Mercury Effects, Sources and Control Measures

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INTRODUCTION

Mercury is but one of the toxic heavy metals that contaminates much of the waters and sediments of the San Francisco Estuary. It has been found throughout the Estuary at elevated concentrations in water, sediment, and biota. It accumulates in tissues and is magnified in higher orders of the food web. The form of mercury that typically bioaccumulates in fish is monomethyl mercury, which can constitute 85% of the total tissue mercury. The balance is the soluble, ionic form of mercury, Hg^{+2} which is commonly found in fish gut lining. However, in edible muscle tissue (fillet), the portion normally consumed, virtually all of the incorporated mercury is in the monomethyl form. Fish at the top of the food web can harbor mercury concentrations in their tissues over one million times the mercury concentration in the water in which they swim.

Bivalves appear to accumulate mercury in a manner different from fish. Mercury in these organisms accumulates principally as Hg^{+2} and only 15–20% of the total mercury is methyl mercury. Consequently, a doubling of the most toxic form of mercury, monomethyl mercury, can occur in bivalves without producing a statistically significant change in concentration of total tissue mercury

Partly as a result of the tremendous increase in mercury production and use in this century, and partly as a result of the many soluble species of mercury, mercury contamination is now virtually world-wide in extent and widespread in our environment. It travels easily through different environmental media, including the atmosphere, in a variety of chemical forms and is toxic to humans and biota in extremely low concentrations. In water environments, conjugation with particles dominates the movement and fate of mercury (PTI, 1994; Schoellhamer, 1996). In addition to experiencing the general, industrially-related, global increase in mercury distribution over the last century, California is unique in also being the site of massive bulk contamination by the element. The California Coast Range contains one of the world's great geologic deposits of mercury. This mercury was mined intensively during the late 1800s and early 1900s, largely to supply Gold Rush era gold mining in the Sierra Nevada, where the mercury was used in the gold extraction process. A legacy of leaking Coast Range mercury mines and lost Sierra Nevada quicksilver now provides a significant, additional, ongoing burden of mercury to the Delta and Bay from both sides of the state.
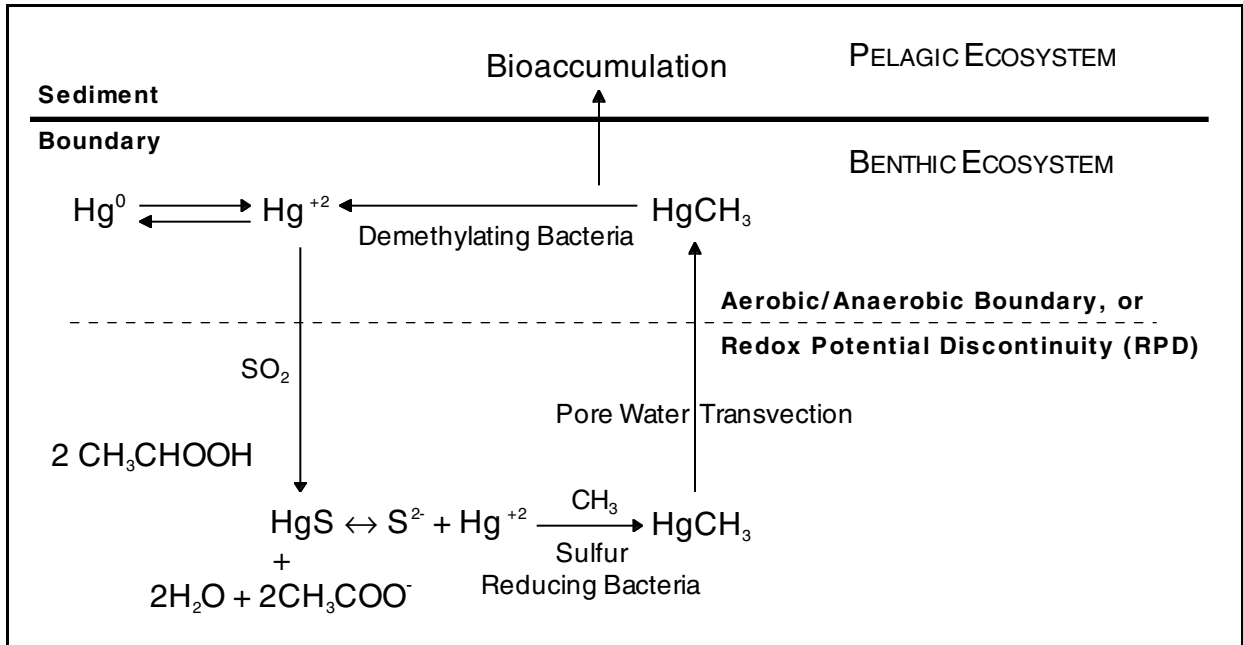
MERCURY SOURCES

Mercury, which occurs as a result of both natural and anthropogenic sources in our environment, continually cycles in the marine environment of the Estuary. The cycle involves different forms and species of mercury as a result of both chemical and biological reactions in aerobic and anoxic microenvironments. Until several years ago, estimates of the natural background level of mercury were unrealistically high due to erroneous data, giving the impression that anthropogenic contributions to the global mercury flux were less than they truly are (Fitzgerald and Clarkson, 1991). The generation of erroneous data arose because of a lack of appreciation for the ease of cross-contamination and the lack of sufficiently sensitive instrumentation to measure mercury in soil, water, and air. A schematic of the cycle is shown in Figure 1.

