

Chapter J

MERCURY GEOENVIRONMENTAL MODELS

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INTRODUCTION

Mercury mines and mines that produce byproduct mercury can impact the environment through the release of mercury-enriched sediment, mercury-rich mine drainage, and mercury vapor released to the atmosphere. Most mercury mines contain mercury contaminated mine wastes and soils that are a source for both soluble and particulate mercury species. Environmental concerns related to mining and processing of mercury-bearing ores consist of contamination of soils, sediments, and waters by mine wastes; mercury vapor released during ore processing and from mine tailings; and mercury mine drainage and toxic metal release into watersheds. Significant environmental impacts on watersheds also are associated with the release and transport of elemental mercury from past and present gold placer operations, and from tailings generated during the processing of precious metal ores where the amalgamation process was used. Although geoenvironmental models of mercury deposits can be used to establish the environmental effects caused by these deposits, the models must be used in the context of global cycling of mercury.

GLOBAL MERCURY CYCLE AND ENVIRONMENTAL

The global atmospheric pool of mercury contributes mercury to watersheds and lakes through both wet and dry depositional processes that are mediated by leaf uptake of mercury by plants (Mason and others, 1994). Because of this atmospheric contribution of mercury, the magnitude of the flux of mercury to the environment from mineralized areas and mine sites reflects both local and global contributions of mercury, although the local source typically predominates in mineralized areas. The primary natural sources of mercury to the atmosphere include, in decreasing importance, the oceans, soil degassing, volcanoes, and geothermal systems (Varekamp and Buseck, 1986, Mason and others, 1994). Anthropogenic sources of mercury to the atmosphere are primarily from coal combustion, waste incineration, and smelters (Nriagu and Pacyna, 1988). Since the beginning of industrial period in the middle 1800s, the global atmospheric mercury deposition increased until about 1970 and then decreased slightly in the past three decades (Fitzgerald and others, 1997). This increase in atmospheric mercury deposition is reflected in the sedimentary record of lakes, estuaries, and bogs. Cores of recently deposited sediments from all these environments record an increase in mercury concentration of about 2 to 5 times over background mercury concentrations established prior to the industrial period (Fitzgerald and others, 1997, Hurley and others, 1994; Verta and others, 1990). For this reason mercury background levels in various media such as soils generally cannot be established and only baseline concentrations can be determined now.

Unlike most metals, plants uptake mercury primarily through leaves rather than through the root system. Under high ambient air mercury concentration, plants uptake and concentrate mercury in their leaves, and conversely, under low ambient air concentrations of mercury, plants give off mercury through their leaves (Lindberg and others, 1992). In mine areas where ambient air concentrations of mercury are high either due to roasting of mercury ores or from emission of mercury vapor from contaminated or naturally anomalous soils, plant communities down wind from these sites concentrate both mercury and methylmercury in their leaves. For example, at mercury contaminated mine sites in southwest Alaska, plant leaves contain elevated mercury and methylmercury concentration, up to 970 ppb and 37 ppb respectively, as compared to baseline values of 190 ppb, and 1.5 ppb, respectively, in unmineralized areas (Bailey and Gray, 1997, Bailey et al., 1999). Wash off and litter fall are the primary routes for introduction of mercury into creeks and lakes from these plant communities. This process will augment any direct contamination of watersheds and lakes by mercury contaminated mine wastes and waters.

The mercury species of greatest environmental concern is methylmercury, because it may become highly concentrated through bioaccumulation in fish and other fish consuming biota. Methylmercury is a neurotoxin and its pathway into humans is primarily through consumption of methylmercury-contaminated fish. A secondary pathway into humans is the direct ingestion of mercury contaminated mine wastes by children displaying pica activity (soil ingestion). Mercury released from point sources and deposited from the atmosphere into streams, wetlands, and lakes may become methylated and incorporated into the food web. Methylation of mercury and its uptake by biota is a complex process and dependent on several variables. As a result, although fisheries downstream from mercury mine sites are generally contaminated, the levels of methylmercury do not always exceed the federal action level of 1.0 ppm (for example see Gray et al., 1996, for fisheries below mercury mines in Alaska). Formation of

methylmercury (CH_3Hg^+) is favored by the presence of ionic mercury and high concentrations of dissolved organic carbon and sulfate. Mercury methylation is a co-metabolic reaction and sulfate-reducing bacteria are the primary mediators in the biotic methylation process (Campeau and Bartha, 1985, Summers, 1986). Acid mine drainage from mercury deposits commonly has both high sulfate and mercury concentration and introduction of these waters into streams, wetlands, and lakes increases the methylation process (Rytuba and Enderlin, 1999). Although methylmercury can be formed at mine sites in mercury-contaminated soils and mine waters, most mercury methylation occurs downstream from the mine site in wetlands and larger aquatic bodies. Detrital particles, such as clays, organic phases, and iron oxyhydroxide, adsorb Hg^{2+} from the water column in streams and lakes, and sedimentation of these particles reduces the methylation process. Sequestration of mercury in sediment is the primary mode of removing mercury from the environment.

MERCURY PRODUCTION

Mercury has been mined in North America since the early 1800's with over 6 million flasks (a flask equals 76 pounds of mercury) of mercury being produced from ten major mercury mineral belts (fig. 1). The mercury mineral belts consist of mercury deposits with significant production (greater than 1000 flasks of mercury), small mercury occurrences having small or no production, and areas of country rock containing elevated concentrations of mercury. In North America, the California Coast Range mercury mineral belt has been the largest producer of mercury and contains fifty-one mines that have produced over 1000 flasks of mercury. The New Almaden mine in central California is the largest mercury mine in North America having produced about four million flasks. Mercury also has been produced as a byproduct from zinc-rich volcanogenic massive sulfide deposits and from hot-spring-type

