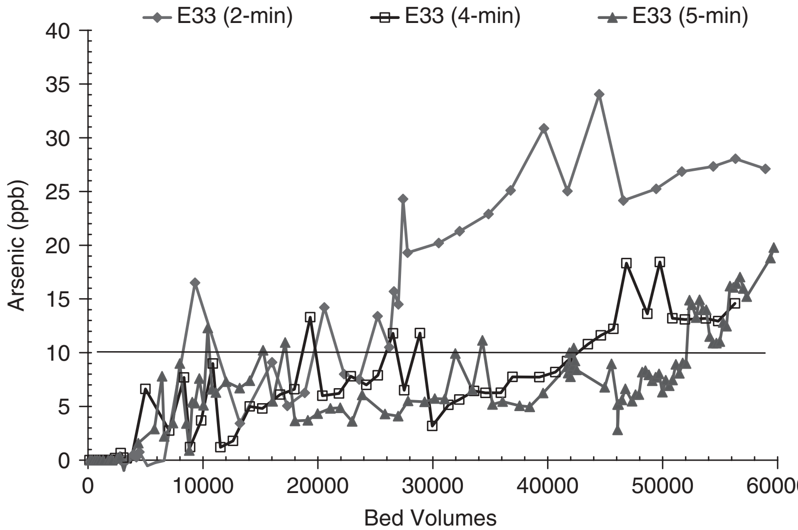

Figure 10 Arsenic concentrations in column effluent as a function of cumulative bed volumes for E33 with different EBCTs. (*See insert for color representation of figure*.)

EBCTs (2, 4, and 5 minutes). The uncertainty in the method used to estimate the breakthrough point (visual examination of the curves) is estimated to be 15%. It is important to note that the EBCTs used in the tests were within the ranges recommended by the vendors and that the relative performance of the media could change if different EBCTs are used.

Table 8 summarizes the results of the pilot tests shown in the figures. The results of the tests are expressed as bed volumes of effluent that passed through the column until the effluent arsenic concentration reached 10 ppb. It can be seen from inspection of Figures 9 and 10 that the number of BVs of influent passing through the column until a target concentration is reached in the effluent can be difficult to estimate if the data are noisy. Thus, the number of BVs until breakthrough can be a very imprecise measure of the arsenic adsorption capacity of the media.

Estimates of the concentration of arsenic (mg As/g media) in the adsorptive media (i.e., the capacity) at effluent concentrations of 10 ppb (10 μg/L), when $C/C_0 = 0.8$ and when $C_e = C_0$ [where the influent (C_0) and effluent (C_e) concentrations are equal] are also shown in the table. The capacities are calculated from the mass balance on arsenic data by integration of the area above the breakthrough curves (BTCs) and below the influent arsenic concentration. These may be a more unbiased measure of sorption than the BV value, as discussed below. The capacity at 10 ppb (10 μg/L) is calculated from raw data from $BV = 0$ to the point in the BTC where the arsenic concentration in the effluent (C_e) reached and

TABLE 8 Summary of Performance Data for Adsorbent Media Using Three Methods

		E33[a]			MetSorb	ArsenX^{np}
Method	Parameter EBCT:[b]	2 min	4 min	5 min	2 min	3 min
Pilot	BV to 10 ppb (10 μg/L)	24,000	43,000	52,000	13,000	27,000
	Capacity at 10 ppb (mg/g)	1.95	3.56	4.21	0.70	1.38
	Capacity at $C/C_0 = 0.8$ (mg/g)	4.03	NA	NA	2.26	2.10
PD RSSCT	BV to 10 ppb (10 μg/L)	15,400	43,000	41,000	12,800	43,000
	Capacity at 10 ppb (mg/g)	1.95	3.39	3.07	0.69	1.33
	Capacity at $C/C_0 = 0.8$ (mg/g)	4.26	4.68	4.71	1.24	1.37
	Capacity at $C_e = C_0$ (mg/g)	5.08	5.61	5.02	1.31	1.38
Freundlich isotherm	Capacity at 10 ppb (mg/g)		4.97		1.18	4.63
	Capacity at 40 ppb (mg/g)		7.67		4.13	9.86

[a] NA, not available.
[b] Empty bed contact time; not applicable to isotherm.

stayed above 10 ppb (10 μg/L). Lower limits for several of the parameters are listed in the table because the experiments were terminated before full or 80% capacity of the columns was reached. Other parameters in the table are discussed in later sections.

RSSCT Studies

Laboratory studies to predict media performance of pilot-scale adsorption columns were conducted using rapid small-scale column tests (RSSCTs). RSSCTs are scaled-down columns packed with smaller-diameter adsorption media that receive higher hydraulic loading rates to significantly reduce the duration of experiments (Aragon et al., 2004; Thomson et al., 2005; Westerhoff et al., 2005). Results for RSSCTs can be obtained in a matter of days to a few weeks, whereas pilot tests can take a number of months to over a year.

This method uses scaling relationships that allow correlation of lab-scale column results operated at accelerated flow rates to full-scale column performance. The RSSCT concept is based on a theoretical analysis of the adsorption processes that govern performance, including solution and surface mass transport and adsorption kinetics. Mass transfer models have been used to determine dimensionless parameters that establish similitude between small- and large-scale columns. Crittenden et al. (1987a,b, 1991) developed scaling equations for both constant and nonconstant diffusivities with respect to particle size. The scaling laws ensure that the RSSCT and the full-scale system will have identical breakthrough profiles. Details of the theoretical basis for the RSSCT method are described in the appendix. Proportional diffusivity (PD) and constant diffusivity (CD) tests were carried out for the media studied in the Socorro Springs pilot test (Siegel et al., 2007). Design, procedures, and results for the proportional diffusivity tests are described in detail in Aragon (2007) and are summarized below.

Methods and Materials Media shipped from vendors was crushed by hand or with an electronic mortar and pestle (shatterbox), separated by a sieve stack into mesh fractions, and rinsed with deionized (DI) water to remove fines. E33 and MetSorb were baked in an oven at 105°C overnight to complete dryness. For column packing, dry medium was weighed according to design calculations described in the Appendix, submerged in DI water, and deaerated by vacuum pump for at least one hour. The PD RSSCT columns were packed with 100 × 200 mesh adsorption media (diameters of 0.15 to 0.075 mm). Deaerated media were loaded into the columns as a slurry using a small spatula. Media were backwashed with DI water for approximately 15 minutes or until the backwash water was clear of fines.

Chlorinated Socorro Springs water was hauled to the SNL in 55-gallon drums for the RSSCTs and stored in 200-L feed tanks. Water was gravity fed to a manifold and to multiple columns, which were operated in down-flow mode. Pressures in the system did not exceed 20 psi. PD RSSCT column influent and effluent were sampled once per day via three-way stopcock sample ports. Samples were filtered through 0.45-μm nylon membranes; approximately 50 mL of sample was collected and preserved with HNO_3 to achieve pH ~ 2. An internal standard and matrix spike (a 1-g 1250 ppb Ge and 1250 ppb As mixture) was added to each sample and analyzed for total arsenic with ICP-MS. Design parameters for RSSCTs and a corresponding pilot-scale test are shown in Table 9. Actual EBCTs for the PD test columns were as follows: E33, 0.23 min (PD 1–2), 0.38 min (PD 2-2), 0.50 min (PD 2–3); ArsenX^{np}, 0.28 min; MetSorb, 0.39 min.

Results Breakthrough curves for the E33 media at 3 EBCTs are shown in Figure 11; curves for MetSorb and ArsenX^{np} are shown in Figures 12 and 13. RSSCT PD and pilot test data are shown for comparison. The shapes of only the 2- and 4-minute EBCT E33 pilot tests correlate well with their corresponding RSSCTs. Results are summarized in Table 8; the RSSCTs are reasonably good predictors of the 10-ppb As BVs for the E33 4-min EBCT and MetSorb pilots tests but less accurate for the other EBCTs for E33 and the ArsenX^{np}. Estimates

TABLE 9 Comparison of Design Parameters for Pilot- and Small-Scale Columns

Parameter	Pilot Scale	RSSCT
Column diameter [cm (in.)]	7.6 (3)	1.0 (0.4)
Particle diameter (mm)	0.25–2.0	0.15–0.18
EBCT (min)	2–5	0.05–0.9
Bed height [cm (in.)]	50–130 (20–50)	8–30 (3–12)
Flow rate [mL/min (gpm)]	1,100–1,900 (0.3–0.5)	20–120 (0.005–0.03)
Hydraulic loading rate [cm/min (gpm/ft^2)]	24–32 (6–8)	15–125 (3–32)

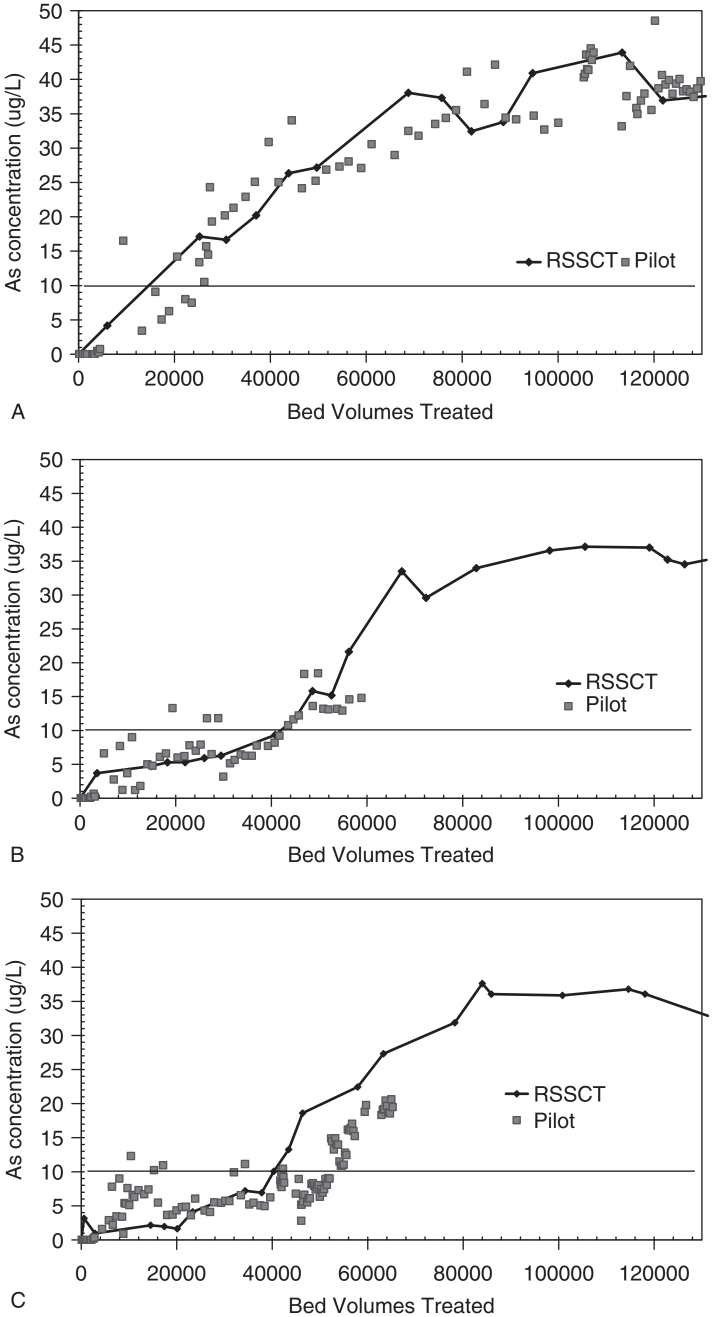

Figure 11 (A) Pilot and RSSCT (PD 1–2) breakthrough curves for E33 media for 2-minute EBCT; (B) pilot and RSSCT (PD 2-2) breakthrough curves for E33 media for 4-minute EBCT; (C) pilot and RSSCT (PD-2-3) breakthrough curves for E33 media for 5-minute EBCT.

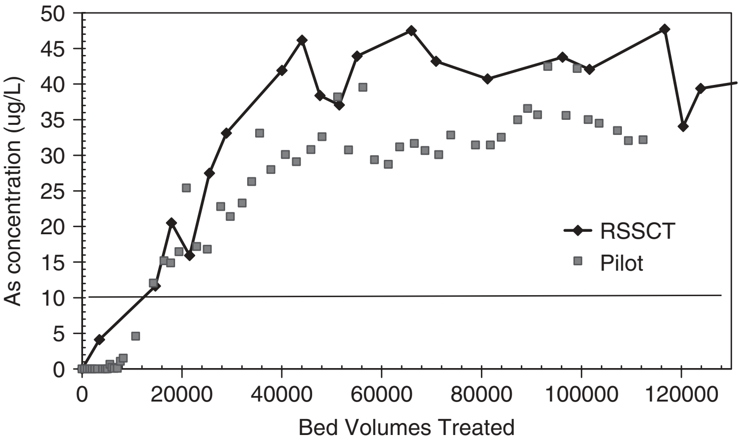

Figure 12 Pilot and RSSCT breakthrough curves for MetSorb media.

of the adsorptive capacity of the media—that is, the concentration of arsenic (mg As/g media) at effluent breakthrough concentrations of 10 ppb (10 μg/L), at $C/C_0 = 0.8$ and at $C_e = C_0$ [where the influent (C_0) and effluent (C_e) concentrations are equal]—are also shown in Table 8. The capacities are calculated from mass balance on arsenic data by integration of the area above the BTC and below the influent arsenic concentration. As discussed previously, these may be a more unbiased measure of sorption than the BV value.

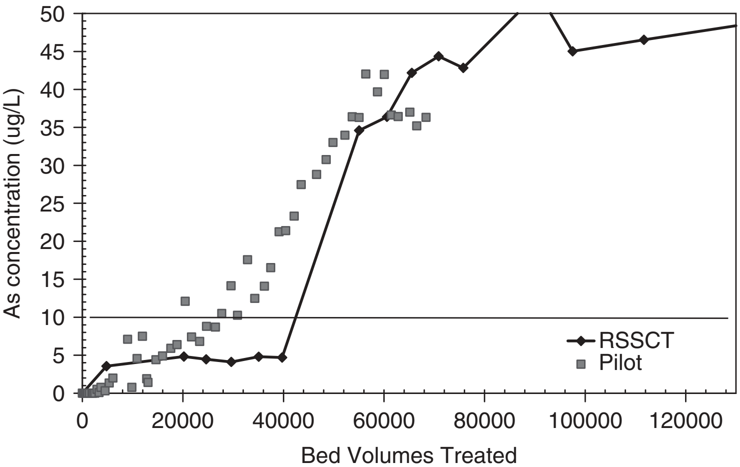

Figure 13 Pilot and RSSCT breakthrough curves for ArsenX^{np} media.

DISCUSSION

Controls on Adsorption of Arsenic in Fixed-Bed Media

To a first approximation, the effectiveness of fixed-bed adsorptive media for arsenic removal depends on three kinds of factors:

1. The chemical nature of the adsorbent, affecting its ability to form electrostatic or specific chemical bonds with arsenic oxyanions
2. The physical properties of the media, including surface area and pore size distribution of the adsorptive media and any changes in hydraulic properties of the media during treatment
3. The chemistry of the water source, including pH, redox speciation of As [i.e., As(III)/As(V) ratio], and the concentration of aqueous species that will interfere with adsorption of arsenic by competing for adsorption sites, modifying adsorptive media surface charge, or physically blocking access of arsenic to the interior of the particles or grains of adsorptive media

This study addressed the first two factors by examining the arsenic sorption capacity of three different metal oxyhydroxide media exhibiting a range of chemical compositions and contrasting physical properties. Comparison of the results of this study to similar studies carried out in other water compositions will allow evaluation of the effect of the third factors and will be the subject of future publications.

As water passes down through a filter vessel containing fixed-bed media, the arsenic concentration declines within the media until it is no longer detectable. As the upper portion of the media becomes saturated, the treatment region (mass transfer zone) progresses downward until all adsorptive capacity is used and complete arsenic breakthrough occurs. When the capacity of the medium is completely exhausted, the arsenic concentrations in the untreated and treated water will be the same.

Figure 14 describes important dynamic processes involved in the uptake of arsenic by adsorbent media. Note the concentration axes on the right side of the figure. The concentration of arsenic decreases from c_b in the bulk solution, to c_s at the fluid solid interface, to c_p in the pores, as q, the concentration in the solid, increases. In dynamic systems, such as fixed-bed treatment systems, the effectiveness of arsenic adsorption is dependent on the relative rates of several processes. These include (1) the kinetics of surface complexation, (2) the rate of mass transfer of arsenic to the interior of the grains, and (3) the hydraulic loading rate (flow rate). The effectiveness of treatment will be highest when the arsenic species form specific chemical bonds quickly to reactive surfaces and the flow rate is low enough to allow arsenic species to migrate to fresh sorption sites in the grain interiors. High surface area and a uniform pore distribution with a mean pore size large enough to allow diffusion of the aqueous species lead to high sorption capacity.

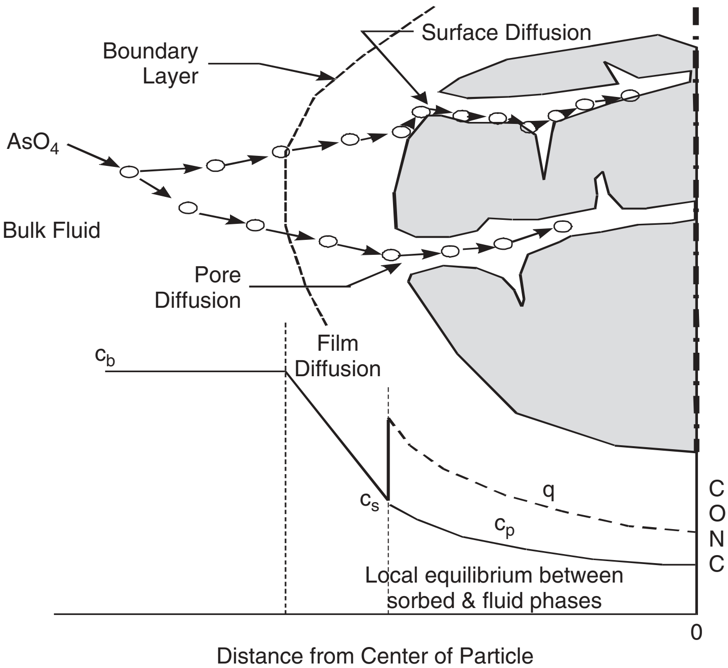

Figure 14 Processes controlling the transport of arsenic from bulk solution to the interior of granular adsorbent media. (Adapted from Crittenden, 1987b.)

The zero point of charge (ZPC) of the oxide is a property of the surface chemistry of the media and is an important determinant of adsorption capacity. Above the pH of the ZPC, the oxide surface has a net negative charge, and there will be an electrostatic repulsion between an anionic species and the surface. In this study, the arsenic adsorption capacities of media containing iron oxyhydroxide (E33, ArsenX^{np}), and titanium oxyhydroxides (MetSorb) were compared. Two iron oxyhydroxide phases were examined: E33 is composed of granules of a mixture of iron oxyhydroxide phase; in ArsenX^{np}, nanoparticulate iron oxide is dispersed within an ion-exchange resin bead. In the alkaline chlorinated water used in the Socorro Springs pilot study, arsenic is predominantly present as the oxyanion arsenate. The ZPCs of the oxide phases in the media are not well characterized, but in general, iron oxyhydroxide and the titanium oxyhydroxides have ZPCs about pH 6.7 (Yoon et al., 1979). Thus, at the ambient pH (about 8), both of the metal sorbents exhibit a negative surface charge. If sorption is to occur by a specific chemical bond, the electrical repulsion must be overcome in these media. Differences in adsorption capacity among the media in batch experiments are probably due to specific chemical adsorption and the physical properties of the media that affect arsenic diffusion into the interior of the grains.

In a flowing system, the balance between the rates of the chemical and physical processes is expressed by the shape of the mass transfer zone (MTZ). In the MTZ, the concentration of the arsenic drops from its initially high value to a lower value, corresponding to equilibrium sorption. The shape of the MTZ is very important to use of adsorptive media in drinking water treatment. The adsorbent bed must be replaced or regenerated when the concentration of arsenic in the effluent exceeds the MCL (10 μg/L). Under favorable conditions where diffusion into the grain interior is rapid relative to flow (hydraulic loading) rate, the mass transfer zone will be relatively sharp, and a large fraction of the potential sorption capacity of the media will be utilized before replacement is warranted. Under unfavorable conditions, the mass transfer zone will be broad, the arsenic concentrations in the effluent will rise rapidly above the MCL, and most of the adsorbent bed will not adsorb arsenic before it needs to be replaced. Prediction of the performance of adsorptive media in pilot tests or full-scale applications relies on information about the adsorptive capacity of the media in batch systems as well as the shape of the MTZ in the dynamic system. In the following section, the use of an analytical model to predict the shape of the MTZ is evaluated.

Modeling Adsorption Breakthrough: The Klinkenberg Model

One of the goals of this project is to determine if the performance of adsorbent media in field-scale tests can be predicted from relatively few laboratory measurements. A mathematical model that could be programmed in an Excel spreadsheet was examined as a potential predictive tool. Details about the model are given in the Appendix and summarized below. This simple solution for an adsorption breakthrough curve is based on the following assumptions: (1) isothermal conditions, (2) no axial dispersion, (3) linear driving force for mass transfer (i.e., constant k), (4) linear adsorption equilibrium [i.e., constant K (ρK_d)]. If the overall mass transfer coefficient (k) and Henry's Law constant (K) are known, it is possible to predict (1) the adsorption breakthrough curve at the bed exit or at any location inside the column [(c/c_f) vs. t], and (2) the concentration profile inside the column [(c/c_f) vs. z] at any time t.

There are two ways to determine the overall mass transfer coefficient k and Henry's Law constant K: (1) from batch experiments (adsorption equilibrium and kinetics) as described in the preceding sections and (2) from breakthrough data obtained in small or large columns by regression. The second approach is applied in this section by modeling the adsorption breakthrough curves of arsenic from the packed columns of E33 and MetSorb media used in the RSSCTs.

Equation (9) is an analytical solution (Klinkenberg, 1948) of the ratio of adsorbate concentration in the fluid phase to that of influent at a given location (z) and a given moment (t).

$$\frac{c}{c_F} \approx \frac{1}{2}\left[1 + \operatorname{erf}\left(\sqrt{\tau} - \sqrt{\xi} + \frac{1}{8\sqrt{\tau}} + \frac{1}{8\sqrt{\xi}}\right)\right] \tag{9}$$

where c_F is the influent adsorbate concentration, τ the dimensionless time coordinate, and ξ the dimensionless distance coordinate. These are defined by

$$\xi = \frac{kKz}{u}\frac{1-\varepsilon_b}{\varepsilon_b} \tag{10}$$

$$\tau = k\left(t - \frac{z}{u}\right) \tag{11}$$

where k is the overall mass transfer coefficient (min^{-1}), K the dimensionless Henry's Law adsorption equilibrium constant, and t the time.

As discussed in the Appendix, the Klinkenberg solution also provides an analytical solution of the ratio of adsorbent loading to the equilibrium adsorption amount at a given location (z) and a given moment (t); therefore, it is possible to predict the adsorbent loading inside the column (i.e., $\overline{q}$ vs. z) at any time.

Modeling Adsorption Breakthrough of Arsenic from Packed Columns RSSCT PD 2-2 data for E33, shown in Table 10, were used as the basis for regressing the overall mass transfer coefficient k and Henry's Law constant K (ρK_d) used in equation (2) for prediction of arsenic adsorption breakthrough at other conditions. The EBCT of this RSSCT corresponded to the 4-minute EBCT of the pilot tests for E33. It was assumed the bed porosity ε_b was 0.5 for all cases. Equations (9) to (11) were programmed into an Excel spreadsheet by fitting the experimental breakthrough data with Equation 9, and the corresponding set of model parameter (k,K) for the column given in Table 10. As shown in Figure 15, the Klinkenberg model fits the adsorption breakthrough curve for PD 2-2 quite well.

Using the Klinkenberg model constants (k,K) determined from the RSSCT data, we should be able to predict the arsenic breakthrough performance of similar adsorbents at different operating conditions. Figure 16 shows that the Klinkenberg model with the model parameters (k,K) regressed from RSSCT data PD-2-2 (small particles, medium EBCT) can predict fairly well the breakthrough curves obtained from RSSCT PD-2-3, which has a longer EBCT. This

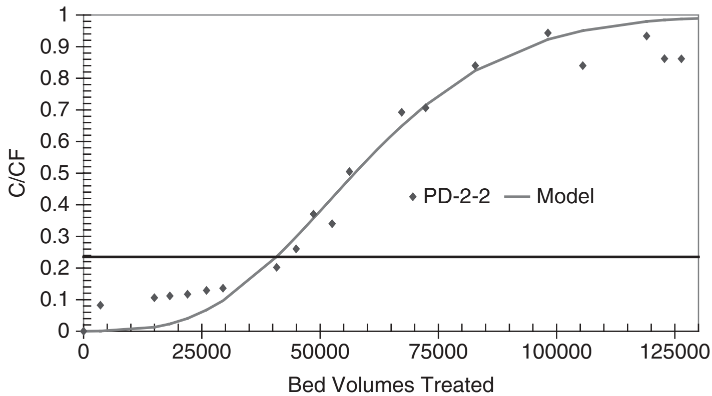

Figure 15 Calibration of As breakthrough data (PD-2-2) with the Klinkenberg model. $k(\text{min}^{-1}) = 0.0005$; $K = 120{,}000$.

TABLE 10 RSSCT Parameters for Klinkenberg Model Calibration

	Column Name		
	PD 2-2	PD 2–3	N/A
Media type	E33, medium EBCT	E33, long EBCT	MetSorb
Mesh size	100 × 200	100 × 200	100 × 200
Column diameter (cm)	0.70	0.70	0.70
Bed height (cm)	9.37	12.38	12.78
Bed volume (cm^3 = mL)	3.61	4.76	4.92
Flow rate (mL/min)	9.50	9.50	12.70
EBCT (min)	0.38	0.50	0.39
Media mass (g)	1.90	2.40	4.00
Average c_F (ppb)	42.5	40.28	44.0

suggests that breakthrough data obtained from a short column with a smaller empty bed contact time (EBCT) can be used to predict the performance in a long column with a larger EBCT. This statement, if validated with other adsorbent media, could significantly reduce the number of RSSCT experiments required to evaluate alternative adsorbent media.

Comparisons of breakthrough curves obtained from pilot tests SC-8, SC-9, and SC-10 to the predictions from the Klinkenberg model using the model parameters (k, K) regressed from RSSCT data from PD-2-2 are shown in Figures 17 to 19. These are scale-ups from the small RSSCT column to a much larger column (scale-up ratio of 2600 times). The pilot test conditions are summarized in Table 7.

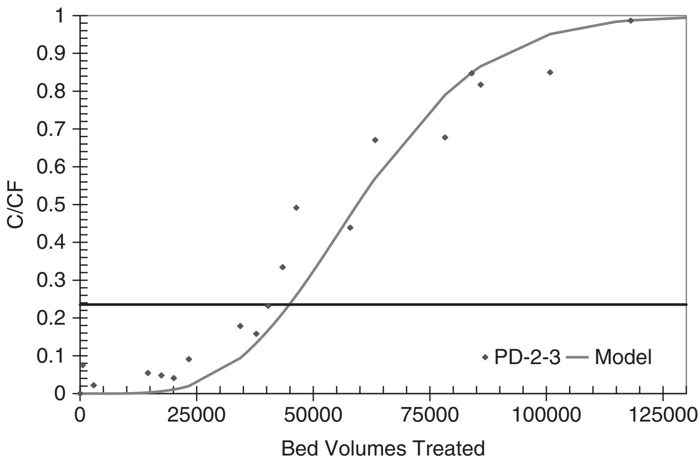

Figure 16 Comparison of breakthrough curves obtained in RSSCT PD 2-3 with predictions from the Klinkenberg model using parameters from RSSCT PD-2-2.

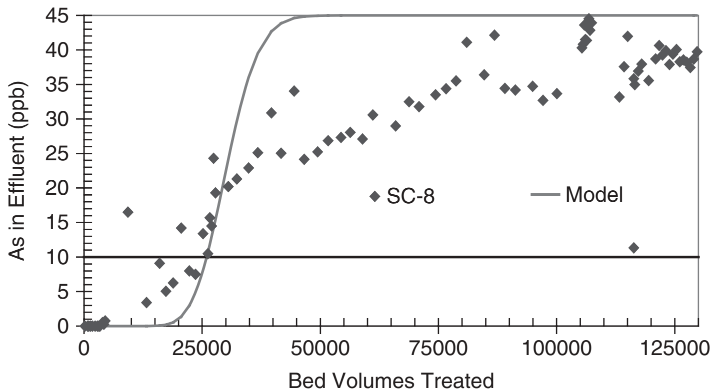

Figure 17 Comparison of breakthrough curves obtained in pilot test column SC-8 with predictions from the Klinkenberg model using parameters from RSSCT PD-2-2. $k(\text{min}^{-1}) = 0.0005$; $K = 120{,}000$.

Although the shape of the breakthrough curve in the SC-8 pilot test column (2-minute EBCT) disagrees with that of the model, both show 10 ppb breakthrough at about 27,000 BV. The model predicts breakthrough in SC-9 at 54,000 BV compared to the 42,000 BV estimated from the pilot test data. The model prediction using RSCCT data PD-2-2 for SC-10 (5-minute EBCT) agrees well with the experimental breakthrough curve and forecasts a value of breakthrough time similar to that of the experimental data (~55,000 BV vs. 52,000 BV). Because there is so much scatter in the pilot test data, any comparison to the exact BV value predicted by the analytical model should be considered semiquantitative at best.

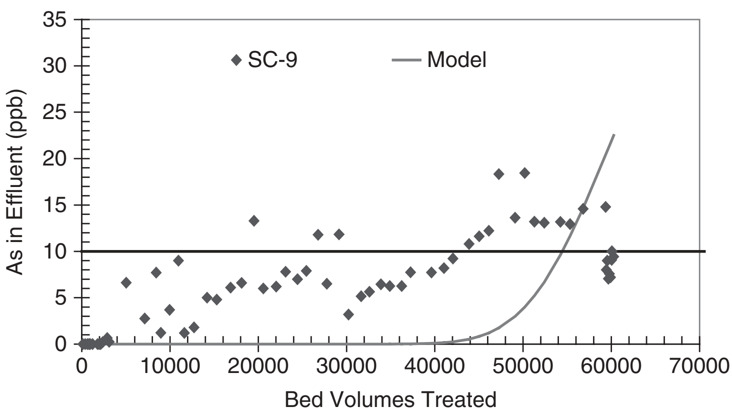

Figure 18 Comparison of breakthrough curves obtained in pilot test column SC-9 with predictions from the Klinkenberg model using parameters from RSSCT PD-2-2.

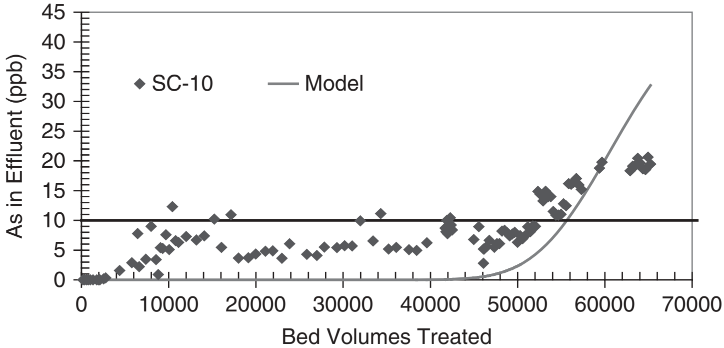

Figure 19 Comparison of experimental breakthrough curves obtained in pilot test column SC-10 with predictions from the Klinkenberg model using parameters from RSSCT PD-2-2.

Figure 20 compares the pore water arsenic concentration profile inside column SC-10 and the arsenic concentration profile predicted from the Klinkenberg model using the values of k and K regressed from RSSCT data PD-2-2. It is interesting to note that the model can semiquantitatively predict the shape of the pore water arsenic concentration profile inside the column. Theoretically speaking, the adsorption breakthrough curve at the column exit and the concentration profile inside the column at the breakthrough time are correspondent. This information can be utilized to design accelerated pilot-scale tests to replaced prolonged breakthrough experiments. Instead of measuring the breakthrough at the column exit for an extended period of time, it may be possible to measure the concentration profile inside the bed once steady state is established. By analyzing

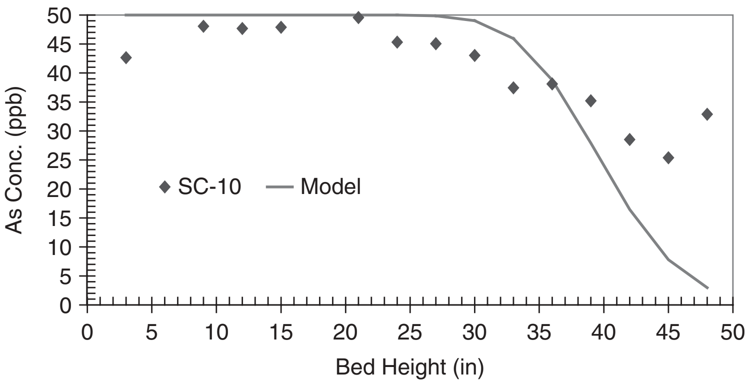

Figure 20 Comparison of the experimental As concentration profile obtained in pilot test column SC-10 with predictions from the Klinkenberg model PD-2-2. $k = 0.0005\,\text{min}^{-1}$, $K = 120{,}000$. (*See insert for color representation of figure*.)

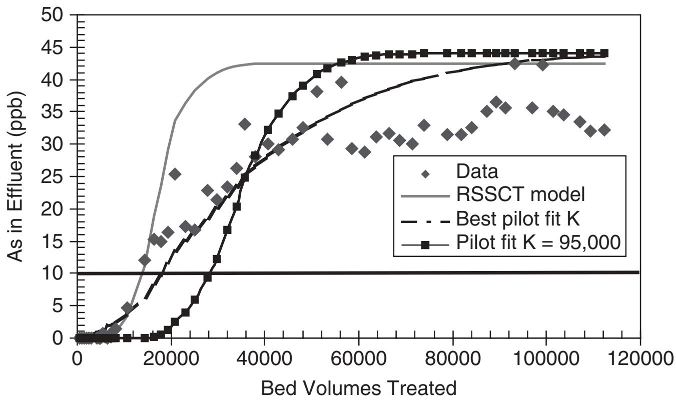

Figure 21 Comparison of breakthrough curves obtained in MetSorb pilot test with predictions from the Klinkenberg Model using parameters from RSSCT and alternative model fits. RSSCT: $k = 0.0004$, $K = 50{,}000$; pilot tests: $k = 0.0004$; $K = 95{,}000$; best pilot fit: $k = 0.000065$; $K = 95{,}000$. (*See insert for color representation of figure*.)

the concentration profile, one can obtain a set of model parameters (k,K) and apply these parameters to predict the adsorption breakthrough at the column exit.

Data from the MetSorb RSSCT column (Figure 12) were also regressed with the Klinkenberg model to obtain values of k (0.004 minute^{-1}) and K (50,000). Figure 21 compares pilot-scale data to predictions made with the Klinkenberg model using these parameters (solid line). The model gives a reasonable estimate of the BV at 10 ppb breakthrough but does not match the rest of the curve. Using a value of K consistent with the best linear fit to the sorption isotherm ($K(\rho K_d) = 95{,}000$; see Table 6) does not improve the fit (curve marked pilot fit $K = 95{,}000$). Decreasing the mass transfer coefficient to $k = 0.000065$ improved the fit considerably (curve marked “Best pilot fit K”). This suggests that the model could be used with batch sorption data in sensitivity analyses to semiquantitatively predict both the breakthrough at the MCL and the shape of the elution curve if independent information about the mass transfer coefficients was available.

The results also suggest that the Klinkenberg equation might be used to estimate the pilot test breakthrough at the MCL for different EBCTs using data from a single RSSCT. Such an application could limit the number of RSSCTs needed to accurately predict breakthrough for full-scale systems of different sizes and costs. In this study, the pilot breakthrough for the three EBCTs is estimated by the model predictions derived from the RSSCT curves run at the intermediate EBCT.

Comparison of Estimates of Media Performance Using Batch and Dynamic Tests

In this study, four experimental methods were used to estimate the performance of adsorbent media in a full-scale treatment system at Socorro Springs: two batch

TABLE 11 Estimated Sorption Capacities from Lab Tests Relative to Pilot Test Results[a]

	Medium		
Test	E33 (4 min)	MetSorb	ArsenX^{np}
RSSCT-PD	0.95	0.99	0.96
Freundlich	1.40	1.69	3.36

[a]Calculated as (capacity in As mg/g media)$_{test}$/(capacity in As mg/g media)$_{pilot}$.

sorption measurements (kinetic and equilibrium), RSSCTs, and a pilot-scale test. Results from all methods are summarized in Table 8 and in Table 11. In Table 11, the capacities predicted by the batch tests and RSSCTs are compared to those measured in the pilot tests. The relative number of bed volumes until breakthrough at 10 ppb predicted by the RSSCT agreed with that of the pilot test (E33 > ArsenX^{np} > MetSorb). The relative adsorptive capacity (mg As/g media) at 10 ppb breakthrough for the pilot test, RSSCT, and sorption isotherm measurements followed the same order. Note that the capacities obtained in the isotherm tests are higher than those estimated from the pilot tests (Table 8). This is consistent with the expectation that the smaller particle sizes and longer contact times in the batch tests would lead to more effective mass transfer of arsenic into the interior of the adsorptive media grains.

