

# Arsenic in Ground Water: A Review of Current Knowledge and Relation to the CALFED Solution Area with Recommendations for Needed Research

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## ABSTRACT

Ground water with arsenic concentrations greater than the U.S. Environmental Protection Agency drinking water standard exists throughout much of the CALFED solution area. These high concentrations are of concern from the standpoint of both existing water supply and development of conjunctive use projects. Much is known about arsenic mobility in ground water subject to different hydrologic and geochemical conditions. However, some important knowledge gaps exist that limit the ability to design water supply projects that could prevent arsenic mobilization or promote arsenic removal from ground water. A few well studied systems could provide a much better understanding of methods for preventing or eliminating high arsenic problems. Within the context of the examination of a few detailed field studies, some important research needs include: 1.) Determining the significance of metal-bridging aqueous complexes involving inorganic arsenic and natural organic matter, 2.) In the context of *in situ* remediation, determining whether

adsorbed arsenic is stabilized or released during crystallization of metal oxides. Little is known about the quantitative significance competition of inorganic arsenic with other inorganic aqueous species in natural systems. Experiments should be conducted with actual aquifer materials, as the effects of aging on arsenic desorption in laboratory studies are quite significant. 3.) Devise methods to detect and quantify rates of oxidation/reduction reactions of arsenic that are carried out by microorganisms at ambient concentrations of arsenic and under *in situ* conditions. The findings from detailed field studies have the potential for greatly reducing the cost of meeting the new drinking-water standard for arsenic. The research would benefit a broad constituency.

## KEYWORDS

arsenic, ground water, groundwater, CALFED, water supply, conjunctive use, geochemistry, adsorption, microbiology

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## INTRODUCTION

An evaluation of the human health effects of arsenic in drinking water (National Research Council 1999; National Research Council 2001), along with estimated compliance costs (Federal Register 2001), resulted in lowering the arsenic drinking-water standard from 50 to 10  $\mu\text{g/L}$ . Estimated costs for compliance in California are \$550 million for capital costs and \$77 million annual operation expenses for existing regulated water supplies (Kennedy/Jenks Consultants 1997). The lower standard has caused concern that conjunctive water use also may be affected in many parts of the CALFED solution area (Saracino-Kirby 2000). CALFED is a consortium of state and federal agencies addressing California's water management issues. An understanding of the biogeochemical and hydrologic processes controlling arsenic solubility and transport are necessary in the management and development of water supplies, particularly where conjunctive use of water is being practiced or considered in the CALFED solution area.

Water management strategies require an understanding of the occurrence of, and controls on, arsenic in ground water. An incomplete understanding of the occurrence and biogeochemical environment of arsenic in ground water limits the ability to develop and manage water supplies. Identification of aquifers likely to have unacceptably high arsenic concentrations would direct water supply development to aquifers with low arsenic concentrations. Understanding the geochemical and physical controls on arsenic in ground water can lead to management strategies that prevent increases in arsenic concentrations in response to withdrawals of ground water. Because the geochemical and physical controls on arsenic in ground water are not fully understood, research that allows better prediction of arsenic concentrations in aquifers used for water supply needs to be identified and pursued, including methods for manipu-

lating aquifer geochemistry to result in acceptable aqueous arsenic levels. A review of the current understanding of the processes that affect arsenic along with a review of the current understanding of arsenic in ground water in the CALFED solution area form the basis for identifying these research needs.

## Arsenic in ground water

Although only present as a trace element in the Earth's crust, the poisonous properties of arsenic compounds have been known since antiquity. Despite a low crustal abundance ( $\sim 0.0005\%$ ), arsenic is widely distributed in nature and is commonly associated with the ores of metals like copper, lead, and gold. Indeed, arsenic was probably first discovered and used in the smelting and alloying of copper, nearly three thousand years ago (Nriagu 2002). Arsenic trioxide ( $\text{As}_2\text{O}_3$ ) eventually gained so much favor as a homicidal agent in the nineteenth century (having the advantage of being colorless, odorless, and tasteless) that James Marsh devised the first chemical test in the 1830s for the presence of arsenic in tissue (Nriagu 2002). This advance in forensic science put such nefarious malefactors on notice that their evil doings could become uncovered. Arsenic trioxide is currently used for the treatment of certain forms of leukemia and other forms of cancer (Pott et al. 2001). Indeed, the properties of arsenic have been alternatively exploited for medicinal and toxicological purposes, the latter category covering the desire to be rid of such undesirable creatures as crop-threatening insects, weeds, rodents, and assorted microbes (Nriagu 2002). Arsenic was also long used as an agent in hide tanning, and as a pigment for paints and dyes, thereby becoming one of the first recognized chemical occupational hazards (Azcue and Nriagu 1994). It was even produced as a chemical warfare agent (e.g., triphenylarsine), the storage of which has polluted soils in eastern Germany (Köhler et al. 2001). Arsenic in the form of cacodylic acid (dimethyl arsenic acid), under the code name agent blue, was used as a herbicide in the Vietnam war prior to the controversial application of agent orange. These past uses, although some are still employed to lesser degree, have had the effect of introducing a large cumulative quantity of anthropogenically-derived arsenic into the environment.

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While the above applications have generally fallen into disuse with the discovery of synthetic dyes and pesticides, arsenic still has considerable application in agriculture. For example, organic arsenicals like roxarsone (4-hydroxy-3-nitrophenylarsonic acid) act as intestinal palliatives and increase the yields and improve pigmentation of feedlot-raised poultry and swine. The roxarsone is not retained in the tissues (or eggs) of the animals but is excreted with feces. Nonetheless, the arsenic in the excrement of these animals puts the element into the environment, accounting for 20-50 metric tons annually just on the eastern seaboard of the United States (Christen 2001a). Roxarsone can be degraded by microorganisms, a process that liberates As(V) (Brown et al. 2005; Gabarino et al. 2003) and enhances its mobility into local surface and ground water (Rutherford et al. 2003). Other anthropogenic sources of pollutant arsenic include slag from smelters, combustion of coal, runoff from mine waste tailings, and industrial sites of former tanning or pesticide manufacture. These point sources of pollution have their most adverse effects at the local scale.

Natural occurrence of arsenic in drinking water, rather than anthropogenic contamination, adversely affects the largest human populations covering the broadest regional areas (Kinniburgh et al. 2003; Smedley and Kinniburgh 2002; Welch et al. 2000). In Bangladesh alone, perhaps 50 million people drink ground water that contains elevated arsenic concentrations, and thousands of new cases of severe arseniasis (“arsenicosis”) occur annually in that country (Christen 2001b; Nickson et al. 1998; Smedley et al. 2001). The epidemiological situation is also widespread in West Bengal, India (Bagla and Kaiser 1996). Symptoms of arseniasis are characterized by painful skin lesions, hair loss, and more serious disorders of the skin, lung, and bladder that eventually lead to cancers, loss of organ function, and death (National Research Council 1999; National Research Council 2001). Increased recognition of the health risks from arsenic ingestion led to recent lowering of the drinking-water standard. Many public water supplies exceed the new lower standard (Frey and Edwards 1997). Large regions of the continental United States have ground water arsenic concentrations that greatly exceed the U.S.

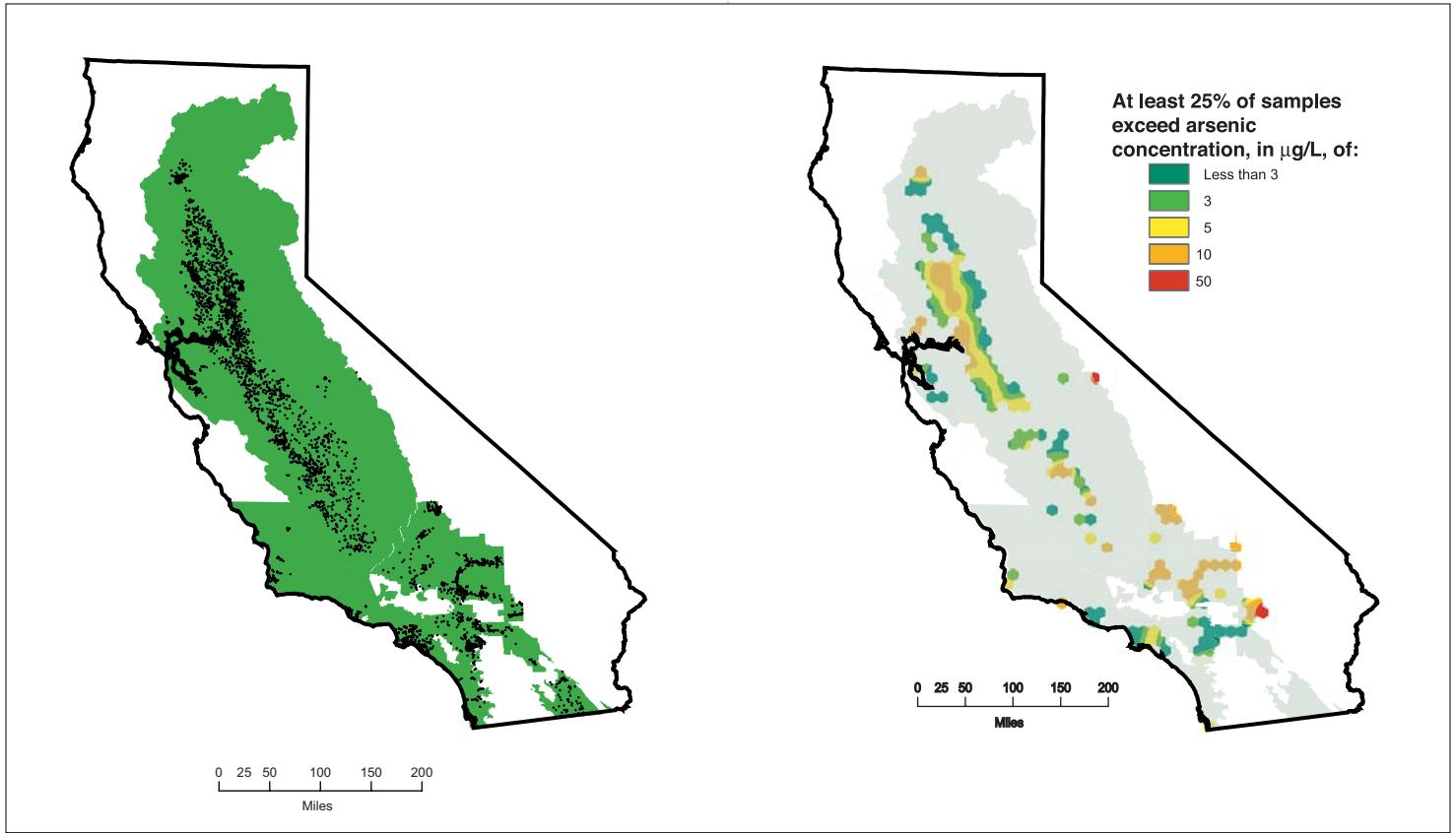
EPA drinking water standard, especially California and other states in the southwest (Welch et al. 2000), including areas where conjunctive use is being considered or already practiced (Saracino-Kirby 2000).

