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Biogeochemical Controls on Arsenic Occurrence and Mobility in Water Supplies

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I. INTRODUCTION

The occurrence of arsenic (As) in potable water supplies is increasingly a cause of concern worldwide. Significant health effects (including cancer of the skin and internal organs) have been linked to chronic exposure to arsenic in drinking water (1). A large-scale shift in water resource allocation from surface water to groundwater in West Bengal, India, and Bangladesh and the inadvertent exposure of local populations to groundwater containing arsenic at concentrations of several hundred $\mu\text{g}/\text{L}$ has resulted in an extreme example of environmental health effects (2,3). Although arsenic concentrations in potable water in the United States are low compared with those regions (e.g., Taiwan, West Bengal, Bangladesh, Chile, etc.) where health effects have been studied, the U.S. Environmental Protection Agency (USEPA) is, in response to these health concerns, re-evaluating the current enforceable standard for arsenic in drinking water of 50 $\mu\text{g}/\text{L}$ (0.67 μM) (4). A standard of 10 $\mu\text{g}/\text{L}$ (0.13 μM) was promulgated in January 2001 (5); the effective date of the rule has been delayed (pending reconsideration of a standard between 3 and 20 $\mu\text{g}/\text{L}$) but the original compliance date in 2006 remains in force (4).

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Since arsenic is characterized as a "minor" constituent of surface water and groundwater (i.e., an element having a (naturally occurring) median concentration between 1 $\mu\text{g/L}$ and 1 mg/L) (6), a standard in the range of 3 to 20 $\mu\text{g/L}$ will pose a substantial challenge to water suppliers. The USEPA estimates that the source waters for 5.4% of groundwater-based community water systems (CWSs) and 0.8% of surface-water-based CWSs would require treatment to comply with an arsenic standard of 10 $\mu\text{g/L}$ (7). Since, in most cases, the least expensive avenue for compliance would involve modification of existing treatment systems to accomplish arsenic removal (8), a standard at this level would be particularly burdensome for groundwater-based CWSs without existing treatment, that is, for 50% of very small systems (serving populations of 25–100) and approximately 25% of small systems (serving populations of 101–10,000) (7). Although the occurrence of arsenic in the source water will determine whether treatment would be required to meet a new standard, other water quality parameters will also influence the feasibility of various treatment technologies. Both the oxidation state of arsenic and the concentrations of co-occurring source water constituents will affect the efficiency of arsenic removal (see Chaps. 6 and 9).

From the perspective of water supply, it is the occurrence and mobility of naturally occurring arsenic in groundwater and (to a lesser extent) fresh, surface water that are chiefly of concern. Although substantial contamination of surface water and groundwater has resulted from mining and smelting, manufacture of arsenical pesticides, and other human activities, such contamination rarely affects potable water supplies in the United States (9). This is not, however, necessarily the case in developing countries; in Thailand, for example, elevated concentrations of arsenic in drinking water are linked to mining activities (10).

The concentration of naturally occurring arsenic in groundwater and surface water can vary quite widely with the most elevated concentrations on the order of tens of mg/L (11). This variability can be attributed both to the variations in the arsenic content of the soils, rocks, and aquifer minerals that serve as the proximate source of arsenic in groundwater and surface water and to the variable extent of processes that release or sequester arsenic from or to solid phases. Numerous reviews of arsenic geochemistry are available (9,11–16) and this chapter seeks to complement them by focusing on the following questions:

- How are surface water and groundwater different or similar with regard to arsenic occurrence, speciation, and cycling?
- How does the proximate source of arsenic influence dissolved arsenic concentrations?
- Are arsenic occurrence, speciation, and mobility dominated by equilibrium or kinetic controls?

II. COMPARISON OF GROUNDWATER AND SURFACE WATER SUPPLIES

The concentration of arsenic in precipitation is quite low, averaging 0.019 $\mu\text{g}/\text{L}$ for precipitation originating from unpolluted ocean air masses and 0.46 $\mu\text{g}/\text{L}$ for that from terrestrial air masses (17). As rain or snowmelt infiltrates through soils, its composition is altered by the chemical weathering of soils and aquifer minerals. The differences in the chemical composition of surface water and groundwater reflect the progress of chemical weathering under varying conditions and for varying durations that are characteristic of these types of natural waters. For a given potable water source (i.e., a surface water intake or groundwater well), the quality of the water supply derives both from the characteristics of the inputs to the river, lake, reservoir, or aquifer and from the evolution of chemical composition during the residence time of water in that system.

A. Discharge to Surface Waters and Groundwater Recharge

Inputs to surface waters include baseflow (i.e., groundwater inputs), surface flow, and interflow occurring during (or soon after) precipitation (or snowmelt) events, and direct precipitation (18). The chemical composition of the interflow component reflects relatively short-term interactions with the soil matrix; surface flows have even less contact with soils and thus correspondingly less alteration of their chemical composition. Inputs to groundwaters include recharge from surface waters and percolation of water through the unsaturated (or vadose) zone of soils in recharge areas. Significant changes in the composition of soil moisture (such as several-fold increases in the total dissolved solids (TDS) concentration relative to that of average precipitation) occur within meters of the surface due both to evapotranspirative concentration and chemical weathering (6). The accumulation of trace constituents is likely to parallel, to some extent, that of the more well-studied major ions in soil waters.

For both surface waters and groundwaters, input of or mixing with geothermal waters can have dramatic impacts on both major ion and trace element composition because of the enrichment of geothermal waters in many chemical constituents. In particular, geothermal waters are often enriched in arsenic (11) and contribute significant amounts of arsenic to surface waters, for example, in the eastern Sierra Nevada in California (19,20).

B. Evolution of Water Quality

The chemical compositions (including arsenic concentrations and speciation) of surface waters and groundwaters evolve under varying conditions during resi-

constituent of surface water (y occurring) median concen- d in the range of 3 to 20 $\mu\text{g}/\text{L}$ liers. The USEPA estimates ed community water systems ould require treatment to com- n most cases, the least expen- ification of existing treatment ndard at this level would be CWSs' without existing treat- ving populations of 25-100) g populations of 101-10,000) source water will determine v standard, other water quality arious treatment technologies. ations of co-occurring source nic removal (see Chaps. 6 and

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1 mobility dominated by equilib-

dence times that range from means of 2 wk for rivers, 10 yr for lakes, and 1700 yr for groundwater. Actual residence times for a given system can, however, differ substantially from the mean; groundwater ages, in particular, can vary from less than decades for shallow aquifers to tens of thousands of years (6). Because of their longer residence times and isolation from the earth's surface, deep groundwaters are subject to only minor seasonal effects, which can be quite pronounced for surface waters and even shallow aquifers. The extent of mixing and heterogeneity can also be quite different in surface water and groundwater systems. Surface waters are subject to large-scale mixing (e.g., by wind) though stratification may develop seasonally and heterogeneities arise at sediment-water interfaces (21). Although mechanical mixing during fluid advection and molecular diffusion does result in some hydrodynamic dispersion of solute concentrations in groundwaters (22), signals of local heterogeneities in the porous medium can be preserved to a significant extent in the contacting groundwater.