The level of absolute agreement between different laboratory and pilot test performance was media dependent. The number of bed volumes until breakthrough at 10 ppb measured by the RSSCTs for E33 and MetSorb were nearly identical to the values from the pilot tests, whereas the breakthrough in the RSSCT for ArsenX^{np} occurred at 63% of the bed volumes in the pilot test. The sorption capacity (mg As/g media) of two of the media (E33, MetSorb) as measured in the pilot tests could be predicted to within about 70% by batch sorption tests, whereas the capacity of the ArsenX^{np} measured in the batch was much higher (336%) than that measured in the pilot test. The PD RSSCTs were accurate predictors of the media capacity for the pilot tests for E33, MetSorb, and ArsenX^{np} media (within 5%) (Table 11).

The poor correlation between isotherm studies and column (RSSCT and pilot) predictions of arsenic removal by ArsenX^{np} is probably due to the behavior during crushing for the batch sorption and RSSCTs. The resin was ground to 325×400 mesh for isotherm studies. Upon crushing, the near perfectly spherical ArsenX^{np} beads were ground into what looked like a fine iron powder. Visually, the media did not seem to have the same physical properties as the precrushed resin. Prior to crushing, the beads were comparable to ball bearings; after crushing, the media no longer seemed to be in a beadlike form. The fine materials were flakes that produced a red stain on contact. The sorptive properties of the ArsenX^{np} in the isotherm tests are probably not indicative of the performance to be expected in column or pilot studies. The properties of this material dominated the results of the batch sorption experiments and to some extent the RSSCT, and make comparisons with the other media questionable. In addition to the effects of crushing on adsorptive properties, it was observed that the hydraulic properties before crushing were more ideal; water flowed through almost without resistance. After crushing, the media tended to stick together, causing columns to "plug" when water pressure was applied. The ArsenX^{np} resin beads were, however, used in the kinetic batch tests and pilot studies without crushing. These studies probably provide more accurate estimates of capacity and performance.

The Klinkenberg model can be used to calculate the breakthrough curves using values of the mass transfer coefficient (k/min) and Henry's constant [dimensionless K_d or (ρK_d)]. When values for these variables are obtained from RSSCT experiments, the number of bed volumes of water treated until the MCL is reached could be predicted within 20% for the E33 media at three EBCTs and for the MetSorb media, however, the shape of the curves did not match the predictions. The inability of the model to match the pilot-scale data may be due to the model assumption of linear sorption and to a dependence of the mass transfer coefficient on particle size. The first limitation is supported by the results of the batch sorption experiments; none of the media exhibited linear sorption (Table 6). The second limitation is supported by the results of other RSSCT experiments that showed a strong dependence on particle size for these and other media (A. Aragon, personal communication; Aragon, 2004). This suggests that a more accurate model of the adsorption breakthrough behavior would be possible with a nonlinear adsorption isotherm and multiple pore diffusion resistances. The adsorption equilibrium and kinetic mass transfer data could be obtained from the batch adsorption experiment and RSSCT adsorption breakthrough data for this modeling effort.

CONCLUSIONS

Rapid, inexpensive tests are needed to predict the arsenic adsorption capacity of adsorptive media to help communities select the most appropriate technology for meeting compliance with the new arsenic MCL. In this study the consistency among capacity estimates made by batch and dynamic methods were compared and their relevance to full-scale performance was evaluated. Each method has inherent limitations and strengths. Pilot tests and RSSCTs provide direct estimates of the volume of water that can be treated in the column or adsorbent bed before arsenic in the effluent exceeds the MCL or other desired concentrations. However, the RSSCTs can only be performed by highly trained specialists, and the pilot tests are relatively expensive and take long times to obtain direct measurements of the treatment capacity. The results of both these tests may be subject to physical effects such as channeling and provide little direct information about plant operations. Batch sorption measurements are relatively rapid and inexpensive; they provide information about the equilibrium sorption capacity and kinetics of uptake of arsenic by relatively small particles. However, the results are not accurate indicators of the long-term performance of the media in full-scale treatment systems because they do not provide direct measurement of the shape of the mass transfer zone within an absorbent media column. In addition, they do not capture the effects of changes in the influent arsenic concentration on capacity.

The Sandia National Laboratories pilot demonstration at the Socorro Springs site obtained arsenic removal performance data for five different adsorptive media under constant ambient flow conditions; results for three of the media are reported here. Two iron oxyhydroxide phases were examined: E33 is composed of granules of a mixture of iron oxyhydroxide phases, whereas in ArsenX^{np}, nanoparticulate iron oxide is dispersed within an ion-exchange resin. The third medium, MetSorb, is a granular titanium oxyhydroxide. Test water was taken from blended well water at Socorro Springs. The water has approximately 50 ppb arsenic in the oxidized [arsenate, As(V)] redox state, with moderate amounts of silica, low concentrations of iron and manganese, and a slightly alkaline pH (about 8).

The amount of arsenic sorption by the media was studied using different methods to allow a clearer comparison of the relative performance. For the flow experiments (pilot and RSSCTs), a measurement was made of the number of bed volumes of water passing through the media columns until the regulatory limit [10 ppb (10 μg/L)] in the effluent was exceeded. For both the batch tests and the flow experiments, the sorption capacity of the media (amount of arsenic adsorbed by the media) when the treated water reached 10 ppb (10 μg/L) was also calculated or measured. For flow experiments, the capacities were calculated from the mass balance on arsenic data by integration of the area above the BTC and below the influent arsenic concentration; these may be a more unbiased measure of sorption than the BV value. For batch tests, a sorption isotherm was fit to the data, and a capacity was calculated at 10 ppb (10 μg/L) or other values. In general, in the batch sorption studies, the media were ground to a smaller particle size than that used in the pilot test to minimize the effects of mass transfer within the grains and thereby reduce the time required to reach steady state. The batch equilibration time of 24 hours was based on kinetic studies. Freundlich isotherms could be fit to sorption data from all of the media.

For pilot tests using the EBCTs recommended by the vendors, the BV value and capacity at 10 ppb (10 μg/L) arsenic show a fairly consistent relationship among the adsorptive power of the media: E33 > ArsenX^{np} > MetSorb. For the Freundlich isotherm, the order of calculated sorption capacity in equilibrium with a solution with 10 ppb arsenic was E33 > ArsenX^{np} > MetSorb. Because the batch studies were designed to minimize kinetic and mass transfer rate effects, they provided upper limits to the arsenic adsorption capacity of the media. The capacities calculated in the Freundlich isotherms at 10 ppb (10 μg/L) were 1.4 to 3.4 times the values measured in the pilot tests.

Rapid small-scale column tests (RSSCTs) are scaled-down columns packed with smaller-diameter adsorption media that receive higher hydraulic loading rates to reduce the duration of experiments significantly. The PD RSSCTs were accurate predictors of the media capacity for pilot tests for E33, MetSorb, and ArsenX^{np} media (within 5%).

The Klinkenberg analytical solution to the mass transfer equation of arsenic adsorption in a packed column can reasonably describe the adsorption breakthrough behavior of arsenic in E33 and MetSorb. Only two adjustable parameters—overall mass transfer coefficient k and the Henry's Law constant K—are needed in this model for predicting the adsorption breakthrough curve, adsorbate concentration profile inside the column, and adsorbent loading inside the column. The results suggest that the Klinkenberg equation calibrated on a single RSSCT might be used to provide reasonable estimates of pilot-scale performance for a range of EBCTs. In this study the predicted breakthrough time is within 20% error of the experimental values obtained in the pilot tests. The model was also able to qualitatively predict the shape of the mass transfer zone by calculating the arsenic concentration profile in the pore fluids of spent core from pilot test column SC-10.

Laboratory tests (batch sorption and RSSCTs) are much less expensive to conduct than pilot tests and provide reasonable qualitative predictions of field-scale performance. The results of this project suggest that laboratory studies could be useful to communities that cannot afford to carry out comparative pilot tests of multiple media, especially if other information about backwash requirements and costs (capital and labor) are already available. The goal of future work is to combine sorption data obtained at another site (Anthony) with the mass transfer coefficient obtained from the Klinkenberg model from the Socorro study to see if breakthrough profiles can be predicted at the second site. Effort will also be devoted to model the adsorption breakthrough behavior with a nonlinear adsorption isotherm and multiple pore diffusion resistances.

APPENDIX

Effective Diffusivity in Adsorbent Particles

To extract the effective diffusivity of arsenic in the macropores of E33, a diffusion equation for a macropore-controlled system can be obtained from a differential mass balance on a spherical shell element of the adsorbent particle (Ruthven, 1984):

$$(1-\varepsilon_p)\frac{\partial q}{\partial t} + \varepsilon_p \frac{\partial c}{\partial t} = \varepsilon_p D_p \left(\frac{\partial^2 c}{\partial R^2} + \frac{2}{R}\frac{\partial c}{\partial R}\right) \tag{A.1}$$

where ε_p is the adsorbent particle porosity, $q(R,t)$ the adsorbed phase concentration (µg/L of adsorbent), t (s) the time, c (µg/L) the adsorbate concentration in the supernate, D_p (cm^2/s) the macropore diffusivity of adsorbate in the adsorbent, and R (cm) the radial distance from the center of the adsorbent particle. The macropore diffusivity (D_p) is assumed to be independent of concentration in equation (A.1).

If the adsorption equilibrium is linear [$q = Kc$, where K is the dimensionless Henry's Law adsorption equilibrium constant defined as a ratio of adsorbed phase concentration per unit volume of particle (µg/L) to adsorbate concentration (µg/L)], equation (A.1) can be rewritten as

$$\frac{\partial c}{\partial t} = D_e \left(\frac{\partial^2 c}{\partial R^2} + \frac{2}{R} \frac{\partial c}{\partial R} \right) \tag{A.2}$$

where D_e (cm^2/s) is the effective diffusivity, defined by

$$D_e = \frac{\varepsilon_p D_p}{\varepsilon_p + (1 - \varepsilon_p) K} \tag{A.3}$$

The initial and boundary conditions for a step change in the feed and surface concentrations are

$$\begin{gathered} c(R, 0) = c_0' \qquad q(R, 0) = q_0' \\ c(R_p, t) = c_0 \qquad q(R_p, t) = q_0 \\ \left(\frac{\partial c}{\partial R} \right)_{R=0} = \left(\frac{\partial q}{\partial R} \right)_{R=0} = 0 \end{gathered} \tag{A.4}$$

where R_p (cm) is the adsorbent particle radius, c_0' the initial adsorbate concentration at a given location R, c_0 the adsorbate concentration at the particle surface, and at a given time t, q_0' the initial adsorbed phase concentration at a given location R and is the adsorbed phase concentration at the particle surface and at a given time $t (q_0 = K c_0)$.

The analytical solution for equation (A.2) with the initial and boundary conditions defined by equation (A.4) is given by Crank (1976) and Ruthven (1984):

$$\frac{\overline{q} - q_0'}{q_0 - q_0'} = \frac{M_t}{M_{\max}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(-\frac{n^2 \pi^2 D_e t}{R_p^2} \right) \tag{A.5}$$

where $\overline{q}$ **(t)** (µg/L) is the average adsorbed phase concentration through the particle, M_t (µg/L) the mass gain of adsorbent at time t, and $M_{\max}$ (µg/L) the mass gain of adsorbent at infinite time.

For fractional adsorption uptake $M_t / M_{\max}$ above 70%, equation (A.5) can be simplified by using only the first term with a 2% error:

$$\frac{M_t}{M_{\max}} \cong 1 - \frac{6}{\pi^2} \exp \left(\frac{\pi^2 D_e t}{R_p^2} \right) \tag{A.6}$$

This solution for the fractional adsorption uptake was used to correlate the adsorption kinetics data shown in Figure 6. A plot of ln[1 − $(M_t / M_{\max})$] versus time generates a straight line with a slope of $-\pi^2 D_e / R_p^2$ and an intercept of ln $\left(6/\pi^2\right)$, from which the effective diffusivity D_e, for arsenic diffusion in the macropores of the meddia was calculated. D_e/R_p^2 is the diffusion time constant (s^{-1}) that measures the diffusion rate of an adsorbate in porous media. A large diffusion time constant suggests a slow diffusion rate of adsorbate molecules in the porous media.

Rapid Small-Scale Column Tests

Theory Laboratory studies to predict media performance of pilot-scale adsorption columns were conducted using rapid small-scale column tests (RSSCTs). RSSCTs are scaled-down columns packed with smaller-diameter adsorption media that receive higher hydraulic loading rates to reduce the duration of experiments significantly. Results for RSSCTs can be obtained in a matter of days to a few weeks, whereas pilot tests can take a number of months to over a year. This method uses scaling relationships that allow correlation of lab-scale column results operated at accelerated flow rates to full-scale column performance. The RSSCT concept is based on a theoretical analysis of the adsorption processes that govern performance, including solution and surface mass transport and adsorption kinetics. Mass transfer models have been used to determine dimensionless parameters that establish similitude between the small- and large-scale columns.

If perfect similitude is maintained, the RSSCTs will have breakthrough profiles that are identical to full-scale columns (Crittenden et al., 1987a). Two mass transfer models are most frequently used to model adsorption columns, the dispersed flow pore and surface diffusion model (DFPSDM), and the homogeneous surface diffusion model (HSDM). The most general model, the DFPSDM, includes pore diffusion and surface diffusion as well as axial dispersion. This model includes many of the known transport and kinetic phenomena that occur in fixed-bed adsorbents; therefore, a dimensional analysis allows the development of scaling factors. The HSDM models surface diffusion while neglecting pore diffusion and axial dispersion. It has been shown that surface diffusion is much greater than pore diffusion for strongly adsorbed species (Hand et al., 1983); therefore, the contribution of pore diffusion to the adsorbate transport has been neglected.

Crittenden et al. (1987a,b, 1991) developed scaling equations for both constant and nonconstant diffusivities with respect to particle size. The scaling laws ensure that the RSSCT and the full-scale system will have identical breakthrough profiles. The basis for the RSSCT scaling laws is described below; variables are defined in Table A.1; definitions of the terms are given in Aragon (2004).

By equating the modulus of surface diffusivity and assuming equal solute distribution parameters, a relationship between EBCTs for small- and large-scale columns is determined:

$$\frac{\mathrm{EBCT_{SC}}}{\mathrm{EBCT_{LC}}} = \left[\frac{R_{\mathrm{SC}}}{R_{\mathrm{LC}}}\right]^2 \frac{D_{s,\mathrm{LC}}}{D_{s,\mathrm{SC}}} \tag{A.7}$$

The dependence of the surface diffusion coefficient on particle radius is defined by the diffusivity factor, x, as follows:

TABLE A.1 Definition of Terms for RSSCT Scaling Equations

D_s	Surface diffusion coefficient, L^2/T
EBCT	Empty bed contact time, T
k_f	Film transfer coefficient, L/T
LC	Subscript denoting large column
R	Particle radius (geometric mean), L
Pe	Peclet number (dimensionless)
Re	Reynolds number (dimensionless)
SC	Subscript denoting small column
Sc	Schmidt number (dimensionless)
x	Diffusivity factor (dimensionless)
ε	Void fraction (dimensionless)
μ	Viscosity of the fluid, M/LT
v	Superficial velocity (hydraulic loading, Darcy velocity), L/T

$$\frac{D_{s,\mathrm{SC}}}{D_{s,\mathrm{LC}}} = \left[\frac{R_{\mathrm{SC}}}{R_{\mathrm{LC}}}\right]^x \tag{A.8}$$

Combining these equations yields

$$\frac{\mathrm{EBCT_{SC}}}{\mathrm{EBCT_{LC}}} = \left[\frac{R_{\mathrm{SC}}}{R_{\mathrm{LC}}}\right]^{2-x} \tag{A.9}$$

A special case of nonconstant diffusivity is a linear relationship between surface diffusivity and particle size (proportional diffusivity, PD). The diffusivity factor, x, becomes equal to 1 and the ratio of EBCTs becomes

$$\frac{\mathrm{EBCT_{SC}}}{\mathrm{EBCT_{LC}}} = \frac{R_{\mathrm{SC}}}{R_{\mathrm{LC}}} \tag{A.10}$$

A minimum value of $\mathrm{Re_{SC}}$ is required to establish a minimum velocity that will not overexaggerate the effects of dispersion and external mass transfer. If the small and large columns maintain a constant ratio of their respective Reynolds numbers, the following relation is established:

$$\frac{Re_{\mathrm{SC,min}}}{Re_{\mathrm{LC}}} = \frac{2v_{\mathrm{SC}}R_{\mathrm{SC}}/\mu\varepsilon}{2v_{\mathrm{LC}}R_{\mathrm{LC}}/\mu\varepsilon} \tag{A.11}$$

Canceling terms and rearranging gives the ratio of the hydraulic loading of the two columns:

$$\frac{v_{\mathrm{SC}}}{v_{\mathrm{LC}}} = \frac{R_{\mathrm{LC}}}{R_{\mathrm{SC}}}\frac{\mathrm{Re_{SC,min}}}{\mathrm{Re_{LC}}} \tag{A.12}$$

Berrigan (1985) showed that dispersion was not important if the product of the Reynolds and Schmidt numbers was in the mechanical dispersion region; therefore, the ratio of hydraulic loadings could be calculated using

$$\frac{v_{\mathrm{SC}}}{v_{\mathrm{LC}}} = \frac{R_{\mathrm{LC}}}{R_{\mathrm{SC}}} \frac{\mathrm{Re}_{\mathrm{SC,min}}\mathrm{Sc}_{\mathrm{SC}}}{\mathrm{Re}_{\mathrm{LC}}\mathrm{Sc}_{\mathrm{LC}}} \tag{A.13}$$

A requirement for using this equation is that the small-scale column Peclet number ($\mathrm{Pe}_{\mathrm{SC}}$) be greater than or equal to $\mathrm{Pe}_{\mathrm{LC}}$; otherwise, a reduction in the hydraulic loading may cause a significant amount of dispersion in the RSSCT.

If the surface diffusivity remains constant with respect to the particle radius (constant diffusivity, CD), the diffusivity factor, x, is equal to zero and the ratio of EBCTs for small columns and large columns is

$$\frac{\mathrm{EBCT}_{\mathrm{SC}}}{\mathrm{EBCT}_{\mathrm{LC}}} = \left[\frac{R_{\mathrm{SC}}}{R_{\mathrm{LC}}}\right]^2 \tag{A.14}$$

The Stanton and Peclet numbers remain equal between the small- and full-scale columns only if the surface diffusivity is independent of particle size (Aragon, 2004). If Stanton numbers are identical between process sizes, the liquid-phase mass transfer coefficients can be related to particle radius by

$$\frac{k_{f,\mathrm{SC}}}{k_{f,\mathrm{LC}}} = \frac{R_{\mathrm{LC}}}{R_{\mathrm{SC}}} \tag{A.15}$$

If this is the case, the hydraulic loading of the columns is inversely proportional to particle size (Crittenden et al., 1987a):

$$\frac{v_{\mathrm{SC}}}{v_{\mathrm{LC}}} = \frac{R_{\mathrm{LC}}}{R_{\mathrm{SC}}} \tag{A.16}$$

This relationship will provide equality between Reynolds numbers for both process sizes.

RSSCT Design The scaling equations discussed above were used to design the RSSCTs. The following input parameters were necessary for the design calculations:

- Particle radius, R (cm)
- Column diameter, d (cm)
- Bulk density, ρ (g/mL)
- Pilot empty bed contact time, $\mathrm{EBCT}_{\mathrm{pilot}}$ (min)
- Estimated bed volumes to be processed (BV)
- Pilot flow rate, Q (gpm)
- Liquid viscosity, μ (Pa · s)
- Liquid density, ρ (kg/m^3)
- Free liquid diffusivity, D_l (m^2/s)
- Bed porosity, ϵ

Equations used for input and design calculations are shown in Table A.2.

TABLE A.2 Input and Design Calculations for RSSCTs

Parameter	Pilot	RSSCT (PD)
Column area, A	$\dfrac{\pi d^2}{4}$	$\dfrac{\pi d^2}{4}$
EBCT	Input	$\text{EBCT}_{\text{pilot}} \dfrac{R_{\text{PD}}}{R_{\text{pilot}}}$
Hydraulic loading rate, v	$\dfrac{Q}{A}$	$V_{\text{pilot(m/h)}} \dfrac{R_{\text{pilot}}}{R_{\text{PD}}} \dfrac{\text{ReSc}_{\text{PD}}}{\text{ReSc}_{\text{pilot}}}$
Particle diameter, D_p	$R_{\text{pilot}} \cdot 2$	$R_{\text{PD}} \cdot 2$
Reynolds number, Re	$\dfrac{\rho v D_p}{\mu \varepsilon}$	$\dfrac{\rho v D_p}{\mu \varepsilon}$
Schmidt number, Sc	$\dfrac{\mu}{\rho D_l}$	$\dfrac{\mu}{\rho D_l}$
Flow rate, Q	$v_{\text{pilot}} A$	$v_{\text{PD}} A$
Bed volume, V_{bed}	$\text{EBCT} \cdot Q$	$\text{EBCT} \cdot Q$
Bed height, h_{bed}	$\dfrac{\text{Vol}_{\text{bed}}}{A}$	$\dfrac{\text{Vol}_{\text{bed}}}{A}$
Mass of media, M	$\text{Vol}_{\text{bed}} \cdot \rho_b$	$\text{Vol}_{\text{bed}} \cdot \rho_b$
Water required, $L_{\text{req'd}}$	$\text{BV} \cdot \text{Vol}_{\text{bed}}$	$\text{BV} \cdot \text{Vol}_{\text{bed}}$
Duration of experiment	$\dfrac{L_{\text{req'd}}}{Q}$	$\dfrac{L_{\text{req'd}}}{Q}$

Klinkenberg Solution

Modeling Adsorption Breakthrough in a Packed Column A simple mathematical model can be derived from the mass balance of an adsorbent bed element. The partial differential equation governing adsorption breakthrough dynamic behavior can be written as (Zouboulis and Katsoyiannis 2002; Seader et al., 2006)

$$D_L \frac{\partial^2 c}{\partial z^2} + \frac{\partial (uc)}{\partial z} + \frac{\partial c}{\partial t} + \frac{1-\varepsilon_b}{\varepsilon_b} \frac{\partial \overline{q}}{\partial t} = 0 \tag{A.17}$$

where D_L (cm^2/s) is the axial dispersion coefficient of adsorabte molecules, z (cm) the distance coordinate in the flow direction, c (μg/L) the adsorabte (arsenic) concentration, u (cm/s) the interstitial fluid velocity, e_b the porosity of the adsorbent bed, t (s) the time, and $\overline{q}$ (μg/L) the average adsorbed phased concentration in the adsorbent particle.

Klinkenberg solved equation (A.17) and obtained a simple solution for the adsorption breakthrough curve based on the following assumptions (Klinkenberg, 1948; Zouboulis and Katsoyiannis 2002; Seader et al., 2006): (1) an isothermal condition, (2) no axial dispersion, (3) a linear driving force for mass transfer, and (4) linear adsorption equilibrium.

$$\frac{c}{c_F} \approx \frac{1}{2}\left[1 + \text{erf}\left(\sqrt{\tau} - \sqrt{\xi} + \frac{1}{8\sqrt{\tau}} + \frac{1}{8\sqrt{\xi}}\right)\right] \tag{A.18}$$

$$\xi = \frac{kKz}{u}\frac{1-\varepsilon_b}{\varepsilon_b} \tag{A.19}$$

$$\tau = k\left(t - \frac{z}{u}\right) \tag{A.20}$$

$$\overline{q}(t) = \frac{1}{R_p^3}\int_0^{R_p} q(R,t)R^2\,dR \tag{A.21}$$

$$\frac{\overline{q}}{q_F^*} \approx \frac{1}{2}\left[1 + \operatorname{erf}\left(\sqrt{\tau} - \sqrt{\xi} - \frac{1}{8\sqrt{\tau}} - \frac{1}{8\sqrt{\xi}}\right)\right] \tag{A.22}$$

where c_F is the influent adsorbate concentration, τ the dimensionless time coordinate, ξ the dimensionless distance coordinate, k the overall mass transfer coefficient (min^{-1}), K the dimensionless Henry's law adsorption equilibrium constant, $q(R,t)$ (µg/L) the adsorbed phase concentration inside a spherical adsorbent particle at location R and time t, R_P the adsorbent particle radius, and q_F^* (µg/L) the equilibrium capacity calculated from $q_F^* = Kc_F$.

Equation (A.18) is an analytical solution of the ratio of the adsorbate concentration in the fluid phase to that of influent at a given location (z) and a given moment (t), and equation (A.22) is an analytical solution of the ratio of adsorbent loading to the equilibrium adsorption amount at a given location (z) and a given moment (t). If the overall mass transfer coefficient k and Henry's Law constant K are known, it is possible to predict:

1. The adsorption breakthrough curve at the bed exit or any location inside the column [(C/C_F) vs. t]
2. concentration profile inside the column [(C/C_F) vs. z] at any time t
3. adsorbent loading inside the column ($\overline{q}$ vs. z) at any time

Acknowledgments

The Arsenic Water Technology Partnership (AWTP) program is a multiyear program funded by a congressional appropriation through the Department of Energy to develop and test innovative technologies that have the potential to reduce the costs of arsenic removal from drinking water. The AWTP members include Sandia National Laboratories, the American Water Works Association (AWWA) Research Foundation, and WERC (a Consortium for Environmental Education and Technology Development). The cooperation and support of members of the Arsenic Water Technology Partnership, including Abbas Ghassemi and Rose Thompson (NMSU) and Albert Ilges (AwwaRF), are gratefully acknowledged.

The contributions of several co-workers are also gratefully recognized: Randy Everett, Brian Dwyer, Justin Marbury, Richard Kottenstette, Pamela Puissant, Jerome Wright, Emily Wright, Katharine North (Sandia National Laboratories), Carolyn Kirby (Comforce Technical Services, Inc.), Frederick Partey, and Dave

Norman (New Mexico Tech). The adsorptive media used in this study were obtained from Graver Technologies, Purolite Company, and Adedge Technologies, Inc.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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11

ARSENIC REMEDIATION OF BANGLADESH DRINKING WATER USING IRON OXIDE–COATED COAL ASH

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INTRODUCTION

In this chapter we describe a novel process for removing arsenic from water. The process is based on using fine particles of coal bottom ash, the ash left at the bottom of a coal-fired boiler after the combustible matter in coal has been burned off, that have been coated with iron oxide.

Relevant Literature on Arsenic Removal from Drinking Water Several approaches have been investigated for removing arsenic from drinking water. Useful reviews of techniques for removing arsenic from water supplies have been presented by Bissen and Frimmel (2003), Ng et al. (2004), and Johnston and Heijnen (2001). Processes that have demonstrated successful arsenic removal include coagulation with ferric chloride or alum followed by filtration (e.g., Hering et al., 1997), removal with iron oxide–coated sand (e.g., Thirunavukkarasu et al., 2003) or iron-impregnated sand (Vaishya and Gupta 2003), direct adsorption on metallic (zero-valent) iron (e.g., Ramaswamy et al., 2001; Campos, 2002; Bang et al., 2005), and adsorption on treated zeolites (e.g., Campos and Buchler, 2006), iron-chelated resins (Rau et al., 2003), or granulated ferric hydroxide (e.g., Badruzzaman et al., 2004; Pal, 2001). Other studies have addressed removal by

Arsenic Contamination of Groundwater: Mechanism, Analysis, and Remediation,
Edited by Satinder Ahuja

membranes or biomembranes (e.g., Velizarov et al., 2004). Daus et al. (2005) report experiments comparing five media, including metallic iron, for adsorptive removal of arsenic from drinking water.

Katsoyiannis and Zouboulis (2002) report experiments using modified polymer beads coated with iron oxides to remove arsenic from water. Although their work is similar to the work reported here, they used synthetic polymer beads, which are significantly more expensive than the substrate explored here. They also used a different method for depositing iron oxides than the one examined here. The method used to deposit iron hydroxide on the substrate surface has been shown to affect the adsorptive capacity of the resulting media significantly (Westerhoff et al., 2006).

CHEMISTRY OF THE ARSENIC REMOVAL PROCESS

The primary ingredients of bottom ash are oxides and complexes of silicon, calcium, iron, aluminum, and magnesium. Bottom ash is the finely powdered residue left after combustion of anthracite and bituminous coal in power plant boilers. Under scanning electron microscope, the ash particles from Indian power plants are revealed to be mostly spherical with smooth glasslike surfaces. This surface morphology is consistent with the ash being heated to near its melting point during the combustion process.

Basic unit operations for this process take place in two stages. The first-stage unit operations involve preparing the arsenic removal medium. Bottom ash (residue left at the bottom of the boiler from coal-fired power plants) is washed and mixed with a solution of ferrous sulfate (0.6 M), and excess solution is decanted. The wet residue is mixed with a dilute solution of sodium hydroxide (0.1 M). Excess solution is again decanted. The residue is dried in air, water-washed several times (usually, four or five), and dried in air again. At this point, the arsenic removal medium, bottom ash coated with ferric hydroxide, is ready. The coated bottom ash is referred to in this chapter as ARUBA (arsenic removal using bottom ash) dust. The reactions involved in the first stage of our process are outlined below in a simplified form, using $Fe(OH)_3$ to represent any of the possible hydrated ferric hydroxides or oxyhydroxides that may be involved.

1. Ash is soaked in $FeSO_4$ solution, depositing hydrated Fe^{II} on the ash surface. The unknown extent of hydration is indicated by x, and $\text{Ash}\cdot\,\text{Fe}(\text{H}_2\text{O})^{2+}_{x,s}$ represents the hydrated ferrous ion on the ash surface:

$$\text{Ash}_s \quad + \text{Fe}^{2+} \quad + x\text{H}_2\text{O} \rightarrow \text{Ash} \cdot \text{Fe}(\text{H}_2\text{O})^{2+}_{x,s} \tag{1}$$

2. OH^- displaces water ligands to produce ferrous hydroxide on the ash surface:

$$\text{Ash} \cdot \text{Fe}(\text{H}_2\text{O})^{2+}_{x,s} \quad + 2\text{OH}^- \quad \rightarrow \text{Ash} \cdot \text{Fe}(\text{OH})_{2,s} \quad + x\text{H}_2\text{O} \tag{2}$$

3. During the drying process, exposure to air oxidizes the ferrous hydroxide to ferric hydroxide on the ash surface. The molar ratios of oxygen, water, and H^+ are indicated below by y, z, and m, respectively.

$$\mathrm{Ash} \cdot \mathrm{Fe^{II}(OH)_{2,\mathit{s}}} + y\mathrm{O_2} + z\mathrm{H_2O} \rightarrow \mathrm{Ash} \cdot \mathrm{Fe^{III}(OH)_{3,\mathit{s}}} + m\mathrm{H^+} \qquad (3)$$

Quantities of reactants used in the first stage: One gram of ARUBA dust contains about 0.5 g of coal ash and about 0.5 g of $Fe(OH)_3$ (all weights after drying in laboratory room air, in a fumehood). This leads to an estimate of 0.7 g of $FeSO_4$ and 0.4 g of NaOH consumed in making 1 g of ARUBA dust. We have demonstrated that the decanted (and thus recovered) quantities of $FeSO_4$ and NaOH solutions can be reused for coating up to three successive subsequent batches of coal ash. Figure 1 shows images of uncoated and coated bottom ash.

The second stage involves mixing the ARUBA dust with arsenic-laced water. Arsenic binds to ferric hydroxide on the ash surface as insoluble adsorbed ferric arsenate. The solid residue, spent ARUBA dust, is filtered out of the processed water. The chemical reactions for arsenic removal in the second stage can be described by these simple equations, but the actual mechanisms are likely to be much more complex:

1. Fe^{III} on the ash surface may oxidize As^{III} to As^{V}, as indicated in this simplified reaction:

$$\mathrm{H_3As^{III}O_3} + 2\mathrm{Ash} \cdot \mathrm{Fe^{III}(OH)_{3,\mathit{s}}} \rightarrow \mathrm{As^{V}O_4}^{3-} + 2\mathrm{Ash} \cdot \mathrm{Fe^{II}(OH)_{2,\mathit{s}}} + 3\mathrm{H^+} + \mathrm{H_2O} \qquad (4)$$

Dissolved oxygen will also oxidize As^{III} and Fe^{II}.

2. Formation of insoluble adsorbed ferric arsenate on the ash surface:

$$\mathrm{Ash} \cdot \mathrm{Fe^{III}(OH)_{3,\mathit{s}}} + \mathrm{As^{V}O_4}^{3-} \rightarrow \mathrm{Ash} \cdot \mathrm{Fe^{III}As^{V}O_4} + 3\mathrm{OH^-} \qquad (5)$$

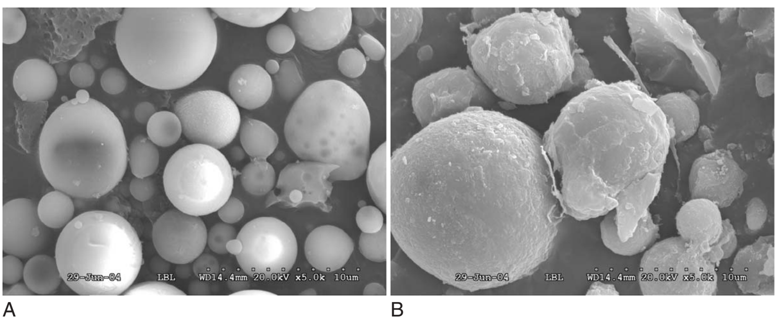

Figure 1 Bottom ash (A) before and (B) after coating with ferric oxide. The 11 square dots near bottom right of each figure span a distance of 10 μm.

We believe that arsenic removal by ARUBA dust is more complex than equation (5) suggests, because the pH usually decreases somewhat after the laboratory-prepared *challenge water* (made using the Grainger Challenge Water recipe, published in 2006 by the National Academy of Engineering) has been treated with ARUBA dust.

Quantities of reactants used in the second stage: We first tested ARUBA dust for the capacity to remove As^V (as sodium arsenate) dissolved in deionized water. Our results from these experiments show that 1 g of ARUBA dust made from Indian bottom ash removes 1 mg of elemental As^V before the endpoint equilibrium concentration of arsenic in water exceeds 10 ppb. The process is not yet optimized, and not all batches turn out to perform identically. Conservatively, we use a capacity of removal of 0.7 mg of As^V per gram of ARUBA dust, although some batches have shown performance as high as 1 mg of As^V per gram of dust. Assuming the 0.7-mg figure, 1 g of ARUBA dust can remediate As^V from 2.3 L of water with initial $[As^V] = 300$ ppb to a final concentration of less than 10 ppb over a period of about an hour. If the target endpoint equilibrium concentration of arsenic in the water is allowed be higher (e.g., 50 ppb), the As^V removal capacity of ARUBA dust is much greater.

The challenge water is comprised of As^{III} and As^V at 150 ppb each, with 2 mg/L $FeSO_4$, and low dissolved oxygen (less than 3 mg/L). Note that this recipe does not incorporate other competing ions (e.g., silicate, phosphates), which could reduce adsorption performance. However, we report laboratory results using this recipe since it has the benefit of being published widely. Laboratory stock deionized water was used to prepare the challenge water. The level of dissolved oxygen in the challenge water was maintained at about 2 mg/L by purging it with argon or N_2. We found that ARUBA dust (1.5 g/L) succeeds in reducing arsenic in the challenge water from $[As^{III} + As^V] = 300$ ppb to < 50 ppb in less than 10 minutes.

Finally, we report results from application of the ARUBA process to remove arsenic from groundwater in a field setting by traveling to Bangladesh to conduct experiments. These experiments in the field (with measurements of samples conducted both in Bangladesh and Berkeley) demonstrated the effectiveness of ARUBA in reducing arsenic concentrations to acceptable levels, but also demonstrated, as expected, reduced capacity for arsenic removal per gram of ARUBA dust with real Bangladesh waters than with the challenge water.

TESTING FOR TOXIC METALS LEACHING FROM THE ARUBA DUST

Investigating Trace Metal Contamination from Unspent (Fresh) Media

An important issue in using coal ash as a media substrate is the possibility that the ash itself might contaminate the treated water with other leachates (e.g., heavy metals), even while it removes the arsenic.

Physical and chemical characterizations of coal ash samples were reviewed by Kim (2003a). The literature (e.g., Walia, 1995; Sheps-Pelig and Cohen, 1999; Daniels et al., 2002; Kim et al., 2003) identifies 20 toxic or objectionable metal leachates from coal ash from the United States, India, and Israel, as follows: aluminum, antimony, arsenic, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, potassium, selenium, silicon, titanium, and zinc. Methods for creating leachates from samples of coal ash were reviewed by Kim (2003b).

Preparation of Leachates We searched for some of the elements listed above in water that was exposed to ARUBA. The first step is to ensure that no serious toxic elements leach from the substrate itself. Leachates were extracted at pH 3, 6, and 10 from untreated bottom ash by mixing the bottom ash with aqueous liquid equal to 10 times the weight of the ash, sonicating for 1 hour at 30° C, followed by filtration through ashless paper. Acetic acid and sodium carbonate were used to make the acidic and basic conditions, respectively. Before adjustment, the pH of laboratory deionized water was 6, due to dissolution of CO_2. All apparatus used in the extractions was borosilicate glass. In real-world applications, the bottom ash would be coated with ferric hydroxide, mixed with water at far higher dilution, with less forceful extraction.

The extracts were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) in the Environmental Measurement Laboratory of the Earth Sciences Division at Lawrence Berkeley National Laboratory (LBNL). The results are shown in Table 1 along with several standards that govern the acceptable concentration of each element in drinking water. Several of the standards for drinking water come from the U.S. Environmental Protection Agency (EPA).