The bulk of the mercury is normally present as Hg^{+2} in the early stages of deposition, but over time it is probably converted by inorganic chemical reactions to the more insoluble cinnabar (HgS). In California, cinnabar is the primary form of the Coast Range mercury deposits. The mercury used in gold mining in the Sierra Nevada was refined liquid quicksilver (elemental mercury, Hg^0), though this elemental mercury likely experienced various transformations once back in the environment. The concentration and rate of formation of $HgCH_3$ (methyl mercury) in anaerobic sediment and water is thought to be proportionate to the amount of HgS, not the amount of total mercury. There are other factors which influence these reactions including pH, temperature, oxygen/redox level, salinity, toxicity, rate of sediment deposition, rate of pore water transvection, rate of mercury deposition, species of mercury deposited (Hg^0 or Hg^{+2}), and the rate of $HgCH_3$ removal by bioaccumulation.

On a world wide scale, volcanic deposits and mining sources are geographically localized but, in California, they are of great importance. Most additional mercury sources are part of a

widespread, global cycle. The release, deposition, and movement of mercury through these global pools has been catalogued, as shown in Table 1.

Figure 1. Mercury Cycling in a Marine Environment

Bioaccumulation

PELAGIC ECOSYSTEM

Sediment

Boundary

BENTHIC ECOSYSTEM

$Hg^0 \rightleftharpoons Hg^{+2} \longleftarrow HgCH_3$

Demethylating Bacteria

Aerobic/Anaerobic Boundary, or

Redox Potential Discontinuity (RPD)

SO_2

Pore Water Transvection

$2\ CH_3CHOOH$

$HgS \leftrightarrow S^{2-} + Hg^{+2} \xrightarrow{CH_3} HgCH_3$

+

Sulfur

Reducing Bacteria

$2H_2O + 2CH_3COO^-$

Table 1. Global Atmospheric Mercury (Fitzgerald and Clarkson, 1991)

Sources	Hg Movement 10^9 g/yr	Reference
Atmospheric Hg Deposition	5–6	Fitzgerald, 1986
	6	Slemr *et. al.,* 1981
Atmospheric Hg Emissions		
Anthropogenic	2	Watson, 1979
Natural	3.6	Nriagu and Pacyna, 1988
Volcanic	0.06	Fitzgerald, 1986
Other Continental Sources	1–2	
Crustal Degassing		
Forest Fires		
Biological Mobilization		
Oceanic Sources		
Equatorial Pacific	0.2	Kim and Fitzgerald, 1986
World Ocean	2	Nriagu and Pacyna, 1988
Fluvial Hg Input	0.2	Gill and Fitzgerald, 1987

Natural Sources

Mercury occurs naturally in the environment and thus has a background concentration independent of man's releases. Mercury can occur naturally in a variety of valence states and conjugations, such as Hg^0 (elemental mercury), Hg^{+2} (dissolved in rainwater, or as the ore cinnabar, HgS), and as an organometal such as methyl mercury (CH_3Hg and $(CH_3)_2Hg$). Moreover, through natural chemical and biological reactions, mercury changes form among these species, becoming alternately more or less soluble in water, more or less toxic, and more or less biologically available.

As with any site on the globe, there is natural mercury contamination in San Francisco Bay. The recent spate of forest fires in Northern California alone undoubtedly contributed some mercury to this environment. Clearly, in California there is an ongoing load of some magnitude associated with the general export of mercury from natural cinnabar deposits, in addition to mining-related point sources. It is difficult to determine just what proportion of mercury in the Bay Area is from natural sources because what is natural varies greatly from one part of the world to the next. Because of airborne mercury pathways, there is no part of the globe today untouched by the world-wide increase in both use and release of mercury by man in this century. Current and proposed research at the University of California at Davis, seeks to differentiate and quantify the generalized global atmospheric contribution of mercury in California, as compared to regional and point sources. One tool in this work is the study of the historic record of mercury deposition, as preserved in lake and estuarine sediment cores from relatively pristine locations such as Lake Tahoe and from contaminated sites in the Valley, Coast Range, and Bay-Delta. The importance, in this region, of localized bulk contamination mercury sources, over and above general deposition from the global cycle, is apparent in elevated mercury levels in tributaries to the Estuary. Concentrations in inflowing rivers often greatly exceed those seen in comparable rivers in regions without local mercury sources.

Volcanic

Mercury is initially released into the biosphere through volcanic activity. Mercury is present in the earth's crust at a concentration of 0.5 ppm. Mercury typically forms the sulfide (HgS)

because of the prevalence of sulfides in volcanic gases. In this fashion it is found naturally in deposits as the red sulfide ore, cinnabar. It is commercially mined as this form. Volcanic sources emit an estimated global total of 60,000 kg of mercury per year.

Forest fires

Biomass, particularly trees and brush, accumulate and harbor a substantial fraction of the biosphere's mercury. When forest fires heat these fuels to temperatures well above the boiling point of mercury (357°C), the mercury may be released to the atmosphere as either Hg^{+2} or the decomposed Hg^0. The Hg^0 released may be oxidized in the atmosphere over time to Hg^{+2} which is also quite soluble in water and so dissolves in the moisture in the air when released in this fashion.

