

Introduction

Present concentrations of mercury in the San Francisco Estuary and the Sacramento and San Joaquin rivers are high enough to warrant concern for the health of humans and wildlife. The CALFED Bay-Delta Program (CALFED) is a collaborative effort among 23 state and federal agencies to restore ecological health and improve water management for the beneficial uses of the San Francisco Estuary (Estuary, that is, the combined Bay and Delta). Tidal wetland restoration on a large scale is being considered by CALFED and other agencies as a means of increasing populations of fish species of concern (Brown 2003). Large scale tidal wetland restoration may lead to increased concentrations of mercury in the estuarine food web and exacerbate the existing mercury problem.

Tidal wetlands are part of the Estuary. They are intimately connected to the open waters of the Estuary through the exchange of water and sediment. Tidal wetlands are generally retentive environments that store most of the materials they receive. Consequently, regional changes in water or sediment quality in the Estuary caused by large scale restoration actions will also affect water and sediment quality in tidal wetlands. For example, increased mobilization of historically contaminated sediment from the Bay floor would result in larger supplies of mercury to Bay tidal wetlands. Conversely, tidal wetlands can also serve as sources of materials that they produce or that they release from their stores. Restoration actions that specifically affect mercury cycling in tidal wetlands or that increase the amount of tidal wetlands in the Estuary can result in changes in methylmercury production and accumulation on a regional scale.

The objective of this article is to evaluate our present ability to predict the local and regional effects of large scale restoration actions on mercury accumulation in aquatic food webs. The article begins by documenting the cause for concern over mercury in the Estuary. Past and present sources of mercury and the mercury cycle are then described to provide context for understanding the possible impacts of restoration actions. This is followed by a discussion of factors influencing mercury accumulation in tidal wetlands. Finally, a set of recommendations is presented to address major uncertainties and provide the information needed to assess and avoid increases in mercury accumulation due to tidal wetland restoration.

Existing Concerns for Human and Wildlife Health

Mercury concentrations increase with each step in the food chain in a process known as biomagnification. Generally, species at the top of the food chain, such as humans and fish-eating wildlife, receive the highest mercury exposure. In the Estuary, birds that are benthic omnivores in tidal wetlands also accumulate relatively high mercury concentrations.

Human Health Concerns

Concern for human health stems primarily from mercury exposure through consumption of contaminated sport fish. This is a concern throughout a large portion of the Estuary, but tidal wetland restoration activities could increase mercury accumulation in sport fish and other species consumed by humans both near specific wetland areas (a local scale) and in the Estuary as a whole (a regional scale).

Mercury is a neurotoxicant, and in humans is particularly hazardous for fetuses and children as their nervous systems develop (OEHHA 1994a). Mercury can cause many types of problems in children, including mental impairment, impaired coordination, and other developmental abnormalities. In adults, mercury has neurotoxic effects that include decrements in motor skills and sensory ability at comparatively low doses, to tremors, inability to walk, convulsions, and death at extremely high exposures.

In 1970 a human health advisory was issued for the Delta advising pregnant women and children not to consume striped bass (*Morone saxatilis*) (Brodberg, personal communication, see "Notes"). The advisory was revised in 1993 upon review of more mercury data for striped bass (Brodberg, personal communication, see "Notes"). The revised advisory included size-specific consumption advice for adults, children aged 6 to 15 years, pregnant women, and children under age 6. Recent studies in the Bay-Delta watershed have continued to find mercury concentrations of potential human health concern in several popular sport fish species. Extensive sampling was conducted in San Francisco Bay in 1994 and 1997 (SFBRWQCB 1995; SFEI 1999). In response to the 1994 results, an interim fish consumption advisory was issued for the Estuary, largely due to concern over human exposure to methylmercury (OEHHA 1994b). Following USEPA guidance (USEPA 1995), a mercury screening value of $0.23 \mu\text{g g}^{-1}$ wet weight was calculated (SFEI 1999). Samples with concentrations above this screening value indicate a potential human health concern. In the Bay in 1997, 44 of 84 samples (52%) exceeded this concentration (SFEI 1999). The species with the highest median concentrations in the Bay in 1997 were leopard shark (*Triakis semifasciata*, $0.88 \mu\text{g g}^{-1}$ wet weight) and striped bass (*Morone saxatilis*, $0.42 \mu\text{g g}^{-1}$ wet weight). (Tissue concentrations in this article are for total mercury, which is less costly to measure than methylmercury. Approximately 95% of the mercury in sport fish is methylmercury [Wiener and Spry 1996], so the total mercury concentration is a good approximation of the methylmercury concentration.)

