

# Arsenic in Ground Water of the United States: Occurrence and Geochemistry

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## Abstract

Concentrations of naturally occurring arsenic in ground water vary regionally due to a combination of climate and geology. Although slightly less than half of 30,000 arsenic analyses of ground water in the United States were  $\leq 1 \mu\text{g/L}$ , about 10% exceeded  $10 \mu\text{g/L}$ . At a broad regional scale, arsenic concentrations exceeding  $10 \mu\text{g/L}$  appear to be more frequently observed in the western United States than in the eastern half. Arsenic concentrations in ground water of the Appalachian Highlands and the Atlantic Plain generally are very low ( $\leq 1 \mu\text{g/L}$ ). Concentrations are somewhat greater in the Interior Plains and the Rocky Mountain System. Investigations of ground water in New England, Michigan, Minnesota, South Dakota, Oklahoma, and Wisconsin within the last decade suggest that arsenic concentrations exceeding  $10 \mu\text{g/L}$  are more widespread and common than previously recognized.

Arsenic release from iron oxide appears to be the most common cause of widespread arsenic concentrations exceeding  $10 \mu\text{g/L}$  in ground water. This can occur in response to different geochemical conditions, including release of arsenic to ground water through reaction of iron oxide with either natural or anthropogenic (i.e., petroleum products) organic carbon. Iron oxide also can release arsenic to alkaline ground water, such as that found in some felsic volcanic rocks and alkaline aquifers of the western United States. Sulfide minerals are both a source and sink for arsenic. Geothermal water and high evaporation rates also are associated with arsenic concentrations  $\geq 10\text{g/L}$  in ground and surface water, particularly in the west.

## Introduction

Arsenic in drinking water can impact human health and is considered one of the prominent environmental causes of cancer mortality in the world (Smith et al. 1992). An understanding of the status and trends of arsenic concentrations in ground water can: (1) assist water managers and users in overcoming adverse health effects through avoidance or treatment; (2) provide a basis for evaluating the costs of adopting a particular value for a drinking water standard (or MCL—maximum contaminant level); and (3) assist epidemiologists interested in evaluating the intake of arsenic from drinking water, which can contribute much of the human exposure to inorganic arsenic (Borum and Abernathy 1994; Smith et al. 1998). Knowledge of the regional distribution of arsenic in ground water is timely because the U.S. Environmental Protection Agency (EPA) must issue a proposed and a final regulation for arsenic in drinking water by 2000 and 2001, respectively.

The following discussion expands upon previous regional evaluations of arsenic occurrence in ground water (Welch et al. 1988; Korte and Fernando 1991) and drinking water within the United States (M. Davis et al. 1994; Frey and Edwards 1997 and references therein). Describing arsenic occurrence in ground water is a major focus of this paper. Additionally, the geochemistry of arsenic in

ground water is discussed with an emphasis on those processes that are associated with widespread high arsenic concentrations. (For the purpose of discussion, the adjectives “high,” “moderate,” “low,” and “very low” are used to indicate arsenic concentrations  $> 50$ ,  $> 10$  to  $\leq 50$ ,  $> 1$  to  $\leq 10$ , and  $\leq 1 \mu\text{g/L}$ , respectively).

Discussions of arsenic in relation to human health, regulation of arsenic in drinking water, analytical and sampling methods, cycling in the environment and other issues can be found in a variety of publications. Some useful publications include Abernathy et al. (1997), Chappell et al. (1994), Lederer and Fensterheim (1983), National Academy of Sciences (1977), Nriagu (1994a, 1994b), and the World Health Organization (1981, 1986, 1996). Overviews of arsenic in the environment by Cullen and Reimer (1989) and Ferguson and Gavis (1972) also contain information pertinent to this discussion.

## Data Compilation and Statistical Methods

Water quality data were retrieved from the U.S. Geological Survey's National Water Information System (NWIS) in 1997, and additional data were obtained from other agencies. Only a single analysis was used for a particular well or spring to prevent bias toward frequently sampled sources. Additional information on the characteristics of the data, such as laboratory and field procedures and reporting levels, is included in Focazio et al. (2000). Discussion in the following sections considers only samples that have been filtered ( $0.45 \mu\text{m}$  or smaller pore-size filter) because excluded arsenic can largely be associated with material that is not moving through the aquifer. For the purpose of brevity, the discussion of arsenic in ground water refers to filtered samples.

The arsenic data—about 20,000 analyses—were grouped according to physiographic province with a separate category for Alaska. Geothermal water (temperature  $> 50^\circ\text{C}$ ) and slightly saline water (dissolved solids  $> 3000 \text{mg/L}$  or specific conductance  $> 4000 \mu\text{S/cm}$ ) were assigned to two additional groups. Multiple

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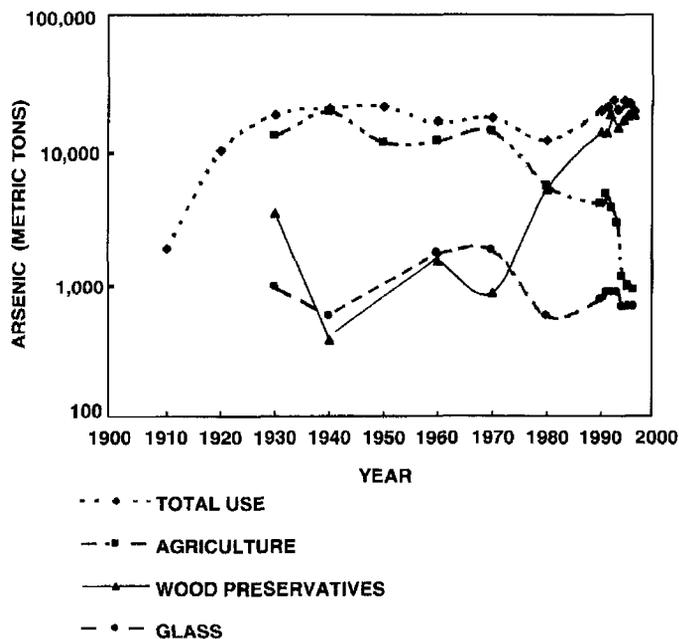


Figure 1. Arsenic use in the United States. Data are from Loebenstein (1994) and Edlestein (1997, 1998).

comparisons of all combinations of these groups, based on Kruskal-Wallis rank sums, were used to identify which groups differed from others (Hollander and Wolfe 1973). Because sample sites are not uniformly distributed across the country, statistical comparison of arsenic concentrations should be interpreted with caution. Sample sites for Alaska are clustered in only a few parts of the state and include an area in the vicinity of Fairbanks that is affected by mining. Accordingly, the data for Alaska may be more representative of the effects of mining than generally of ground water in that state.

### Arsenic Occurrence in Relation to Anthropogenic Sources

Although arsenic has been used for a wide variety of purposes in the United States (Abernathy 1983; Lederer and Fensterheim 1983; Azcue and Nriagu 1994), agricultural applications, wood preservation, and glass production have been the dominant uses. Inorganic arsenic has been used as a wood preservative for more than 60 years and currently represents the single greatest use of arsenic compounds in the United States (Figure 1). Agricultural use of arsenical chemicals is now less than 10% of peak use and only slightly exceeded the amount used for glass production in 1996. Monosodium methanearsonate (MSMA) was the primary form of arsenic applied to agricultural land in 1996, primarily on cotton (U.S. Department of Agriculture 1997). Relatively small quantities of disodium methanearsonate (DMSA) and dimethyl arsenic acid (cacodylic acid) were also applied in 1996. Arsenic also is added to poultry and swine feed.

Inorganic arsenic was widely applied prior to being banned for pesticide use in the 1980s and 1990s. Lead arsenate ( $PbHAsO_4$ ) was the primary insecticide used in fruit orchards prior to the introduction of DDT in 1947 (Shepard 1951). Inorganic arsenicals also have been applied to citrus, grapes, cotton, tobacco, and potato fields. Historic annual arsenic loading rates up to approximately 490 kg/ha (approximately 440 lb./acre) on apple orchards in eastern Washington (Benson 1976) led to arsenic concentrations in soil in excess of

100 mg/kg (Davenport and Peryea 1991). Agricultural soils in other parts of the United States also have high arsenic concentrations exceeding 100 mg/kg due to long-term application (20 to 40 years or more) of calcium- and lead-arsenate (Woolson et al. 1971, 1973; Wauchope 1983). Early studies suggested that arsenic in eastern Washington orchards was largely confined to the topsoil, although evidence for movement into the subsoil also has been cited (Peryea 1991). This apparent movement of arsenic suggests a potential for contamination of shallow ground water. In contrast, most soils unaffected by human activities contain < 10 mg/kg of arsenic (Wauchope 1983; Shacklette and Boerngen 1984).

Application of phosphate fertilizers creates the potential for releasing arsenic into ground water. Laboratory studies suggest that phosphate applied to soils contaminated with lead arsenate can release arsenic to soil water (Woolson et al. 1973; Davenport and Peryea 1991). Increased use of phosphate at relatively high application rates has been adopted to decrease the toxicity of arsenic to trees in replanted orchards (Davenport and Peryea 1991). Laboratory results suggest that this practice may increase arsenic concentrations in subsoil and shallow ground water (Davenport and Peryea 1991; Peryea 1991; Peryea and Kammereck 1997). Application of phosphate onto uncontaminated soil also may increase arsenic concentrations in ground water by releasing adsorbed arsenic.

Few analyses of ground water samples for methylated arsenic compounds are available compared with the number of inorganic arsenic determinations. Analyses of about 30 ground water samples in northwestern Nevada for monomethyl arsonate and di-methyl arsonate suggest that ground contains < 1  $\mu\text{g/L}$  of these methylated species (analyses were all < 0.3  $\mu\text{g/L}$ ; page 486 in Bostic et al. 1997 and unpublished USGS data). Based on limited sampling, arsenic in runoff from areas where DMSA and MSMA are applied appears to be low (< 1  $\mu\text{g/L}$ ; Thurman 1997). One notable exception to the observation that methylated-arsenic compounds are low in ground water is where arsenic and organic waste have been mixed, which can produce locally high organic arsenic concentrations (A. Davis et al. 1994). Reviews of biotransformation of arsenic in the environment provide insight into processes affecting organic arsenic where present in ground water (Andreae 1983; Cullen and Reimer 1989; Maeda 1994).

Arsenic concentrations in ground water are high at many sites with contaminated ground water (Tables 1 and 2). About 30% of 1191 Superfund sites list arsenic as a "contaminant of concern" in the record of decision (ROD) abstract or in the contaminant list, suggesting that high arsenic in ground water associated with waste disposal is common. Sites associated with the production of inorganic arsenic pesticides locally have exceedingly high concentrations in ground water, although not all sites appear to have an anthropogenic source for the arsenic. Ground water at one site in Texas has arsenic concentrations exceeding  $2 \times 10^6 \mu\text{g/L}$  (Table 2).

Arsenic in the ground water appears largely to be from aquifer materials at some Superfund sites that are contaminated with volatile organic compounds (VOCs). Comparison of arsenic concentrations in surficial samples at one site with nearby off-site surficial samples suggests that arsenic is not from waste disposal (Ogden 1990). Ongoing investigations of waste disposal sites in the northeast suggest that naturally occurring arsenic associated with iron oxide is being mobilized at some sites (Nikolaidis 1998) including at a VOC-contaminated site in Maine that does not have an identified anthropogenic source of arsenic (Colman 1998). Because ground water affected by petroleum products and landfill

**Table 1**  
**Selected Superfund Sites with High Arsenic in Ground Water at Concentrations Described in the Record of Decision (ROD) as Being "Of Concern"**

States	ROD <sup>1</sup>
<b>Sites associated with the use or disposal of inorganic arsenic</b>	
California, South Carolina	R05-89/099 R09-88/025 R06-88/023
Texas (2)	R04-87/026 <sup>2</sup>
Ohio, Texas	R05-88/068 R06-88-030
<b>Sites containing primarily municipal waste</b>	
Pennsylvania	R03-88/056
<b>Sites containing industrial waste (may also contain municipal waste)</b>	
Delaware, Iowa, Massachusetts, Montana, New Jersey, New York, Ohio, Pennsylvania	R08-89/022 R03-88/062 R02-89/081 R05-89/099 R02-88/075 R01-88/029 R03-88/052 R07-89/022
Arkansas	R06-88/036
Massachusetts, Minnesota, New Jersey, New York	R01-88/030 R05-87/058 R02-92/179 R02-92/176
Michigan	R06-89/111
California, Minnesota, New Jersey, New Mexico, Oregon, Pennsylvania, Virginia	R02-89/076 R03-88/055 R05-88/065 R06-88/039 R03-88/058 R10-88/017 R09-88/023

<sup>1</sup>ROD—U.S. EPA Record of Decision. Record of Decisions were retrieved from <http://www.epa.gov/superfund/oeri/imp/products/rodsites/rsitedoc.htm> March 21, 1998. Not all decisions were final.

<sup>2</sup>Sites are associated with the use or disposal of inorganic arsenic in wood preservatives.

**Table 2**  
**Arsenic in Ground Water in Areas Associated with the Use, Production, or Disposal of Arsenical Pesticides**

Geographic Area	As, µg/L	Source of Arsenic	References
<b>Groundwater Is Affected by Anthropogenic Sources</b>			
Massachusetts	1–11,300	Disposal of arsenical pesticides	A. Davies et al. 1994 <sup>1</sup>
Maryland	Maximum 2240	Disposal of chemical warfare agents	Vroblecky et al. 1989; Nemoff and Vroblecky 1989
Texas	—	Disposal of cotton waste containing arsenical pesticides	Aurelius 1988
Texas	< 50 to < 2,500,000	Disposal of inorganic arsenic pesticides <sup>2</sup>	Geraghty & Miller Inc. 1996
<b>Groundwater Does Not Appear to Be Affected by Anthropogenic Sources</b>			
Minnesota (two sites)	General $\gamma > 6$	As much as 11,500 pounds of PbAsO <sub>4</sub> buried	Stark et al. 1987
North Dakota	> 50	Arsenic-laden bait for grasshoppers	Roberts et al. 1985
South Dakota	3–110	Arsenic-laden bait for grasshoppers	Carter et al. 1998
Washington	—	Agricultural use of inorganic arsenical pesticides	Erickson and Norton 1990
Wisconsin	< 10 (223 samples)	Mixing and use of PbAsO <sub>4</sub> for agricultural use	Woo 1991

<sup>1</sup>Also see Aurillo et al. 1994.