Forest fires and rain are responsible for the transport and deposition of mercury over much of the world's surface, regardless of its source.

Oceanic releases

Mercury is also a component of seawater and is released naturally through the evaporation of elemental mercury from the ocean's surface. Both elemental and ionic mercury are soluble in water, although elemental mercury to a much smaller degree. As less soluble elemental mercury evaporates, the equilibrium reaction is pulled towards more elemental mercury, which then releases more elemental mercury from the ocean's surface. The equilibrium reaction between ionic and elemental mercury is shown below in Equation 1:

$$Hg^{+2}{}_{Aq} + 2e^- \leftrightarrow Hg^0{}_{Atmos} \qquad \text{Equation 1}$$

Ionic mercury can form from the oxidation of elemental mercury or from the demethylation of monomethyl mercury.

Anthropogenic Sources

Mercury is used in a broad array of more than 2,000 manufacturing industries and products (Kurita, 1987). These include barometers, thermometers, hydrometers, pyrometers, mercury arc lamps, switches, fluorescent lamps, mercury boilers, mercury salts, mirrors, catalysts for the oxidation of organic compounds, gold and silver extraction from ores, rectifiers, cathodes in electrolysis/electroanalysis, and in the generation of chlorine and caustic paper processing, batteries, dental amalgams, as a laboratory reagent, lubricants, caulks and coatings, in pharmaceuticals as a slimicide, in dyes, wood preservatives, floor wax, furniture polish, fabric softeners, and chlorine bleach (Volland, 1991). Individual industries use different forms of mercury as well, as shown in Table 2.

The United States produced about 3,435 tons of mercury in 1986 and imported another 6.5 tons. It is estimated that the US exported about 32.5 tons of mercury that year, yielding a net domestic annual use of about 3,409 tons of mercury (HSD, 1991). Of this use, 50% to 56% was used in the electrical industry, 12% to 25% was used in chloralkali plants to generate chlorine and caustic soda, 10% to 12% was used in paint manufacturing, and about 3% was used in the preparation of dental amalgams (Sills, 1992).

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Table 2. Sources and Uses of Mercury (USDHHS, 1992)

Name	Form	Source or Use
Mercury	Metallic or Elemental (Hg^0)	Chlorine-alkali manufacturing
		Dental fillings
		Gold mining
		Electrical equipment (batteries, switches)
		Instruments (thermometers, barometers)
Mercuric mercury	Inorganic (Hg^{+2})	Electrical equipment (batteries, lamps)
		Skin care products
		Medicinal products
Mercurous mercury	Inorganic (Hg^{1+})	Electrical equipment (batteries)
		Medicinal products
Methyl mercury	Organic (CH_3Hg^{1+})	Diet (e.g., contaminated fish)
		Polluted sediment
Phenylmercury	Organic ($C_6H_5Hg^{1+}$)	Fungicides
		Pigments (paints)

Mining

In addition to the generalized global and local industrial sources of mercury described above, the watershed of the San Francisco Estuary contains a tremendous amount of mining-related, bulk mercury contamination. Historically, mercury was mined intensively in the Coast range and transported across the Central Valley for use in Sierra Nevada placer gold mining operations. Virtually all of the quicksilver used in these operations was ultimately lost into Sierran watersheds. It has been estimated that, in river drainages of the Mother Lode region alone, approximately 7,600 tons of refined quicksilver was inadvertently deposited in conjunction with Gold Rush era mining (CVRWQCB, 1987). Additional mercury was used throughout the gold mining belt of the northwestern and central Sierra Nevada. The majority of Coast Range mercury mines which supplied this practice have since been abandoned and remain unreclaimed. As a result of these two activities, bulk mercury contamination exists today on both sides of the Valley.

Larry Walker and Associates (1995) measured mercury concentrations and loads at index stations on the Sacramento, Feather and Yuba Rivers. A particular focus was placed on the Yuba River, upstream and downstream of Englebright Reservoir, to investigate the effects of foothill reservoirs on downstream mercury transport. In related work, Slotton *et al.* (1995a) have, since 1993, evaluated the local bioavailability of mercury in all major river tributaries throughout the northwestern Sierra Nevada. The water quality data indicate that a significant amount of Gold Rush era mercury still exists in sediment in the upper Yuba watershed and that this is being transported down into Englebright reservoir, where it is largely trapped. Bioavailability studies confirm that the reservoir acts as an interceptor of not only inorganic, sediment-based mercury, but of bioavailable methyl mercury as well. Despite the fact that elevated levels of mercury are found in the heavily mined upstream tributaries and, particularly, within Englebright Reservoir itself, the aquatic biota below the impoundment consistently demonstrate significantly reduced concentrations of mercury, as compared to above the reservoir. The bioindicator organisms used in this work represent time-integrated measures of in-stream mercury bioavailability and indicate that the reservoir acts to consistently intercept bioavailable mercury that would otherwise be available for downstream transport, ultimately to the Bay/Delta system. The assumption is that mercury cycling in other Sierra watersheds is similar to that observed in the Yuba. However, as a cautionary note, the United States Geological Survey (USGS) observed high concentrations of mercury associated with particulate matter in high flows downstream of

Englebright Reservoir last winter. The USGS believes the mercury was deposited in the streambed before construction of the dam and is only now being eroded away (Joseph Domagalski, personal communication). Therefore, much, but clearly not all, of the mercury remaining in the Sierras from historic gold mining may be unavailable for downstream transport and biomagnification in the Estuary. In the few high mercury rivers without dams, particularly the Consumnes, direct transport of historic gold mining mercury into the Estuary remains unimpeded.