TABLE 1 Leachates from Uncoated Bottom Ash Extracted at High Concentration in Aqueous Media of Various pH Values

Element	EPA MCLG[a] (ppb)	MCL (ppb)	WHO MCL (ppb)	NSF MCL (ppb)	Most Stringent Standard (ppb)	pH 3 (ppb)	pH 6 (ppb)	pH 10 (ppb)	Deionized Water (ppb)
Arsenic	0	10	10	10	10	88	17	33	1
Beryllium	4	4	—	—	4	1	<1	<1	<1
Cadmium	5	5	3	5	3	13	39	<1	1
Chromium	100	100	50	100	50	18	2	90	2
Copper	1300	1300	2000	1300	1300	17	30	16	9
Lead[b]	0	15	10	15	10	<10	<10	<10	<10
Selenium	50	50	10	50	10	17	6	8	<1

[a]MCLG, maximum contaminant level goals; MCL, maximum contaminant level.
[b]Lead has an "action level" of 15 ppb, but we have shown it under the MCL column.

Others have been established by the World Health Organization (WHO) and NSF International.

Toxicity Testing of Spent Media

Spent media are media that have adsorbed arsenic from water and must be discarded as waste. The spent media need to be tested against the possibility that they should not leach arsenic or other toxic chemicals and again contaminate the environment (e.g., see Ali et al., 2003; Badruzzaman, 2003). We tested the toxic chemical leaching from spent media prepared with U.S. fly ash substrate. The leachates from spent media were tested using EPA Method 1311 [Toxicity Characteristics Leaching Procedure (TCLP)].[1] The spent media were not toxic, based on the results of the TCLP.

EQUIPMENT FOR APPLICATION IN THE FIELD

The ARUBA process is currently at the laboratory stage with limited field data. At the time of this writing, it is under discussion regarding licensing for commercial application. The licensee will select a plan for ARUBA technology implementation and media delivery as integral components of the business plan.

We anticipate that in all cases, large-scale manufacture of ARUBA dust (the first stage of the chemical process) will be conducted at a centralized facility. Bottom ash used to make ARUBA dust is readily available; it is a sterile waste product from South Asian coal-fired power plants. The other chemicals needed are also locally available in Bangladesh and India.

We sketch here two alternative implementation models as possibilities for the second stage of the chemical process described earlier. In one approach to the provision of safe drinking water, small community-based safe water centers will be set up throughout the country, along a model currently demonstrated successfully in neighboring India by Water Health International (www.waterhealth.com). These centers, which may employ one or two local residents, treat local groundwater with ARUBA dust and make that water available for sale to local residents at a modest price. We estimate that 10 L of safe drinking water could be sold for less than $0.10 at a reasonable business profit. This price would be affordable to someone making about a dollar a day, and the price could be brought down if there is domestic or international aid for provision of safe and affordable drinking water.

A second possible approach may be to sell ARUBA dust through the existing supply channels of village grocery stores, much like tea, matchboxes, and other commodities. In the latter scenario, ARUBA dust will be sold with a measuring

[1]Testing done by Curtis and Tompkins Ltd., 2323 Fifth Street, Berkeley, CA 94710 (www.curtisandtompkins.com), a commercial laboratory certified for environmental chemical analysis by the California Department of Health Services, U.S. Air Force, U.S. Navy, U.S. Army Corps of Engineers, and other government organizations.

scoop, with instructions to add one scoop per bucket of water, and then filter out the spent media. For removing ARUBA dust, one could use a a household sand filter (e.g., a modified version of the biosand filter developed at the University of Calgary by David Manz). The filter could be preloaded with some ARUBA media to improve effectiveness. We have built and tested a prototype of the biosand filter at LBNL to confirm that it will trap ARUBA dust and let out only clear water with an acceptably low concentration of arsenic. However, we have not conducted life-cycle testing of the filter to its limit of loading and breakthrough. In any case, field testing and feedback from focus groups could change the method of choice for separating the spent medium from the treated water at the household level.

PERFORMANCE TESTING OF ARUBA DUST

Laboratory Testing

The ARUBA dust has undergone extensive testing, starting in late 2003 in a range of water environments, first with deionized laboratory water spiked with As^{V}, then with As^{III}, and finally, with challenge water. Arsenic concentrations were measured in near real time using initially AcuStrip (Acustrip Inc., Mountain Lakes, New Jersey) arsenic test strips and later with QuickTest arsenic test kits (Industrial Test Systems Inc., Rock Hill, South Carolina). Inductively coupled plasma mass spectrometry (ICP-MS) is used routinely for slower but more accurate measurements. We generally obtained good agreement between the results from the rapid methods (within their limits of accuracy) and those from ICP-MS. Note that QuickTest provides arsenic concentration estimates that are generally within (20% $\pm$ 2 ppb) of the high-quality ICP-MS results.

Capacity Laboratory results for the ability of ARUBA dust to remove arsenic are given in Table 2, expressed as mg (elemental) arsenic bound per gram of ARUBA dust, in equilibrium with 50 ppb of arsenic in solution, with the initial solutions being prepared with laboratory deionized water. These data show that ARUBA dust can remove about five times more As^{V} than As^{III} and about three times more As^{V} alone than in solutions with equal initial concentrations of each species. These data are consistent with results reported for arsenic removal by iron oxides.

TABLE 2 Arsenic Adsorption Capacity of ARUBA Dust for Laboratory Deionized Water

	As^{III}	As^{V}	As^{III}, As^{V}
Initial [As] (ppb)	300	2000–2240	150, 150
pH	6.6	4.7–5.6	6.6
Capacity (mg As/g ARUBA dust)	0.20 ± 0.05	1.0 ± 0.2	0.36 ± 0.07

We also note that these data are for arsenic-spiked deionized laboratory water. In real water with competing ions, the performance of ARUBA dust in removing arsenic will be lower, depending on the concentrations of various competing ions. Since the concentrations of competing ions vary from site to site, it is impractical to provide a single number for arsenic removal capacity of ARUBA dust in real waters.

Kinetics Figure 2 shows laboratory results for [As] versus time in challenge water treated with ARUBA dust at 1.0, 1.5, and 2.0 g/L. Challenge water was prepared from ACS-certified standards and had initial $[As^{III}] = 150$ ppb, $[As^{V}] = 150$ ppb, and $[Fe^{II}] = 2$ mg/L. The error bars are derived from replicated experiments. Challenge water was prepared daily from standard solutions and deionized water through which argon had flowed until the dissolved oxygen level dropped below 3 mg/L. Immediately after mixing the ARUBA dust and challenge water, the pH was measured and adjusted to 6.5 to 6.7 using dilute $NaHCO_3$ solution. Our results (not shown here) with individual solutions of As^{III} and As^{V} had shown that this pH range would give the best overall As removal when both species were present. (In the 2007 field tests described below, no such adjustment of pH was made. At the time of the laboratory testing in 2005, we believed that such pH adjustment will be needed in the field.) The ARUBA dust slurry was stirred for the time shown on the graph and then allowed to settle for at least 15 minutes before filtering. AcuStrip measurements were performed immediately and samples were collected for later ICP-MS.

The results show that 1.0 and 1.5 g ARUBA dust per liter of challenge water reduced total [As] to 80 and 40 ppb after 10 minutes of mixing, respectively. In contrast, 1.0 g ARUBA dust per liter of water with only As^{V} and an initial concentration of 400 ppb reduced the $[As^{V}]$ to between 5 and 10 ppb in

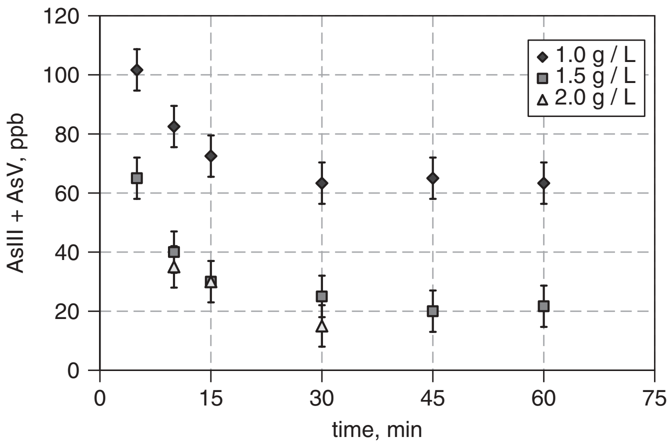

Figure 2 Kinetics of arsenic removal for various doses of ARUBA dust. [As] in treated water with initial $[As^{III} + As^{V}] = 300$ ppb and $[Fe^{II}] = 2$ ppm.

10 minutes. Although the ARUBA process is more effective in removing As^{V} than As^{III}, it does meet the challenge of reducing both species to below the target concentration of 50 ppb with inexpensive materials and simple methods.

Field Testing

Our efforts to procure stable samples of arsenic-contaminated groundwater from Bangladesh were fraught with problems. Some water samples arrived in Berkeley with a precipitate. In response, we consulted with experts from Bangladesh who advised that the samples should be digested on-site with nitric acid before being shipped to Berkeley. These samples were received in Berkeley clear (without a precipitate); however, adjusting the pH of these samples with NaOH solution to reflect field conditions again produced a precipitate.

In the spring of 2007, two graduate students at UC Berkeley (Susan Amrose and Johanna Mathieu) tested the effectiveness of ARUBA dust in removing arsenic from groundwater in Bangladesh by actually conducting experiments on-site. They first visited contaminated tube wells in five villages in Jhikargachha Upazila (Bangladeshi subdistrict) and Abhaynagar Upazila (both of the Jessore district in the Khulna division), where they treated water samples from eight different tube wells. Subsequently, they tested water samples from a tube well from another village in Sonargaon Upazila, just outside Dhaka. The objective of the trip was to demonstrate the ability of ARUBA dust to reduce the concentration of arsenic in Bangladeshi contaminated groundwater to below the Bangladeshi standard of 50 ppb.

Field Testing Methods Villages containing tube wells with high levels of arsenic were identified by BRAC, a Bangladeshi nongovernmental organization using the final report of their 1999–2000 arsenic study ("Combating a Deadly Menace: Early Experiences with a Community-Based Arsenic Mitigation Project in Bangladesh," published in August 2000). Contaminated tube wells were identified by consulting with local community leaders and BRAC employees. At each tube well, water samples were collected for further testing only if the initial screening test of the tube well's arsenic concentration (measured by QuickTest) were sufficiently high (in most cases, greater than 200 ppb). The samples were collected after pumping the tube well for 5 minutes to access the aquifer, not the water standing in the tube well column.

Samples were treated with ARUBA dust in the late evening or early the following morning. In one case, they also treated water with ARUBA dust 30 minutes after collection to ensure that the lag time between collection and treatment did not affect the results. Most commonly, there was a delay of several hours between sample collection and testing the effectiveness of ARUBA dust in arsenic remediation. The arsenic concentration in the water sample was checked again immediately before ARUBA dust treatment. At this time, they also prepared a sample for ICP-MS analysis in the United States.

Treatment of the water sample was undertaken by adding a single dose of ARUBA media (1 g) to 250 mL of water and shaking for 30 minutes. After filtration (using Whatman No. 1 filter paper), they measured the posttreatment arsenic concentration using the QuickTest and prepared another sample for ICP-MS. If the arsenic level did not go below 50 ppb after the first treatment, they repeated the treatment using a fresh water sample and twice as much ARUBA dust (2 g per 250 mL). In two cases, they treated with a quadruple dose of ARUBA dust (4 g per 250 mL). Note that quadruple doses were always given as two consecutive double doses; after initial treatment with a double dose, they added another double dose to the filtrate, as opposed to adding all 4 g at once. Also note that all these measurements were performed in the field with QuickTest (with its inherent lower accuracy). So sometimes the students stopped adding ARUBA dust, believing that a low enough arsenic concentration had been reached. However, for brevity we report in Table 3 only the more accurate results obtained with ICP-MS analysis of U.S. samples. This explains why the treated samples for wells 2 and 8 in Table 3 show concentrations higher than 50 ppb. We believe that if more ARUBA dust were added to these water samples in the field, arsenic concentrations lower than 50 ppb would surely have been obtained.

Field Testing Results The students collected a total of nine water samples from arsenic-contaminated tubewells in six different villages. In all cases, QuickTest indicated that they were able to reduce the amount of arsenic in the water to below the Bangladeshi standard of 50 ppb (see Figure 2 and Table 3). In three cases, a single dose of ARUBA dust was adequate, four cases required a double dose, and two wells with very high arsenic levels (greater than 500 ppb) required quadruple doses. The students did not attempt to reduce arsenic concentrations in each well to below the WHO standard of 10 ppb, but based on the extremely low arsenic values obtained after double and quadruple doses, we believe it possible with the addition of more ARUBA dust. Note, as explained above, that Table 3

TABLE 3 ICP-MS Measurements

Tube Well	Upazila	Union	Village	Initial Arsenic (ppb)	Final Arsenic (ppb)	Dose of ARUBA (g)
1	Jhikargachha	Godkhali	Kamalpoura	667	38	2
2	Jhikargachha	Godkhali	Jafornagar	433	62	2
3	Jhikargachha	Godkhali	Yousufpur	333	37	1
4	Jhikargachha	Godkhali	Patuapara	67	12	1
5	Abhaynagar	Prembug	Prembug	311	7	2
6	Abhaynagar	Prembug	Prembug	1067	3	4
7	Abhaynagar	Prembug	Prembug	344	32	2
8	Abhaynagar	Prembug	Prembug	356	58	1
9	Sonargaon	Aminpur	Bugmusha	522	17	4

shows the more accurate ICP-MS results, so some "final" concentrations are higher than the < 50 ppb indicated in the field by QuickTest. We believe that addition of more ARUBA dust would have brought the concentrations down to below 50 ppb in samples from wells 2 and 8.

Field Testing Conclusions In six of the eight samples of Bangladeshi groundwater collected from two geographically distinct areas of Bangladesh and across six different villages, the students successfully demonstrated the ability of ARUBA to reduce arsenic concentrations to below the Bangladeshi standard of 50 ppb. For water samples from the two remaining wells, numbers 2 and 8, where the final concentration measured with ICP-MS was above 50 ppb, a larger dose of ARUBA dust will certainly lower the concentration to below 50 ppb. They also demonstrated the feasibility in some samples of reducing arsenic concentrations in the water to below the WHO standard of 10 ppb by adding more ARUBA. As shown in Figure 3, the amount of ARUBA needed to treat arsenic-contaminated water is roughly proportional to the amount of arsenic in

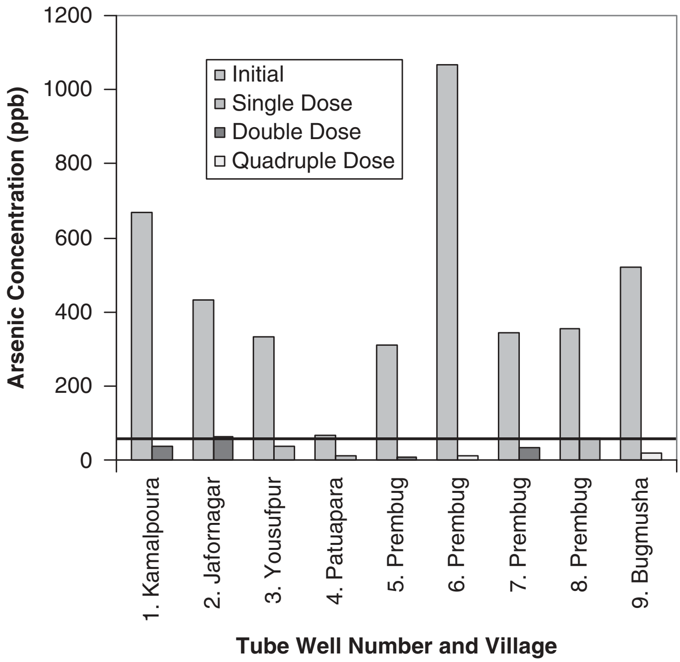

Figure 3 Arsenic concentrations of tube well water before and after treatment with ARUBA dust. Data are as measured with ICP-MS (with an accuracy of ±10%). In each case only the initial and final (lowest) concentrations are plotted. Colors of bars for posttreatment concentrations of arsenic for tube wells 4, 5, 6, and 9 may be difficult to discern. Posttreatment bar for well 4 is green (single dose); 5, red (double dose); and 6 and 9, yellow (quadruple dose). One dose is 1 g of ARUBA dust. (*See insert for color representation of figure*.)

the water. Therefore, with higher doses we believe that ARUBA should be able to remove arsenic to below the WHO standard in all cases.

MANUFACTURE, OPERATION, AND MAINTENANCE

Scaling up the manufacture of ARUBA dust from the laboratory benchtop scale to an industrial scale is a chemical engineering task yet to be undertaken. We estimate that sufficient coal ash is produced annually in South Asian power plants to supply the full requirement for all of arsenic-affected Bangladesh, should the market potential be realized. Once ARUBA dust has been procured, removing arsenic with it does not require advanced technical skills.

If the water is treated at the local safe water centers, the process would involve adding the requisite amount of ARUBA dust to a tank of water, which would be stirred gently (to avoid settling) for about an hour, followed by removal of ARUBA dust from the water by any of the standard methods (e.g., flocculation and coagulation, followed by settling and filtration, or simply settling followed by filtration).

If the water is treated at the individual household level, the end-user family would purchase a simple down-flow sand filter, and thereafter purchase ARUBA dust periodically. One concept of operation is that before collecting water from the local hand pump, a measured volume of ARUBA dust (calibrated to the degree of local arsenic contamination) is added to a recently rinsed empty collection bucket. The ARUBA dust will mix turbulently with the water while it is pumped into the bucket and while the bucket is transported back home. Once the user has returned home, the water collected is simply poured into the diffuser basin and the lid is replaced on the sand filter. Within a short period of time, the user obtains clear, arsenic-free water. The flow rate of the filter ranges from 12 to 25 L/h.

The filter requires maintenance when the flow rate becomes too slow (less than 8 L/h). Maintenance involves agitating the sand through gentle mixing or stirring to loosen the small trapped particles. Our best current estimate is that the sand (and spent ARUBA dust trapped in it) will need to be replaced twice a year.

RESIDUE MANAGEMENT

ARUBA dust removes arsenic by binding it to form ferric arsenate. Ferric arsenate is insoluble (pH 4 to 8 under nonreducing conditions) and thus is harmless enough for disposal in a landfill. The TCLP tests confirm this expectation. Spent ARUBA dust will be produced daily at the safe water centers or will be produced in those households treating their own drinking water, depending on how the second step of ARUBA application is implemented. The safe water center will be operated on a commercial basis, and the same supply chain that provides fresh ARUBA dust to the safe water center can be used to collect the spent ARUBA dust and ship it away to a landfill. As the sand in the household is used to trap ARUBA dust, the entire sand bed is treated as the residue of this arsenic removal process. When the sand bed becomes so clogged that agitation no longer restores the flow rate to acceptable levels, the sand must be replaced. Our best current estimate is that sand replacement must occur on a semiannual basis.

COSTS

The raw materials needed for the manufacture of ARUBA are FeSO4, NaOH, bottom ash, and industrial water for processing. We estimate that per kilogram of ARUBA, the cost of these materials adds up to $0.11. The addition of energy and labor costs, and packaging and shipping, might raise this to $0.50. Other costs of doing business (e.g., management salaries, interests on bank loans, marketing, and profit on equity) will raise the cost further.

If the first of the two dissemination models (safe water centers offering water for sale), each 10-L can of water will use up about 40 g of ARUBA (based on the field test data above, assuming no further improvements in ARUBA dust performance). If ARUBA dust is priced at $1 per kilogram, the price of ARUBA dust needed to clean up 10 L of water is $0.04. Salaries, other costs, and profit would add up to at most $0.06. In a pay-as-you-go model, this is affordable to a Bangladeshi making about a dollar a day.

SOCIAL ACCEPTABILITY

Different technical innovations have been observed to have different speeds of diffusion in social structures. Sociologists have studied the diffusion of innovations in societies for over a century, resulting in more than 5000 papers on this subject by 2003. Everett Rogers's book ontitled *Diffusion of Innovations* is widely considered the standard reference on the subject (Rogers, 2003). More specifically, the study of diffusion of innovations in societies in the developing countries spans about the past half century. Numerous detailed studies of diffusion of specific technologies in specific contexts have been analyzed in the literature to extract lessons that cut across technologies and contexts. We describe here the five attributes of technological innovation (from among a few dozens of attributes) that consistently emerge as the most relevant and important in influencing ease and speed of diffusion of innovation in social structures (in both industrialized and developing countries). These five top attributes are discussed below in the context of ARUBA technology.

1. *Relative advantage* (perceived relative advantage over nonadoption: can be economic or social convenience and/or satisfaction). Arsenic poisoning from drinking water is readily recognized to be a serious health threat by the exposed populations in Bangladesh and nearby regions of India and Nepal.

The advantages of drinking water free of arsenic are correctly perceived to be clear skin (free of hyperkeratosis) and a much lower risk of serious adverse health outcomes such as ulcers, gangrene, vascular disease, and cancer. The key question relates to what economic value end users place on avoiding these risks. This is important because the cost of arsenic-removal technology must be compatible with the perceived value placed on avoiding this risk. For example, bottled drinking water is widely understood to be free of arsenic, but its price is perceived to be too high compared to the value of risk avoided. A water and sanitation program (WSP) study conducted by the World Bank and BRAC entitled *Willingness to Pay for Arsenic-free, Safe Drinking Water in Bangladesh* addresses this question for the relevant population in Bangladesh and yields useful guidance regarding such valuation (Ahmad et al., 2003). The survey, which covered 2900 households (a family of five), concluded that the average value of arsenic-free water to households was \$2.04 to \$2.64 per month, which is equivalent to \$24.48 to \$31.68 per year. Our technology cost estimates are well within this valuation. The large relative advantage, and low cost compared to the value of risk avoidance, make ARUBA very likely to succeed in the field.

2. *Compatibility* (with existing social norms, past experience, and value systems). Purchasing either safe water at a central safe water center in a village, or purchasing ARUBA dust and treating the water collected at home does not clash with existing social norms or value systems as far as we can tell by discussion with Bangladesh and West Bengal residents and past residents. In the case of direct purchase of ARUBA dust, the at-home filtering will require education and explanation; however, no serious conflict is noted with existing social norms or practices. This is a strong positive feature of ARUBA. Purchasing the water at the village safe water center, or having safe water delivered to one's home for a small additional fee, also seem acceptable.
3. *Complexity* (difficulty of understanding the innovation or of acquiring new skills to use it). Fortunately, using ARUBA does not require acquiring new skills. The broad popular concept to be explained will be that this additive powder removes the toxic contaminant from water as a medicine removes a disease. Purchasing safe water from a central safe water center is the easiest thing to understand for a population that already purchases other household goods (and even an occasional soft drink) from the village grocery store. This is not difficult to explain or understand. Admittedly, home treatment (adding a spoonful of powder to the water, waiting a few minutes, and then removing the powder by filtering) is easy to comprehend, but it is somewhat less convenient.
4. *Trialability* (degree to which innovation can be experimented with on a limited basis). Some technical innovations lend themselves only to an all-or-none trial, such as signing up for a cell phone service contract. However, others can be experimented with on a limited basis (e.g., a new fertilizer can be tried on only a portion of a farm). ARUBA can be used easily on a

trial basis. Long-term commitment or a lock-in period (which can present a barrier to adoption) are nonexistent with ARUBA. In a village, a household can purchase arsenic-free water from a safe water center one week, and not purchase it the next week. In the market, packets of various sizes of ARUBA dust will be available for sale, and a new user will get some free samples. In either case, the users can try the technology without fear of a long-term financial or technical commitment. The high trialability of ARUBA adds to the ease of its social diffusion.

5. *Observability* (degree to which adoption of an innovation by one user can be observed by others in the social group). High observability of an innovation leads to validation of the innovation in the eyes of others in the social group, as well as opportunities for discussions about it in the social group. An example is the use in public of a transistor radio. On the other hand, low or minimal observability leads to lack of such validation and lack of opportunity for discussion (e.g., the choice of technology for contraception). Highly observable technologies diffuse faster and with more ease than others.

   In this regard, ARUBA falls somewhere in the middle. The routine purchase of safe water from a safe water center would be highly visible. The purchase of ARUBA dust from a public place would certainly be observable, although a bit less easily, and addition of a spoonful of ARUBA dust to an empty bucket brought to a hand pump will also be observable to others obtaining water at the same time. However, it will be less visible or observable than, say, a loud boom-box on the shoulders of a teenager—anyway, a rarity in rural Bangladesh.

The literature suggests that of these five important attributes, the first two (i.e., relative advantage and compatibility) are the two most critically important. We are pleased that ARUBA does not seem to face any social acceptability resistance in these two, and only a minor possible problem (if any) within the other three. Also, it is evident that a community-based treatment system meets the last three criteria much better than a household-based treatment system does.

FUTURE TASKS

We envision that the following preparatory tasks remain to be undertaken to launch ARUBA:

1. Conduct additional field testing on the product (e.g., range of pH and temperatures, media exposure duration, optimization of overall treatment protocol).
2. Design the manufacturing facility needed to mass-produce ARUBA dust successfully.

3. Identify and negotiate contracts to establish a supply chain, distribution network, and plant location.
4. Prepare and conduct market analysis in conjunction with the field tests to identify market segments and price sensitivity.
5. Begin community education programs in villages where field tests are being conducted.

SUMMARY AND CONCLUSIONS

We describe a method to coat particles of bottom ash (from South Asian coal-fired power plants) with complexes of iron oxides. The coating process and the raw materials are both low cost, resulting in a low estimated cost for the manufactured product (here called ARUBA dust). Laboratory measurements of arsenic-removal kinetics are presented for three different doses of ARUBA dust to arsenic-laced water, and these show that arsenic is removed from the water in tens of minutes. ARUBA dust was then transported to Bangladesh and used to treat samples of water from nine tubewells from six different villages from two widely separated locations within Bangladesh. We found that the (at this point unknown) trace chemical ions in the real waters in Bangladesh reduced the arsenic-removal performance of ARUBA dust by about a factor of 10 compared to that with synthetically constituted Bangladesh groundwater in the laboratory. Even under these conditions, we estimate that arsenic removal with ARUBA will remain highly affordable to average rural residents of Bangladesh. In all cases, ARUBA removed (or showed potential to remove) arsenic from groundwater to levels below the maximum comtaminat level (MCL) for arsenic in drinking water promulgated in Bangladesh.

We then review the open issues related to large-scale implementation of this technology in Bangladesh and discuss the remaining tasks and sociological parameters that will influence the social adoption of arsenic removal with ARUBA dust as a large-scale method to remove arsenic from drinking water in Bangladesh.

Acknowledgments

We gratefully acknowledge significant contributions to this research from many dedicated persons, especially Yanbo Pang, Ray Dod, Heena Patel, Ebere Chukwueke, Tasnuva Khan, Matthew Jeung, Clete Reader, Melissa Quemada, Duo Wang, Jeiwon Deputy, Meghana Gadgil, Susan Amrose, Johanna Mathieu, Girish Champhekar, Rajesh Shah, and Iqbal and Kamal Quadir

We gratefully acknowledge partial financial support from several agencies. The Blue Planet Run Foundation and LBNL's Technology Transfer Office supported this research in critical early stages. The field trip to Bangladesh was partially supported by CleanWater LLC and NCIIA. NCIIA also partly supported some of the costs of experiments. The U.S. Department of Energy supported some of the researchers through the Student Undergraduate Laboratory Internship Program and the Community College Internship Program. The David Scholars Program at UC Berkeley partially supported Heena Patel's participation. We also received partial support from the student entrepreneurship competition held by UC Berkeley's College of Engineering.

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12

DEVELOPMENT OF A SIMPLE ARSENIC FILTER FOR GROUNDWATER OF BANGLADESH BASED ON A COMPOSITE IRON MATRIX

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INTRODUCTION

Arsenic in groundwater used for drinking is now regarded as a worldwide public health crisis and identified as one of the worst natural disasters on Earth. This problem is particularly severe in southern and eastern Asia. It is estimated that of the 140 million people in Bangladesh, between 77 to 95 million are drinking groundwater containing more than 50 μg/L (50 ppb or 0.05 mg/L), the maximum contamination level (MCL), from 10 million tube wells [1,2]. Prolonged drinking of this water has caused serious illnesses, in the form of hyperkeratosis on the palms and feet, fatigue symptoms of arsenicosis, and cancer of the bladder, skin, and other organs [3]. In the long term, one in every 10 people could die of arsenic poisoning if they have high concentrations of arsenic in their water [4].

The only solution to this crisis is to provide clean potable water for the masses. Clean and potable water imply that the water should be free from toxic chemical species and biological pathogens and conform the local standard. In this endeavor

Arsenic Contamination of Groundwater: Mechanism, Analysis, and Remediation,
Edited by Satinder Ahuja

we have developed a filtration system to clean groundwater. The filter has been studied thoroughly and passed through several environmental technology verification programs for arsenic mitigation (ETVAM) projects and approved by the government of Bangladesh (GOB) for household use [5]. Recently, the filtration technology has been given the highest award from the National Academy of Engineering's Grainger Challenge Prize for Sustainability [6] after testing 15 other competitor technologies. NAE has recognized this innovative technology for its affordability, reliability, ease of maintenance, social acceptability, and environmental friendliness, which met or exceeded the local government's guidelines for arsenic removal.

The arsenic measurement and mitigation research by the group started in 1997. Our measurement papers and protocols were described elsewhere [7,8]. The ability to measure ppb-level As(III) and As(V) allowed us to test the filtration technology with real groundwater in the field. The first mitigation technology paper was published in 2000 [9]. Since then several other papers were published on improvement of the technology [10–12]. The technology was patented in 2002.

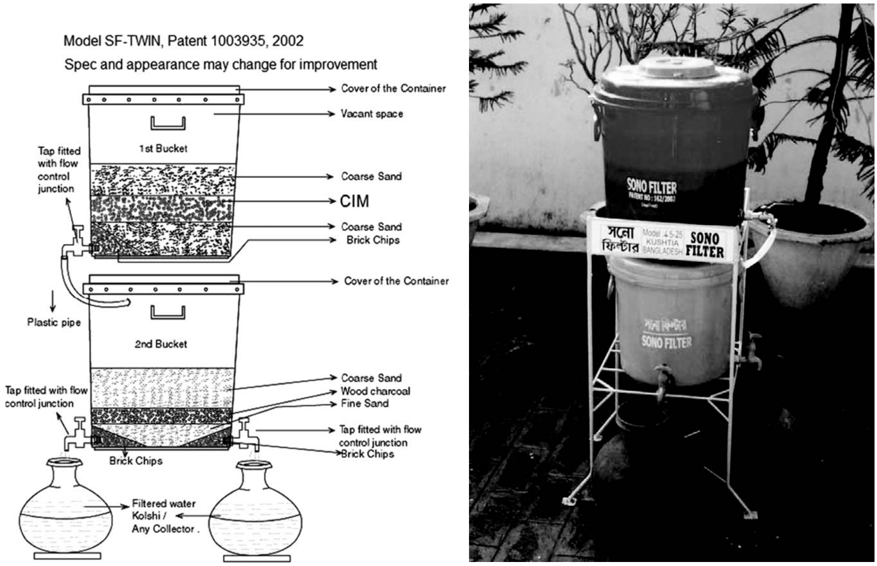
More than 30,000 arsenic filters (hereafter known as SONO filters) were deployed in 16 districts all over Bangladesh. Many of these filters have been in continuous use for five years without a breakthrough. We estimate that more than 1 billion liters of clean drinking water was consumed from these filters, and they continue to provide high-quality water for drinking and cooking. The following is a description of the SONO filter and its performance based on the data obtained from our research, development, and extensive participation in ETVAM. These results were compared with that of other filter technologies.

MATERIALS AND METHODS

Analytical methods, protocols, speciation procedures, and analytical method validation were described elsewhere [5,7,8,13]. Standard laboratory instruments and practices were followed for other water quality parameters. The detection limit for arsenic was 2 μg/L with all instrumental techniques. The unit SONO filter is shown in Figure 1. A list of basic materials and their characteristic functions is provided in Table 1.

RESULTS AND DISCUSSION

In groundwater (pH 6.5 to 7.5) arsenic is present in two oxidation states [As(III) in H_3AsO_3 and As(V) in $H_2AsO_4^-$ and $HAsO_4^{2-}$]. It is known that in most groundwater in Bangladesh, more than 50% of total arsenic is present as the neutral H_3AsO_3 at groundwater pH. The other 50% is divided equally in two As(V) species, $H_2AsO_4^-$ and $HAsO_4^{2-}$. An ideal filter must remove all three species without chemical pretreatment, without regeneration, and without producing toxic wastes. The unit SONO filter and its predecessor 3-Kolshi filter (Kolshi



A B

Figure 1 (A) Filter schematic; (B) SONO filter in use. (From ref. 14.) (*See insert for color representation of part B.*)

is the round container shown in Figure 1B) had satisfied these requirements. The original SONO 3-Kolshi filtration systems also passed a rapid assessment test, and a system made similarly was tested in Nepal by an MIT group with an arsenic removal capacity of 20 μg/L [15,16].

Filter Tests and Performance Evaluation

The SONO filters were tested only with real groundwater contaminated with arsenic and other species. From the inception of our work, we realized that the fastest way to test for filter performance was to use real groundwater containing varied concentrations of arsenic, iron, and other inorganic species and compare them with the potable water quality parameters. We have selected six tube wells with varied water chemistry in six different households where SONO filters were installed. Table 2 shows that all the filters remove arsenic to less than10 μg/L from an input range of 32 to 2423 μg/L As(total). All filters removed soluble Fe below 0.26 mg/L even from the highest input iron of 21 mg/L. We found arsenicosis patients in the last three locations, where arsenic cocentrations were above the suggested 300 μg/L. These experimental filters continue to provide clean potable water for households.

In combination with the composite iron matrix (CIM), the sand, the charcoal, and the optimum arrangement of the materials, the SONO filter removes arsenic, iron, manganese, and many other inorganic species, to provide a potable water. Figure 2A shows typical test results in which 62,680 L of tube well water

TABLE 1 Materials Used in SONO Filters[a]

Material[b]	Function and Characteristics	Brief Manufacturing Method and Availability
Top bucket (32 kg)		
Coarse river sand (CRS), 10 kg wet ($F_m = 1.5$–2, 95% SiO_2, 5% other metal oxides)	CRS is an inactive material used as coarse particulate filter, disperser, flow stabilizer, and to provide mechanical stability. Groundwater with high soluble iron is oxidized and preicpitates as $Fe(OH)_3(s)$ in this medium.	CRS is obtained from a local river and washed thoroughly before use.
Composite iron matrix (CIM), 8–10 kg	CIM is the active surface for complexation and immobilization of inorganic arsenic and many toxic metal cations. The final product is porous, lighter than original turnings, and produces less fines for filter stability.	CIM is manufactured from various iron turnings through a proprietary process.
Coarse river sand and brick chips (BCs)	CRS and BCs are inactive materials and have similar functions. In combination these are used as a protection barrier for the free-flow junction outlet.	Same as top. BCs are from local brick manufacturer, washed thoroughly, and disinfected with bleach.
Bottom bucket (25 kg)		
Coarse river sand	Similar to above. This stage retains residual iron leached from the first-stage CIM as hydrons ferric oxide. Filter life span can be estimated from the residual iron from the top bucket.	Same as above.

Wood charcoal (WC)	Wood charcoal is known to adsorb organics (odor-causing compounds, pesticide residues, etc). WC is passive to arsenic but imparts better-tasting water.	WC is obtained from firewood used for cooking. Large quantitites are collected from local hotels and villagers.
Fine river sand (FRS) and brick chips[c]	FRS is a fine filtration medium used to catch any residual particulates. BCs are used as flow-stabilizing media.	Both obtained from local manufacturers; washed thoroughly.
Other materials		
Plastic buckets, 40 L	Container. Only food-grade high-density polypropylene (HDPP) buckets are used.	Local plastic molding industries. Buckets were retrofitted with top cover and outlets for flow controller taps.
Flow controllers	Control flow to maintain optimum residence time for best arsenic removal. This is fixed in the factory.	Molded plastic or metal taps are available in local hardware stores.
Metallic filter stand	Support for the buckets.	Made by local welders.

[a] General filter specifications. Top bucket (red): 45 L, diameter/height: 46/44 cm. Flow rate: 20–30 L/h continuous.
[b] See Figure 1.
[c] Brick chips: silica 55%, alumina 30%, iron oxide 8%, magnesia 5%, lime 1%, and others 1%. Some materials are subject to change for continuous improvement of the filtration technology.