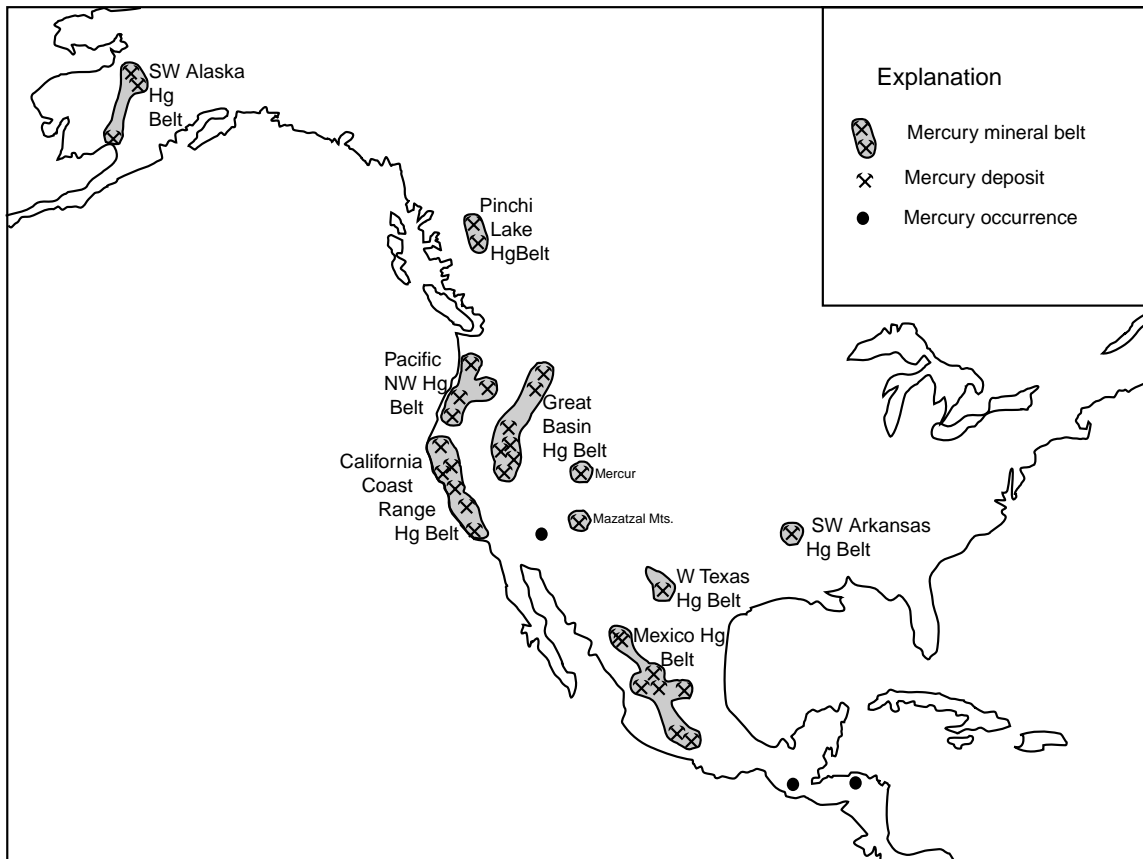


Figure 1. Mercury mineral belts in North America consist of mercury deposits with significant production and mercury occurrences with little or no production. Shaded areas in mineral belts indicate areas that include altered areas with elevated mercury concentration.

gold-silver deposits. Much of the mercury produced has been used in the recovery of gold from placer deposits and in the processing of precious metal ores that utilized the mercury amalgamation process. Because of environmental concerns and the consequent low price of mercury, large scale mercury mining ceased by 1980 in North America

except for some small scale mercury mining in Mexico. Primary mercury production continues in the Almaden mercury district in Spain, which contains the largest and richest mercury ore bodies in the world, as well as from mercury deposits (listed in decreasing amount of production) in Kyrgystan, China, Algeria, Russia, Slovakia, Tajikistan, Ukraine, Mexico, and Slovenia. Mercury also continues to be produced in Finland as a byproduct from massive sulfide deposits. Similar deposits in the Urals, (former Soviet Union) and India also produce mercury, but it is released to the atmosphere rather than recovered during the smelting process. In the United States, gold mines are the only producers of byproduct mercury, because the mercury content of gold and silver ores from hot-spring-type, and Carlin-type gold deposits can be as high as several hundred $\mu\text{g/g}$ (ppm). However, some of these mines still release significant mercury to the atmosphere. In Mexico, significant byproduct mercury production continues to come from the reprocessing of silver and gold mine tailings, such as in the Zacatecas precious metal district.

MERCURY DEPOSIT TYPES

Most mercury deposits that occur in the large mercury mineral belts in North America can be classified as either silica-carbonate-type or hot-spring-type mercury deposits (Rytuba, 1996). However, the largest mercury deposits in the world are the Almaden-type deposits, but this deposit type is primarily restricted to the Almaden district in Spain. Silica-carbonate-type and hot-spring-type mercury deposits are usually spatially separate but in the California mercury mineral belt, hot-spring type mercury mineralization can overprint earlier formed silica-carbonate type mercury deposits, such as in the Knoxville district (Rytuba, 1996).

Silica-carbonate-type mercury deposits are associated spatially with serpentinite that has been altered to a mineral assemblage of silica and carbonate minerals. These deposits are generally small to moderate in size, and contain from 0.1 to 10 million metric tons of ore containing from 0.2 to 0.8 weight percent mercury. The deposits consist of vein and replacement ore bodies developed within and adjacent to silica-carbonate altered serpentinite. Silica-carbonate alteration is localized along regional faults that separate serpentinite from adjacent country rock and the alteration commonly extends up to several kilometers beyond the margins of the ore bodies. The alteration assemblage is zoned from a central core of quartz-chalcedony-magnesite-pyrite-marcasite to a peripheral zone of magnesite-calcite-dolomite-magnetite. The initial alteration process consists of the addition of carbonate to the serpentinite followed by introduction of silica into the central core (Sherlock, et al., 1993). The peripheral zone of calcite-dolomite veining may extend for several kilometers outward from the mercury deposit. In addition to mercury, these deposits commonly have elevated concentrations of antimony (0.1 – 1,000 ppm), arsenic (2-200 ppm), nickel (10-3,000 ppm), cobalt (5 – 100 ppm), thallium (1-12 ppm), and zinc (2 –50 ppm). Copper is generally low, less than 50 ppm, and lead is essentially absent in these deposits. Pyrite and marcasite comprise from 2 to 10 volume percent in the ores except in deposits that formed adjacent to mafic volcanic vents where iron sulfide can comprise up to 50 volume percent. The grain size of both iron sulfides ranges from 0.5 to 5 mm. Cinnabar is generally fine grained, about 0.2 mm, but can be have a larger grain size, up to 5 mm, in veins and vugs. This deposit type formed from low-temperature, less than 120°C, CO₂-CH₄-H₂S-rich fluids that commonly contained petroleum compounds (Peabody, 1992; Sherlock et al., 1993). The impermeable serpentinite bodies are important in the localization of silica-carbonate-type mercury deposits because their fault-bounded margins impede and channel the flow of mercury-bearing hydrothermal fluids (Rytuba, 1996). Elevated levels of mercury and small mercury occurrences are present in the silica-carbonate-alteration zones. The large productive mercury deposits formed in structural traps, such as antiformal structures, where fluids were localized below impermeable strata. In the large deposits, the ore bodies are hosted both in silica-carbonate altered serpentinite and in adjacent clastic sedimentary rocks.

Hot-spring-type mercury deposits are associated closely with volcanic centers and form in the near surface environment. The volcanic host rocks and associated clastic sedimentary rocks are altered to an assemblage of adularia, quartz, and sericite at depth, and in the near surface, to an advanced argillic alteration assemblage of kaolinite, alunite, and cristobalite that commonly contains elemental sulfur. Some of these deposits are hosted in hot-spring sinter that was deposited at the surface and that consists of banded silica phases and beds of hydrothermal eruption breccia. These deposits have a trace element association of lithium, boron, arsenic, antimony, gold, silver, thallium, and tungsten. Hot-spring-type mercury deposits are often the near-surface expression of hot-spring type gold deposits that occur at deeper levels below mercury-enriched sinter, such as at the McLaughlin gold deposit (Lehrman, 1986). The hydrothermal fluid source for the hot-spring-type mercury and associated gold deposits ranges in composition from dominantly meteoric to mixed meteoric-magmatic and the fluids are typically low-salinity, moderate-temperature (about 200°C) (Rytuba 1993).

Almaden-type mercury deposits are the largest and highest-grade mercury deposits. These deposits commonly contain from 10 to 100 million metric tons of ore that ranges from 2.0 to 20 weight percent Hg. The Almaden deposit in central Spain is the single largest mercury deposit in the world. These deposits are associated spatially

with mafic submarine vent complexes that consist of mafic dikes and sills, and oval craters typically with dimensions of 300 m by 150 m (Hernandez, 1985), and submarine calderas, such as at the Las Cuevas deposit (Rytuba et al., 1988). Juvenile magma clasts within the craters are typically alkali basalts. The deposits consist of massive cinnabar and elemental mercury replacement bodies hosted in quartzite, tuff breccias, submarine mafic to intermediate composition pyroclastic flows, mafic dikes, and organic-rich black shales. Primary veins in these deposits are uncommon and cinnabar veins that are present consist of gash fractures developed during later regional metamorphism of these deposits (Rytuba et al., 1988). The replacement deposits hosted in quartzite consist of stratiform zones of cross cutting ore consisting of cinnabar, native mercury, pyrite, calcite, and quartz. The grade and thickness of ore bodies is highest near the margin of the volcanic craters and decreases systematically away from the craters. Mercury is the only ore metal in these deposits and the only other trace metal present is zinc. No other mineral deposit type is associated with these mercury deposits.