Recent work suggests that the Coast Range, rather than the Sierra Nevada, may be a dominant source of mercury to Central Valley Rivers and the Estuary. The Larry Walker and Associates Sacramento River mercury mass balance work indicated that the export of mercury from northwestern Sierra Nevada rivers was considerably less than that contributed by drainages in the north central and northwestern portions of the state, possibly largely due to trapping of mercury by foothill reservoirs. At the confluence of the Feather and Sacramento Rivers at Verona, the upstream Sacramento River was, somewhat surprisingly, found to contribute 75–80% of the total mercury load at that river mile.

Another mercury mass load export study was undertaken by the Central Valley Regional Board in the southwestern part of the Sacramento River watershed during 1995. The spring of 1995 was wet, and water from the Sacramento Valley entered the Estuary through both the Sacramento River and Yolo Bypass. Highly elevated concentrations of mercury were repeatedly observed in the Bypass. The source of a significant portion of the mercury was traced to Cache Creek, which drains Clear Lake and which is estimated to have exported about a thousand kilograms of mercury to the Estuary in 1995. The drainage is known to be enriched in mercury and has several large abandoned mercury mines. Long-term sediment mercury mass balance work by the Slotton research team on just one small tributary, Davis Creek, has documented mobile, in-stream loads of approximately 200 kg of mercury in single wet seasons (Reuter *et al.,* 1996). For perspective, a single gram of mercury has been found to be sufficient to contaminate the typical midwestern lake (Watras *et al.,* 1994). The majority of mine-related mercury from the Davis Creek sub-drainage is currently intercepted by the dam at Davis Creek Reservoir, though mercury from other similar mercury mine regions remains available for downstream transport. Follow-up studies by the Central Valley Regional Water Quality Control Board and Slotton *et al.* are underway to determine (1) whether the source(s) of the mercury are localized to mines and (2) to determine the spatial trends in *in situ* bioavailability of mercury throughout the watershed.

Also in 1995, a comprehensive synoptic study was undertaken in the small Marsh Creek watershed of Contra Costa County (Slotton *et al.,* 1996). This research was conducted during a period of steady high flow, immediately following a series of large storms, to identify and quantify mercury sources and local aquatic bioavailability. All significant tributaries were sampled. The small drainage was found to export 10–20 grams of mercury per day, with greater amounts during actual storm events. Mass balance calculations indicated that about 95% of the entire watershed's mercury load originated from the Mount Diablo mining area; about 93% of this was from a relatively small patch of exposed mine tailings. A generalized source of mercury from the elevated-mercury natural terrain was not indicated by the data, despite the fact that the great majority of the watershed's flow and suspended solids load emanated from non-mining regions. Most of the mercury exported from the mine workings was found to initially leave the site in dissolved form, highly mobile and potentially more easily methylated by bacteria than cinnabar particles. Bioaccumulation studies indicated that aquatic organisms immediately below the mine tailings had the highest tissue concentrations in the watershed. Even small invertebrates contained up to 60 times the 0.5 ppm health guideline concentration of mercury for edible fish. Body burdens fell with increasing distance from the mining area, but were significantly elevated above upstream, control levels for the 10 miles downstream to Marsh Creek Reservoir, where they were also significantly elevated.

Coal-Fired Power Plants

Coal is known to contain mercury as a result of testing done upon the flue gas emitted from power plant stacks. The quantity released by burning coal is estimated to be on the order of 3,000 tons per year globally, about the same amount released through all industrial processes (Joensuu, 1971). The concentration of mercury in coal varies form as low as 70 ng/g up to 22,800 ng/g

(ppb). During the burning of coal, mercury is initially decomposed to elemental mercury and then, as the flue gas cools and exits the plant, the majority of the mercury is quickly oxidized, probably catalytically due to the presence of other metals in the gas, to its water-soluble, ionic form, Hg^{+2}.

Gasoline and Oil Combustion

Crude petroleum is known to contain small but measurable amounts of mercury. A study performed on the mass of metals in crude oils from 32 different sources stored in the nation's Strategic Petroleum Reserves (SPR) in salt domes in Oklahoma has determined that the average amount of mercury in petroleum is 0.41 ppm (Shur and Stepp, 1993). The standard deviation for this average was a rather large (0.90 ppm) with one crude oil (Arabian) containing 5.2 ppm mercury. Another study of metals performed on petroleum found a range of mercury concentration from 0.03 to 0.1 ppm (Speight, 1991). Both of these studies were performed using older mercury analysis methods with method detection limits of approximately 0.11 ppm. However, these studies also indicate minimum mercury concentrations in crude oil.