TABLE 2 Results from Six SONO Filters Monitored for 2.3 to 4.5 Years in Active Use by Householders[a]

Parameter	Filter 1, Fatic	Filter 2, Courtpara	Filter 3, Zia	Filter 4, Alampur	Filter 5, Kaliskhnpur	Filter 6, Juniadah
Years in use	2.32	4.5	2.66	3.6	4.4	2.5
Water yield (L)	67,760	125,000	77,840	104,960	128,480	72,960
Number of measurements	10	110	12	14	56	8
As(total) input (μg/L)	32 ± 7	155 ± 7	243 ± 9	410 ± 15	1139–1600	2423 ± 87
As(total) filter (μg/L)	<2	7 ± 1	7 ± 1	8 ± 2	7 ± 2	8 ± 4
Fe(total) input (mg/L)	20.7 ± 0.6	4.85 ± 0.25	7.35 ± 0.3	10.86 ± 0.56	1.53 ± 0.08	0.6 ± 0.03
Fe(total) filter (mg/L)	0.22 ± 0.02	0.228 ± 0.04	0.25 ± 0.03	0.242 ± 0.03	0.25 ± 0.05	0.26 ± 0.03
Cost per liter (Taka), (1 Taka = \$0.016)	0.031	0.016	0.026	0.02	0.016	0.028

[a]Location: Kushtia district, Bangladesh. Test period: 2000–2005. Flow rate: 20–30 L/h. Other water chemistry parameters are similar to those in Table 1. Consumption: 60 to 180 L/day. As(total) was measured by ASV on a thin-film gold electrode validated by IAEA interlaboratory comparison studies at SDC/MSUK, Kushtia, Bangladesh and with the graphite furnace AA at the GMU Chemistry Department. Iron was measured spectrophotometrically at SDC/MSUK. The cost per liter decreases as more water is filtered.

containing 180 to 1600 μg/L As (total) was filtered to produce potable water with less than 14 μg/L As (total) until reaching the detection limit (2 μg/L). Figure 2B shows the progressive decrease in effluent arsenic with a SONO CIM filter. In contrast, activated alumina shows the opposite behavior, as shown in Figure 2C. This is also confirmed in recent ETVAM tests, in comparison to activated alumina, cerium hydroxide ion-exchange resin, and microfine iron oxide–based filters [5]. We attribute this unique property of the SONO filter to the generation of new complexation sites on CIM through in situ iron oxidation and surface chemical reactions, as discussed later. It also indicates that the arsenic removal reaction has a zero-order kinetics with respect to the influent As(total) concentration. This indicates a high arsenic removal capacity independent of input As(total) (up to 2400 μg/L), and also implies no breakthrough of arsenic for the life of the filter. The filter life span can be estimated by assuming a 1As : 1Fe mole ratio reaction in which all available CIM Fe is used and where the filter loses 500 μg/L of iron (from CIM) at 200 L/day use. It would take 274 years to lose 1000 g of iron when 20,000,000 L of water is filtered. The filters contain 8 to 10 times the assumed iron. This calculation assumes that all insoluble iron complexes remain trapped in the filtration assembly. The filter life span can also be estimated from our data on a Freundlich isotherm with CIM [$\log(X/M) = \log K + (1/n)\log C_f$, where X is the μg/L of As adsorbed, M the grams of CIM used, and C_f the free arsenic in μg/L] with an adsorption capacity $K = 4250$ and adsorption intensity $n = 2.61$. It was found to take about 6 years to reach the 50-μg/L MCL breakthrough from influent water containing 300 μg/L As(total) at an 80-L/day usage rate and a filter with 10,000 g of CIM. Although these calculations are disparate, it shows that the filter will work for many years before a breakthrough occurs. The MCL breakthrough is extended further by the coprecipitation of arsenate by HFO produced from Fe(II) present in groundwater even at low concentrations. Our oldest filter is still functioning without any changes and without a breakthrough. It was shown that the filter can even work at a 60-L/h flow rate without a

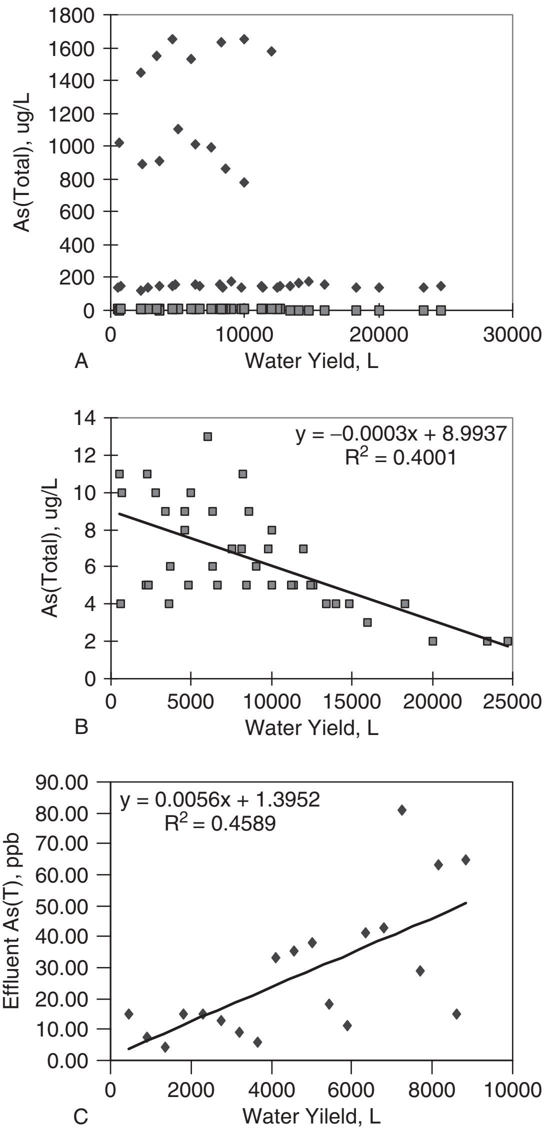


Figure 2 (A) Influent water containing arsenic from four different tubewells (diamonds) with concentrations of 180 to 1600 μg/L were passed through the filtration system to yield a total of 62,680 L of filtered water (squares) with 6 ± 3 μg/L (median 5 μg/L) total arsenic and no detectable As(III) as shown in (B). (C) Results for activated alumina filter from ETVAM test data.

breakthrough. However, due to the unknown water chemistry and varied As(total) in groundwater, we fixed the flow rate at 20 to 30 L/h to ensure long-term use and effluent As(total) below 30 μg/L [17]. On the other hand, it was found that blank filter breakthrough occurs at 88 L groundwater, whereas the plain sand filter broke through the MCL almost instantaneously [17].

Several nongovernmental organizations (NGOs) have installed SONO filters in many arsenic-affected areas of Bangladesh. One such highly affected area is Hajigong, where 165 SONO filters were installed to supply water for 300 arsenicosis patients and 3000 family members. The results published show that As (total) in filtered water was < 2 μg/L (70% samples), < 10 μg/L (20% samples), < 30 μg/L (10% samples), and none above 30 μg/L from the influent As(total) 600 to 700 μg/L with at least 50% in the form of more toxic As(III) [18]. The study also found no change in flow rate and no maintenance required for 12 months.

System Validation and Comparative Studies

The SONO filtration system was tested extensively by us and in several technology verification projects (ETVAMs) run by the government of Bangladesh (Bangladesh Arsenic Mitigation Water Supply Projects) and compared with other filters [5]. Table 3 summarizes the results of more than 590,000 L of groundwater filtered in 10 experimental filters located throughout Bangladesh. Of these, 577,000 L was tested by the authors at six locations, as described in Table 2, and 17,334 L was tested by ETVAMs at five locations throughout Bangladesh (Bera-Pabna, Hajigong-Comilla, Manikgang-Dhaka, Faridpur, and Nawabgang-Rajshahi) under varied groundwater chemistry conditions. Clearly, the filter water parameters met and exceeded U.S. Environmental Protection Agency (EPA), World Health Organization (WHO), and Bangladesh standards. It is noted that the SONO filter removes the most toxic As(III) species from groundwater without chemical pretreatment below the detection limit (2 μg/L). Table 4 compares four ETVAM-approved filters for household use. It shows that SONO was tested for all parameters and the only technology that removed manganese. Manganese is now implicated as a toxic trace metal in Bangladesh groundwater [19]. It is also interesting to note that many groundwater sources do not meet the potable water quality standard even in the absence of arsenic; in these locations SONO filters are also used.

Naturally occurring soluble iron and phosphate can affect the performance of most filtration technologies. Table 3 shows that SONO filters not only removed the arsenic but also removed 99% of the soluble iron and made the water potable. Phosphate is often considered the competing ion for arsenate and has the potential to affect the performance of the filter negatively. We find no clear effect of phosphate on the removal capacity of arsenic. Our observations indicate that phosphate does not affect the performance of SONO filter even at 40 to 50 mg/L concentration [17].

TABLE 3 Comparison of Water Quality from Use of a SONO Filter

Constituent[a]	EPA (MCL)	WHO Guideline	Bangladesh Standard[b]	Influent Groundwater	SONO Filter Water[c]
Arsenic(total) (μg/L)	10	10	50	5–4000[d]	3–30
Arsenic(III) (μg/L)	—	—	—	5–2000[e]	<5
Iron(total) (mg/L)	0.3	0.3	0.3 (1.0)	0.2–20.7	0.19 ± 0.10
pH	6.5–8.5	6.5–8.5	6.5–8.5	6.5–7.5	7.6 ± 0.1
Sodium (mg/L)	—	200	—	<20.0	19–25
Calcium (mg/L)	—	—	75 (200)	120 ± 16	5–87
Manganese (mg/L)	0.5	0.1–0.5	0.1 (0.5)	0.04–2.00	0.22 ± 0.12
Aluminum (mg/L)	0.05–0.2	0.2	0.1(0.2)	0.015–0.15	0.11 ± 0.02
Barium (mg/L)	2.0	0.7	1.0	<0.30	<0.082
Chloride (mg/L)	250	250	200 (600)	3–12	4.0–20.0
Phosphate (mg/L)	—	—	6	<12.0	0.9 ± 0.12
Sulfate (mg/L)	—	—	100	0.3–12.0	12 ± 2
Silicate (mg/L)	—	—	—	10–26	18 ± 6

[a] 1 mg/L = 1000 μg/L.
[b] Bangladesh standard values are given as maximum desirable concentration with maximum permissible concentration in parentheses.
[c] SONO filters. ICP multielement measurements of Cu, Zn, Pb, Cd, Se, Ag, Sb, Cr, Mo, and Ni show concentrations below the EPA and WHO limits at all times. All other measurements show an average of semicontinuous measurement of more than 394,000 L of groundwater filtered by us and ETVAM in at least eight different water chemistries in different regions of Bangladesh. Water chemistry parameters were recoded for 23 metals, nine anions, Eh, pH, temperature, dissolved oxygen, conductivity, and turbidity for hundreds of samples. All prescribed parameters passed the drinking water standards of WHO and Bangladesh.
[d] One tube well at Bheramara was found to contain As(total) 4000 μg/L. The filtered water had 7 μg/L. This well was later capped by the government.
[e] In some wells, As(III) concentrations exceeded 90% of the As(total).

Chemistry and Possible Mechanisms

The most probable chemical reactions taking place in various locations of the filter media are shown in Table 5. The process of arsenic removal from groundwater is based on active surface oxidation, surface complexation, and precipitation of arsenic (III and V) on CIM. Based on literature data [20–22] and our research [23], the arsenic removal process can be summarized as follows:

- First, in situ oxidation of CIM continuously generates hydrous ferric oxide (HFO), which has a higher active surface area than that of simple oxides of iron. Dynamic electrochemical study (a Tafel plot) shows that water is the primary oxidant for iron [22]. The main active material in the SONO filter is the composite iron matrix (CIM), a mass made of cast iron turnings through a process to maintain active CIM integrity for years. The CIM removes the inorganic arsenic species quantitatively through the possible reactions shown in Table 5. Infrared spectroscopy (IRS) [20] and extended

TABLE 4 Comparison of Four Filter Technologies Tested by the ETVAM and Approved for Household Use in Bangladesh

Parameter	Bangladesh Standard	Alumina	Composite Iron Matrix (SONO)	Cerium Ion-Exchange Resin	Microfine Iron Oxide
As(total) (ug/L)	50	57 ± 24	6 ± 1	7 ± 5	22 ± 4
As(III) (ug/L)	—	36 ± 19	4 ± 1	5 ± 2	6 ± 4
Fe(total) (mg/L)	0.3 (1.0)	0.6 ± 0.2	0.06 ± 0.04	0.16 ± 0.21	0.2 ± 0.1
Phosphate (mg/L)	6	0.5 ± 0.2	0.9 ± 0.6	0.9 ± 0.6	1.1 ± 1.5
Sulfate (mg/L)	100	68 ± 77	12 ± 2	No data	No data
Silicate, SiO_2 (mg/L)	—	11 ± 2	18 ± 6	No data	No data
Al (mg/L)	0.1 (0.2)	0.17 ± 0.07	0.11 ± 0.02	No data	No data
Ca (mg/L)	75 (200)	No data	104 ± 18	No data	No data
Mn (mg/L)	0.1 (0.5)	1.4 ± 0.2	0.22 ± 0.12	No data	0.5 ± 0.4
Mg (mg/L)	—	No data	50 ± 17	No data	No data
pH	6.5–8.5	7.3 ± 0.17	7.6 ± 0.1	7.4 ± 0.4	7.4 ± 0.3
Flow rate (L/h)	—	128 ± 7	17 ± 3	61 ± 6	264 ± 37

[a]Data exclude one outlier test performed at Hajigang. "No data" indicates that no tests were performed.

x-ray absorption fine structure (EXAFS) [21] show that arsenate and arsenite form bidentate, binuclear surface complexes with $=$ FeOH (or $=$ FeOOH or hydrous ferric oxide, HFO) as the predominant species tightly immobilized on the iron surface. The primary reactions are $= \mathrm{FeOH} + \mathrm{H_2AsO_4}^- \rightarrow= \mathrm{FeHAsO_4}^- + \mathrm{H_2O}$ ($K = 10^{24}$) and $= \mathrm{FeOH} + \mathrm{HAsO_4}^{2-} \rightarrow =\mathrm{FeAsO_4}^{2-} + \mathrm{H_2O}$ ($K = 10^{29}$). These intrinsic equilibrium constants indicate very strong complexation and immobilzation of inorganic arsenic species. It is known that excess Fe^{2+}, Fe^{3+}, and Ca^{2+} in groundwater enhance the positive charge density of the inner Helmholtz plane of the electrical double layer and specifically bind anionic arsenates to form surface complexes. In addition to arsenic species, $=$ FeOH is also known to remove many other toxic species [10–12].

- Also, inorganic As(III) species are oxidized to As(V) species by the active $O_2^{-\cdot}$ produced by the oxidation of soluble Fe(II) with dissolved oxygen. Manganese (1 to 2 wt%) in CIM catalyzes the oxidation of more toxic arsenite As(III) to arsenate As(V) for rapid removal of arsenic. Therefore, the process requires no pretreatment of groundwater with external oxidizing agents such as hypochlorite bleach or potassium permanganate. This is a clear advantage of SONO technology.
- We found (Table 2) that the As(III) and As(V) removal process was independent of the input arsenic concentration (i.e., a zero-order reaction). This may imply that new reaction sites generated in CIM and the subsequent aging of $Fe(OH)_3(s)$ to produce HFO is a zero-order process with respect to arsenate removal. This ensures a high arsenic removal capacity independent of the concentration of input arsenic and better performance with time.

TABLE 5 Possible Physicochemical Reactions in Various Parts of the Filtration Process

Reaction Location[a]	Reactions[b]
Top layer: oxidation of As(III) (Equations are balanced for reactive species only)	$As(III)+O_2{}^{\cdot -} \rightarrow As(IV) + H_2O_2$ $As(III) + CO_3{}^{\cdot -} \rightarrow As(IV) + HCO_3{}^-$ $As(III)OH^{\cdot -} \rightarrow As(IV)$ $As(IV) + O_2{}^{\cdot -} \rightarrow As(V) + O_2{}^{\cdot -}$
Top bucket: oxidation of soluble iron Oxidation of ferrous to ferric through active oxygen species	$Fe(II) + O_2 \rightarrow O_2{}^{\cdot -} + Fe(III)OH_2{}^+$ $Fe(II) + O_2{}^{\cdot -} \rightarrow Fe(III) + H_2O_2$ $Fe(II) + CO_3{}^{\cdot -} \rightarrow Fe(III) + HCO_3{}^-$
CIM hydrous ferric oxide (HFO) Fe(III) complexation and precipitation	$= FeOH + Fe(III) + 3H_2O \rightarrow Fe(OH)_3$ (s, HFO) $+ = FeOH + 3H^+$ (= FeOH is surface of hydrated iron)
CIM–HFO surface Surface complexation and precipitation of As(V) species	$= FeOH + AsO_4{}^{3-} + 3H^+ \rightarrow = FeH_2AsO_4 + H_2O$ $= FeOH + AsO_4{}^{3-} + 2H^+ \rightarrow = FeHAsO_4{}^- + H_2O$ $= FeOH + AsO_4{}^{3-} + H^+ \rightarrow = FeAsO_4{}^{2-} + H_2O$ $= FeOH + AsO_4{}^{3-} \rightarrow = FeOHAsO_4{}^{3-}$
Top two buckets: precipitation of other metals Bulk precipitation of arsenate with soluble metal ions	$M(III) + HAsO_4{}^{2-} \rightarrow M_2\ (HAsO_4)_3$ (s), M = Fe, Al $M(II) + HAsO_4{}^{2-} \rightarrow M(HAsO_4)$ (s) and other arsenates, M = Ba, Ca, Cd, Pb, Cu, Zn, and other trace metals
CIM and sand interface Reactions with iron surface and sand can produce a porous solid structure with extremely good mechanical stability for the filter known as solid CIM	$= FeOH + Si(OH)_4 \rightarrow = FeSiO\ (OH)_3\ (s) + H_2O$ $= FeOH + Si_2O_2(OH)_5{}^- + H^+ \rightarrow = FeSi_2O_2(OH)_5\ (s) + H_2O$ $= FeOH + Si_2O_2(OH)_5{}^- \rightarrow = FeSi_2O_3(OH)_4{}^-\ (s) + H_2O$ $= FeOHAsO_4{}^{3-} + Al(III) \rightarrow = FeOHAsO_4Al$ (s) $= FeOHAsO_4{}^{3-} + Fe(III) \rightarrow = FeOHAsO_4Fe(s)$ $= FeOH.HAsO_4{}^{2-} + Ca(II) \rightarrow = FeOH.HAsO_4Ca$ (s)

Source: Data from refs. 24 to 28.
[a] CIM, composite iron matrix.
[b] All surface species indicated by "=X" are solids.

- At groundwater neutral pH, the HFO formed on the CIM is found to be porous and partially protects the underlying iron matrix from further reactions, thus ensuring long operational stability without compromising water quality.
- Further reactions involving HFO arsenate, silicate from sand [29], and other cations render the products as extremely insoluble spent material with properties very similar to those of naturally occurring Fe-arsenic minerals. Therefore, the solid waste leaching shows no detectable waste disposal hazard.

Detailed thermodynamics and kinetics of the arsenic removal process are, however, yet to be firmly established.

Management of Spent Material

Measurements on used sand and CIM-Fe by total available leaching protocol (TALP) show that the spent material is completely nontoxic, with less than 5 μg/L As(total), which is 1000 times less than the EPA limit [30]. The procedure was also followed with Bangladesh rainwater (adjusted to pH 7), where the primary mode of transport of water-soluble species could take place during the rainy season. TALP is similar to EPA's toxicity characteristic leaching procedure (TCLP) except that the samples were ground to fine powder before leaching at two different pH values. Similar results were also reported by ETVAM using EPA's TCLP methods. Further tests on backwash of filter waste showed that SONO produced the lowest concentrations of As(total), 93 mg/kg, compared to commercial filters based on microfine iron oxide 2339 mg/kg, cerium hydroxide–based ion-exchange resin 105 mg/kg, and activated alumina 377 mg/kg in solid waste versus the EPA limit of 500 mg/kg. Arsenic species in the filter's used sand and CIM are in the oxidized form and firmly bound with insoluble solid CIM. This is similar to a self-contained naturally occurring compound in the Earth's crust. It is almost like disposing soil on soil. Most important, NAE tests of the used CIM of SONO filter was characterized as "non detectable and non hazardous (limit 0.50 mg/L)" by the TCLP [31]. It may be noted that the EPA recommended a land disposal limit for arsenic of 2 kg/hta per year. This corresponds to arsenic from 10 million liters of water with 200 μg/L concentration (A. H. Khan, personal communication). According to this prescription, 4 m^2 of land is good enough for the disposal of the spent media from household filters used for 274 years at 100 L/day.

Technology Use, Dissemination, and Social Acceptability

The SONO filter has been designed with Bangladesh village people in mind. It does not require any special maintenance other than replacement of the upper sand layers when the apparent flow rate decreases. Experiments show that the flow rate may decrease 20 to 30% per year if groundwater has high iron (>5 mg/L) due to formation and deposition of natural HFO in sand layers. The sand layers (about an inch thick) can be removed, washed, and reused or replaced with new sand. The presence of soluble iron and formation of HFO precipitate is also a common problem with other filtration technologies.

The use of tube wells to extract groundwater was done to avoid drinking surface water contaminated with pathogenic bacteria. However, pathogenic bacteria can still be found in drinking water due to unhygienic handling practices in many shallow tube wells, possibly located near unsanitary latrines and ponds [32]. To investigate the issue of bacterial growth in SONO filters, a Bangladesh NGO named the Village Education Resource Center (VERC) recently tested 193 SONO filters at 61 locations in one of the remotest fields, Sitakundu, Bangladesh [33]. The report shows that of the 264 tests, 248 were found to have zero count of thermo-tolerance coliforms (ttc) per 100 mL and 16 with 2 ttc/100 mL. Pouring 5 L of hot water in each bucket every month has been shown to kill pathogenic bacteria and eliminate coliform count. This protocol can be followed once a week where coliform counts are high. We have no records of diarrhea or other water-borne diseases from drinking SONO-filtered water. It appears that the SONO filtration system does not foster pathogenic bacteria on its own.

Except for basic training in hygiene, no special skill is required to maintain the filter. The maintenance process requires about 20 to 30 minutes. Because the SONO filter has no breakthrough, the active media does not require any processing, such as backwashing or chemical regeneration. The filter will produce potable water for at least five years (time span of our continuing test results). The actual filter life span is determined by the life span of the six experimental filters (in Table 2) running in the field. Except for manufacturing defects, mechanical damage due to mishandling, transportation, and natural disasters (flooding), none of the filters showed MCL breakthrough to this date.

The filter is now manufactured by an NGO [Manob Sakti Unnyan Kendro (MSUK), Kushtia, Bangladesh] from indigenous materials at 200 to 500 units per lot (Figure 3). The filter materials are available almost anywhere in the world except the CIM, which can be produced with an appropriate licensing agreement. Large-scale transportation of the filters takes place with flatbed trucks, and filter distribution in villages occurs with flatbed rickshaws. Following simple instructions and without setup costs, the user can set up a system in 20 minutes.

At the time of writing, about 35,000 filters had been distributed in 16 districts throughout Bangladesh. The large-scale deployment was accomplished through participation of a dozen local NGOs and international institutions. For example, MSUK has distributed 825 filters to 325 primary schools serving 67,000 students and teachers. The SONO filter is also used by many local restaurants, tea/candy shops, and villagers in remote places. We estimate that about half-a-million people are the direct beneficiaries of the filtration system. It is worth noting that many people, the authors included, use this water, free from arsenic and other toxic species, for drinking and cooking. The filtration system can be scaled up by connecting units in parallel. This can easily enhance the flow rate for small community use.

A B

Figure 3 (A) SONO filter production center at Kushtia, Bangladesh; (B) filters loaded on a flatbed truck for distribution. (*See insert for color representation of figure.*)

Presently, at $35 to $40 each five years (equivalent to the one-month income of a village laborer in Bangladesh), SONO is one of the most affordable water filters in Bangladesh. Affordability has been enhanced by monthly payment schedules through NGOs distributing the filters. The filter does not require chemicals or consumables. The estimated operating cost is no more than $10 over five years only if the flow controller needs replacement, which is rare. One unit can serve two families' need for drinking and cooking water for at least five years. The SONO filter setup and maintenance do not require any special skill. Potable water is collected within 2 to 3 hours after discarding the first two batches. After overcoming the initial skepticism of drinking different water from a filter, people liked the taste of soft water. Our experience shows that mostly women participate in the water collection and maintenance of the filter. The filter has been accepted extremely well because women do not have to go far to find arsenic-free wells (painted green); they can still use their contaminated wells. Users drinking this water for two years show some disappearance of arsenical melanosis, with a general sense of well-being and improvement in health. These data are now being collected and will be reported. Besides drinking and cooking, at a 20-L/h flow rate the filters produce enough water to be used for other purposes, such as cleaning and washing cooking utensils. Except for the inconvenience of sharing filtered water with neighbors, we found no social and cultural issues that hinder dissemination and use of the filter. We found schoolchildren who drink SONO water carrying bottles of water home at the end of the school day. Many NGOs have also implemented intensive training and cultural programs to motivate people to drink arsenic-free water.

CONCLUSIONS

It is now clear that in Bangladesh and many other countries, while the surface water is not potable without treatment and filtration, a major portion of the groundwater is also not potable, due to the presence of many toxic species. It appears that the development of low-cost filters is the only way to solve the present drinking water crisis in many countries of the world.

Acknowledgments

The authors deeply appreciate the workers of SDC/MSUK, Bangladesh for their unwavering support in all aspects of this work. We also acknowledge assistance from Abul Barkat, Department of Economics, and Amir H. Khan, Department of Chemistry, Dhaka University, Bangladesh.

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13

COMMUNITY-BASED WELLHEAD ARSENIC REMOVAL UNITS IN REMOTE VILLAGES OF WEST BENGAL, INDIA

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INTRODUCTION

Arsenic (As) has long been known for its acute toxicity. Minerals such as orpiment, realgar, and arsenopyrite are common subsurface sources of arsenic, which due to geochemical and biogeochemical weathering contribute to high

Arsenic Contamination of Groundwater: Mechanism, Analysis, and Remediation,
Edited by Satinder Ahuja

levels of dissolved arsenic in groundwater. There are other anthropogenic sources of arsenic which are responsible for discharging arsenic into the environment. Arsenic contamination in groundwater poses serious health threats where people generally use groundwater as their source of drinking water. Arsenic in the drinking water is a problem in several regions around the globe, the worst ever being the widespread arsenic poisoning in the Indian subcontinent. In Bangladesh and the neighboring Indian state of West Bengal, nearly 100 million people who use arsenic-contaminated drinking water from underground sources are at risk of developing adverse health effects; arguably, such widespread human calamity is one of the most catastrophic incidents in recent times [1–3]. There are differences of opinion about the genesis of arsenic contamination in groundwater for this area; however, geochemical weathering of subsurface soil, not industrial pollution, is the sole contributor of arsenic in the groundwater. The concentration of dissolved arsenic in several drinking water wells in this geographic area exceeds well over 200 μg/L, while the maximum permissible arsenic concentration in drinking water in India and Bangladesh is 50 μg/L [4]. The World Health Organization (WHO) guideline for recommended maximum contaminant level (MCL) for arsenic is 10 μg/L [5]. The presence of unacceptable levels of arsenic does not alter the taste, color, or odor of water. Also, health-related impairments caused by arsenic poisoning from drinking water take several years before becoming obvious and are mostly irreversible and fatal.

Rainfall in this region is quite significant and often exceeds 1500 mm/yr and is sufficient to develop a surface water–based drinking water system, which has only a small possibility of contamination from arsenic. However, the lack of infrastructural funds and poor sanitation practices prevailing in this region makes surface water practically unusable for drinking purposes, due to susceptibility to microbial contamination. In many remote villages in this area, arsenic-contaminated groundwater remains the only feasible source of drinking water. Cost-effective arsenic removal technology is thus a bare necessity to provide safe drinking water. The groundwater is, otherwise, free of contaminants and safe for drinking.

Arsenic is a borderline element between metals and nonmetals, commonly known as a metalloid. In all contaminated groundwater, dissolved arsenic exists as inorganic compounds in the oxidation states + III and + V. They are commonly referred to as As(III), or arsenite, and As(V), or arsenate. Environmental separation of dissolved arsenic from groundwater essentially involves removal of inorganic arsenic species from the contaminated water. Organoarsenical compounds are not found in the groundwater and result primarily from industrial discharges, so essentially most arsenic removal technologies focus on the removal of inorganic arsenic compounds from the groundwater. Inorganic arsenic in the groundwater remains either as oxyacid or in oxyanionic form, depending on the pH of the aqueous phase. Table 1 summarizes various forms of inorganic arsenic oxyacids and oxyanions encountered in groundwater. It may be observed that at nearly neutral pH, monovalent $H_2AsO_4^-$ and divalent $HAsO_4^{2-}$ are the

TABLE 1 Forms of Inorganic Arsenic Species in Water

Parent Oxyacid	pK_a Values	Predominant Species at pH 5.5	Predominant Species at pH 8.5
As(V): H_3AsO_4	p$K_{a1} = 2.2$ p$K_{a2} = 6.98$ p$K_{a3} = 11.6$	$H_2AsO_4^-$	$HAsO_4^{2-}$
As(III): $HAsO_2$	p$K_{a1} = 9.2$	$HAsO_2$	$HAsO_2$

predominant species, but in identical conditions an electrically neutral $HAsO_2$ is the major As(III) species.

The existing and emerging arsenic removal technologies are summarized below:

- Activated alumina sorption
- Polymeric anion exchange
- Sorption on iron oxide–coated sand particles
- Ferric chloride or alum coagulation followed by filtration
- Granulated iron oxide particles
- Polymeric ligand exchange
- Nanomagnetite particles
- Sand with zero-valent iron
- Hybrid cation-exchange resins
- Hybrid anion-exchange resins
- Reverse osmosis or nanofiltration

The technical details of the foregoing processes and their relative advantages and disadvantages are available in the literature [6–27]. Except for reverse osmosis and nanofiltration, which are essentially nonselective physical processes of exclusion of ions across a semipermeable membrane, for all other processes the underlying chemistry includes either or both of the following two types of interactions: (1) As(V) oxyanions are negatively charged in the near-neutral pH range and therefore can undergo coulombic or ion-exchange types of interactions, and/or (2) As(V) and As(III) species, being fairly strong ligands or Lewis bases, are capable of donating lone pairs of electrons. They participate in Lewis acid–base (LAB) interactions and often show high sorption affinity toward solid surfaces that have Lewis acid properties.

Adsorption using activated alumina in fixed-bed columns has been a candidate technology for the Indian subcontinent since 1997, when the Bengal Engineering and Science University (formerly Bengal Engineering College) in Howrah, India, in technical collaboration with Lehigh University in Pennsylvania initiated installation of activated alumina-based wellhead arsenic removal units in remote villages in the state of West Bengal, India, which borders Bangladesh. Since then, through financial support received from Water for People in the United States and other private donations from various countries, the institution has installed over 150 such community-level units. Each of these units serves as the source of arsenic-free drinking and cooking water for approximately 200 families, thereby benefiting about 150,000 people altogether. The units are essentially fixed-bed adsorption columns mounted on the top of the existing hand-pump units. The entire process of arsenic removal, from the operation and maintenance of the wellhead unit to the regeneration of exhausted media as well as disposal of treatment residuals, achieves essentially the following goals:

- Avoidance of chemical addition, pH adjustment, and use of electricity during daily operation of the units
- Simple manual operation
- Construction using materials available from indigenous sources only
- Maintenance and monitoring of units by villagers
- Avoidance of indiscriminate disposal of arsenic removed from contaminated groundwater through retention in the same premises
- Using regenerable media to promote reuse
- Detoxification of treatment residuals and containment to avoid further leaching of arsenic to the environment

Apart from elucidating on the design and a brief description of the technology, in this chapter we also discuss the methodology of regeneration, sustained performance of the units over multiple cycles after regeneration, and protocols for containment of arsenic in spent regenerant as a small-volume sludge. We also discuss the leaching potential of treatment residual under various environmental conditions, the environmental fate of arsenic, and the overall mass balance of the system.

WELLHEAD TREATMENT UNIT

The adsorption column mounted on top of the existing wellhead hand pump is essentially a cylindrical stainless steel (SS-304) tank. The general configuration of the sorption column and its operational features are presented schematically in Figure 1A, while the specific details are provided in Figure 1B. Inside the column there are two distinct chambers. In the upper part of the column a sufficiently large head space is kept to contain a spray and splash distributor and atmospheric vent connections. As the hand pump is operated manually, the groundwater enters the top part of the column, where it is fragmented into tiny droplets at the spray and splash distributor. The vent connections allow the top part to remain aerated

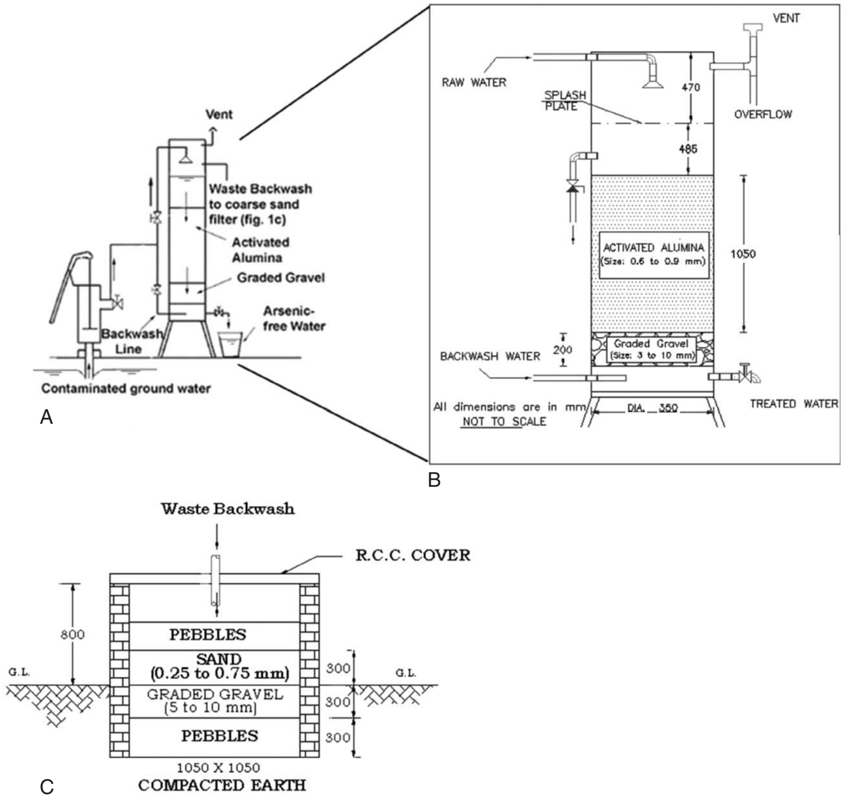

Figure 1 (A) Schematic of a wellhead arsenic removal unit; (B) details of the activated alumina adsorption column; (C) coarse sand filter.

so that the atmospheric oxygen is dissolved in the aqueous phase in the droplets as well as in the water standing in the headspace. The dissolution of oxygen in the water in the top part of the column ensures oxidation of dissolved iron into insoluble hydrated Fe(III) oxides (HFOs), or HFO particles and minimal conversion of As(III) to As(V). Underneath the headspace is fixed-bed activated alumina followed by graded gravels and the treated water collection chamber. The design flow rate of the gravity-fed unit is 8 to 10 L/min. The HFO particles produced due to oxidation of dissolved iron are trapped within the activated alumina bed. To maintain the flow rate the column is routinely backwashed for 10 to 15 minutes every day. The backwashed water is contaminated with arsenic-laden HFO particulates. It is passed through a coarse sand filter located at the same premise to retain the HFO particulates. Figure 1C provides the pertinent details of the coarse sand filter. The unit is shown in Figure 2.

Activated alumina was procured from an indigenous manufacturer (Oxide India Chemicals, Durgapur, India) after performing a series of laboratory studies

Figure 2 Wellhead arsenic removal unit. (*See insert for color representation of figure*.)

validating its suitability for long-term column operation. Each column is provided with an inexpensive locally made mechanical paddle-type flow totalizer to record the total volume of water treated by the column.

PERFORMANCE OF THE TREATMENT UNITS

Figure 3A shows the influent and effluent arsenic histories for a wellhead unit at Debnagar village in the Murshidabad district of West Bengal. It may be noted that the arsenic concentration of contaminated groundwater fluctuates around 500 μg/L and is significantly greater than the arsenic concentrations that are normally encountered in contaminated wells in this area. Nevertheless, the wellhead unit was able to treat nearly 12,000 bed volumes before 50 μg/L of arsenic breakthrough was observed. Total dissolved iron content in this particular location was quite high (i.e., in the vicinity of 10 mg/L). Figure 3B shows the influent and effluent histories of total iron at the same site; a removal of over 90% influent

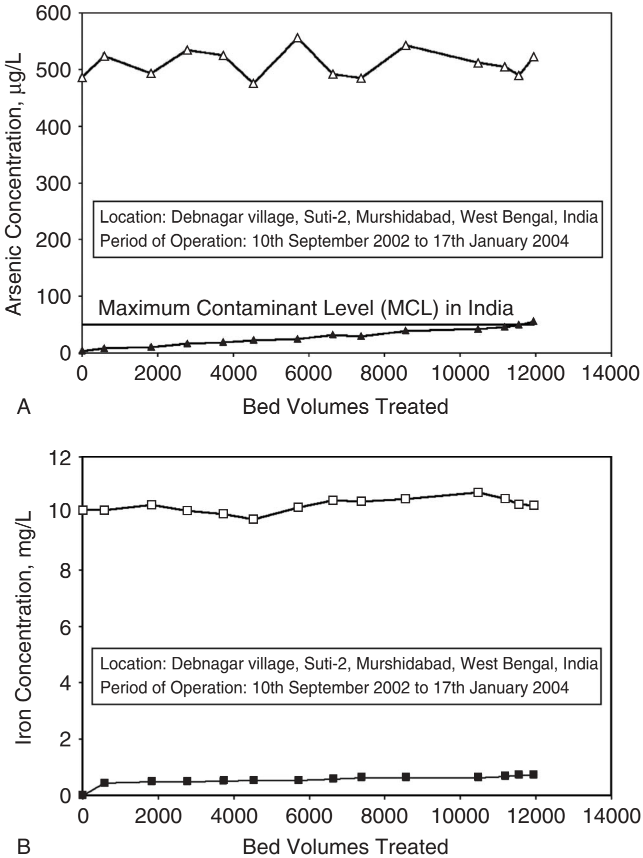

Figure 3 Influent (open symbols) and effluent (closed symbols) histories of the treatment unit at Debnagar village in Murshidabad, West Bengal, for (A) arsenic and (B) iron.

iron was obtained within the column, due primarily to the oxidation of Fe(II) into HFO precipitates. Figure 4A shows the influent and effluent arsenic histories in another site at Sadpur village at Maslandpur in the North 24 Parganas district of West Bengal. For an influent arsenic concentration varying near 90 to 100 μg/L, the column run showed almost similar performance, running for about 12,000 bed volumes (BV), before reaching breakthrough. Figure 4B shows the iron histories in the influent and effluent of the column at the same location. Significant iron removal was also observed in this case. In both cases the length of run was considerably long, being over one year on the time scale. The length of the column run varied depending on the influent arsenic and iron concentrations; run length varied from 10 months (6000 BV) to more than two years (20,000 BV). The breakthrough for all the cases was gradual, typical of plug flow adsorption columns. Also, these plug flow columns are forgiving toward variation in the

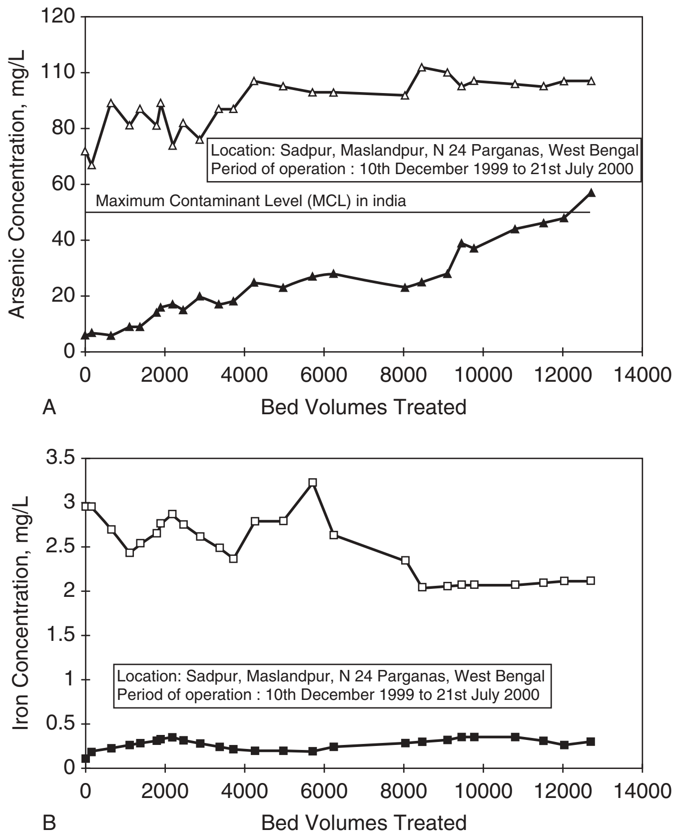

Figure 4 Influent (open symbols) and effluent (closed symbols) histories of the treatment unit at Sadpur village in North 24 Parganas, West Bengal, for (A) arsenic and (B) iron.

influent arsenic concentrations (i.e., there was no effect of variation in influent arsenic concentration on the effluent arsenic concentration from the treatment unit). So there was no danger of the arsenic concentration in the treated water at the exit of the column suddenly exceeding the MCL. Therefore, it is safe to test the effluent water for arsenic in an interval of one month. Every treatment unit is tested for arsenic and iron concentration in the treated water monthly.

