

ARSENIC: CHEMISTRY, FATE, TOXICITY, AND WASTEWATER TREATMENT OPTIONS

HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
PUBLICATION NUMBER 4676
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Arsenic: Chemistry, Fate, Toxicity, and Wastewater Treatment Options

Health and Environmental Sciences Department

API PUBLICATION NUMBER 4676

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ABSTRACT

Arsenic is a naturally occurring element present in rocks, soils, water, sediments and biological tissues in the parts per billion to parts per million range. It is also present in fossil fuels such as crude oils, shale oils and coal, with concentrations varying largely with the geology of the source. Concentrations in refinery wastewaters are typically below detection levels (e.g., <10 ppb), but can range as high as several hundred ppb. Arsenic in the environment has both anthropogenic and natural sources, and certain anthropogenic sources have caused localized adverse effects on ecological systems and human health. Based on an extensive review of the literature, this monograph is intended to serve as a reference volume on the sources of arsenic in the environment, the chemistry and fate of arsenic compounds, biomedical effects, the toxicity of arsenic to aquatic and terrestrial species, wastewater treatment options, and regulatory standards for arsenic in the environment.



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EXECUTIVE SUMMARY

This monograph is intended to serve as a reference volume for the petroleum industry on the sources, chemistry, fate, biomedical effects, aquatic and terrestrial toxicity, wastewater treatment options, and regulatory standards for arsenic (As) in the environment.

Arsenic is naturally present in each of the environmental media (air, surface and groundwaters, soils, sediments, tissues) as well as in fossil fuels such as coal and crude oils. World production of arsenic trioxide in 1995 was 43,000 metric tons, all of which was produced outside of the United States. Current uses of arsenic compounds include wood preservatives, agricultural chemicals, glass manufacturing, metal alloys, semiconductor materials and medical uses. Specific uses have shifted in recent years, largely as a result of environmental regulations.

Although its poisonous properties have been recognized for thousands of years, there is significant controversy about the risks of low-level arsenic exposure to human health and ecological communities. There is considerable evidence suggesting that arsenic has a nutritional function, but its role as an “essential trace nutrient” has not yet been conclusively demonstrated. Unlike other trace elements that are both highly toxic and essential, arsenic appears to be unique in that the same forms that appear to be essential have also been implicated as carcinogens. The discussion on the biomedical aspects of arsenic exposure emphasizes the current debate over the carcinogenicity of arsenic to human populations. Cancer risk guidelines presently suggest that although arsenic is a carcinogen (via ingestion or inhalation), the response curve is probably non-linear at low concentrations, indicating that there is a “virtually safe dose” below which effects are not expected.

The toxicity of arsenic to ecological receptors is discussed in detail. The discussion includes terrestrial and wetland vegetation, terrestrial wildlife, birds, and aquatic fish and invertebrates. Tables are used to summarize the extensive literature on the acute and chronic toxicity and bioaccumulation of arsenic compounds. The toxicity of arsenic varies among the different chemical forms and the species being evaluated.

Removal of arsenic from wastewaters can be achieved by various techniques including oxidation, precipitation, coprecipitation, adsorption, membrane technologies or ion exchange resins. Only As^{+5} compounds can be separated from the aqueous phase effectively. If As^{+3} is present, it must first be oxidized to As^{+5} before it can be effectively removed from the effluent. The selection of a treatment option(s) will depend upon the concentration of arsenic in the wastewater, the chemical forms of the arsenic, wastewater characteristics (e.g., pH, total dissolved and suspended solids, organic composition), wastewater flow rates, and the effluent limit. The current literature indicates that no single treatment technology is completely suitable for achieving the low arsenic concentrations required in some wastewater permits (<10 ppb).

As a result of the documented adverse effects on human health and aquatic and terrestrial species, arsenic compounds are of concern to many federal and state regulatory agencies. Regulatory standards for arsenic in water, sediments, foods and drugs, sewage sludge, and hazardous wastes are briefly discussed.

Section 1

INTRODUCTION

This monograph presents information on the chemistry, fate and toxicity of arsenic in the environment. It also includes a discussion of treatment options for removing arsenic from petroleum industry wastewaters. Chapter 2 describes the natural and anthropogenic sources of arsenic in the environment (including coal and crude oil), presents data indicating measured concentrations in both pristine and altered systems, and discusses the historic and current uses of arsenic in manufacturing and industry. Chapter 3 addresses the environmental fate and transport of arsenic in the environment with emphasis on water. Chapter 4 reviews the sampling and analysis of environmental samples (air, water, wastewater, sediment, soil, and tissue), and provides information on alternate analytical methods and lower detection levels. Chapters 5 and 6 address toxicological aspects of arsenic. Chapter 5 briefly discusses the toxicology of arsenic to humans. Chapter 6 presents extensive tables and text on the acute and chronic toxicity of arsenic compounds to terrestrial wildlife and plants and aquatic species. Chapter 7 discusses technologies for removing arsenic from waters and wastewaters, and Chapter 8 presents regulatory standards/criteria/guidance values for arsenic in environmental media.

BACKGROUND

Arsenic is naturally present in rocks, soils, water, sediments, and biological tissues in the parts per billion to parts per million range. It has both anthropogenic and natural sources, the atmosphere being the major transport pathway. Anthropogenic inputs in specific areas, however, can be significant and can cause adverse effects on ecological systems and human health. Total arsenic emissions into the atmosphere from anthropogenic sources are of the order of 30,000 tons/year, about 60 percent of which comes from the two major sources—copper smelting and coal combustion. In the United States, anthropogenic sources and concentrations of arsenic have changed substantially over the past 15 years. The sole U.S. arsenic producer ceased operations in 1985. This resulted in complete dependence upon foreign importation of arsenic.

Although its poisonous properties have been recognized for thousands of years, there is significant controversy about the risks of low-level arsenic exposure to human health and ecological communities. Arsenic is the twelfth most abundant mineral in the human body, and there is considerable recent evidence suggesting that arsenic is involved in methionine metabolism and has a nutritional function for several species of research mammals. Its “essentiality” to humans, however, has not been conclusively demonstrated. Unlike other trace elements that appear to be both highly toxic and essential, arsenic appears to be unique in that the same forms that appear to be essential have also been implicated as carcinogens (i.e., tri- and pentavalent oxyarsenical ions).

SCOPE OF THE REVIEW

This monograph is intended to serve as a reference volume on the sources, chemistry, fate, aquatic and terrestrial toxicity, and wastewater treatment options for arsenic. The literature on environmental aspects of arsenic is massive. For example, computerized searches of the key information databases for the term “arsenic” indicated the following numbers of references: BIOSIS Previews (3,524 for the period 1985-96); CA Search (1,529 for 1957-96), Scisearch (5,654 for 1988-96), and U.S. Environmental Protection Agency’s (U.S. EPA’s) AQUIRE database (>1,000). As a result, the reader may need to consult more specific articles, including those that have been cited in text, and referenced at the end of each chapter.

Concentrations are reported throughout this report as they were cited in the original sources. It was not feasible to verify and convert all concentrations to a consistent atomic/formula basis (e.g., mg/kg as As vs. total compound).

Section 2

ENVIRONMENTAL SOURCES AND USES OF ARSENIC

This chapter addresses the natural and anthropogenic sources of arsenic in the environment and discusses the current and historic uses of arsenic in manufacturing and industry. Over the last 10 years, the sources and uses of arsenic in the United States have changed substantially as a result of evolving environmental regulations and improved source controls. As a result, older information may not be accurate, and more contemporary data have not yet been generated.

ENVIRONMENTAL SOURCES AND CONCENTRATIONS OF ARSENIC

Arsenic is naturally present in rocks, soils, water, sediments, and biological tissues at concentrations in the parts per billion (ppb) to parts per million (ppm) range [National Academy of Sciences, (NAS), 1977]. Higher concentrations are associated with igneous and sedimentary rocks, particularly with sulfidic ores. With an average concentration of approximately 3 ppm, arsenic ranks between 20th and 50th among the abundant elements in the earth's crust, depending upon the cited reference. Extensive discussions of the sources, concentrations, and chemical species are presented in NAS (1977), Eisler (1994) and Cullen and Reimer (1989).