Approximately 16 to 18 million barrels (672 to 756 million gallons) of crude oil are consumed daily in the United States. At an average concentration of 0.41 ppm mercury and an average density for crude oil of 6.9 lbs per gallon, the minimum total amount of mercury vaporized daily is therefore 1,901 lbs. This value represents an annual discharge of 347 tons of mercury nationwide, assuming that all of the oil is combusted. Certainly, the greatest proportion of the petroleum used in the United States is burned in vehicles. It is unclear whether the mercury present in crude oil is vaporized during the refining process or whether it remains in the refined petroleum. Because of the very large volumes of oil consumed, even a small concentration of mercury clearly represents a major source of atmospheric deposition of mercury. More work with the more sensitive analytical methods developed in the past few years should be performed to confirm these numbers.

Smelting

The smelting of ores to yield pure metals is thought to release some mercury into the atmosphere. Most metal ores are thought to have higher concentrations of mercury than coal, although the volumes of ore that are smelted each year pale in comparison with the volume of coal burned for power generation.

Chlor-Alkali Plants

Elemental mercury is employed as the electrode in the electrochemical production of chlorine gas and caustic soda (sodium hydroxide). Near most paper and pulp facilities which employ this technology to bleach the paper product white, the sediment is contaminated with high concentrations of mercury.

Mildew Suppression, Laundry facilities

An infrequent and historical point source of mercury contamination has been the use of mercury compounds for mildew suppression by laundry facilities, which have a chronic problem with moisture and bacterial growth (Sills, 1992). This contamination source type should no longer be a problem. The use of mercury as a fungicide in interior latex paints has been similarly banned by the US EPA.

Sewage Treatment

Sewage treatment represents the focal point of today's urban industrial, commercial, and domestic liquid waste streams. The secondary treatment of sewage involves dewatering, which necessarily concentrates the solids and all non-volatile contaminants, but does little to treat or remove inorganic dissolved contaminants. Mercury is commonly found in urban sewage through point source discharges from dental offices and industrial manufacturing processes such as battery fabrication. As the sewage is dewatered and the solids concentrated, mercury can be either sequestered by the organic humus of sludge or, if the sludge is caked and dried, can be released to the atmosphere in the drying process.

If the sludge has been dried, the fate of the sludge itself then dictates the extent of mercury contamination. Commonly, the dried product is incinerated or spread upon tree farms as a fertilizer and organic material. Sewage sludge incineration probably accounts for no more than 3,000 kg/yr in mercury emissions (EPA, 1990). The distribution of sludge in this fashion also spreads concentrated mercury over a large area where it is either taken up in the biomass or contributes to surface water runoff and consequently downstream contamination.

Difficulties can arise when dissolved inorganic contaminants are not removed from treated waste water prior to its reintroduction to receiving sewage. In Michigan's upper peninsula, the sediments and fish of 900-acre Deer Lake near Ishpeming were found in 1981 to be severely contaminated with mercury as a result of releases from the Ishpeming waste water treatment plant and combined storm sewer overflows (Sills, 1992). The upstream discharge that contaminated the sewage releases was from the laboratories of an iron ore mining company.

Mercury dumping from naval vessels

The US Navy has surfaced as a major source of near-shore marine mercury pollution because of the use of mercury as ballast in its subsurface vessel fleet. During inter-ship ballast transfer operations, elemental mercury is occasionally spilled into marine waters, resulting in contamination of both sediment and water. This could be a significant point source of mercury directly within the Estuary.

Influences upon Mercury Pollution

pH

The pH of inland surface waters has been found to dramatically affect the amount of mercury taken up by biota (Gilmour and Henry, 1991). Specifically, mercury in fish tissue is present predominantly as methyl mercury, so changes in the biogeochemistry of this compound of mercury may account for any increase in bioaccumulation. It has been determined that inorganic mercury binds to organic matter more strongly as the pH declines (Schindler *et al.,* 1980), thus decreasing mercury's solubility. Conversely, in sediments a lower pH may increase the solubility of HgS (Ramal *et al.,* 1995). Alkalinity and pH affect the biogeochemistry of mercury in numerous ways, including the binding capacity of the various species, the rate of methyl mercury production, and even the uptake efficiency of methyl mercury by aquatic organisms (Cope *et al.*, 1990; Slotton 1991). The most important result of these combined effects is that methyl mercury is produced, transported, and accumulated by aquatic organisms significantly more efficiently at low alkalinity and pH; i.e., conditions to the acidic side of neutrality (< pH 7) (Winfrey and Rudd, 1990). Because of this, many thousands of lakes in north central and north eastern United States, central and eastern Canada, and northern Europe can, and do, develop mercury accumulations in edible fish well above health guidelines, from global atmospheric deposition alone and with no local point sources. In California, the naturally moderate to high alkalinity of surface waters maintains the pH at levels typically well above acidic conditions. This is very fortunate, in light of the bulk mercury contamination that supplements global loads in many parts of the Estuary watershed. Under prevailing conditions of high alkalinity and above neutral pH, even grossly contaminated water bodies such as Clear Lake frequently do not demonstrate edible fish mercury levels dramatically higher than those from relatively unpolluted, but acidic, waters. With hypothetical lower levels of alkalinity and pH, surface waters with bulk mercury contamination

(i.e., much of the San Francisco Estuary watershed) could be expected to develop fish mercury accumulations far above those seen today.