MINERALOGIC CHARACTERISTICS

The primary ore mineral in all mercury deposit types is cinnabar, (HgS). Elemental mercury is also common in all deposit types but generally in small amounts. Only in one deposit of the Almaden type, Las Cuevas, Spain, is elemental mercury the primary ore mineral. The high temperature polymorph of mercury sulfide, metacinnabar, commonly is present in silica-carbonate-type mercury deposits and in a few of these deposits, it is the primary ore mineral. More rarely, under extreme oxidizing and low pH conditions, mercury sulfates and chlorides may form as coatings on surface exposures. These yellow and green minerals are photosensitive and typically turn black on exposure to the sun and can be easily confused with manganese oxides. Mercury silicates and chromates also are present in silica-carbonate-type deposits. All of these minerals can be present in very small amounts except in a few silica-carbonate-type deposits where they comprise the main ore minerals. In hot-spring type mercury deposits, mercury sulfate, chloride, and oxide minerals are present in the upper parts of the ore bodies and these phases may form during supergene alteration of the ore body. Because these phases are very soluble, they commonly are preserved in sealed vugs and fracture coatings within the upper parts of ore bodies. The mineral corderoite, a mercury chloro-sulfide, is the dominant ore mineral at only one hot-spring type mercury deposit, the McDermitt deposit, Nevada.

Other sulfide minerals present in silica-carbonate type deposits include pyrite, and marcasite and in hot-spring-type deposits, pyrite and native sulfur are present. In silica-carbonate deposits iron sulfides comprise from 5-10 percent by volume of the ores and altered country rock except where these deposits are localized adjacent to mafic volcanic centers and sulfidation of the country rock results in up to 50 percent iron sulfides being present in the ores. Pyrite and marcasite are the primary acid-generating sulfides in silica-carbonate type deposits. In hot-spring-type and Almaden-type deposits, pyrite is the primary acid generating sulfide. Cinnabar is the most insoluble of the metal sulfides under ambient oxidizing conditions, and as a result, its acid-generating capacity is very limited. Other sulfide minerals present in silica-carbonate and hot-spring-type deposits are stibnite, realgar, and orpiment, but the small amount of these phases contributes minimally to acid generation.

MINING AND PROCESSING METHODS

Mercury mining operations typically are small and their surface impact covers an area of a square kilometer or less. In the larger mercury districts, deposits commonly are localized along the same regional fault zone and mines may extend for several kilometers along the mineralized structure. Most mines were underground operations with open stope mining of high-grade ore shoots. Waste rock often was used to backfill underground workings resulting in only a small fraction of waste rock being brought to the surface. The high-grade ore zones usually have sharp contacts with low-grade ore or unmineralized country rock. Because low-grade ore is only rarely mined, stopes tend to follow the outline of high-grade ore bodies and are irregular in shape. Ore bodies that were present in the near surface were mined by open pit methods but only a few mines have been exclusively open pit operations.

The primary processing method for mercury ores utilizes the comparatively simple and inexpensive process of heating ores above the upper stability temperature of cinnabar to volatilize mercury and sulfur followed by a condensing process to recover elemental mercury. This procedure permitted the recovery of elemental mercury at most mine sites without the need to ship ores to a central processing facility. At some of the mines, a beneficiation process was used to minimize the amount ore being processed. Beneficiation processes included screening, jigging, tabling, or flotation, the latter process especially being used at the more recently developed mines. In the mid-1960's, flotation plants located at Gabbs and Mina, Nevada, processed ores from several deposits within the Great Basin mercury belt. The largest of the flotation plants was established in 1975 at the McDermitt mine, Nevada, where ores from the unusual ore body consisting of both cinnabar and corderoite, $\text{Hg}_3\text{S}_2\text{Cl}_2$, were concentrated prior to roasting in a Herreshoff furnace.

Mercury ores have been heated in a variety of retorts and several types of furnaces. Furnaces differ from retorts in that furnaces internally heat the ores, mix fuel and mercury vapor, and process a continuous feed of ore. Retorts consist of one or more pipes that contain a single charge of ore. In retorts, the ore is externally heated and vapors from the fuel do not mix with the volatilized mercury. Retorts generally have a small capacity, about 500 pounds of ore per pipe. Because of their low cost, retorts have been utilized at small mines having small but high-grade ore bodies. Two basic types of retorts have been utilized. The Rossi type consists of several iron tubes that serve both as ore roasting and condensing systems. The D type retorts, are "D" shaped in cross section and are either used for roasting ore and condensing, and in the Pan type retorts, the roasting is done in a separate chamber. In some of the larger mines with ore processing furnaces, retorts were utilized to purify sooty mercury recovered from the furnace condensing system. Furnaces that have been utilized include the Scott, Herreshoff, and several types of rotary furnaces. The capacity of furnaces ranged from less than 10 tons to 350 tons per day. The rotary furnace was the most commonly utilized. It consists of a rotating, inclined iron cylinder into which ore is continuously fed and from which the roasted ore, calcine, is removed. Mercury vapors and other gases are drawn from the upper end of the cylinder into a dust collector (cyclone) and then processed in a condenser before being released through a stack. The Herreshoff furnace was used at larger mines and consists of a series of circular hearths into which ore is continuously fed and mechanically advanced to successive hearths of higher temperature. In the Herreshoff furnace, calcine is removed from the base and gases are fed through a dust collector and then a condensing system. The Scott furnace generally was built from brick and consisted of a series of baffles upon which the ore migrated downward as it was heated. The calcines were drawn from the base. The Scott furnaces initially were inefficient until considerable ore had been processed through them and the bricks had become saturated with elemental mercury. At the end of mining, the bricks from the furnace were processed in a retort to recover the mercury.

Condensing systems, which cool the vapor from the furnaces in order to separate the liquid mercury from other stack gases, range from simple single pipe to complex multiple pipe condensers. The condensing system usually consists of a pipe 8-15 inches in diameter and several hundred feet in length that is folded into inverted U shapes. The bases of the condensing system pipes are immersed in water tank and equipped with a drain hole at the base so that condensed elemental mercury can be collected in the tank. Both air- and water-cooled condensing systems have been utilized. In the more simple retorts, the condensing system consists of an iron pipe 2-4 inches in diameter and 5-10 feet long sloping downward from the top of the retort to a collection tank. About two thirds of the product recovered from the condensers consists of elemental mercury and the remainder consists of fine soot composed of rock dust, mercury sulfides and sulfates, fuel soot, water, and finely dispersed elemental mercury. In the older mines this material was dried on steam tables. However, this process released mercury to the atmosphere and often was a serious source of mercury poisoning. Calcium carbonate was used to aid in the mechanical coagulation of finely condensed particles of mercury from soot and collected from the table through a small pipe leading to a collecting tank. In the larger and more modern mines, mechanical mixers or a centrifuge was employed to remove mercury from the soot.