Surface waters are exposed to sunlight and the atmosphere, which support the growth of photosynthetic organisms. "Nutrient-like" behavior of arsenic (i.e., surface depletion in its total concentration) has been observed in surface seawater (23) and in some lakes (24), though, in other cases, surface depletions were not observed (25-28). The occurrence of arsenic in the (thermodynamically unstable) +III oxidation state and of monomethylated and dimethylated arsenic species in oxic surface waters has been attributed to the activity of phytoplankton (25-27,29).

Exchange with the atmosphere can be limited, thus allowing depletion of dissolved oxygen, even in some surface waters (e.g., hypolimnetic water) as well as in groundwater. Changes in redox potential then occur as oxygen and other terminal electron acceptors (such as nitrate, manganese oxides, etc.) are consumed by both microbial and abiotic reactions (see Sec. IV.A). Microbial processes in groundwater systems can have a significant impact on the distribution of arsenic between solid and aqueous phases (see Sec. IV and Chaps. 8 and 11). The uptake of arsenic by the biota is, however, less likely to affect dissolved arsenic concentrations in groundwater than in surface waters where uptake by biota provides a mechanism for transport of arsenic from the water column to the sediments.

C. Comparison of Arsenic Occurrence in Surface Water and Groundwater

Several surveys have been performed in the United States to determine the occurrence of arsenic in potable water supplies and the likelihood of exceedences of drinking water standards set at various levels (7,9,11,30-32). Of these, Frey and Edwards (31) provided data specifically for source waters (rather than finished waters, whose compositions reflect effects of water treatment) and obtained sam-

ples representative of 1, distinct regional concentrations four except North Central in groundwater the occurrence of arsenic by Frey and Edwards CWSSs in the United States of the survey were lower arsenic source waters this survey of CWSSs 50 µg/L. As an example result in elevated arsenic in the arid south 17 mg/L arsenic of TDS preclude

D. Surface Water

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III. PROXIMITY

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ples representative of various regions of the United States. As shown in Figure 1, distinct regional patterns are observed in arsenic occurrence with the lowest concentrations found in the Mid-Atlantic and Southeast regions. In all regions except North Central, arsenic concentrations above 5 $\mu\text{g/L}$ occur more frequently in groundwater than in surface waters. Only one region (North Central) has any occurrence of arsenic above 20 $\mu\text{g/L}$ in surface waters. The data set presented by Frey and Edwards (31), however, represents only about 500 of the 54,432 CWSs in the United States. Furthermore, since potable water supplies at the time of the survey were subject to the arsenic standard of 50 $\mu\text{g/L}$ and substituting a lower arsenic source water would have been an attractive alternative to treatment, this survey of CWSs may have excluded source waters with arsenic in excess of 50 $\mu\text{g/L}$. As an extreme example, evaporative concentration has been shown to result in elevated concentrations of arsenic (up to mg/L levels) in groundwater in the arid southwestern United States (33) and in terminal alkaline lakes (e.g., 17 mg/L arsenic in Mono Lake) (25). In these cases, however, the high levels of TDS preclude these waters from use as potable water supplies.

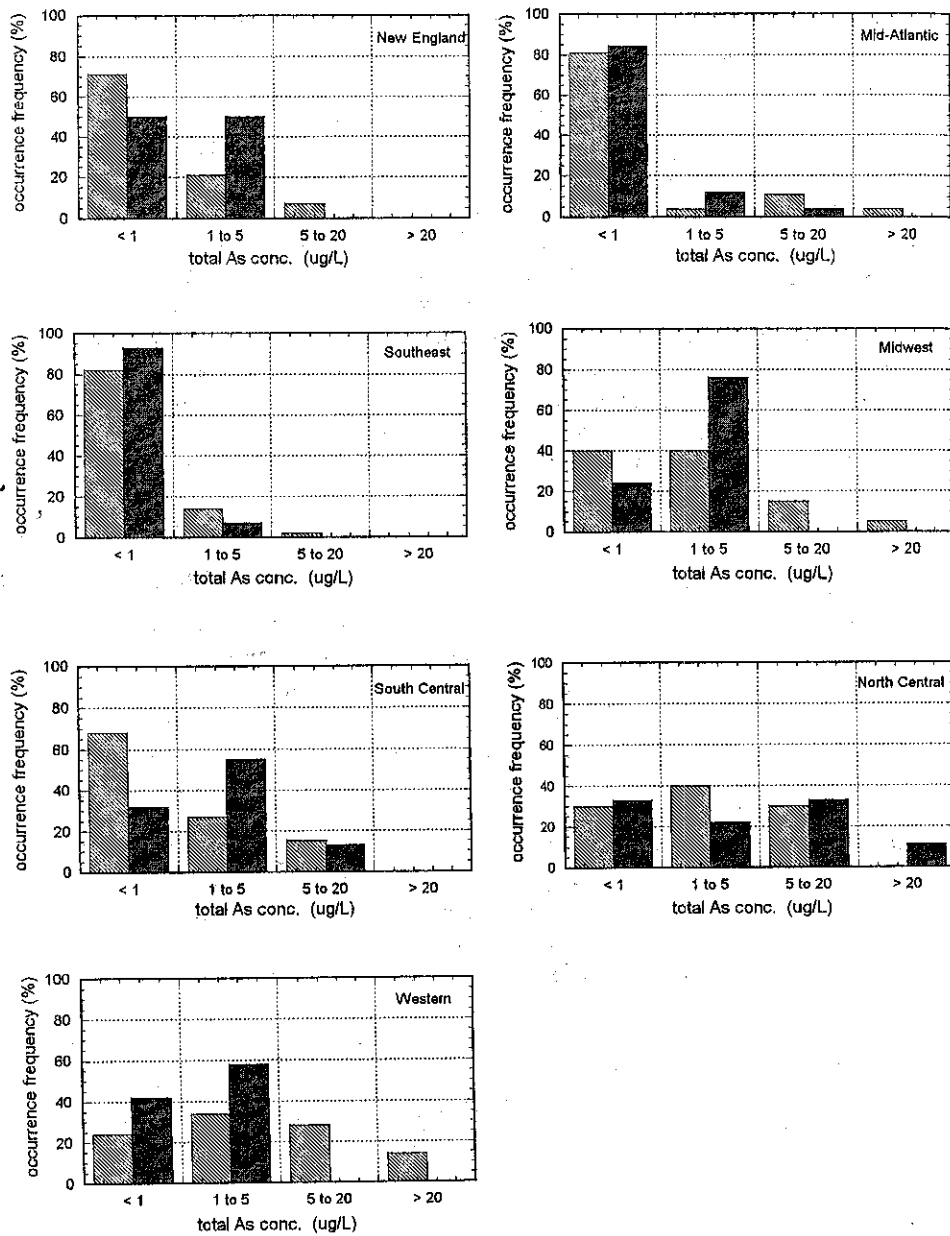
D. Surface Water and Groundwater as a Coupled System