<sup>2</sup>Lee 1998.

wastes can dissolve iron oxide, arsenic in the iron oxide may be an important source of arsenic in ground water at waste-disposal sites.

A few regional studies of agricultural use of inorganic arsenic pesticides do not suggest that widespread high concentrations of arsenic in ground water is common. In some areas, high arsenic concentrations regionally coincide with agricultural use, but these concentrations do not appear to result from agricultural use. Although some contribution of arsenic from historic uses is possible, studies in North Dakota, South Dakota, Wisconsin, and Minnesota all conclude that ground water is largely unaffected by use of arsenical pesticides (Table 2). High arsenic concentrations in ground water of northern Texas has been attributed to disposal of cotton gin waste, which has been found to contain arsenic concentrations up to 240 mg/kg (Aurelius 1988). Organic arsenicals in poultry and swine waste result from approved use in feed as arsanilic acid. Arsenic concentrations in poultry waste up to 32 mg/kg have been reported (Isaac et al. 1978), which is consistent with earlier studies. Some arsenic in soil water, which can exceed 50 µg/L, beneath field plots treated with chicken waste has been attributed to the waste (Isaac et al. 1978). The form and concentration of arsenic in ground water from application of arsenic-bearing poultry and swine waste does not appear to be well described in the scientific literature, although much of the arsanilic acid is not metabolized by pigs and chickens (Aschbacher and Feil 1991). Other possible anthropogenic sources of arsenic in ground water include codisposal with municipal waste (Blakey 1984), arsenic in phosphate detergents (Angino et al. 1970), and Civil War-era embalming fluid (Konefes and McGee 1996).

## Arsenic Occurrence in Relation to Natural Sources

### Arsenic Occurrence in Atmospheric Precipitation and Surface Water

Atmospheric precipitation, surface water, and aquifer materials are potential sources of arsenic in ground water. Precipitation in unpolluted areas generally contains much less than 1 µg/L dissolved arsenic (Andreae 1980). Substantially greater concentrations have been found in precipitation affected by anthropogenic sources. For instance, arsenic concentrations averaging 17 µg/L (Crecelius 1975) were found in rain and snow collected downwind from a smelter (now dismantled) in Tacoma, Washington. In the absence of anthropogenic sources, precipitation contributes little to arsenic concentrations in most ground water.

Most rivers and streams in the United States contain arsenic concentrations ≤ 1 µg/L (Smith et al. 1987; Lettenmaier et al. 1991). A notable exception is surface water draining geothermal areas. Geothermal springs in Yellowstone National Park commonly have arsenic concentrations exceeding 1000 µg/L (Stauffer and Thompson 1984; Ball et al. 1998). Discharge of geothermal water results in arsenic concentrations as high as 360 µg/L in the Madison River at the park boundary, and as high as 19 µg/L arsenic in the Missouri River at a point 470 km downstream (Nimick 1994; Nimick et al. 1998). Geothermal water is the primary source of arsenic in other parts of the United States, including some surface water in the eastern Sierra Nevada (Eccles 1976; Wilkie and Hering 1998). Water draining mineralized areas also can have very high arsenic concentrations.

### Arsenic Occurrence in Ground Water

Arsenic concentrations in ground water of the Appalachian Highlands and the Atlantic Plain generally are very low (Figure 2).

Although arsenic concentrations in these two provinces are significantly different, the 75th percentile for both regions is  $\leq 1 \mu\text{g/L}$ . Ground water in some bedrock units that underlie an area extending from Massachusetts into Maine (area 1 on Figure 3) contains high arsenic concentrations. Ground water in the coal-bearing portion of the Appalachian Highlands generally does not have high arsenic concentrations, although concentrations up to  $180 \mu\text{g/L}$  have been reported in drainage from an anthracite coal mine (Wood 1996). Arsenic concentrations in ground water and coal of the Warrior Basin of Alabama are high, most likely because of alteration of the coal by thermal water (Goldhaber et al. 1997). Because pyrite generally contains the bulk of arsenic in most coal (Coleman and Bragg 1990), this sulfide mineral is the most likely source of the arsenic in coal mine drainage.

Median arsenic concentrations are the same for the Interior Plains and the Rocky Mountain System ( $\leq 1 \mu\text{g/L}$ ), and their 75th and 90th percentiles are similar (Figure 2). Studies during the last decade suggest that high arsenic may be more widespread in the Interior Plains than previously recognized (Figure 3). Sulfide minerals appear to be a source of arsenic in the ground of north-eastern Wisconsin and, perhaps, eastern Michigan (areas 3 and 5 on Figure 3). In Michigan, authigenic pyrite in consolidated sand-

stone containing  $\leq 6.5\%$  arsenic (Kolker et al. 1998) appears to be an important source of arsenic in ground water. Similarly, pyrite and marcasite are the source of arsenic in some ground water in Wisconsin (area 5 on Figure 3; Schreiber et al. 2000). Alluvial and glacial aquifers of the upper Midwest contain high aqueous arsenic concentrations, including areas 4, 6, and 7 (Figure 3). The widespread association between glacial deposits and high arsenic in ground water suggests that other parts of the upper Midwest may also have high concentrations.

Arsenic concentrations in the Intermontane Plateaus are significantly different from those in all other provinces (Figure 2). Among provinces, the 50th (median), 75th, and 90th arsenic concentration percentiles are highest for the Intermontane Plateaus (Figure 2). As in the Intermontane Plateaus, arsenic concentrations in the Pacific Mountain System are significantly different from those in all other provinces—the 50th (median), 75th, and 90th arsenic percentiles are greater than in other provinces, except for the Intermontane Plateaus (Figure 2). The climate of much of the Intermontane Plateaus and parts of the Pacific Mountain System is relatively arid. This aridity can lead to evaporative concentration of arsenic in shallow ground water, particularly in the hydrologically closed basins of eastern Oregon, Nevada, western Utah, and east-

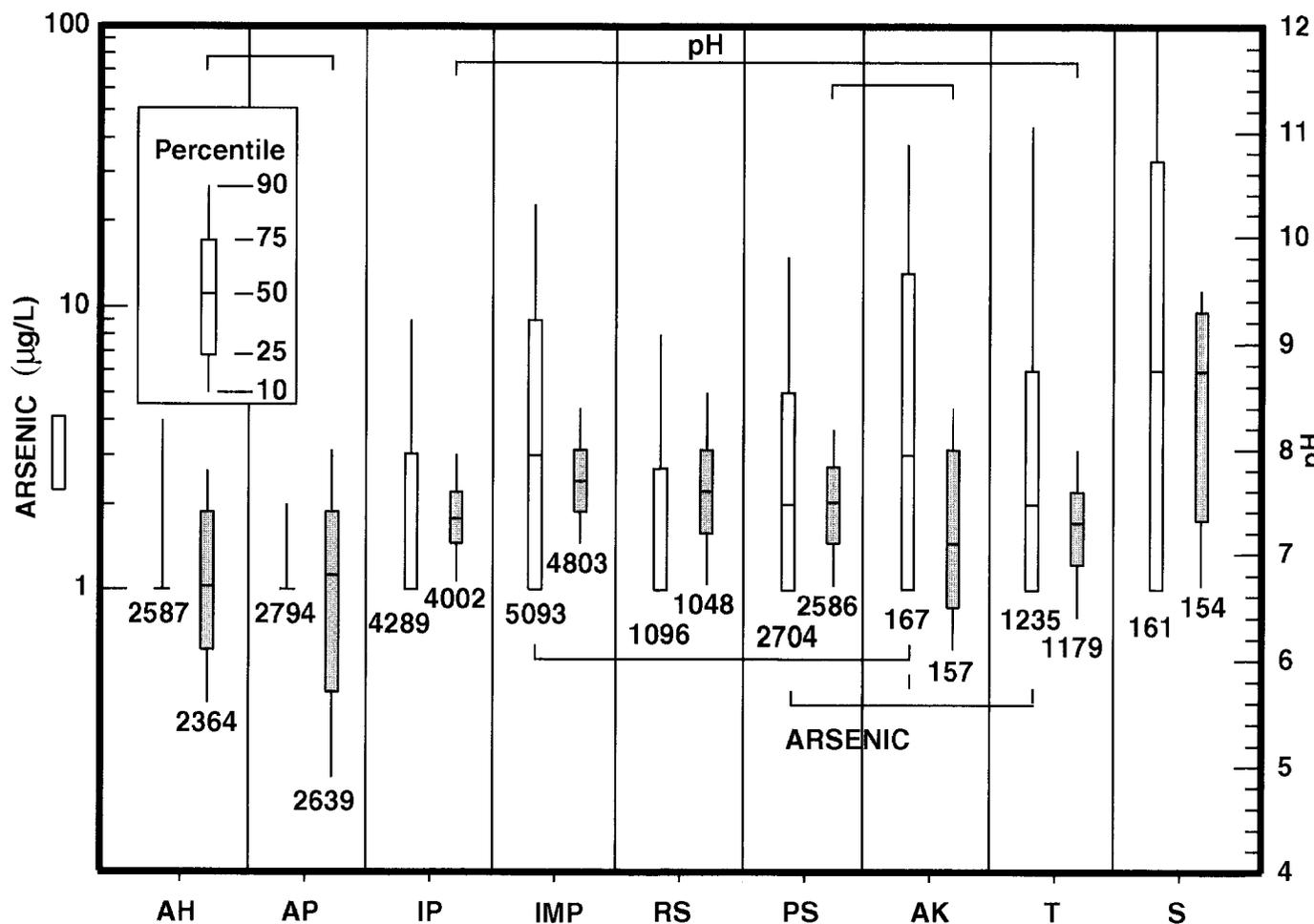
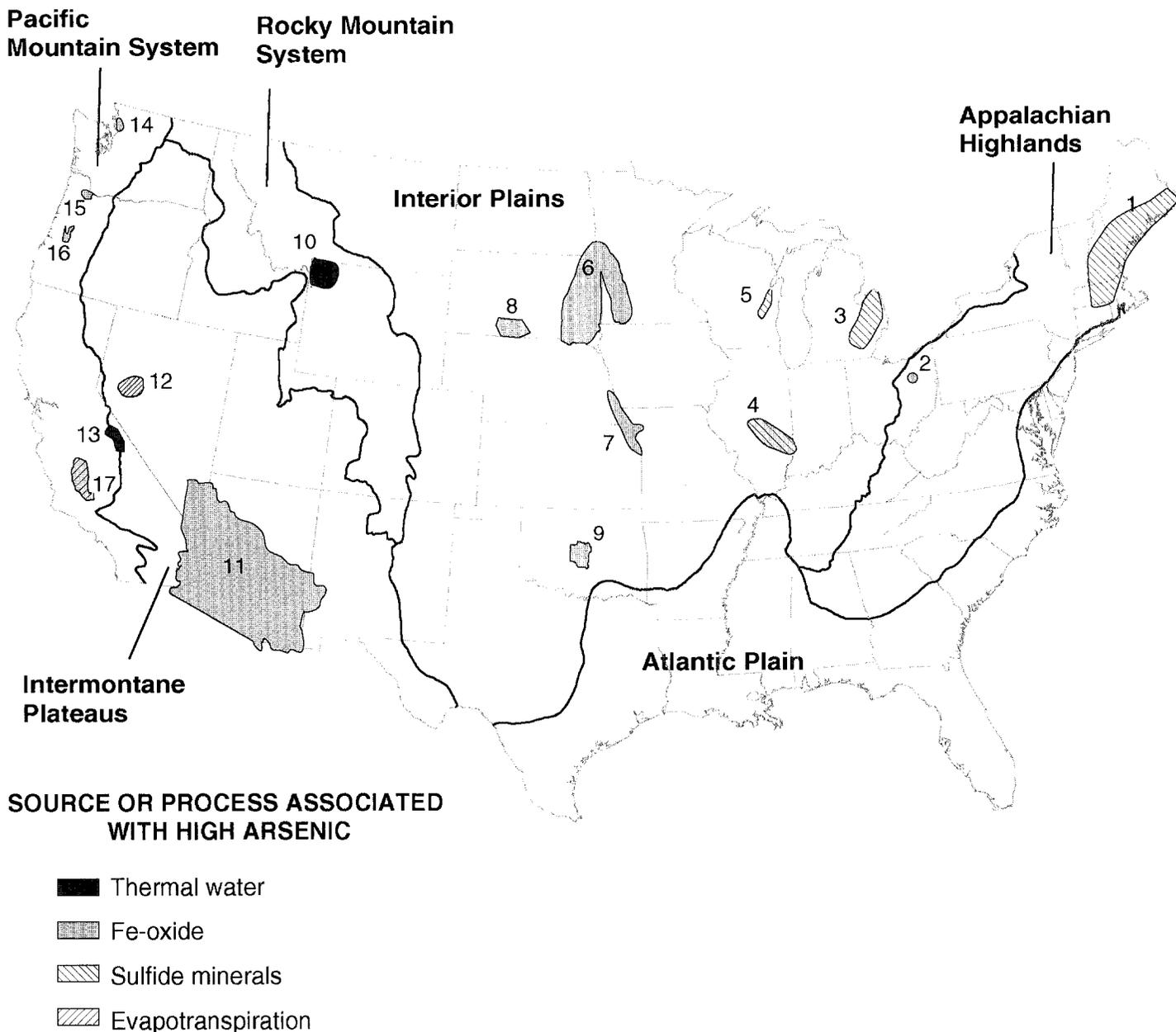


Figure 2. Summary statistics for arsenic and pH in ground water. Physiographic provinces follow Fenneman (1931) except for the inclusion of the Laurentian Upland and Interior Highlands with the Interior Plains, and inclusion of the Caribbean with the Atlantic Plain. The horizontal brackets connect boxplots that are not significantly different, as indicated by results of Kruskal-Wallis rank sums test. The 75th percentile arsenic concentration for the Appalachian Highlands and Atlantic Plain is  $\leq 1 \mu\text{g/L}$ . The minimum reporting level for arsenic is  $\leq 1 \mu\text{g/L}$ . The values beneath the boxes indicate the number of analyses available for each province. Abbreviations: AH—Appalachian Highlands, AP—Atlantic Plain, IP—Interior Plains, IMP—Intermontane Plateaus, RM—Rocky Mountain System, PM—Pacific Mountain System, AK—Alaska, T—thermal, and S—high dissolved solids.