### Aggregation of data in the CALFED solution area

USGS data were retrieved from the California District NWIS (National Water Information System; <http://waterdata.usgs.gov/ca/nwis/nwis>). The 7,838 water quality observations were retrieved using the site identification number as a primary key. The data were further reduced to one observation per station by retaining at each station the most recent observation with the greatest number of chemical variables. The most recent observation was selected because analytical precision, accuracy, and detection levels are believed to have generally improved over time. After this reduction, 4,745 observations remained. In addition, all site locations and well construction information were retrieved and loaded into separate data files, using the site identification number as a primary key.

The 4,745 observations were designated shallow or deep based on well depth, where shallow wells were 30.5 m (100 feet) or less in depth. Well depths were available for only 3,394 observations; 673 were designated shallow, and 2,721 were designated deep. Both one-way analysis of variance and the Wilcoxon rank sum test indicated no significant difference in arsenic concentration between shallow and deep groundwater samples. Data for the deep wells provide a guide for identifying areas where arsenic concentrations may be high or low.

A graphical display of ground water arsenic concentrations within the CALFED solution area is presented in [Figure 1](#). The approach used to produce the colored areas followed the approach described by Ryker (2001). Briefly, hexagons with a 50 km distance from side-to-side were defined for the map area. A 75th percentile for arsenic was calculated for each hexagon that contained five or more ground water stations. A color was assigned to each hexagon based on the 75th percentile and the colors were ‘blurred’ near the edges, but the color assignments were maintained in the center. Although the shallow and deep arsenic concentrations are not statistically different populations, only data for

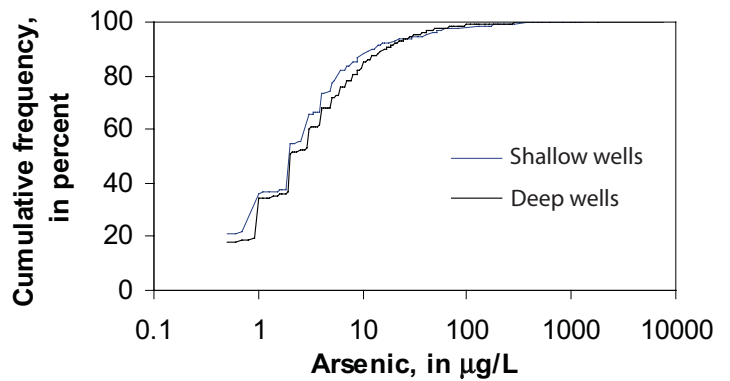


**Figure 1.** Maps showing arsenic in deep ground water within the CALFED solution area (shown in green). The shaded hexagons were constructed using the approach described by Ryker (2001). Inset map shows samples locations.

deep wells were retained for the purpose of constructing the map because the shallow ground water is less likely to represent a source of drinking water.

**Arsenic in ground water within the CALFED solution area**

Arsenic concentrations in ground water exceed the current standards throughout much of the CALFED solution area (Figure 1). About 15 percent of the water from wells deeper than 30.5 m (100 feet) produce water with arsenic concentrations greater than the 10 µg/L drinking-water standard (Figure 2). If this population of wells is an approximate representation of the ground water resources of the CALFED solution area, then about one seventh of the ground water contains unacceptable arsenic concentrations. More than one fourth (about 28 percent) of the water has reported arsenic concentrations greater than 5 µg/L, a level that has been considered as a standard. Shallow wells in the database yield water with similar exceedance levels.



**Figure 2.** Exceedance probability for arsenic in water from shallow (>100 feet) and deep (greater than or equal to 100 feet) wells within the CALFED solution area. All values less than 0.5 µg/L were set to 0.5 for the purposes of this graph.

Arsenic concentrations are notably elevated in the San Joaquin and Sacramento Valleys and in the desert valleys of southern California. Arsenic concentrations

appear to be higher near the center of the Sacramento Valley than along the margins. Arsenic in shallow ground water in the Tulare Lake basin is well documented and largely attributed to release from iron oxide (Fujii and Swain 1995; Gao et al. 2004). The city of Hanford in the southern San Joaquin Valley has several wells that produce high arsenic water (Hering and Chiu 2000; Johnson 1990). Variations in arsenic concentrations appear to be related to ground water levels, with higher concentrations being associated with periods of shallower depth to water. This relation has been tentatively attributed to oxidation and release of arsenic from aquifer sediments during periods of lower water levels (Johnson 1990). Several other areas in the southern San Joaquin Valley have high arsenic ground water (Swartz 1995; Swartz et al. 1996). Much of this water is distinctly alkaline (pH values greater than 8), which suggests that arsenic may be a result of desorption from aquifer materials (Swartz 1995; Swartz et al. 1996).

Arsenic concentrations are of particular concern in the vicinity of some mining areas, particularly in the Mother Lode (Foster and Ashley 2002; Savage et al. 2000). Increased human development of areas in the vicinity of mineralized areas can be expected to be impacted by the presence of high arsenic concentrations in both surface and ground water. Although the source of the arsenic is clearly associated with sulfide mineralization, the extent of the problem is not well known. As discussed below, lowering of the water table in aquifers containing sulfide minerals can lead to sulfide mineral oxidation with consequent release of arsenic to ground water.

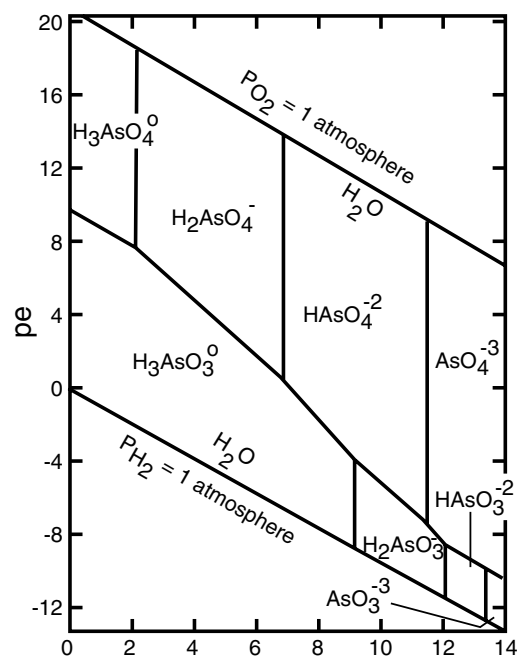
Arsenic concentrations in exceeding 10  $\mu\text{g/L}$  are common throughout much of southern California (Figure 1 and Davis et al. 1994). The causes of the high concentrations do not appear to have been determined. Evaporative concentration may be a contributing factor leading to high arsenic concentrations in areas such as the desert basins in southeastern California and the southern San Joaquin Valley (Fujii and Swain 1995; Welch and Lico 1998). Arsenic does not appear to partition into evaporite minerals until very high salinities are attained ( $> 9$  molar), which can lead to arsenic concentrations in excess of 100,000  $\mu\text{g/L}$  (Levy et al. 1999).

## METHODS/DISCUSSION

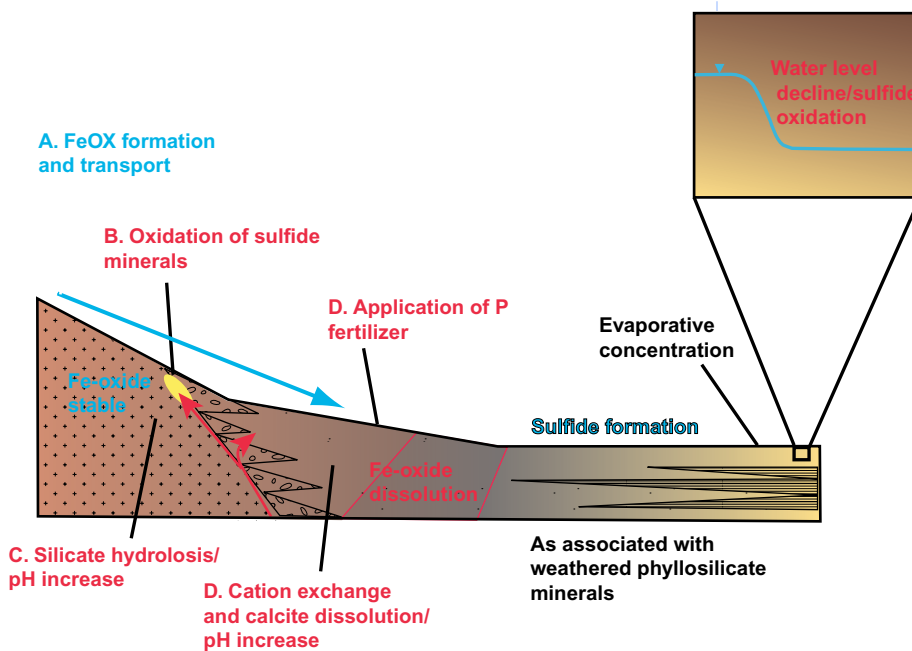
### Controls on Arsenic in Ground Water

#### Overview of Arsenic Cycling in the Environment

Overviews of the aqueous chemistry of arsenic in the environment (Cullen and Reimer 1989; Le 2002), and more specifically in ground water (Welch et al. 2000), form the basis for the following brief summary. Aqueous arsenic in ground water exists primarily as oxyanions with formal oxidation states of III and V. Either arsenite [As(III)] or arsenate [As(V)] can be the dominant inorganic form in ground water (Figure 3). Arsenate ( $\text{H}_n\text{AsO}_4\text{n}^{-3}$ ) generally is the dominant form in oxic waters. In contrast, arsenite ( $\text{H}_n\text{AsO}_3\text{n}^{-3}$ ) dominates in sulfidic and methanic waters including most geothermal water. Reexamination of the suggestion that aqueous arsenic-carbonate species may be common in natural water (Kim et al. 2000) has raised serious questions about the existence of such species (Wallschläger et al. 2003). In highly reducing, sulfide-rich water, thioarsenites (mono-, di-, and tri-) can form (Hollibaugh et al. 2005; Wilkin et al. 2003). Equilibrium generally is not obtained between arsenic and other redox couples commonly present in ground water.



**Figure 3.** Aqueous arsenic dominance diagram at 25°C. Constructed using Geochemists Workbench (Bethke 2000), with thermodynamic data from WATEQ2F (Ball and Nordstrom 1991).