As mentioned above, groundwater can be recharged from and also discharge into surface waters and thus surface water and groundwater cannot be considered independently. In Montana, arsenic concentrations in groundwater of 16 to 176 $\mu\text{g/L}$ have been attributed in part to direct aquifer recharge by Madison River water with concentrations of geothermally derived arsenic as high as 100 $\mu\text{g/L}$ (as well as to leaching of arsenic from aquifer sediments) (34). Groundwater inputs can contribute substantially to streamflow; in a U.S. survey, groundwater contributions ranged from 14–90%, with a median value of 55% (35). Elevated concentrations of chemical constituents in groundwater can influence the composition of surface waters though these impacts may be modified by processes occurring in the hyporheic zone (36).

Artificial recharge of aquifers with surface water, which offers a mechanism for water storage in the arid Southwest, also raises issues of water quality. For example, arsenic occurs in groundwater in the Kern Fan element of the Kern water bank (a proposed groundwater recharge project) at concentrations up to 211 $\mu\text{g/L}$ (37). The extent to which the composition of recharged surface water will evolve to resemble the ambient groundwater during storage is not known.

III. PROXIMATE SOURCES OF ARSENIC

In both surface waters and groundwaters, arsenic in the aqueous (mobile) phase is derived from the arsenic contained in soils, rocks, and aquifer minerals. Arsenic



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is a widely distributed constituent of geological materials, with an average crustal abundance of 1.8 mg/kg. Relatively low concentrations of arsenic (<0.1 to not more than 20 mg/kg) occur in igneous rocks, schists, carbonates, and sandstones. Elevated concentrations of arsenic (ranging up to hundreds of mg/kg) occur in basalts, slate, marine shale, and phosphorites (11). The arsenic content of soils ranges from <0.1 to hundreds of mg/kg; elevated concentrations are found in soils derived from shales and in soils in mineralized areas or areas of volcanic or geothermal activity (11,38,39).

Elevated arsenic concentrations in soils or aquifer minerals are not, however, required to support dissolved arsenic concentrations in the range of a few to hundreds of $\mu\text{g/L}$. For a solid with an arsenic content (M) of 1.8 mg/kg (i.e., equal to the crustal abundance), the fraction (f) of arsenic that would need to be released to support a given dissolved arsenic concentration in the contacting porewater ($[\text{As}]_{\text{diss}}$ in $\mu\text{g/L}$) can be calculated from the equation:

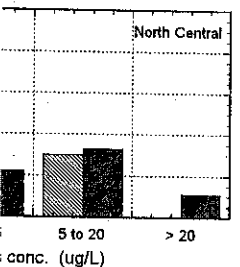
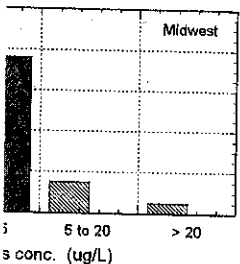
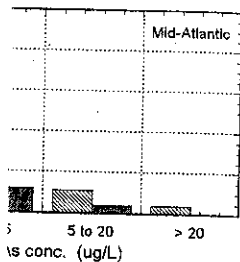
$$f = \frac{[\text{As}]_{\text{diss}} (\phi)}{(M)(D)(1 - \phi)(1000)} \quad (1)$$

where D is the specific gravity of the solid (in g/cm^3) and ϕ is porosity (11). For typical values of specific gravity ($D = 2.6 \text{ g/cm}^3$ for plagioclase) and porosity ($\phi = 0.3$) and $M = 1.8 \text{ mg/kg}$, it requires the solubilization of only 0.09% of the arsenic contained in the solid to support a dissolved arsenic concentration of 10 $\mu\text{g/L}$.

Despite this, a substantial proportion of U.S. groundwaters [42% in the Frey and Edwards (31) study] have arsenic concentrations below 0.5 $\mu\text{g/L}$. In addition, the variability of arsenic concentrations in groundwaters suggests that arsenic is differentially mobilized from various source materials under different environmental conditions. Thus the speciation of arsenic in the solid phase and its susceptibility to leaching by contacting porewater as well as mechanisms for the sequestration of arsenic from the aqueous to solid phases must be considered.

Arsenic in soils, sediments, and rocks subject to weathering is present largely in association either with sulfides or iron oxyhydroxides. In mineralized areas, arsenic is associated with sulfide minerals (i.e., as arsenopyrite and as a trace element in pyrite and other minerals) and with secondary arsenate and arse-

Figure 1 Arsenic occurrence in U.S. source waters in groundwater (diagonal hashed bars) and surface water (shaded bars). Regions: New England (ME, NH, VT, MA, RI, CT, NY, NJ), Mid-Atlantic (PA, MD, DE, VA, DC, WV, KY, NC, SC), Southeast (TN, GA, FL, AL, MS), Midwest (OH, IN, MI, IL, WI, MN, IA), South Central (MO, AR, LA, TX, OK, NM, KS, NE, CO), North Central (MT, ND, SD, WY), Western (AZ, CA, NV, ID, OR, WA, AK, HA). (Data from Ref. 31.)



nate-sulfate minerals (e.g., bukovskyite, kankite, pitticite, and scorodite) formed by weathering processes (40). Authigenic precipitation of arsenic in sulfide solids can occur as a result of bacterial sulfate and/or arsenate reduction (41,42). In contrast, elevated arsenic contents in alluvial sediments has been attributed to its deposition in association with iron oxides (43) and arsenic and iron contents are also correlated in phosphate rock (44). The enrichment of (easily leachable) arsenic in pegmatites has been related to elevated concentrations of arsenic in groundwater from drilled bedrock wells in New Hampshire (45). Clearly, these different associations of arsenic in solid phases will confer differing susceptibility to mobilization.