Studies of mercury contamination in sport fish have also been conducted in freshwater portions of the Estuary and its watershed in the past few years. Sport fish sampling was conducted throughout much of the Delta (the "Delta Study") in the summer of 1998 (Davis and others 2000b). This sampling focused on largemouth bass (*Micropterus salmoides*) and white catfish (*Ameiurus catus*), which had average mercury concentrations in composite samples from the Delta of $0.29 \mu\text{g g}^{-1}$ wet weight and $0.27 \mu\text{g g}^{-1}$ wet weight, respectively. Sport fish were also sampled in the Sacramento River under the Sacramento River Watershed Program (Larry Walker Associates 1999) and in the San Joaquin River as part of the Delta Study.

Average mercury concentrations in Sacramento River largemouth bass ($0.65 \mu\text{g g}^{-1}$ wet weight) and white catfish ($0.43 \mu\text{g g}^{-1}$ wet) were higher than the concentrations in these species in the Delta (Figures 1 and 2). The average concentration in San Joaquin River largemouth bass ($0.49 \mu\text{g g}^{-1}$ wet weight) was also elevated relative to the Delta (Figures 1 and 2). Overall, the freshwater sampling has detected concentrations that are frequently above the mercury screening value and generally similar to those for which consumption advice has been issued for the Estuary. Studies of mercury in sport fish in the Delta and the Sacramento River are continuing with funding from CALFED and the Sacramento River Watershed Program. The objective of these studies is to provide the data needed to determine whether additional consumption advisories are needed for these regions.

Wildlife Health Concerns

Aquatic ecosystems tend to have higher rates of mercury bioaccumulation and biomagnification than do terrestrial ecosystems (USEPA 1997). There are several factors contributing to this difference. Fish store most mercury as methylmercury in their muscle while mammals and birds store much of their methylmercury burden in feathers and fur, items poorly digested or rarely eaten (and affording mammals and birds a mercury excretory pathway unavailable to fish). Aquatic systems have more complex food webs and more trophic levels, and the primary producers in aquatic systems may themselves accumulate more mercury from water and sediment than do soil-based primary producers in terrestrial systems (USEPA 1997). Top predators in aquatic systems therefore are at greatest risk from mercury bioaccumulation.

In all vertebrates, including fish, developing embryos are the life stage most vulnerable to mercury exposure. The transfer of methylmercury to the embryo represents the greatest hazard. In addition to the hazard to top avian, reptilian, and mammalian predators in aquatic systems, fish and amphibian species, particularly long-lived species, may also be at risk from mercury. Of all of these groups, avian embryos appear to face the greatest risk. Risks to mammalian predators, such as river otters, mink, and seals, may also be high, but have not been studied as extensively to date.

Toxicology of Mercury to Wildlife

Symptoms of acute methylmercury poisoning in birds include reduced food intake leading to weight loss, progressive weakness in wings and legs, difficulty flying, walking, and standing, and an inability to coordinate muscle movements (Scheuhammer 1987). There are also significant adverse effects at lower tissue-mercury concentrations representing chronic mercury exposures. Embryological exposure may lead to impaired hearing (Heinz 1979), and impaired vision or tunnel vision has been demonstrated in other adult vertebrate species (humans and monkeys) (Wolfe and others 1998). These sensory deficits could reduce ability to locate and catch prey, impair ability to find a mate through visual or auditory clues, or impair ability to detect and escape predators. Mercury may also suppress the immune system and increase susceptibility to disease (Sundloff and others 1994).