**Figure 4.** Conceptual model of arsenic cycling in ground water.

The most common source of arsenic in ground water is release from aquifer materials (Foster 2003; Welch et al. 2000), although anthropogenic inputs represent a significant source in some cases. Quantitatively, small amounts of dissolved arsenic in drinking water can trigger human health effects. The amount of arsenic present in most aquifer materials is quite sufficient to supply amounts that can cause acute health problems. For instance, the arsenic content of sediments associated with the high arsenic concentrations in the Bengal Delta of Bangladesh and West Bengal are not abnormally high compared with surficial sediments found elsewhere in the world.

Partitioning of arsenic between water and aquifer material is affected by a variety of factors, some of which are schematically represented in Figure 4. In the near surface, environmental arsenic cycles between ground water and a variety of aquifer materials. Chemical weathering of uplands, such as the igneous and metamorphic rocks of the Sierra Nevada and the San Gabriel Mountains, commonly leads to the formation of iron oxide coatings on sediment. This weathering also releases arsenic that adsorbs or coprecipitates

with the oxide. After deposition, several processes can cause the release of the arsenic from this sediment into ground water. An increase in pH can lead to desorption of arsenic from iron oxides (Smedley et al. 2005; Welch et al. 2000 among many others), which has been cited as the cause of high arsenic in the Kern fan in the southern San Joaquin Valley (Swartz et al. 1996). Two common causes of high pH ground water are silicate hydrolysis and calcite dissolution enhanced by cation exchange. Hydrolysis of common silicate minerals such as feldspars can produce progressively higher pH values along a ground-water flow path. Consequently, in a given system older ground water may have more arsenic because of the higher pH.

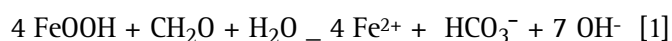
Silicate hydrolysis of felsic volcanic rocks can produce fairly high pH in relatively young ground water, which is a contributing factor to the common association of high arsenic with this rock type (Welch et al. 1988; Welch et al. 2000).

A second process that can cause a pH increase is exchange of sodium on sediments for calcium and magnesium in ground water, which enhances carbonate mineral dissolution. High arsenic concentrations associated with this process have been well documented in central Oklahoma where ground water contacts sediments that were previously in contact with brines formed from seawater (Parkhurst et al. 1996). High pH and arsenic concentrations associated with sediments that were in contact with continental brines formed by evaporation in a closed basin have been documented in northern Nevada (Welch and Lico 1998). High pH ground water in the Tulare Lake basin (Fujii and Swain 1995; Gao et al. 2004) is likely due to this same process, among others. High pH ground water can be expected in closed basins elsewhere in California, such as in the Mojave Desert. Coastal aquifers may be similarly affected where ground water flows through sediments previously in contact with sea water.

Deposition of iron oxide along with sedimentary-organic matter is a common feature of basin-fill

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deposits that constitute many of the most productive aquifers in California. These two phases can react and release arsenic present in the oxide. This reaction is a commonly invoked cause of high arsenic in ground water (Kelly et al. 2005; Nickson et al. 2000; Welch and Lico 1998, among many others). The reaction increases the pH and releases iron, carbonate species and arsenic into ground water as represented by the reaction:



Reaction 1 can proceed to the extent that the iron-carbonate mineral siderite forms (see Magaritz and Luzier 1985, among many others). The formation of siderite is consistent with the observation that ground water with high arsenic and iron concentrations are common, but that the concentrations are not correlated.

The most common arsenic minerals in aquifer materials include arsenic-rich pyrite ( $\text{FeS}_2$ ) and various arsenic sulfide phases that can form authigenically in sulfidic environments (Kirk et al. 2004; McRae 1995; Moore et al. 1988; Rittle et al. 1995; Williams et al. 1996). Arsenic in trace amounts is commonly present in pyrite, but can reach concentrations as great as 8.5 percent (Kolker et al. 2003). The arsenic sulfide  $\text{As}_2\text{S}_3$  can form abiotically or biotically from nonthermal water (Newman et al. 1997a) and from geothermal water (Webster 1990; Webster and Nordstrom 2003). Arsenic adsorption or coprecipitation with iron monosulfide minerals, such as greigite or mackinawite, has been suggested to occur in shallow (< 10 cm), arsenic-contaminated sediments in two lakes; arsenic-containing pyrite forms beneath these sediments (Huerta-Diaz et al. 1998). Arsenopyrite, or a chemically equivalent amorphous phase ( $\text{FeAsS}$ ), also can be a sink for arsenic (Rittle et al. 1995).

Oxidative dissolution of these sulfide minerals can cause the release and redistribution of arsenic in the aquifer as As(III) and As(V). Ground water level declines can expose sulfide minerals to atmospheric oxygen with consequent release of arsenic (Appleyard et al. 2006; Kinniburgh et al. 1994; Schreiber et al. 2003). Under near surface conditions pyrite can react with oxidants (most commonly dissolved oxygen, but also nitrate) resulting in the liberation of arsenic. It

has been recognized for a long time that microbes, particularly under acidic conditions, greatly increase these oxidation reactions (Nordstrom and Alpers 1999 and references therein). Although pyrite oxidation is a complex chemical process that may involve 15 or more steps, the reaction is commonly written as (Drever 1997):

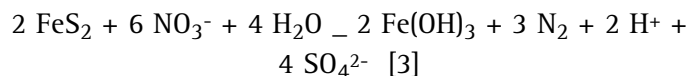


Iron hydroxide, a product of reaction [2], can incorporate some of the released arsenic through adsorption or co-precipitation. Accordingly, quantitative release of arsenic into ground water should not be expected.

Extensive pyrite oxidation, and consequent release of arsenic to ground water, can result from exposure of pyrite in aquifer materials to atmospheric oxygen due to the lowering of the water table in response to ground water development (Appleyard et al. 2004; Kinniburgh et al. 1994; Schreiber et al. 2003).

Similarly, mining of sulfide ore deposits, including gold ore in the Mother Lode in the Sierra Nevada, has led to the release of arsenic because of increased contact of pyrite and other sulfide minerals with atmospheric oxygen (Foster and Ashley 2002; Savage et al. 2000). Arsenic in water flowing from mined areas can be attenuated by adsorption onto iron oxide (e.g., Carrillo-Chavez et al. 2000; Carrillo and Drever 1998a; Courtin-Nomade et al. 2005)

Although much less common than reaction with dissolved oxygen, nitrate can produce arsenic concentrations well above 50  $\mu\text{g/L}$  (Appelo and Postma 1993) by reacting with pyrite through the overall reaction:



Clay and other aluminosilicate minerals are known to be significant adsorbents of arsenic (Stollenwerk 2003). With the possible exception of sediments of the Bengal Basin, these phases have not been identified as an important source of widespread high arsenic concentrations in ground water. Only recently has a clear association of high As(III) concentrations with weathered biotite been demonstrated through the use of spectroscopy and chemical extractions (Breit et al. 2001a; Breit et al. 2001b; Breit et al. 2001c; Foster et

al. 2000a). This association of arsenic with the phyllosilicate mineral biotite may be more widespread than is currently recognized. Several factors may contribute to a lack of recognition of the significance of biotite as an arsenic adsorbent. One factor is that obtaining XANES spectra, as has been done for some Bangladesh sediments by Foster et al. (2000a), is time consuming and requires an advanced photon source, of which only three are available in the United States.

Another factor that can lead to under-recognition of the importance of As(III)

associated with biotite is a result of inadequate sample handling. Sediment sample preservation employing an argon atmosphere and freezing at the time of collection was required to maintain the oxidation states of Fe(II) and As(III) of the chemically reduced Bengal Delta sediments. Exposure of the sediments to atmospheric oxygen for only a few hours resulted in considerable conversion of the Fe(II) and As(III) to Fe(III) and As(V), respectively. Results of subsequent extraction of these sediments could easily be misinterpreted as indicating the presence of iron oxide containing As(V).

Evaporation greatly increases solute concentrations in many parts of California and is a contributing factor that leads to high arsenic concentrations.

Hydrologically closed basins in southeastern California with high arsenic concentrations include the Salton Sea (Setmire et al. 1993) and Owens Lake (Levy et al.

1999; Ryu et al. 2002). Evaporation also increases arsenic concentrations in the Tulare Lake basin (Fujii and Swain 1995).

Geothermal water commonly contains high arsenic concentrations (Webster and Nordstrom 2003). Geothermal water is a principal source of arsenic in Long Valley in eastern California, which in turn is a source of water supply for the Los Angeles Aqueduct (Eccles 1976; Mariner and Willey 1976; Wilkie and Hering 1998).

A brief description of aquifer materials and water quality often associated with high arsenic concentrations, along with some example of localities that have been described as having these characteristics, is shown in Table 1. Recognition of these hydrogeologic settings may be useful in identifying potential areas with high arsenic in ground water.

Dominant arsenic-bearing phase	Source	Process releasing arsenic to ground water	Distinguishing water quality	Hydrogeologic setting	Examples <sup>1</sup> CALFED area
Fe-oxide	Weathering and transport of sediment in an oxic environment	Desorption from iron-oxide	High pH, dissolved oxygen present, low Fe, Mn, N species dominantly as nitrate	'Old' ground water <sup>2</sup> and felsic volcanic rocks	Kern fan
				Areas with abundant exchangeable sodium	Possible in coastal aquifers
		Dissolution of iron oxide	High dissolved iron concentrations, dissolved oxygen absent, N species dominantly as ammonia	Sediments containing iron oxide and sedimentary organic carbon	Tulare Lake basin
				Organic-rich contaminant plumes	SHAD Superfund site
Weathered biotite	Intense chemical weathering	Unknown		Basin-fill sediments affected by seasonal changes in oxidation state induced by wetting and drying cycles	Tulare Lake basin (?)
Sulfide minerals	Sulfide mineralization	Oxidation	Low pH, increasing sulfate, dissolved oxygen absent	Mineralization near the water table	Mother Lode, Iron Mountain
Geothermal water	High temperature weathering	Silicate mineral dissolution	High silica, fluoride, boron, sodium-dominated	Thermal features	Eastern Sierra Nevada

<sup>1</sup> Most of the examples are cited in table 3 of Welch and others (2000), where the reader can find additional information on the examples (including additional reference material). The examples are for illustrative purposes and as such is not intended to represent a complete list.

<sup>2</sup> The term 'old' in this context refers to water that has been affected by relatively extensive silicate hydrolysis, resulting in a high pH.

**Table 1.** Water chemistry and hydrogeology commonly associated with ground water containing high arsenic concentrations.