Arsenic can exist in four oxidation states: +5, +3, 0, and -3. In water and sediment, arsenic occurs in the two highest oxidation states, +5 and +3. The metallic (0) state occurs in some mineral deposits, and the reduced state (-3) occurs in gaseous arsine (AsH_3) (Callahan *et al.*, 1979).

Air

Arsenic enters the atmosphere from many natural sources (e.g., volcanic activity, wind erosion, volatilization from soils, forest fires, sea spray) and anthropogenic sources (e.g., smelting operations, fossil fuel combustion, herbicide application, burning of arsenic treated wood). These atmospheric sources are balanced by removal processes such as precipitation and dry deposition. Eisler (1994) reported that in general, atmospheric levels of arsenic are higher in

winter because of the increased use of coal for heating. The ratio of natural to anthropogenic inputs is approximately 60:40. The ratio is expected to increase with stricter regulations on anthropogenic sources. (Cullen and Reimer, 1989). Natural sources of atmospheric arsenic are largely due to low temperature volatilization from soils. Data indicate that anthropogenic emissions are dominated by metal production, especially from copper smelting which has accounted for approximately 40 percent of the total anthropogenic emissions (Cullen and Reimer, 1989).

Eisler (1994) reported mean air concentrations of arsenic in remote areas as $<0.021 \mu\text{g}/\text{m}^3$, and 0 to $0.16 \mu\text{g}/\text{m}^3$ in urban areas. Concentrations near smelters were substantially higher, ranging from 0.5 to $1.9 \mu\text{g}/\text{m}^3$. Dust from near a smelter in Tacoma, Washington had concentrations of $1,300 \text{ mg}/\text{kg}$, whereas dust from areas remote from the smelter had arsenic concentrations of $70 \text{ mg}/\text{kg}$. Orchard spraying of lead arsenate resulted in a maximum air concentration of $260,000 \mu\text{g}/\text{m}^3$, and burning arsenic-treated vegetation had a maximum air concentration of $400 \mu\text{g}/\text{m}^3$.

U.S. EPA (1995) compiles air pollutant emission factors for point sources. These emission factors are not regulatory criteria or goals, rather they represent long-term averages for all facilities in a particular source category. Selected emission factors (or ranges) are presented below (Table 2-1). Much more detailed information for other industries and chemicals is presented in U.S. EPA's (1995) AP-42 report.

Arsenic emission factors for coal and oil-fueled electric power generating stations were evaluated by Gratt and Levin (1994). Emission factors from residual oil fueled facilities were estimated to be 0.3 to $5.5 \text{ lbs}/10^{12} \text{ BTUs}$. For coal fired plants, emission factors ranged from 1.1 to $69.1 \text{ lbs}/10^{12} \text{ BTUs}$, depending upon the type of coal and the pollution control system.

Drinking Water

Davis *et al.* (1994) presented results from 140 water utilities throughout the U.S. and reported that 56 percent of the surveyed utilities had arsenic levels $>0.5 \mu\text{g}/\text{L}$, 16 percent had values >2

TABLE 2-1. SELECTED EMISSION FACTORS BY INDUSTRY CATEGORY

Industry Category	Emission Factor	Units
Bituminous coal combustion	231-684	lb/10 ¹² BTU
Anthracite coal combustion	BDL - 2.4 E-04	lb/ton
Uncontrolled lignite combustion	235-2,730	lb/10 ¹² BTU
Fuel oil combustion sources No. 6 oil fired	19-114	lb/10 ¹² BTU
Fuel oil combustion sources Distillate oil fired	4.2	lb/10 ¹² BTU
Wood waste combustion	1.4 E-06 - 2.4 E-04	lb/ton
Waste oil combustion Small boilers	1.1 E-01	lb/1,000 gal
Waste oil combustion Space heaters	2.5 E-03 - 6.0 E-02	lb/1,000 gal

Note: BTU = British thermal unit

BDL = Below detection level

$\mu\text{g/L}$, and 5 percent had values $>5 \mu\text{g/L}$. Utilities using groundwater averaged $2.4 \mu\text{g/L}$ and ranged from <0.5 to $38.6 \mu\text{g/L}$. Utilities using primarily surface water had lower concentrations of arsenic, with an average of $0.6 \mu\text{g/L}$, and a range of <0.5 to $4.6 \mu\text{g/L}$. The survey clearly showed higher arsenic levels in the western and southwestern U.S. compared to areas east of the Mississippi River.

Surface Waters

The concentration of arsenic in freshwaters is highly dependent on the geology of the drainage area and the anthropogenic sources to the watershed. Cullen and Reimer (1989) report dissolved arsenic data for rivers in Europe, and North and South America. The overall geometric mean was 1.4 ppb, with a range of 0.1 to 75 ppb. The North American average was ~ 0.5 ppb. Sixteen California and Florida rivers averaged 2.3 ppb, with a high value of 43 ppb (Cullen and Reimer, 1989). Eisler (1994) reported a range for Lake Superior of 0.1 to $1.6 \mu\text{g/L}$.

Anthropogenic sources, however can greatly increase surface water concentrations. Thornton (1994) reported concentrations in areas of Britain and Wales with significant contamination from the mining industry. Water concentrations in rivers with arsenic-contaminated sediments ranged from 10 to 50 $\mu\text{g-As/L}$, with one tributary exceeding 250 $\mu\text{g/L}$. Searles Lake, California, has a reported range of 198,000 to 243,000 $\mu\text{g/L}$, and Finfeather Lake, Texas had a maximum concentration of 240,000 $\mu\text{g/L}$ (Eisler, 1994).

Oceanic concentrations tend to be less variable than freshwaters. Background concentrations of arsenic from selected saline environments are shown in Table 2-2.

TABLE 2-2. BACKGROUND ARSENIC CONCENTRATIONS REPORTED FROM SALINE WATERS

Location	Reported Concentration (in $\mu\text{g/L}$ unless otherwise specified)	Citation
Worldwide Sea Water	mean = 2 range = 0.15 to 6.0	Eisler, 1994
Deep Pacific and Atlantic Waters	1 to 1.8 ppb	Cullen and Reimer, 1989
Norwegian Fjords	total As = 0.65 to 2.03 trivalent As = 0 to 0.84	Abudullah <i>et al.</i> , 1995
Chesapeake Bay	total As = 0.07 to 0.09	cited in Abudullah <i>et al.</i> , 1995
Loire Estuary	total As = 1.46	cited in Abudullah <i>et al.</i> , 1995
Port Hacking, Australia	total As = 0.97 to 2.40	cited in Abudullah <i>et al.</i> , 1995

Effluents and Wastewaters

As part of U.S. EPA's (1982) program to develop technology-based limits for the petroleum refining industry, the Agency conducted several short-term sampling programs for toxic pollutants. For the refinery effluent "screening program," arsenic was detected at only 4 of the 17 direct discharge facilities. Of the 21 samples from these 17 facilities, all but 2 were $<10 \mu\text{g/L}$. One value was $31 \mu\text{g/L}$ and another was reported as $734 \mu\text{g/L}$. A similar Regional Surveillance and Analysis Dataset (U.S. EPA, 1982) sampled final effluents from seven refineries. Arsenic was detected at only one of the seven refineries, with a range of values of 5 to $28 \mu\text{g/L}$. The predominant source of arsenic in refinery effluents appears to be from crude oil as opposed to process chemicals and catalysts.

Tang *et al.* (1995) investigated concentrations of arsenic and other trace metals that partition into tank bottom waters at petroleum product distribution terminals. The results indicated that arsenic compounds generated in the refining process were highly soluble in water and caustic solutions, and preferentially partitioned from the refined products (primarily catalytic gasoline and alkylate) into the aqueous tank bottoms. Tank bottoms from regular unleaded product tanks contained very high arsenic concentrations (17, 191, and 282 ppm), while the tank bottoms from super-unleaded and regular-leaded tanks were ~ 0.005 and <1 ppb, respectively. The differences in the concentrations were attributed to the blending components, their proportions in the blend, and the actual blending process. Arsenic speciation studies in the tank bottom waters identified monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), arsenite, arsenate, and several other organoarsenic compounds.