**Figure 3. Areas underlain with ground water containing high arsenic concentrations (> 50 mg/L) and known or inferred source or process responsible for the high concentrations.**

ern California. Evaporative concentration is a contributing factor leading to high arsenic concentrations in areas such as the Carson Desert and the southern San Joaquin Valley (areas 12 and 17, respectively, on Figure 3). The high pH of saline ground water may be a factor affecting arsenic by limiting adsorption. Arsenic does not appear to partition into evaporite minerals until a very high salinity is attained (> 9 molar), which can lead to arsenic concentrations in excess of 100 mg/L (Levy et al. 1999). Ground water with somewhat elevated dissolved solids content tends to have high arsenic concentrations (Figure 2). These relations suggest that evaporative concentration together with limited adsorption can lead to moderate to high arsenic concentrations in ground water.

High arsenic concentrations in Alaska are common in the ground water of the Kenai Peninsula (Glass 1996) and ground water associated with gold mining near Fairbanks (Wilson and Hawkins 1978). Because of the relatively high proportion of samples from wells in the vicinity of Fairbanks, the data for Alaska are probably biased toward areas affected by mining than the data for

ground water elsewhere in the state.

Typically, arsenic concentrations in geothermal water generally are greater than those found in nonthermal water (Welch et al. 1988). Geothermal water as a whole compared with nonthermal data for the various physiographic provinces supports this observation (Figure 2). Much of the high arsenic in ground water within the Madison and upper Missouri River valleys appears to be directly or indirectly related to the Yellowstone geothermal system (Nimick 1994, 1998; Sonderegger and Ohguchi 1988). Arsenic concentrations in some ground water of southwestern Idaho also are influenced by geothermal water. The cluster of moderate and high arsenic values in north-central Nevada includes samples of geothermal ground water associated with dewatering of sulfide-bearing gold deposits (Maurer et al. 1996).

An association between an alkaline ground water (pH > 8) and high arsenic has been found in several areas of the United States. (Table 3). High arsenic ground water in aquifers composed of felsic volcanic rocks, which commonly is alkaline, is found in South

**Table 3**  
**Areas with High Arsenic Concentrations Derived From Natural Sources**

Source of Arsenic <sup>1</sup>	Hydrologic Units and Number of Area Shown in Figure 3	References
<b>Sulfide minerals</b>	Bedrock (1) <sup>2</sup>	Zuena and Keane 1985; Boudette et al. 1985; Marvinney et al. 1994; Ayotte et al. 1998; Peters et al. 1999
Fe-oxide (D)	Paleozoic sandstone (2)	Matisoff et al. 1982
Sulfide minerals	Glacial deposits, sandstone and shale <sup>3</sup> (3)	Westjohn et al. 1998; Kolker et al. 1998
Fe-oxide (D)	Glacio-fluvial deposits <sup>4</sup> (4)	Voelker 1986; Holm and Curtiss 1988; Panno et al. 1994; Holm 1995
<b>Sulfide minerals</b>	Ordovician carbonate and clastic rocks (5)	Simo et al. 1996; Schreiber et al. 2000
Fe-oxide (D, P)	Glacial deposits and shale (6)	Roberts et al. 1985; Kanivetsky, in press
Fe-oxide (D)	Alluvium (7)	Ziegler et al. 1993; Korte 1991
Fe-oxide (P)	Volcanic ash (8)	Carter et al. 1998
<b>Fe-oxide (P)</b>	Sandstone and mudstone (9)	Scholotmann and Breit 1992; Norvell 1995
Black shale lithic fragments	Glacio-fluvial deposits	Yarling 1992
<b>Geothermal water</b>	Volcanic rocks (10)	Stauffer and Thompson 1984; Ball et al. 1998
<b>Fe-oxide (P)</b>	Basin fill sediments, including volcanic, alluvial, and lacustrine deposits (11)	Owen-Joyce and Bell 1983; Owen-Joyce 1984; Robertson 1989
<b>Fe-oxide (D, P) and evaporative concentration</b>	Basin fill sediments, including alluvial and lacustrine deposits (12)	Welch and Lico 1998
<b>Geothermal water</b>	Volcanic rocks (13)	Mariner and Willey 1976; Eccles 1976; Wilkie and Hering 1998
Fe-oxide <sup>5</sup> (P)	Alluvium (14)	Goldstein 1988; Ficklin et al. 1989; Davies et al. 1991
Fe-oxide (D)	Basin-fill deposits (15)	Hinkle 1997; Hinkle and Polette 1999
Fe-oxide (P)	Felsic-volcanic tuff (16)	Goldblatt et al. 1963; Nadakavukaren et al. 1984
<b>Fe-oxide and evaporative concentration</b>	Basin-fill sediments, including alluvial and lacustrine deposits (17)	Fujii and Swain 1995; Swartz 1995; Swartz et al. 1996

<sup>1</sup>Known or inferred—where the source of arsenic appears well documented are shown in bold text otherwise the source is given with a normal font. For areas with iron oxide as a source of arsenic, dissolution of the oxide and desorption are important processes that can release to ground water. The letters “D” and “P” in parentheses refer to the processes of dissolution and pH-influenced desorption of arsenic, respectively.

<sup>2</sup>Arsenic concentrations in ground water are generally higher in bedrock aquifers compared with overlying glacial aquifers.

<sup>3</sup>The sandstone contains arsenic rich pyrite, which may be a source of the arsenic in the overlying glacial aquifer. Pyrite has not been identified in the glacial deposits.

<sup>4</sup>May include a contribution of arsenic from underlying coal-bearing units. Arsenic-rich ground water may extend into the upper Kankakee River basin within Indiana, as suggested by high arsenic in surface water, sediment and biota (Fitzpatrick et al. 1998; Schmidt and Blanchard 1997).

<sup>5</sup>Although arsenopyrite has been mentioned as a possible source of arsenic. However, high pH (the median pH of 11 samples with arsenic > 50 µg/L is 8.25) and generally low sulfate concentrations (< 25 mg/L; Ficklin et al. 1989) imply that sulfide mineral oxidation is limited, suggesting that the arsenic may be from iron oxide that was formed from the oxidation of arsenopyrite. The ground water with the highest arsenic concentration (15,000 µg/L) also had the highest pH (9.23).

Dakota, Oregon, and Arizona (areas 8, 11, and 16 in Table 3). Other aquifers with high arsenic, alkaline ground water have been reported in central Oklahoma and northwestern Washington (areas 9 and 14 in Table 3). A general relation of arsenic with dissolved phosphate has been noted in ground water (including areas 12, 15, and 16), which in some cases also is alkaline. The assembled data suggest that arsenic tends to increase with increasing pH and phosphate, as suggested by rank correlations (the Spearman’s rho in Figure 4). These relations are consistent with adsorption onto iron oxide being one factor affecting arsenic concentrations.

Mining of sulfide-bearing rocks in many parts of the United States has led to high arsenic concentrations in surface and ground water (Table 4). The western United States has some well known examples of high arsenic concentrations in water that result from sulfide oxidation in mined areas, including the upper Clark Fork River in Montana (Brumbaugh et al. 1994; Moore 1994), the Cour d’Alene mining district of northern Idaho (Mok et al. 1988), Bryant Creek drainage of California (Hammermeister and Walmsley 1985),

the Whitewood Creek–Cheyenne River surface water system of western South Dakota (Cherry et al. 1986a, 1986b, 1986c; Goddard 1989), and the Fairbanks mining district of Alaska (Wilson and Hawkins 1978). Oxidation of arsenopyrite associated with gold ore is an obvious source of arsenic at some of these deposits. Arsenic concentrations in ground water and sediment can be affected for hundreds of kilometers downstream from mined areas (Moore 1994). Not all mineralized areas produce arsenic-rich ground water, however. Arsenic concentrations in ground water of the Colorado Mineral Belt, for instance, generally are low (Klusman and Edwards, 1977).

Water associated with many abandoned mines and mine waste commonly is acidic due to the oxidation of sulfide minerals (Alpers and Blowes 1994). Perhaps less well known is the existence of arsenic-rich water with circum-neutral to alkaline pH conditions associated with sulfide minerals. Examples include arsenic-enriched water in the Mother Lode in California and water associated with polymetallic vein deposits of Nevada (Table 4).

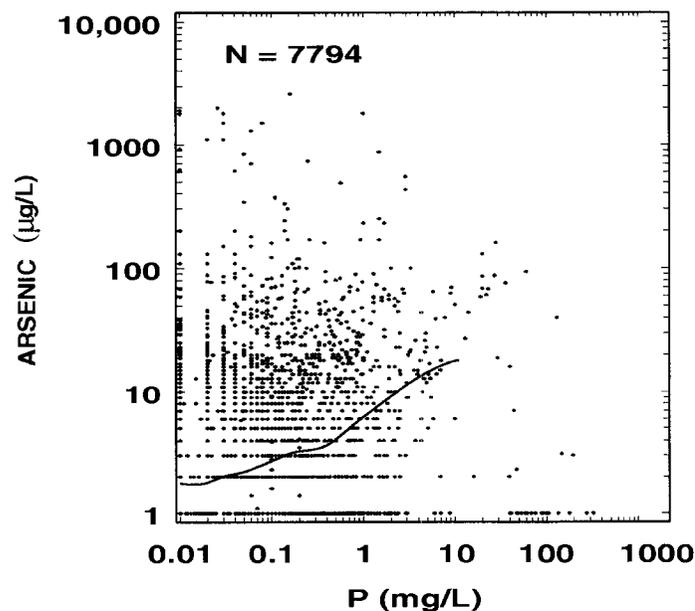
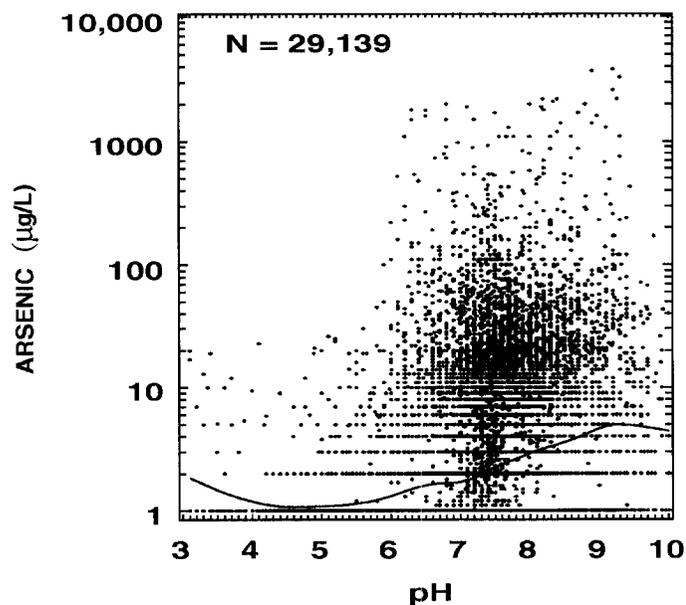


Figure 4. Relation of arsenic with pH and phosphate in ground water. The lines represent a cubic spline fit. The N value indicates the number of data points. The Spearman's  $\rho$  (rho; Hollander and Wolf 1973) for arsenic with pH and phosphate are 0.19 and 0.22, respectively. Both rank correlations are highly significant ( $r < 0.001$ ).

### Geochemical Controls on Arsenic in Ground Water

A brief discussion of arsenic geochemistry follows, couched in the terminology for oxidation/reduction (redox) conditions as proposed by Berner (1981) for sedimentary deposits. These are: (1) oxic (dissolved oxygen  $> 1$  mg/L); (2) post-oxic (dissolved oxygen  $< 1$  mg/L and no sulfide present); (3) sulfidic (dissolved oxygen  $< 1$  mg/L with sulfide present); and (4) methanic (methane present).

Aqueous arsenic in ground water exists primarily as oxyanions with formal oxidation states of III and V (e.g., Ficklin et al. 1989; Holm and Curtiss 1988; Welch et al. 1988). Either arsenate [As(V)] or arsenite [As(III)] can be the dominant inorganic form in ground

Table 4  
Arsenic and pH in Water Associated with Selected Mined Areas with Sulfide Minerals

Location and Deposit Type	As, $\mu\text{g/L}^1$	pH	Number of Samples <sup>2</sup>	Reference
Bald Mountain, Massachusetts – massive sulfide	2–430	5.9–8.0	11	Seal et al., in press
Bunker Hill Mine, Idaho – polymetallic vein	140–300 110–460	2.7–2.8 2.9–3.0	—	Mok et al. 1988 <sup>3</sup>
Mother Lode, California – low-sulfide gold-quartz	6–740	7.1–8.2	5/3	Ashley 1997
Iron Mountain, California – massive sulfide	150,000– 40,000	–0.7–2.6	3	Nordstrom and Alpers 1995
Leviathan Mine, California – volcanic-exhalative sulfur	8400–33,000	2.1–3.8	4	Hammermeister and Walmsley 1985
Nevada–Quartz – adularia with high sulfur	$< 5$ –830	2.8–3.8	3/2	Price et al. 1995
Nevada–Quartz – alunite	10–1600	2.4–3.0	1/2	Price et al. 1995
Nevada – polymetallic vein deposits	$< 5$ –13,000 $< 5$	6.8–7.8 3.8, 4.0	15/12 2/2	Price et al. 1995

<sup>1</sup>Rounded to the nearest 0.1.

<sup>2</sup>Where more than one district was sampled, the number followed by a slash represents the number of mining districts sampled.