Mercury has been bottled at the processing site in iron flasks that contain 76 pounds of elemental mercury. More recently the metric ton flask has been used. Inefficiencies and spillage during the bottling process has caused mercury contamination of mill sites and calcines. For a more complete discussion of the processing techniques, the reader is referred to Von Bernewitz (1937) and Schuette (1931, 1938).

ENVIRONMENTAL CONCERNS ASSOCIATED WITH MINERAL PROCESSING

Because of the inefficiencies in the roasting process, mercury vapor and mercury- enriched particles were released to the atmosphere and deposited down wind from furnace and retort sites causing local enrichment of mercury in soils. Mercury content is highest in organic rich, surface soils, ranging from 5 to 25 $\mu\text{g/g}$ (ppm), and decreases to background levels at a maximum depth of 0.5 meters. A typical vertical profile of soils impacted by long term furnace release is shown in figure 2 from the New Idria district, the second largest producer of mercury in North America. The background concentration of mercury, 100 ng/g (ppb), is reached at a depth of 33 cm. The leaching and transport of mercury into the soil column indicates that the mercury phases deposited from furnace release are soluble and include elemental mercury and other chloride and sulfates of mercury (see discussion below on speciation). In the larger mercury districts where processing occurred over a long period, the loading of mercury to soils adjacent to the mine site constitutes a potential source of mercury- enriched sediment. Soils naturally accumulate mercury deposited from the global atmospheric pool of mercury, and as result, even soils present outside of mineralized areas have mercury concentrations that reflect increased mercury deposition since the inception of the industrial period. Although soils from mercury mine areas have significantly elevated levels of total mercury, the ratio of methylmercury to total mercury is lower in mine areas than in the baseline sites in unmineralized areas (Bailey and others, 1999). This is because an enzyme-catalyzed (organomercurial lyase) microbial demethylation

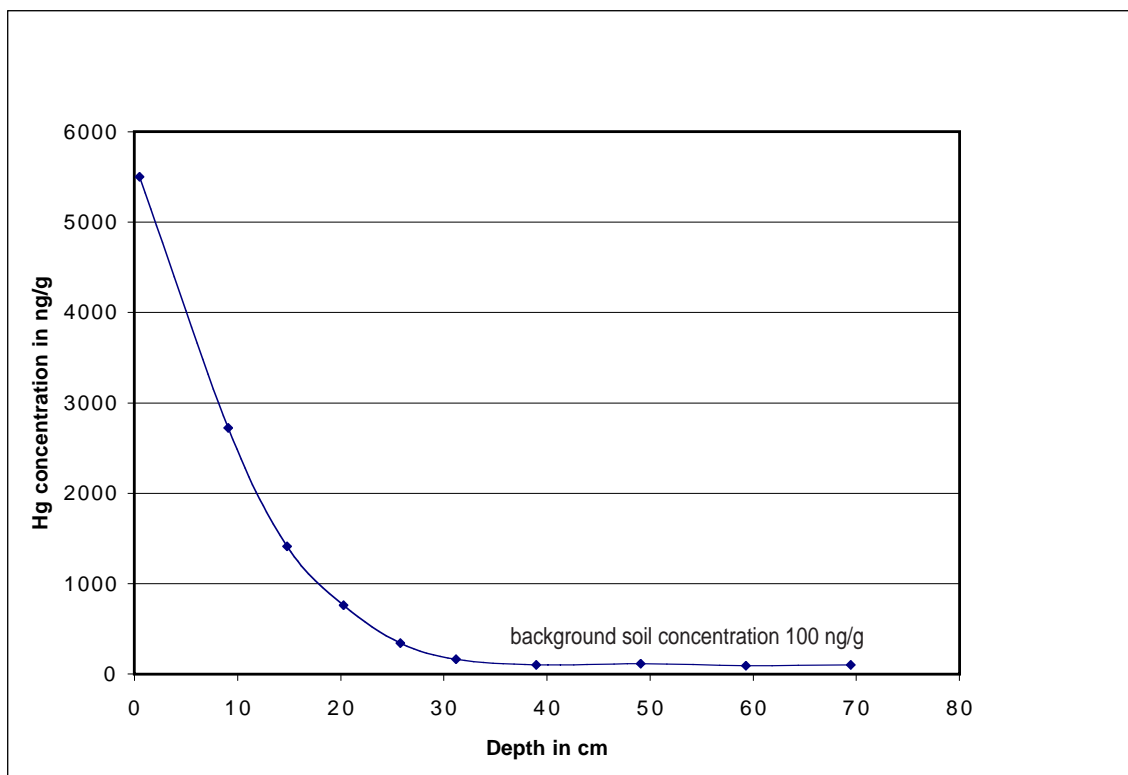


Figure 2. Profile of mercury concentration in soil impacted by release of particulate mercury and vapor from mercury mines in the New Idria mercury district, California.

reaction breaks the Hg-C bond to produce Hg (II) and CH₄ (Summers, 1986), thus preventing high concentrations of methylmercury from accumulating in these soils (Hines and others, 1999).

The potential environmental impact of mercury-mine wastes varies considerably depending on the total mercury concentration and speciation of phases present in the mine waste. Mercury mine wastes, listed in increasing content of mercury, include waste rock, low grade ore, mine tailings, condenser soot, and cyclone dust. Dust generated during roasting of the ores was collected in a cyclone prior to the mercury-rich vapor entering the condensing system at the larger mines that employed rotary furnaces. Cyclone dust has a distinctive maroon color and can contain up to several weight percent mercury. Soot that accumulates in the condensing columns represents the fine material that escaped the cyclone collectors or that was directly released from the furnace to the condenser at mines that did not have collectors. This fine-grained, well-sorted material can contain up to several tenths of a percent of mercury that is present as elemental mercury and as mercury sulfate and chloride phases. Condenser soot was generally collected and reprocessed in a retort. A major environmental concern is posed by soot that was not reprocessed and was discarded on waste dumps, because of its high concentration of soluble mercury phases. Condenser soot has the consistency of fine silt and can be readily transported by the wind throughout mine site. The mercury vapor flux from condenser soot to the atmosphere also can be very high especially under hot and sunny weather conditions where it can pose a risk to humans through the inhalation pathway.

Mercury mine ore tailings, termed calcines, have a characteristic red color that results from the oxidation of iron sulfides during the roasting of the sulfide ores. The term calcine comes from the common historic practice of adding lime (CaO) to the mercury ore as a desulfurizer. Calcines were typically deposited adjacent to the furnace site or discarded into nearby stream channels. Flood events periodically removed the tailings from the stream channel thus providing space for continuous tailings disposal during the life of the mine. As a result, mercury mine tailings commonly occur within stream channels and in overbank deposits for several to tens of kilometers downstream from mine sites. Transport of mercury from mercury mine sites where the source of mass loading is from mine tailings occurs primarily in the particulate phase and most of the mercury flux occurs during peak flow events (Whyte and Kirchner, 1999; Whyte, 1998). Mine tailings can impact waters at great distances the mine area. For example, downstream from the Idrija mine in Slovenia, the second largest mercury district in the world, sediments in the River Soca and in the seawater of the Gulf of Trieste are contaminated with inorganic mercury more than 50 km

from the mine area (Horvat et al. 1999). Sediments contaminated with tailings are a concern because they are a source of elemental mercury and ionic mercury that can become methylated in downstream aquatic environments. For example, inorganic mercury phases in mine tailings from the Idrija mine introduced into Gulf of Trieste contribute to methylation of mercury in bottom seawater sediments (Horvat et al. 1999). Stream sediments that drain mercury mineralized areas contain from 2 to 200 ppm mercury, and heavy mineral concentrates contain metal concentrations, in ppm, as high as the following: Hg, 4,400; Ba, 10,000; Cr, 7,000; Cu, 150; Ni, 500; Pb, 200; Sn, 300; and Zn, 500. The fine-grained nature of the calcine also contributes to water turbidity. Calcines also were commonly used for road material and most dirt roads adjacent to mines were covered with calcines. Recovery of mercury during retorting of ores ranges from 90 to 95percentresulting in calcine that may contain from 5 to 10percentof the original mercury in the ore. The amount of mercury removed during the roasting process in small mines is extremely variable so that calcine in these operations may contain significant mercury concentrations. Mercury content in calcine ranges from 10 to 1500 µg/g (ppm) depending on the efficiency of the retort or furnace used. Other trace metals originally present in elevated concentration in silica-carbonate mercury ores, such as nickel and chrome, also are present in high concentrations, 100 to 5,000 ppm. Calcines adjacent to condensing systems where mercury was recovered and bottled into flasks may have very high mercury content, up to several 1000 ppm, because the mercury commonly was spilled in this area and was adsorbed by the iron oxide phases in the calcine fragments.