IV. EQUILIBRIUM VERSUS KINETIC CONTROLS OF ARSENIC REMOBILIZATION AND SEQUESTRATION

Dissolved arsenic concentrations can be limited either by the solubility of minerals containing arsenic as a constituent element (or in solid solution) or by sorption of arsenic onto various mineral phases. For both the precipitation-dissolution of arsenic-containing minerals and sorption-desorption of arsenic onto solid phases, equilibrium calculations can indicate the level of control over dissolved arsenic concentrations that can be exerted by these processes. However, neither of these types of reactions is necessarily at equilibrium in natural waters. The kinetics of these reactions can be very sensitive to a variety of environmental parameters and to the level of microbial activity. In particular, a pronounced effect of the prevailing redox conditions is expected because potentially important sorbents (e.g., Fe(III) oxyhydroxides) are unstable under reducing conditions and because of the differing solubilities of As(V) and As(III) solids.

A. Redox Controls

In aquatic environments with restricted contact with the atmosphere, sub-oxic and anoxic conditions are generated by the biological oxidation of organic carbon and concomitant reduction of oxygen, nitrate, manganese and iron oxides, and sulfate. Although the concentrations of redox-active species formally define the redox potential (pe or E_H) of the system, it is often the case that redox potentials calculated from different redox couples do not agree with each other or with the measured redox potentials (23,46) unless extraordinary care is exercised (47). These discrepancies indicate that concentrations of redox-active species reflect the kinetics of operative redox reactions in the system (which establish steady-state concentrations) rather than redox equilibrium. Modeling of the distribution of porewater and sediment constituents in coastal marine sediments suggests that the rates of microbial and abiotic redox reactions can be comparable (48).

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Arsenic occurs in aquatic environments in multiple oxidation states, most commonly +III and +V (12,13,16). Although As(V) is thermodynamically favored in oxic waters and As(III) under reducing conditions, coexistence of As(III) and As(V) has been observed in both oxic surface waters and anoxic groundwaters and hypolimnetic waters (24,25,49). Such coexistence has been attributed to biologically mediated interconversions of As(III) and As(V) and to the inertness of arsenic species toward reaction with chemical oxidants, particularly oxygen (50,51), and reductants, such as sulfide at circumneutral pH values (52). Microorganisms can directly mediate reduction of As(V) to As(III) (41,42,53,54) and also oxidation of As(III) to As(V) (55-58). However, abiotic oxidation of As(III) by manganese oxides can also be rapid (59-64). Oxidation of As(III) in lake sediments has been attributed to reactions with manganese oxides (65) and the heterogeneous oxidation of As(III) by soils has been shown to be related to the level of oxalate-extractable manganese (66). Abiotic reduction of As(V) by sulfide may be important at low pH values where sulfide is present as H_2S (52).

Although coexistence of As(III) and As(V) in solution (inconsistent with the calculated or measured redox potential) is frequently observed, speciation of arsenic in the solid phase is closely coupled to the redox status of the sediments (67-71). Sequential extraction of arsenic-contaminated sediments has shown that the solid-phase speciation of arsenic shifts from the iron and manganese oxyhydroxide fraction in the oxidized region to the sulfide fraction in the reduced zone (69). In soils amended with arsenate and subjected to flooding (under N_2) and subsequent aeration, arsenopyrite was identified in the flooded soils but not after aeration. During aeration, arsenic appeared to be sorbed and/or coprecipitated with iron oxyhydroxides (72). Release of arsenic from sediments has been found to be related to reductive dissolution of Fe(III) oxides and oxidative dissolution of sulfide minerals as well as to the redox cycling of arsenic (67-69,71,73-77). Correlation of sediment profiles also suggests some control of arsenic mobility by manganese, possibly due to redox reactions of manganese oxides with As(III) (74,78). Redox conditions (whether subject to equilibrium or kinetic controls) will thus profoundly affect the distribution of arsenic between the aqueous and solid phases.

B. Dissolution-Precipitation

Limits on the dissolved concentrations of arsenic due to precipitation of authigenic minerals (with arsenic as a constituent ion) are unlikely in oxic systems. Most arsenate minerals are too soluble to precipitate under environmental conditions. Scorodite, $FeAsO_4(s)$, is observed as a weathering product of arsenopyrite and is likely to have formed under conditions of elevated concentrations of dissolved As(V) and Fe(III) and at low pH (40). At circumneutral pH, scorodite is unstable with respect to transformation to Fe(III) oxyhydroxide phases, which

may then serve as sorbents for As(V) solubilized by scorodite dissolution (see Sec. IV.C). Calcium arsenates have been identified at a contaminated site where acid mine drainage water with very elevated As(V) concentrations (tens to hundreds of mg/L) interact with a limestone substratum (79). Although Wagemann (80) calculated that barium arsenate, $Ba_3(AsO_4)_2(s)$, was oversaturated in natural waters, redetermination of the solubility product for this solid by Essington (81) demonstrated that these calculations were based on a grossly incorrect constant. Based on a reinterpretation of previously reported solubility data, Essington (81) also reported a solubility product for $BaHAsO_4(s)$, $K_{sp} = 10^{-26.64}$. Figure 2 shows that the concentration of total, dissolved As(V) in equilibrium with both $BaHAsO_4(s)$ and barite, $BaSO_4(s)$, at fixed pH varies inversely with the sulfate concentration. Thus water with, for example, a sulfate concentration of 50 mg/L would be oversaturated with respect to $BaHAsO_4(s)$ (at pH 8.3) if the total, dissolved As(V) concentration exceeded about 30 $\mu\text{g/L}$. However, the kinetics of solid precipitation at a low degree of oversaturation can be quite slow and barium arsenates have not been identified in natural environments.