<sup>3</sup>Also see Wai and Mok 1989 and Spruill 1993.

water. Arsenate ( $\text{H}_n\text{AsO}_4^{n-3}$ ) generally is the dominant form in oxic waters (Robertson 1989). In contrast, arsenite ( $\text{H}_n\text{AsO}_3^{n-3}$ ) dominates in sulfidic and methanic waters (Holm and Curtiss 1989; Korte and Fernando 1991; Pokrovski et al. 1996), including deeply circulating geothermal water (Ballantyne and Moore 1988; Criaud and Foulliac 1989; Webster 1990). In strongly sulfidic environments that are near saturation with respect to orpiment, arsenic sulfide complexes may form, probably with the generic formula  $\text{H}_n\text{As}_3\text{S}_6^{n-3}$  (Spycher and Reed 1989; Webster 1990; Helz et al. 1995). In solutions that have lower sulfide concentrations and that are greatly undersaturated with respect to orpiment, arsenic-sulfide monomeric species are likely to form (Helz et al. 1995). Formation of arsenic-sulfide complexes probably does little to enhance the solubility of arsenic in geothermal water, as demonstrated by a negative correlation between the partial pressure of  $\text{H}_2\text{S}$  and arsenic concentration in many geothermal systems (Ballantyne and Moore 1988). In low-temperature environments (approximately  $25^\circ\text{C}$ ), arsenic-sulfide complexes are probably an insignificant percentage of the overall dissolved arsenic speciation (Webster 1990). Redox couples, such as arsenic and iron, are generally not in equilibrium in ground water (Lindberg and Runnells 1984; Welch et al. 1988). Thus, the suggestion that ratios of As(III)/As(V) in environmental water may be used to calculate Eh (Cherry et al. 1979; Tallman and Shaikh 1980) should be followed with extreme caution. This lack of redox equilibrium has also been reported for surface water, where As(III) has been observed in oxic water and As(V) have been found in highly sulfidic water (Spliethoff et al. 1995).

Aqueous and solid-water reactions, some of which are bacterially mediated studies (Turner 1949; Johnson 1972; Freeman et al. 1986; Ahmann et al. 1997; Laverman et al. 1995; Dowdle et al. 1996; Harrington et al. 1998), can oxidize or reduce aqueous arsenic. Mn(IV)-oxide prepared in the laboratory rapidly oxidizes As(III) to As(V) (Oscarson et al. 1981a, 1983; Moore et al. 1990; Driehaus et al. 1995; Scott and Morgan 1995; Nesbitt et al. 1998). Studies of arsenic interaction with lake (Oscarson et al. 1980, 1981b; Kuhn and Sigg 1993) and marine sediments (Peterson and Carpenter 1983) are consistent with these observations. Reduction of As(V) may occur in some sediment (Brannon and Patrick 1987). A mixed [Fe(II)-Fe(III)]-oxide of undetermined structure has been found to reduce Se(VI) to Se(IV) (Myneni et al. 1997). By analogy, reduction of As(V) also might occur with this mixed oxide as the reductant. As(V) reduction by Fe(III)-oxide, although thermodynamically favorable, is extremely slow (Oscarson et al. 1981a).

The foregoing discussion is based on the assumptions of relatively low concentrations of total arsenic in solution and temperatures near 25°C. In hydrothermal environments the arsenite species still predominate, but solubility controls may vary based on temperature and sulfide activity (Pokrovski et al. 1996). In low temperature environments with very high arsenic concentrations (> 1000 µg/L) oligomeric species might predominate in solution (cf. Tossell 1997 and references therein). For example, in some waters that are known to be contaminated with arsenic, concentrations in excess of 100 mg/L have been observed (cf. Geraghty and Miller Inc. 1996). In these waters, oligomeric species such as  $As_3O_3(OH)_3$ ,  $As_6O_6(OH)_6$ , and  $As_4O_6$  are thermodynamically stable relative to the mono-arsenite species (Tossell 1997).

### Arsenic in Areas of Intense Evaporation

Evaporative concentration can increase arsenic concentrations. This process is particularly important in closed hydrologic basins of the semiarid western United States where evaporation rates exceed precipitation. For example, in the Carson Desert and southern San Joaquin Valley (areas 12 and 17 in Figure 3), evaporation appears to be a contributing factor producing high arsenic concentrations. Another factor that appears to affect arsenic concentrations in these two areas is adsorption or co-precipitation of arsenic on iron oxide (Fujii and Swain 1995; Welch and Lico 1998). Because arsenic is not incorporated in most evaporite minerals, the concentrations in ground water associated with these minerals can have high arsenic concentrations (Levy et al. 1999).

### Arsenic-Iron-Oxide Relations

Adsorption (or co-precipitation) of arsenic on iron oxides has been cited as a concentration-limiting process in ground water (Matisoff et al. 1982; Robertson 1989; Welch and Lico 1998), rivers (Johnson and Thornton 1987; Fuller and Davis 1989), soil water (Masscheleyn et al. 1991), lake water (Crecelius 1975; Belzile and Tessier 1990; DeVitre et al. 1991; Moncure et al. 1992; Soma et al. 1994; Huerta-Diaz et al. 1998), and in estuaries (Sullivan and Aller 1996). Several lines of evidence suggest that iron oxides affect arsenic in water, including: (1) correlation between iron and arsenic concentrations in sediments (Crecelius 1975) and sediment extracts (Huang and Liaw 1979; Maher 1984; Moore et al. 1988; Belzile and Tessier 1990; Sullivan and Aller 1996) along with adsorption modeling (Belzile and Tessier 1990; Welch and Lico 1998); (2) observations that arsenic concentrations vary with diel pH cycles (Davis et al. 1989; Fuller and Davis 1989; Brick and

Moore 1996; Nimick et al. 1998); and (3) studies of arsenic adsorption in laboratory solutions (e.g., references in Dzombak and Morel 1990).

The structure of arsenate and arsenite adsorption and co-precipitation on iron oxide has been investigated using a variety of approaches (Fuller et al. 1993; Hsia et al. 1994; Manceau 1995; Waychunas et al. 1993, 1995, 1996; Sun and Doner 1996 and 1998; Jain et al. 1999). Adsorption of arsenic onto  $Fe(OH)_3$  is affected by a variety of factors, including pH, the chemistry and amount of  $Fe(OH)_3$  present, and concentrations of competing ions. Co-precipitated arsenic is released from iron oxide as the crystalline growth of the oxide proceeds. Studies of arsenic adsorption kinetics reveal a short period of rapid uptake (less than five minutes) followed by a longer period during which arsenate adsorption is limited by diffusion into aggregated iron-oxide colloidal particles (Fuller et al. 1993). Adsorption of As(III) is faster than for As(V), although greater than 90% adsorption was achieved within 24 hours in laboratory solutions for both As(V) and As(III) (Raven et al. 1998).

A biologically mediated reaction that can release arsenic from iron oxide, commonly referred to as dissimilatory iron reduction, involves organic carbon and iron oxide (Lovley 1991). Dissolution of iron oxide is the primary process responsible for high arsenic concentrations in some ground water (e.g., Welch and Lico 1998; Nagorski and Moore 1999). Sources of organic carbon include sedimentary-organic matter and anthropogenic organic compounds. A model simulation indicates dissolution of  $Fe(OH)_3$  initially in equilibrium with water containing 2 µg/L of arsenic can lead to water with arsenic concentrations > 200 µg/L. Modeled reactions producing the results shown in Figure 5 consist of an initial equilibration between water with an aqueous arsenic concentration of 2 µg/L and sediment containing  $Fe(OH)_3$  (see the Appendix for a description of the model simulations). This initial equilibration precedes the dissolution reactions and simulates equilibration during the transport and deposition of iron oxide coated sediment in oxic water. Subsequent reaction of the arsenic-bearing  $Fe(OH)_3$  with organic carbon in water has an initial pH of 7, then proceeds in a stepwise fashion with: (1) release of arsenic, and (2) equilibration of the solution with the remaining  $Fe(OH)_3$ . Each step simulates complete replacement of ground water and equilibration with the oxide. As  $Fe(OH)_3$  dissolution and adsorption of arsenic proceeds, a nearly constant  $As_{aq}$  concentration is reached. A notable feature of the simulation is the relatively high and persistent aqueous arsenic concentration as the  $Fe(OH)_3$  becomes depleted. The constant concentration occurs when the mass of arsenic released from the  $Fe(OH)_3$  dissolution is equal to the mass in the water after equilibration. The concentrations > 200 µg/L persist for more than 20 pore volumes until the  $Fe(OH)_3$  is completely consumed after 50 steps.

The effect of pH on arsenic concentrations is illustrated by comparing simulations of the reaction of  $Fe(OH)_3$  with water having a different initial pH value (Figure 5). Reaction of water with an initial pH of 8 produces higher arsenic concentrations than found with the pH 7 inflow water, followed by a rapid decrease. The high concentrations reflect greater desorption at the higher pH.

Inclusion of phosphate in water reacting with the arsenic-bearing  $Fe(OH)_3$  results in much greater arsenic concentrations during the early phase of the simulation (Figure 5). These greater concentrations are a consequence of competition for adsorption sites. This simulation is a conceptual example of the possible effect of the application of phosphate fertilizer on arsenic concentrations.

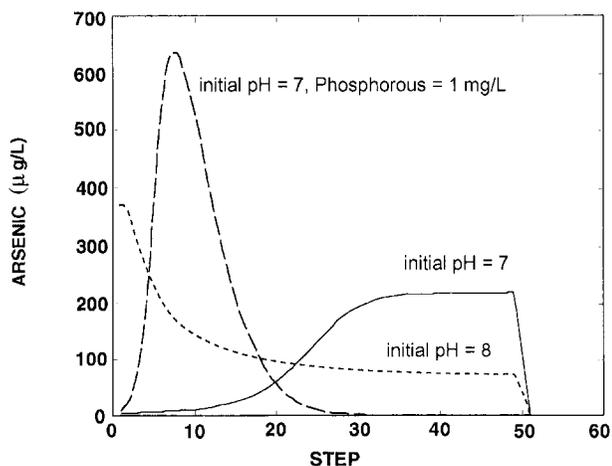


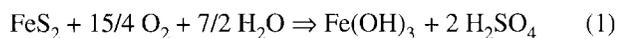
Figure 5. Arsenic associated with dissimilatory reduction of iron oxide. The numerical simulation is described in the appendix. The  $\text{pH}_i$  indicates the initial pH at the beginning of each simulated reaction step.

### Arsenic-Sulfide Mineral Relations

In oxic water, dissolution of sulfide minerals, most notably pyrite and arsenopyrite, contributes arsenic to ground and surface water in many parts of the United States. Arsenopyrite is the most common arsenic mineral (O'Neil 1995). Other common sulfide minerals can contain 1% or more arsenic as an impurity (e.g., pyrite, galena, sphalerite, marcasite, and chalcopyrite; Onishi 1978). Scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ) can be stable in low-pH water with high arsenic/iron ratios (Langmuir et al. 1999), although breakdown to iron oxide can occur. Sulfide minerals are an important sink for arsenic in some sulfidic water.

Sulfide mineral oxidation has long been studied primarily because of concerns with the production of acid mine drainage that commonly contains toxic concentrations of inorganic constituents. Pyrite is the most common gangue sulfide mineral associated with ore deposits, and therefore its effect on mine drainage is the most thoroughly studied. Because of the voluminous literature and the availability of recent summaries (Moses et al. 1987; Nicholson et al. 1988; Nicholson 1994; Rimstidt et al. 1994), the following discussion of pyrite oxidation is limited to a broad overview. Dissolution of arsenopyrite ( $\text{FeAsS}$ ) recently has received increased attention because of environmental concerns and because of an interest in increasing recovery of gold from refractory sulfide ores.

Pyrite oxidation is a complex chemical process that may involve 15 or more steps resulting in an overall reaction commonly written as

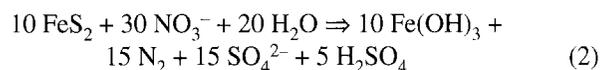


Because arsenic concentrations in pyrite generally range from about 0.02% to 0.5%, and may be as large as 6.5% (Kolker et al. 1998; also see page 16, National Academy of Sciences 1977), this reaction (Equation 1) can release a considerable amount of arsenic to the aqueous phase. The bacteria *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans*, and *Leptospirillum ferrooxidans* can increase reaction rates for sulfide mineral oxidation by about five orders of magnitude compared with abiotic reaction rates (Schrenk et al. 1998). *T. ferrooxidans* and *L. ferrooxidans* increase the oxidation rate indirectly by catalyzing the reaction between dissolved oxygen and Fe(II) to form Fe(III). The ferric iron can then oxidize pyrite, which is a much faster reaction than the reaction of pyrite directly by dissolved oxygen.

Bacterial oxidation of pyrite involving oxygen appears to

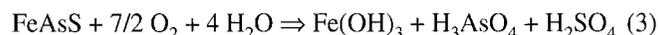
occur only in water with a pH less than 4 (Arkesteyn 1980), except in water with high nitrate concentrations. Sulfide-mineral oxidation in circum-neutral ground water commonly is attributed to abiotic oxidation. Although abiotic oxidation is slow, because bacteria do not catalyze the reaction of dissolved oxygen with Fe(II) (Moses and Herman 1991), field studies clearly demonstrate pyrite oxidation in neutral and slightly alkaline ground water (Postma et al. 1991; Kinniburgh et al. 1994; Schreiber 2000). Arsenic concentrations exceeding 1000  $\mu\text{g/L}$  in ground water can be produced where sulfide minerals are present near or above the water table (Schreiber 2000; Kinniburgh et al. 1994). Microbial examination of ground water in a zone with ongoing pyrite oxidation suggests that the oxidation is abiotic (Kinniburgh et al. 1994).

Aqueous nitrate in the presence of oxygen can oxidize pyrite at pH values greater than 5 (Appelo and Postma 1993). The overall reaction may be written as



Bacterial oxidation of Fe(II) by *Gallionella ferruginea* and sulfur in pyrite by *T. denitrificans* promotes this reaction. Pyrite oxidation involving nitrate has produced arsenic concentrations well above 50  $\mu\text{g/L}$  (van Beek et al. 1989; Appelo and Postma 1993).

Arsenopyrite oxidation by Fe(III) is about 10 times faster than the reaction with pyrite and is more rapid in the presence of *T. ferrooxidans*. Comparison of reaction rates is complicated by other factors, including surface area, degree of crystallinity, and mineral purity. As is the case for pyrite oxidation, *T. ferrooxidans* increases the reaction rate (Dorofeev et al. 1990; Fernandez et al. 1995; Zeman et al. 1995) by oxidizing Fe(II) to Fe(III). The overall reaction may be written as



Arsenopyrite oxidation can lead to precipitation of scorodite under acidic conditions, but this product commonly breaks down to iron oxide (Dove and Rimstidt 1985; Alpers et al. 1994; Fernandez et al. 1995). For example, scorodite has been observed as an apparently stable alteration product of arsenic-rich sulfides in some mine dumps (Dove and Rimstidt 1985). Although the solubility of scorodite is somewhat uncertain (Dove and Rimstidt 1985; Robins, 1987; Dove and Rimstidt 1987; Nordstrom and Parks 1987; Rimstidt and Dove 1987; Krause and Ettel 1988), it appears to be relatively soluble at intermediate pH values, and thus may not be an important control on arsenic in most ground water. Under higher pH conditions, iron oxide is the dominant oxidation product, and this reaction product adsorbs or co-precipitates arsenic.