Soils and Sediments

Arsenic is ubiquitous in soils, with concentrations reflecting the geology of the region, and in anthropogenic inputs. Arsenic is a constituent of numerous minerals and is found most frequently in association with sulfur, most commonly as arsenopyrite (FeAsS). Inorganic arsenate can also be bound to iron and aluminum cations, or any other cation that may be present (e.g., calcium, zinc, magnesium, lead). Arsenic may also be bound to the organic matter in soils.

The average concentration in the continental crust is 3 ppm (Cullen and Reimer, 1989). NAS (1977) reports that natural, uncontaminated soils vary from 0.1 to 40 ppm with an average of 5 to 6 ppm.

Arsenic in phosphorites ranges from 1 to 180 ppm, with a mean of about 23 ppm (NAS, 1977). Concentration ranges in igneous and sedimentary rocks are 0.4 to 100 ppm. Average concentrations in limestone, sandstone and shales were reported as 1.7, 2.0, and 14.5 ppm, respectively (NAS, 1977). African soils associated with gold deposits contain between 300 and 500 ppm (Cullen and Reimer, 1989).

Highest concentrations are in soils and sediments near anthropogenic sources (e.g., smelters, sites where arsenic pesticides were manufactured and/or sprayed, mining wastes). Surficial soils from the “impacted area” near a smelter which operated in southwest Montana between 1884 and 1980 were sampled more than ten years after operations ceased. Results showed a mean surface concentrations of 408 ppm (0-5 cm depth profile) and 295 ppm (0-15 cm). Concentrations in the site “reference area” had soil concentrations of 90 and 60 ppm for these same two depths (Galbraith *et al.*, 1995). Thornton (1994) investigated contaminated agricultural lands in southwest England and reported concentrations ranging from 60 to 2,500 ppm in soils near upland mining areas compared to “normal” agricultural soil concentrations of 2 to 53 ppm. In the vicinity of roasting ovens and smelter stacks, Thornton (1994) reported surface soil arsenic concentrations as high as 10,000 to 100,000 ppm.

Arsenic concentrations in freshwater and saline sediments are much higher than in overlying waters. Long and Morgan (1990) evaluated NOAA’s National Status and Trends Program database for sediments throughout the U.S. to determine concentrations associated with biological effects. Arsenic concentrations ranged from 1 to 2,257 ppm. Sediment arsenic concentrations reported from different areas of the world are presented in Table 2-3.

TABLE 2-3. SEDIMENT CONCENTRATIONS OF ARSENIC

Locations	Reported As Concentration (in dry weight)	Citation
19 Estuaries in the UK	4.8 to 1,740 ppm dry weight most were <50 ppm dry weight	Bryan and Langston, 1992
England and Wales	5 to 15 ppm	Thornton, 1994
Puget Sound, WA	22 to 1,005 ppm	Long and Morgan, 1990
San Francisco Bay, CA	10 to 70 ppm	Long and Morgan, 1990
Newport, RI	2.8 ppm	Long and Morgan, 1990
Trinity River, TX	2.2 to 3.4 ppm	Long and Morgan, 1990
Baltimore Harbor, MD	32 to 92 ppm	Long and Morgan, 1990
Kishwaukee River, IL	3.7 to 5 ppm	Long and Morgan, 1990

Fossil Fuels

Cullen and Reimer (1989) reported that the mean arsenic content of bituminous coals in the U.S. was 150 ppm, and the average concentration of 799 different coals of varying types was 15 ppm.

Shale oil typically contains between 10 and 100 ppm of arsenic as oxides and organic complexes. Such levels can be a problem because at concentrations greater than ~1 ppm, arsenic poisons downstream catalysts used to upgrade the quality of the oil (Singhal *et al.*, 1994). Tang *et al.* (1994) reviewed the literature on shale oil production and concluded that although arsenic was distributed over a wide range of boiling points, the highest concentrations were found in fractions derived from the higher distillation temperatures (i.e., the higher molecular weight fractions). Concentrations in the shale oil, naptha, light distillate, heavy distillate, and residuum were 4.6, below detection level (<DL), 1.4, 4.4, and 12 ppm, respectively. Arsenic in the ppm level was determined in the oil shale retort waters (Tang *et al.*, 1994).

The concentration of arsenic in crude oils can approach the low parts per million level, but more typically it is in the parts per billion range (Hofstader, 1976). Cullen and Reimer (1989) present

an average value of 0.015 ppm, although higher averages (up to 0.263 ppm) are quoted. Davis and Associates (1968) obtained analyses of 110 oils and reported an average concentration of 0.042 ppm, or about 5.2 kg/million barrels. Reported concentrations of arsenic in different types of crude oils are summarized in Table 2-4.

TABLE 2-4. ARSENIC CONTENT IN DIFFERENT CRUDE OILS

Type of Crude	Arsenic Concentration (ppm)	Citation
US (median concentration)	<0.03	Kirk-Othmer, 1981
Alamein	0.0024	Tang <i>et al.</i> , 1994
Alberta	0.0024 to 0.111	Tang <i>et al.</i> , 1994
California	0.063 to 1.112	Tang <i>et al.</i> , 1994
Libya	0.077 to 0.343	Tang <i>et al.</i> , 1994
Louisiana	0.046	Tang <i>et al.</i> , 1994
Venezuela	0.02 to 0.284	Tang <i>et al.</i> , 1994
Wyoming	0.111	Tang <i>et al.</i> , 1994

Filby (1975) examined trace metals in crude oils by using distilled water to extract metals from a California crude. In a 1:1 crude/water extraction, 37 percent of the arsenic (by weight) was extracted to the water phase. Filby (1975) also studied the distribution of trace metals in a California tertiary oil which was separated into asphaltene, resin, and methanol soluble fractions. The study showed that 59 percent of the arsenic was associated in the methanol soluble fraction, 20 percent in the resin, and 21 percent in the asphaltene.

Tang *et al.* (1995) also reviewed the literature on the distribution of trace metals in crude oil and several distillation products. For a Venezuelan crude, the raw crude contained 20 ppm arsenic, and about 15 percent of this was removed by the desalting treatment process. The distribution of arsenic in the eight distillation fractions increased with increasing average molecular weight (MW). More specifically, 65 percent of the arsenic was in the pitch (MW >1,000), 28 percent was in the heavy vacuum oil (MW 580), and only 4 percent was in the light vacuum oil (MW 350).

As noted by Tang *et al.* (1995), very little information is available in the literature on the concentrations of arsenic in refined petroleum products. Regular and premium gasoline “contained almost non-detectable arsenic” (~5 ppb) and one fuel oil had 58 ppb. No arsenic data were reported for jet fuel (type A) or aviation gas. Finished and unfinished diesel oil contained 20 to 40 ppb arsenic.

Hosterman *et al.* (1990) evaluated 27 samples from natural bitumen and heavy oil deposits for 40 different trace elements. Collected from the U.S. and several other western hemisphere countries, the range of arsenic concentrations in the reservoir rock was 0.128 to 16.2 ppm, the sediment residue ranged from 0.058 to 17.1 ppm, and the bitumen or heavy oil ranged from 0.039 to 22.0 ppm.

ROLE OF ARSENIC IN MANUFACTURING AND INDUSTRY

Historic uses of arsenic have been extremely diverse and have changed significantly in recent years. This change is a result of a better understanding of the uses of arsenic, the development of alternate products, and much stricter environmental regulations. For example, during the 1980s, the primary market for arsenicals shifted from cotton farming where its use is now restricted, to the production of wood preservatives (primarily chromated arsenate). The production and uses of arsenic are discussed below.

Production of Arsenic

World production of arsenic trioxide in 1995 was 43,000 metric tons, and world reserves are believed to be 20 to 30 times annual world production (USGS, 1996). The largest producers of arsenic trioxide were China (13,000 metric tons), Chile (6,300), France (6,000), and Mexico (4,400). Other major producers were Namibia, Belgium, Phillippines, Russia, Kazakstan, and Ghana.