Under reducing conditions, As(III) may precipitate with sulfide as orpiment, $As_2S_3(s)$, realgar, $As_4S_4(s)$, or arsenopyrite, $FeAsS(s)$. However, even if such solids form, the dissolved As(III) concentrations in equilibrium with them are not necessarily low. A study of orpiment solubility demonstrated that, in

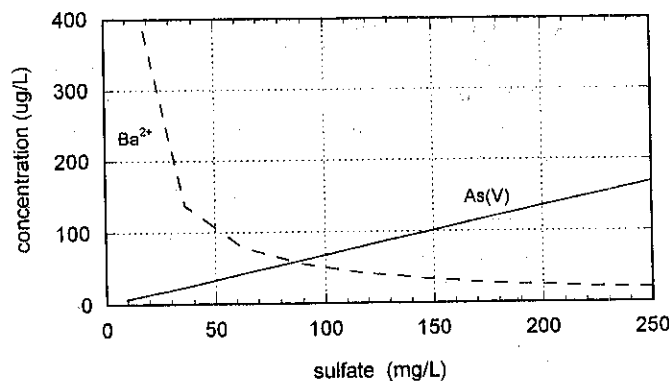


Figure 2 Dissolved concentrations of barium and As(V) (in $\mu\text{g/L}$) in equilibrium with the solids $BaHAsO_4(s)$ and $BaSO_4(s)$ calculated as a function of the dissolved sulfate concentration (mg/L) using MINEQL⁺ (133). Calculations were performed at pH 8.3 with ionic strength fixed at 0.01 M and major ion composition in mg/L (mM in parentheses): SiO_2 9.3 (0.16), Ca 72 (1.8), Mg 29 (1.2), Na 93 (4.1), K 4.5 (0.12), HCO_3 154 (2.5), Cl 87 (2.4), F 0.29 (0.015), B 0.14 (0.013). The solubility constants for $BaHAsO_4(s)$ and $Ba_3(AsO_4)_2(s)$ were taken from Essington(81).

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the absence of excess sulfide, the concentrations of dissolved As(III) (present as H_3AsO_3) in equilibrium with orpiment were about 750 $\mu\text{g/L}$ over a pH range of about 2–6 and were predicted to increase with pH above pH 6. In the presence of excess sulfide, solubility was lower at $\text{pH} < 3$ but substantially higher at circumneutral pH (in the tens of mg/L); this increased solubility was attributed to the formation of the dissolved complex $H_2As_3S_6^-$ (82). The presence of this species in solutions saturated with orpiment was supported by analysis of solubility data by Helz et al. (83) who also provided spectroscopic evidence for the monomeric dissolved species $H_2AsS_2^-$ and $HAsS_2^{2-}$ in undersaturated alkaline solutions. Formation of carbonato complexes of As(III) has also been proposed (84). Dissolved As(III) concentrations in equilibrium with mixed metal sulfides can be lower than those controlled by orpiment solubility as demonstrated for the assemblage $\text{CuS(covellite)-Cu}_{1.8}\text{S(digenite)-Cu}_3\text{AsS}_4$ (85). Even in this case, however, dissolved As(III) concentrations were between 12 and 160 $\mu\text{g/L}$ for pH values of 8–8.5 and varying concentrations of dissolved sulfide.

Such sulfide phases are unstable in the presence of dissolved oxygen. In eastern Wisconsin, release of arsenic from a sulfide-bearing secondary cement horizon has been attributed to introduction of oxygen in water supply wells. The intersection of static water levels in residential wells with this horizon was found to correlate strongly with concentrations of arsenic in groundwater, which were as high as 12 mg/L (86). An x-ray photoelectron spectroscopic study of arsenopyrite oxidation showed that arsenic diffuses from the interior of the mineral to the surface during oxidation, suggesting that arsenic would be preferentially leached from the solid (87).

Under either reducing or oxidizing conditions, the solubilization of arsenic from sulfide phases can be subject to kinetic limitations. Mass transfer constraints, particularly in porous media, can result in localized saturation conditions near the surface of the solid. For oxidative dissolution, depletion of dissolved oxygen may limit dissolution kinetics. Microorganisms may also play a role in catalyzing such oxidative dissolution as has been demonstrated for pyrite oxidation (88) and thus dissolution rates may reflect the level of microbial activity (which may be subject, for example, to nutrient limitation). Thus, although equilibrium calculations indicate solubility constraints on dissolved arsenic concentrations, actual concentrations may be lower than the predicted equilibrium values due to slow dissolution kinetics or greater due to slow precipitation kinetics.

C. Sorption–Desorption

Unlike authigenic mineral precipitation, sorption is clearly an important mechanism controlling dissolved As(V) concentrations. Arsenic adsorption onto oxide minerals (specifically iron oxides and hydroxides) has been invoked in interpreting the occurrence and mobility of arsenic in lake sediments (68,69,73,74,89,90),

equilibrium with dissolved sulfate and at pH 8.3 with (in parentheses): As_2O_3 , 154 (2.5), Cl $3\text{aHAsO}_4(\text{s})$ and

observed diel cycles of dissolved arsenic concentrations in streamwater (91), scavenging of arsenic from seawater at hydrothermal vents (92,93), and the association of iron and arsenic in alluvial sediments (43,94-96). Arsenate sorbs strongly on many mineral phases, particularly Fe(III) and Al(III) oxyhydroxides and clay minerals (97-107). Retention of arsenate by soils has been correlated with the amounts of oxalate-extractable aluminum and (108) and with citrate-dithionite extractable iron (104). Sorption is also the basis for many water treatment technologies for arsenic removal, such as coagulation and packed-bed media filtration (see Chaps. 6 and 9).

Sorption of As(III) to Fe(III) oxyhydroxides has been widely observed (101,105-107,109). At high pH values, As(III) can be sorbed to a greater extent than As(V). Sorption of As(III) on clays and amorphous aluminum hydroxide has been reported (102). However, removal of As(III) by coagulation with alum is generally poor (110,111). Adsorption experiments conducted with hydrous aluminum oxide under conditions comparable to water treatment with coagulants (pH 6, 120 μ M total Al) showed 99% removal of As(V) but only 3% removal of As(III) at initial arsenic concentrations of 10 and 100 μ g/L (112).

The extent of arsenic sorption in natural waters will be influenced by many factors, relating to both the sorbent and the water composition. As(V) and As(III) have different affinities for various sorbent phases that may be present in sediment, soils, and aquifers. Thus the redox speciation of arsenic and the characteristics of available sorbents will strongly affect the extent of arsenic sorption as will the pH and concentrations of co-occurring inorganic and organic solutes in the aqueous phase. Since sorption is a surface phenomenon and is limited by the availability of surface sites on the sorbing phase(s), the extent of competition between arsenic and other sorbates will depend not only on the affinity of each sorbate for the surface but also on their concentrations relative to each other and to the surface site concentration. Elevated concentrations of phosphate have been used to desorb arsenic from clays (51) and from soils contaminated with arsenical pesticides (113).

