

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 ≤ 50 , > 1 to ≤ 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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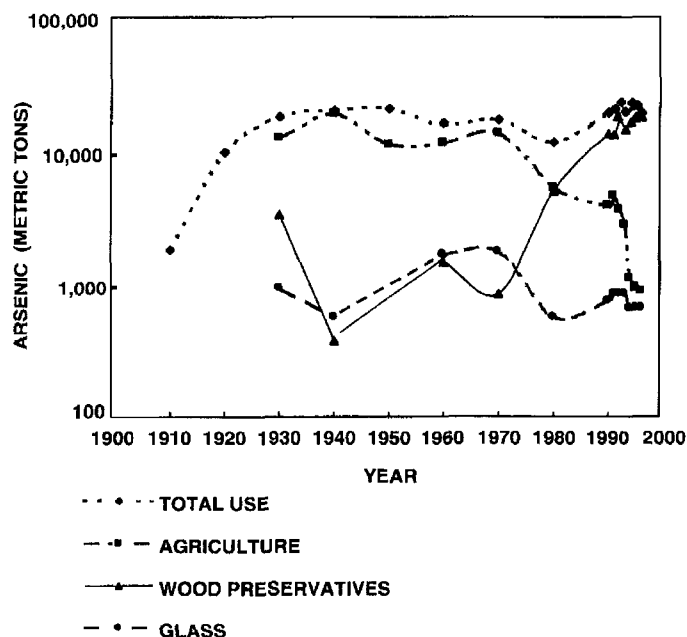


Figure 1. Arsenic use in the United States. Data are from Loebenstein (1994) and Edlestein (1997, 1998).

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

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

²Sites 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
Groundwater Is Affected by Anthropogenic Sources			
Massachusetts	1–11,300	Disposal of arsenical pesticides	A. Davies et al. 1994 ¹
Maryland	Maximum 2240	Disposal of chemical warfare agents	Vroblesky et al. 1989; Nemoff and Vroblesky 1989
Texas	—	Disposal of cotton waste containing arsenical pesticides	Aurelius 1988
Texas	< 50 to < 2,500,000	Disposal of inorganic arsenic pesticides ²	Geraghty & Miller Inc. 1996
Groundwater Does Not Appear to Be Affected by Anthropogenic Sources			
Minnesota (two sites)	General y > 6	As much as 11,500 pounds of PbAsO ₄ 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 ₄ for agricultural use	Woo 1991

¹Also see Aurillo et al. 1994.