Sulfide minerals, and perhaps amorphous sulfide phases, can be important sinks for arsenic in sulfidic water (Moore et al. 1988; McRae 1995; Rittle et al. 1995). The arsenic sulfide  $\text{As}_2\text{S}_3$  can form abiotically or biotically from nonthermal water (Newman et al. 1997) and from geothermal water (Webster 1990). Arsenic adsorption or co-precipitation with iron mono-sulfide 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).

**Table 5**  
**Principal Reactions Affecting Inorganic Arsenic Concentrations in Ground Water**

Redox Condition	Important Phases	Important Reactions	Conditions That Affect Arsenic Mobility	Examples or References
Oxic (dissolved oxygen present)	Fe-oxides	Adsorption/desorption	pH; presence of competing adsorbent; oxygen and Fe <sup>3+</sup> concentrations	Areas 2, 8, 12, 14, and 16; Peryea and Kammereck 1997
		Precipitation		Dead Indian Spring; Welch et al. 1988
	Sulfide minerals	Sulfide oxidation	pH and microbial activity; oxygen and NO <sub>3</sub> transport	Areas 1 and 3 and many mining sites (see text); Appelo and Postma 1993
Post-oxic (dissolved oxygen and sulfide not present)	Fe-oxides	Adsorption/desorption and precipitation	Oxidation state of As; also see Oxic discussion above	Dzombak and Morel 1990
		Adsorption/desorption	pH	See text
		Dissolution	Presence of organic carbon	Area 12; Nagorski and Moore 1999
	Sulfide minerals	See Oxic discussion above		
Sulfidic (sulfide present)	Sulfide minerals	Precipitation	Sulfide, iron, and As concentrations	Moore et al. 1988; McRae 1995; Rittle et al. 1995; Huerta-Diaz et al. 1998

## Discussion of Arsenic Occurrence and Geochemistry

Anthropogenic sources contribute arsenic to ground water at some waste disposal sites. Reaction of synthetic organic compounds with iron oxide appears to be one cause of locally high arsenic concentrations. Less well understood are the effects of historic and current use of arsenical chemicals for agricultural purposes. Although the data assembled for this evaluation do not suggest that widespread high arsenic concentrations result from agricultural use, the relationship between arsenic in ground water and the use of arsenic on agricultural land is not well documented at a national scale.

Concentrations of naturally occurring arsenic in ground water vary regionally due to a combination of climate and geology. Although slightly less than half of 30,000 arsenic analyses of ground water in the United States were  $\leq 1 \mu\text{g/L}$ , about 10% exceeded  $10 \mu\text{g/L}$ . At a broad regional scale, moderate to high arsenic concentrations appear to increase from east to west across the United States, although high concentrations exist in all physiographic provinces. Arsenic concentrations in ground water of the Appalachian Highlands and the Atlantic Plain generally are very low. Concentrations are somewhat greater in the Interior Plains and the Rocky Mountain System. Ground water in the Intermontane Plateaus and Pacific Mountain System of the western United States more commonly contains arsenic concentrations  $> 10 \mu\text{g/L}$  compared with that in the eastern physiographic provinces. Investigations during the last decade in New England, Michigan, Minnesota, South Dakota, Oklahoma, and Wisconsin suggest that moderate to high arsenic concentrations ( $> 10 \mu\text{g/L}$ ) are more widespread and common than previously recognized.

The preceding discussion has largely focused on ground water with moderate to high arsenic concentrations, possibly leaving an impression that a large proportion of the ground water in the United States has high arsenic. The assembled data suggest that ground water in the United States typically contains low to very low

arsenic concentrations ( $\leq 1 \mu\text{g/L}$ ), particularly in the two eastern provinces where 75% or more of the sampled ground water contains arsenic concentrations  $\leq 1 \mu\text{g/L}$ . In most of the areas outlined in Figure 3, which shows areas that tend to have high arsenic concentrations, some ground water with low to very low arsenic concentrations also exists. In areas with naturally high arsenic concentrations, steep lateral and vertical concentration gradients in arsenic concentration are commonly observed. Examples include areas 4, 6, 11, and 17 (Figure 3), where steep gradients exist between zones of low to very low concentrations and zones with high arsenic concentrations.

Although some of the relations between geology and arsenic concentrations in ground water can be inferred from individual studies, a statistically based evaluation requires further work. Development of a lithochemical geologic coverage would be an important component in such an evaluation. Earlier work suggests, along with data and studies discussed previously, that unaltered (unmineralized) basalt and limestone commonly contain ground water with low arsenic concentrations. Aquifers with alkaline ( $\text{pH} > 8$ ) ground water, such as felsic-volcanic tuffs and ash, are known to contain high concentrations, including parts of areas 8, 12, 14, and 16. Reduction and dissolution of iron oxide through reaction with organic matter appear to produce high arsenic ground water in some parts of the country. In addition to areas previously discussed, ground water with high arsenic concentrations on the Kenai Peninsula (Glass 1996) and in shallow ground water of Louisiana (Dial and Huff 1989) may be caused by an interaction between iron oxide and chemically reduced carbon. Black shale, which can contain sulfide minerals, also has been cited as a source of arsenic.

Some of the most common reactions affecting arsenic concentrations are summarized in Table 5. Arsenic release from iron oxide, from desorption or dissolution, appears to be the most common cause of regionally high arsenic concentrations. Desorption can be promoted by a high pH or the introduction of a competing adsorbent in oxic and post-oxic ground water. Iron oxide can release arsenic to ground water through dissimilatory-iron reduc-

tion involving either naturally occurring or anthropogenic (i.e., waste disposal, presence of petroleum products, etc.) organic carbon. After precipitation of amorphous iron oxide containing arsenic, the conversion to a more crystalline form releases arsenic. The oxidation state of inorganic arsenic has an important effect on mobility. In the presence of iron oxide, As(III) is adsorbed to a lesser degree than As(V) (Dzombak and Morel 1990).

Sulfide minerals can be a source or sink for arsenic (Moore et al. 1988; McRae 1995; Rittle et al. 1995). Oxidation of arsenic bearing sulfide minerals produces high arsenic concentrations in many parts of the country, particularly where rocks have undergone mineralization. Except in very acidic water, where scorodite can form, the most common arsenic-bearing product is iron oxide. Precipitation of sulfide minerals, which can occur in sulfide-rich water, can remove arsenic from water.

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### Appendix

Version 2.1 of PHREEQC (Parkhurst 1995) was used for the adsorption modeling displayed in Figure 5. The program and WATEQ4 thermodynamic data are available from <http://brrcrftp.cr.usgs.gov>. Note that the WATEQ4 data files include data for adsorption from Dzombak and Morel (1990). The chemical analyses are for the Carson Desert, an area with ground water containing high arsenic concentrations (Welch and Lico 1998). The initial simulation forms an iron oxide in equilibrium with a solution containing 2 µg/L arsenic in water using the following input:

```
TITLE d7_15
# EQUILIBRATE HFO WITH 2 µg/L As - SAVE SURFACE
KNOBS
-pe 5
-diagonal
-iterations 400
```

```
SOLUTION 1
units ppm
TEMP      25.0
pH        7.
pe        10.
O(0)     1.20
Ca        1.20
Mg        .80
Na       500.00
K         11.00
Cl        92.00 charge
S(6)     190.00
```

```
Alkalinity 840.00 as HCO3
Si         29.00
As         2 ppb
SURFACE 1
-equil solution 1
Hfo_w Fe(OH)3(a) 0.027 600
```

```
EQUILIBRIUM_PHASES 1-2
# moles of Fe(OH)3 initially present
Fe(OH)3(a) 0.0 .0297
```

```
END
The saved oxide was then reacted with organic matter in a stepwise manner until the oxide was entirely consumed using the following input code.
```

```
SOLUTION 0 Arsenate = 0
units ppm
```

```
TEMP      25.0
pH        7.
pe        2.5
Ca        1.20
Mg        .80
Na       500.00
K         11.00
Cl        92.00 charge
S(6)     190.00
Alkalinity 840.00 as HCO3
Si        29.00
```

```
USE SURFACE 1
EQUILIBRIUM_PHASES 1
  Calcite  0.0  0.1
  Siderite 0.0  0.0
  Fe(OH)3(a) 0.0 .0297
```

```
# moles of Fe(OH)3 initially present
```

```
REACTION 1
CH2O .00015
```

```
ADVECTION
-cells 1
-shifts 51 1
```

```
SELECTED_OUTPUT
-file d_15.pun
-totals As
```

```
END
```

This model input corresponds to the results labeled “pH<sub>i</sub> = 7” in Figure 5. The results labeled “pH<sub>i</sub> = 8” use the same input except the pH of the initial solution and the reaction solution was set equal to 8. The line labeled “pH<sub>i</sub> = 7” and “P = 1 mg/L” included a phosphate concentration of 1 mg/L in the second part of the simulation. The pH values at the end of each simulated step were about 7.26 and 8.52. Calcite and siderite are allowed to precipitate as the dissolution reaction proceeds.

### References

- Abernathy, J.R. 1983. Role of arsenical chemicals in agriculture. In *Arsenic: Industrial, Biomedical, Environmental Perspectives*, ed. W.H. Lederer and R.J. Fensterheim 57–60. New York: Van Nostrand Reinhold.
- Abernathy, C.O., R.L. Calderon, and W.R. Chappell (eds.). 1997. *Arsenic Exposure and Health Effects*. New York: Chapman and Hall.