### **Arsenic adsorption reactions on common aquifer minerals**

The common oxides of iron, aluminum, and manganese appear to be the most important adsorbents of arsenic in aquifers (Bowell 1994; Driehaus et al. 1995; Manning and Goldberg 1997a; Manning and Goldberg 1997b; Oscarson et al. 1983; Stollenwerk 2003). Recent studies suggest that As(III) associated with chemically weathered biotite may be an important source of arsenic in some aquifers in the lower Bengal Delta (Breit et al. 2001a; Breit et al. 2001b; Foster et al. 2000a; Foster et al. 2000b). As(V) is known to strongly react with iron oxides in soils, sediments, and aquifer materials (Carrillo and Drever 1998b; Foster et al. 1998; Livesey and Huang 1981; Matisoff et al. 1982), and studies have documented the association of arsenic with iron oxides in various terrestrial systems (Fuller and Davis 1989; Pichler and Veizer 1999; Rancourt et al. 2001) .

Adsorption of both As(V) and As(III) on pure iron oxide phases has been widely studied (Arai et al. 2004; Belzile and Tessier 1990; Fuller et al. 1993; Kneebone et al. 2002; Waychunas et al. 1993). For As(V) adsorption on goethite and ferrihydrite (also commonly referred to as ferric oxyhydroxide and hydrous ferric oxide), at low surface coverage, a monodentate complex is favored, whereas at high surface coverage, two different bidentate complexes are favored (Fendorf et al. 1997; Sun and Doner 1998; Waychunas et al. 1996). The monodentate bonds are presumably stronger than the bidentate bonds, because they form at the lower arsenic concentrations and do not change with time to bidentate bonds. Once the more energetic monodentate sites are consumed, As(V) binds at the bidentate sites. The change in As(V) binding with As(V) concentration may be important, because chemical conditions that lead to extensive desorption of As(V) in contaminated aquifers might not produce the same degree of desorption in uncontaminated systems.

As(III) also has a high affinity for the iron oxide surface, with evidence for inner sphere complexation confirmed in the literature from spectroscopic studies (Manning and Goldberg 1996b; Raven et al. 1998; Wilkie and Hering 1996). As(III) can be more strongly

bound than As(V) at neutral to alkaline pH values (Jain and Loeppert 2000; Kent and Fox 2004; Manning et al. 1998). Column experiments with sands have also been conducted under alkaline pH conditions that showed As(V) to be more mobile than As(III) (Stollenwerk 2003).

As(V) adsorbs on aluminum oxides somewhat less strongly than on iron oxides of similar structure (Manning and Goldberg 1996b), but generally has the same type of pH dependence as observed with iron oxides (Halter and Pfeifer 2001; Xu et al. 1988). As(V) adsorbs even more weakly on kaolinite, illite, and clay minerals (Lin and Puls 2000; Manning and Goldberg 1996a). Clean quartz does not adsorb As(V) at all or only weakly at low pH values (Stollenwerk 2003); however, quartz grains in aquifers commonly have significant Fe- and Al-rich secondary mineral coatings to which As(V) and As(III) can adsorb (Kent and Fox 2004).

In contrast to As(V), adsorption of As(III) by hydrous Al oxides and clay minerals is substantially lower than observed on iron oxides (Arai et al. 2001; Manning and Goldberg 1997a). Both inner-sphere and outer-sphere As(III) complexes have been observed on aluminum oxides (Arai et al. 2001; Goldberg and Johnston 2001).

As(III) associated with weathered biotite (hydrobiotite) in grey (chemically reduced) sediments of the Bengal Delta co-occurs with high concentrations of aqueous arsenic (Breit et al. 2001a; Breit et al. 2001b; Foster et al. 2000a; Foster et al. 2000b). Although the mechanism for release of the arsenic to ground water is not understood, the lack of iron oxide in these sediments suggests that reductive dissolution is not the sole cause of high arsenic in ground water of the Bengal Delta.

### **Competitive adsorption with other ground-water ligands**

As(V) and As(III) compete with other adsorbing ground-water ligands for mineral surface sites. The ligands commonly observed at higher concentrations in ground water (e.g. carbonate, silicate, and organic acids) may significantly decrease arsenic adsorption and thereby increase dissolved arsenic concentrations and mobility in aquifers. For example, studies of

As(V), As(III) and fulvic acid competitive adsorption on natural, low surface-area alumina, hematite, quartz, and kaolin showed that fulvic acid greater than 10,000  $\mu\text{g/L}$  reduced As(V) and As(III) adsorption in the pH 5-7 range (Xu et al. 1988; Xu et al. 1991). Fulvic acid has also been shown to decrease As(V) and As(III) adsorption on iron oxides (Redman et al. 2002). However, at low fulvic acid concentrations typical of uncontaminated aquifers, Hering et al. (1997) demonstrated a decrease in As(III) adsorption and little effect on As(V) adsorption by ferrihydrite at pH 6. At higher organic acid concentrations, such as in amended soils, arsenic mobility may be increased by the presence of natural organic matter (Jackson and Miller 1999). The effects of natural organic matter on arsenic adsorption may be more complex than realized, as Redman et al. (2002) recently argued that humic substances are capable of forming aqueous metal-bridging complexes with As(V) and As(III) and also can oxidize As(III) to As(V).

Moderate concentrations of bicarbonate seem to have little effect on As(V) and As(III) adsorption by iron oxides (Arai et al. 2004; Fuller et al. 1993; Meng et al. 2000); however, modeling predictions at higher concentrations suggest that As(V) adsorption would be decreased (Appelo et al. 2002; Arai et al. 2004). These "higher" concentrations are actually representative of bicarbonate concentrations observed in ground water, which usually has partial pressures of carbon dioxide gas greater than that in the atmosphere. Sulfate, another common ground-water ligand, only decreases As(V) adsorption at high sulfate concentrations [As(V)/S ratios less than 10] and at pH values less than 7 (Jain and Loeppert 2000).

Phosphate concentrations greater than arsenic decreases As(V) and As(III) adsorption by iron oxides across a broad pH range, although the effect on As(III) adsorption at high pH is low because of low phosphate adsorption (Jain and Loeppert 2000). Similar observations have been made in systems with kaolinite, illite, and other clays (Lin and Puls 2000; Manning and Goldberg 1996b; Manning and Goldberg 1997b). Adding phosphate to soils can increase the mobility of arsenic (Melamed et al. 1995), and Darland and Inskeep (1997b) showed that phosphate increases As(V) mobility in column experiments packed with sand.

Welch and Lico (1998) argued that phosphate was at least partly responsible for higher arsenic concentrations observed in an aquifer. Abundant phosphate in near surface sediments may play a role in removing arsenic from water under some conditions. An iron-phosphate phase containing up to two weight percent arsenic has recently been reported in Holocene sediments of Bangladesh (Breit et al. 2004; Foster et al. 2003). Clearly, this phase can concentrate arsenic in sediments that typically contain arsenic concentrations in the 2-10  $\text{mg kg}^{-1}$  range (Breit et al. 2004).

Several studies have shown that silicate adsorbed on iron oxides reduces As(V) adsorption, especially in the alkaline pH range (Davis et al. 2001; Swedlund and Webster 1999). Meng et al. (2000) evaluated the effect of silicate on arsenic adsorption during co-precipitation experiments with ferrihydrite and observed that the presence of silicate decreased arsenic uptake.

### **Sorption kinetics and incorporation into crystal structures.**

Many adsorbing ions exhibit biphasic kinetics where a fast adsorption phase is followed by slower and sometimes more significant sorption (Davis and Kent 1990). This type of kinetic behavior for As(V) adsorption has been observed for many different oxides (Arai et al. 2004; Fuller et al. 1993; Raven et al. 1998). Desorption rates for As(V) are generally slower and pH dependent (Darland and Inskeep 1997a; Darland and Inskeep 1997b; Fuller and Davis 2004). Slow rates of adsorption and desorption likely influenced the As(V) breakthrough curves observed in column experiments in which phosphate was introduced in the influent to sand-sized quartz and feldspar grains (Darland and Inskeep 1997a; Darland and Inskeep 1997b). As(V) desorption was incomplete in the case where phosphate was added after As(V) was already adsorbed on the quartz and feldspar materials in the column.

Slow adsorption and desorption kinetics do not necessarily mean slow rates of bond formation or disassociation. Slow rates of desorption can be caused by slow rates of diffusion through aggregated nanoparticles (Fuller et al. 1993). These types of aggregated particles are common in natural systems and As(V) can adsorb on the nanoparticles prior to aggregation during a co-

precipitation process (Ford 2002; Fuller et al. 1993; Pichler and Veizer 1999). Slow rates of adsorption and desorption are also caused by mass transfer limitations for diffusion in and out of nanofractures in rock matrices and sediment grains. Such mass transfer limitations may partly explain some observations that the reversibility of As(V) adsorption decreases with contact time (Fuller and Davis 2003; Puls and Powell 1992). Lin and Puls (2000) investigated the effects of aging on desorption of As(III) and (V) from clay minerals (caused by adding phosphate for 10 hours). Aging for 30-75 days greatly decreased desorption from halloysite and kaolinite. Generally, some As(V) desorption can occur quickly when changing chemical conditions occur (Kent and Fox 2004); however, the relative contributions of mass transfer and chemical hysteresis to the amount of slow desorption are not well understood.

More As(V) is adsorbed on ferrihydrite during co-precipitation than during adsorption on the already precipitated phase (Fuller et al. 1993). As the ferrihydrite is transformed to the more crystalline phases, hematite and goethite, the As(V) may be desorbed because the ideal crystal structures of hematite and goethite would not accommodate the tetrahedral arsenate anion. Fuller et al. (1993) observed significant desorption of As(V) from As-ferrihydrite co-precipitates at pH 8 during aging for several weeks. However, Ford (2002) found that very little As(V) was desorbed in a study of As-ferrihydrite co-precipitate aging conducted at pH 6, suggesting that arsenic could be stabilized with time in crystalline iron oxide phases by variants from the ideal crystal structure. Also, since As(V) is more strongly adsorbed at pH 6 than at pH 8, there would be more tendency for the evolving mineral surfaces to retain As(V) during low-temperature, near-neutral pH aging. Arsenic is likely trapped in the crystalline structure (rather than adsorbed on the surface of the hematite or goethite) because it becomes very difficult to extract the As(V) with acid after transformation (Ford 2002), particularly at lower As(V) concentrations.