²Lee 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-

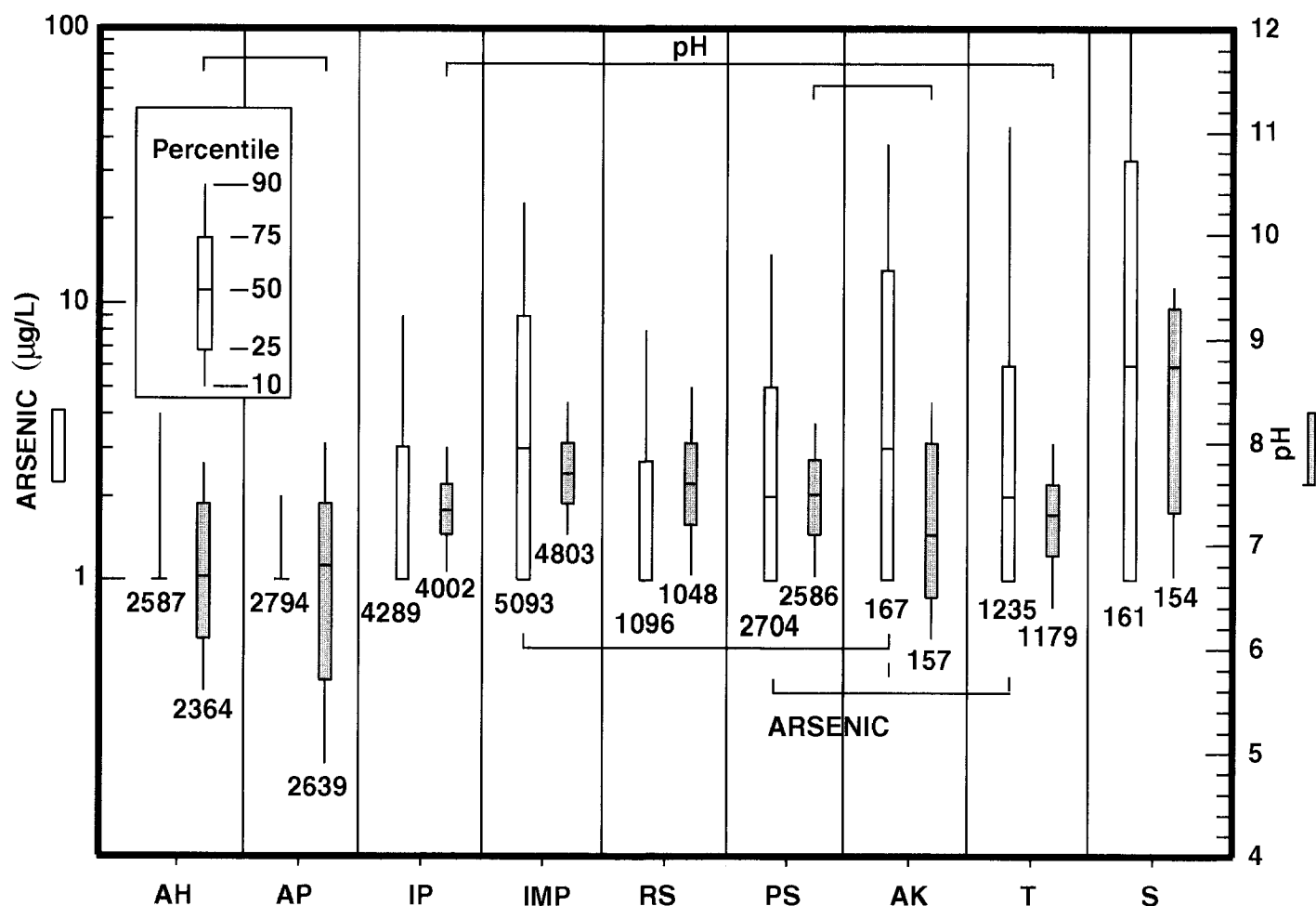


Figure 2. Summary statistics for arsenic and pH in ground water. Physiographic provinces follow Fenneman (1931) except for the inclusion of the Laurentian Upland and Interior Highlands with the Interior Plains, and inclusion of the Caribbean with the Atlantic Plain. The horizontal brackets connect boxplots 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.