- Ahmann, D., L.R. Krumholz, H. F. Hemond, D.R. Lovley, and F.M.M. Morel. 1997. Microbial mobilization of arsenic from sediments of the Aberjona watershed. *Environmental Science and Technology* 31, 2923–2930.
- Alpers, C.N., D.W. Blowes, D.J. Nordstrom, and J.L. Jambor. 1994. Secondary minerals and acid mine-water chemistry. In *The Environmental Geochemistry of Sulfide Mine-Wastes*, ed. J.L. Jambor and D.W. Blowes, 247–438. Short Course Handbook 22. Waterloo, Ontario: Mineralogical Association of Canada.
- Alpers, C.N., and D.W. Blowes. 1994. *Environmental Geochemistry of Sulfide Oxidation*. Symposium Series 550. Washington, D.C.: American Chemical Society.
- Andreae, M.O. 1980. Arsenic in rain and the atmospheric mass balance of arsenic. *Journal of Geophysical Research* 85, no. C8: 4512–4518.
- Andreae, M.O. 1983. Biotransformation of arsenic in the marine environment. In *Arsenic: Industrial, Biomedical, Environmental Perspectives*, ed. W.H. Lederer and R.J. Fensterheim, 378–391: New York: Van Nostrand Reinhold.
- Angino, E.E., L.M. Magnuson, T.C. Waugh, O.K. Galle, and J. Bredfeldt. 1970. Arsenic in detergent: Possible danger and pollution hazard. *Science* 168, 389–390.
- Appelo, C.A.J., and D. Postma. 1993. *Geochemistry, Groundwater and Pollution*. Roderdam: A.A. Balkema.
- Arkesteyn, G.J.M.W. 1980. Pyrite oxidation in acid sulphate soils: The role of microorganisms. *Land and Soil* 54, no. 1: 119–134.
- Aschbacher, P.W., and J.J. Feil. 1991. Fate of [<sup>14</sup>C] arsanilic acid in pigs and chickens. *Journal Agricultural Food Chemistry* 38, 146–149.
- Ashley, R.P. 1997. Environmental geochemistry of gold deposits in the Mother Lode Belt. Coalifying. In *4th International Symposium on Environmental Geochemistry Proceedings*, ed. R.B. Wanty, S.P. Marsh, and L.P. Gough, 7. USGS Open-File Report 97-496.
- Aurelius, L. 1988. Investigation of arsenic contamination of groundwater occurring near Knott, Texas. Austin, Texas: Texas Department of Agriculture.
- Aurillo, A.C., R.P. Mason, and H.F. Hemond. 1994. Speciation and fate of arsenic in three lakes of the Aberjona Watershed. *American Chemical Society* 28, no. 4: 577–585.
- Ayotte, J.D., M.G. Nielson, and G.R. Robinson. 1998. Relation of arsenic concentrations in ground water to bedrock lithology in eastern New England. *Geological Society of America Annual Meeting Abstracts with Programs: A-58*.
- Azcue, J.M., and J.O. Nriagu. 1994. Arsenic: Historical perspectives. In *Arsenic in the Environment, Part I: Cycling and Characterization*, ed. J.O. Nriagu, 1–16. New York: John Wiley & Sons.
- Ball, J. W., D.K. Nordstrom, E.A. Jenne, and D.V. Vivit. 1998. Chemical analyses of hot springs, pools, geysers, and surface waters from Yellowstone National Park, Wyoming, and vicinity, 1974–1975. USGS Open-File Report 98-182.
- Ballantyne, J.M., and J.N. Moore. 1988. Arsenic geochemistry in geothermal systems. *Geochimica et Cosmochimica Acta* 52, no. 2: 475–483.
- Belzile, N., and A. Tessier. 1990. Interactions between arsenic and iron oxyhydroxides in lacustrine sediments. *Geochimica et Cosmochimica Acta* 54, 103–109.
- Benson, N.R. 1976. Retardation of apple tree growth by soil arsenic residues from old insecticidal treatments. *Journal American Society of Horticultural Science* 101, no. 3: 251–253.
- Berner, R.S. 1981. A new geochemical classification of sedimentary environments. *Journal of Sedimentary Petrology* 51, no. 2: 359–365.
- Blakey, N.C. 1984. Behavior of arsenical wastes codisposed with domestic solid wastes. *Journal of the Water Pollution Control Federation* 56, no. 1: 69–75.
- Borum, D.R., and C.O. Abernathy. 1994. Human oral exposure to inorganic arsenic. In *Arsenic Exposure and Health*, ed. W.R. Chappell, C.O. Abernathy, and C.R. Cothorn, 21–30. Northwood: Science and Technology Letters.
- Bostic, R.E., R.L. Kane, K.M. Kipfer, and A.W. Johnson. 1997. Water resources data, Nevada, water year 1996. USGS Water-Data Report NV-96-1.
- Boudette, E.L., F. C. Canney, J. E. Cotton, R. I. Davis, W.H. Ficklin, and J.M. Motooka. 1985. High levels of arsenic in the groundwater of southeastern New Hampshire. A geochemical reconnaissance. USGS Open-File Report 85-202.
- Brannon, J.M., and W.H. Patrick Jr. 1987. Fixation, transformation, and mobilization of arsenic in sediments. *Environmental Science and Technology* 21, 450–459.
- Brick, C.M., and J.N. Moore. 1996. Diel variation of trace metals in the upper Clark Fork River, Montana. *Environmental Science and Technology* 30, 1953–1960.
- Brumbaugh, W.G., C.G. Ingersoll, N.E. Kemble, and T.W. May. 1994. Chemical characterization of sediments and pore water from the upper Clark Fork River and Milltown Reservoir, Montana. *Environmental Toxicology and Chemistry* 13, no. 12: 1971–1983.
- Carter, J.M., S.K. Sando, T.S. Hayes, and R.H. Hammond. 1998. Source occurrence, and extent of arsenic contamination in the Grass Mountain area of the Rosebud Indian Reservation, South Dakota. USGS Water Resources Investigation Report 97-4286.
- Chappell, W.R., C.O. Abernathy, and C.R. Cothorn (eds.) 1994. *Arsenic Exposure and Health*. Northwood: Science and Technology Letters.
- Chen, S.L., S.R. Dzung, M.H. Yang, K.H. Chiu, G.M. Shieh, and C.M. Wai. 1994. Arsenic species in groundwaters of the blackfoot disease area, Taiwan. *Environmental Science and Technology* 28, no. 5: 877–881.
- Cherry, J.A., A.U. Shaikh, D.E. Tallman, and R.V. Nicholson. 1979. Arsenic species as an indicator of redox conditions in groundwater. *Journal of Hydrology* 43, no. 1-4: 373–392.
- Cherry, J.A., F.M.M. Morel, J.V. Rouse, J.L. Schnoor, and M.G. Wolman. 1986a. Hydrogeochemistry of sulfide and arsenic-rich tailings and alluvium along Whitewood Creek, South Dakota (Part 1 of 3 parts). *Mineral & Energy Resources* 29, no. 4: 12.
- Cherry, J.A., F.M.M. Morel, J.V. Rouse, J.L. Schnoor, and M.G. Wolman. 1986b. Hydrogeochemistry of sulfide and arsenic-rich tailings and alluvium along Whitewood Creek, South Dakota (Part 2 of 3 parts). *Mineral & Energy Resources* 29, no. 5: 15.
- Cherry, J.A., F.M.M. Morel, J.V. Rouse, J.L. Schnoor, and M.G. Wolman. 1986c. Hydrogeochemistry of sulfide and arsenic-rich tailings and alluvium along Whitewood Creek, South Dakota (Part 3 of 3 parts). *Mineral & Energy Resources* 29, no. 6: 15.
- Coleman, S.L., and L.J. Bragg. 1990. Distribution and mode of occurrence of arsenic in coal. In *Recent Advances in Coal Geochemistry*, ed. L.L. Chyi and C.L. Chou, 13–26. Special Paper 248. Boulder, Colorado: Geological Society of America.
- Colman, J. 1998. Oral communication, Northborough, Massachusetts.
- Crecelius, E.A. 1975. The geochemical cycle of arsenic in Lake Washington and its relation to other elements. *Limnology and Oceanography* 20, no. 3: 441–451.
- Criaud, A., and C. Fouillac. 1989. The distribution of arsenic (III) and arsenic (V) in geothermal waters: Examples from the Massif Central of France, the Island of Dominica in the Leeward Islands of the Caribbean, the Valles Caldera of New Mexico, U.S.A., and southwest Bulgaria. *Chemical Geology* 76, 259–269.
- Cullen, E.R., and K.J. Reimer. 1989. Arsenic speciation in the environment. *Chemical Reviews* 89: 713–764.
- Davenport, J.R., and F.J. Peryea. 1991. Phosphate fertilizers influence leaching of lead and arsenic in a soil contaminated with lead and arsenic in a soil contaminated with lead arsenate. *Water, Air and Soil Pollution* 57-58, 101–110.
- Davies, J., R. Davis, D. Frank, F. Frost, D. Garland, S. Milham, R.S. Pierson, R.S. Raasina, S. Safioles, and L. Woodruff. 1991. Seasonal study of arsenic in ground water: Snohomish County, Washington. Snohomish Health District and Washington State Department of Health.
- Davis, A., H. Kempton, and A. Nicholson. 1994. Groundwater transport of arsenic and chromium at a historical tannery, Woburn, Massachusetts. *Applied Geochemistry* 9, no. 5: 569–582.
- Davis, J.A., C.C. Fuller, B.A. Rea, and R.G. Claypool-Frey. 1989. Sorption and coprecipitation of arsenate by ferrihydrite. In *Water-Rock Interaction*, ed. D.L. Miles, 187–189. Balkema: Rotterdam.
- Davis, M.K., K.D. Reich, and M.W. Tikkanen. 1994. Nationwide and California arsenic occurrence studies. In *Arsenic Exposure and Health*, ed. W.R. Chappell, C.O. Abernathy, and C.R. Cothorn, 31–40. Northwood: Science and Technology Letters.
- DeVitre, R., N. Belzile, and A. Tessier. 1981. Speciation and adsorption of arsenic on diagenetic iron oxides. *Limnology and Oceanography* 36, no. 7: 1480–1485.

- Dial, D.C., and G.F. Huff. 1989. Occurrence of minor elements in ground water in Louisiana including a discussion of three selected sites having elevated concentrations of barium. State of Louisiana Department of Transportation and Development Water Resources Technical Rept. No. 47.
- Dorofeev, A.G., T.A. Pivovarova, and G.I. Karavaiko. 1990. The kinetics of oxidation of ferrous oxide by *Thiobacillus ferrooxidans*: Effect of products of arsenopyrite oxidation and pH. *Microbiology* 59, no. 2: 126-131.
- Dove, P.M., and J.D. Rimstidt. 1985. The solubility and stability of scorodite,  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ . *American Mineralogist* 70, no. 7-8: 838-844.
- Dove, P.M. and J.D. Rimstidt. 1987. The solubility and stability of scorodite,  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ . *American Mineralogist* 72, no. 7-8: 845-848.
- Dowdle, P.R., A.M. Laverman, and R.S. Oremland. 1996. Bacterial dissimilatory reduction of arsenic (V) to arsenic (III) in anoxic sediments. *Applied Environmental Microbiology* 62, no. 5: 1664-1669.
- Driehaus, W., R. Seith, and M. Jenkel. 1995. Oxidation of arsenate(III) with manganese oxides in water treatment. *Water Research* 1, 297-305.
- Dzombak, D.D., and F.M.M. Morel. 1990. *Surface Complex Modeling*. New York: John Wiley & Sons.
- Eccles, L.A. 1976. Sources of arsenic in streams tributary to Lake Crowley California. USGS Water Resources Investigation Report 76-36.
- Edelstein, D. 1997. *Arsenic, Annual Review-1996*. Mineral Industry Surveys. U.S. Geological Survey.
- Edelstein, D. 1998. *Arsenic, Annual Review-1997*. Mineral Industry Surveys. U.S. Geological Survey.
- Erickson, D., and D. Norton. 1990. Washington state agriculture chemicals pilot study. Final report. Olympia, Washington: Washington State Department of Ecology, Ground Water Monitoring Section.
- Fenneman, N.M. 1931. *Physiography of Western United States*. New York: McGraw-Hill.
- Ferguson, J.F., and J. Gavis. 1972. A review of the arsenic cycle in natural waters. *Water Research* 6, no. 11: 1259-1274.
- Fernandez, M.G.M., C. Mustin, P. Dedonato, O. Barres, P. Marion, and J. Berthelin. 1995. Occurrences at the mineral-bacteria interface during the oxidation of arsenopyrite by *Thiobacillus ferrooxidans*. *Journal of Biotechnology and Bioengineering* 46, no. 1: 13-21.
- Ficklin, W.H., D.G. Frank, P.K. Briggs, and R.E. Tucker. 1989. Analytical results for water, soil, and rocks collected near the vicinity of Granite Falls, Washington, as part of an arsenic-in-groundwater study. USGS Open-File Report 89-148.
- Fitzpatrick, F., T.L. Arnold, and J.A. Colman. 1998. Surface-water-quality assessment of the Upper Illinois River Basin in Illinois, Indiana, and Wisconsin—Spatial distribution of geochemicals in the fine fraction of streambed sediment, 1987. USGS Water Resources Investigation Report 98-4109.
- Focazio, M.J., A.H. Welch, S.A. Watkins, D.R. Helsel, and M.A. Horn. 2000. A retrospective analysis on the occurrence of arsenic in public ground-water resources of the United States and limitations in drinking-water-supply characterizations. USGS Water Resources Investigation Report 99-4279, 21.
- Freeman, M.C., J. Aggett, and G. O'Brien. 1986. Microbial transformations of arsenic in Lake Ohakuri, New Zealand. *Water Research* 20, no. 3: 283-294.
- Frey, M.M., and M.A. Edwards. 1997. Surveying arsenic occurrence. *Journal American Water Works Association* 89, 105-117.
- Fujii, R., and W.C. Swain. 1995. Areal distribution of trace elements, salinity, and major ions in shallow ground water, Tulare basin, Southern San Joaquin Valley, California. USGS Water Resources Investigation Report 95-4048.
- Fuller, C.C., and J.A. Davis. 1989. Influence of coupling of sorption and photosynthetic processes on trace element cycles in natural waters. *Nature* 340, 152-154.
- Fuller, C.C., J.A. Davis, and G.A. Waychunas. 1993. Surface chemistry of ferrihydrite: Part 2. Kinetics of arsenate adsorption and coprecipitation. *Geochimica et Cosmochimica Acta* 57, 2271-2282.
- Geraghty and Miller Inc. 1996. Status report on the groundwater extraction system Elf Atochem North America Inc., Bryan, Texas. Supplement to the annual report for February 1996, vol. 1.
- Glass, R.L. 1996. Ground-water conditions and quality in the western part of Kenai Peninsula, Southcentral Alaska. USGS Open-File Report 96-466.
- Goddard, K.E. 1989. Composition, distribution, and hydrologic effects of contaminated sediments from the discharge of gold mine wastes to the Whitewood Creek at Lead and Deadwood, South Dakota. USGS Water Resources Investigation Report 87-4051.
- Goldblatt, E.L., S.A. Van Denburgh, and R.A. Marsland. 1963. The unusual and widespread occurrence of arsenic in well waters of Lane County, Oregon. Lane County Health Department Report.
- Goldhaber, M.B., J.R. Hatch, J.C. Pashin, T.W. Offield, and R.B. Finkelman. 1997. Anomalous arsenic and fluorine concentrations in carboniferous coal, Black Warrior Basin, Alabama: Evidence for fluid expulsion during Alleghanian thrusting. *Geological Society of America Annual Meeting Abstracts with Programs*, 51. Boulder, Colorado: GSA.
- Goldstein, L. 1988. A review of arsenic in ground water with an emphasis on Washington state. M.S. thesis, Department of Environmental Science, Evergreen State College, Olympia, Washington.
- Hammermeister, D.P., and S.J. Walmsley. 1985. Hydrologic data for Leviathan Mine and vicinity, Alpine County, California, 1981-83. USGS Open-File Report 85-160.
- Harrington, J.M., S.B. Fendorf, and R.F. Rosenzweig. 1998. Biotic generation of arsenic(III) in metal(loid)-contaminated sediments. *Environmental Science and Technology* 32, no. 16: 2425-2430.
- Helz, G.R., J.A. Tossell, J.M. Charnock, R.A.D. Patrick, D.J. Vaughan, and C.D. Garner. 1995. Oligomerization in As(III) sulfide solutions: Theoretical constraints and spectroscopic evidence. *Geochimica et Cosmochimica Acta* 59, no. 22: 4591-4604.
- Hinkle, S.R. 1997. Quality of shallow ground water in alluvial aquifers of the Willamette Basin, Oregon, 1993-95. USGS Water Resources Investigation Report 97-4082-B.
- Hinkle, S.R., and D.J. Polette. 1999. Arsenic in ground water of the Willamette Basin, Oregon. USGS Water Resources Investigation Report 98-4205.
- Hollander, M., and D.A. Wolfe. 1973. *Nonparametric Statistical Methods*. New York: John Wiley.
- Holm, T.R. 1995. Ground-water quality in the Mahomet Aquifer, McLean, Logan, and Tazewell Counties. Illinois State Water Survey Contract Report 579.
- Holm, T.R., and C.D. Curtiss. 1988. *Arsenic Contamination in East-Central Illinois Ground Waters*. Illinois Department of Energy and Natural Resources, Energy and Environmental Affairs Division.
- Holm, T.R., and C.D. Curtiss. 1989. A comparison of oxidation-reduction potentials calculated from the As(V)/As(III) and Fe(III)/Fe(II) couples with measured platinum-electrode potentials in groundwater. *Journal of Contaminant Hydrology* 5, no. 1: 67-81.
- Hsia, T.H., S.L. Lo, C.F. Lin, and D.Y. Lee. 1994. Characterization of arsenate adsorption on hydrous iron oxide using chemical and physical methods. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 85, 1-7.
- Huang, P.M., and W.K. Liaw. 1979. Adsorption of arsenite by lake sediments. *International Revue der Gesamten Hydrobiologie* 64, no. 2: 263-271.
- Huerta-Diaz, M.A., A. Tessier, and R. Carignan. 1998. Geochemistry of trace elements associated with reduced sulfur in freshwater sediments. *Applied Geochemistry* 13, 213-233.
- Isaac, R.A., S.R. Wilkenson, and J.A. Stuedemann. 1978. Analysis and fate of arsenic in broiler litter applied to coastal Bermuda grass and Kentucky-31 tall fescue. In *Proceedings of a Symposium on Environmental Chemistry and Cycling Processes*, ed. D.C. Adriano and I.L. Brisbin Jr. 207-220. U.S. Department of Energy.
- Jain, A., K.P. Raven, and R.H. Loeppert. 1999. Arsenite and arsenate adsorption on ferrihydrite: Surface charge reduction and net OH-release stoichiometry. *Environmental Science and Technology* 33, 1179-1184.
- Johnson, D.L. 1972. Bacterial reduction of arsenate in sea water. *Nature* 240, no. 5357: 44-45.
- Johnson, C.A., and I. Thornton. 1987. Hydrological and chemical factors controlling the concentrations of Fe, Cu, Zn and As in a river system contaminated by acid mine drainage. *Water Research* 21, no. 3: 359-365.