In 1985, the sole U.S. producer of arsenic (the ASARCO smelter located in Tacoma, WA) ceased operation, resulting in complete dependence on foreign imports. Annual import data collected by

the U.S. Geologic Survey are summarized in Table 2–5 below (USGS, 1996). In recent years, most of the imported arsenic trioxide was used for the production of wood preservatives, primarily chromated copper arsenate (CCA). The remainder was used in glass manufacturing, agricultural chemicals, nonferrous alloys, the semiconductor industry, and other miscellaneous applications. Each of these is discussed below.

TABLE 2-5. SUMMARY OF USGS ANNUAL IMPORT DATA, 1991-1995

U.S. Imports (values in metric tons)	1991	1992	1993	1994	1995
Arsenic Metal	1,010	740	767	1,330	800
Arsenic Trioxide	27,100	30,700	27,500	27,500	31,000
Arsenic Compounds	374	40	--	5	350

Wood Preservatives

According to recent USGS (1996) data, approximately 80 percent of the imported arsenic trioxide is used in the formulation of wood preservatives. Three principal U.S. manufacturers of wood preservatives consume most of the arsenic trioxide for the production of arsenic acid, which is then used to produce chromated copper arsenate ($\text{CrO}_3 \cdot \text{CuO} \cdot \text{As}_2\text{O}_5$) for treating lumber and other wood products (e.g., telephone poles and railroad ties).

Agricultural Uses

Agricultural uses of arsenic products have changed considerably in recent years. Monosodium methanearsonate (MSMA), disodium methanearsonate (DSMA), and cacodylic acid are used as post-emergence herbicides for the control of Johnson and nutsedge grass and other weeds (primarily in cotton fields). Arsenic acid and cacodylic acid are used as desiccants to defoliate the cotton boll before harvesting. Calcium arsenate was once used extensively for the control of the boll weevil and cotton worm but is no longer used. Though its use is restricted by regulation, lead arsenate is still applied as a pesticide on fruit crops (Kirk-Othmer, 1992). Lead arsenate is used to control codling moths, plum curculio, cabbage worms, potato bugs, and tobacco hornworms (Tamaki and Frankenberger, 1992). As a feed additive, arsanilic acid and Roxarsone

are used to improve feeding efficiency in chickens and swine, and to control swine dysentery. Carbarsone and nitarsones are used as antihistomonads in turkeys (Tamaki and Frankenberger, 1992). Sodium arsenite is also used for cattle and sheep dips.

Glass Manufacturing

Nearly all glass contains small quantities of arsenic as an additive (NAS, 1977). Refined arsenic trioxide (>99% pure) was used in glass manufacturing as a decolorizer and fining agent for removing gasses during the production of bottleglass and other types of glassware, but has been replaced by arsenic acid (Kirk-Othmer, 1992).

Metal Alloys

Because of its semi-metallic properties, arsenic is used in small quantities to create metal alloys, primarily in combination with lead, and to a lesser extent, copper. Trace quantities are added to lead-antimony grid alloys that are used in lead-acid batteries to minimize the self-discharging characteristic of these batteries (Kirk-Othmer, 1992). Arsenic additions of up to 3 percent to lead-based bearing alloys improves their mechanical properties, particularly at high temperatures. Arsenic is also used to increase hardness and castability, and can create a desirable fine-grain effect in electrotpe metal without affecting hardness or ductility. It has also been used to improve the sphericity of lead shot used in ammunition. Added to copper and copper alloys, arsenic raises the recrystallization temperature and resistance to corrosion. Arsenical copper is also used for heat exchangers and condenser tubes (Kirk-Othmer, 1992).

Semiconductor Industry

About 15 tons of very high purity (>99.99%) arsenic was consumed in the manufacture of semiconductor materials in 1995 (USGS, 1996). When alloyed with aluminum, gallium, and indium, high purity arsenic forms important semiconductor compounds, including aluminum arsenide, gallium arsenide, and indium arsenide. Gallium arsenide is used in diodes, transistors, high efficiency solar cells, integrated circuits, microwave devices, fiber optics, and lasers. High purity arsenic is also used in the manufacture of photoreceptor arsenic-selenium alloys for plain paper copiers (Kirk-Othmer, 1992).

Medical Uses

Arsenic compounds have been used in medicines for more than 2,000 years. Modern studies of arsenical drugs began in 1905 when it was determined that Atoxyl could cure trypanosomiasis, and subsequent experimentation led to several drugs that could cure syphilis. By 1932, it is estimated that 12,500 arsenic compounds had been synthesized by medical researchers, and some had been clinically tested. Further research was virtually abandoned when it was determined that penicillin was a more effective therapy for syphilis (Kirk-Othmer, 1992). Although no new arsenical drug has been introduced in recent years, arsenicals such as Melarsoprol are still important in the treatment of African trypanosomiasis. In veterinary medicine, arsenamide is an important drug for the treatment of adult heartworms.

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Section 3

ENVIRONMENTAL FATE AND TRANSPORT OF ARSENIC

This section discusses the speciation of arsenic and the chemical and physical processes affecting speciation and concentration – oxidation, reduction, biomethylation, coprecipitation, and sorption. Separate subsections are devoted to fate and transport in water, sediment, and air.

The fate of arsenic in the natural environment, including the atmosphere, aquatic and terrestrial systems, and organisms, was reviewed comprehensively by Cullen and Reimer (1989). Much of the information summarized in this chapter comes from that review and earlier reviews by McComish and Ong (1988), Callahan *et al.* (1979), the National Academy of Sciences (1977), and Ferguson and Gavis (1972), plus several papers in Nriagu (1994). Additional illustrative material has been added from papers published after those reviews.

PHYSICAL AND CHEMICAL PROPERTIES OF ARSENIC

Arsenic (atomic number 33) is the third member of group V_A of the periodic table of elements. The other members (with their atomic number) are nitrogen (7), phosphorus (15), antimony (51), and bismuth (83). The stable elemental form of arsenic is a steel gray, brittle, crystalline, semimetallic solid (Weast, 1986). Its physical properties (Weast, 1986) are:

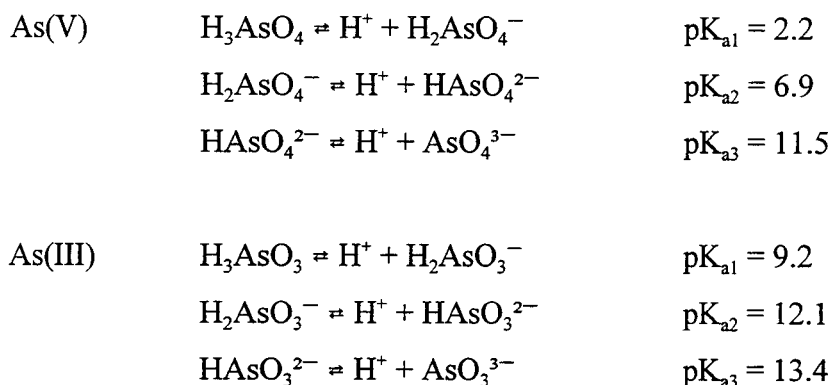
Atomic weight	74.91
Specific gravity	5.72
Melting point	817°C at 28 atm
Boiling point	613°C (sublimes)

ARSENIC IN WATER

Speciation

In the aquatic environment, arsenic occurs in the two highest oxidation states: +5 and +3. The pentavalent form of inorganic arsenic, As(V), exists as one of the protonated forms of arsenic

acid (often collectively referred to as arsenate), and the trivalent form, As(III), occurs as arsenious acid (often referred to as arsenite) (Cullen and Reimer, 1989):



At 25°C, equal concentrations of the two forms of arsenic on both sides of the equilibrium equation will exist at a pH equal to the pK_{a} . At pH levels below the pK_{a} value, the arsenic form on the left side of the equation dominates, and at pH levels above the pK_{a} value, the arsenic form on the right side of the equation dominates. Therefore, for As(V) at pH values typical of fresh water, 5–9, H_2AsO_4^- predominates below pH 6.9 and HAsO_4^{2-} above 6.9. For As(III), H_3AsO_3 is the dominant form over the entire range of normal pH.