Every well studied to date has been found to contain both As(III) and As(V), but their relative distribution varies; the presence of As(III) along with As(V) has also been reported in Bangladesh and elsewhere [28,29]. The effectiveness of the wellhead unit is assessed by its overall arsenic removal ability (i.e., for removal of both arsenates and arsenites). Selected sets of influent and treated water analyses were carried out for a number of wellhead units in the region after significant arsenic breakthrough took place. Table 2 provides the names of the villages, As(V) and As(III) analyses of influent and effluent water, and their

TABLE 2 Distribution of As(III) and As(V) in Well Water and Their Percentage Removal

Location of Wellhead Units	Arsenic (μg/L) Influent AS(III)	Influent AS(V)	Influent Total	Effluent AS(III)	Effluent AS(V)	Effluent Total	% Removal AS(III)	% Removal AS(V)
Debnagar, Murshidabad	219	144	363	10	23	33	95.43	84.03
Rampur, N 24 Parganas	140	80	220	13	25	38	90.71	68.75
Prithiba, Guma, N 24 Parganas	90	57	147	3	25	28	96.67	56.14
Banipur, Habra, N 24 Parganas	154	63	217	13	47	60	91.56	25.40
Dakshin Chatra, N 24 Parganas	53	53	106	8	13	21	84.91	75.47
South Betpool, N 24 Parganas	108	144	252	22	2	24	79.63	98.61
South Chatra, N 24 Parganas	50	30	80	14	4	18	72.00	86.67
Sendanga, N 24 Parganas	70	30	100	9	12	21	87.14	60.00
Potapara, N 24 Parganas	62	58	120	20	15	35	67.74	74.14
Ashrafabad, N 24 Parganas	115	78	193	20	20	40	82.61	74.36

percentage removal. Note that As(III) removal is equally good or even better than As(V) removal in several locations. Activated alumina is not efficient for removal of As(III) species but can remove As(V) quite efficiently [30]. Since activated alumina is not effective in removing As(III), the role of dissolved iron or, more specifically, hydrous ferric oxide (HFO) precipitates in arsenic removal process can readily be recognized [7, 30–32]. Oxidation of dissolved iron alone in the absence of activated alumina is, however, unable to bring the total arsenic concentration below 50 μg/L, as evidenced from independent laboratory batch studies.

An earlier study demonstrated that the dissolved oxygen concentration in the influent water at the top portion of the column is quite high; oxygen concentration in the water drops to near-zero value at the end of the column [33]. This observation proves that the oxygen has been consumed to oxidize influent Fe(II) to Fe(III). Freshly precipitated amorphous HFO fines coalesced rapidly in the presence of activated alumina and are accumulated primarily near the top of the bed. As discussed earlier, the HFO particulates were removed from the column through backwash every morning and stored in the coarse sand filter next to the unit. The arsenic removal mechanism inside the column is elucidated in the following section.

ARSENIC REMOVAL: INTERPLAY OF VARIABLES

The arsenic removal data presented in the previous section and analyzed for many of the field removal units clearly suggest that the overall process of arsenic removal in these fixed-bed activated alumina adsorption columns is greatly influenced by three variables:

1. Dissolution of oxygen in water
2. Presence of iron in the well water and its rapid oxidation to HFO
3. The relative presence of As(III) compared to the total arsenic present in the groundwater

Arsenic removal in the wellhead units takes place in steps. First, the dissolution of oxygen from the air takes place at the air–water interface. The inlet chamber of the column is so designed that it offers passage of atmospheric air in and out of the column. At the inlet to the column, water is sprayed inside the filter. The droplets thus formed provide high specific surface area, facilitating enhanced diffusion of air to the aqueous phase. Also, the free space kept in the upper part of the filter over the activated alumina bed allows a longer residence time for the inlet water so as to facilitate further reactions.

Dissolved Fe(II) present in the raw water is oxidized to Fe(III) by the dissolved oxygen according to the following reaction:

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH_3)(s) + 8H^+ \qquad \Delta G^0_{reac} = -18 \text{ kJ/mol} \quad (1)$$

It may be noted that the standard state of free-energy change for reaction (1) is a high negative value which indicates that the forward reaction is thermodynamically very favorable. The insoluble ferric hydroxides or hydrated ferric oxides particles are formed at nearly neutral pH. The hydrogen ions generated in reaction are neutralized by the alkalinity (HCO_3^-) present in the groundwater. That is why no significant change in the pH is observed in the effluent at any installed wellhead units, regardless of its dissolved iron content. The HFO particles that are produced are mostly intercepted in the top part of the column. X-ray diffraction studies have confirmed that the HFO particles remain in an amorphous state and no crystalline iron oxide (e.g., goethite, hematite, magnetite) was formed even after several weeks of operation.

Next, arsenite and arsenates are adsorbed onto activated alumina and HFO. As activated alumina is weak in adsorbing arsenite, its contribution for removal of As(III) is not significant. However, it contributes significantly to removal of As(V). HFO particles adsorb both As(III) and As(V). As(III) oxidation to As(V), for which +0.206 V is necessary, may be accomplished easily by dissolved oxygen in water and is a thermodynamically feasible process. However, the kinetics of such oxidation is rather slow [34], and simple conversion of arsenite to arsenate through oxidation by dissolved oxygen can be ruled out. It may also be hypothesized that a portion of precipitated HFO particles first oxidize As(III) to As(V), which is subsequently sorbed strongly onto HFO particles or activated alumina [35,36]. Dissolved Fe(II) thus formed is oxidized back to ferric hydroxide by oxygen in accordance with the following scheme:

$$HAsO_2 + 2Fe(OH)_3 + 3H^+ \longrightarrow H_2AsO_4^- + 2Fe^{2+} + 4H_2O \qquad (2)$$

dissolved oxygen

However, analyses of samples collected at different bed depths from an arsenic removal unit suggested minimal oxidation of As(III) to As(V). Even after complete exhaustion of the unit, where the influent contained about 95% of total arsenic as As(III), less than 25% of the total arsenic was present as As(V) in the effluent. Several previous studies also confirmed that As(III) oxidation by dissolved oxygen and/or hydrated Fe(III) oxide are kinetically slow and significant only in plug-flow fixed beds containing HFO particles [36,37]. Significant As(III) or arsenite removal in every wellhead unit is attributed to selective arsenite sorption onto freshly precipitated HFO particles [38]. Previous spectroscopic studies validated arsenite binding onto HFO particles through the formation of inner-sphere complexes [39,40]. In fact, at a pH around 7.5, the As(III) sorption capacity of HFO is significantly greater than that of As(V) [40]. So it may be concluded that HFO takes up both As(V) and As(III) with almost comparable capability. Figure 5 attempts to illustrate the roles of different variables and components for removal of total arsenic from contaminated groundwater. The concentrations of As(III), As(V), Fe(II), and HCO_3^- vary from one place to another but remain within an envelope where the aforementioned mechanism remains operative. Thus, it may be concluded that although activated alumina plays a major role in arsenic removal, a significant role is also played by HFO.

REGENERATION OF AN EXHAUSTED UNIT

Upon exhaustion, the adsorption medium in each unit is replaced by fresh or previously regenerated media. The exhausted activated alumina is taken to a central regeneration facility where the medium is regenerated inside a stainless steel batch reactor that can be rotated about its horizontal axis manually. Figure 6 shows a batch reactor employed in regeneration. A 2% NaOH solution is used as the regenerant; an exhausted medium is rotated with two bed volumes of regenerant solution in the batch reactor for about 45 minutes. The process is repeated once with a fresh regenerant solution. During regeneration, pH remains

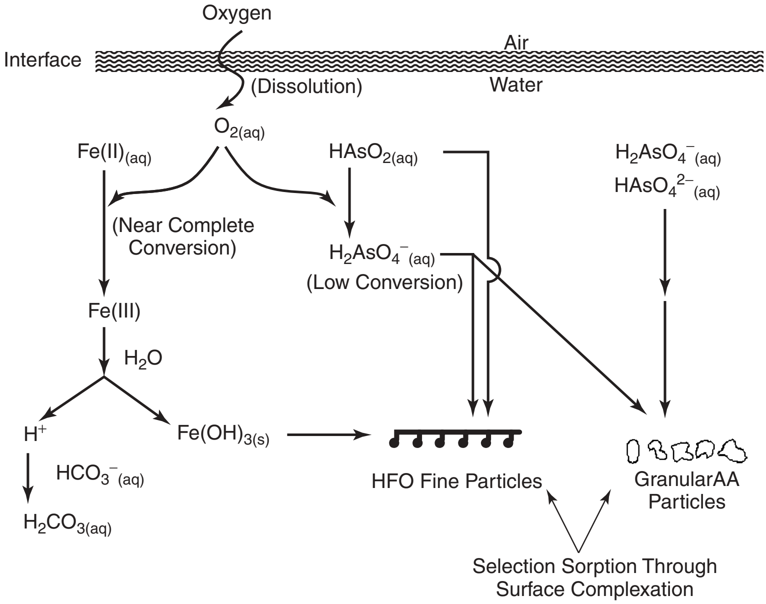

Figure 5 Interplay of variables for simultaneous removal of As(III) and As(V) in an adsorption column. AA, activated alumina; HFO, hydrated Fe(III) oxides.

Figure 6 Batch reactor employed to carry out regeneration at the central regeneration facility. (*See insert for color representation of figure*.)

near 12.0. The spent alkali is subsequently drained off and collected. After a rinse with well water, the medium is subjected to about two bed volumes of 1% HCl in order to neutralize the media. Subsequently, the spent acid is drained and collected. The medium is then rinsed thoroughly with water for half an hour. The medium is dried in the sun and kept in a safe place for reuse. At the end of the regeneration, spent acid, alkali, and rinse water are mixed, and pH is adjusted to around 6.5 by adding 10% hydrochloric acid. A thick brown slurry is formed immediately and is kept standing overnight before it is disposed of at the top of a coarse sand filter. The arsenic-laden solids and HFO particles are intercepted and retained at the top of the filter. The entire regeneration, including the spent regenerant treatment, is completed in about 5 hours.

CONSECUTIVE RUNS

Several of these arsenic removal units have been operated successfully for many cycles. When the arsenic concentration in the treated water nears 50 μg/L, the adsorption medium is regenerated and reused for the next cycle of operation. Figure 7 shows the concentration of dissolved arsenic in contaminated groundwater (influent) and in treated water (effluent) from one representative unit located at Habra village in the North 24 Parganas district in West Bengal, India for three consecutive cycles of operation. However, at the second and consecutive cycles of operation, an initial leakage of arsenic, of the order of 20 to 25 μg/L, was observed. It may be noted that although there were variations in the influent

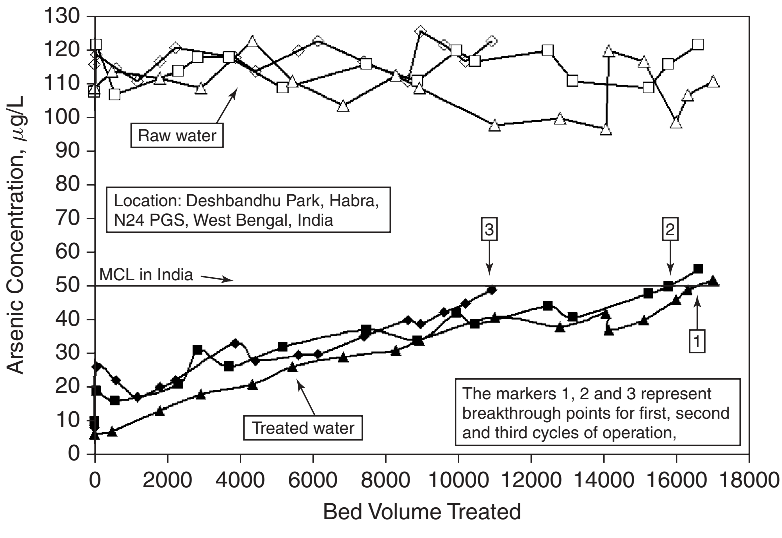

Figure 7 Sustained performance of arsenic removal for three consecutive cycles of operation.

arsenic concentrations, arsenic concentration in the treated water was not affected by the short-time peak concentrations. The initial leakage of arsenic might not be considered significant, due to the fact that the concentration of arsenic in treated water remained well below 25 μg/L. Moreover, regeneration and reuse of the adsorption media help to reduce the unit's operation cost.

REGENERATION AND SAFE TRANSFORMATION OF TREATMENT RESIDUES

Regeneration of exhausted media is carried out at a central facility following the general procedure as indicated earlier. Since 2003 there have been numbers of regenerations at the facility. As already noted, the spent regenerants and water rinses that contain high arsenic concentrations are not disposed of unless they are treated to convert the waste to environmentally benign substances. The spent regenerant and rinse solutions are mixed together and the pH is lowered to approximately 6.5. Immediately after the adjustment of pH of the mixed solution, a thick brown sludge is precipitated. After they are kept standing overnight, the aqueous phase and the sludge are slowly disposed on top of a coarse sand filter; the sludge is effectively retained at the top, whereas the aqueous phase (treated wastewater) percolates through the filter and into the soil. Pertinent details of one such regeneration and subsequent sludge formation are indicated in Table 3. The treated wastewater has a significantly low concentration of arsenic, which can be considered safe for disposal to surface runoff or water bodies.

An independent laboratory experiment with spent regenerants collected during regeneration of exhausted medium from another unit showed that aqueous arsenic and iron concentrations are lowest at pH 6.0. Figure 8 shows the result of the experiment. Field results are very similar to these laboratory data except for a significant concentration of aluminum in the field solution. A mass balance of the regeneration data demonstrates that the dry weight of the sludge generated as a residue of the regeneration should not be more than 600 g even if there is a significant quantity of ferric hydroxide precipitate. The aqueous phase has a fairly low concentration of arsenic, which means that the arsenic in the spent regenerant has been confined in the tiny amount of solid sludge, and hence the sludge has a very high concentration of arsenic on a dry weight basis.

TABLE 3 Volumes and Compositions of Individual Regenerant Streams for Regeneration of Exhausted Media Used at South Betpool, N 24 Parganas, West Bengal, India

Description	Volume (L)	pH	Total Arsenic (μg/L)	Total Iron (mg/L)
Spent caustic	400	12.5	2872	86.8
Spent acid	200	3.9	951	245.3
Spent rinse	200	5.5	840	34.1
Treated wastewater	800	7.1	30	0.96

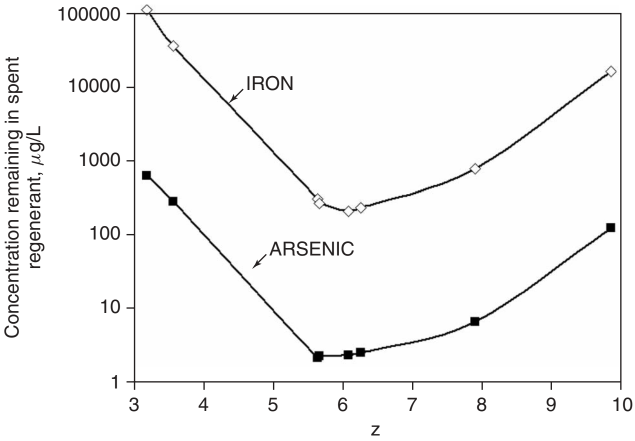

Figure 8 Concentrations of dissolved arsenic and iron in the aqueous phase of the mixed solution of spent regenerants and rinses at different pHs.

STORAGE AND LEACHING POTENTIAL OF TREATMENT RESIDUE

The arsenic-laden solid treatment residue generated at the central regeneration facility is stored on top of a coarse sand filter. The construction details of the coarse sand filter are similar to those next to the treatment units (Figure 1C), with size adequate to hold sludge produced from regenerations of all 150 units for at least 30 years. Laboratory tests were conducted to determine the leaching potential of the sludge kept under these conditions. Standard toxic characteristic leading procedure (TCLP) tests were carried out with the sludge at standard conditions [41]. Apart from the conventional TCLP tests, another set of leaching tests, called extended TCLP (ETCLP), were carried out. ETCLP tests are similar to TCLP but carried out at different pH levels so that the leaching potential at different pH conditions can be assessed [42]. Results of the TCLP test are indicated

TABLE 4 Results of TCLP and Chemical Analysis of Sludge from Regeneration of Unit at Potapara, N 24 Parganas, West Bengal

Chemical content of sludge	
Arsenic content (mg/g of dry sludge)	8.811
Iron content (mg/g of dry sludge)	150.91
TCLP results	
pH of extracting solution	2.84
pH of solution after extraction	4.87
Arsenic concentration after extraction (μg/L)	102.8
Iron concentration after extraction (mg/L)	1.2

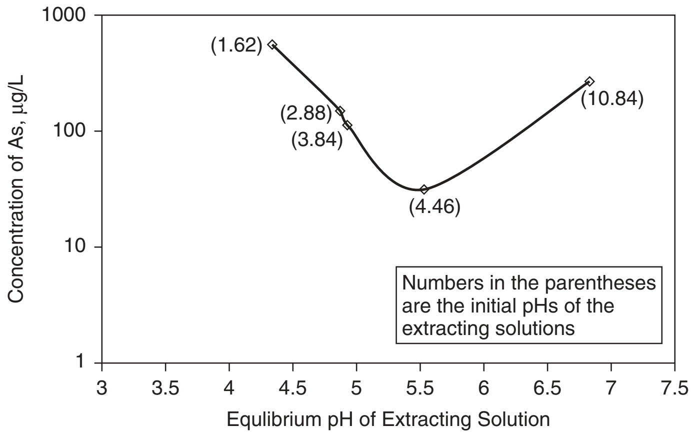

Figure 9 Arsenic leachability determined by an extended TCLP test for the treatment residue obtained from the top of a coarse sand filter at the central regeneration facility.

in Table 4. Figure 9 Indicates the results of the ETCLP test. The similarity of the curves in Figures 8 and 9 suggests that arsenic release from the sludge takes place as a result of and is controlled by dissolution of ferric hydroxide particulates. Further leaching tests conducted in the laboratory with minicolumns using tap water and deionized (DI) water under an atmospheric condition indicated minimal leaching of arsenic. The arsenic leaching with tap water and DI water was found to be 10 and 15 µg/L, respectively. In both cases, all arsenic in leachate was found to be in As(V) form. Tap water and deionized water resemble surface runoff and rainwater, respectively.

RESIDUE MANAGEMENT

Managing and containing the arsenic removed from groundwater is as important as removing arsenic to provide safe drinking water. The local environmental laws/guidelines with regard to the safe disposal of arsenic-containing residual either do not exist or are not enforceable. However, to avoid any potential hazard in the future, proper management of treatment residuals is considered an important part of the overall treatment scheme.

Regeneration of the media is the first step to reducing the volume of treatment residuals. If there were no regeneration, every wellhead unit would produce 100 kg of disposable adsorbent media at the end of each cycle, posing a sizablee obstacle to safe waste management. Following regeneration and containment of arsenic as 600 g of solid sludge, the amount of treatment residue is reduced more than 150-fold. The sludge is contained and stored at the top of a coarse sand filter, which is designed specifically to maintain atmospheric condition inside.

The slightly oxidizing environment inside coarse sand filters helps to keep iron in the form of Fe(III) and arsenic in As(V) form. Figure 10 presents a pe–pH or

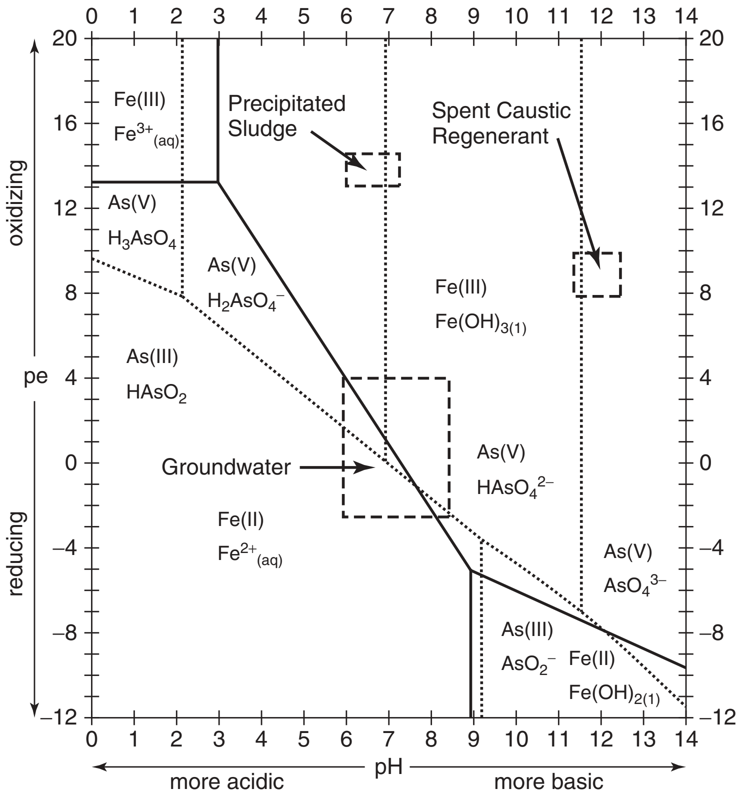

Figure 10 pE−pH diagram of iron and arsenic, confirming the predominance of As(V) and Fe(III) in the sludge precipitated after spent regenerant treatment.

predominance diagram for arsenic and iron. During the regeneration procedure, all the solutions are nearly saturated with atmospheric oxygen. The following half-reaction and the resulting pe value tend to determine the redox environment for them [43]:

$$\tfrac{1}{4}O_2 + H^+ + e^- = \tfrac{1}{2}H_2O \qquad pe^0 = 20.79 \tag{3}$$

$$pe = pe^0 + \tfrac{1}{4}\log\, PO_2 - pH \tag{4}$$

where PO_2, the partial pressure of oxygen, = 0.21 atm for atmospheric oxygen. For spent alkali regenerant at pH 11.5 to 12.5 and PO_2 = 0.21 atm, pe = 9.12 to 8.12. For precipitated sludge at pH 6 to 7 and PO_2 = 0.21 atm, pe = 14.62 to 13.62.

The estimated boundary of pe−pH conditions for both spent alkali regenerant and the precipitated sludge are marked on the pe−pH diagram. It may be noted that As(V) is the dominating species in both situations. Experimental observations indicated earlier support that fact. Since any reduction of HFO particles, which is the predominant constituent of the sludge, to Fe(II) will result in enhanced leaching of arsenic, the top of the coarse sand filter is deliberately kept open to the atmosphere through the provision of vents. Also, it may be noted from the pe–pH diagram that under conditions of pH 5 to 10, the pe value under atmospheric conditions is 15.6 and 10.6, respectively. In this region, the presence of Fe(III) and As(V) is thermodynamically favorable. Hence, there will not be any significant leaching of arsenic as long as an oxidizing condition prevails and the pH of the water passing through the storage chamber is in the range 5 to 10. Experimental observations of the leaching study carried out under such conditions indicated a very minimal leaching of arsenic, as indicated earlier.

On the other hand, if the sludge is kept under a reducing environment, such as in sanitary landfills, the pe–pH diagram dictates that thermodynamically both arsenic and iron will be reduced to As(III) and Fe(II). This condition causes enhanced leaching. TCLP may indicate minimal leaching of arsenic from the sludge as it is performed under an oxidizing environment. However, under reducing conditions such as those inside landfills, there will be enhanced leaching of arsenic. The evidence of such leaching is observed by Delemos et al. [44] and commented on by Blaney and SenGupta [45]. Also, there is evidence of research findings that TCLP underestimates leaching of arsenic [46], as the protocol essentially proposes to carry out tests with a headspace of air in the bottles.

COST OF TREATED WATER AND WATER TARIFF

One of the key attributes for a sustainable technology is the economic sustainability of that technology. The cost involved with the technology can be divided broadly into categories like fixed capital cost (cost of stainless steel column with internals and fittings, adsorption media, and civil cost); operation and maintenance cost (wages for caretaker responsible for backwashing and upkeep, cost of monthly water analysis and minor maintenance); and cost of regeneration (cost of chemicals, cost of labor). The itemized costs are indicated in Table 5 both in U.S. dollars and in Indian rupees.

In many villages the stainless steel adsorption unit has been operating for more than six years and the adsorption media have been regenerated and reused several times. The estimated life of the stainless steel arsenic removal units is more than 20 years. However, for calculation of the cost of water, a conservative life estimate of 10 years is considered. The interest rate is considered to be 6%. The amortization factor

$$a = \frac{i \cdot (i+1)^n}{(1+i)^n - 1} = 0.1358 \qquad (5)$$

where n, the number of years = 10 years, and i, the rate of interest = 6%.

TABLE 5 Costs Associated with the Wellhead Arsenic Removal Unit

Item	Cost in Rupees	Cost in U.S. Dollars
Fixed Capital Cost		
Stainless steel (SS-304) adsorption column with valves, internals, water meter, and connections with the existing wellhead hand pump	30,000	700
Adsorbent media: activated alumina	20,000	460
Civil work and installation, including labor	5,000	115
Total	55,000	1,275
Maintenance Cost (Annual)		
Wage to the caretaker responsible for daily backwashing and minor maintenance	15,000	340
Water testing (once every month with a replicate) in Bengal Engineering College or other private local laboratory	2,500	60
Total	17,500	400
Cost of Regeneration		
Cost of once-a-year regeneration and spent regenerant treatment, including labor and chemicals	4,500	110

For simplicity of calculation, assume that regeneration is done once a year; then the regeneration cost may be included in the annual cost. Thus,

$$\begin{aligned} \text{total annual cost for one unit} &= \text{amortization factor} \times \text{fixed capital cost} \\ &\quad + \text{annual maintenance cost} + \text{cost of regeneration} \\ &= 0.1358 \times \$1275 + \$110 + \$400 = \$683 \end{aligned} \quad (6)$$

From the data for 150 running units, it is estimated that the total volume of water treated by a unit in one year on average is about 8000 BV (i.e., 800,000 L). So the cost of water per 1000 L is 85 cents. The estimated amount of arsenic-safe water used by a family of six members for drinking and cooking purposes in a month at the rate of 5 L per capita per day is 900 L. The water tariff for a family of six for one month is around 75 cents or 30 rupees. However, capital costs for the existing 150 units have been provided by Water for People, Rotary International, Hilton Foundation, and other private donors; therefore, the present water tariff is only 15 rupees for a family per month, which is insignificant if the cost of suffering and the cost of medicine for arsenic- related diseases are considered. While regeneration helps reduce the volume of the sludge about 150-fold, reusability of the sorbent media helps decrease the cost of treated water significantly. Instead of regeneration and reuse of the media, if the media is replaced every cycle, leaving aside the environmental cost of safe disposal of the huge amount of exhausted media, the cost of water would have been much higher. The replacement of media would have cost about \$500 (22,000 rupees), including the cost of labor and transportation. This would have necessitated a water tariff of \$1.34 per 1000 L, which is 1.5 times more costly. The family burden for paying for water would have been 50 rupees per month, which is very high compared to the economic conditions of the rural Indian population.

CONCLUSIONS

Over 150 wellhead arsenic removal units are currently being operated by local villagers in the Indian state of West Bengal, bordering Bangladesh. The units are maintained and run by the beneficiaries. The units do not require chemical addition, pH adjustment, or electricity for regular operation. Each unit serves approximately 250 to 350 families living within a short distance of the unit, and the flow rate is modest at approximately 10 L/min. Arsenite, As(III), as well as arsenate, As(V), from the groundwater is effectively removed to render it safe for drinking and cooking. Regenerability and durability of the adsorbent allows for a low-cost, sustainable solution to the widespread arsenic poisoning in this area. After regeneration, the spent regenerants, containing a high concentration of arsenic, are converted to a small volume of sludge, which is stored under oxidizing conditions to prevent future arsenic leaching. This process offers superior economic advantages in regard to treatment and management of dangerous treatment residuals compared to conventional adsorbent-based processes, where regeneration and reuse are not practiced. Also, for conventional processes, the huge amount of media in landfills leaches out dangerous concentrations of arsenic. A global scheme for the overall process of arsenic removal including the management of treatment residues, is presented in Figure 11. Input to the process is groundwater contaminated with arsenic and caustic soda and acid for regeneration, whereas the outputs are simply treated drinking water and neutralized brine solution. Thus, the technology, besides being most appropriate for the rural settings of the affected area in terms of ease of use and economics, also offers considerable ecological sustainability. Similar community-level arsenic treatment technology, which is economically and environmentally sustainable, may be replicated in developing countries such as Bangladesh and Vietnam, where arsenic poisoning is a deadly menace.

Acknowledgments

The authors gratefully acknowledge the funding received from Water for People, Rotary International, Hilton Foundation, and other private donors for installation of community-level arsenic removal units on the Indian subcontinent. One of the authors is grateful to Lehigh University for providing opportunity to carry out related research work at Fritz Laboratory. The authors also thank the field workers for their enormous efforts, which have been instrumental in achieving success for the project.

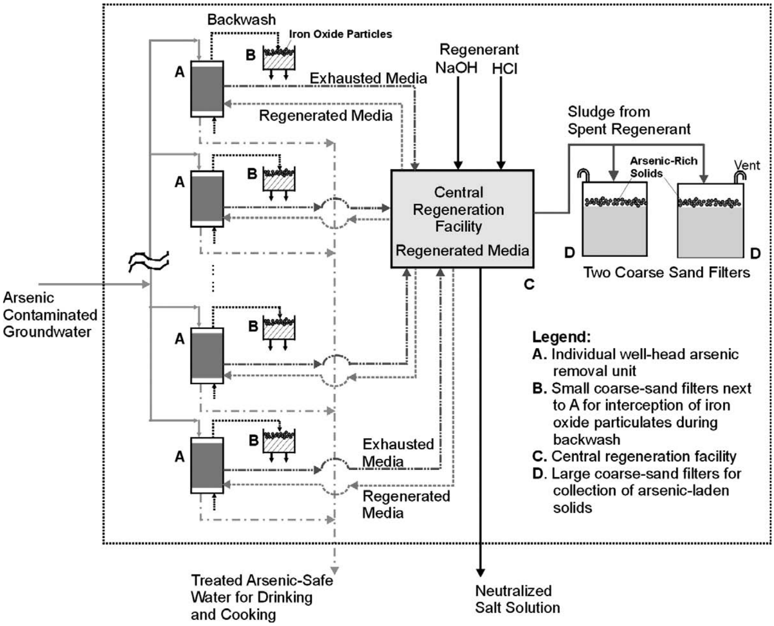

Figure 11 Global treatment scheme for arsenic removal and arsenic containment. (*See insert for color representation of figure*.)

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14

WATER SUPPLY TECHNOLOGIES FOR ARSENIC MITIGATION

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INTRODUCTION

Arsenic contamination of groundwater is a major water supply problem in many countries of the world. The estimated populations exposed to arsenic exceeding the national standard of 50 μg/L from drinking water are 29 million in Bangladesh, 5.63 million in China, 5.31 million in India, and 0.550 million in Nepal [1]. Apart form these, a significant percentage of the population is exposed to arsenic from drinking water in the United States, Argentina, Chile, Mexico, Hungary, Mongolia, Cambodia, Vietnam, Laos, and Taiwan. As a result, arsenic has become a major public health problem in many of these countries. Thousands of people have been identified as being affected by arsenic poisoning. Arsenic toxicity has no known effective treatment, but drinking of arsenic contamination–free water can help arsenic-affected people at the preliminary stage of their illness to get rid of the symptoms of arsenic toxicity. Hence, provision of arsenic contamination–free water is urgently needed for mitigation of arsenic toxicity and protection of the health and well-being of people living in acute arsenic problem areas in these countries.

Development of water supply systems avoiding arsenic-contaminated water sources and removal of arsenic to acceptable levels are two options for safe water supply. Arsenic-free water is not available in nature; hence the option to avoid arsenic is to develop water supply systems based on sources having very low

Arsenic Contamination of Groundwater: Mechanism, Analysis, and Remediation,
Edited by Satinder Ahuja

dissolved arsenic. Rainwater, well-aerated surface water, groundwater in both very shallow and deep aquifers are well-known arsenic-safe sources of water. Rainwater has very low arsenic, often undetectable by conventional detection and measurement techniques. The arsenic content of most surface water sources ranges from less than 1 μg/L to 2 μg/L. Very shallow groundwater replenished by rainwater or surface water and relatively old deep aquifers show arsenic content within acceptable levels.

Treatment of arsenic-contaminated water for the removal of arsenic to an acceptable level is the alternative option for a safe water supply in arsenic-affected areas. Arsenic treatment technologies can effectively make use of the existing water sources and the people will not be required to shift immediately to an unfamiliar water supply option. Since detection of arsenic in groundwater, a lot of effort has been mobilized for treatment of arsenic-contaminated water to make it safe for drinking purpose. During the last few years, many small-scale arsenic removal technologies for use at the community and household levels have been developed, field tested, and used under action research programs in Bangladesh, India, Nepal, Vietnam, and other countries. Some of these have been tested and evaluated under different technology verification programs and accepted for deployment under certain conditions.

In this chapter we present a short review of small-scale water supply technologies used in household and community water supplies for arsenic mitigation in different countries of the world. We update technological development in small-scale water supplies and discuss the problems, prospects, limitations, and conditions of deployment of different treatment processes. We also delineate areas of further improvement for successful implementation and adaptation of technologies to local conditions.

TECHNOLOGIES BASED ON ARSENIC-SAFE WATER SOURCES

Technologies for producing drinking water using water sources known to have low arsenic content include:

- Treatment of surface water by slow sand filtration, combined roughing and slow sand filtration, conventional coagulation–sedimentation–filtration and disinfection. Rivers, lakes, and ponds are the main sources of surface water and the degree of treatment required varies with the level and type of impurities present in water.
- Dug wells/ring wells or very shallow tube wells to abstract low-arsenic groundwater from very shallow aquifers.
- Deep tube wells to collect arsenic-safe water from deep protected aquifers.
- Rainwater harvesting systems to collect, store, and use rainwater before it joins the surface water and groundwater.

Treatment of Surface Waters

Surface water is arsenic-safe but invariably contains microorganisms of greater immediate health concerns. Surface water requires treatment for a desired level of clarification and disinfection to make it safe for water supply. Protection of sources from contamination makes treatment easier, and an unprotected source requires elaborate treatment for removal of impurities of different origins. Most important, the surface water sources must be perennial, and the availability of such sources is difficult in many areas. The methods of surface water treatment in use in developing countries and their suitability and conditions of deployment are stated below.

Slow Sand Filtration Slow sand filtration (SSF) is a low-cost technology with very high efficiency in turbidity and bacterial removal that is suitable for the treatment of surface water with low levels of contamination. The water from the pond/river is pumped by a mechanical or manually operated pump to feed the filter bed, which is raised from the ground, and the treated water is collected through tap(s) or pumped to an overhead water tank for distribution through pipe networks. The removal of impurities from the raw water is brought about by a combination of processes, such as sedimentation, adsorption, straining, and most important, biochemical and microbial actions [2]. It has been found that the treated water from a slow sand filter is normally clear and bacteriologically safe or within tolerable limits. It is suitable for the development of a surface water–based water supply system in developing countries. The main purposes of slow sand filters are to:

- Reduce the number of microorganisms present in the water
- Retain fine organic and inorganic solid matters and reduce turbidity
- Oxidize organic compounds dissolved in water

The main features of a slow sand filter consist of an inlet, the filter box, and an outlet control box, as shown in Figure 1. The shape of filter box has no influence on filter performance and can be rectangular, square, or circular. The filtration rate should be on the order of 0.1 to 0.2 m/h. Clean sand free of clay, silt, and organic matter is used as filter material. The sand should not be too fine, to avoid high initial head loss. The sand used for the filter bed should have an effective size, d_{10}, between 0.1 and 0.3 mm and a uniformity coefficient d_{60}/d_{10} below 3. The sand may require sieving to discard fine and coarse fractions. The underdrain system is usually composed of a gravel layer with a total height of 0.3 to 0.5 m which supports sand and provides enough space for a perforated pipe system to collect filtered water evenly. The installation of a false floor made of concrete blocks or bricks can be used as an alternative to perforated pipes.