In addition to the concentration of mercury present in mine tailings, the speciation of mercury phases in mine wastes is important in determining the amount of mercury that is bioavailable when the exposure pathway is through direct ingestion of mine tailings. The speciation of mercury phases also determines the amount of mercury that is released from tailings and that becomes available for methylation and subsequent incorporation into biota as methylmercury. A variety of techniques have been used to determine mercury speciation. The mineralogy of mercury phases in mine tailings has been examined using indirect methods such as sequential extraction (Revis et al., 1989, Sakamoto et al., 1992) and thermal desorption (Azzaria and Aftabi, 1991, Biester and Nehrke, 1997). More recently x-ray absorption spectroscopy has been used to directly identify mercury phases (Kim and others, 1998). Extended x-ray adsorption fine structure spectroscopy (EXAFS) indicates that several mercury phases are formed during roasting of mercury ores: metacinnabar (high temperature polymorph of HgS), corderoite (HgS₂Cl₂), schuetteite (HgSO₄·H₂O) and mercury chlorides (Kim and others, 2000). All of these minerals are more soluble than cinnabar, and thus mine tailings can be a significant source of soluble mercury. Metacinnabar commonly is the dominant mercury phase in calcines derived from silica-carbonate-type mercury deposits, because during the roasting process cinnabar is converted to metacinnabar and impurities introduced into the metacinnabar structure impedes its reversion back to cinnabar upon cooling to ambient conditions (Kim and others, 1998).

Table 1. Geologic and geochemical factors that control mine drainage composition

	Silica-carbonate type mercury deposits	Hot-spring type mercury deposits
<u>Trace Metals</u>	Ni-Co-Cr-Sb-Zn-Cu	Au-As-Sb-Li-Tl-W
<u>Alteration</u>	Carbonates-quartz	Adularia-quartz-clays
<u>Sulfides</u>	Pyrite-marcasite 5-50% +/- millerite(NiS)	Pyrite 2-5% +/- native sulfur
<u>Host Rocks</u>	Serpentinite-(shale)	Clastic and volcanic rocks
<u>Structural Control</u>	Serpentinite contacts- faults	Faults-volcanic vents
<u>Ore Minerals</u>	Cinnabar-metacinnabar (HgS)- elemental Hg	Cinnabar (HgS)- corderoite (Hg ₃ S ₂ Cl ₂)
<u>Secondary Minerals</u>	Mercury sulfates- chlorides-chromates	Mercury sulfates- chloride-oxides

MERCURY MINE DRAINAGE COMPOSITION

The geology of the mercury deposit type provides an important control on the composition of mercury mine drainage. Geologic factors (table 1) such as ore mineralogy, host- rock composition, and type and amount of iron sulfides present are important in determining the pH, and metal and anion concentrations in mine drainage. Acidity of mine drainage from silica-carbonate-type deposits is mitigated by the carbonate alteration mineral assemblage

and serpentinite host rocks of this deposit type (fig. 3). However, in silica-carbonate-type deposits that are localized adjacent to mafic vent complexes where large amounts of pyrite have been introduced into the country rock, mine drainage can have extreme acidity, as low as pH 2.4. The content of iron sulfides (pyrite and marcasite) in these mercury ores can be as high as 50 volume percent and the acid-generating capacity of these sulfides exceeds the neutralizing capacity of the serpentinite and carbonate minerals in the alteration assemblage. Mine drainage from hot-spring-type mercury deposit are only moderately acidic, because the pyrite content is typically low, 2-5%, and the host rock buffering capacity is sufficient to partially mitigate the acidity. The sum of the base metal concentrations (nickel, cobalt, chrome, antimony, zinc, and copper) in mine drainage from silica-carbonate-type mercury deposits is moderate to high, from 100 to 100,000 $\mu\text{g/L}$ (ppb) (fig. 3). In contrast, hot-spring type mercury deposits have an epithermal geochemical suite of elements associated with them: gold, silver, antimony, arsenic, lithium, and tungsten (table 1). The sum of the base-metal concentrations is typically low because this suite of trace metals characterizes the base metal composition of mine drainage from this type of mercury deposit (Rytuba, 1997).

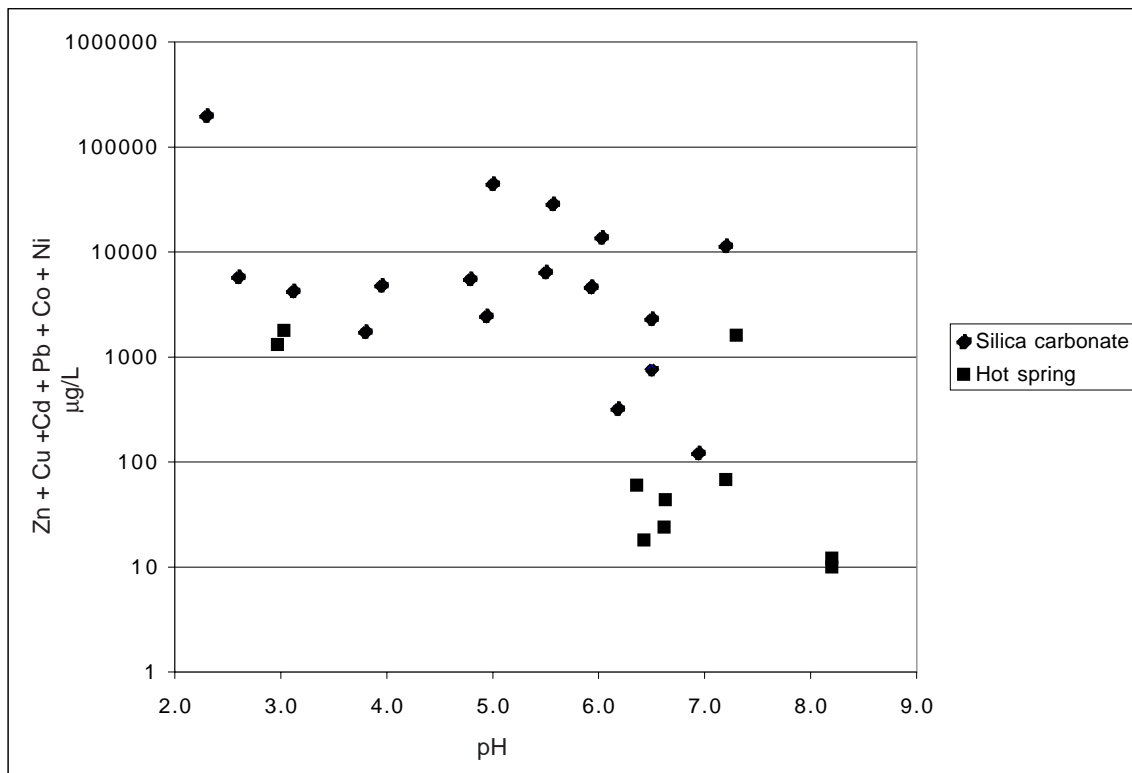


Figure 3. The sum of the base metals Zn, Cu, Cd, Pb, Co, and Ni versus pH (Ficklin plot) for mercury mine drainage from silica-carbonate and hot-spring type mercury deposits.