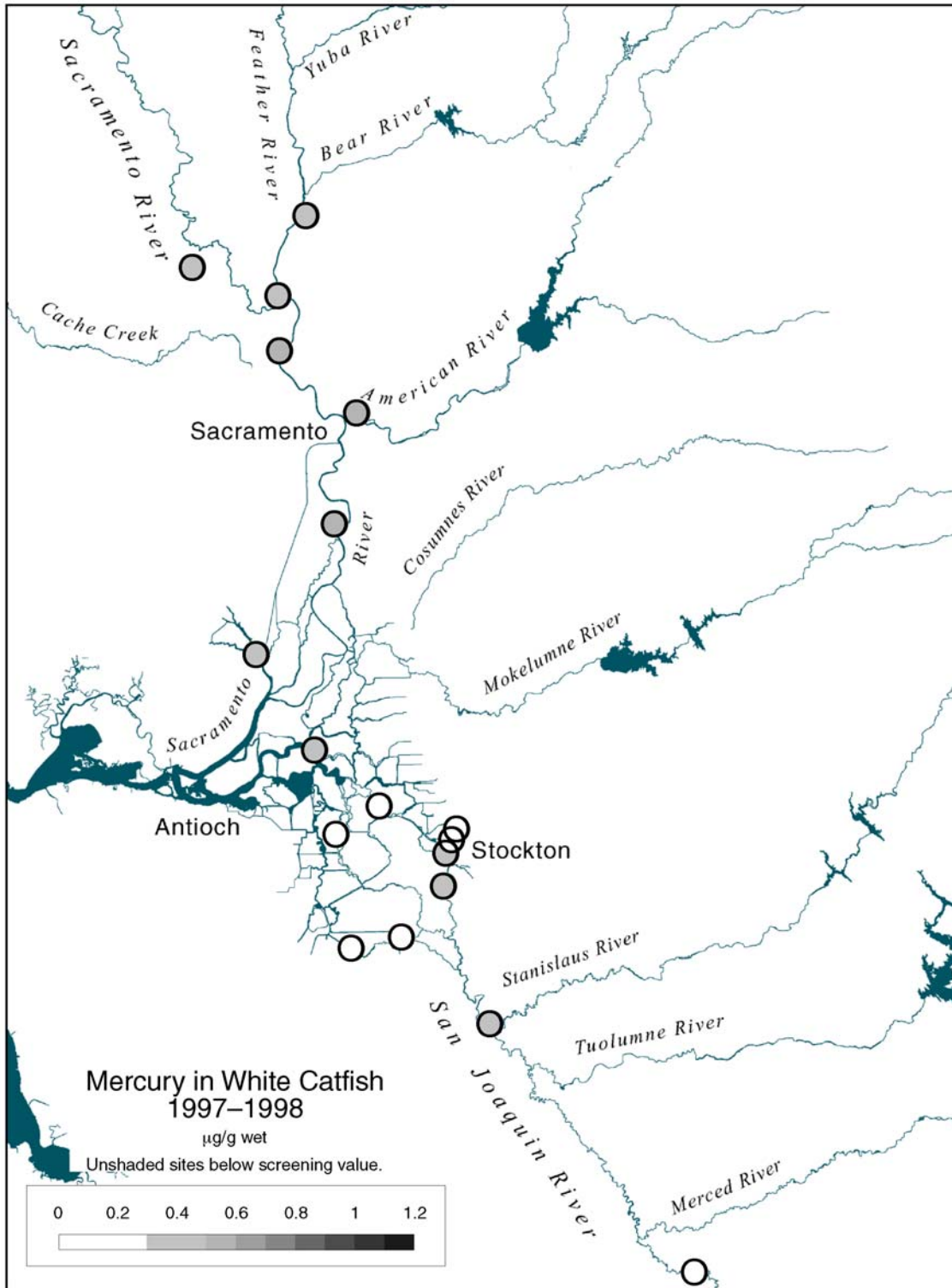


Figure 2 Mercury in white catfish, 1997 and 1998. Data generated by the SRWP and the Delta Study (Davis and others 2000b).

Impaired reproduction is one of the most sensitive toxicological responses, with effects occurring at very low dietary concentrations. In birds, concentrations in the egg are typically most predictive of mercury risk to reproduction, but concentrations in liver have also been evaluated for predicting reproductive risk. The documented effects of mercury on reproduction range from embryo lethality to sublethal behavioral changes in juveniles at low dietary exposure. Reproductive effects in birds typically occur at concentrations of about twenty percent of the concentrations causing mortality of adult birds (Scheuhammer 1991).