### **Microbiological processes contributing to the mobilization or immobilization of arsenic in drinking water**

Inorganic arsenic (As) is a well-known poison, and its acute toxicity is largely controlled by its chemical ox-

idation state. While arsenic is toxic to metazoans, a number of taxonomically diverse microorganisms have evolved biochemical defense mechanisms that either prevent arsenic from entering cells in the first place or rapidly extrude it back to the environment if it does enter. These detoxification reactions are mostly centered on redox changes between the As(III) and As(V) oxidation states, and can alter the speciation of arsenic found in the surrounding aqueous medium. Other defense mechanisms of microorganisms include a variety of methylation reactions that produce methylated oxyanions of both As(III) and As(V), or form highly toxic methylated arsine gases where the arsenic end product is in its most chemically reduced form [As(-III)]. A more recent discovery was that a wide diversity of microorganisms can actually gain energy from the oxidation or reduction of arsenic oxyanions, and use this energy to achieve arsenic-dependent cellular growth. Thus, certain anaerobes can grow by respiring As(V), thereby reducing it to As(III). Another group of microorganisms can use As(III) as an electron donor in lieu of organic substrates and conserve the energy gain in its oxidation to As(V) (as ATP) using either oxygen or nitrate as the biological oxidant. Because these microorganisms in a sense employ arsenic as an energy-generating nutrient, they could act as biological pioneers in organic-poor subsurface aquifers that have an abundant arsenic content. These energy-yielding microbial activities could ultimately cause the mobilization of arsenic by attacking solid mineral phases that contain As(III) (oxidation) or are adsorbed to surfaces as As(V) (reduction). This section will focus primarily upon what is currently known about these two types of energy-conserving microbial reactions involving arsenic. Directions for future research that would be relevant to the integrity of drinking water supplies will be presented along with other needed research topics.

Microbes are responsible for the formation of trace quantities of toxic arsine gases (e.g., trimethylarsine) emanating from anoxic environments, although these are quantitatively unimportant reactions in the soil systems studied (Turpeinen et al. 2002). A number of diverse prokaryotes, including anaerobic methanogenic archaea (McBride and Wolfe 1971) and

aerobic eubacteria (e.g., Honschopp et al. 1996) can form methylated arsines from inorganic arsenic, but the metabolism of arsenic by these microbes is an ancillary rather than central part of their biochemistry. As(V) and As(III) comprise the bulk of the arsenic encountered in the natural environment, and include a number of methylated organoarsenicals (e.g., methylarsonic and dimethylarsenic acids) commonly found in natural waters as breakdown or excretory products from aquatic biota (Millward et al. 1996; Reimer and Thompson 1988), or as urinary excretions of animals, including humans (Aposhian et al. 2000; Healy et al. 1998). Recent review chapters by Francesconi and Kuehnelt (2002) and Le (2002) give further details on the occurrence of organoarsenicals in nature.

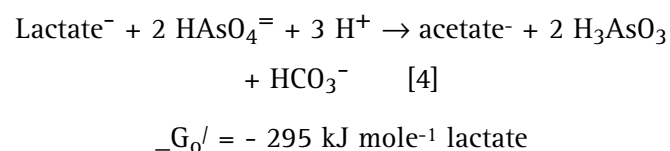
### **Arsenic toxicity and arsenic resistant microorganisms**

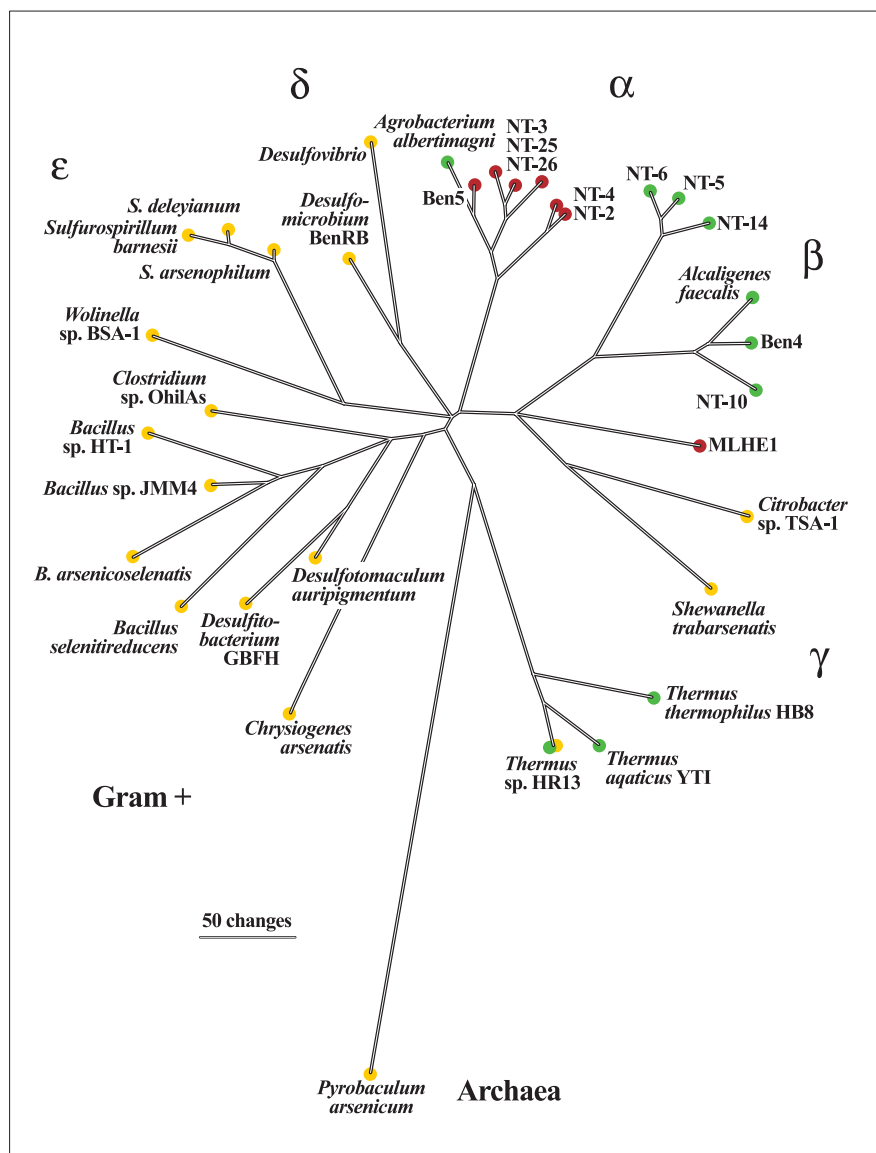
Arsenate is a molecular analog of phosphate, and inhibits oxidative phosphorylation, thereby short-circuiting life's main energy generation system. Arsenite is even more broadly toxic because it binds to sulfhydryl groups, thereby impairing the function of many proteins, including respiratory enzymes. For these reasons, once inorganic arsenic has entered a cell either in the case of As(V) via phosphate transporters, or for uncharged As(III) (at pH values < 9.2) via aqua-glycerolporins (Rosen 2002), it is in the immediate interest of the organism to be rid of it. This can be achieved by either rendering the arsenic innocuous, or by facilitating its immediate excretion. In the first instance, compounds like arsenobetaine and arsenic-containing sugars are found in high abundance in various marine animals and algae (and in some terrestrial plants and animals), but the arsenic is in a benign form. Certain plants, especially ferns, can hyper-accumulate large amounts of arsenic from contaminated soil and hence may be useful in phytoremediation (Francesconi et al. 2002; Ma et al. 2001). In contrast to marine life, most of the arsenic found in these ferns remains in the inorganic form either as As(III) or As(V) (Webb et al. 2003). In the second case, a number of prokaryotes and eukaryotes have evolved mechanisms that confer resistance to inorganic arsenic, allowing for them to live in the presence of relatively high concentrations of As(V). The well-studied "ars" gene system in bacteria and

certain genes related to tyrosine phosphatases in yeast are geared to removing internal arsenic pools (Mukhopadhyay et al. 2002; Rosen 2002). The common theme is to first reduce As(V) to As(III), which in bacteria is achieved by low molecular weight (~ 15 kilo-Dalton) soluble As(V) reductases ("ArsC") that are present in the cytoplasm. The As(III) is then pumped out of the cell by ArsA and ArsB cell membrane proteins, a process that requires expenditure of energy in the form of ATP. Although this process has been studied in detail in common lab microorganisms like *Escherichia coli* and *Staphylococcus aureus*, this process is apparently widely spread amongst other bacteria, and occurs in strict anaerobes like *Clostridia* (Langner and Inskeep 2000) and *Desulfovibrio* (Macy et al. 2000). Arsenate reduction to As(III) has been noted in a number of aerobic bacteria isolated from As-contaminated soils and mine tailings (Jones et al. 2000; Macur et al. 2001), suggesting that As(V)-resistance can play a role in the biogeochemical cycling of this element. The resistance genes controlling As(V) reduction in *E. coli* have been inserted into the plant *Arabidopsis thaliana* which, when inserted with genes for glutamylcysteine synthetase, result in sequestration and hyperaccumulation of arsenic within the leaves of this plant (Dhanker et al. 2002).

### **Arsenic respiration by anaerobic prokaryotes**

Considering that some bacteria have developed modes of resistance to arsenic, it came as a surprise that As(V) could actually serve as a respiratory oxidant to sustain the growth of other types of anaerobic bacteria and Archaea. We refer to these microbes as dissimilatory arsenate reducing prokaryotes ("DARPs"). Two closely-related representatives of the  $\alpha$ -Proteobacteria, *Sulfurospirillum arsenophilum* and *S. barnesii* were the first reported microbes that could achieve this feat (Ahmann et al. 1994; Laverman et al. 1995; Stolz et al. 1999). They conserve energy by linking the oxidation of organic matter or H<sub>2</sub> to the reduction of As(V) to As(III):





**Figure 5.** Phylogenetic diversity of representative arsenic-metabolizing prokaryotes. Dissimilatory arsenate respiring prokaryotes (“DARPs”) are indicated by the yellow circles, heterotrophic arsenite oxidizers (“HOAs”) are indicated by the green circles, and chemoautotrophic arsenite oxidizers (“CAOs”) are indicated by the red circles. In some cases (e.g., *Thermus* sp. Strain HR13) the microbe has been found able to both respire As(V) and oxidize As(III). From Oremland and Stolz, 2003.

To date, no “obligate” DARPs have been found, and all the strains examined can use other electron acceptors for growth. This makes them not only opportunists, but also flexible in their mode of metabolism, a facet that allows them to adapt and survive in a changing environment. For example, *S. barnesii* can also respire

selenate, nitrate, nitrite, fumarate, Fe(III), thio-sulfate, and elemental sulfur, in addition to other substances (Laverman et al. 1995; Oremland et al. 1995). Several novel species of DARPs have been isolated from freshwater sediments. Other anoxic niches include sediments from estuaries, soda lakes, hot springs, and gold mines (see the reviews by Newman et al. 1998; Oremland and Stolz 2003; Stolz and Oremland 1999). Recently, they have been found in the gastrointestinal tracts of animals (Herbel et al. 2002). At present, detailed or preliminary reports of about 16 reported pure cultures of DARPs, including thermophilic Eubacteria and Crenarchaea are available. The original discovery of two species of *Sulfurospirillum* that respire As(V) suggested that DARPs would be confined to this clade of the  $\gamma$ -Proteobacteria, a convenience that would have allowed for their detection and enumeration using simple 16S rDNA-based molecular probes. However, subsequent work proved that this was not the case. Indeed, as can be seen in Figure 5, DARPs make up a highly diverse phylogenetic assemblage. These assemblages include not only “garden varieties” of microbes, physiologically suited for living at circum-neutral pH, mesophilic temperatures, and low salinity, but also several extremophiles that are well adapted to high temperature, pH, and/or salinity (Gihring and Banfield 2001; Huber et al. 2000; Switzer et al. 1998). Indeed, DARPs are ubiquitous in

nature and can be easily enriched in uncontaminated soils or sediments merely by the addition of As(V) and the establishment of anoxic conditions. The organic matter normally present in these soils and sediments serves as the biological substrate to fuel the reduction of As(V) to As(III) as mediated by the respiratory activity of the DARPs. Both Gram positive (*Desulfotomaculum auripigmentum*) and Gram negative (*Desulfomicrobium* strain RB) sulfate-reducing bacteria can respire As(V), and in addition, will form arsenic trisulfide precipitates as an end product of the reduction of both arsenate and sulfate (Macy et al. 2000; Newman et al. 1997a; Newman et al. 1997b). Other DARPs include halo-respiring members of the

genus *Desulfotobacterium* (Niggenmeyer et al. 2001), and well recognized enterics such as *Citrobacter* sp., and *Wolinella succinogenes* (Herbel et al. 2002).