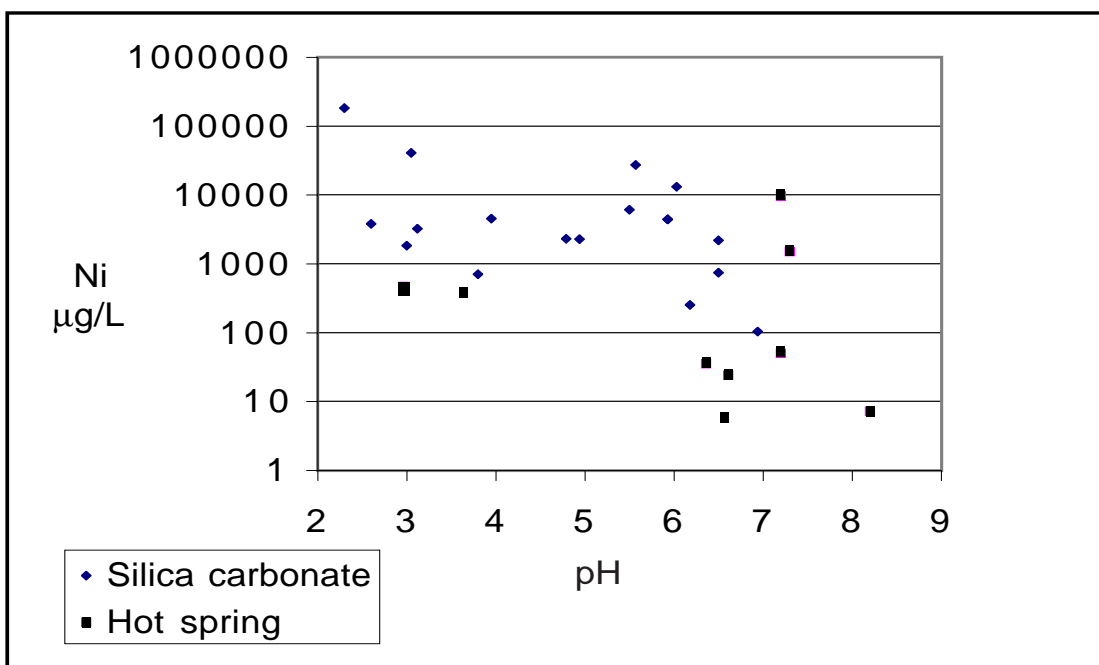


Figure 4. Nickel concentration versus pH in mercury mine drainage from silica-carbonate type and hot-spring type mercury deposits.

Nickel concentration in mine drainage waters associated with silica-carbonate-type mercury deposits are very high (fig. 4), often exceeding 10,000 µg/L (ppb), and commonly accounts for most of the total base metal loading in these waters (fig. 3). The unusually high nickel content of these waters reflects the high nickel content of serpentinite host rocks that are associated with this deposit type (Rytuba and Kleinkopf, 1995). The protolith for the serpentinite is seafloor basalt and associated mafic cumulates. During hydrothermal alteration of serpentinite to the silica-carbonate alteration assemblage, the nickel sulfide, millerite, was deposited in vugs and fractures within alteration zones and mercury ore bodies (Bailey and Everhart, 1964). Although not abundant, millerite is widespread throughout silica-carbonate alteration zones and is readily oxidized in mine workings and mine wastes exposed to oxygenated surface waters. Nickel sulfates formed from oxidation of millerite are readily soluble as Ni(H₂O)₆ complex at a pH less than 8 and remain in solution unless adsorbed onto iron hydroxides. Above pH of 8, nickel is precipitated as the NiOH. Because silica-carbonate alteration zones extend along major fault zones beyond mercury districts for several kilometers, springs and seeps developed along these fault zones can be expected also to have high nickel concentrations. Toxicity of nickel to fish occurs at concentrations above 50 µg/L (ppb) and the drinking water standard of 200 µg/L (ppb) is often exceeded in streams impacted by this deposit type.

Total mercury concentration (dissolved and adsorbed onto particulate phases) in mine drainage shows extreme variability even within deposit type, ranging from less than 1 µg/L to over 200 µg/L (ppb) (fig. 5). The mercury concentration often exceeds the drinking water standard, 2 µg/L (ppb), and the aquatic criteria for continuous concentration, 0.012 µg/L (ppb).

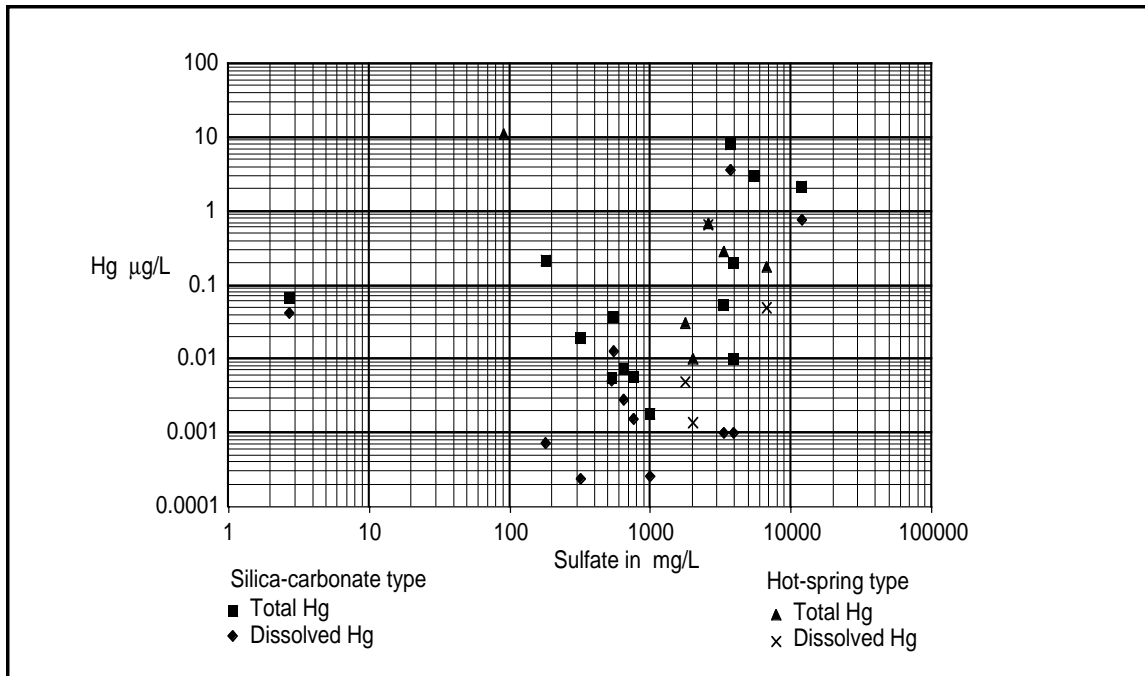


Figure 5. Mercury concentration in mercury mine drainage from silica-carbonate type and hot-spring type mercury deposits.