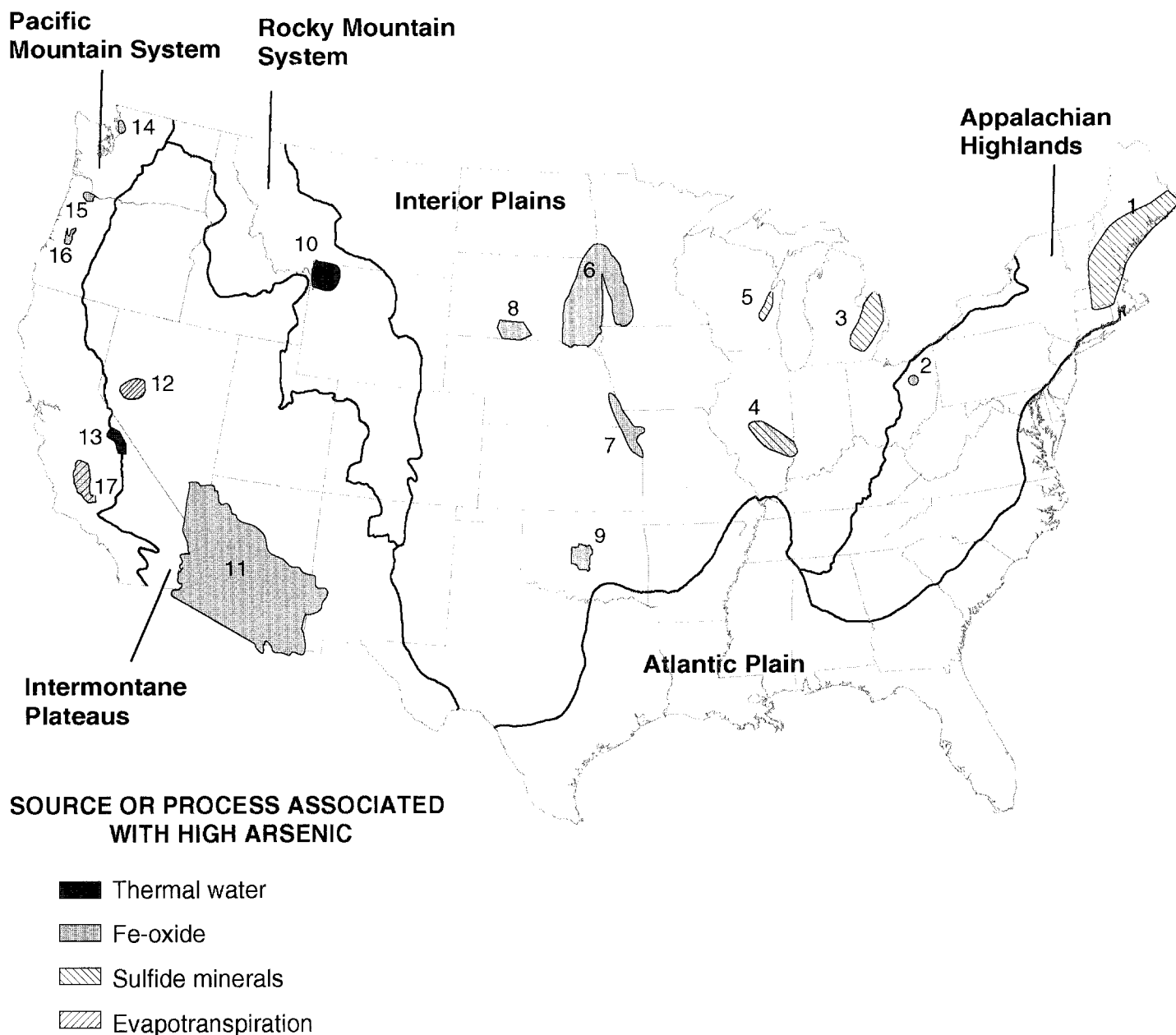


Figure 3. Areas underlain with ground water containing high arsenic concentrations (> 50 mg/L) and known or inferred source or process responsible for the high concentrations.

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 ¹	Hydrologic Units and Number of Area Shown in Figure 3	References
Sulfide minerals	Bedrock (1) ²	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 ³ (3)	Westjohn et al. 1998; Kolker et al. 1998
Fe-oxide (D)	Glacio-fluvial deposits ⁴ (4)	Voelker 1986; Holm and Curtiss 1988; Panno et al. 1994; Holm 1995
Sulfide minerals	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
Fe-oxide (P)	Sandstone and mudstone (9)	Scholttmann and Breit 1992; Norvell 1995
Black shale lithic fragments	Glacio-fluvial deposits	Yarling 1992
Geothermal water	Volcanic rocks (10)	Stauffer and Thompson 1984; Ball et al. 1998
Fe-oxide (P)	Basin fill sediments, including volcanic, alluvial, and lacustrine deposits (11)	Owen-Joyce and Bell 1983; Owen-Joyce 1984; Robertson 1989
Fe-oxide (D, P) and evaporative concentration	Basin fill sediments, including alluvial and lacustrine deposits (12)	Welch and Lico 1998
Geothermal water	Volcanic rocks (13)	Mariner and Willey 1976; Eccles 1976; Wilkie and Hering 1998
Fe-oxide ⁵ (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
Fe-oxide and evaporative concentration	Basin-fill sediments, including alluvial and lacustrine deposits (17)	Fujii and Swain 1995; Swartz 1995; Swartz et al. 1996

¹Known 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.

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

³The 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.

⁴May 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).

⁵Although 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).

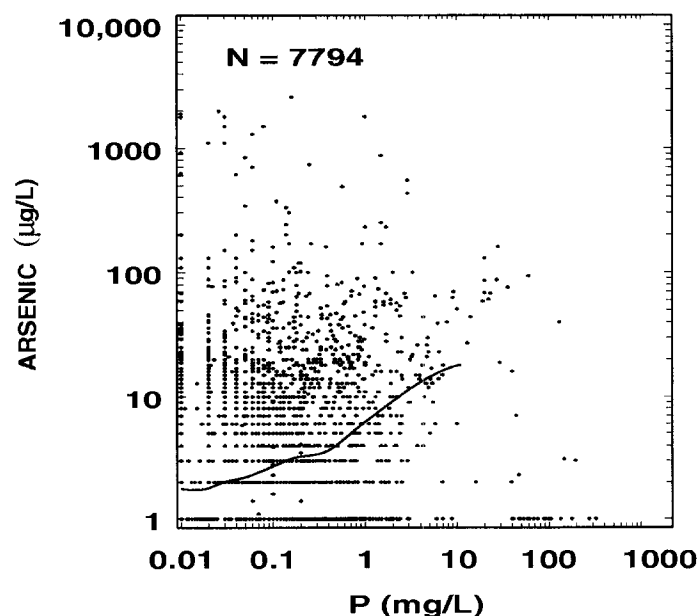
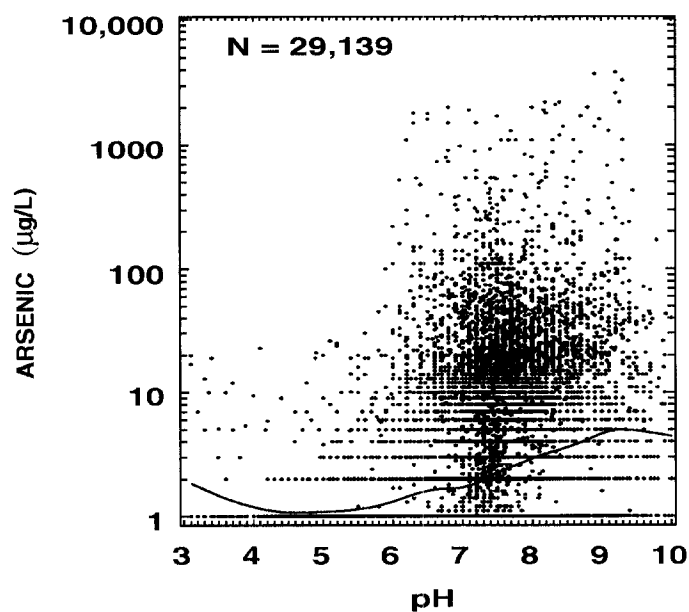