In DARPs, the enzymes for arsenate respiration are located on the periphery of the cell that is associated with the membrane and or in the case of Gram negative organisms, its periplasm (Krafft and Macy 1998; Oremland et al. 2002b). Although these enzymes are in the process of being fully characterized, preliminary results show that they are mostly molybdenum-containing enzymes of the DMSO family of respiratory reductases (McBride and Wolfe 1971; McEwan et al. 2002). They are relatively large, and sometimes multi-component structures, encompassing not only the reductases but electron carriers as well as cytochrome *b*. Thus, *Crysiogenes arsenatis* has a dissimilatory As(V) reductase composed to two fractions: a 89 kilo-Dalton (kD) plus a 29 kD component (Krafft and Macy 1998). An analogous type of arrangement appears to occur in *Bacillus selenitireducens*, *Desulfotobacterium* GBFH, and *Shewanella* ANA-3 (J.F. Stolz, unpublished data). On the other hand, *Sulfurospirillum barnesii* and *S. arsenophilum* As(V) reductases, although also relatively large (~ 48 kD), seem to differ from the former type in being a hydrophobic monomer and lacking molybdenum (J.F. Stolz, unpublished data). Work is continuing on the detailed characterization of these enzymes and the genomes that encode them with the ultimate purpose of designing functional gene probes. This will someday allow for the detection (and enumeration) of DARPs in the natural environment, as well as for detection of the resident population's ability to synthesize dissimilatory As(V) reductases.

As mentioned in the previous section, the As(V)-detoxifying reductases are cytoplasmic rather than being associated with the cell membrane, and are low molecular weight, soluble structures. However, as some As(V) may still enter the cells of DARPs via phosphate transporters, these two processes of As(V)-respiration and As(V)-detoxification are not necessarily mutually exclusive. Indeed, it appears that *Shewanella* ANA-3 has both the resistance and respiratory types of As(V) reductases (Saltikov et al. 2003). Mutants of this strain that lack the As-detoxifying enzyme do not grow as rapidly as does the wild type when coupling its growth to dissimilatory As(V) reduction.

The activity of DARPs can be readily discerned upon incubation of anoxic sediment slurries amended with millimolar As(V) (Dowdle et al. 1996). Although much of the early work conducted on the microbiology of arsenic was with natural materials taken from As-contaminated ecosystems, the activity of DARPs can be readily elicited from pristine samples as well. This indicates that DARPs have a ubiquitous presence in nature, and will reduce As(V) when present and when it is advantageous for them to do so. In addition to respiring aqueous As(V), DARPs can also attack As(V) within the mineral matrix of scorodite, or that which is adsorbed to solid phases like ferrihydrite and alumina (Ahmann et al. 1997; Zobrist et al. 2000). This contrasts with detoxifying reductases present in As-resistant bacteria which cannot attack As(V) bound or embedded in a solid phase (Langner and Inskeep 2000). Arsenate adsorbed onto the surface of ferrihydrite can also be mobilized back into the aqueous phase by iron-respiring bacteria that reduce Fe(III) to Fe(II), thereby destroying the capacity of ferrihydrite to adsorb As(V) (Cummings et al. 1999).

The ecological significance of As(V) as a terminal electron acceptor for the oxidation of autochthonous organic matter is not generally known, but is thought to be minor because arsenic is, after all, a trace element. However, in Mono Lake, California, a particularly arsenic-rich environment (dissolved inorganic arsenic = 15,000 µg/L), *in situ* measurements of As(V) respiration in its stratified water column were made with the radiotracer <sup>73</sup>As(V) (Oremland et al. 2002a). It was found that as much as 14% of annual primary productivity can be mineralized to CO<sub>2</sub> in the anoxic water column of the lake by the activity of DARPs (Oremland et al. 2000).

To date, the determination of the numbers of As(V)-respiring bacteria in environmental samples has been limited to classic serial-dilution culture-based techniques (i.e., Most-Probable-Numbers) that demonstrate growth and As(III) production in medium that contains As(V) as the sole respiratory oxidant. In the anoxic water column of Mono Lake, DARPs number between 10<sup>2</sup> and 10<sup>3</sup> per ml, while sediments from As(V)-contaminated lakes contain between 10<sup>4</sup> to 10<sup>5</sup> cells per gram (Harrington et al. 1998; Kuai et al. 2001). These numbers appear to be low and are probably biased

that way because the method requires that they achieve growth in the medium provided. Culture-independent polymerase chain reaction (“PCR”) techniques have not yet emerged to enumerate DARPs, in part because their diverse phylogeny negates the utility of 16S rDNA probes, and the fact that DARPs isolated are “opportunists” capable of respiring electron acceptors other than As(V). As mentioned previously, more research needs to be conducted on the enzymes and genetics of DARPs’ dissimilatory As(V) reductases before more accurate molecular techniques will emerge that enables the detection of these functional genes in the environment.

Nonetheless, some initial research has been conducted using established phylogenetic 16S rDNA techniques to examine arsenate respiration in nature. Denatured gradient gel electrophoresis (“DGGE”) of DNA extracted from anoxic Mono Lake water incubated with 1 mM As(V) gave resolved bands indicating that members of the *\_- (Thiomicrospira) and \_-Proteobacteria (Desulfovibrio) were enriched by this procedure and were probably respiring As(V) in the incubated samples (Hoeft et al. 2002). However, the dominant in situ phylogenetic genome of DNA isolated from bottom water indicated the Bacillus/Clostridium genera of low G+C Gram positive bacteria (Humayoun et al. 2003). That the two DARPs isolated from Mono Lake sediments were bacilli is significant (Switzer et al. 1998). The electron donors that drive As(V) reduction were thought to be typical organic acids and sugars (e.g., lactate, acetate, glucose); however, these substrates did not significantly stimulate activity when they were added to As(V)-enriched bottom water (Hoeft et al. 2002). Recent work indicates that sulfide may partially drive microbial arsenate reduction in Mono Lake (Hoeft, Kulp, and Oremland, unpublished data).*

### Microbial arsenite oxidation

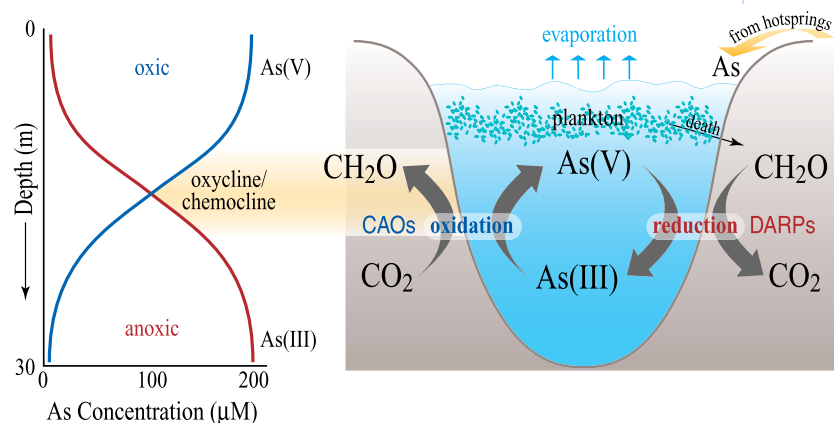
Another important microbiological process is the oxidation of As(III) back to As(V). This phenomenon has been known for many years and has been recently reviewed (Ehrlich 2002; Mukhopadhyay et al. 2002; Santini et al. 2002). Arsenite oxidation has now been found to occur in a broad diversity of aerobic heterotrophic prokaryotes (heterotrophic arsenite oxidizers, or “HAO”s), as well as in some chemoautotrophs

(chemoautotrophic arsenite oxidizers, or “CAO”s), cumulatively accounting for about 30 species thus far. The latter microbes use As(III) as their energy source (“electron donor”) whereby they can fix CO<sub>2</sub> into organic cellular material and achieve growth. The taxonomic diversity of these microbes is also shown in Figure 5, in addition to that of the DARPs. Arsenite oxidation by HAOs has been a recognized scientific phenomenon for a much longer time (about 90 years) than that of CAOs (e.g., see the references cited by Phillips and Taylor 1976), and subsequently more is known about the physiology and genetics of the former organisms than the latter. For example, the As(III) oxidase of various HAOs have been characterized, and are molybdenum-containing enzymes of the DMSO reductase family (Stolz and Basu 2002). The arsenite oxidases of CAOs have yet to be described. HAOs cannot grow with As(III) as their energy source, although some have electron carriers associated with their As(III) oxidases that suggest As(III) may serve as a supplemental source of reducing power. The arsenite-oxidase genes (*aox*) have been identified in a recently isolated metal-resistant bacterium, and they had high sequence identity (64-72%) to that of *Alcaligenes faecalis* (Muller et al. 2003).

With regard to CAOs, the isolation of strain NT-26, a fast-growing member of the *Rhizobium* clade of the *\_-Proteobacteria* has stimulated recent interest in chemoautotrophic As(III) oxidation (Santini et al. 2001a; Santini et al. 2001b). Strain NT-26 has a “flexible” metabolism in that it can grow as an autotroph with As(III) as its energy source, but it can also grow as a conventional heterotroph by using organic compounds (sugars, fatty acids, alcohols) in lieu of As(III). Heterotrophic oxidation of As(III) is viewed primarily as a detoxification reaction that converts As(III) encountered on the cell’s outer membrane into the less toxic form, As(V), thereby making it less likely to enter the cell. NT-26 is also being studied as the basis for bioremediation of aquatic systems where As(III) is a pollutant, because the As(V) can be immobilized onto strong adsorbents like ferrihydrite, which can be subsequently removed from water treatment systems (Battaglia-Brunet et al. 2002; Lièvremonet et al. 2003). Interest in this subject has resulted in the recent isolation of several novel species of both heterotrophic and

autotrophic aerobic As(III) oxidizers from As-rich environments (Salmassi et al. 2002; Santini et al. 2002). Included here is a curious thermophilic species of *Thermus* (strain HR 13), a Eubacterium isolated from an As-rich hot spring that, under aerobic conditions, will oxidize As(III) for detoxification purposes without conserving the energy gain of the reaction. However, under anaerobic conditions, strain HR 13 can grow on lactate using As(V) as its electron acceptor, and is thus both a HAO and a DARP (Gihring and Banfield 2001).