Two organic forms of pentavalent arsenic often found in natural water are monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) (Aurilio *et al.*, 1994):

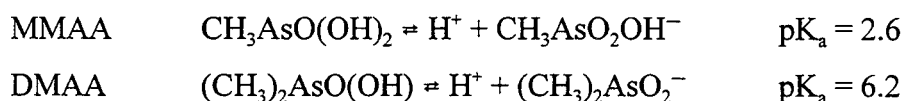


Table 3-1 lists numerous other organoarsenicals that have been found in tissue and, in some cases, water or sediment.

TABLE 3-1. DISTRIBUTION AND PROPERTIES OF ENVIRONMENTALLY IMPORTANT ORGANOARSENICALS^(a)

Compound	Occurrence	Comments
Monomethylarsonic acid $\text{CH}_3\text{AsO}(\text{OH})_2$ (MMAA)	Both	Stable and water soluble, easily detected, can be reduced to CH_3AsH_2 , and reacts with RSH to give $\text{CH}_3\text{As}(\text{SR})_2$; $\text{pK}_a = 3.6, 8.2$
Dimethylarsinic acid $(\text{CH}_3)_2\text{AsO}(\text{OH})$ (DMAA)	Both	Stable and water soluble, easily detected by conventional methods, can be reduced to $(\text{CH}_3)_2\text{AsH}$, and reacts with RSH to give $(\text{CH}_3)_2\text{As}(\text{SR})$; $\text{pK}_a = 6.2$
Trimethylarsine oxide $(\text{CH}_3)_3\text{AsO}$	Both	Limited detection in environment may be due to facile reduction to $(\text{CH}_3)_3\text{As}$; reacts with H_2S to give $(\text{CH}_3)_3\text{AsS}$
Tetramethylarsonium ion $(\text{CH}_3)_4\text{As}^+$	Tissue	Has only been found in tissues to date, but is likely to be more widely distributed
Arsine AsH_3	Environment	Oxidized to AsO_4^{3-} or $\text{As}_2\text{O}_5(\text{s})$; limited observation in environment
Monomethylarsine CH_3AsH_2	Environment	Easily oxidized to $\text{CH}_3\text{AsO}(\text{OH})_2$
Dimethylarsine $(\text{CH}_3)_2\text{AsH}$	Environment	Easily oxidized to $(\text{CH}_3)_2\text{AsO}(\text{OH})$
Trimethylarsine $(\text{CH}_3)_3\text{As}$	Environment	Easily oxidized to $(\text{CH}_3)_3\text{AsO}$ and $(\text{CH}_3)_2\text{AsO}(\text{OH})$; may escape detection by some analytical procedures
$(\text{CH}_3)_2\text{AsSR}$	Not yet observed	May be formed in anoxic soils and sediments; reacts with O_2 to give $(\text{CH}_3)_2\text{AsO}(\text{OH})$
$\text{CH}_3\text{As}(\text{SR})_2$	Not yet observed	May be formed in anoxic soils and sediments; reacts with O_2 to give $\text{CH}_3\text{AsO}(\text{OH})_2$
Arsenocholine $(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{CH}_2\text{OH}$	Tissue	Easily converted to arsenobetaine
Arsenobetaine $(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{CH}_2\text{COO}^-$	Tissue	Has been found, and is the most abundant arsenical, in most marine animals so far investigated; can give $(\text{CH}_3)_3\text{AsO}$ and $(\text{CH}_3)_2\text{AsO}(\text{OH})$ on reaction with base
Arsenosugars	Tissue	Found mainly in algae, stable at neutral pH, and react with acid/base to give $(\text{CH}_3)_2\text{AsO}(\text{OH})$

^(a) Adapted from Cullen and Reimer (1989)

Thermodynamic stability for arsenic in fresh water at 25 °C is illustrated in Figure 3–1.¹ The total dissolved arsenic concentration is 50 µg/L (0.68 µM). For oxic water, with typical pE values of 5–8 and pH values of 5–9, the arsenic acid [As(V)] species H_2AsO_4^- and HAsO_4^{2-} are thermodynamically stable. Arsenious acid [As(III)] only becomes stable as HAsO_3^{2-} under low pH, reducing (low pE) conditions.

Because arsenic forms anions with oxygen, it does not form complexes with other aqueous anions, such as carbonate or sulfate, as many other trace elements do. Significant ion pairing with calcium and magnesium in seawater has been reported (Cullen and Reimer, 1989).

When sulfide is introduced into the thermodynamic calculations, the pE-pH diagram changes for the reducing conditions, as shown in Figure 3–2 for a sulfide concentration of 32 µg/L (1 µM). At low pH and low pE, the solids orpiment (As_2S_3) and realgar (AsS) become stable, as indicated by the dashed lines in Figure 3–2. At higher pH levels in reducing conditions, dissolved As(III) is stable in the form of thioarsenite, AsS_3^{3-} .

The natural world is not at thermodynamic equilibrium. Although As(V) dominates over As(III) in oxic water, it does not do so to the extent predicted by thermodynamics. Cullen and Reimer (1989) reported that, based on the thermodynamic equations, As(V)/As(III) ratios should be 10^{15} to 10^{26} in seawater, which would make As(III) species undetectable. However, As(III) is routinely found in most natural waters. Even in oxic water, As(III) can be found at concentrations that equal as much as 50 percent of As(V), i.e., $\text{As(V)}/\text{As(III)} = 2$. This deviation from the theoretical predictions of thermodynamics results from very slow kinetics and biological mediation, which are discussed further in the section on [Fate and Transport](#)

¹pE-pH diagrams show the combined effects of oxidation-reduction reactions, acid-base equilibria, and solubility on the thermodynamic stability of the chemical species that an element may form. pE (the negative logarithm of electron activity) is a measure of the availability of electrons in solution, just as pH (the negative logarithm of hydrogen ion activity) is a measure of the availability of protons in solution. High pE values reflect oxidizing conditions and low pE values reducing conditions. Although pE-pH diagrams are useful for understanding the thermodynamic tendency of a defined system, they may not accurately represent natural conditions because of reaction kinetics and biological mediation.

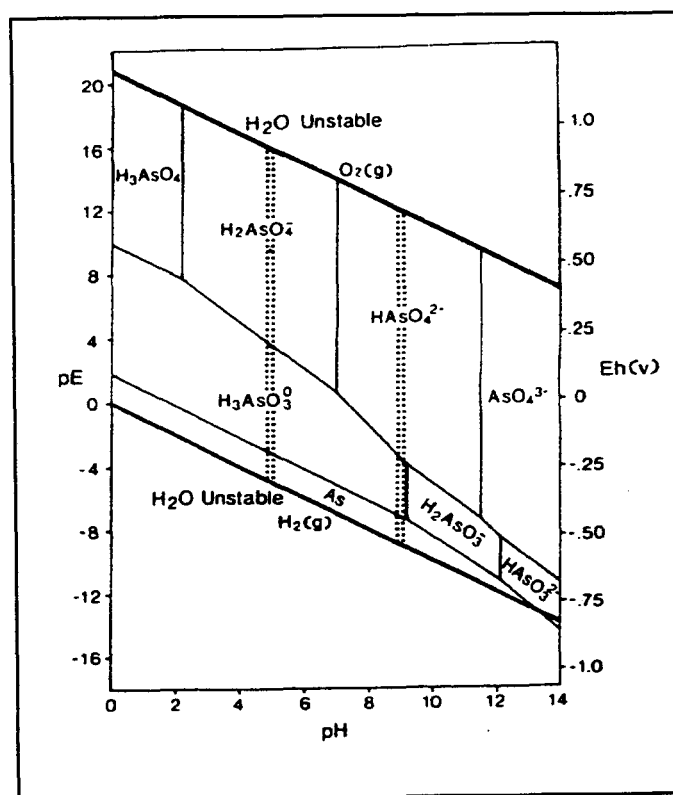


Figure 3-1. pE-pH diagram for the As-H₂O system at 25°C. (Total dissolved arsenic = 50 µg/L.) Reprinted from Cullen and Reimer, 1989 with kind permission from Elsevier Science-NL, Sara Burgerhartstraat 25, 1055 KV, Amsterdam, The Netherlands.