Figure 4. Relation of arsenic with pH and phosphate in ground water. The lines represent a cubic spline fit. The N value indicates the number of data points. The Spearman's ρ (rho; Hollander and Wolf 1973) for arsenic with pH and phosphate are 0.19 and 0.22, respectively. Both rank correlations are highly 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 ²	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 ³
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

¹Rounded to the nearest 0.1.

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

³Also 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 Fouillac 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 H_2S and arsenic concentration in many geothermal systems (Ballantyne and Moore 1988). In low-temperature environments (approximately 25°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 $\text{As}_3\text{O}_3(\text{OH})_3$, $\text{As}_6\text{O}_6(\text{OH})_6$, 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 $\text{Fe}(\text{OH})_3$ is affected by a variety of factors, including pH, the chemistry and amount of $\text{Fe}(\text{OH})_3$ 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 $\text{Fe}(\text{OH})_3$ 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 $\text{Fe}(\text{OH})_3$ (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 $\text{Fe}(\text{OH})_3$ 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 $\text{Fe}(\text{OH})_3$. Each step simulates complete replacement of ground water and equilibration with the oxide. As $\text{Fe}(\text{OH})_3$ 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 $\text{Fe}(\text{OH})_3$ becomes depleted. The constant concentration occurs when the mass of arsenic released from the $\text{Fe}(\text{OH})_3$ 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 $\text{Fe}(\text{OH})_3$ is completely consumed after 50 steps.

The effect of pH on arsenic concentrations is illustrated by comparing simulations of the reaction of $\text{Fe}(\text{OH})_3$ 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 $\text{Fe}(\text{OH})_3$ 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.

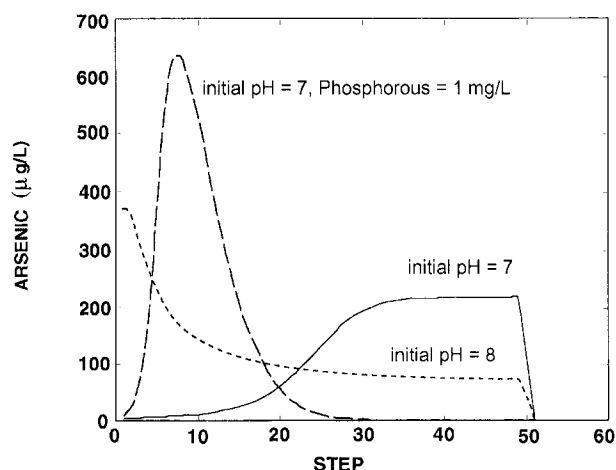


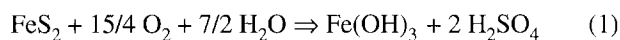
Figure 5. Arsenic associated with dissimilatory reduction of iron oxide. The numerical simulation is described in the appendix. The pH_i indicates the initial pH at the beginning of each simulated reaction step.

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 (FeAsO₄·2H₂O) 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 (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

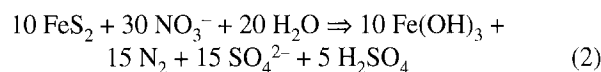


Because arsenic concentrations in pyrite generally range from about 0.02% to 0.5%, and may be as large as 6.5% (Kolker et al. 1998; also see page 16, National Academy of Sciences 1977), this reaction (Equation 1) can release a considerable amount of arsenic to the aqueous phase. The bacteria *Thiobacillus 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

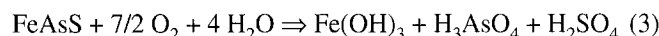
occur only in water with a pH less than 4 (Arkesteyn 1980), except in water with high nitrate concentrations. Sulfide-mineral oxidation in circum-neutral ground water commonly is attributed to abiotic oxidation. Although abiotic oxidation is slow, because bacteria do not catalyze the reaction of dissolved 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 µg/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 µg/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 As₂S₃ 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 (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 ³⁺ 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 ₃ 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_i = 7” in Figure 5. The results labeled “pH_i = 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_i = 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.

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