Precipitation reactions cannot decrease dissolved arsenic concentrations below that in equilibrium with the solid. In contrast, the dissolved arsenic concentrations controlled by equilibrium sorption will decrease with increasing sorbent concentration. This effect is illustrated in Figure 3, which shows the calculated distribution of As(V) between sediment and porewater where this distribution is controlled by As(V) adsorption onto hydrous ferric oxide (HFO). Increasing the concentration of iron (present as HFO) in the sediment from 1 to 1.5 mg/g significantly decreases the predicted concentration of As(V) in the porewater. This modeling follows the approach used by Welch and Lico (33) except that we have used a published constant for the sorption of silica on ferrihydrite (114) rather than the estimated constants used by Welch and Lico (33). The choice of the

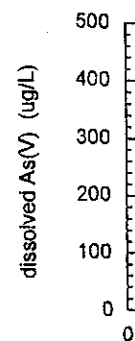


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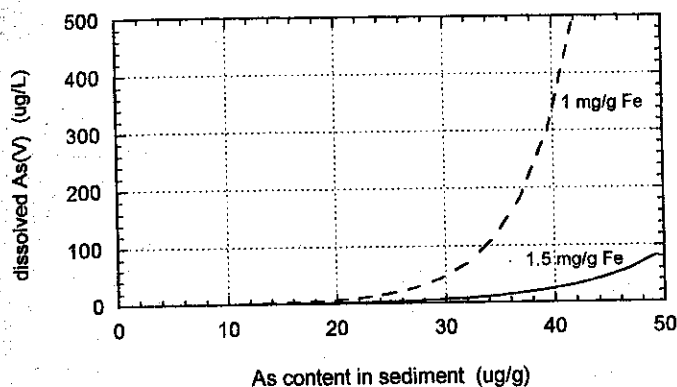


Figure 3 Dissolved As(V) concentrations in porewater ($\mu\text{g/L}$) as a function of the arsenic content of the sediment ($\mu\text{g/g}$) where partitioning between the solid and solution is controlled by sorption onto hydrous ferric oxide (HFO) with 1 or 1.5 mg/g Fe(III) (as HFO) present in the sediments. Modeling was performed using MINEQL⁺ (133) which incorporates constants for sorption onto HFO from Dzombak and Morel (134). Constants for sorption of silica from Hansen et al. (114) and of fluoride estimated by Dzombak and Morel (134) were included in the modeling. Calculations were performed at pH 8 with ionic strength fixed at 0.01. Dissolved concentrations of major ions were fixed at the values reported for Figure 2 (i.e., sorption of these ions onto HFO was not allowed to deplete their concentration in the porewater). Contents of As and Fe in the sediments were calculated based on Eq. (1) using $D = 2.6 \text{ g/cm}^3$ and $\phi = 0.3$.

constant for silica sorption does significantly affect the results of the calculations (for the conditions used here). Consistent with our choice of constants, previous studies of As(V) removal by sorption/coprecipitation with ferric chloride in electrolyte solutions amended with silica (115) or in whole water samples (110) indicate that silica has only a modest effect on the sorption of As(V). However, Welch and Lico (33) did find that, for sediment samples obtained from the Carson Desert in Nevada, the predicted concentration of arsenic adsorbed to HFO agreed with the concentrations obtained from sediment extraction within a factor of 10. Miller (116) has also successfully described the observed partitioning of arsenic in sediment water systems with an adsorption model.

The equilibrium distribution of arsenic between the surface and solution can be destabilized by changes in environmental conditions. Changes in pH or in the concentration of competing ions could shift a pre-existing sorption equilibrium to release arsenic into the contacting fluid. Consistent with competitive desorption, correlations between dissolved arsenic and other (competing) anions

have been observed in oxic groundwater (96). Changes in environmental conditions that result in dissolution of the sorbing phase could also increase the dissolved arsenic concentration. Enhanced release of arsenic associated with dissolution of iron oxides has been demonstrated in selective leaching experiments with the strong organic complexing agent EDTA (ethylenediaminetetraacetic acid) (117).

Redox conditions and pH have been shown to be crucial factors influencing the release of arsenic from contaminated sediments (75,78). Changes in redox conditions, specifically a decreasing redox potential, can affect arsenic sorption both by altering the redox speciation of arsenic and by favoring reductive dissolution of some sorbents, particularly Fe(III) oxyhydroxides. These effects are illustrated in studies of microbial reduction. When a microorganism capable of reducing both Fe(III) and As(V) was incubated with a coprecipitate of As(V) and Al(III) oxyhydroxide, all the As(III) produced was released into solution. With a coprecipitate of As(V) and Fe(III) oxyhydroxide, most of the As(III) produced remained associated with the solid, though some Fe(II) was also released into solution (54). When an Fe(III)-reducing bacterium was incubated with scorodite or As-contaminated sediments, Fe(II) and As(V) were released into solution and no As(III) was detected (118). The importance of the redistribution of arsenic between sorbent and solution as the sorbing phase is progressively dissolved is illustrated by a calculation of dissolved arsenic concentrations in groundwater by Welch et al. (9).

A role of microbial processes in release of arsenic into groundwater concomitant with the reductive dissolution of Fe(III) oxyhydroxides has been suggested based on the observed correlation between dissolved arsenic and bicarbonate concentrations (94,95). Increased bicarbonate concentrations are attributed to the oxidation of organic matter with Fe(III) oxyhydroxides as the terminal electron acceptor. Like oxidative dissolution, reductive dissolution may be kinetically limited. Rates of microbial reduction may be limited by the supply (and nature) of organic carbon.

D. Sequestration and Release of Arsenic in the Los Angeles Aqueduct System

The importance of the availability of Fe(III) oxyhydroxide as a sorbent and of the diagenetic alteration of this sorbent under changing environmental conditions on the mobility of arsenic is illustrated by the Los Angeles Aqueduct (LAA) system.