Salinity

Salinity has been statistically linked to dissolved mercury concentrations in an inverse relationship, suggesting that local runoff may be an important source of dissolved mercury in the South Bay. As runoff increases and salinity decreases, the concentration of dissolved mercury increased (SFEI, 1993). Increasing salinity has also been associated with a decline in the rate of mercury methylation and in equilibrium methyl mercury concentrations (Compeau and Bartha, 1984).

Sulfate concentration

The microbial methylation of mercury is thought to proceed through the metabolic action of sulfur- reducing bacteria (SRB) in anoxic environments (Gilmour and Henry, 1991). The concentration of sulfate in marine waters is approximately 28 mM, which is considerably higher than freshwater sulfur concentrations. In freshwater systems, it is clear that an increase in sulfur concentration increases sediment sulfate-reduction rates (Rudd *et al.,* 1986). However, there appears to be a window of sulfate concentration that promotes the highest mercury methylation rate. Optimum mercury methylation by SRB in sediments is at 200–500 mM. Above this range, the formation of sulfide appears to inhibit methylation. At the same time, the presence of other sulfide-forming metals, such as iron, may affect the equilibrium between sulfate and sulfide in the pore water of the system.

Percent Fines

In aquatic sediments, mercury and other heavy metal contamination is most strongly correlated with the proportion of fine particles. This is particularly the case when the heavy metal load entering the system is largely in a very diffuse, molecular form, such as in atmospheric deposition, mine leakage of dissolved metals, and direct introduction to the environment of liquid or vaporized elemental mercury. Fine sediment particles contain a disproportionate amount of surface area and adsorption sites, and thus tend to accumulate far greater concentrations of diffuse heavy metals than do larger sediment particles such as sand and gravel. In local research at a Sierra Nevada foothill reservoir, bottom sediment concentrations of mercury, as well as copper, zinc, and cadmium, were found to increase exponentially at average sediment grain sizes of less than 24 micrometers (Slotton *et al.,* 1994; Slotton and Reuter, 1995). In addition to largely determining the concentration of mercury in the sediments, sediment particle size also affects the diffusion of oxygen, minerals, and ions which therefore affects bacterial activity and the production of methyl mercury.

Aerobic and Anaerobic Microenvironments

Each transformation of mercury from one valence state or one species to another takes place in specific microenvironmental compartments (Figure 1). At the aerobic/anaerobic boundary in sediment, which is the limiting depth for oxygen penetration into the sediment, there is a redox potential discontinuity (RPD). In the oxygen-rich environment of the upper sediment, the electrochemical potential is oxidizing, thus favoring oxygen metabolism and the ionized (soluble) states of metals (e.g., Hg^{+2}). Conversely, the oxygen-poor lower sediment exhibits a reducing electrochemical potential that favors sulfur metabolism by sulfur reducing bacteria (SRBs). Two products of microbial sulfur metabolism are HgS (which is highly insoluble) and CH_3Hg (which is the form of mercury most commonly found in tissue), when mercury is present in the sediment.

Where the water itself becomes anaerobic, methyl mercury production can increase dramatically and transfer rapidly and efficiently into the aquatic food web. Research at Davis Creek Reservoir in the Berryessa/Clear Lake historic mercury mining district found that the seasonally anoxic bottom waters of the reservoir provided a large annual pulse of methyl mercury to the reservoir food chain (Slotton 1991; Slotton *et al.* 1995a). Piscivorous largemouth bass in this system accumulated fillet mercury at concentrations up to 10 times the 0.5 ppm health guideline.

Both the proportions of total and dissolved mercury concentrations in the water and their absolute values can change due to shifts in the electrochemical potential of the sediment and/or water. Hydrological impacts such as the deposition of abnormally high volumes of silt, scouring, growth of algae or other oxygen-scavenging flora can dramatically alter mercury biogeochemistry and, consequently, the production, transformation, and concentration of the different mercury species.

MERCURY'S HEALTH EFFECTS

As mercury cycles through various forms and media, its bioavailability and toxicity change through both biological and chemical reactions. Because mercury is found throughout the environment, everyone is exposed to low levels of mercury. Dental amalgams are themselves about half mercury and it is known that mercury in the breath of persons with mercury amalgam fillings is higher than those without. However, the health effects of dental amalgams is unknown. Mercury emanating from amalgams is, at least initially, entirely in inorganic forms, which are not readily accumulated by the body as compared to methyl mercury. Other principal means of human mercury exposure are through the use of skin care products and, particularly, through the consumption of methyl mercury contaminated fish. The three pathways of exposure are then inhalation, absorption, and ingestion.

The principal target of long-term exposure to low levels of metallic and organic mercury is the nervous system. The principal target of long-term exposure to low levels of inorganic mercury appears to be the kidneys (USDHHS, 1992). Short-term exposure to higher levels of any form of mercury can result in damage to the brain, kidneys, and fetuses. Mercury has not been found to be carcinogenic. However, there are significant differences in the toxicity of the major forms of mercury. Mercury has been found to have a deleterious effect upon a wide range of systems including the respiratory, cardiovascular, hematologic, immune, and reproductive systems.

The bioaccumulation of mercury in various forms contributes in large measure to its toxicity. Table 3 lists concentrations that have been documented in a typical freshwater lake food web.