SSF is an alternative water supply system for medium-sized settlements in arsenic-affected areas provided that the level of contamination of water at source is low. Slow sand filters perform best under continuous operation and

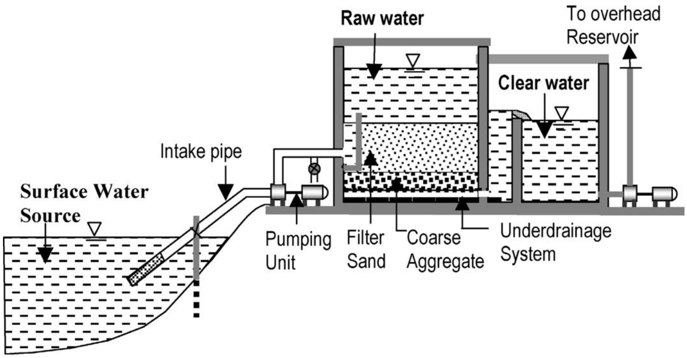

Figure 1 Slow sand filtration unit with a mechanical pumping system.

constant-flow conditions. A 24-hour operation makes maximum use of the plant. The biological activities must first be allowed to develop in a newly installed filter bed. This ripening period will take two to four weeks after installation. The purification process is located primarily in a thin layer located at the surface of the sand bed called “Schmutzdecke.”

The proven method of cleaning a slow sand filter is by scraping off the sand surface with hand shovels to remove the top 1.5 to 2.0 cm of dirty sand. The scraped-off mixture of sand and impurities may be discarded and replaced by new sand or washed for re-use if it is cheaper than buying new sand. The thoroughly washed, scraped sand may be applied during the next cleaning operation. The cleaning frequency for well-operated slow sand filters is approximately one to three months. After removal of the top layer, the filter operation is immediately started to minimize interference with the biological activity within the filter bed. A cleaned filter will regain full biological activity within two to three days provided that the cleaning procedure is of a few hours’ duration [3].

Slow sand filtration can only treat relatively clear water. Higher turbidity will rapidly clog the filter bed, interfere with the biological process, and reduce the filter runs between filter cleanings. The presence of small numbers of algae is beneficial to the treatment process, but algal bloom will result in filter failure. The operation conditions of slow sand filters include [4]:

- Low turbidity, not exceeding 30 NTU (nephelometer turbidity units)
- Low bacterial count
- No algal bloom; absence of cyanobacteria
- Free of bad smell and color

A protected surface water source is ideal for slow sand filtration. The problems encountered for not maintaining the foregoing operation conditions include low discharge, need for frequent washing, and poor effluent quality. Since these are small units, community involvement in operation and maintenance is absolutely essential to keep a system operational. Although SSF has a very high bacterial removal efficiency, it may not reduce the bacterial count to acceptable levels in case of heavily contaminated surface water. In such cases, the treated water may require chlorination to meet drinking water standards.

The requirement for frequent washing of filter media resulting from filtration of water of high turbidities is the main reason for abandoning many existing slow sand filters in Bangladesh and India. Apart from turbidity, the presence of algal blooms in stagnant water bodies makes the water unsuitable in certain seasons of the year. The presence of cyanobacteria in some area is another constraint for slow sand filtration of surface waters. A study in Bangladesh shows that about 95% of the pond sand filters (PSFs) produce water with high thermotolerant coliform (TTC) counts due to the poor quality of pond water and lack of proper operation and maintenance [5]. Disinfection of PSF water is needed to produce water of acceptable quality for drinking purposes.

A large number of slow sand filters have been installed in Bangladesh under different programs, including arsenic mitigation, a significant proportion of which remains out of operation for poor maintenance. The major limitations mentioned by different organizations in Bangladesh involved in the installation of PSFs are as follows [6]:

- The discharge is low due to filter clogging.
- Operation and maintenance are difficult.
- PSFs are not suitable for heavily contaminated ponds.
- People complained of a foul taste in pond water, and many resorted to using it for cooking only.
- PSFs conflict with fish culture.
- It is difficult to find an appropriate/reserve pond for installation of PSFs.
- Many ponds dry up in the dry season in some parts of the country.
- Secondary contamination takes place due to lack of proper maintenance.

Multistage Filtration A multistage filter consisting of roughing filters and a slow sand filter can remove impurities of moderately contaminated surface waters to acceptable levels for drinking water. It is introduced to overcome the frequent clogging encountered in SSF due to high suspended solids in surface waters. Multistage filters can operate effectively when the turbidity of surface water exceeds 30 mg/L. The roughing filtration unit is used for pretreatment of highly polluted water and makes the water suitable for slow sand filtration. The turbidity reduction by upflow, downflow, and horizontal flow roughing filters amounts to about 70 to 90%, while the bacteriological water quality improvement by roughing filters was of about the same order [7]. The roughing and slow sand filter units have been constructed in many parts of the world with success in reduction of very high turbidities and coliform counts. Operation and maintenance are relatively easy, and less frequent attention is needed for a longer duration of

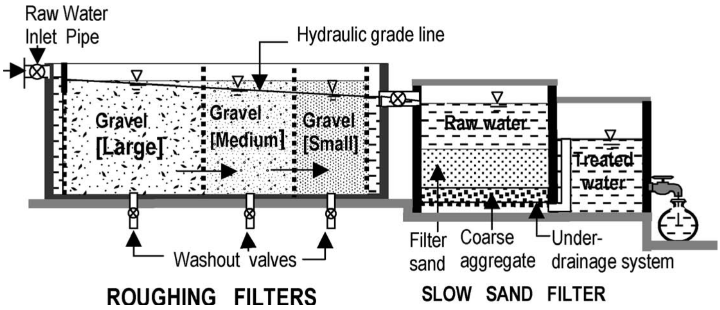

Figure 2 Horizontal-flow multistage filtration unit.

operation between cleaning. Experimental units are in operation in Bangladesh. A multistage filter is shown in Figure 2.

Flow through a roughing filter bed is controlled by inlet and outlet valves. The flow rate is adjusted in the inlet valve and the outlet at the start of the filtration operation. The inlet-controlled slow sand filter is easier to operate. In the case of slow sand filtration units the water depth on the filter bed will gradually increase with the running of the filter and the development of head loss.

Conventional Treatment of Surface Water Conventional treatment plants can be scaled down to meet the requirements for the treatment of surface waters for relatively larger communities. The conventional treatment for surface water involves presettling, coagulation, sedimentation, filtration, and disinfection processes, which can effectively remove the high levels of impurities commonly present in surface waters. It is relatively costly and requires skilled personnel for operation and maintenance. The per capita cost of treatment can be reduced significantly if a large number of consumers can be brought under one unit by a piped water supply.

Conditions for deployment of surface water treatment for drinking water supply are as follows [8]:

- Availability of a perennial water source of acceptable quality
- Evaluation of water quality and installation of the right processes to suit the prevailing water quality of the source
- Monitoring of water quality, particularly turbidity and bacteriological quality, and adopting measures as appropriate
- Acceptability of the community and willingness to operate and maintain the system
- Protection of the source from contamination
- Large enough unit for conventional treatment to maintain a full-time trained operator for operation and maintenance of the system
- Adoption of a water safety plan for greater health benefit (if feasible)

Dug or Ring Wells

The withdrawal of groundwater by digging wells is the oldest method of water supply. Dug/ring wells collect water from the top of the aquifer, which is replenished each year by infiltration of arsenic-free rainwater or by percolation of surface water through an aerated zone. The oxidation of dug well water due to its exposure to open air and agitation during water withdrawal may also be the cause of low dissolved arsenic and iron in dug well water. Dug wells are widely used in many countries of the world for domestic water supplies. Flow in a dug well is actuated by lowering the water table in the well due to withdrawal of water. Usually, no special equipment or skill is required for the construction of dug wells. The wells should be at least 1.2 m in diameter for construction by manual digging. Large-diameter wells may be constructed for community water supplies. The depth of the well is dependent on the depth of the water table and its seasonal fluctuations. Wells should be at least 1 m deeper than the lowest water table. Community dug wells should be deeper to provide a larger surface area for the entry of enough water to meet the higher water demand. Private dug wells are less that 10 m deep, but dug wells for communal use are usually 20 to 30 m deep.

Dug wells cannot be constructed and maintained in loose sandy silt. Soils with clay and silt produce a very small amount of water per day for the water supply. Traces of organic debris in soil strata produce water with unacceptable odor, color, and turbidity. Sanitary protection and careful monitoring of water quality are essential components of dug well–based water supplies. The upper part of the well lining and the space between the wall and soil require proper sealing. The construction of an apron around the well can prevent entry of contaminated used water by seepage into the well.

A study conducted on the risk assessment of arsenic mitigation options (RAAMO) showed that microbial contamination of dug well water indicated by TTC counts is high, while the number of TTCs in dug well water increases drastically in a monsoon [5]. Dug wells are vulnerable to arsenic, iron, manganese, and bacterial contamination [9]. Water in a dug well is very easily contaminated if the well is open and the water is drawn using bucket and rope. Dug wells constructed closer to habitations are more vulnerable to contamination, while drinking water sources nearer households are needed for accessibility and convenience. Satisfactory protection against bacteriological contamination is obtained by sealing the well top with a watertight concrete slab. Water may be withdrawn by installation of a manually operated handpump. An unprotected and a protected dug well are shown in Figures 3 and 4.

The experience in dug well–based water supplies for arsenic mitigation is not very encouraging in Bangladesh and India. In acute arsenic problem areas, a significant proportion of dug wells have been found to be arsenic contaminated. Bacterial contamination, bad smell, and high turbidity are characteristic water quality problems in many affected areas of Bangladesh and India. Since the presence of organics in soil is the cause of arsenic contamination of groundwater in many areas, dug wells do not provide a suitable water supply option in those

Figure 3 Water collection from an open dug well. (*See insert for color representation of figure.*)

areas. The low or no dissolved oxygen and very low oxidation–reduction potentials of dug well water is unfavorable for the oxidation of arsenic and iron and improvement of water quality [10]. The difficulty in the control of microbial contamination of dug wells by a disinfectant has also been reported in West Bengal [11]. An improved small-diameter (1.2 m) dug well can, on average, supply drinking and cooking water to only about 15 households in the dry season.

Figure 4 Water collection from a protected (covered) dug well. (*See insert for color representation of figure.*)

Dug wells can be constructed for drinking water supplies in arsenic-affected areas when the following conditions are met:

- The presence of water-bearing sandy strata and fluctuation of the water level within the depth of the well are required, whereas the presence of clayey soil, black/organic-rich soil, and loose silty soil are not suitable for a dug well.
- After construction of a well, the water should be treated with lime and disinfected with bleaching powder.
- A prescribed set of water quality parameters, including the presence of pesticide residues, is required to be analyzed before the well can be commissioned.
- Sanitary protection is required to prevent dug well water from contamination.
- Water quality monitoring, particularly of arsenic content and bacteriological quality, is required at regular intervals. Disinfecion of well water may be required during operation if bacteriological contamination cannot be controlled.
- Acceptability by the community and willingness of the community to operate and maintain the system are considered essential for sustainability.

Very Shallow Shrouded Tube Wells In many areas, groundwater with a low arsenic content is available in shallow aquifers composed of fine sand at shallow depths. This may be due to accumulation of rainwater in the upper part of the aquifer or dilution of arsenic-contaminated groundwater by fresh water recharged each year by surface and rain waters. However, the particle size of soil and the depth of the aquifer are not suitable for installing a normal tube well. To get water through these very fine-grained aquifers, artificial sand packing called shrouding is required around the screen of the tube well. This packing increases the yield of the tube well and prevents the entry of fine sand into the screen. However, shrouding is not required if the productivity of the aquifer is good at the level of the strainer.

Deep Tube Wells

Deep aquifers in many countries are relatively free of arsenic contamination. The aquifers in many countries are stratified and in some places are separated by relatively impermeable strata. Deep tube wells (DTWs) installed in those protected deeper aquifers are producing arsenic-safe water. The British Geological Survey (BGS) and Department of Public Health Engineering (DPHE) study in Bangladesh has shown that only about 1% of deep tube wells 150 m or more deep are contaminated with arsenic exceeding 50 μg/L [12]. The RAAMO study reported very low levels of arsenic and microbial contamination of DTW water and found that the disease burden of DTW water is the lowest among all alternative water supply options [5]. Hence, deep tube wells may be installed to avoid shallow arsenic-contaminated aquifers where suitable arsenic-safe deep aquifers are available to produce water of acceptable quality for a water supply. Manually operated deep tube wells have very low drawdown and insignificant impact on the hydraulics of deep aquifers. The identification of areas having suitable deep aquifers and a clear understanding of the mechanism of recharge of these aquifers are needed to develop DTW-based water supply systems. A manually operated DTW is shown in Figure 5.

In general, permeability, specific storage capacity, and specific yield usually increase with depth because of the increase in the size of aquifer materials. Experience in the design and installation of tube wells shows that reddish sand/dupitila aquifer produces the best quality water in respect to dissolved iron and arsenic. Aquifers below marine clay in the coastal areas also produce arsenic-safe water. Manually operated deep tube wells are a source of safe and reliable water supply in most parts of the coastal areas of Bangladesh. Tube wells are a very popular technology for water supply in arsenic-affected areas, hence an arsenic-safe deep tube well in place of a shallow contaminated tube well is the most popular option for arsenic mitigation. An assessment of progress in arsenic mitigation in Bangladesh shows that despite the restrictions in the National Policy and Implementation Plan for Arsenic Mitigation [13], about 12% of people living in some arsenic-affected areas in Bangladesh have been provided with arsenic-safe water by installing deep tube wells [14].

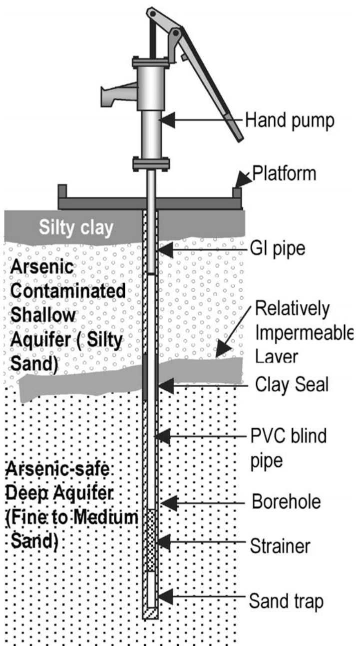

Figure 5 Deep tube well with hand pump.

However, there are many areas where the separating impermeable layers are absent and aquifers are formed by stratified layers of silt and medium sand. Deep tube wells in such areas may yield arsenic safe water initially but the arsenic content of the water is likely to increase with time, due to mixing of contaminated and uncontaminated waters. Again the possibility of contamination of deep aquifers by interlayer movement of large quantities of groundwater cannot be ignored. If a deep aquifer is recharged primarily by vertical percolation of contaminated water from the shallow aquifer above, the deep aquifer is soon likely to be contaminated with arsenic. For the installation of a tube well in a deeper layer, sealing the annular space of the borehole by impermeable clay or sand–cement slurry as shown in Figure 5 is necessary to prevent intralayer movement of water. However, recharge of deep aquifers by infiltration through coarse media and replenishment by the horizontal movement of water are likely to keep the aquifer arsenic-free even after prolong water abstraction. Since many people in rural areas in developing countries still use surface water for cooking and bathing, installation of a deep tube well in an area can be a source of drinking water for a large number of people. A protocol for the installation of a deep tube well to abstract arsenic-safe water from a deeper aquifer in an arsenic-contaminated area has been developed in Bangladesh [13], naming the following conditions of deployment:

- The presence of relatively impermeable layers between arsenic-safe deep aquifers and shallow contaminated aquifers is important for the installation of a deep tube well.
- The annular space of boreholes in deep tube wells must be sealed at the level of impermeable strata to avoid percolation of arsenic-contaminated water. With a thick overlying clay layer, sealing is not required.
- A prescribed set of water quality parameters, including possible toxic substances in DTW water, must be analyzed before the tube well is commissioned.
- Water quality monitoring, particularly changes in the arsenic content of the water, is required at least once in a year.

Rainwater Harvesting

Rainwater is the main source of fresh water available in inland surface water and groundwater resources. Rainwater harvesting (RWH) is the process of collecting rainwater before it joins the surface water and groundwater resources. Rainwater is relatively free of impurities, except those picked up from the atmosphere, but the quality of rainwater may deteriorate during the process of harvesting and unsanitary practices in storage and consumption [15]. RWH has good potential as a water supply in arsenic-affected areas in most of the countries affected. The advantages of RWH are that the quality of rainwater is relatively good, the system is independent and suitable for a scattered population, no energy costs are incurred, and the system is easy to construct and maintain with materials available locally. The availability of rainwater is regulated by rainfall intensity, distribution of rainfall throughout the year, and availability of suitable catchment areas.

Rainwater is harvested using roof and surface catchments and stored in tanks for use. The roof catchment is connected with a gutter and downpipe system to lead rainwater to the storage tank. A rainwater-based water supply system requires determination of the capacity of the storage tank and catchment area for rainwater collection in relation to water requirements, rainfall intensity, and rainfall distribution. Because of the requirements for large catchment areas and storage tanks, due to unequal distribution of rainfall throughout the year in many countries, rainwater harvesting is relatively costly and designed to meet the demand for drinking and cooking water of only one household. Community rainwater harvesting systems have also been developed for schools and in other common use areas where large catchment areas are available.

The catchment area for rainwater collection is usually the roof, which is connected to a gutter system to lead rainwater to the storage tank. (Figure 6). Rainwater can be collected from any type of roof but concrete, tile, and metal roofs give the cleanest water. Poorer people are in a disadvantageous position with respect to the utilization of rainwater as a source of water supply in developing countries, as they often have smaller thatched roofs or no roof at all. A thatched roof can be used as a catchment area by covering it with polyethylene, but it requires good skills to guide water to the storage tank. In coastal areas of Bangladesh, pieces of cloth fixed at four corners with a pitcher underneath are used for rainwater collection. Plastic sheets (Figure 7) have also been tried as a catchment for rainwater harvesting for people who do not have a roof suitable for rainwater collection.

Figure 6 Rainwater harvesting by roof catchment. (*See insert for color representation of figure.*)

Figure 7 Plastic sheet catchment for rainwater harvesting. (*See insert for color representation of figure.*)

The use of a land surface as a catchment area, with an underground gravel/sand-packed reservoir as a storage tank, can be an alternative system of rainwater collection and storage. In this case, the water has to be channeled toward the reservoir and allowed to pass through a sand bed before entering underground reservoirs. This process is analogous to recharge of an underground aquifer by rainwater during a rainy season for utilization in a dry season.

The quality of rainwater is relatively good, but it is not free of all impurities. Windblown dirt, leaves, fecal droppings from birds, insects, and animals, and contaminated litters in catchment areas are the main sources of contamination of rainwater. Microbial contamination of rainwater as indicated by coliform counts is quite common, and some is of fecal origin. Such pathogens as *Cryptosporidium, Giardia, Campylobacter, Vibrio, Salmonella, Shigella*, and *Pseudomonas* spp. have been found in rainwater [15]. The highest microbial counts are found in the first flush of rainwater; the level of contamination decreases as the rain continues. A significant reduction of microbial contamination was found in the rainy season, when flush washing of a catchment is frequent. Long storage of rainwater in a poorly managed system is associated with the growth of algae, aquatic organisms, and breeding of dengue mosquitoes inside the storage tanks. Risk assessment of alternative water supply technologies used for arsenic mitigation in Bangladesh showed that rainwater, despite some microbial contamination, offered the second-best option after deep tubewells with respect to the estimated disease burden from drinking water [5].

The quality of rainwater is directly related to the cleanliness of catchments, gutters, and storage tanks. The first flush of rainwater carries most of the contaminants. A system is therefore necessary to divert the contaminated first flow of rainwater from roof surfaces. If the storage tank is clean, the bacteria or parasites carried with the flowing rainwater will tend to die off. Several devices and good practices have been suggested to store or divert the first foul flush away from the storage tank. The important factors in preserving the quality of stored rainwater include proper design and installation/construction of the rainwater harvesting system, covering the storage tank, and screening of inlet and outlet holes. Sunlight reaching the water will promote algae growth. The storage tank requires cleaning and disinfection when the tank is empty, or at least once a year. Disinfection of rainwater should also be practiced when microbial contamination and sanitary risk observed during operational monitoring warrant such remedial action. Disinfection with chlorine can make rainwater safe for drinking.

Minerals such as calcium, magnesium, iron, and fluoride in appropriate concentrations are considered essential for health, but rainwater is essentially lacking in minerals. The mineral salts in natural ground and surface waters sometimes impart a pleasing taste to water. Mineral-deficient rainwater tastes flat and may not be acceptable to people used to drinking mineral-rich water.

The following conditions are required for the installation of a deep tube well for arsenic mitigation:

- A suitable catchment area must be available, together with a properly constructed and well-maintained storage tank.
- A rainwater harvesting system can be a supplementary source of drinking water.
- Control of microbial contamination is necessary.
- A water safety plan can provide water with greater health benefits.

TREATMENT OF ARSENIC-CONTAMINATED WATER

Aresenic removal from contaminated water for drinking water supplies has attracted enormous attention in recent years. The most commonly used processes include oxidation and sedimentation, coagulation and filtration, lime treatment, adsorption onto sorptive media, ion exchange, and membrane filtration [16–21]. A detailed review of arsenic removal technologies is presented by Sorg and Logsdon [22]. Jackel [23] has documented several advances in arsenic removal technologies. In view of the lowering of drinking water standards by the U.S. Environmental Protection Agency (EPA), a review of arsenic removal technologies was made to consider the economic factors involved in implementing lower drinking water standards for arsenic [24]. Many of the arsenic-removal technologies have been discussed in detail in the AWWA reference book [25]. A review of low-cost well-water treatment technologies for arsenic removal, with a list of companies and organizations involved in arsenic removal technologies, has been compiled by Murcott [26]. Comprehensive reviews of arsenic removal processes have been documented by Johnston et al. [27], Ahmed [1], and Ahmed et al. [28].

Some units developed for the treatment of arsenic at the household and community levels and installed for experimental use in various parts of Bangladesh, India, Nepal, Vietnam, and other countries have shown good potential for use as water supplies in arsenic-affected areas. All the technologies have merits and demerits and are being refined to make them suitable for use in rural areas. Modifications based on pilot-scale implementation of the technologies are being made to improve effectiveness, reduce the capital and operation costs, make the technology more user friendly, and overcome operational and maintenance problems.

Oxidation and Sedimentation Processes

Arsenic is present in groundwater in As(III), arsenite, and AS(V), arsenate, forms in different proportions depending on the groundwater environment and degree of oxidation after abstraction. Most treatment methods are effective in removing arsenic in pentavalent form and hence include an oxidation step as pretreatment to convert arsenite to arsenate. Arsenite can be oxidized by oxygen, ozone, free chlorine, hypochlorite, permanganate, hydrogen peroxide, and Fulton's reagent, but atmospheric oxygen, hypochloride, and permanganate are commonly used for oxidation in developing countries. Atmospheric oxygen is the most readily available oxidizing agent, and many treatment processes utilize oxidation by air. But air oxidation of arsenic is a very slow process that can take weeks [29]. Chemicals such as chlorine and permanganate can rapidly oxidize arsenite to arsenate under a wide range of conditions. Ozone and hydrogen peroxide are very effective oxidants, but their use in developing countries is limited. Filtration of water through a bed containing solid manganese oxides can oxidize arsenic rapidly without releasing excessive manganese in the water filtered.

Passive Sedimentation

Passive sedimentation received considerable attention because of rural people's habit of drinking stored water from pitchers. Oxidation of water during collection and subsequent storage in houses may cause a reduction in arsenic concentration in stored water (*bashi pani*). Experiments conducted in Bangladesh showed no to high reduction in arsenic from drinking water by passive sedimentation. Arsenic reduction by plain sedimentation appears to be dependent on water quality, particularly the presence of precipitating iron in water. Ahmed et al. [30] showed that more than a 50% reduction in arsenic content is possible by sedimentation of high-alkalinity tube well water containing iron but cannot be relied upon to reduce arsenic to the desired level when the concentration is high. High alkalinity and the presence of iron in tube well water increase arsenic removal by storage. Most studies showed a reduction of zero to 25% of the initial concentration of arsenic in groundwater. Passive sedimentation failed to reduce arsenic to the desired level of 50 μg/L in a rapid assessment of technologies conducted in Bangladesh [31].

In Situ Oxidation In situ oxidation of arsenic and iron in aquifers was tried under an arsenic mitigation pilot project. The aerated tube well water was stored in the 500-L-capacity feed water tank shown in Figure 8 and released back into the aquifers through the tube well by opening a valve in a pipe connecting the water tank to the tube well pipe under the pump head. The dissolved oxygen in water oxidizes arsenite to less mobile arsenate and the ferrous iron in the aquifer to ferric iron, resulting a reduction in arsenic content in tube well water. Experimental results show that arsenic in the tube well water following in situ oxidation is reduced to about half, due to underground precipitation and adsorption on ferric iron [32].

Solar Oxidation SORAS is a simple method of solar oxidation of arsenic in transparent bottles to reduce the arsenic content of drinking water [33]. Ultraviolet radiation can catalyze the process of oxidation of arsenite in the presence of other oxidants, such as oxygen [34]. Experiments in Bangladesh show that, on average, the process can reduce the arsenic content of water to about one-third of the original concentration.

Coagulation and Filtration

In the process of coagulation and flocculation, arsenic is removed from solution through three mechanisms: precipitation, coprecipitation, and adsorption [35]. Arsenic removal by precipitation, co-precipitation, and adsorption by coagulation with metal salts and lime followed by filtration is the most heavily documented

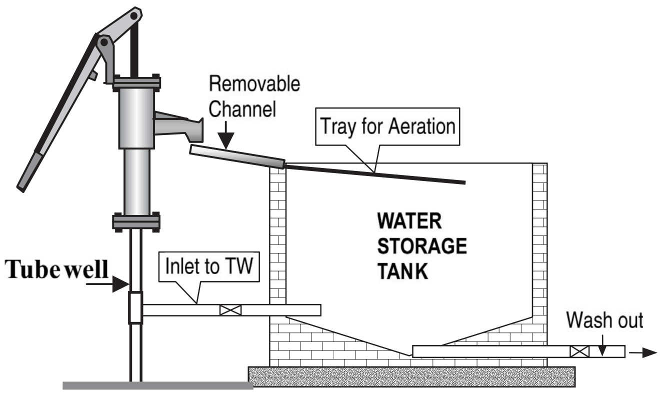

Figure 8 Feed water tank for in situ arsenic removal. (Based on Sarker and Rahman [32].)

method of arsenic removal from water. This method can effectively remove arsenic and many other suspended and dissolved solids from water, including iron, manganese, phosphate, fluoride, and microorganisms, and improve turbidity, color, and odor, resulting in a significant improvement in water quality. Water treatment with coagulants such as aluminum alum [$Al_2(SO_4)_3 \cdot 18H_2O$], ferric chloride ($FeCl_3$), and ferric sulfate [$Fe_2(SO_4)_3 \cdot 7H_2O$] are effective in removing arsenic from water, but ferric salts have been found to be more effective in removing arsenic than alum on a weight basis and over a wider range of pH. In both cases pentavalent arsenic can be removed more effectively than trivalent arsenic [3].

In the coagulation–flocculation process, aluminum sulfate, ferric chloride, or ferric sulfate is added and dissolved in water under efficient stirring for one to a few minutes. Aluminum or ferric hydroxide microflocs are formed rapidly. The water is then stirred gently for a few minutes for agglomeration of microflocs into larger, easily settlable flocs. During this flocculation process all kinds of microparticles and negatively charged ions are attached to the flocs electrostatically. Arsenic is also adsorbed onto coagulated flocs. As trivalent arsenic occurs in nonionized form, it is not subject to significant removal. Oxidation of As(III) to As(V) is thus required as a pretreatment for efficient removal. This can be achieved by the addition of bleaching powder (chlorine) or potassium permanganate.

Bucket Treatment Unit The bucket treatment unit (BTU), developed by the DPHE-Danida Project in Bnagladesh, is based on the principles of coagulation, coprecipitation, and adsorption. It consists of two buckets, each 20 L in capacity, placed one above the other (Figure 9). Chemicals are mixed manually with arsenic-contaminated water in the upper red bucket by vigorous stirring with a wooden stick for 30 to 60 seconds and then flocculated by gentle stirring for about 90 seconds. The mixed water is then allowed to settle for 1 to 2 hours. The water from the red bucket is then allowed to flow via plastic piping into the lower green bucket and a sand filter box installed in the lower bucket. The flow is initiated by opening a valve fitted slightly above the bottom of the red bucket to avoid inflow of settled sludge in the upper bucket. The lower green bucket is practically a treated water container. The units were reported to have very good performance in arsenic removal in both field and laboratory conditions [36]. Extensive study of DPHE-Danida BTU under Bangladesh Arsenic Mitigation Water Supply Project (BAMWSP), Department for International Development (DFID), UK, WaterAid [31] rapid assessment program showed mixed results.

Bangladesh University of Engineering and Technology (BUET) modified the BTU and obtained better results by using 100 mg/L of ferric chloride and 1.4 mg/L of potassium permanganate in modified BTUs. The arsenic contents of treated water were mostly below 20 mg/L and never exceeded 37 mg/L, while arsenic concentrations of tubewell water varied between 375 and 640 mg/L. The BUET modified bucket treatment units have been found to be very effective in removing iron, manganese, phosphate, and silica. Initially, the presence of few

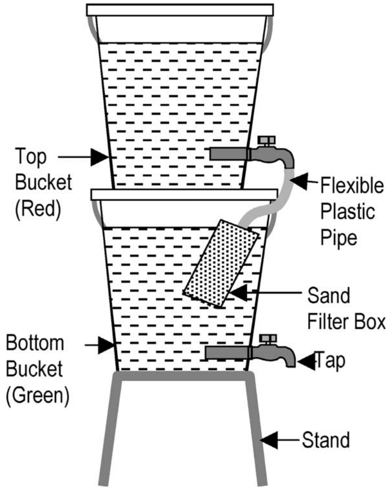

Figure 9 Double-bucket household arsenic treatment unit.

fecal coliform was found in the treated water. This secondary contamination of water may be due to handling of materials by contaminated hands. This problem was eliminated by introducing bleaching powder in the chemical packets. The BTU appears to be a promising technology for arsenic removal at the household level at low cost. It can be build by locally available materials and is effective in removing arsenic if operated properly.

Star Filter The star filter developed by Stevens Institute of Technology in the United States also uses two buckets, one to mix chemicals (iron coagulant and hypochloride) supplied in packets and the other to separate flocs by the processes of sedimentation and filtration. The second bucket has a inner bucket with slits on the sides as shown in Figure 10 to help sedimentation and keep the filter sand bed in place. The chemicals form visible large flocs on mixing by stirring with stick. Clean water is collected through a plastic pipe fitted with an outlet covered with a cloth filter to prevent entry of sand. The unit has been field-tested extensively in Bangladesh, and the efficiency of the star filter in removing arsenic has been described by Meng and Korfiatis [37].

Fill-and-Draw Units A fill-and-draw unit is a 600-L-capacity community type of treatment unit designed on the basis of coagulation, sedimentation, and filtration. The tank is filled with arsenic-contaminated water collected from a community tubewell in the evening, and the required quantity of oxidant and coagulant are added to the water. The water is then mixed for 30 seconds by rotating a manually operated mixer with flat-blade impellers at the rate of 60 rpm, and the water is left overnight for sedimentation. Initially, the coagulant and the disinfectant are mixed with water during fast rotation, but the rotating speed of

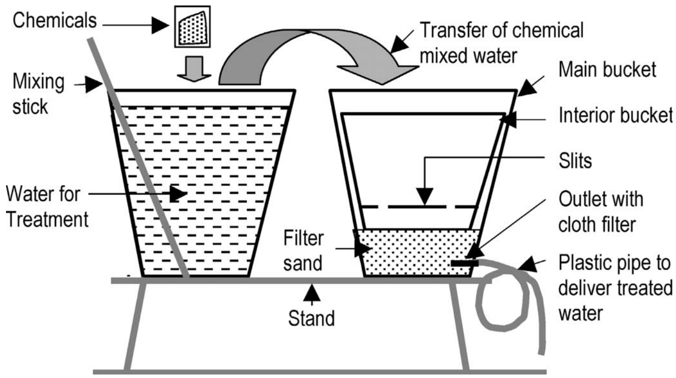

Figure 10 Star arsenic filter.

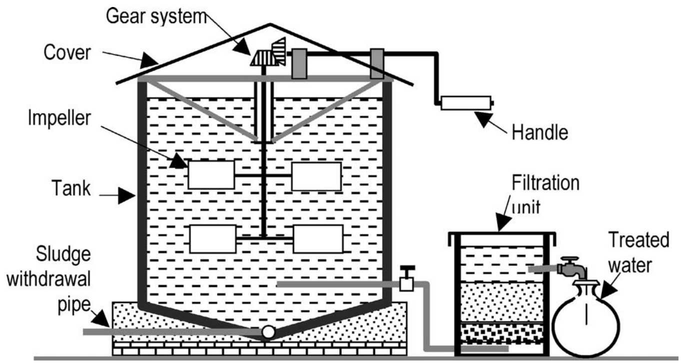

Figure 11 Fill-and-draw arsenic removal unit.

water decreases with time and finally ceases. Floc formation is caused by the hydraulic gradient of the slow rotational motion of the water in the tank, which continues long after mixing has stopped. The settled water is then drawn through a pipe fitted at a level a few inches above the bottom of the tank, passed through a sand bed, and finally, collected through a tap for drinking purposes (Figure 11). The sludge deposited at the bottom is flushed out with unused water before the next operation of the unit. The mixing and flocculation processes in this unit are autoregulated to effect higher removal of arsenic. The dose of chemical can be fixed depending on the quality of raw water to be treated. These units are intended to serve clusters of families and educational institutions.

Arsenic Removal Unit Attached to a Tube Well The All India Institute of Hygiene and Public Health, India developed a small arsenic removal unit attached to tube wells. The principles of arsenic removal by alum coagulation, sedimentation, and filtration have been employed in a compact unit for water treatment

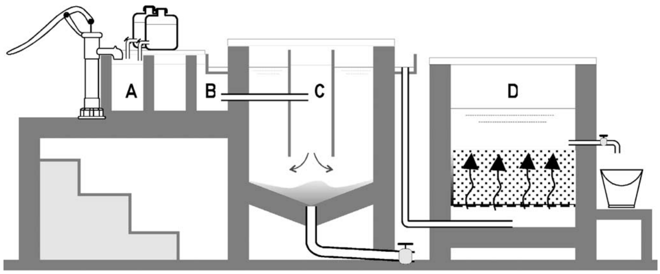

Figure 12 Arsenic removal plants attached to a tube well. A, mixing; B, flocculation; C, sedimentation; D, filtration (up-flow).

at the village level in West Bengal. An arsenic removal plant attached to a hand tube well as shown in Figure 12 has mixing, flocculation, sedimentation, and filtration chambers. The compact unit has been found effective in removing 90% of the arsenic from tube well water having initial arsenic concentrations of 300 μg/L. The treatment process involves the addition of sodium hypochloride (Cl_2) and aluminum alum in diluted form in the mixing chamber.

Iron–Arsenic Removal Plants Groundwater rich in iron and arsenic can be coprecipitated by simple aeration when the water is alkaline. The iron precipitates [$Fe(OH)_3$] formed by oxidation of dissolved iron [$Fe(OH)_2$] present in groundwater have an affinity for the adsorption of arsenic. Iron removal plants (IRPs) in Bangladesh and Vietnam constructed on the principles of aeration, sedimentation, and filtration in a small unit have been found to remove arsenic without added chemicals. Depending on the operating principles, conventional community IRPs work more or less like arsenic removal plants.

A study suggests that As(III) is oxidized to As(V) in IRPs to facilitate higher efficiency in arsenic removal in IRPs constructed in an arsenic-affected area in Bangladesh [38]. The evaluation of IRPs shows that most units can lower the arsenic content of tube well water from four-fifths to one-fifth of the original concentrations. The efficiency of these community-type Fe–As removal plants can be increased by increasing the contact time between arsenic species and iron flocs. Community participation in operation and maintenance at the local level is absolutely essential for effective use of these plants.

Some production wells supplying water in urban areas in Bangladesh have been found to be contaminated with arsenic. A few medium-scale Fe–As removal plants of capacity 2000 to 3000 m^3/day have been constructed for water supplies in those district towns based on the principle of iron–arsenic removal by aeration. The working principles of the unit are shown in Figure 13.