Conversely, in anoxic water where As(III) should dominate, appreciable concentrations of As(V) are usually found (e.g., Peterson and Carpenter, 1983; Abdullah *et al.*, 1995).

Fate and Transport

The primary chemical and physical processes affecting arsenic in water are reduction of As(V) to As(III), oxidation of As(III) to As(V), biomethylation, coprecipitation with iron or manganese hydroxides, and sorption. Each of these processes is discussed in this section. Photolysis is of importance only to the extent that it may increase oxidation, and volatilization is not important for the arsenic species commonly found in water.

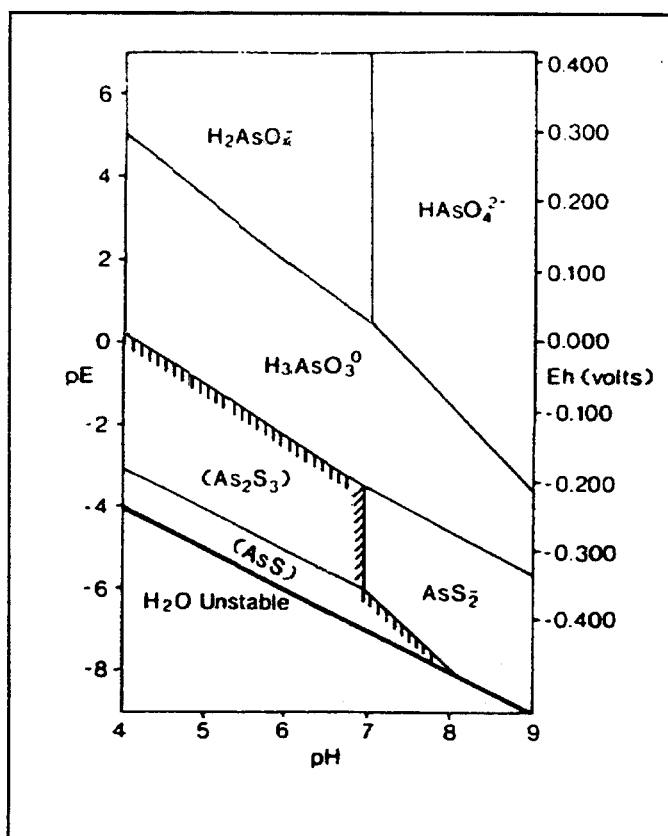


Figure 3-2. pE–pH diagram for the As–S–H₂O system at 25°C. (Total dissolved arsenic = 50 µg/L; total dissolved S = 32 µg/L.) Reprinted from Cullen and Reimer, 1989 with kind permission from Elsevier Science-NL, Sara Burgerhartstraat 25, 1055 KV, Amsterdam, The Netherlands.

Reduction. As(V) is generally the most prevalent form of arsenic in water, but it is reduced to As(III) under anoxic conditions such as lake hypolimnia (Anderson and Bruland, 1991; Aurilio *et al.*, 1994) and deep ocean waters (Abdullah *et al.*, 1995; Peterson and Carpenter, 1983).

However, As(V) can remain as the predominant arsenic species in anoxic water for long periods because bacterially mediated reduction or chemical reduction is kinetically slow. The rate of reduction of As(V) to As(III) estimated by several investigators is summarized in Table 3–2.

As(V) concentrations in the anoxic hypolimnion of Upper Mystic Lake (Massachusetts) were found to increase during stratification in 1992, which was attributed to the release of As(V) from

sediment at faster rates than chemical/biological reduction in the water column could convert it to As(III) (Aurilio *et al.*, 1994). In the following year, however, when sulfide was detected at the bottom of the hypolimnion toward the end of stratification (no sulfide was detected in 1992), total arsenic concentrations in the hypolimnion were an order of magnitude higher, and As(III) accounted for about 60 percent of the total (Spliethoff *et al.*, 1995). Release of As(III) from the completely anoxic sediments was postulated to account for the increase in As(III) and total arsenic. From anoxic sediments of the watershed upstream of Upper Mystic Lake, Ahmann *et al.* (1994) isolated a vibrio-shaped microorganism that reduces As(V) to As(III) and uses the energy for growth.

Appreciable amounts of As(III) can also occur in oxic water where As(V) is the thermodynamically stable form and there are no external sources of As(III). The presence of As(III) in oxic water is attributed to biologically mediated reduction by a variety of phytoplankton and bacteria (Aurilio *et al.*, 1994; Cullen and Reimer, 1989; Sanders *et al.*, 1994). Dissolved arsenic in the surface water of Lake Greifen (Switzerland) in late summer was 100 percent As(III), which was attributed to uptake of As(V) and production of As(III) by phytoplankton and slow oxidation of As(III) remaining after the bloom dissipated (Kuhn and Sigg, 1993).

Oxidation. As(III) is oxidized slowly to the more stable As(V) in oxic water (Table 3–2).

Research has shown that oxidation in estuarine water occurred five times faster in the presence of bacteria. Oxidation rate increases with initial arsenite concentration, temperature, and salinity. In solutions exposed to sunlight, the oxidation rate increased 5–10 times (Cullen and Reimer, 1989).

As(III) is oxidized chemically by Mn(IV) and Fe(III) oxides (Oscarson *et al.*, 1981; De Vitre *et al.*, 1991). Kuhn and Sigg (1993) attributed the oxidation of As(III) in the anoxic hypolimnion of Lake Greifen to chemical oxidation by manganese oxides.

TABLE 3-2. OXIDATION, REDUCTION, AND METHYLATION RATES

Water Source	Rate ($\mu\text{g/L/day}$)	Rate (% of Total As/day)	Reference
Reduction of As(V) to As(III)			
Upper Mystic Lake (Mass.) (<i>in situ</i>)	0.009 $\pm$ 0.003	0.5	Aurilio <i>et al.</i> (1994)
<i>Skeletonema costatum</i> (<i>in vitro</i>)		11.4 (log growth phase)	Cullen and Reimer (1989)
Patuxent River (Md.) (<i>in situ</i>)	0.13 $\rightarrow$ 0.33		Cullen and Reimer (1989)
Black Sea (<i>in situ</i>)	0.0056		Cutter (1992)
Oxidation of As(III) to As(V)			
Upper Mystic Lake (Mass.) (<i>in situ</i>)	0.019–0.023	2	Aurilio <i>et al.</i> (1994)
Distilled water		1.4	Cullen and Reimer (1989)
Filtered seawater, Saanich Inlet (British Columbia)	0.003 (antibiotics) 0.024 (no antibiotics)	1.6 14	Peterson and Carpenter (1983)
Narragansett Bay (R.I.) (<i>in vitro</i>)	0.023 (sterile) 0.11 (with bacteria)	5 25	Cullen and Reimer (1989)
Methylation of As(V) to DMAA			
Upper Mystic Lake (Mass.) (<i>in situ</i>)	0.011 $\pm$ 0.002	0.6	Aurilio <i>et al.</i> (1994)
<i>Skeletonema costatum</i> (<i>in vitro</i>)		1.5 (log growth phase)	Cullen and Reimer (1989)
Demethylation of DMAA to As(V)			
Davis Creek Reservoir (Calif.) (<i>in vitro</i>)	Anoxic: 0.0063–0.0085 Oxic: >0.029	Anoxic: 1.1–1.4 Oxic: >7	Anderson and Bruland (1991)
Mixed estuarine bacterial cultures (<i>in vitro</i>)	0.001		Cullen and Reimer (1989)

Biomethylation. After methods were developed to separate and measure the methylarsenicals, MMAA (0.08–0.15 $\mu\text{g/L}$) and DMAA (0.02 $\mu\text{g/L}$) were found in surface water of the Pacific Ocean, but not in deeper water. Since then, the two compounds have been found widely in surface waters. Increased MMAA and DMAA concentrations have been associated with phytoplankton blooms, and the production of methylarsenic compounds from As(V) has been demonstrated in phytoplankton cultures (Anderson and Bruland, 1991; Aurilio *et al.*, 1994; Cullen and Reimer, 1989; Sanders *et al.*, 1994). However, methylarsenicals are not found in all estuaries during phytoplankton blooms, which has been attributed to the absence of species with the ability to methylate arsenic (Sanders *et al.*, 1994).