The large range in mercury concentration is caused by several factors. The most important factors are the solubility of the mercury phases with which the mine drainage interacts and the amount and adsorption capacity of the particulate phases present. Mercury speciation, as well as the concentration of mercury in mine drainage, is also an important variable in assessing the potential environmental impact that mine drainage may have on water quality and biota. Elevated levels of mercury, as well as high sulfate concentration in mine drainage, enhance methylation of mercury by sulfate-reducing bacteria in environments impacted by mine drainage. The mercury species present in mine drainage are strongly affected by chemical processes that occur when mine drainage reacts with mine wastes and surface waters. For this reason the composition of mine drainage is discussed for three different mine environments: (1) at the point of discharge from underground mine workings; (2) mine drainage that has reacted with mine wastes; and (3) mine drainage that has mixed with stream water.

Mine Drainage from Underground Mine Workings

At the point of discharge from underground mine workings, the pH of mine drainage from silica-carbonate type mercury deposits is moderately to weakly acidic ranging from 3.1 to 6.9. The pH of hot-spring type mercury deposits is variable, because these deposits are hosted in a variety of rock types that have varying degrees of neutralizing capacity. Low pH is associated with deposits hosted in clastic sedimentary rocks, or volcanic rocks that have been intensely altered to an advanced argillic assemblage of quartz-kaolinite-cristobalite-alunite. Neutral to alkaline pH is associated with deposits hosted in mafic volcanic rocks and in recently formed deposits that contain thermal waters having a high alkalinity (Donnelly-Nolan and others, 1993; Janik and others, 1994). Some mine drainage is composed dominantly of thermal water, such as at the Elgin mine, California, where the pH is alkaline, 8.15. The iron concentration in mine drainage ranges from 0.1 to 7600 mg/L, and is present dominantly in the reduced form, Fe (II). The highest iron concentrations are associated with silica-carbonate type deposits that are localized in and adjacent to mafic intrusions where large amounts of pyrite and marcasite, up to 50 percent by volume, were introduced into the country rock. Mine drainage waters from hot-spring type deposits have lower concentrations of iron because the deposits have lower iron sulfide content. The range in total (unfiltered) mercury concentration is comparable for both deposit types ranging from .005 to 8.0 µg/L for silica-carbonate type deposits and from .01 to 10.0 µg/L for hot-spring type deposits (fig. 5). For both deposit types, filtered samples (0.45 µm) of mine drainage always have lower concentrations of mercury indicating that a significant portion of the mercury present is adsorbed onto particulate phases and colloids (fig. 5). Oxidation and weathering of iron sulfides exposed in underground mine workings and in back fill waste rock contributes to the high sulfate concentration in both

deposit types. Sulfate concentration exceeds several thousand mg/L and is highest in silica-carbonate type mercury deposits that have a high iron sulfide content. Total methylmercury concentration of mine drainage ranges from <.003 to 1.26 ng/L with highest concentrations associated with silica-carbonate type deposits (fig. 6). Filtered samples of mine drainage typically contain lower concentration of methylmercury indicating that methylmercury is also adsorbed onto particulate phases and colloids (see discussion below). Highest methylmercury concentrations occur in waters with high sulfate concentration indicating that underground mines provide an environment for sulfate-reducing bacteria to methylate mercury but methylation is limited by the availability of dissolved organic carbon in this environment.

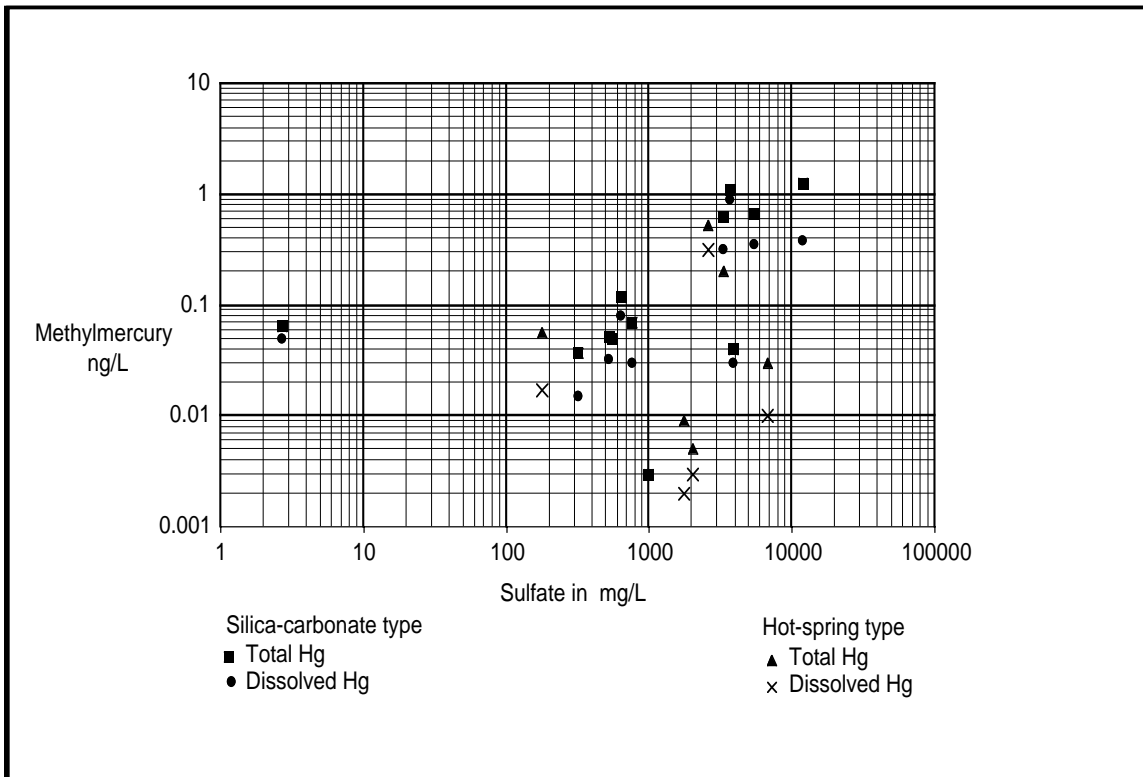


Figure 6. Methylmercury concentration in mercury mine drainage from silica-carbonate type and hot-spring type mercury deposits.

Mine Drainage Composition after Reaction with Atmospheric Oxygen and Mine Wastes

After mine drainage exits the underground mine workings, reaction with atmospheric oxygen results in the oxidation of the dissolved iron (II) to iron (III) and precipitation of iron oxyhydroxide. Mine drainage from silica-carbonate type deposits that have high iron concentration can develop extreme acidity (pH as low as 2.6) (fig. 3) after reaction with atmospheric oxygen causes precipitation of iron oxyhydroxide. Mine drainage often flows over and through mercury-enriched waste rock and mine tailings, because this material typically was disposed in and adjacent to a stream channel that was closest to the mine workings. In mine tailings, mercury commonly is present in soluble phases such as mercury sulfates and oxy-chlorides that were formed during the ore-roasting process (Kim and others, 1998, 2000). As mine drainage reacts with calcines, mercury and methylmercury concentrations in the water increase dramatically, up to two orders of magnitude, because soluble mercury phases are dissolved and the addition of sulfate to the calcines allows sulfate-reducing bacteria to methylate the dissolved mercury (fig. 5) (Rytuba, 2000). Mercury-contaminated soils, especially those that are saturated with water, have been shown to provide a favorable environment for methylation of mercury (Hines and others, 1999). The saturation of mercury-contaminated soils and various types of mine wastes by mine drainage having a high sulfate concentration enhance methylation of mercury in these mine environments.