- Kanivetsky, R. In press. Arsenic in ground water of Minnesota: Hydrogeochemical modeling and characterization. Minnesota Geological Survey Report of Investigation 55.
- Kinniburgh, D.G., I.N. Gale, P.L. Smedley, W.G. Darling, J.M. West, R.T. Kimblin, A. Parker, J.E. Rae, P.J. Aldous, and M.J. O'Shea. 1994. The effects of historic abstraction of groundwater from the London Basin aquifers on groundwater quality. *Applied Geochemistry* 9, no. 2: 175–196.
- Klusman, R.W., and K.W. Edwards. 1977. Toxic heavy metals in ground water of the Front Range, Colorado. *Ground Water* 15, no. 2: 160–169.
- Kolker, A., W.F. Cannon, D.B. Westjohn, and L.G. Woodruff. 1998. Arsenic-rich pyrite in the Mississippian Marshall Sandstone: Source of anomalous arsenic in southeastern Michigan ground water. *Geological Society of America Annual Meeting Abstracts with Programs*, A-59. Boulder, Colorado: GSA.
- Konefes, J.L., and M.K. McGee. 1996. Old cemeteries, arsenic, and health safety. *Cultural Resource Management* 19, no. 10: 15–18.
- Korte, N.E. 1991. Naturally occurring arsenic in groundwaters of the mid-western United States. Oak Ridge National Laboratory Environmental Technology Section Publication no. 3501. Oak Ridge, Tennessee: Oak Ridge National Laboratory.
- Korte, N.E., and Q. Fernando. 1991. A review of arsenic (III) in groundwater. *Critical Reviews in Environmental Control* 21, no. 1: 39.
- Krause, E., and V.A. Ettl. 1988. Solubility and stability of scorodite,  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ : New data and further discussion. *American Mineralogist* 73, no. 7-8: 850–854.
- Kuhn, A., and L. Sigg. 1993. Arsenic cycling in eutrophic Lake Greifen, Switzerland: Influence of seasonal redox processes. *Limnology Oceanography* 38, no. 5: 1052–1059.
- Langmuir, D.D., J. Mahoney, A. MacDonald, and J. Rowson. 1999. Predicting arsenic concentrations in the porewaters of buried uranium mill tailings. *Geochimica et Cosmochimica Acta* 63, no. 19/20: 3379–3394.
- Laverman, A.M., J.S. Blum, J.K. Schaefer, E.J.P. Phillips, D.R. Lovley, and R.S. Oremland. 1995. Growth of strain SES-3 with arsenate and other diverse electron acceptors. *Applied Environmental Microbiology* 61, no. 10: 3556–3561.
- Lederer, W.H., and R.J. Fensterheim (eds.) 1983. *Arsenic: Industrial, Biomedical, Environmental Perspectives*. New York: Van Nostrand Reinhold.
- Lee, R. 1998. Oral communication, USGS, Austin, Texas.
- Lettenmaier, D.P., E.R. Hooper, C. Wagoner, and K.B. Faris. 1991. Trends in stream water quality in the continental United States, 1978–1987. *Water Resources Research* 27, no. 3: 327–339.
- Levy, D.B., J.A. Schramke, J.K. Esposito, T.A. Erickson, and J.C. Moore. 1999. The shallow ground water chemistry of arsenic, fluorine, and major elements: Eastern Owens Lake, California. *Applied Geochemistry* 14, no. 1: 53–65.
- Lindberg, R.D., and D.D. Runnells. 1984. Ground water redox reactions: An analysis of equilibrium state applied to Eh measurements and geochemical modeling. *Science* 225, 925–927.
- Loebenstein, J.R. 1994. The materials flow of arsenic in the United States. U.S. Bureau of Mines Information Circular IC9382.
- Lovley, D.R. 1991. Dissimilatory Fe(III) and Mn(IV) reduction. *Microbiological Reviews* 55, no. 2: 259–287.
- Maeda, S. 1994. Biotransformation of arsenic in the freshwater environment. In *Arsenic in the Environment, Part I: Cycling and Characterization*, ed. J.O. Nriagu, 155–188. New York: John Wiley & Sons.
- Maher, W.A. 1984. Mode of occurrence and speciation of arsenic in some pelagic and estuarine sediments. *Chemical Geology* 47, no. 3-4: 333–345.
- Manceau, A. 1995. The mechanism of anion adsorption on iron oxides: Evidence for the bonding of arsenate tetrahedra on free  $\text{Fe}(\text{O},\text{OH})_6$  edges. *Geochimica et Cosmochimica Acta* 59, no. 17: 3647–3654.
- Mariner, R.H., and L.M. Willey. 1976. Geochemistry of thermal waters in Long Valley, Mono County, California. *Journal of Geophysical Research* 81, no. 5: 792–800.
- Marvinney, R.G., M.C. Loisel, J.T. Hopeck, D. Braley, and J.A. Krueger. 1994. Arsenic in Maine groundwater: An example from Buxton, Maine. In *Proceedings of the 1994 Focus Conference on Eastern Regional Ground Water Issues*, 701–714. Dublin, Ohio: National Ground Water Association.
- Masscheleyn, P.H., R.D. Delaune, and W.H. Patrick Jr. 1991. Arsenic and selenium chemistry as affected by sediment redox potential and pH. *Journal of Environmental Quality* 20, no. 3: 522–527.
- Matisoff, G., C.J. Khourey, J.F. Hall, A.W. Varnes, and W.H. Strain. 1982. The nature and source of arsenic in northeastern Ohio ground water. *Ground Water* 20, no. 4: 446–456.
- Maurer, D.K., R.W. Plume, J.M. Thomas, and A.K. Johnson. 1996. Water resources and effects of changes in ground-water use along the Carlin Trend, north-central Nevada. USGS Water Resources Investigation Report 96-4134.
- McRae, C.M. 1995. Geochemistry and origin of arsenic-rich pyrite in the Uphapee Creek, Macon County, Alabama. M.S. thesis, Department of Geology, Auburn University, Alabama.
- Mok, W.M., J.A. Riley, and C.M. Wai. 1988. Arsenic speciation and quality of groundwater in a lead-zinc mine, Idaho. *Water Research* 22, no. 6: 769–774.
- Moncure, G., P.A. Jankowski, and J.I. Drever. 1992. The hydrochemistry of arsenic in reservoir sediments, Milltown, Montana. In *Water-Rock Interaction*, ed. Y.K. Kharaka and A.S. Maest, 513–516. Rotterdam: Balkema.
- Moore, J.N. 1994. Contaminant mobilization resulting from redox pumping in a metal-contaminated river-reservoir system. In *Environmental Chemistry of Lakes and Reservoirs*, 451–471. Washington, D.C.: American Chemical Society.
- Moore, J.N., W.H. Ficklin, and C. Johns. 1988. Partitioning of arsenic and metals in reducing sulfidic sediments. *Environmental Science and Technology* 22, 432–437.
- Moore, J.N., J.R. Walker, and T.H. Hayes. 1990. Reaction scheme for the oxidation of As(III) to As(V) by birnessite. *Clays and Clay Minerals* 38, no. 5: 549–555.
- Moses, C.O., and J.S. Herman. 1991. Pyrite oxidation at circumneutral pH. *Geochimica et Cosmochimica Acta* 55, no. 2: 471–482.
- Moses, C.O., D.K. Nordstrom, J.S. Herman, and A.L. Mills. 1987. Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. *Geochimica et Cosmochimica Acta* 51, no. 6: 1561–1571.
- Myneni, S.C.B., T.K. Tokunaga, and G.E. Brown Jr. 1997. Abiotic selenium redox transformations in the presence of Fe(II, III) oxides. *Science* 278, no. 5340: 1106–1109.
- Nadakavukaren, J.J., R.L. Ingermann, and G. Jeddelloh. 1984. Seasonal variation of arsenic concentration in well water in Lane County, Oregon. *Bulletin of Environmental Contamination and Toxicology* 33, no. 3: 264–269.
- Nagorski, S.A., and J.N. Moore. 1999. Arsenic mobilization in the hyporeic zone of a contaminated stream. *Water Resources Research* 35, no. 11: 3441–3450.
- National Academy of Sciences. 1977. Arsenic. In *Medical and Biological Effects of Environmental Pollutants*. Washington, D.C.
- Nemoff, P.R., and D.A. Vroblecky. 1989. Hydrogeologic and chemical data for the O-Field Area, Aberdeen Proving Ground, Maryland. USGS Open-File Report 89-238.
- Nesbitt, H.W., G.W. Canning, and G.M. Bancroft. 1998. XPS study of reductive dissolution of 7A-birnessite by  $\text{H}_3\text{AsO}_3$ , with constraints on reaction mechanism. *Geochimica et Cosmochimica Acta* 62, no. 12: 2097–2110.
- Newman, D.K., T.J. Beveridge, and F.M.M. Morel. 1997. Precipitation of arsenic trisulfide by *Desulfotomaculum auripigmentum*. *Applied Environmental Microbiology* 63, no. 5: 2022–2028.
- Nicholson, R.V. 1994. Iron-sulfide oxidation mechanisms—Laboratory studies. In *The Environmental Geochemistry of Sulfide Mine-Wastes*, ed. J.L. Jambor and D.W. Blowes, 163–183. Short Course Handbook 22. Waterloo, Ontario: Mineralogical Association of Canada.
- Nicholson, R.V., R.W. Gillham, and E.J. Reardon. 1988. Pyrite oxidation in carbonate-buffered solutions. 1. Experimental kinetics. *Geochimica et Cosmochimica Acta* 52: 1077–1085.
- Nikolaidis, N. 1998. Oral communication, University of Connecticut.
- Nimick, D.A. 1994. Arsenic transport in surface and ground water in the Madison and upper Missouri River Valleys, Montana. American Geophysical Union Fall Meeting, 247.