Elevated arsenic concentrations in the LAA water supply derive from geothermal inputs of arsenic in the Owens Valley. Eccles (19) estimated that about 60% of the arsenic input to Crowley Lake, the first reservoir in the LAA system resulted from inputs of geothermal water with arsenic concentrations of approxi-

mately 1 mg/L in Hot Creek Gorge. Although rapid oxidation of As(III) to As(V) was observed downstream of the geothermal inputs, total arsenic concentrations remained constant (119). This observation is consistent with an earlier study that showed that comparable discharges of geothermal water in Hot Creek Gorge could be calculated based on arsenic, chloride, and boron (120). In contrast, losses of arsenic up to 50% were reported for geothermally influenced streams in Lassen Volcanic National Park; the difference between the conservative behavior of arsenic in Hot Creek Gorge and its nonconservative behavior at Lassen was explained by the different inputs of iron in these systems (121). The paucity of iron and the abundance of phosphate are also likely factors affecting the conservative transport of arsenic through Crowley Lake (27).

The conservative transport of arsenic through the LAA system is deliberately perturbed as part of the interim arsenic management plan implemented in 1996 by the Los Angeles Department of Water and Power (LADWP) in order to provide LADWP customers with drinking water that contains less than 10 $\mu\text{g/L}$ arsenic (as compared with the historical annual average of 20 $\mu\text{g/L}$) (122). Under the interim arsenic management plan, the Cottonwood Treatment Plant (originally built in 1973 and operated intermittently to reduce turbidity) has been operated nearly continuously since March 1996 for arsenic removal. For this purpose, ferric chloride (at an average dose of 5.7 mg FeCl_3/L) and cationic polymer (at an average dose of 1.7 mg/L) are introduced into the LAA through diffusers at the Cottonwood Treatment Plant. Flocculated solids resulting from this treatment are deposited in North Haiwee Reservoir, 27 km downstream of the treatment plant.

A field study conducted in December 1999 (123,124) confirmed the efficacy of this treatment process. The LAA discharges into North Haiwee Reservoir in a channel about 25 m wide, bordered on the eastern side by a small peninsula. Samples of overlying water, sediment, and sediment porewaters were collected in this channel and in a control site on the eastern side of the peninsula. In the channel, an orange-brown floc was visible floating in the water and was observed to settle near the banks, where flow velocity was reduced. In the water sample collected closest to the LAA discharge, the comparison between arsenic and iron concentrations in unfiltered samples (17 $\mu\text{g/L}$ As and 1.9 mg/L Fe) and samples filtered through 0.45- μm membrane filters (3.3 $\mu\text{g/L}$ As and 0.13 mg/L Fe) indicated that both As and Fe were largely associated with the particulate phase. In contrast, at the control site, the concentrations of arsenic in unfiltered and filtered samples were quite similar; unfiltered samples contained 5.7 and filtered samples 4.6 $\mu\text{g/L}$ As.

The sediments collected in the channel were enriched in both arsenic and iron relative to the sediments collected at the control site. A 20-cm core was collected at the control site and a 40-cm core in the channel; sediments were digested using a modification of the U.S. Environmental Protection Agency

(EPA) Method 6010. Based on analysis of these digests, the average concentrations in the sediments (on a dry weight basis) were 240 and 8 $\mu\text{g/g}$ for arsenic and 4.4 and 0.2% for iron in cores from the channel and control sites, respectively.

Sediment porewaters were collected to a depth of 28 cm at a vertical resolution of 0.5 cm with a gel probe device modified from Krom et al. (125). The patterns in the concentrations of manganese, iron, and arsenic in sediment porewater indicated that the sediments became more reducing with depth and were consistent with a shift in terminal electron acceptors from O_2 to Mn oxides to Fe oxides. Dissolved manganese concentrations increased below 5 cm. Dissolved iron and arsenic concentrations increased below 10 cm and were closely correlated. The maximum dissolved arsenic concentration observed in the porewater was 1.3 mg/L.

These data can be used to examine the delivery of iron and arsenic to the sediments and their diagenetic behavior within the sediments. Based on 4-yr average values of the arsenic concentrations above Cottonwood (24.8 $\mu\text{g/L}$) and below Haiwee (8.3 $\mu\text{g/L}$) and the ferric chloride dose (5.7 mg/L), the molar ratio of iron to arsenic in the floc is 160. The same value is observed in the particulate fraction in the water samples collected below the LAA discharge. Figure 4 shows the molar ratios of iron to arsenic in the sediments from the channel core and in

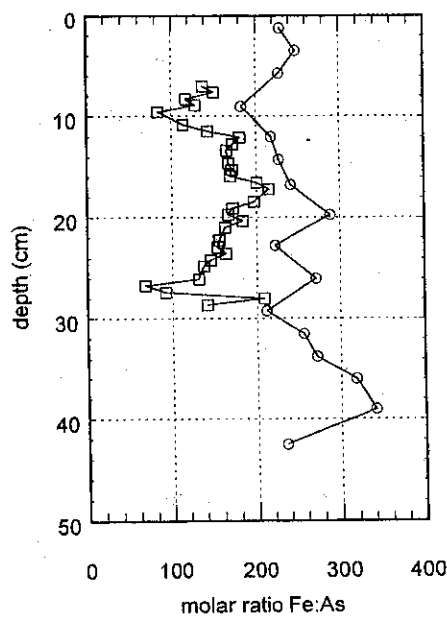


Figure 4 Molar ratios of arsenic and iron in porewaters (□) and sediments (○) as a function of depth.

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the porewaters (excluding the near-surface samples that are very low in both arsenic and iron). The average values of these molar ratios are 250 for the sediment and 150 for the porewaters; neither the sediment nor porewaters exhibit any clear trend in the Fe/As molar ratio with depth. The correspondence of these values for the initial floc, particulate material in the overlying water, sediments, and porewaters suggests that the sediment composition at this site is dominated by the effects of the coagulant input at Cottonwood and that iron and arsenic are released congruently from the sediments during diagenesis.