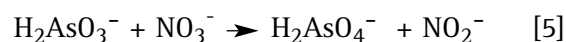
Hot springs often contain high concentrations of As(III) in the emerging hydrothermal waters, and thus rapid, biologically-driven As(III) oxidation occurs as these hot, anoxic waters become aerated (Langner et al. 2001; Wilkie and Hering 1998). Characterization of the microbes involved in these oxidations has been mostly confined to investigations of HAOs, either as classical isolations (Salmassi et al. 2002), or in the use of established molecular techniques such as DGGE or



**Figure 6.** The chemical speciation of arsenic in the stratified water column of Mono Lake, California (left panel), as explained by the metabolism of arsenic by microbial populations present in the water column (right panel). Arsenic cycling occurs in the region of the chemocline. Arsenate reduction is mediated by DARPs that use released organic matter from dying plankton to fuel their respiration. Arsenite oxidation (aerobic and anaerobic) is mediated by CAOs that also contribute to secondary production by “fixing” CO<sub>2</sub> into organic matter. Arsenic first enters this alkaline (pH=9.8), saline (~90 g/L) lake as a dissolved component contained in the discharge from hydrothermal springs. Arsenic, as well as other dissolved constituents, reaches high concentrations because of the predominance of evaporation over precipitation in this semi-arid region. From Oremland and Stolz, 2003.

Fluorescent *In situ* Hybridization (FISH) to characterize natural populations (Gihring et al. 2001; Jackson et al. 2001).

Recently, a novel species of the *Ectothiorhodospira* clade of Eubacteria was isolated from Mono Lake that grew under anaerobic conditions using As(III) as its electron donor and nitrate as its electron acceptor:



$$-G_0' = -87.2 \text{ kJ mole}^{-1}$$

This non-photosynthetic bacterium, strain MLHE-1, also grew as an autotroph with sulfide or hydrogen gas in lieu of As(III), and additionally grew as a heterotroph on acetate with air or with nitrate as the electron acceptor (Oremland et al. 2002a). Curiously, it was unable to grow on or oxidize As(III) under aerobic conditions. The occurrence of anaerobic As(III) oxidation suggested that there might be a tight coupling in nature between respiratory reduction of As(V) at the expense of electron donors like organic compounds and H<sub>2</sub>, and its re-supply as carried out by microbial As(III) oxidation at the expense of commonly-occurring strong oxidants like nitrate, nitrite, or perhaps Fe(III). Such a theoretical coupling is illustrated in Figure 6 for a stratified system like Mono Lake, in which the abundance of arsenic in the lake is from natural hydrothermal inputs coupled with evaporative concentration. Final proof of a coupling would require that *in situ* experiments be performed with <sup>73</sup>As(III) in Mono Lake and other systems.

Mono Lake is an “extreme” environment in terms of its high pH (9.8), high salinity (~90 g L<sup>-1</sup>), and high content of other toxic minerals. Nitrate-linked microbial oxidation of As(III) was recently shown to occur in a freshwater lake contaminated by anthropogenic sources of arsenic (Senn and Hemond 2002), thereby underscoring that this phenomenon is probably widespread in its natural occurrence. Indeed, experimental injection of nitrate into ground water of Bangladesh resulted in the immobilization of arsenic (Harvey et al. 2002), suggesting an oxidation of As(III) to As(V) resulting in the adsorption of the latter species onto surfaces of minerals like ferrihydrite. The occurrence therein of such a microbial oxidation with-

in the subsurface suggests the presence of microorganisms that are physiologically analogous to strain MLHE-1. It remains to be determined what types of microorganisms carry out this reaction in freshwater aquifers, lakes, or marine systems, as compared to those found in soda lakes.

## DISCUSSION: THE MICROBIAL ARSENIC CYCLE IN GROUND WATER: WHAT IS KNOWN?

The microbiology of arsenic appears to be mostly confined to microorganisms that either gain energy from the redox changes associated with the transitions between As(III) and As(V), or those that carry out these reactions for the purpose of detoxification.

Energy-yielding biochemical reactions mediating the reduction of As(III) to As(0) or As(-III) (or their corresponding reverse biochemical oxidations) have not as yet been reported, although they could certainly be possible. The formation and destruction of organoarsenicals and arsine gases by microorganisms, while certainly of interest, does not appear to be of quantitative importance in natural systems. Thus, the "ecology" of arsenic is rather simple if we focus only on the redox reactions occurring between As(III) and As(V). In contrast to this simplified view, however, understanding the contribution that these microorganisms make to the hydrologic mobility of arsenic in aquifers is a highly complex, interdisciplinary environmental question that is nonetheless of critical importance to the health of millions of people worldwide. Factored into such complexity are the competing chemical reactions that affect both the speciation and the partitioning of arsenic between the aqueous phase and the solid mineral phase of the aquifer matrix. In addition, as should be apparent from the preceding discussion, most of what we have learned to date about the microbial biogeochemistry of arsenic has been confined to studies of accessible surface environments (e.g., soils, sediments, lakes, estuaries, mine wastes) or with novel bacterial cultures originally isolated from these locales. As yet, little information exists regarding the microbiology related to arsenic mobility in the subsurface. Very little experimental microbiological work has been conducted either using the recovered aquifer materials themselves, or by conducting *in situ* manipulative hydrological experiments

of ground waters. However, some chemical/hydrological investigations have been done to date that suggest the importance of microbial activities in the observed mobility or redox changes of arsenic.

In light of the above theoretical framework, a preliminary report is notable because it demonstrates the presence of both DARPs and As(III) oxidizing bacteria in aquifer sediments taken from subsurface locations in Bangladesh (Saikat et al. 2001). In addition, some recent manipulation experiments were conducted *in situ* with Bangladesh ground water (Harvey et al. 2002). These researchers found that injection of molasses resulted in the mobilization of arsenic into the aqueous phase while in contrast, injection of nitrate immobilized arsenic. These results can be explained by the molasses acting as an electron donor in the first case, thereby stimulating the activity of DARPs and resulting in the reduction of adsorbed As(V) and its release into solution as As(III). Injection of nitrate on the other hand probably stimulated the activity of anaerobic CAOs, which in turn oxidized As(III) back to As(V). Hydrological tracer tests with arsenic were conducted at an experimental aquifer site at Cape Cod, Massachusetts (Höhn et al. 2001; Stadler et al. 2001). When As(V) was injected into the anoxic subsurface (iron reducing zone) down gradient breakthroughs of As(III) were observed. Conversely, when As(III) was injected into the aerobic and suboxic zones (nitrate reducing), the appearance of As(V) was noted down gradient. These results are consistent with and can be explained by the activities of DARPs and both aerobic and nitrate-reducing CAOs, respectively. Finally, a large scale aquifer storage and recovery experiment was conducted by injecting surface water into a pristine aquifer in southwest Florida (Arthur et al. 2002). Although the "native" levels of dissolved arsenic were below 10 µg/L, they rose to as high as 50 µg/L during the recovery phase, implying that the re-injection process itself, possibly coupled with the activities of microorganisms, resulted in an unpredicted mobilization of arsenic into the aqueous phase.

As(V) can be reduced by bacteria even under aerobic conditions as a detoxification mechanism (Macur et al. 2001). How important such bacteria might be in uncontaminated environments is not known, but such bacteria could explain the observations of As(III) in

oxic surface waters (Sohrin et al. 1997).

## Transport of arsenic in ground water

### Adsorption modeling in aquifers

In current engineering practice, the retardation of contaminant transport in solute transport models is generally done by utilizing the distribution coefficient (constant- $K_d$ ) approach to describe retardation by adsorption (Bethke and Brady 2000). Significant uncertainty in the calculation of retardation may be introduced when the constant- $K_d$  modeling approach is used, due to temporal or spatial variations in ground-water chemistry (Davis and Curtis 2003; Glynn 2003). For As, one reason this may occur is because  $K_d$  values are very sensitive to chemical conditions and to the type of mineral adsorbent and may range by several orders of magnitude (Smedley and Kinniburgh 2002).

In contrast to the constant- $K_d$  modeling approach, surface complexation models (SCM) have the capability of describing changes in arsenic adsorption as chemical conditions and aqueous speciation vary (Gao and Mucci 2001). SCM describe the equilibria between aqueous chemical species and species formed at mineral surfaces (i.e., surface complexes) through mass-action equations, and SCM can be readily incorporated within solute transport models (Kent et al. 2000; Parkhurst et al. 2003; Stollenwerk 1998).

Considerable experimental data is available that describes arsenic adsorption in systems with one mineral phase, and SCM have been developed to accurately describe these data (e.g., Gao and Mucci 2001; Hsia et al. 1992; Manning et al. 1998; Manning and Goldberg 1997a; Swedlund and Webster 1999). Nevertheless, the application of SCM to the mixtures of minerals in soils and sediments is difficult because of the presence of secondary mineral and organic coatings that affect the stoichiometry and coulombic correction factors of surface complexation reactions (Coston et al. 1995; Padmanabhan and Mermut 1996; Penn et al. 2001).

Two major approaches for applying the SCM concept to soils and sediments are: 1.) The Component Additivity (CA), and 2.) The Generalized Composite (GC) approaches (Davis et al. 1998; Davis et al. 2004).

In the CA approach, a mineral assemblage is assumed to be composed of a mixture of one or more reference phases, whose surface chemical reactions are known from independent studies of each phase. Then, based on a measurement of the relative amounts or surface areas of each mineral present in the soil or sediment, adsorption by the mixture of phases can be predicted by an equilibrium calculation, without any fitting of experimental data for the mixture.