The main treatment processes involved as shown in Figure 13 are aeration, sedimentation, and rapid sand filtration, with provision for addition of chemical, if required. Units operating on the natural iron content of water have a low efficiency, varying between 40 and 80%. These plants are working well except

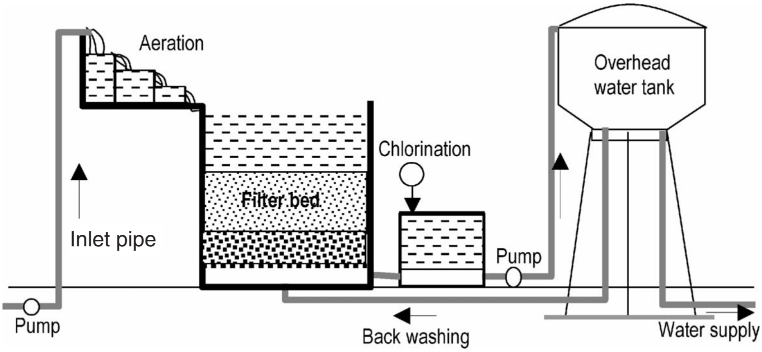

Figure 13 Fe–As removal plant for small towns.

that the water requirement for washing the filter beds is very high. Operations of small and medium-sized Fe–As removal plants in Bangladesh suggest that arsenic removal by co-precipitation and adsorption on natural iron flocs has good potential to reduce arsenic to an acceptable level of 0.05 mg/L in Bangladesh and India when the arsenic content lies within about 0.10 mg/L.

Sorptive Filtration

Arsenic removal by adsorption onto active natural and synthetic sorptive media has a high potential to remove arsenic from drinking water to trace levels. The most widely used sorptive media include activated alumina, activated carbon, iron- and manganese-coated sand, metallic iron, granulated ferric hydroxide, cerium oxide, and many natural and synthetic media. The efficiency of some sorptive media depends on the use of oxidizing agent as aids to sorption of arsenic. Saturation of the sorptive media takes place when the sorptive sites of the media are exhausted and the media are no longer able to remove arsenic from water. Saturation of media by different contaminants and components of water takes place at different times of operation, depending on the specific sorption affinity of the medium to the given component.

BUET-Activated Alumina Activated alumina in different forms has been used extensively for adsorption of arsenic from drinking water. The BUET-activated alumina arsenic removal unit (ARU) consists of subunits for oxidation–sedimentation, filtration, and activated alumina adsorption. Oxidation and sedimentation are done in a plastic bowl, 25 L in capacity, placed at the top with a tap above the bottom to draw settled water. Around 1 mg/L of potassium permanganate is added to water to oxidize As(III) to As(V) and is stirred vigorously with a wooden stick and allowed to settle for about one hour. The settled water is first filtered through a sand bed in a plastic bucket and then passed through the activated alumina column. The unit is very effective in removing arsenic

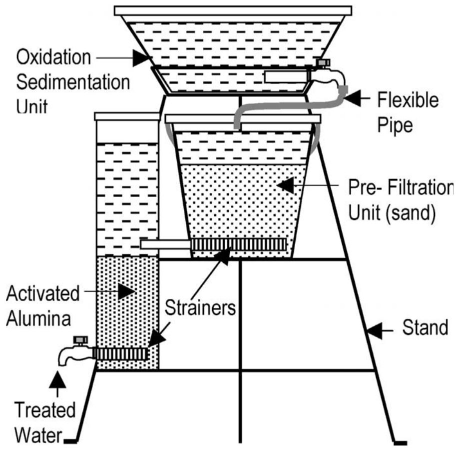

Figure 14 BUET-activated alumina arsenic removal unit.

and iron from tube well water. The social assessment conducted on the unit indicated some practical problems, including difficulty for women to raise water to the level required for gravity flow through the subunits [31]. The problems have been addressed, and the total height of the unit has been reduced by design modification. The modified BUET-activated alumina ARU is shown in Figure 14.

Alcan-Enhanced Activated Alumina In this process, water from a tube well is allowed to pass through enhanced activated alumina beds in two containers, and the treated water is collected from the outlet. The unit is simple and robust in design. No chemicals are added during treatment, and the process relies wholly on the active surface of the media for adsorption of arsenic from water. Other ions, such as iron and phosphate, present in natural water may compete for active sites on alumina and reduce the arsenic removal capacity of the unit. Iron present in shallow tube well water at elevated levels eventually accumulates in the activated alumina bed and interferes with flow of water through the bed. Alcan's enhanced activated alumina is designed as a single-use medium and requires replacement after use. Environmentally safe disposal of spent activated alumina, about 40 kg per batch of treatment, is required.

Apyron Arsenic Treatment Unit Apyron Technologies Inc.(ATI) in the United States has developed arsenic treatment unit (ATUs) in which Aqua-Bind media is used for groundwater arsenic reduction. An ATU consists of a cylindrical adsorber vessel with two proprietary ATI media. The AquaBind arsenic medium used by ATI consists of nonhazardous aluminum oxide (Al_2O_3) and manganese oxide (Mn_2O_3) that can selectively remove As(III) and As(V) from water. The column receives water under slight pressure from a manually operated lift pump shown in (Figure 15). Water flows downward through the two-chamber housings to capture particulate iron and adsorb arsenic. The water exits through a discharge

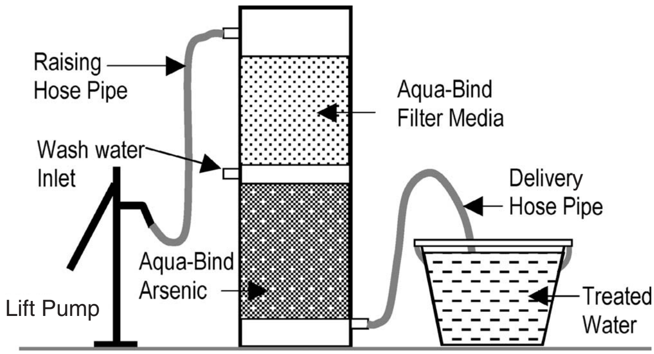

Figure 15 Apyron arsenic treatment unit.

hose into the designated container at approximately 15 L/min. It is claimed that the units installed in India and Bangladesh in experimental schemes consistently reduced arsenic to less than 10 μg/L. The medium in the top chamber used for removal of iron precipitates requires washing by a backflow of water.

Granular Ferric Hydroxide Granular ferric hydroxide (AdsorpAs) is a highly effective adsorbent, developed at the Technical University of Berlin, Germany, specially for the selective removal of arsenic from natural water. The proponents claimed that arsenic treatment capacities of AdsorpAs ranged from 40,000 to 60,000 bed volumes, until the permissible level of 0.01 mg/L for arsenic was exceeded. AdsorpAs has 0.2 to 2.0 mm grain size, 72 to 77% porosity, 250 to 300 m^2/dm^3 specific surface, 1.22 to 1.29 kg/dm^3 bulk density, and 52 to 57% active substances [$Fe(OH)_3$ and β-FeOOH]. It has an adsorption capacity of 45 g/kg for arsenic and 16 g/kg for phosphorus on a dry weight basis [39]. The granular ferric hydroxide reactors are fixed-bed adsorbers that operate like a conventional filter with a downward flow of water. The units require iron removal as pretreatment to avoid clogging the adsorption bed. Typical orientation of a granular ferric hydroxide–based arsenic removal unit is shown in Figure 16. The water, containing high dissolved iron and suspended matter, is first pretreated by aeration and filtration through a gravel/sand filter bed. It is then passed through AdsorpAs in the adsorption tower for removal of arsenic.

M/S Pal Trockner(P) Ltd., India and Sidko Limited, Bangladesh installed several granular ferric hydroxide–based arsenic removal units in India and Bangladesh, respectively. Proponents of the unit claim that AdsorpAs has very high arsenic removal capacity, 5 to 10 times higher than that of activated alumina. As a result, it produces smaller residual spent solids. The typical residual mass of spent AdsorpAs is in the range 5 to 25 g/m^3 of treated water. The spent granular ferric hydroxide is a nontoxic solid waste. Under normal conditions, no leaching of arsenic takes place out of the spent AdsorpAs.

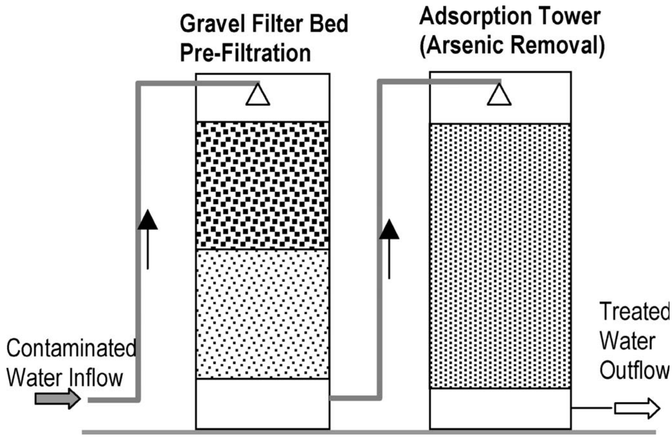

Figure 16 Granular ferric hydroxide–based arsenic removal unit.

READ-F Arsenic Removal Unit READ-F is an adsorbent produced and promoted by Nihon Kaisui Co. Ltd in Japan and Brota Services International for arsenic removal in Bangladesh. READ-F displays high selectivity for arsenic ions under a broad range of conditions and effectively adsorbs both arsenite and arsenate. Oxidation of arsenite to arsenate is not needed for arsenic removal, nor is adjustment of pH required before or after treatment. READ-F is an ethylene–vinyl alcohol copolymer–borne hydrous cerium oxide in which hydrous cerium oxide ($CeO_2 \cdot nH_2O$) is the adsorbent.

The READ-F sorptive medium has shown its best performance in field testing of arsenic mitigation technologies in Bangladesh under the Environmental Technology Verification–Arsenic Mitigation Program [40]. The units need iron removal by sand filtration to avoid clogging of resin bed by iron flocs. Brota Services International is promoting READ-F-based household, wellhead, and community-based arsenic removal units in Bangladesh. The wellhead and community units are attached to tube wells. In the household unit both the sand and resin beds have been arranged in one container, as shown in Figure 17 while in the community unit sand and resin beds are placed in separate containers. Community unit with a large quantity of resin have been constructed close to wells with multiple water points at the outlet.

READ-F can be regenerated by adding sodium hydroxide, then sodium hypochloride, and finally, washing by water. The regenerated READ-F needs neutralization by hydrochloric acid and washing with water for reuse. The wastewater can be treated by a small amount of adsorbent after pH adjustment for safe disposal. Proponents claim that the basic characteristic property of READ-F is that it adsorbs arsenic from water but under normal conditions, never discharges arsenic. Experiments in Japan confirmed that no arsenic was leaching from arsenic adsorbed by READ-F after disposal in soil.

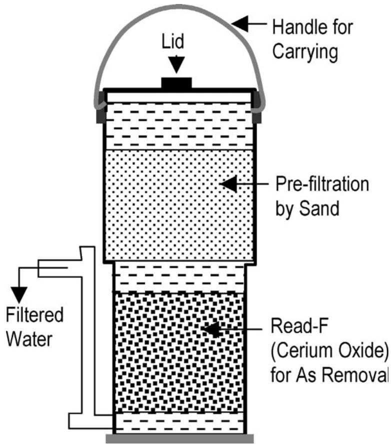

Figure 17 READ-F arsenic removal unit.

Iron-Coated Sand BUET constructed and tested iron-coated sand based on the small-scale unit shown in Figure 18 for the removal of arsenic from groundwater. To avoid clogging the active filter bed, the unit needs pretreatment for the removal of excess iron. The pretreatment system consists of a bucket where water is poured and stirred for some time to accelerate the precipitation of iron. The water is then allowed to flow through a sand filter, where the excess iron is filtered out. The water from the pretreatment unit passes through an iron-coated sand filter and is placed in a polyvinyl chloride chamber, where the arsenic is removed. A strainer connected to a tap is placed in an iron-coated sand layer above the bottom of the chamber. Water enters the strainer and eventually flows through the tap for collection by consumers. Iron-coated sand has been prepared following a procedure similar to that adopted by Joshi and Chaudhury [21]. The saturated medium is regenerated by passing 0.2 N sodium hydroxide through the column or soaking the sand in 0.2 N sodium hydroxide followed by washing with distilled water [41]. No significant change in bed volume in arsenic removal was found after five regeneration cycles. Iron-coated sand has been found equally effective in removing both As(III) and As(V).

Shapla Arsenic Filter The Shapla arsenic filter, a household arsenic removal unit, has been developed and is being promoted by International Development Enterprises (IDE), Bangladesh. The adsorption medium is iron-coated brick chips manufactured by treating brick chips with ferrous sulfate solution and works on the same principles as iron-coated sand. The water collected from a contaminated tube well is allowed to pass through filter media placed in an earthen container having a drainage system underneath. The arrangement of the Shapla filter is shown in Figure 19.

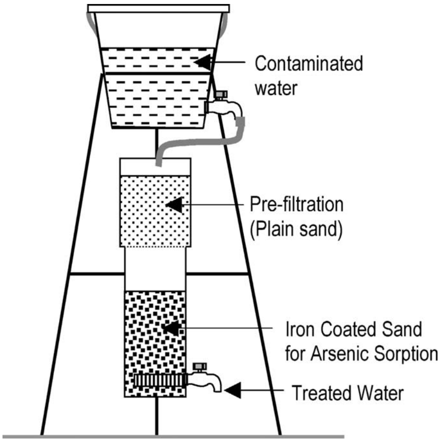

Figure 18 Household arsenic removal unit based on iron-coated sand.

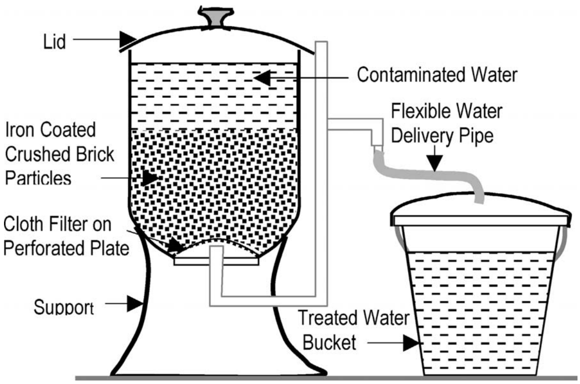

Figure 19 Shapla filter for arsenic removal at the household level.

SONO Filter The SONO filter uses metallic (cast iron turnings), sand, brick chips, and wood coke to remove arsenic and other trace metals from groundwater [42,43]. The filtration system originally consisted of 3-Kolshi (burned clay pitcher), used widely in many countries for storage of water for drinking and cooking. The top pitcher contained coarse sand and metal iron filings and brick chips; the second pitcher contained wood charcoal, fine sand, and brick chips; and the third served as storage. The primary active material are the cast iron turnings, used to remove arsenic and many other toxic species from water. The secondary active material is the charcoal, made from cooking woods to remove organic species in water (if present). The inactive (or less active) materials are the sand and brick chips, used to maintain the flow, retention, and mechanical stability of the filtration device. The significant drawbacks of the 3-Kolshi filter was that the filter materials could nor be taken out for washing and regular maintenance. To overcome these problems, the filter media are housed in two plastic buckets, as shown in Figure 20. The cast iron turnings have been transformed by proprietary process into a complex iron matrix (CIM), which is capable of maintaining its active CIM integrity for years. Manganese in a CIM catalyzes oxidation of As(III), and all As(V) is removed by a surface-complexation reaction between a surface of hydrated iron (=FeOH) and arsenic species [44]. The new =FeOH is generated in situ as more water is filtered.

Earlier, Nikolaidis and Lackovic [45] showed that 97% of the arsenic can be removed by adsorption on a mixture of zero-valent iron fillings and sand and recommended that arsenic species could have been removed through formation of coprecipitates and mixed precipitates and by adsorption on ferric hydroxide solids. The principles of adsorption of arsenic by metallic iron have been used successfully in the SONO filter in Bangladesh and in the Kanchan arsenic filter (KAF) in Nepal. The SONO filter has been certified provisionally with a reduction in the claims of the proponent and conditionally approved for sale in Bangladesh after verification [40].

In 2007, the U.S. National Academy of Engineering declared the Grainger Challenge Prize competition for innovative solutions to removing arsenic from drinking water. The winning systems had to be affordable with low life-cycle cost, robust, reliable, easy to maintain, socially acceptable, and environmentally friendly. As sustainable technologies, they also had to be within the manufacturing capabilities of the countries where they would be deployed and not degrade

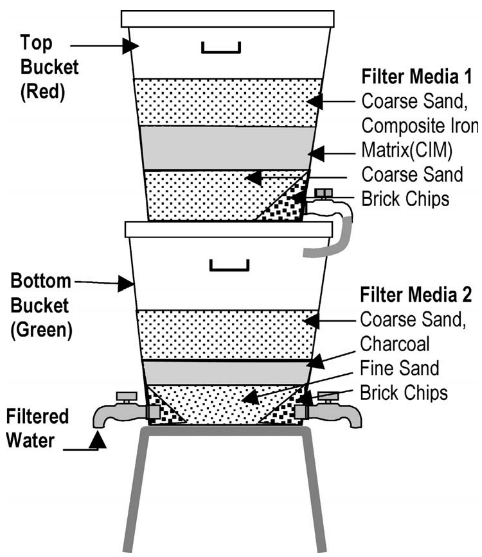

Figure 20 SONO arsenic filter.

other water-quality characteristics or introduce pathogens. The SONO filter competed for the Grainger Challenge Prize for Sustainability and won the first prize of $1 million.

Kanchan Arsenic Filter **T**he Kanchan arsenic filter (KAF) was developed by researchers at Massachusetts Institute of Technology (MIT), the Environment and Public Health Organization (ENPHO) of Nepal, and the Rural Water Supply and Sanitation Support Programme (RWSSSP) of Nepal, based on slow sand filtration and iron hydroxide adsorption principles [46]. Like the SONO filter, the KAF uses metallic iron, in the form of iron nails covered with brick chips, followed by a slow sand filter (Figure 21). The exposure of iron to air and water helps the development of ferric hydroxide particles. When arsenic-contaminated water is poured into the filter, a surface complexation reaction occurs and arsenic is rapidly adsorbed onto the surface of the ferric hydroxide particles [46]. This technology is a result of seven years of multidisciplinary research and has been optimized based on socioeconomic conditions in the Terai region of Nepal.

The KAF has won prestigious awards: at the MIT IDEAS Design Competition 2002, the World Bank Development Marketplace Global Competition 2003, the World Bank Nepal Country-level Development Marketplace Competition 2005, the U.S. Environmental Protection Agency P3 Design Competition 2005, and the Wall Street Journal Technology Innovation Award, 2005 (Environmental Category). The current Gem505 version is a fourth-generation design, promoted since March 2004 [46].

Ion Exchange

The process is similar to that of activated alumina except that the medium is a synthetic resin of better defined ion-exchange capacity. The synthetic resin is based on a cross-linked polymer skeleton called the matrix. The charged functional groups are attached to the matrix through covalent bonding and fall into strongly acidic, weakly acidic, strongly basic, and weakly basic groups [47]. The resins are normally used for the removal of a specific undesirable cation or anion

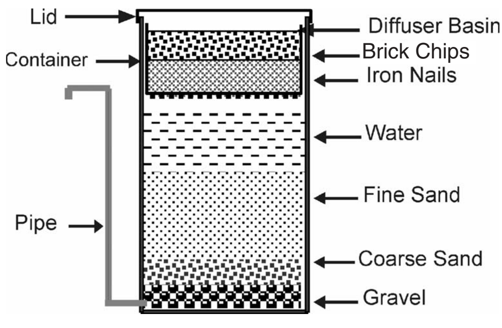

Figure 21 Kanchan arsenic filter.

from water. The strongly basic resins can be pretreated with anions such as Cl^- and used for the removal of wide ranges of negatively charged species, including arsenate.

The arsenic removal capacity is dependent on the sulfate and nitrate contents of raw water, as sulfate and nitrate are exchanged before arsenic. The ion-exchange process is less dependent on the pH of water. Arsenite, being uncharged, is not removed by ion exchange. Hence, preoxidation of As(III) to As(V) is required for removal of arsenite by an ion-exchange process, but the excess of oxidant often needs to be removed before the ion exchange to avoid damage to sensitive resins. Development of ion-specific resin for exclusive removal of arsenic can make the process very attractive.

Tetrahedron Technology Tetrahedron in the United States promoted ion-exchange-based arsenic removal technology in Bangladesh. The technology proved its arsenic removal efficiency even at high flow rates. Figure 22 is a schematic diagram of tetrahedron technology. It consists of a stabilizer and an ion exchanger (resin column) with facilities for chlorination using chlorine tablets. Tube well water is pumped or poured in the stabilizer through a sieve containing the chlorine tablets. The water mixed with chlorine is stored in the stabilizer and subsequently flows through the resin column when the tap is opened for collection of water. Chlorine from a chlorine tablet dissolved in water kills bacteria and oxidizes arsenic and iron. The stabilizer removes flow rate pulses from the pump and traps iron and other hydroxide precipitates formed in water, and finally, the ion exchanger adsorbs arsenic, sulfate, and phosphate from tube well water. The residual chlorine was found to minimize bacterial growth in the media. The saturated resin requires regeneration by recirculation of NaCl solution. The liquid wastes rich in salt and arsenic produced during regeneration require special treatment. Units tested under field conditions in Bangladesh showed fluctuations in performance.

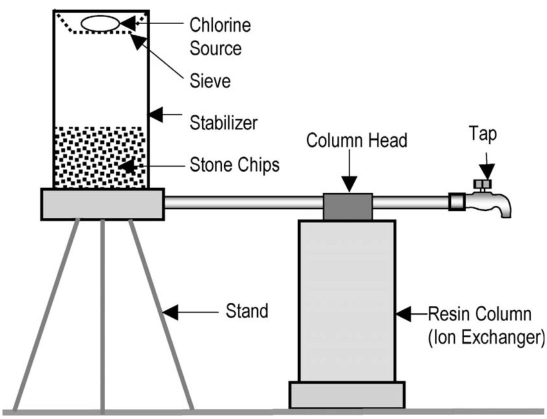

Figure 22 Tetrahedron arsenic removal technology.

Membrane Techniques

Synthetic membranes can remove many contaminants from water, including bacteria, viruses, salts, and various metal ions. Usually, two types of membrane filtration—nanofiltration (NF) and reverse osmosis (RO)—have the appropriate pore sizes for the removal of arsenic. In recent years, new-generation RO and NF membranes have been developed; those operate at lower pressure and are less expensive. Arsenic removal by membrane filtration is independent of pH and the presence of other solutes but is affected adversely by the presence of colloidal matter. Iron and manganese can also lead to scaling and membrane fouling. Once fouled by impurities in water, the membrane cannot be backwashed. Water containing high suspended solids requires pretreatment for arsenic removal by membrane techniques. Most membranes cannot, however, withstand an oxidizing agent. The EPA [48] reported that NF was capable of over 90% removal of arsenic, while RO provided removal efficiencies of greater that 95% under ideal pressure. Water rejection (about 20 to 25% of the influent) may be an issue in water-scarce regions [48]. A wider variety of reverse osmosis systems was promoted in Bangladesh. Experimental results showed that the systems could effectively reduce arsenic along with other impurities in water. The capital and operational costs of a reverse osmosis system would be relatively high.

Oh et al. [49] applied reverse osmosis and nanofiltration membrane processes for the treatment of arsenic-contaminated water, applying low pressure with a bicycle pump. A nanofiltration membrane process coupled with a bicycle pump could be operated under conditions of low recovery and low pressure, ranging from 0.2 to 0.7 MPa. Arsenite was found to have a lower rejection rate than arsenate in ionized forms, hence water containing higher arsenite levels requires preoxidation for reduction of total arsenic to acceptable levels. The reverse osmosis process, coupled with a bicycle pump system operating at 4 MPa, can be used for arsenic removal because of its high arsenite rejection. The study concluded that low-pressure nanofiltration with preoxidation or reverse osmosis with a bicycle pump device could be used for the treatment of arsenic-contaminated groundwater in rural areas [49].

Sludge Disposal

All arsenic treatment technologies ultimately concentrate arsenic in sorption media, sludges, or liquid media. Arsenic from these arsenic-rich media can again dissolve in water or contaminate soil. Hence, environmentally safe disposal of sludges, saturated media, and liquid wastes rich in arsenic is a concern.

The EPA has developed a toxic characteristic leaching procedure (TCLP) test to identify wastes likely to leach toxic chemical into groundwater. The TCLP test conducted on different types of wastes collected from arsenic treatment units by Brewster [50], Chen et al. [24], Eriksen-Hamel and Zinia [51], Ali et al. [52], and BCSIR [40] showed very little leaching of arsenic from sludges. These arsenic levels in leachate are well below the level required for classification as hazardous wastes. However, TCLP may not be an appropriate tool to assess the stability of arsenic-rich wastes. TCLP does not duplicate environmental and redox conditions conducive to mobilization of arsenic in groundwater.

Experiments were conducted to assess the transformation of arsenic from aqueous solutions in the presence of cow dung [52]. The results from this study suggest that a biochemical (e.g., biomethylation) process in the presence of fresh cow dung may led to significant reduction of arsenic from arsenic-rich treatment wastes. However, the process appeared to slow down significantly with time under the experimental conditions followed in the study. Fixation of arsenic in engineering materials is a method of preventing arsenic contamination of the environment. Hazardous wastes are often blended into stable waste or engineering materials such as glass, brick, concrete, or cement block. There is a possibility of air pollution or water pollution downstream of kilns burning brick containing arsenic-contaminated sludge, due to volatilization of arsenic during burning at high temperatures. In Hungary, experiments showed that some 30% of arsenic in the coagulated sludge was lost to the atmosphere in this way [27]. Sludge or spent filter media with a low arsenic content can be disposed off on land or in landfills without significant increase in the background concentrations of arsenic. Wastes with high concentrations of arsenic may need solidification or confinement before final disposal.

The requirements for deployment of arsenic removal technologies for the water supply are as follows:

- Verification of the technology by the authorized organization in the country. Adherence to the limitations of the technology, conditions of deployment, and monitoring requirements.
- Evaluation of the quality of water to assess the suitability of the arsenic removal technology proposed.
- Monitoring of the water quality, particularly the arsenic content of the treated water to understand the performance of the system, requirement for media replacement, and regeneration and regulation of chemical dose.
- Acceptability of the community and willingness to pay for sustained operation and maintenance of the system.
- Proper disposal of sludge and arsenic concentrates as prescribed in the protocol for disposal adopted by the appropriate authority of the country.

COSTS OF TECHNOLOGY

The cost of technology is an important factor for the adoption and sustainable use of the technology for water supply. The main components of cost of technology include the cost of acquisition of the technology/materials, transportation cost, installation/construction cost, operation and maintenance (O&M) costs, and cost of waste management. However, the first three components are nonrecurring cost and can be considered as total capital cost (TCC). To estimate the annual TCC, the total capital cost of the technology needs to be annualized and expressed as cost per year. For up-front capital costs, the annualization includes compound interest charged over the period of repayment of the capital. For water supply technology, it is assumed that the payment plan will spread the TCC over the lifetime of the technology. To find the annualized effective cost, the capital cost is to be multiplied by the capital recovery factor (CRF) or amortization factor.

The capital recovery/amortization factor is calculated using the formula

$$\text{CRF} = \frac{(1+i)^N}{[(1+i)^N - 1]/i} \tag{1}$$

where CRF is the capital recovery/amortization factor, i the interest rate, and N the number of years (lifetime of the technology). The operation and maintenance costs include salary of personnel, costs of consumable chemicals and power, costs of replacement and repair of parts, costs of media replacement and regeneration, monitoring and service costs, and opportunity cost of time and efforts of users. However, the costs of treatment and safe disposal of wastes generated from the technologies are considered as operational cost and included under the O&M cost of the technology.

The costs of major arsenic mitigation water supply technologies calculated by Ahmed [53] and the World Bank [4] under its Operational Response to Arsenic Contamination of Groundwater in South and East Asian Countries assuming an annual interest rate of 12% are summarized in Table 1.

A rainwater harvesting system is a household option, and hence the cost is comparatively high. It is not a suitable option for poorer people who have no suitable roof catchment for rainwater collection. A deep tubewell can provide safe water at low installation and nominal operation and maintenance costs, but deep tube wells are not feasible at all locations. Water supply options based on arsenic-safe water sources produce drinking water at lower costs. The SSF is a low-cost surface water treatment option, but deployment of this option is restricted by the increasing level of contamination of surface water in developing countries. The conventional treatment processes have more flexibility in respect to raw water quality, but the operational cost for small conventional systems is very high, due to the requirements of chemicals, power, and skilled operators. A dug/ring well is the next lowest cost option, which can provide water at low installation and nominal O&M costs. It is not likely to be a good option in arsenic-affected areas.

Most arsenic removal plants are costlier than alternative water supply options. The cost of arsenic removal technology appears to be an important factor for adoption and sustainable use in a rural context. Verification of some technologies in Bangladesh showed that the performance of the technologies were very dependent on pH and the presence of phosphate and silica in natural groundwater, and most of the technologies did not meet the claims of proponents in respect to treatment capacity [40]. A reduction in the rated capacity will further increase the cost of treatment per unit volume of water. However, most technologies have been installed and are being operated under field testing and pilot-scale

TABLE 1 Cost of Water Supply Options for Arsenic Mitigation

Technology	Tech. Life	Annualized Capital Recovery ($)	Annual O&M Cost ($)	Water Production (m^3)	Unit Cost ($\$/m^3$)
Alternative WS					
Rainwater harvesting	15	30	5	16.4	2.134
Deep tube well	20	120	4	820	0.151
				4,500	0.028[a]
Slow sand filter	15	117	15	820	0.161
				2,000	0.066[a]
Dug/ring well	25	102	3	410	0.256
				1,456	0.072[a]
Conventional treatment	20	2,008	3,000	16,400	0.305
Piped water supply	15	5,872	800	16,400	0.375
				73,000	0.084
Arsenic treatment (household units) based on:					
Coagulation–filtration	3	5.0	25	16.4	1.70
Iron-coated sand/brick dust	6	0.9	11	16.4	0.73
Metallic iron/iron fillings	5	3.0	1	16.4	0.24
Synthetic media	5	1.2	29	16.4	1.84
Activated alumina	4	3.2	36	16.4	2.39
Arsenic treatment (community units) based on:					
Coagulation–filtration	10	44	250	246	1.21
Granulated ferric hydroxide/oxide	10–15	500–600	450–500	820–900	1.20
Activated alumina	10–15	30–125	500–520	164–200	3.20
Ion exchange	10	50	35	25	3.40
Reverse osmosis	10	440	780	328	3.72
As–Fe removal by air oxidation–filtration	20	32,000	7,500	730,000	0.054

[a]Development of full potential of the system.

operations. Hence, the costs of installation, operation, and maintenance of all the arsenic removal system are not known or are yet to be standardized based on modifications to suit the local conditions.

CONCLUSIONS

A wide range of technologies based on arsenic-safe water sources are available for water supplies at low cost, but the performance of the technologies varies widely depending on the quality of raw water. Community participation in operation and maintenance of small surface water–based technologies and RWHS are not encouraging. The performances of medium-sized to large systems that can support a full-time operator are comparatively better. Tube well technologies are the preferred option of people in arsenic-affected areas, but tube wells are not always successful in producing arsenic-safe water at all locations. Substitution of an arsenic health risk by a microbial health risk due to shifting from a tube well–based water supply to a surface water–based water supply is a great concern.

The problem of treatment of groundwater for arsenic removal arises from the requirement for its removal to very low levels to meet stringent drinking water quality standards and the guideline value for arsenic. Arsenic removal technologies have improved significantly during the last few years, but reliable, cost-effective, and sustainable treatment technologies are yet to be identified and developed further to meet the requirements. All treatment technologies concentrate arsenic at some stage of treatment in different media. Large-scale use of an arsenic removal system may generate significant quantities of arsenic-rich treatment wastes, and indiscriminate disposal of these wastes could lead to environmental pollution. Safe disposal of arsenic-rich media is a concern and needs to be addressed.

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15

SOLUTIONS FOR ARSENIC CONTAMINATION OF GROUNDWATER

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WORLDWIDE ARSENIC CONTAMINATION PROBLEM

As mentioned earlier, arsenic contamination has been found in regional water supplies in Argentina, Bangladesh, Cambodia, Canada, Chile, China, Ghana, Hungary, India, Laos, Mexico, Mongolia, Nepal, Pakistan, Poland, Taiwan, Thailand, the UK, the United States, and Vietnam. Recognizing the fact that inorganic arsenic is a documented human carcinogen, the World Health Organization (WHO) set a standard at no more than 10 μg/L (or 10 ppb) of arsenic (As) in drinking water in 1993. This standard was finally adopted in the United States in 2006; however, 50 μg/L (50 ppb or 0.05 mg/L) is the maximum contamination level (MCL) considered acceptable in Bangladesh. It is estimated that of the 140 million people of Bangladesh, 29 million are drinking groundwater from approximately 9 million tube wells containing arsenic at levels greater than 50 ppb. The estimated number of people affected elsewhere are 5.6 million in China, 5.3 million in India, and over 0.5 million in Nepal. The population at risk approaches 100 million in Bangladesh at the MCL set by the WHO. This suggests that as many as 200 million people could be affected by this problem worldwide. It should be noted that a number of toxicologists (see Figure 1) consider even a 10-ppb level of arsenic to be too high because even at 1 ppb, the risk of getting cancer is 1 in 3000. The fact remains that prolonged drinking of this water has caused serious illnesses in the form of hyperkeratosis on the palms and

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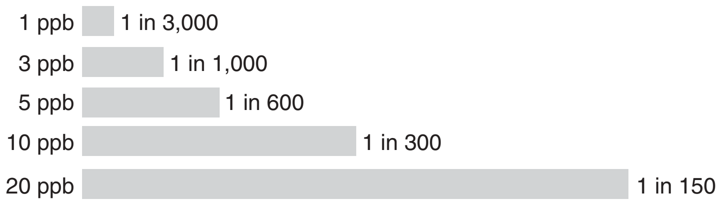

Figure 1 Risk of cancer with arsenic contamination of water. Over long periods of time, a small amount of arsenic can cause harm. This chart shows the estimated odds of getting bladder or lung cancer for a person who drinks about a quart of arsenic-laced water a day for 70 years. For women, the chances are slightly lower; for men, slightly higher. (From the National Research Council's 2001 study for the U.S. Environmental Protection Agency.)

feet, fatigue symptoms of arsenicosis, and cancer of the bladder, skin, and other organs. In the long term, one in every 10 people could die of arsenic poisoning if they continue using water with high concentrations of arsenic.

SEVERITY OF THE PROBLEM IN SOUTH ASIA

As discussed earlier in the book, naturally occurring arsenic contaminates groundwater in Bangladesh, where thousands of shallow (10 to 40 m) tube wells installed in the 1970s were found in the 1980s to be contaminated by arsenic. This occurred because the original focus was to solve the bacterial contamination of surface water, not elemental contamination, and the project did not include adequate testing to avoid the arsenic problem. This unfortunate calamity could have been avoided, as analytical methods that can test for arsenic down to the ppb levels have been available for a long time [1].

According to a report from the Arsenic Policy Support Unit of Bangladesh [2], the progress in monitoring arsenic in water supplies is ongoing. The blanket arsenic screening of 4.73 million tube wells showed 1.29 million wells contained arsenic above the acceptable level of 50 μg/L in Bangladesh. Since the estimated number of tube wells is approximately 9 million, it can be concluded that some 6.2% of all the wells in Bangladesh are contaminated above the Bangladesh limits for arsenic. Mitigation options have been made available to some 38% of the contaminated wells in Bangladesh, and over the next 5 years, most villages will receive some support. Since the population of Bangladesh is expected to rise in the near future from 140 million to 250 million, the problem will be exacerbated further.

For the last 18 years, Chakraborti et al. (D. Chakraborti, personal communication, 2007) have analyzed 225,000 tube well water samples from Ganga–Meghna–Brahamaputra, a plain covering an area of 569,749 km^2 and a population of more than 500 million. They found that a number of states in India (such as Uttar Pradesh, Bihar, West Bengal, Jharkhand, and Assam) and Bangladesh are affected by a concentration of arsenic >50 μg/L. On the average, about 50% of the water samples contain arsenic above 10 μg/L and 30% above 50 μg/L. Of the 2000 arsenic removal devices installed in villages in West Bengal, India, four out of five have either been abandoned or they deliver odorous or discolored water.

Most of the discussion in this chapter is focused on Bangladesh, as the problem has reached horrendous proportions there. The lessons learned there can help provide workable solutions to this problem in other parts of the world as well.

ARSENIC MITIGATION

The estimated impact of arsenic mitigation in Bangladesh is shown in Table 1. It appears that nearby private wells are still the primary source of water. The microbial contamination is of concern in alternative water supplies or remediation systems. Since a great number of people are dependent on nearby wells, it is important to assure that they are safe. If not, the villagers are to be discouraged from using it or at a minimum they should be provided with reliable arsenic removal units (see Chapters 9 to 13). It should be noted here that the quality of groundwater in an area can impair the performance of these units. A large number of deep tube wells are being installed to correct this problem. However, for a great number of these wells, the status of arsenic contamination is unknown. No steps have been taken to prevent future potential contamination with arsenic, as the wells are not necessarily being installed within the guidelines.

To address this problem, the Bangladesh government's National Policy for Arsenic Mitigation [4] states that access to safe water for drinking and cooking must be ensured through implementation of alternative water supply options in all arsenic-affected areas. The policy also states that all mitigation programs must follow the Bangladesh standards for drinking water, and preference will be given

TABLE 1 Estimated Impact of Various Forms of Arsenic Mitigation in Bangladesh

New Water Source	Number Installed	Users/ Unit	Estimated Impact (% of Population at Risk)
Nearby private well	—	—	29
Deep tube well	74,809	50	12
Arsenic removal unit	33,074	6	0.66
Dug well	6,268	30	0.63
Pond sand filter	3,521	50	0.59
Rainwater collector	13,324	6	0.27
Piped water system	65	240	0.05

Source: Adapted from ref. 3. The compilation relies primarily on reports from the Arsenic Policy Support Unit, with additional information from other studies.

to surface water as the source of water supply over groundwater, and it also states that a safe source of drinking water is available to people at a reasonable distance on an emergency basis.