When present, DMAA typically accounts for 10 to 20 percent of the total dissolved arsenic, and MMAA is usually present at 10 percent or less of the concentration of DMAA (Cullen and Reimer, 1989). In contrast to this generalization, proportions of DMAA as high as 60 percent of total arsenic have been reported in California lakes sampled by Anderson and Bruland (1991). In a 13-month monitoring program on the estuarine Patuxent River, Maryland, DMAA was the predominant form of arsenic in 2 of the months, whereas inorganic forms predominated in the other 11 months. MMAA concentrations were equal to or greater than DMAA concentrations in 5 of the months (Sanders *et al.*, 1994).

MMAA and DMAA are stable in sterile water, but are slowly demethylated to HAsO_4^{2-} by bacteria (Table 3–2). Demethylation may explain the virtual absence of methylarsenicals in water below the photic zone. Methylarsenicals could be transported below the photic zone by mixing of the water column and sinking of phytoplankton, but they could not be produced there.

Coprecipitation. Under oxic conditions, dissolved Fe(II) and Mn(II) are oxidized to Fe(III) and Mn(IV) and precipitate as oxyhydroxides. Several dissolved elements, including arsenic, can be incorporated in the precipitate and thereby removed from the water column. Iron oxyhydroxide precipitation is particularly important in estuaries at the saltwater interface, and coprecipitation of arsenic has been postulated as an explanation for the nonconservative behavior of arsenic in

some estuaries (Howard *et al.*, 1984). In estuaries where conservation of dissolved arsenic has been found, the formation of arsenic-organic matter complexes has been proposed as a competing mechanism for coprecipitation with iron or manganese (Waslenchuk and Windom, 1978). Anderson and Bruland (1991) attributed increased dissolved arsenic in an anoxic hypolimnion to release of arsenic concurrently with reduction and dissolution of iron and manganese oxyhydroxides. Seyler and Martin (1989) also proposed the coprecipitation of arsenic with iron sulfide to form arsenopyrite (FeAsS) in anoxic water at the bottom of a 90-m deep French lake.

Sorption. Studies on the adsorption of arsenic to aluminum and iron oxyhydroxides as well as other particles—carbon, organic matter, and various soils and sediments—have been summarized by Bhumbra and Keefer (1994), Huang (1994), and Mok and Wai (1994). Sorption constants for arsenic on soils and sediments have been compiled by McComish and Ong (1988). Prasad (1994) discusses three models for describing the adsorption of arsenic.

Generally, sorption maxima for As(V) occur at neutral or acidic pH (Jekel, 1994; Pierce and Moore, 1982; Prasad, 1994). Maximum adsorption of As(V) occurred on iron oxyhydroxides at pH 4–7, depending on initial arsenic concentration; on kaolinite and montmorillonite at pH 5; on alumina at pH 5.5–6; on hematite (Fe_2O_3) at pH 4.2; on feldspar (SiO_2 , Al_2O_3) at pH 6.2; and on alumina, bauxite, and carbon at pH 7. Iron oxyhydroxides have a zero point of charge of pH 8.6, and aluminum oxyhydroxides have a zero point of charge of pH 8.5 (Mok and Wai, 1994). These solids, therefore, have a net positive charge at acid and neutral pH and preferentially adsorb anions such as H_2AsO_4^- and HAsO_4^{2-} . Manganese oxyhydroxides, with a zero point of charge of 2.3 (Mok and Wai, 1994), have a net negative surface charge at typical aquatic pH levels. However, they may develop a positive surface charge by adsorbing other divalent cations and, therefore, still have the ability to adsorb arsenic at natural circumneutral pH.

Anions can compete with arsenic for adsorption sites (Bhumbra and Keefer, 1994). Phosphate can displace As(V) or As(III) from aluminum and iron oxyhydroxides and suppress arsenic

adsorption by soils. The order of effectiveness for anion competition is $\text{H}_2\text{PO}_4^- > \text{H}_2\text{AsO}_4^- > \text{SO}_4^{2-} > \text{CO}_3^{2-}$ for As(V) and $\text{H}_2\text{PO}_4^- > \text{H}_3\text{AsO}_3 > \text{F}^- > \text{SO}_4^{2-} > \text{CO}_3^{2-}$ for As(III).

In the bottom of the upper layer of a deep crater lake, Seyler and Martin (1989) observed simultaneous decreases in Fe(III) and As(V) concentrations, while As(III) concentrations remained constant. Coprecipitation and preferential sorption of As(V) to iron oxyhydroxides were proposed as the mechanisms for the relative enrichment of the As(III).

Diamond (1995) reported field data from three stations in Moira Lake (Ontario) where total, dissolved, and particulate arsenic were measured after filtration through 0.45- μm membrane filters. Based on the particulate arsenic data, 13–16 percent of the arsenic was sorbed to suspended solids. However, based on the difference between the total and dissolved concentrations, only 3–10 percent was sorbed. Regardless of the discrepancy between the two ways of measuring particulate arsenic, the data show that 85–95 percent of the arsenic in the lake was dissolved and only a minor amount was sorbed to suspended solids. Tanizaki *et al.* (1992) also found that 85–95 of the arsenic in seven river samples was dissolved ($<0.45 \mu\text{m}$); in one other sample, only 46 percent was dissolved.

Spliethoff *et al.* (1995) calculated the scavenging of arsenic by iron oxyhydroxides in Upper Mystic Lake using the Dzombak and Morel (1990) surface complexation model. They predicted that 40–60 percent of the As(V) and none of the As(III) in the surface water would be adsorbed to the iron oxyhydroxides. In the hypolimnion during the height of anoxia, only 5–25 percent of the As(V) was expected to be adsorbed, whereas after the lake mixed and oxic conditions returned, 80–95 percent of the As(V) was expected to be adsorbed. The redox-driven dissolution and precipitation of iron therefore was expected to control the dissolved concentration of As(V) in the hypolimnion.

Speciation Modeling

Equilibrium speciation modeling is often employed as a tool for investigating the fate and transport of inorganic contaminants in the environment. Geochemical equilibrium speciation

models include MINTEQ (Felmy *et al.*, 1984), MINEQL (Westall *et al.*, 1976), REDEQL (Ingle *et al.*, 1978), WATEQ3 (Ball *et al.*, 1981), and more recently MINTEQA2 (Allison *et al.*, 1991). These models employ thermodynamic relationships, such as those described earlier in this report, to predict which dissolved, precipitated, or adsorbed species are likely to be found in the environment. They are valuable in that they allow the investigation of the effect of changes in reduction potential (pE), pH, or other chemical conditions on the speciation of inorganic chemicals.

Equilibrium speciation models can be used to predict the concentration of the various protonated states of arsenate and arsenite ions as a function of pH (Allison *et al.*, 1991). Speciation models also can be used to estimate the amount of arsenic adsorbed as a function of pH and competing ions, (Allison *et al.*, 1991; Dzombak and Morel, 1990; McComish and Ong, 1988). Speciation models also are often used to suggest whether and which precipitates are likely to form.

While speciation models commonly are employed to estimate the relative concentrations of oxidation/reduction couples, Cullen and Reimer (1989) point out that As(III) and As(V) often are found together and in proportions that do not reflect equilibrium conditions. Evidence suggests that slow kinetics and/or biotransformation of arsenic species are the principle reasons for this lack of equilibrium. This observation is problematic to modeling oxidation/reduction reactions as it indicates that equilibrium speciation modeling cannot adequately predict As(III)/As(V) ratios in the environment. For this reason, equilibrium speciation predictions of As(III)/As(V) interconversion should be used with caution. Field observations may be the only reliable test of actual As(III)/As(V) ratios. Kinetic approaches may be necessary to adequately address this aspect of arsenic speciation.