In the GC approach, the surface of the mineral assemblage is considered too complex to be quantified in terms of the contributions of individual phases to adsorption. The complexity is caused, in part, by the difficulties in quantifying the electrical field and proportions of surface functional groups at the mineral-water interface in the mixture of mineral phases and associated surface coatings. In this approach adsorption is assumed to be described by mass laws written with "generic" surface functional groups, with the stoichiometry and formation constants for each mass law determined by fitting experimental data for the mineral assemblage as a whole (Davis et al. 1998; Davis et al. 2004). Laboratory experiments are conducted with sediments from the field site to be modeled, and mass law relationships are derived that describe the change in contaminant adsorption with variations in ground-water chemical conditions observed or anticipated in the aquifer (Davis et al. 1998; Davis et al. 2004). Usually a non-electrostatic model is used in GC adsorption modeling. In general, the goal of the GC approach is to develop the simplest model possible that describes the major features of adsorption as chemical conditions are varied over field-relevant ranges (Davis et al. 1998). Thus, for modeling the transport of arsenic in a given aquifer, it would be necessary to collect As(V) [and perhaps As(III)] adsorption data for representative sediments collected by coring or other methods of subsurface sample collection. These data would need to be collected as a function of variable water composition, e.g., varying the concentrations of bicarbonate and phosphate over the ranges observed or anticipated within the aquifer. At field sites where significant temporal or spatial variation in chemical conditions exist, the uncertainty in simulated retardation can be reduced with the use of the semi-empirical GC modeling approach (Davis and Curtis

2003; Kent et al. 2000).

Advantages of the CA modeling approach are that the model parameters are transferable from one field site to another and that the models are supported by detailed experimental investigations published in the literature. This approach allows for the development of databases of self-consistent model parameters, tabulated for individual mineral phases (e.g., Dzombak and Morel 1990). Such databases allow the testing of the effects of competitive adsorption on the adsorption of anions, based on adsorption constants determined for individual anions, which has met with limited success (Gao and Mucci 2001; Manning and Goldberg 1996a; Manning and Goldberg 1996b; Swedlund and Webster 1999). However, another problem is that the adsorption constants determined in the laboratory with pure mineral phases do not correspond perfectly with field-derived adsorption constants (Kent et al. 1995; Stollenwerk 1995). These latter studies illustrated that the absolute magnitude of the laboratory-derived stability constants were overestimated by more than an order of magnitude. Reasons for these errors include: 1.) estimation of surface site types and surface area abundances of minerals, and 2.) a lack of fundamental data on the effects of common ground-water solutes on surface charge and potentials (Davis et al. 2004). The calculations with laboratory constants, however, may provide useful estimates of the relative effects of competitive anion adsorption that might be observed in natural systems and of the adsorptive reactivity with freshly precipitated iron oxyhydroxides in remediation schemes.

#### **In-situ remediation**

Overall management of arsenic concentrations in ground water should include an understanding of methods of altering the geochemical conditions in a manner that can either decrease or limit an increase in arsenic concentrations. Based on the preceding discussion, changes in pH and redox conditions are clearly important factors affecting arsenic mobility. Altering geochemical conditions can reduce arsenic concentrations in aquifers used for municipal water supply. This practice, which is commonly termed '*in situ* removal', has been accomplished using co-precipitation or adsorption involving iron oxide (Appelo and deVet

2003; Appelo et al. 2002; Mettler 2002; Rott and Friedle 1999; Welch et al. 2003). Potential advantages of *in situ* removal include lower capital, land, operational, and sludge disposal costs compared with above ground treatment (Mettler et al. 2001; Rott and Friedle 1999). The basic approaches used for *in situ* treatment can be used as a basis for designing conjunctive use projects to either remove arsenic or prevent arsenic mobilization.

The most common approach consists of withdrawing iron-rich ground water and introducing atmospheric oxygen or potassium permanganate (Matthess 1981; Meyerhoff 1996; Rott and Friedle 1999) to promote the formation of iron oxide and conversion of any dissolved As(III) to As(V), followed by injection and withdrawal for use. This approach may be applicable where iron- and arsenic-rich ground water is present or may be formed in response to artificial recharge. Alternatively, lowering of arsenic concentrations in high pH ground water may be feasible by lowering the pH (Welch et al. 2003). Recent efforts to model arsenic removal (Appelo et al. 1999; Appelo et al. 2002) may lead to a basic understanding of the removal processes that could be applied to many systems.

Various hydraulic approaches can be employed to cycle the water through an aquifer, including injecting and withdrawing from a well (a 'push-pull' approach), or continuous withdrawal from a production well in conjunction with injection into one or more wells. The push-pull approach consists of a period of injection followed by pumping. Removal of arsenic increased in field studies after continued cycles without well or aquifer clogging, even after operation for decades (Appelo and deVet 2003; Appelo et al. 2002; Meyerhoff 1996).

Iron oxide appears to be the most important phase responsible for removing the arsenic from the ground water (Mettler et al. 2001). The arsenic removal process associated with iron removal may be described as a series of reactions involving dissolved oxygen, aqueous and exchangeable cations including Fe(II), and arsenic (Appelo and deVet 2003; Appelo et al. 1999). Injection of water containing dissolved oxygen and Fe(II) can lead to rapid attachment of Fe(II) onto the aquifer and subsequent Fe(II) oxidation to form

ferrihydrate. Upon reversing the flow direction, the injected water has lower arsenic and iron concentration. Characterization of precipitates formed by *in situ* removal of iron after ten years of operation suggests that goethite (crystalline iron oxide) is the long-term stable iron phase (Mettler et al. 2001), which probably forms after initial precipitation of ferrihydrate. Because arsenic is more tightly bound in these recrystallized iron oxides, release would be expected to be slow or insignificant. The presence of increased iron oxide in the sediments could be beneficial because they commonly adsorb many trace elements, a feature that has been long recognized (Jenne 1976). If trace elements were released to the ground water in the vicinity of the *in situ* project their concentrations could be decreased by adsorption onto the iron oxide.

Because *in situ* remediation has not been widely adopted in drinking water systems of the United States, a discussion of some of the commonly expressed concerns with this approach seems appropriate. Among the more often expressed concerns are: 1.) Increasing the iron content of an aquifer will result in lowered yields from production wells, and 2.) After remediation ends, concentrations of arsenic or other trace elements will rise to values greater than before the remediation began.

The first two issues are, at least in part, related to the amount of arsenic and iron that would be added to some volume of an aquifer. Current understanding of the fate of iron entering an aquifer during *in situ* remediation suggests that iron oxide is not concentrated near a well bore, but rather moves some distance out into an aquifer. This understanding is based on geochemical modeling of the reactions that result in the formation of the iron oxide (Appelo and deVet 2003; Appelo et al. 1999), examination of aquifer material that has been affected by *in situ* remediation for decades (Mettler 2002; Mettler et al. 2001), and the observation that well yields have not been lowered (Rott and Friedle 1999 and references therein).

Incorporation of arsenic into sulfide minerals has been suggested as a possible *in situ* remediation strategy (Kirk et al. 2004). Addition of sulfate into ground water with high dissolved arsenic and iron could stimulate sulfate-reducing bacteria thereby promoting sul-

fide precipitation with concomitant arsenic removal. The viability of this approach would depend greatly upon the kinetics of sulfide formation, among other factors. Nonetheless, this approach could be a low cost treatment approach for arsenic removal in chemically reduced, low sulfate ground water.

### **SUMMARY: RESEARCH NEEDED FOR MANAGEMENT OF ARSENIC IN GROUND WATER**

Development of water resources projects could be more efficient if the arsenic content of ground water was well known. Compiling existing data and identifying the likelihood of high and low arsenic concentrations in aquifers with sparse data could be a useful resource for water resource managers. The conceptual model describing arsenic cycling in ground water presented above could form the basis for predicting the presence of high or low arsenic concentrations. For instance, the presence of sulfide minerals in the shallow subsurface or alkaline, oxic water could be used to infer that high arsenic concentrations may be present. The long term impact of human activities on arsenic concentrations also is not well understood. Scrutiny of existing data could prove useful in identifying long-term trends. A long term monitoring program in selected urban and agricultural settings would be useful in determining the impacts, if any, on the arsenic content of ground water.

A basic understanding of the short and long term effects of conjunctive use projects on arsenic concentrations is desirable. Understanding arsenic mobility in ground water in response to different hydrologic and geochemical conditions could lead to design of projects that could prevent arsenic mobilization or promote arsenic removal from ground water. A few well studied systems could provide a much better understanding of the methods for preventing or eliminating high arsenic problems. Within the context of the conceptual model of arsenic cycling discussed above, careful study of at least two types of geochemical settings suggest themselves. First, oxic, alkaline ground water in the San Joaquin Valley and the desert basins of California appears to be commonly associated with high arsenic concentrations. High arsenic concentrations also are commonly associated with chemically reduced ground water, particularly in the southern San Joaquin Valley.

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Effectiveness of *in situ* arsenic removal methods in typical reduced ground water should be evaluated.

Sites should be selected that are chemically and hydrologically similar to other existing and proposed conjunctive use projects in the CALFED solution area. The goal of the studies is to identify chemical, physical, and biologic processes that affect arsenic mobility and methods for minimizing arsenic concentrations. The recent advances in spectroscopic, chemical techniques combined with the development of chemical modeling techniques provide a basis for greatly improved water-quality management strategies of conjunctive use projects. Within the context of the field studies some basic research is envisioned, including:

As(V) and As(III) may be capable of forming metal-bridging aqueous complexes with natural organic matter (Redman et al. 2002). Such complexes could be quite significant in that they could affect the adsorption, mobility, toxicity, and rates of redox reactions of arsenic. Research is needed to determine the significance of such species in ground-water environments such as in the reduced ground water in the southern San Joaquin Valley.

In the context of *in situ* remediation, research is needed to resolve the question of whether arsenic is stabilized during crystallization or released during crystallization. Little is known about the quantitative significance of inorganic arsenic competition with other inorganic aqueous species in natural systems.

Experiments should be conducted with actual aquifer materials rather than pure and clean mineral phases, as the effects of aging on arsenic desorption in laboratory studies are quite significant.

Devise methods to detect and quantify rates (and novel reactants/products) of oxidation/reduction reactions of arsenic that are carried out by microorganisms at ambient concentrations of arsenic and under *in situ* conditions. This can be achieved by incubating sediment aquifer microcosms with radiotracers (e.g.  $^{73}\text{As}$ ; Oremland et al., 2000) and following the kinetics of either microbial arsenate reduction or arsenite oxidation. These measured rates of microbial arsenic transformations can be put into various ground water flow models that include arsenic speciation. In addition, both traditional culture (e.g., most-probable-number) and non-cul-

ture (quantitative PCR or "qPCR") based methods for the detection, enumeration, and physiological/genetic assessment of arsenic-metabolizing bacteria residing in aquifers need to be developed further. For qPCR to succeed, more research will be needed to devise widely applicable molecular primers for the amplification of key functional genes involved in arsenic biotransformation, be they for respiratory arsenate reductase (i.e., *arrA*) or for arsenite oxidase (i.e. *aoxA/aroA*).

Conduct of both detailed field studies along with compilation and assessment and prediction of arsenic concentrations in ground water has the potential for greatly reducing the cost of meeting the new drinking-water standard for arsenic. The research would benefit a broad constituency, ranging from very large to very small water suppliers.

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