- Nimick, D.A. 1998. Arsenic hydrogeochemistry in an irrigated river valley: A reevaluation. *Ground Water* 36, no. 5: 743-753.
- Nimick, D.A., J.N. Moore, C.E. Dalby, and M.W. Savka. 1998. The fate of arsenic in the Madison and Missouri rivers, Montana and Wyoming. *Water Resources Research* 34, no. 11: 3051-3067.
- Nordstrom, D.K., and C.N. Alpers. 1995. Remedial investigations, decisions, and geochemical consequences at Iron Mountain Mine, California. In *Sudbury '95, Conference on Mining and the Environment*, ed. T.P. Hynes and M.C. Blanchette, 633-642. Sudbury, Ontario: Canada Centre for Mineral and Energy Technology.
- Nordstrom, D.K., and G.A. Parks. 1987. The solubility and stability of scorodite,  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ : Discussion. *American Mineralogist* 72, no. 7-8: 849-851.
- Norvell, J.L.S. 1995. Distribution of, sources of, and processes mobilizing arsenic, chromium, selenium, and uranium in the central Oklahoma aquifer. M.S. thesis, Department of Geology, Colorado School of Mines, Golden, Colorado.
- Nriagu, J.O. (ed.) 1994a. *Arsenic in the Environment, Part I: Cycling and Characterization*. New York: John Wiley & Sons.
- Nriagu, J.O. (ed.) 1994b. *Arsenic in the Environment, Part II: Human Health and Ecosystem Effects*. John Wiley & Sons, New York.
- Ogden, P. R. 1990. Arsenic behavior in soil and groundwater at a Superfund site. In *Superfund '90*, 123-127. Silver Spring, Maryland: Hazardous Materials Control Research Institute.
- O'Neil, P. 1995. Arsenic. In *Heavy Metals in Soils*, ed. B.J. Alloway, 107-121. London: Blackie Academic & Professional.
- Onishi, Y. 1978. Arsenic. In *Handbook of Geochemistry*, II/3: 33-A-1 to 33-O-1. Berlin: Springer-Verlag.
- Oscarson, D.W., P.M. Huang, and W.K. Liaw. 1980. Oxidation of arsenite by aquatic sediments. *Journal Environmental Quality* 9, no. 4: 700-703.
- Oscarson, D.W., P.M. Huang, C. Defosse, and A. Herbillon. 1981a. Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. *Nature* 291, no. 5810: 50-51.
- Oscarson, D.W., P.M. Huang, and W.K. Liaw. 1981b. Role of manganese in the oxidation of arsenite by freshwater lake sediments. *Clays and Clay Minerals* 29, no. 3: 219-225.
- Oscarson, D.W., P.M. Huang, W.K. Liaw, and U.T. Hammer. 1983. Kinetics of oxidation of arsenite by various manganese dioxides. *Soil Science Society America Journal* 47, no. 4: 644-648.
- Owen-Joyce, S.J., and C.K. Bell. 1983. Appraisal of water resources in the Upper Verde River area, Yavapai and Coconino counties, Arizona. Arizona Department of Water Resources Bulletin 2.
- Owen-Joyce, S.J. 1984. Hydrology of a stream-aquifer system in the Camp Verde area, Yavapai County, Arizona. Arizona Department of Water Resources Bulletin 3.
- Panno, S.V., K.C. Hackley, K. Cartwright, and C.L. Liu. 1994. Hydrochemistry of the Mahomet bedrock valley aquifer, east-central Illinois: Indicators of recharge and ground-water flow. *Ground Water* 32, no. 4: 591-604.
- Parkhurst D.L. 1995. Users guide to PHREEQC: A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations. USGS Water-Resources Investigation Report 95-4227.
- Peryea, F.J. 1991. Phosphate-induced release of arsenic from soils contaminated with lead arsenate. *Soil Science Society America Journal* 55, 1301-1306.
- Peryea, F.J., and R. Kammereck. 1997. Phosphate-enhanced movement of arsenic out of lead arsenate-contaminated topsoil and through uncontaminated subsoil. *Water, Air and Soil Pollution* 93, no. 1-4: 243-254.
- Peters, S.C., J.D. Blum, B. Klaue, and M.R. Karagas. 1999. Arsenic occurrence in New Hampshire ground water. *Environmental Science and Technology* 33, no. 9: 1328-1333.
- Peterson, M.L., and R. Carpenter. 1983. Biogeochemical processes affecting total arsenic and arsenic species distributions in an intermitently anoxic fjord. *Marine Chemistry* 12, no. 4: 295-321.
- Pokrovski, G., R. Gout, J. Schott, A. Zotov, and J.C. Harrichoury. 1996. Thermodynamic properties and stoichiometry of As(III) hydroxide complexes at hydrothermal conditions. *Geochimica et Cosmochimica Acta* 60, no. 5: 737-749.
- Postma, D., C. Boesen, H. Kristiansen, and F. Larsen. 1991. Nitrate reduction in an unconfined sandy aquifer: Water chemistry, reduction processes, and geochemical modeling. *Water Resources Research* 27, no. 8: 2027-2045.
- Price, J.G., L. Shevenell, C.D. Henry, J.G. Rigby, L.G. Christensen, P.J. Lechler, M.O. Desilets, R. Fields, D. Driesner, B. Durbin, and W. Lombardo. 1995. Water quality at inactive and abandoned mines in Nevada. Nevada Bureau of Mines and Geology Open-File Report 95-4.
- Raven, K.P., A. Jain, and R.H. Loeppert. 1998. Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes. *Environmental Science and Technology* 32, no. 3: 344-349.
- Rimstidt, J.D., J.A. Chermak, and P.M. Gagen. 1994. Rates of reaction of galena, sphalerite, chalcopyrite, and arsenopyrite with Fe(III) in acidic solutions. In *Environmental Geochemistry of Sulfide Oxidation*, ed. C.N. Alpers and D.W. Blowes, 2-13. Symposium Series 550. Washington, D.C.: American Chemical Society.
- Rimstidt, J.D., and P.M. Dove. 1987. The solubility and stability of scorodite,  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ : Reply. *American Mineralogist* 72, no. 7-8: 852-855.
- Rittle, K.A., J.I. Drever, and P.J.S. Colberg. 1995. Precipitation of arsenic during bacterial sulfate reduction. *Geomicrobiology Journal* 13, no. 1: 1-11.
- Roberts, K., B. Stearns, and R. L. Francis. 1985. Investigation of arsenic in southeastern North Dakota ground water. A superfund remedial investigation report. North Dakota State Department of Health.
- Robertson, F.N. 1989. Arsenic in ground-water under oxidizing conditions, south-west United States. *Environmental Geochemistry and Health* 11, no. 3-4: 171-186.
- Robins, R.G. 1987. The solubility and stability of scorodite,  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ : Discussion. *American Mineralogist* 72, no. 7-8: 842-844.
- Schrenk, M.O., K.J. Edwards, R.M. Goodman, and J.F. Banfield. 1998. Distribution of *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*: Implications for generation of acid mine drainage. *Science* 279, 1519-1522.
- Schlottmann, J.L., and G.N. Breit. 1992. Mobilization of As and U in the central Oklahoma aquifer. In *Water-Rock Interaction*, ed. Y.K. Kharaka and A.S. Maest, 835-838. Rotterdam: Balkema.
- Schmidt, A.R., and S.F. Blanchard. 1997. Surface-water-quality assessment of the upper Illinois River Basin in Illinois, Indiana, and Wisconsin—Results of investigations through April 1992. USGS Water Resources Investigation Report 96-4223.
- Schreiber, M.E., J.A. Simo, and P.G. Freiberg. 2000. Stratigraphic and geochemical controls on naturally occurring arsenic in groundwater, eastern Wisconsin, USA. *Hydrogeology Journal* 8, no. 2: 161-176.
- Scott, M.J., and J.J. Morgan. 1995. Reactions at the oxide surfaces. 1. Oxidation of As(III) by synthetic birnessite. *Environmental Science and Technology* 29, no. 8: 1898-1905.
- Seal, R.R., D.P. Haffner, A.L. Meier, and J. Caldwell. In press. Preliminary report of ground and surface water geochemistry in the vicinity of the unmined Bald Mountain massive sulfide deposit. U.S. Geological Survey.
- Shacklette, H.T., and J.G. Boerngen. 1984. Element concentrations in soils and other surficial materials of the conterminous United States. USGS Professional Paper 1134-A.
- Shepard, H.H. 1951. *The Chemistry and Action of Insecticides*, 1st ed. New York: McGraw-Hill.
- Simo, J.A., P.G. Freiberg, and K.S. Freiburg. 1996. Geologic constraints on arsenic in groundwater with applications to groundwater modeling. Groundwater Research Report WRC GRR 96-01, University of Wisconsin.
- Smith, A.H., M. Goycole, R. Haque, and M.L. Biggs. 1998. Marked increase in bladder and lung cancer mortality in a region of northern Chile due to arsenic in drinking water. *American Journal of Epidemiology* 147, no. 7: 660-669.
- Smith, A.H., C. Hopenhayn-Rich, M.N. Bates, H.M. Goeden, I. Hertz-Picciotto, H.M. Duggan, R. Wood, M.J. Kosnett, and M.T. Smith. 1992. Cancer risks from arsenic in drinking water. *Environmental Health Perspectives* 97, 259-267.
- Smith, A.S., R.B. Alexander, and M.G. Wolman. 1987. Water-quality trends in the nation's rivers. *Science* 235, no. 4796: 1607-1615.

- Soma, M., A. Tanaka, H. Seyama, and K. Satake. 1994. Characterization of arsenic in lake sediments by X-ray photoelectron spectroscopy. *Geochimica et Cosmochimica Acta* 58, no. 12: 2743–2745.
- Sonderegger, J.L., and T. Ohguchi. 1988. Irrigation related arsenic contamination of a thin, alluvial aquifer, Madison River Valley, Montana, U.S.A. *Environmental Geology and Water Sciences* 11, no. 2: 153–161.
- Splithoff, H.M., R.P. Mason, and H.F. Hemond. 1995. Interannual variability in the speciation and mobility of arsenic in a dimictic lake. *Environmental Science and Technology* 29, no. 8: 2157–2161.
- Spycher, N.F., and M.H. Reed. 1989. As(III) and Sb(III) sulfide complexes: An evaluation of stoichiometry and stability from existing experimental data. *Geochimica et Cosmochimica Acta* 53, 2185–2194.
- Spruill, T.B. 1993. Preliminary evaluation of the hydrogeology and ground-water quality in valley sediments in the vicinity of Killarney Lake, Kootenai County, Idaho. USGS Water Resources Investigation Report 93-4091.
- Stark, J.R., J.D. Strudell, P.A. Bloomgren, and P. Eger. 1987. Ground-water and soil contamination near two pesticide-burial sites in Minnesota. USGS Water Resources Investigation Report 87-415.
- Stauffer, R.E., and J.M. Thompson. 1984. Arsenic and antimony in geothermal waters of Yellowstone National Park, Wyoming, USA. *Geochimica et Cosmochimica Acta* 48, no. 11: 2547–2561.
- Sullivan, K.A., and R.C. Aller. 1996. Diagenetic cycling of arsenic in Amazon shelf sediments. *Geochimica et Cosmochimica Acta* 60, no. 9: 1465–1477.
- Sun, X., and H.E. Doner. 1996. An investigation of arsenate and arsenite bonding structures on goethite by FTIR. *Soil Science* 161, no. 12: 865–872.
- Sun, X., and H.E. Doner. 1998. Adsorption and oxidation of arsenite goethite. *Soil Science* 163, 278–287.
- Swartz, R.J. 1995. A study of the occurrence of arsenic on the Kern Fan element of the Kern Water Bank, southern San Joaquin Valley, California. M.S. thesis, Department of Geology, California State University, Bakersfield, California.
- Swartz, R.J., G.D. Thyne, and J.M. Gillespie. 1996. Dissolved arsenic in the Kern Fan San Joaquin Valley, California: Naturally occurring or anthropogenic. *Environmental Geosciences* 3, no. 3: 143–153.
- Tallman, D.E., and A.U. Shaikh. 1980. Redox stability of inorganic arsenic(III) and arsenic(V) in aqueous solution. *Analytical Chemistry* 52, no. 1: 196–199.
- Thurman, M. 1997. Oral communication, USGS, Lawrence, Kansas.
- Tossell, J.A. 1997. Theoretical studies on arsenic oxide and hydroxide species in minerals and in aqueous solution. *Geochimica et Cosmochimica Acta* 61, no. 8: 1613–1623.
- Turner, A.W. 1949. Bacterial oxidation of arsenite. *Nature* 164, 76–77.
- U.S. Department of Agriculture. 1997. Agricultural chemical usage 1996 field crops summary. National Agricultural Statistics Service Publication.
- van Beek, C.G.E.M., F.A.M. Hettinga, and R. Straatman. 1989. The effects of manure spreading and acid deposition upon groundwater quality in Vierlingsbeek, the Netherlands. *International Association of Hydrologic Sciences Publication*, 155–162.
- Voelker, D.C. 1986. Observation-well network in Illinois, 1984. USGS Open-File Report 86-416.
- Vroblesky, D.A., M.M. Lorah, and J.P. Oliveros. 1989. Ground-water, surface-water, and bottom-sediment contamination in the O-Field Area, Aberdeen Proving Ground, Maryland, and the possible effects of selected remedial actions on ground water. USGS Open-File Report 89-399.
- Wai, C.M., and W.M. Mok. 1989. Distribution and mobilization of arsenic and antimony species in the Coeur D'Alene River system. Technical Completion Report 12-08-0001-G1222-07. Moscow, Idaho: Idaho Water Resources Research Institute.
- Wauchope, R.D. 1983. Uptake, translocation and phytotoxicity of arsenic in plants. In *Arsenic: Industrial, Biomedical, Environmental Perspectives*, ed. W.H. Lederer and R.J. Fensterheim, 348–375. New York; Van Nostrand Reinhold.
- Waychunas, G.A., J.A. Davis, and C.C. Christopher. 1995. Geometry of sorbed arsenate and ferrihydrite and crystalline FeOOH; Re-evaluation of EXAFS results and topological factors in prediction sorbate geometry, and evidence for monodentate complexes. *Geochimica et Cosmochimica Acta* 59, no. 17: 3655–3661.
- Waychunas, G.A., C.C. Fuller, B.A. Rea, and J.A. Davis. 1996. Wide angle X-ray scattering (WAXS) study of “two-line” ferrihydrite structures: Effect of arsenate sorption and counterion variation and comparison with EXAFS results. *Geochimica et Cosmochimica Acta* 60, no. 10: 1765–1781.
- Waychunas, G.A., B.A. Rea, C.C. Fuller, and J.A. Davis. 1993. Surface chemistry of ferrihydrite: Part I. EXAFS studies of the geometry of arsenate adsorption and coprecipitation. *Geochimica et Cosmochimica Acta* 57, no. 10: 2251–2269.
- Webster, J.G. 1990. The solubility of  $As_2S_3$  and speciation of As in dilute and sulphide-bearing fluids at 25 and 90°C. *Geochimica et Cosmochimica Acta* 54, no. 4: 1009–1017.
- Welch, A.H., M.S. Lico, and J.L. Hughes. 1988. Arsenic in ground water of the western United States. *Ground Water* 26, no. 3: 333–347.
- Welch, A.H., and M.S. Lico. 1998. Factors controlling As and U in shallow ground water, southern Carson Desert, Nevada. *Applied Geochemistry* 13, no. 4: 521–539.
- Westjohn, D.B., A. Kolker, W.F. Cannon, and D.F. Sibley. 1998. Arsenic in ground water in the “thumb area” of Michigan. In *The Mississippian Marshall Sandstone Revisited, Michigan: Its Geology and Geologic Resources*, 5th symposium, 24–25. East Lansing, Michigan: Michigan Dept. of Environmental Quality.
- Wilkie, J.A., and J.G. Hering. 1998. Rapid oxidation of geothermal arsenic(III) in streamwaters of the eastern Sierra Nevada. *Environmental Science and Technology* 32, 657–662.
- Wilson, F.H., and D.B. Hawkins. 1978. Arsenic in streams, stream sediments, and ground water, Fairbanks Area, Alaska. *Environmental Geology* 2, no. 4: 195–202.
- Woo, N.C. 1991. Ground water contamination from lead arsenate mixing sites in Door County, Wisconsin. In *Environmental Threats to Wisconsin's Water Resources; Concerns for the Future*, 25. Oshkosh, Wisconsin: American Water Resources Assoc.
- Wood, C.R. 1996. Water quality of large discharges from mines in the anthracite region of eastern Pennsylvania. USGS Water Resources Investigation Report 95-4243.
- Woolsen, E.A., J.H. Axley, and P.C. Kearney. 1971. The chemistry and phytotoxicity of arsenic in soils: I. Contaminated field soils. *Soil Science Society America Proceedings* 35, no. 6: 938–943.
- Woolsen, E.A., J.H. Axley, and P.C. Kearney. 1973. The chemistry and phytotoxicity of arsenic in soils: II. Effects of time and phosphorous. *Soil Science Society America Proceedings* 37, no. 2: 254–259.
- World Health Organization. 1981. Arsenic. *Environmental Health Criteria* 18, 174. Geneva: WHO.
- World Health Organization. 1986. Review of potentially harmful substances—Arsenic, mercury and selenium. Reports and Studies, no. 28: 171. Geneva: WHO.
- World Health Organization. 1996. *Guidelines for Drinking-Water Quality*, Vol. 2, 156–167. Geneva: WHO.
- Yarling, M. 1992. Anomalous concentrations of arsenic in the groundwater at Wakarusa, Indiana: A byproduct of chemical weathering of shales. Indiana Department of Environmental Management.
- Ziegler, A.C., W.C. Wallace, D.W. Blevins, and R.D. Maley. 1993. Occurrence of pesticides, nitrite plus nitrate, arsenic, and iron in water from two reaches of the Missouri River alluvium, northwestern Missouri—July 1988 and June–July 1989. USGS Open-File Report 93-101.
- Zuena, A.J., and P.E. Keane. 1985. Arsenic contamination of private potable wells. In *EPA National Conference on Environmental Engineering Proceedings*, 717–725. Boston, Massachusetts: U.S. EPA.
- Zeman, J., M. Mandl, and P. Mrnustikova. 1995. Oxidation of arsenopyrite by *Thiobacillus ferrooxidans* detected by a mineral electrode. *Biotechnology Techniques* 9, no. 2: 111–116.