The fractions of iron and arsenic in the sediments that would have to be released to support the observed concentrations of dissolved iron and arsenic in the porewaters can be calculated using Eq. (1) with appropriate values of specific gravity, $D = 2.5 \text{ g/cm}^3$ for coagulant sludge (126), and porosity ($\phi = 0.9$). Figure 5 illustrates that the calculated fractional solubilization is quite low, less than 2.5% for all samples, and is similar for iron and arsenic for most samples. The

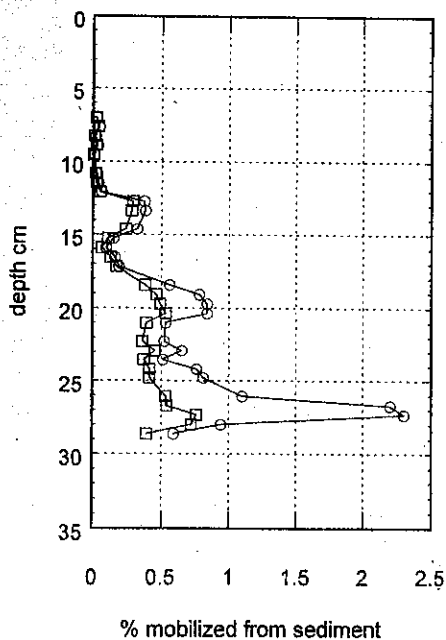


Figure 5 Fractions of arsenic (O) and iron (□) that would need to have been mobilized from the sediment to support the observed concentrations of dissolved arsenic and iron in the porewaters. Note that the porewater data had finer vertical resolution than the sediment samples. Arsenic and iron contents in the sediment sampled at a given depth interval were applied for all porewater data within that interval. Calculations were based on Eq. (1) using $D = 2.5 \text{ g/cm}^3$ and $\phi = 0.9$.

fractional solubilization shows a general increase with depth in the sediments but also exhibits a local maximum between 12 and 15 cm. These observations indicate that the rate of release of iron and arsenic from the sediments is not uniform and is not controlled by their sediment concentrations. Other factors, such as the rate of supply of organic matter, may be influencing the rate of arsenic release from the sediments.

The goal of the interim arsenic management plan is accomplished by coagulant addition to the LAA water supply at Cottonwood. Arsenic is removed from the water supply and deposited with the iron floc in North Haiwee Reservoir. Although the deposited floc becomes unstable under the reducing conditions in the deeper sediments, only a small fraction of the deposited arsenic is released to the porewaters. The uppermost (presumably oxic) layer of the sediment provides a barrier to the diffusive flux of arsenic from the deep porewater into the overlying water. However, physical disturbance of the sediment would allow the elevated concentrations of dissolved arsenic in the porewater to be dispersed into the overlying water. Diffusive flux of arsenic into the overlying water could occur if the oxygen demand in the surficial sediments increased sufficiently that the oxic-anoxic boundary coincided with the sediment-water interface. The deposition of arsenic-rich floc and consequent supply of arsenic to the porewater may also pose a threat to groundwater if shallow groundwater is recharged from the reservoir.

V. IMPLICATIONS FOR WATER SUPPLY AND TREATMENT

The occurrence of arsenic in source waters (and particularly groundwater) can be rationalized by examining the mechanisms of arsenic release from the aquifer solids to the contacting water. Equilibrium calculations provide a constraint on arsenic concentrations that may be expected for water in contact with various solids but slow kinetics (e.g., of dissolution) may result in significant discrepancies between predicted and observed concentrations of dissolved arsenic.

Only a small fraction of U.S. source waters would require treatment to comply with a drinking water standard of 10 $\mu\text{g/L}$. Although most of the systems that would be out of compliance with this standard without treatment would be small groundwater systems, some large groundwater systems (e.g., Albuquerque, NM) and large surface water systems (e.g., Los Angeles, CA) would also be affected by a standard at this level.

Because of the spatial variability in arsenic occurrence in groundwater, selective siting or screening of wells may provide an acceptable water supply. This approach was successfully applied in the City of Hanford, CA (located in the San Joaquin Valley) to comply with the (current) MCL of 50 $\mu\text{g/L}$. Arsenic

concentrations in shallow wells, constructed prior to 1981, routinely exceeded this value. These wells were constructed with maximum depths of approximately 203 m and long, gravel-packed perforated intervals extending within 42 m of the surface. After 1981, deeper wells were constructed (to depths of 460 m) with short perforated intervals located only in coarse-grained sediments not shallower than 216 m and sealed above and below the perforated intervals (127). This strategy is, however, unlikely to be sufficient to comply with a standard of 10 $\mu\text{g/L}$ (128).

When treatment systems must be installed to achieve arsenic concentrations below 10 $\mu\text{g/L}$, constituents other than arsenic must also be considered in choosing a treatment technology. Common groundwater constituents, such as iron, can interfere with treatment technologies for arsenic removal, such as ion-exchange (see Chap. 9). The redox speciation of arsenic in the source water must also be considered in designing treatment systems. Since As(V) is more effectively removed than As(III) by most treatment technologies, preoxidation will generally be required except for technologies, such as manganese greensand filtration, that incorporate an oxidant (7). Simple aeration is insufficient to oxidize As(III) to As(V) (128,129) but many conventional oxidants are suitable for this purpose (130).

A subsurface treatment strategy for groundwaters has been recently field tested in Germany (131). At a municipal well field, extraction of groundwater was alternated, on a 24-hr cycle, with aeration and reinjection of a portion of the extracted water. Introduction of oxygen into the subsurface resulted in the oxidation of ambient (reduced) iron and manganese and precipitation of the corresponding oxyhydroxides in the aquifer. No change in permeability was observed. Arsenic was immobilized in the subsurface; with ambient As(III), however, a "ripening" period, attributed to biofilm formation and onset of biological oxidation of As(III) to As(V), was required for efficient arsenic removal.

This treatment strategy relies on the ambient iron to form a subsurface treatment zone. In iron-poor groundwaters, it is possible that iron could be injected into the subsurface (as a solution of ferric or ferrous salts) and precipitated as Fe(III) oxyhydroxides by subsequent injection of a neutralizing solution (i.e., either base or an oxidant). In calcite-bearing aquifers, precipitation may occur as the ferric salt solution contacts aquifer minerals as has been demonstrated in laboratory experiments by Morrison et al. (132). Principal concerns in implementing such an in situ treatment strategy would be to avoid clogging the porous medium in the subsurface treatment zone, exceeding the capacity for arsenic retention within the treatment zone, or remobilizing arsenic from the treatment zone.

Although groundwaters generally contain higher concentrations of trace constituents (derived from water-rock interactions) than do surface waters, they also often provide superior protection against pathogens and greater reliability

of supply. A thorough assessment of groundwater quality is particularly important when major changes in water resource allocation are made (e.g., the large-scale shifts from surface water to groundwater use in West Bengal, India, and Bangladesh) to avoid exposure to naturally occurring groundwater constituents, such as arsenic.

ACKNOWLEDGMENTS

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