Table 3. Methyl mercury Concentrations in the Food Web (PTI 1994 p. 2)

Planktivores	0.680 mg/kg wet	Piscivores	1. 130 mg/kg wet
Zooplankton	0.260 mg/kg wet	Benthivores	0.480 mg/kg wet
Phytoplankton	0.032 mg/kg wet	Benthic Macroinvertebrates	0.025 mg/kg wet
Lake Water	0.0000003 mg/L (0.3 ng/L)	Pore Water	0.000002 mg/L (2 ng/L)

The common markers for human mercury exposure are blood, hair, and urine mercury concentrations. The mean total mercury levels in whole blood and urine of the general human population are approximately 8 µg/L and 4 µg/L, respectively (WHO, 1990). This background level of mercury can vary considerably, however, with the incidence of dental mercury amalgams and the consumption of fish. Individuals whose diet consists of large amounts of fish can have blood methyl mercury levels as high as 200 µg/L with a daily intake of 200 µg of mercury.

DATA TRENDS IN THE REGIONAL MONITORING PROGRAM

One of the apparently striking conclusions that can be drawn from the data is the lack of bioaccumulation of mercury in the bivalves transplanted for periods of 90 to 100 days to various locations in the Bay for any of the three years of the RMP. Bivalves generally do not accumulate dramatically elevated mercury concentrations, and the mercury they do contain (primarily inorganic mercury) is transferred to consumers far less efficiently than is methyl mercury. The food chain pathway of methyl mercury through larger, piscivorous fish is typically of primary

importance in consumption-related toxicity to higher order consumers, including humans. In recent research at EPA mercury Superfund site Clear Lake California, sedentary, wild Corbicula clams collected from numerous sites around the lake demonstrated consistently low mercury levels and only very small variations in concentration, even across sediment inorganic mercury concentrations that varied by over two orders of magnitude (D.G. Slotton, unpublished data). The pathways of methyl mercury through larger, piscivorous fish appear to be of prime importance in consumption-related toxicity to higher order consumers, including humans. Mercury bioaccumulation in larger piscivorous fish has resulted in tissue concentrations 105 times higher than concentrations in adjacent water (PTI 1994). No piscivorous fish or any organism at the higher end of the food chain has been studied by the RMP for trace metal bioaccumulation. However, as part of the Bay Protection and Toxic Cleanup Program, a fish contamination study was conducted for the San Francisco Estuary (Taberski *et al.,* 1992), and findings revealed tissue concentrations above levels of human health concern in several fish species analyzed.

There has been an appreciable correlation between sediment mercury concentrations and the percentage of fines in the sediment for each of the three years. The greatest proportion of most metals, including mercury (Reimers and Krenkel, 1974), in marine environments is associated with particulates and specifically with the small size fractions of sediment (Schoellhamer, 1996). Local freshwater sediment research at Camanche Reservoir reported similar findings (Slotton *et al.*, 1994, Slotton and Reuter, 1995).

It has been estimated that there is an optimum sulfate concentration for the methylation of mercury by SRB in sediments. Below 200–500 mM sulfate, mercury methylation (a by-product of metabolic sulfate reduction) is suboptimal and above this concentration, sulfide formation would inhibit methylation. This range is below the concentration of sulfate in marine waters, which are also highly buffered compared to freshwaters. In any marine environment, there is still a question as to whether sediment mercury is the source of methyl mercury that can be bioaccumulated, in part because it is probable that the reactions controlling the methylation of mercury in sediment and water are different (Gilmour and Henry, 1991). In marine waters, vigorous sulfide formation probably inhibits the methylation of mercury.

Dissolved Hg^{+2} concentrations appear to be controlled by chelation reactions rather than by dissolution in aerobic waters, while precipitation may control mercury solubility in anaerobic sediments (Nelson and Campbell, 1991).

In some years, variations in mercury concentrations in sediment were correlated with total organic carbon (TOC) and redox potential (Eh), and in some years they were not. As a result, there do not appear to be seasonal correlations with variations in mercury concentrations. Redox conditions can clearly alter the proportion of soluble to insoluble mercury, and so ultimately may alter the amounts of total mercury that lay in the sediment. It is likely, however, that variations in TOC and redox conditions are variables that are impacted by Bay influences other than those which impact mercury concentrations.

POTENTIAL CONTROL MEASURES

Control of anthropogenic sources of mercury pollution involves both point source and area source control. Point source control is often wielded through mechanical or chemical means, while area control is often executed by administrative means. It is always true that it is easier to recover mercury at the source, where it is more concentrated, than it is to recover it after it has dispersed in different forms and species throughout the environment. The continuous cycling of mercury through its many different forms also dramatically complicates the job of devising effective technologies to remove mercury from the environment.

Source Control

Investigators of point sources of mercury pollution have been very effective in isolating sources in the environment. Extremely sensitive analytical instrumentation is now available to monitor total mercury emissions or to analyze mercury's different forms down to the picogram level.