ARSENIC IN SEDIMENT

In addition to direct anthropogenic sources, arsenic can reach sediments through sedimentation of inorganic particulates and deposition of algal and bacterial detritus. However, arsenic resists burial, as evidenced by higher concentrations in surficial oxic sediments than in deeper anoxic

sediments (Aggett and O'Brien, 1985; Holm, 1988; Nakashima, 1987; Riedel *et al.*, 1987). Oxidation/reduction mechanisms are responsible for this arsenic cycling in sediments (Bryan and Langston, 1992; Cullen and Reimer, 1989). As sediments are buried and become anoxic, Mn(IV) and Fe(III) oxyhydroxides are reduced to Mn(II) and Fe(II) and solubilized. Adsorbed and/or coprecipitated arsenic then is released into the interstitial water. If the surface layer of sediment is oxic, the arsenic that diffuses upward may become resorbed or reprecipitated with manganese and iron oxyhydroxides, resulting in higher surficial sediment concentrations. As(III) in interstitial water may also be oxidized chemically by Mn(IV) and Fe(III) oxyhydroxides in surficial sediment, thereby minimizing the flux of As(III) to the water column (Oscarson *et al.*, 1981; De Vitre *et al.*, 1991). If the overlying water is anoxic, the arsenic may be released to the water column.

In the presence of dissolved sulfide in anoxic sediment, arsenic that has been dissolved from iron or manganese oxyhydroxides will precipitate as arsenious sulfide or iron-arsenic sulfides, thereby removing arsenic from interstitial water (Aggett and O'Brien, 1985; Moore *et al.*, 1988). In such cases, higher concentrations of arsenic may occur in deep sediments because the arsenic sulfides are resistant to resolubilization (Moore *et al.*, 1988). Conversely, when sulfide ores are exposed to the atmosphere in mine tailings, oxidation of the sulfides results in the release of iron, arsenic, and other metals. The arsenic is quickly adsorbed by the red-orange iron oxyhydroxide precipitate characteristic of acid-mine streams, thereby reducing water concentrations and enriching sediment concentrations (Mok and Wai, 1994).

Ahmann *et al.* (1994) reported the discovery and isolation from anoxic, fresh-water sediment of a microorganism that reduces As(V) to As(III) and gains energy from this reduction. As(V) was not reduced in sterilized media, showing that active microbial metabolism was necessary for As(V) reduction.

Riedel *et al.* (1987) measured the flux of arsenic from sediment to the overlying water column in laboratory chambers with and without a burrowing polychaete, *Nereis succinea*, present.

Without the worms, As(V) flux (17, 39 ng/cm²/day in two treatments) compared well to flux calculated from molecular diffusion based on Fick's Law (14, 44 ng/cm²/day). However, measured As(III) flux (1.5, 3.4 ng/cm²/day) was lower than predicted (40, 14 ng/cm²/day), presumably because of oxidation of As(III) to As(V) during diffusion through the aerobic surface layer. With the worms present, total As(V) flux increased 3–5 times, and flux of As(III) increased 9–17 times. The greater surface area associated with the burrows apparently allowed increased diffusion of arsenic from deeper in the sediment.

Belzile and Tessier (1990) calculated apparent adsorption constants for As(V) on iron oxyhydroxides in 16 Canadian lakes, and found that the constants agreed well with those obtained in laboratory experiments with amorphous iron oxyhydroxides. They concluded that the partitioning of arsenic between surficial sediments and the overlying water could be described by a simple model of surface complexation, i.e., water concentrations were kept low by adsorption of As(V) on iron oxyhydroxides in the oxic surface layer of the sediment.

Lake sediments can be a sink for anthropogenic inputs of arsenic. The sediments of two lakes in the southeastern U.S. accumulated arsenic that was contributed to the lakes over 10–20 years by the effluents from fly ash ponds (Crecelius *et al.*, 1994). Average surficial sediment concentrations of total arsenic were 46 and 37 µg/g in the two lakes, compared to 5 µg/g in a nearby lake with no anthropogenic inputs. On the basis of sediment concentrations measured in Lake Rotorua, New Zealand (mean of 224 mg/kg), Clayton and Tanner (1994) concluded that all of the arsenic sprayed on the lake in 1959 for weed control was still trapped in the sediment.

ARSENIC IN SOIL

The literature on arsenic concentrations and fate in soils has been reviewed recently by Huang (1994) and Bhumbra and Keefer (1994). Arsenic occurs in contaminated soils primarily as the inorganic As(V) and As(III), but soil microorganisms can produce MMAA, DMAA, arsine, monomethylarsine, dimethylarsine, and trimethylarsine. MMAA, but not DMAA, was found in soil pore waters of a valley in England heavily contaminated by mining (Cullen and Reimer,

1989). As(V) was the predominant arsenic form in contaminated agricultural soils in Japan, but lower levels of MMAA and DMAA were also found (Huang, 1994). Transformations among these inorganic and organic compounds are controlled by the oxidation-reduction, precipitation/adsorption, and biomethylation processes described above, with the additional mechanisms of biological production and volatilization of the arsines.

The availability or solubility of arsenic in soils depends on its source (natural or anthropogenic) and the soil's clay content, redox potential (measured as E_H), and pH (Huang, 1994). Generally, factors that tend to increase arsenic availability are anthropogenic source (e.g., pesticides), low clay content, low E_H (reducing conditions), and high pH (alkaline conditions). As(III) in soils can be oxidized to As(V) by Mn(IV) dioxides or by Fe(III) oxides (Bhumbla and Keefer, 1994).

Overburden materials in mining areas typically have high concentrations of arsenic associated with sulfur in arsenopyrite. As these materials oxidize, iron, sulfate, and arsenic are released. The arsenic then can accumulate in subsoils where it is adsorbed to aluminum and iron oxyhydroxides (Bhumbla and Keefer, 1994).

Masscheleyn *et al.* (1991) studied the solubility and speciation of arsenic in a contaminated (555 mg As/kg) upland, loamy soil. In oxic soils ($E_H > 200$), arsenic solubility was low—less than 4 mg/kg solubilized—and As(V) was the predominant species in solution (65–98 percent). Under moderately reducing conditions (0–100 mV), solubility increased to 10 to 50 mg/kg, and As(III) became the dominant species, although As(V) was still present in appreciable amounts (up to 50 percent). The authors concluded that the solubilization of iron oxyhydroxides released As(V), which was slowly reduced to As(III).

ARSENIC IN THE ATMOSPHERE

The primary sources of arsenic to the atmosphere are believed to be low-temperature volatilization of methylarsines from soil and release of arsenic trioxide, As_2O_3 , from metal smelting and combustion of fossil fuels (Bhumbla and Keefer, 1994; Cullen and Reimer, 1989).

Most airborne arsenic is found on particles; less than 10 percent is found in the vapor phase. Trimethylarsine is typically the predominant organic form, with smaller amounts (15–25 percent) of dimethylarsine, and little or no monomethylarsine. The methylarsines may be found over land but typically not over the oceans, and atmospheric concentrations are higher in the summer than the winter. Both of these observations are consistent with the presumed soil biomethylation source of methylarsines.

As summarized in Scudlark and Church (1988), arsenic concentrations measured in precipitation around the world ranged from 0.005 to 6 $\mu\text{g/L}$. At a Delaware coastal site, Scudlark and Church (1988) measured total arsenic concentrations of 0.00075 to 1.1 $\mu\text{g/L}$ over 17 months. Arsenic concentrations in precipitation from ocean storms were low, $<0.03 \mu\text{g/L}$, and concentrations in all events correlated well with acidity, nitrate, and excess sulfate, suggesting that fossil fuel combustion may be the source. No organic arsenic was detected, and As(V) accounted for 60 to 90 percent of the total arsenic, although As(III)₂O₃ is the form released in combustion. Scudlark and Church (1988) postulated that aqueous oxidation rates are too slow to account for the predominance of As(V) and that atmospheric oxidative catalysts (e.g., O₃, H₂O₂, uv light, other trace metals such as manganese or iron) may be responsible.

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