It is considered desirable at this stage to review the Implementation Plan for Arsenic Mitigation mentioned earlier in the book. The plan states that while research to devise appropriate options are ongoing, the arsenic mitigation programs will promote the following options:

- Improved dug well
- Surface water treatment
  - Pond sand filters
  - Large-scale surface water treatment
- Deep hand tube well
- Rainwater harvesting
- Arsenic removal technology
- Piped water supply system

Of these options, preference is being given to pond sand filters and dug wells. The government's role in rainwater harvesting is limited to promotional activities only; in the case of arsenic removal technology, the implementation plan recommended waiting until issues relating to the safety of these technologies, in terms of chemical and biological water quality and the disposal of liquid and solid wastes, are better understood.

Phased responses will be used to provide alternative water supplies. Under the emergency response, a water supply point will be provided for 50 families on an emergency basis, adopting a supply-driven approach in the hot-spot villages where more than 80% of the tube wells are contaminated. Under medium-term response (in areas where 40 to 80% of the tube wells are contaminated), a water supply will be provided at the rate of one water point for 25 to 30 households on a demand-driven basis. In a long-term response, arsenic mitigation programs will promote proven and sustainable technology options.

Reasons for Poor Progress

As discussed earlier in the book, the progress in arsenic mitigation has been very slow, and only about 4 million people in Bangladesh have been provided with arsenic-safe water during the last five years. It appears that financial backers are not very enthusiastic about the arsenic mitigation policies and implementation plans. Arsenic mitigation programs have been bogged down in the absence of adequate follow-through on the strategy and guidelines for the selection of the best technology. A study on the progress of arsenic mitigation options, trend in installation of different arsenic mitigation technologies and operational monitoring, and evaluation of performance of technologies revealed the following constraints in the progress in arsenic-safe water supplies:

- The problem of selection of appropriate technology for arsenic mitigation in different areas remains a major hindrance.
- The trial of prioritized options in the implementation plan before installation of an appropriate technology in an area is an impractical, time- and resource-consuming approach.
- The overwhelming demand of deep tube wells from communities and local arsenic committees restricts the installation of other technologies prioritized in the implementation plan.
- The large-scale abundance and poor water quality of some arsenic mitigation technologies has deterred the implementing agencies from deployment of these technologies.
- The implementation of a national policy has received poor support from donor agencies.

POTENTIAL SOLUTIONS

A number of symposia and workshops have been organized over the years to address this problem; however, a real solution to the problem has yet to be found. The author persuaded the American Chemical Society, International Union of Pure and Applied Chemistry, and U.S. National Science Foundation to hold a joint workshop with the Bangladesh Academy of Sciences, the Bangladesh Arsenic Mitigation Water Supply Project, the Arsenic Policy Support Unit, and the Bangladesh Chemical Society to come up with some solid recommendations. This international workshop [2], entitled Arsenic Contamination and Safe Water, was held at the Atomic Energy Center, Dhaka, Bangladesh, on December 11–13, 2005. In a well-attended closing session, the participants offered a large number of recommendations. Salient recommendations follow.

General

- An inventory should be made of current research in arsenic pollution.
- A better communications network should be developed within the research community.
- More research needs to be done on the treatment of surface waters.
- Where appropriate, piped water systems need to be installed with central purification.
- More research needs to be done on the relationships between arsenic and the incidence of disease.

Geochemistry

- More local information is needed, especially research on hydrology and microbiology.

- Existing knowledge of arsenic sources must be expanded to cover the entire region.
- Anaerobic studies need to be made of microbial environments.
- It would be desirable to map the aquifer.

Analytical

- Economical and reliable analytical methods are needed. There is great need for additional training, especially of analytical technicians.
- The number of service-oriented analytical laboratories available is woefully inadequate and needs to be increased.
- International assistance is needed to develop quality control guidelines.
- More funds are needed for analytical equipment. It is very important that instrumentation acquired be reliable and accurate, but it does not need to be state of the art.
- An inexpensive method for detection of arsenic in the field and at home needs to be developed.
- The aqueous chemistry of arsenic, especially the environmental effects of speciation, must be investigated further.
- The presence of arsenic in the food chain needs to be analyzed and its effects elucidated.

Remediation

- It is necessary to narrow the choice of remediation devices to no more than three to allow better monitoring of these devices and to allow scale-up for larger communities.
- A project on sludge disposal should be initiated.

Policies

- Efforts should be made to engage the private sector.
- Better coordination is needed between the operations of governmental and nongovernmental organizations.
- The policies that have already been promulgated need to be implemented.
- The maximum acceptable level of arsenic in drinking water should be reduced to 10 ppb.

The international workshop was followed by symposia [5] held at the American Chemical Society meeting in Atlanta, Georgia, March 26–30, 2006. Several speakers compared the cost-effectiveness and efficacy of arsenic removal technologies applied to groundwater with the risks and benefits of purifying surface water, which is plentiful in Bangladesh. The consensus was that all technologies are potentially useful, but those actually chosen for use must vary according to the conditions in each region.

The risks from bacterial contamination of various sources of water supply reveal that with current technologies, the worst overall public safety risks from bacterial contamination are obtained with pond sand filters, with risks decreasing in order as follows: pond sand filters > dug wells > rainwater harvesting > tube wells. Of these, pond sand filter systems, rainwater harvesting, and deep tube wells are generally free of arsenic pollution but not free of bacterial contamination.

Removal of arsenic to acceptable levels and development of water supply systems with water sources not contaminated with arsenic are two feasible options for safe water supply. Totally arsenic-free water is not available in nature; hence the option to avoid arsenic is to develop water supply systems based on sources having very low dissolved arsenic levels. Rainwater, well-aerated surface water, groundwater in very shallow wells, and deep aquifers are well-known arsenic-safe sources of water. The arsenic content of most surface water sources ranges from less than 1 μg/L to 2 μg/L. Very shallow groundwater replenished by rainwater or surface water and relatively old and deep aquifers show arsenic content within acceptable levels.

Rainwater Rainwater has a very low arsenic content, often undetectable by conventional detection and measurement techniques. Problems relate to improper storage and bacterial contamination during storage. This source for providing potable water should be given greater importance.

Dug Wells Dug wells are a good alternative for clean water if they are constructed according to the World Health Organization and other guidelines. They must be covered; water must be removed by a pump, not with a bucket. Water must not be allowed to enter the well directly but must be forced to filter through surrounding sand and soil. According to R. Wilson (personal communication, 2007), to keep dug wells safe from bacterial contamination, they have to be cleaned occasionally, surface contamination has to be avoided, and they should be chlorinated frequently.

Deep Tube Wells Deep tube well technology is a preferred option of people in arsenic-affected areas [3], but tube wells are not always successful in producing arsenic-safe water at all locations. Potential contamination of arsenic from upper strata needs to be controlled. Furthermore, contamination from manganese, boron, or uranium should be checked. Even without withdrawals for irrigation, a small but significant proportion of deep wells that are low in arsenic are likely to fail over time as stress disconnects the PVC pipe sections that went into their construction.

Remediation Technologies

Treatment of arsenic-contaminated water for the removal of arsenic to an acceptable level is an alternative option for safe water supplies in arsenic-affected areas. Arsenic treatment technologies can effectively make use of existing water sources, and people will not be required to shift to an unfamiliar water supply option.

A wide number of technologies based on arsenic-safe water sources are available for water supplies at low costs, but performance of the technologies varies widely, depending on the quality of raw water. Community participation in operation and maintenance of small surface water–based technologies is not encouraging. The performances of medium-sized to large systems that can support a full-time operator are comparatively better. The problem of treatment of groundwater for arsenic removal arises from the requirement for its removal to very low levels to meet the stringent drinking water quality standards and guideline values for arsenic. Arsenic-removal technologies have improved significantly in the last few years, but reliable, cost-effective, and sustainable treatment technologies are yet to be identified and developed further to meet requirements. All treatment technologies concentrate arsenic at some stage of treatment in different media. Large-scale use of arsenic removal systems may generate significant quantities of arsenic-rich treatment wastes, and indiscriminate disposal of these wastes may lead to environmental pollution. Safe disposal of arsenic-rich media is a concern and needs to be addressed.

In 1978, the government of Bangladesh instituted a program called ETV–AM (Environment Technology Verification–Arsenic Mitigation) to verify the claims regarding the efficacy of arsenic removal technologies and appointed the Bangladesh Council of Scientific and Industrial Research to carry out this program, assisted by the Ontario Center for Environmental Technology Advancement of Canada. This program is supported by the Bangladesh Arsenic Mitigation Water Supply Project, financed by the World Bank. Under the current regulations, no arsenic removal technology may be deployed in Bangladesh unless it is cleared by the ETV–AM program. In February 2004, four technologies were approved for "provisional" use and are now being sold: READ-F, SONO 45-25, Sidko, and MAGC/ALCAN.

Recently, the SONO filtration technology useful for a single family (see details of this system in Chapter 12) was given the highest award from the U.S. National Academy of Engineering (NAE), the Grainger Challenge Prize for Sustainability, after testing 15 competitive technologies. The NAE has recognized this innovative technology for its affordability, reliability, ease of maintenance, social acceptability, and environmental friendliness, which met or exceeded the local government's guidelines for arsenic removal.

A community-based system (see details of this system in Chapter 13) was given the silver medal by the NAE. Over 150 wellhead arsenic removal units of this system are currently being operated by local villagers in West Bengal, India, which borders Bangladesh. The units are maintained and run by the beneficiaries, and the wells do not require chemical addition, pH adjustment, or electricity for their regular operation. Each unit serves approximately 250 to 350 families living within a short distance of the unit, and the flow rate is modest, approximately 10 L/min. Arsenite, As (III), as well as arsenate, As(V), from groundwater is effectively removed to render it safe for drinking and cooking. Regenerability and durability of the adsorbent permit a sustainable, low-cost solution for the widespread arsenic poisoning in this area.

Although many technologies have been developed to treat arsenic-contaminated water, on scales ranging from individual kitchen filters that sell for less than $40 to very expensive industrial-sized plants, none has yet emerged as optimal for the conditions encountered. In most cases, the materials used are not fully characterized, and the systems sold commercially have not been fully validated. However, whereas it is relatively easy to remove arsenic by adsorption on supported iron oxides, small point-of-use filters may become clogged after an indeterminate period of time. It should be noted that no provision has been made to assure that systems remain functional once they are in use. Finally, technologies must be developed for safe disposal of the waste or recycling of the active materials.

Even in advanced countries such as the United States, arsenic removal technologies are scarce; the few that are available are generally very expensive. They are needed in communities where well water is used for drinking and cooking. It is anticipated that the family- or community-level arsenic removal technologies that are being developed for Bangladesh and India, which are also economically and environmentally sustainable, can be replicated or further improved for use in developing and developed countries where arsenic poisoning is a menace.

CONCLUSIONS

Discussion of the advantages of alternative water supply options, including pond sand filters, river sand filters, rainwater harvesting, dug wells, sharing safe shallow tube wells, deep tube wells, and arsenic removal technologies, has led to the conclusion that it is very important to integrate water hygiene and sanitation programs and that community choice will be very important in selecting the type of water supply utilized locally. There is a great need for continual water quality testing.

To assure remediation, it is not necessary to limit options to any given number. Furthermore, use of some of the options is dependent on local conditions in a given country. Based on inputs from various participants of the workshop and symposia, the following priority list appears to be logical:

1. Clearly, piped surface water must have the highest priority. This will require total commitment from the governments of countries where problems of arsenic-contaminated water exist and the funding agencies that deem this a desirable option. Along these lines, other surface water options, such as rainwater harvesting, sand water filters, and dug wells, should be tapped as much as is reasonably possible.

2. The next best option would be safe tube wells. More than likely, they must be deep tube wells. It is important to assure that they are located properly and do not contain other contaminants that can add to the problem. Furthermore, they should be installed properly such that surface contaminants cannot get into them.
3. Arsenic removal units (filters) can work on a small scale; however, their reliability initially or over a period of time remains an issue. Reliable low-price test kits are needed that can address this issue.
4. There is a need to identify a reliable filter that can be scaled up for larger communities so that both maintenance and reliability issues can be addressed.
5. Education and training of local scientists and technicians need to be encouraged so that these problems can be addressed directly. There is a need for more analytical scientists, instrumentation, and testing laboratories.
6. People who continue to drink contaminated water need to be educated because their reluctance to switch wells or to take other steps to purify water will surely lead to future cases of arsenicosis.

These recommendations, along with those published earlier [3,6,7], should be given important consideration by the governments of various underdeveloped and developed countries and funding agencies. It is important to remember that local scientists and other well-meaning people are the final arbiters as to what is best for their region.

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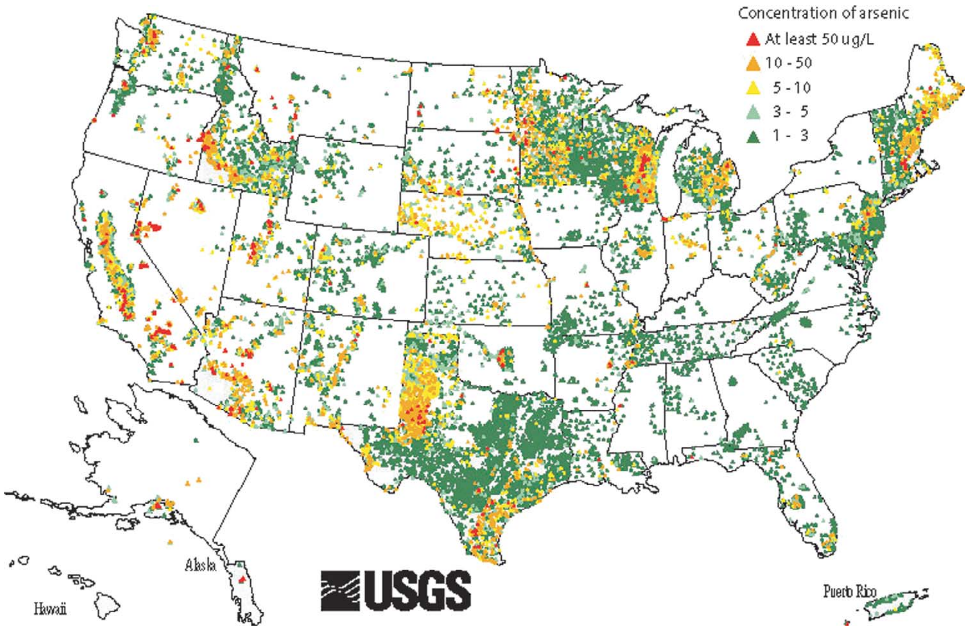
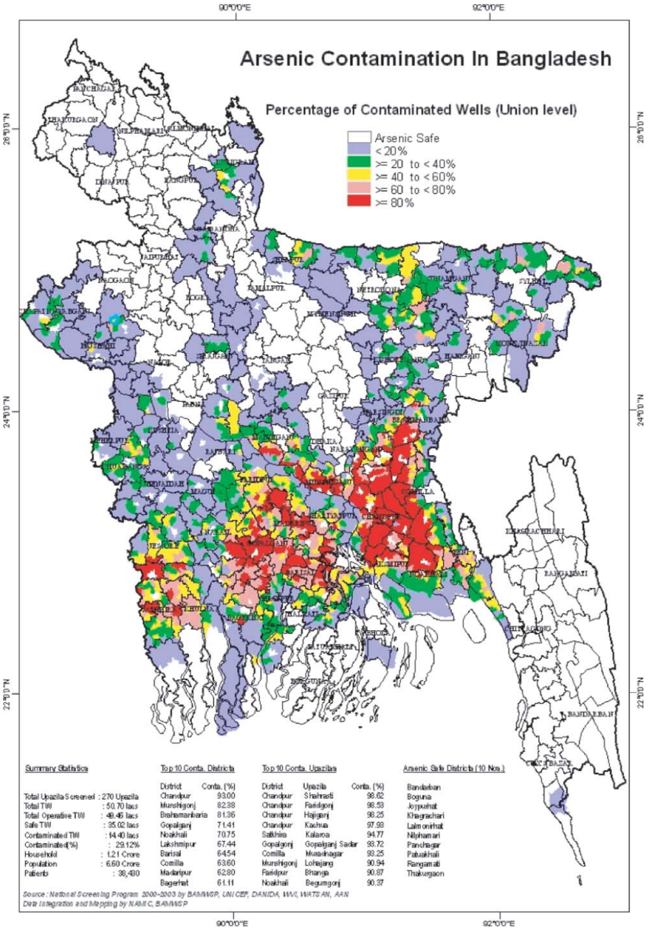
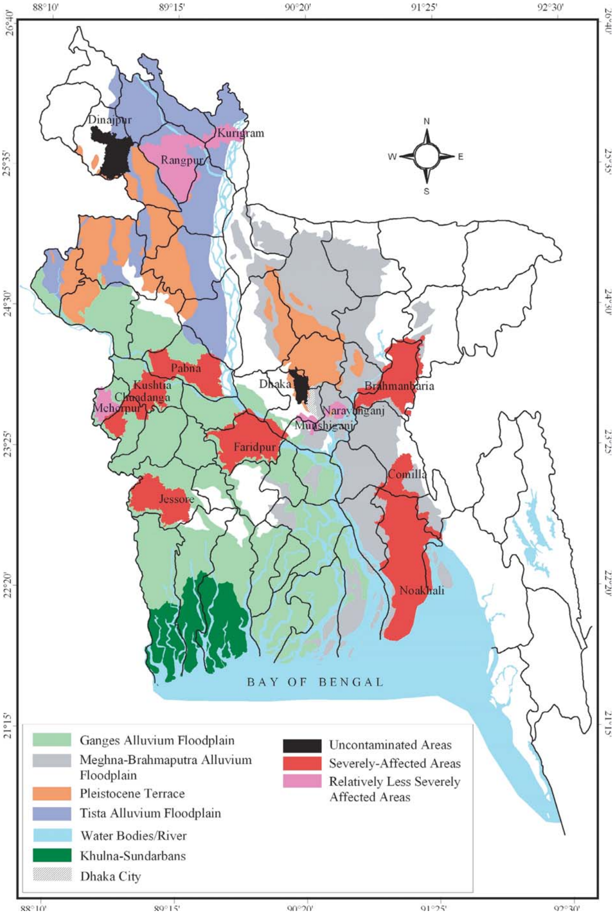


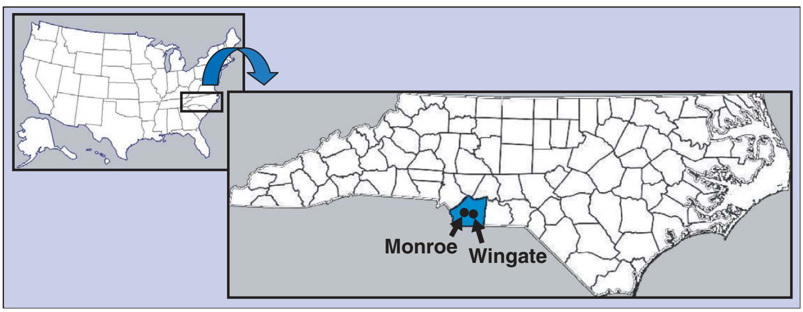
Chapter 1, Figure 1 Arsenic concentration in groundwater in the United States.



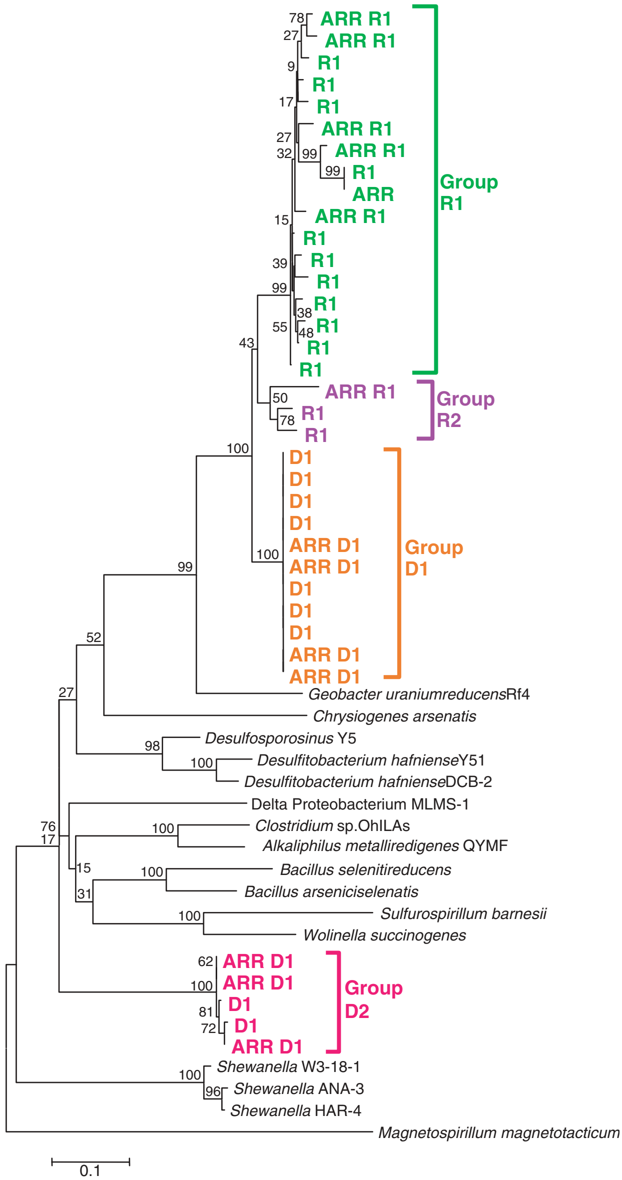
Chapter 2, Figure 1 Arsenic-affected areas of Bangladesh.



Chapter 2, Figure 2 Location of sampling sites.

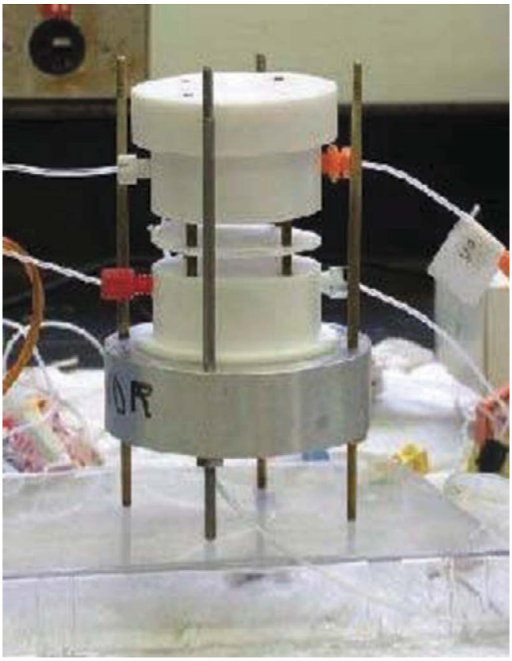


Chapter 4, Figure 1 Well water sampling sites in western North Carolina.



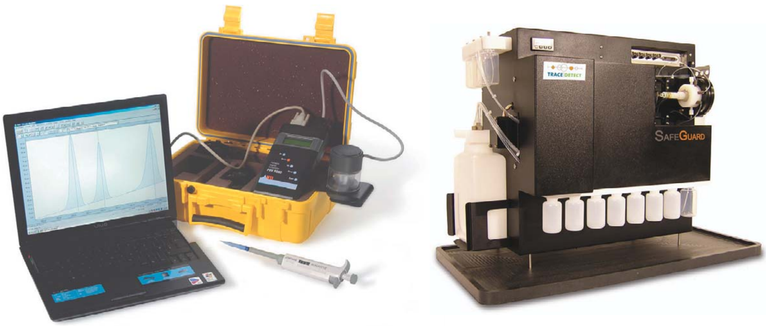
Chapter 4, Figure 2 Phylogenetic tree of *arr*A genes from wells R and D.

Chapter 7, Figure 2 Container for bromide strips showing printed color chart corresponding to solutions 0, 10, 30, 50, 70, 300, and 500 μg/L of arsenic.



Chapter 7, Figure 5 Pervaporation vessel showing the Teflon membrane that separates the lower (donor) chamber from the upper (acceptor) chamber.

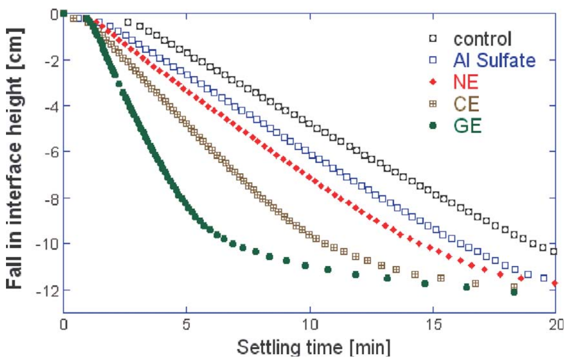
Chapter 8, Figure 1 Colorimetric field test kits with corresponding colored scale chart.



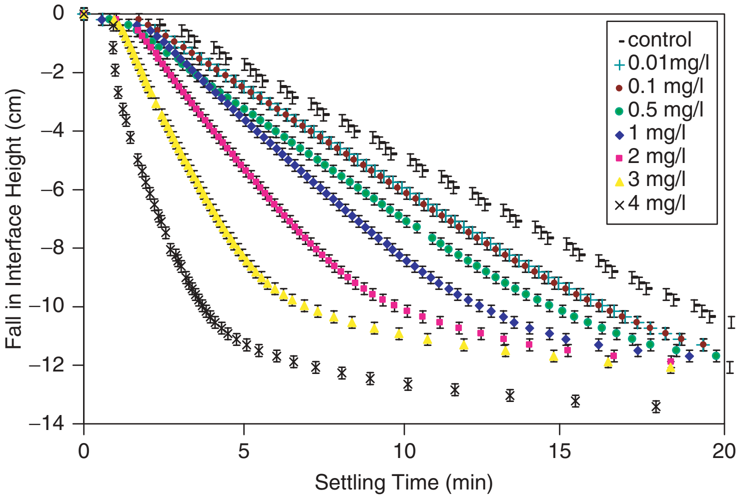
A B

Chapter 8, Figure 3 Example of voltammetric field tests kits: (A) PDV6000 with laptop; (B) benchtop analysis system SafeGuard.

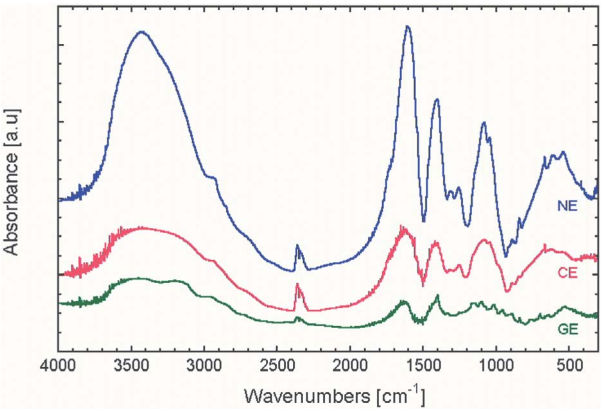
Chapter 9, Figure 1 *Opuntia ficus-indica* (OFI; prickly pear or nopal) mucilage is a thick substance comprised of proteins, monosaccharides, and polysaccharides [10]. The nopal grows abundantly and is very inexpensive and edible. Nopal pads are formed of complex carbohydrates that have the ability to store and retain water, allowing these plants to survive in extremely arid environments. Nopal mucilage is a neutral mixture of approximately 55 high-molecular-weight sugar residues composed basically of arabinose (67.3%), galactose (6.3%), rhamnose (5.4%), and xylose (20.4%) [13,14]. It also contains several ionic species. In fact, its composition gives the OFI the capacity to interact with metals, cations, and biological substances [11]. Cactus mucilage swells but does not dissolve in water [12]. Natural gums have unique surface activity characteristics, which make them ideal candidates for enhancing dispersion properties, creating emulsifications, and reducing the surface tension of high-polarity liquids.



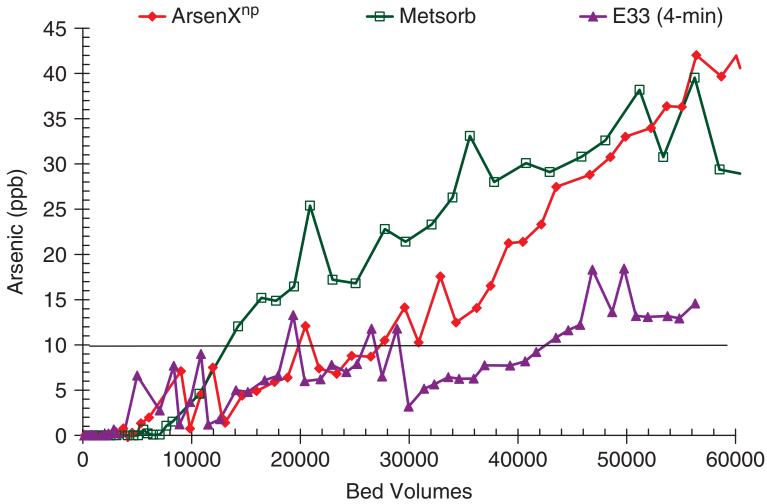
Chapter 9, Figure 2 Flocculation rates comparison at 3 mg/L flocculant dosages. The concentration of the kaolin solution is 5 g/L. Kaolin was used to mimic contaminated water containing a high concentration of particulates. The control refers to the settling of a solution without flocculant. A commercial flocculant was used to establish a baseline $[Al_2(SO_4)_3]$ and to compare the efficiencies of the three mucilage extracts: NE, CE, and GE. GE performed best.



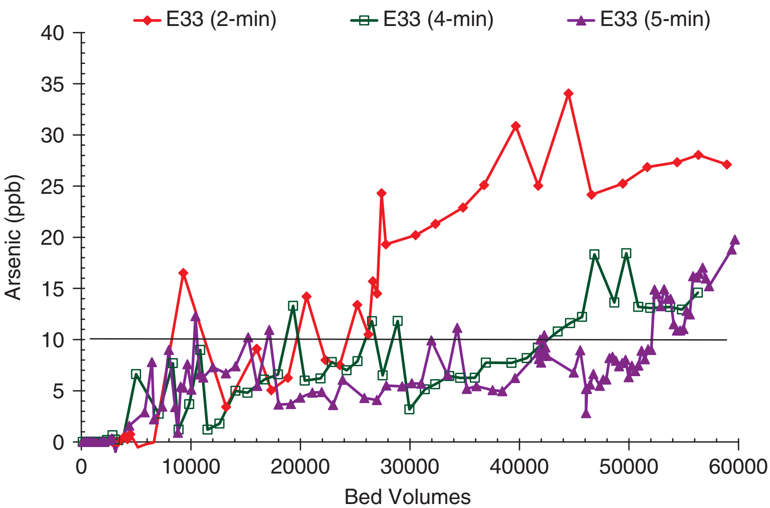
Chapter 9, Figure 3 Effect of dose on the settling rates of GE. The concentrations range from 0.01 to 4 mg/L. Kaolin is used to determine the performance of this flocculant against particulates. The control is the first curve on the right. The initial kaolin concentration is 5 g/L.



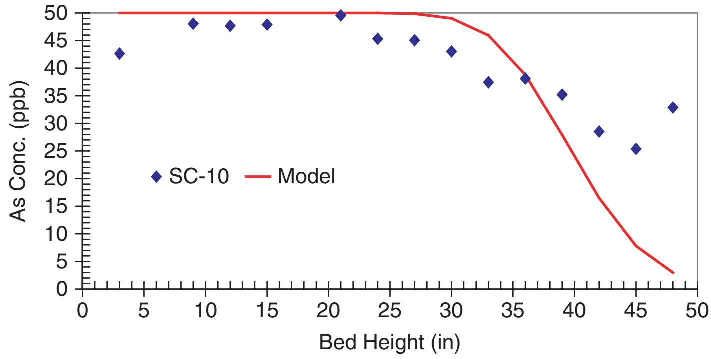
Chapter 9, Figure 5 Raman spectra for NE, CE, and GE mucilage extracts, showing different structures. The lower curve corresponds to GE extract, the upper curve corresponds to NE, and the intermediate curve corresponds to CE.



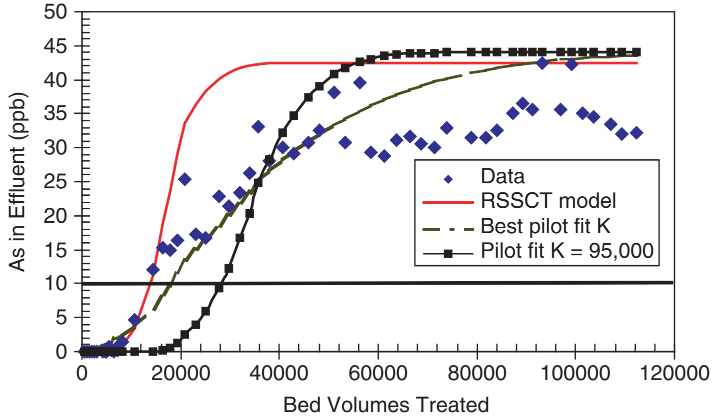
Chapter 10, Figure 9 Arsenic concentrations in column effluent as a function of cumulative bed volumes.



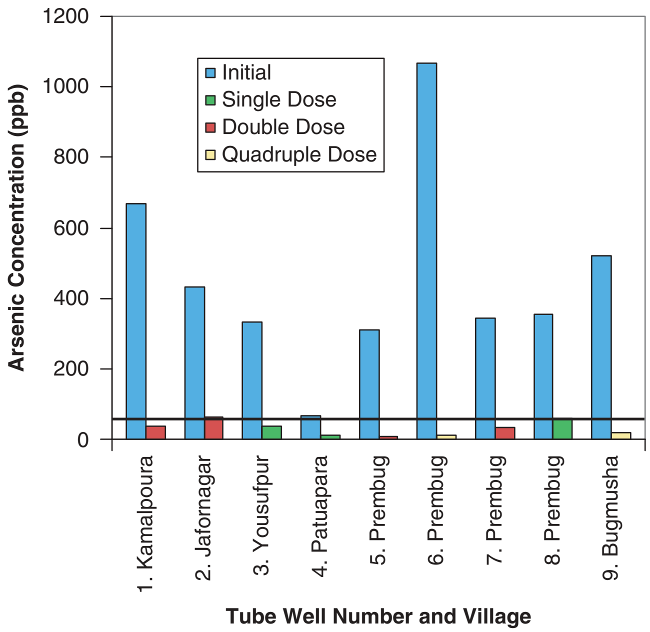
Chapter 10, Figure 10 Arsenic concentrations in column effluent as a function of cumulative bed volumes for E33 with different EBCTs.



Chapter 10, Figure 20 Comparison of the experimental As concentration profile obtained in pilot test column SC-10 with predictions from the Klinkenberg model PD-2-2. $k = 0.0005\,\text{min}^{-1}$, $K = 120{,}000$.



Chapter 10, Figure 21 Comparison of breakthrough curves obtained in Metsorb pilot test with predictions from the Klinkenberg Model using parameters from RSSCT and alternative model fits. RSSCT: $k = 0.0004$, $K = 50{,}000$; pilot tests: $k = 0.0004$; $K = 95{,}000$; best pilot fit: $k = 0.000065$; $K = 95{,}000$.



Chapter 11, Figure 3 Arsenic concentrations of tube well water before and after treatment with ARUBA dust. Data are as measured with ICP-MS (with an accuracy of ±10%). In each case only the initial and final (lowest) concentrations are plotted. Colors of bars for posttreatment concentrations of arsenic for tube wells 4, 5, 6, and 9 may be difficult to discern. Posttreatment bar for well 4 is green (single dose); 5, red (double dose); and 6 and 9, yellow (quadruple dose). One dose is 1 g of ARUBA dust.

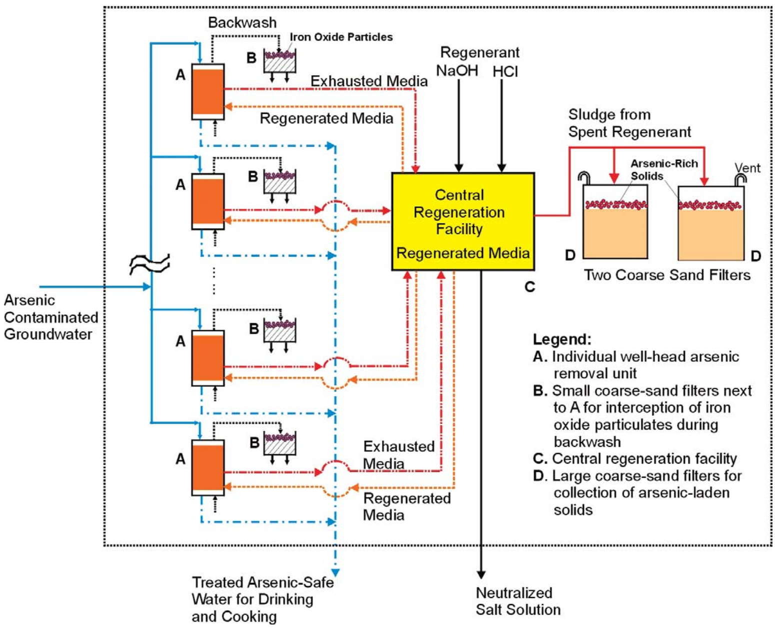
Chapter 12, Figure 1B SONO filter in use.

A B

Chapter 12, Figure 3 (A) SONO filter production center at Kushtia, Bangladesh; (B) filters loaded on a flatbed truck for distribution.

Chapter 13, Figure 2 Wellhead arsenic removal unit.

Chapter 13, Figure 6 Batch reactor employed to carry out regeneration at the central regeneration facility.



Chapter 13, Figure 11 Global treatment scheme for arsenic removal and arsenic containment.

Chapter 14, Figure 3 Water collection from an open dug well.

Chapter 14, Figure 4 Water collection from a protected (covered) dug well.

Chapter 14, Figure 6 Rainwater harvesting by roof catchment.

Chapter 14, Figure 7 Plastic sheet catchment for rainwater harvesting.