Remediation of Abandoned Mines

As a result of the Coast Range mercury deposits, soils in several locations throughout the San Francisco Estuary watershed are naturally high in mercury, and a great number of abandoned mines exist that, to this day, release substantial amounts of mercury into surface waters as rain falls onto mine tailings. When high sulfur ore is exposed to the combination of water and oxygen, sulfuric acid is produced. The resulting acidic drainage from man-made tailings piles and mine workings dissolves mercury and transports the dissolved metal, as well as mercury-bearing particles, into creek channels. Ongoing research in the Marsh Creek watershed has found the source of downstream mercury to be highly localized to upstream mine tailings, as opposed to a generalized, regional source (Slotton *et al.,* 1996). This work has identified potentially effective control and remediation strategies, and has developed site-specific biological and chemical markers which will be used to guide future remediation efforts and quantify their effectiveness. On a larger areal scale, the Cache Creek project is currently underway to evaluate potential mercury control strategies in that important drainage. Both of these projects may serve as models for control and remediation of abandoned mines throughout the San Francisco Estuary watershed.

In contrast, the gold-mining mercury in the Sierra Nevada has been found to be largely dispersed and unsuitable for point-source cleanup approaches (Slotton *et al.,* 1995b). However, a considerable amount of mercury is extracted from Sierran rivers in the course of ongoing placer gold mining. A buy-back program is currently being developed by the Central Valley Regional Water Quality Control Board to encourage the collection and removal of this mercury.

Waste Stream Capture

Dental offices contribute a fair portion of municipal mercury waste. Mercury constitutes almost 50% of the material in dental amalgam tooth fillings. When this material is removed or when a new amalgam is fitted, some particulate-associated mercury is invariably released into waste water. Entrapment of this particulate mercury waste stream could appreciably reduce the mass of mercury entering municipal waste water. It is estimated that each dentist in the US uses an average over 1 kg of amalgam annually (Goering *et al.,* 1992). It is not yet clear whether the highly bound, inorganic mercury of dental amalgams is appreciably available for methylation and incorporation into the food web. Indeed, a very important future area of research involves the determination of the short and long term dissolution and methylation potential of all the major inorganic forms of mercury, including cinnabar, elemental mercury (quicksilver), and dental amalgams.

A good deal of the anthropogenic mercury released world-wide is dissolved in waste water streams. In many industries that use large amounts of mercury, dissolved mercury is routinely captured from waste streams through a variety of technologies utilizing either the ionic nature of most dissolved mercury or the unique and consistent size of dissolved mercury ions. The installation of such traps and filters can be a very effective measure at preventing mercury releases from low volume emitters particularly, because the capacity of such systems can be engineered to require regular but infrequent changeouts.

Flue Gas Scrubbing

Scrubbers are added as air emission control devices to a variety of incinerators to remove toxic or hazardous compounds, most commonly the sulfates. Mercury is present in some concentration in virtually all incineration processes. Commonly, the emitted gas is scrubbed by an aqueous counter-current to both cool the gas and to solubilize compounds in the gas. Other common scrubbing technologies are scrubber/fabric filters, lime injection directly into the combustion chamber, and electrostatic precipitators. At the high temperatures used in most incinerators (or in any process with a temperature greater than $900°C$), all forms of mercury are decomposed to reduced elemental mercury, Hg^0. As the temperature of flue gas quickly drops, Hg^0 is oxidized to soluble Hg^{+2} (probably in part due to the catalytic contributions of other trace metals in the gas) and thus most mercury scrubbed from incinerator gas will dissolve in the cooling water and be transported to the settling ponds.

If flue gas is not scrubbed, mercury can be conveyed both far (as elemental mercury by the wind) and near (as Hg^{+2} dissolved in atmospheric moisture and deposited as rain). In municipal waste

incineration, most mercury is released as the volatile mercuric chloride, $HgCl_2$ (Braun and Gerig, 1991).

Area Control

The mercury that evaporates from dental amalgams and is inhaled can have a surprisingly large impact upon the human body's mercury burden, particularly for inorganic mercury (Goering *et al.,* 1992). However, in many parts of the US and the world, ingestion of fish and other seafood contaminated with methyl mercury is an additional and often dominant source of mercury exposure. Administrative controls to limit the exposure of humans to mercury include warning limits on the amount of fish consumed in a given period.

When sediments are determined to be contaminated with mercury, capping is often a useful measure to limit exposure to the environment. Capping naturally produces an anoxic environment in the underlayment which, over time, can promote the formation of insoluble HgS if sufficient amounts of sulfate are present. Capping also eliminates the potentially harmful effects associated with some forms of dredging to remove contaminated sediments. Dredging can mix sediments with relatively high concentrations of mercury where it can disperse into the water column, aerate sediments and thus promote transformation of mercury to oxidized, soluble Hg^{+2}, and result in the frequently more onerous issue of remediating or disposing of highly contaminated dredge spoils on-land.

Some forms of dredging have been deliberately engineered to minimize the hazards outlined above. The watertight clamshell is one, and vacuum suction dredging is another. These technologies seek to recover only contaminated sediment without mixing with the water column and without further contaminating clean, underlying sediment.

Finally, mercury-contaminated soil and sediment can be washed with any of a variety of surfactants, solvents, or redox reagents to concentrate and/or chemically alter the mercury. The mercury can either be recovered as the element or condensed as the vapor to prevent merely exchanging a problem in one medium for one in another.

In the Estuary, mercury contamination is probably far too widespread for direct/physical areal control measures to be effective or economically feasible. However, significant opportunities may exist for effective point source remediation of important mercury discharges, which would otherwise continue to be transported into the Estuary.

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