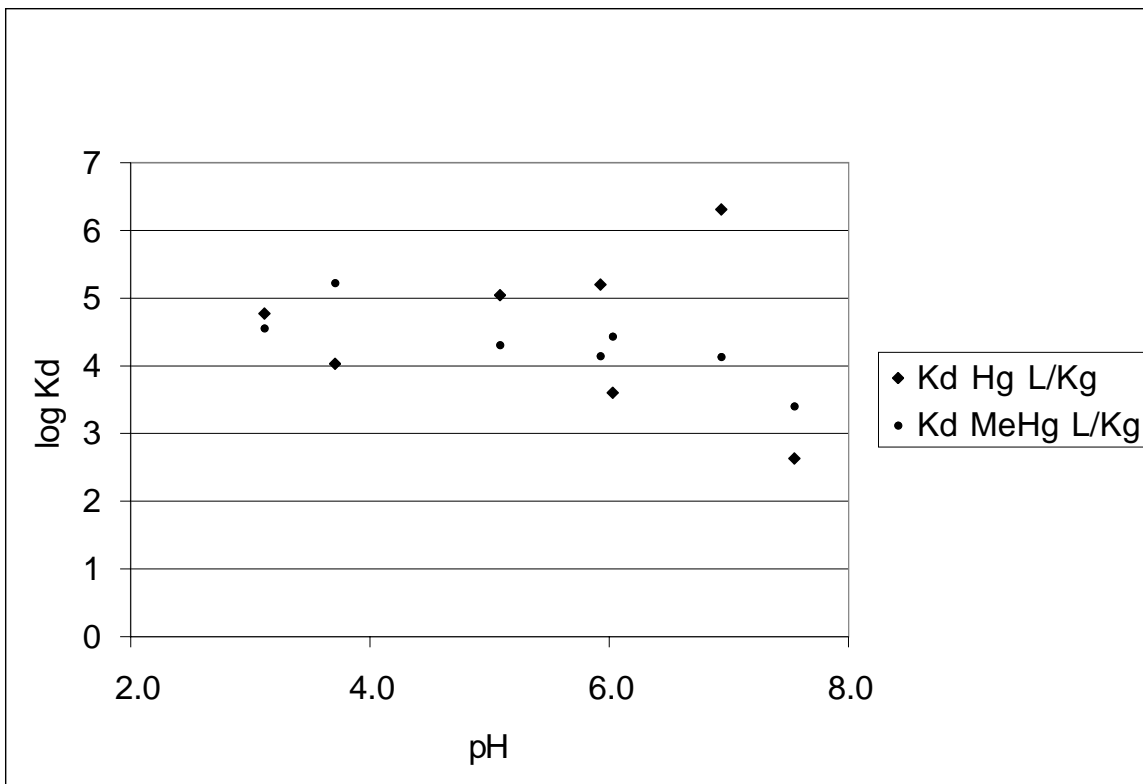


Figure 7. Distribution coefficient, log Kd in L/kg, for mercury and methylmercury with respect to iron oxyhydroxide versus pH (Rytuba, 2000).

Methylmercury Formation and Adsorption in Streams Impacted by Mine Drainage

Streams impacted by mercury mine drainage have elevated levels of mercury, methylmercury, and anions such as sulfate, low pH, and streambeds that are coated by iron oxyhydroxides. Both sulfate- and iron-reducing bacteria (Marvin-DiPasquale and others, 2000) are important methylators of mercury in this high iron and sulfate environment, and stream waters may contain up to several ng/L methylmercury (Rytuba, 1997). As mercury mine drainage mixes with oxygenated stream waters, dissolved iron (II) is oxidized to iron (III) and precipitated as iron oxyhydroxide. High concentration of dissolved iron (up to 8800 ppm) results in iron oxyhydroxide being the most abundant particulate phase present in streams impacted by mine drainage. Aluminum hydroxide and other aluminum silicate phases are also important adsorption substrates. Adsorption of mercury and methylmercury onto iron oxyhydroxide and other aluminum phases is an important process that controls the concentration of mercury species in streams impacted by mercury mine drainage. As a result, most of the mercury species present in streams impacted by mine drainage are present in the particulate phases and the concentration of dissolved mercury species concentrations is very low (Rytuba, 2000). Over the pH range of 3.2 to 7.1, the concentration of mercury in iron oxyhydroxide may be as much as three orders of magnitude greater than that in the coexisting stream water and be as high 220 $\mu\text{g/g}$. Above pH 7.1, mercury adsorption is less effective and macroscopic experiments have demonstrated that the sorptive behavior of mercury (II) onto goethite exhibits a gradual decrease with increasing pH after reaching a maximum adsorption at neutral pH (Barrow and Cox, 1992). Over the pH range 3.2 to 7.1, methylmercury is also strongly adsorbed. Methylmercury concentration is as much as two orders of magnitude greater than that in the coexisting water, up to 105 ng/g. In waters with high sulfate concentration, the negatively charged sulfate complex, $\text{CH}_3\text{HgSO}_4^-$ predominates at low pH (Sanz and others, 1999). It is more effectively adsorbed by iron oxyhydroxide in low pH stream waters than is the neutral methylmercury hydroxide species that is the predominant species in alkaline waters. The distribution coefficient, Kd in L/kg (fig. 7), for both mercury and methylmercury with respect to iron oxyhydroxide significantly decreases at pH above 7.1. Thus, the total amount of mercury and methylmercury present in mine drainage impacted streams primarily reflects the amount of mercury- and methylmercury-enriched iron and aluminum phases present as particles in the water column. The concentration of dissolved mercury species is very low as a consequence of effective adsorption.

Environmental Impact of Mercury Mine Drainage

Mine drainage provides a favorable environment for methylation of mercury because the high concentration of sulfate typically present in these low pH waters is microbially reduced and ionic mercury (Hg^{2+}) is methylated as part of a cometabolic process carried out by sulfate-reducing bacteria. In watersheds impacted by mercury mine wastes and drainage, mercury and methylmercury adsorbed onto iron precipitates, clays, and organic particles accumulate in the streambed during the dry season when water flow is low. A relatively small amount of mercury and methylmercury is transported downstream into larger aquatic systems during this period. During the wet season when stream flows are high, mercury- and methylmercury-enriched sediment is removed from the bed load of the stream and distributed downstream into wetlands, lakes, and reservoirs. The process of sediment redistribution from watersheds impacted by mercury mine drainage and mercury-enriched mine tailings provides a seasonal supply of mercury into aquatic systems where microbial methylation causes methylmercury to enter the trophic levels of the aquatic food web. Methylmercury is biomagnified as it passes upward through the food web to higher organisms, such as fish. Because historic mercury mine sites and active hot springs (or combinations of the two) typically generate the highest concentrations of iron-rich mercury-bearing precipitates, these sites tend to be a primary sources for new mercury entering the cycle.

CLIMATE

In wet climates oxidation and dissolution of pyrite and marcasite increase the possibility of acid-mine drainage and enhance the release of mercury from mine wastes. Wet climates have a higher biologic productivity and as a result dissolved organic carbon concentrations are higher, thus increasing the potential for methylation of mercury by sulfate-reducing bacteria. In dry, high temperature climates, soil-gas emission of elemental mercury is important, and this process may increase the area affected by elevated mercury if adjacent plant communities are present to uptake mercury in their leaves.

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