Embryos of birds are extremely sensitive and vulnerable to relatively minute concentrations of mercury in the egg. Almost all of the mercury in bird eggs is methylmercury (Wolfe and others 1998). Toxic effects of mercury in bird eggs have been documented by many investigators in both laboratory and field studies (Barr 1986; Birge and others 1976; Fimreite 1971, 1974; Heinz 1974, 1979; Heinz and Locke 1975; Hoffman and Moore 1979; Finley and Stendell 1978; Tejning 1967). Egg concentrations in the range of 0.5 to 1.0 $\mu\text{g g}^{-1}$ (all concentrations given are wet weight, unless stated otherwise) have been associated with toxic effects on embryos. In a field study of common terns, Fimreite (1974) estimated the threshold level in eggs for toxic effects on nest success to be between 1.0 and 3.6 $\mu\text{g g}^{-1}$. Heinz (1979) fed ducks 0.5 $\mu\text{g g}^{-1}$ methylmercury over three generations and found decreased reproductive success and altered behavior of ducklings. Heinz (1979) remains the benchmark study which established the lowest observed adverse effect concentration in avian diet of 0.064 g mercury per g (body weight) per day (Sample and others 1996). The mean mercury concentration in eggs associated with these intake rates was 0.86 $\mu\text{g g}^{-1}$. Fimreite (1971), in a feeding study with ring-necked pheasants, found significant reduction in hatchability associated with egg mercury concentrations between 0.5 and 1.5 $\mu\text{g g}^{-1}$. Fimreite (1971) established the lowest adverse concentration (0.5 $\mu\text{g g}^{-1}$) observed in avian eggs. Hoffman and Moore (1979) externally applied mercury to mallard eggs and found dose-related effects on survival, growth, and development. The lowest dose applied which affected survival was 27 g, which corresponds to about 0.5 $\mu\text{g g}^{-1}$ in a mallard egg. Based on these studies, mercury in eggs greater than 0.5 $\mu\text{g g}^{-1}$ is considered harmful. In waterbirds, concentrations greater than 1 $\mu\text{g g}^{-1}$ in blood and 5 $\mu\text{g g}^{-1}$ in liver are additional conservative thresholds for potential adverse effects (Wolfe and others 1998).

Developmental abnormalities due to mercury exposure of embryos can adversely affect juvenile survival. Mercury in the eggs of mallards caused brain lesions in hatched ducklings. Mallards were fed 3.0 $\mu\text{g g}^{-1}$ methylmercury dicyandiamide over two successive years. Mercury was accumulated in the eggs to an average of 7.2 and 5.5 $\mu\text{g g}^{-1}$ in two successive years. Lesions included demyelination, neuron shrinkage, necrosis and hemorrhage in the meninges overlying the cerebellum (Heinz 1975). Fish reproduction can be quite sensitive to methylmercury (Wiener and Spry 1996), but data on exposures and sensitivities specific to the Bay-Delta are not available.

Current Mercury Exposure in Birds in the Bay and Delta

Avian eggs have been used to monitor bioavailability and ecological risk from mercury in the Bay, but much less frequently in the Delta. Mean concentrations of mercury greater than $0.5 \mu\text{g g}^{-1}$ have been found in avian eggs from a variety of species from both North and South San Francisco Bay. Schwarzbach and others (1997b) summarized egg mercury data from 11 species in San Francisco Bay (Figure 3). Among randomly sampled eggs, the highest mean concentrations have been found in Caspian terns from both the North and South bays. Black-crowned night herons from New Almaden Lake (South Bay), least terns from Alameda Naval Air Station (South Bay), clapper rails from both North and South bays, and black-necked stilts from Hayward Marsh (south central Bay) also had mean mercury concentrations in eggs above the lowest observed adverse effect level (LOAEL). Means for other species from San Francisco Bay including coots, mallards and snowy plovers, were usually below the LOAEL, but generally higher than found in other areas of California.

Piscivorous species are generally considered to have the greater rates of mercury bioaccumulation. Indeed, in the Bay, the exclusively piscivorous birds such as terns had the highest concentrations of mercury and the predominantly herbivorous birds like coots the lowest concentrations of mercury. However, the endangered California clapper rail, a benthic omnivore found exclusively in tidal marshes, appears to be an exception. The greatest range in mercury concentrations among any species observed from San Francisco Bay was in the fail-to-hatch eggs of California clapper rails ($n = 44$) from south San Francisco Bay where concentrations in a 1992 investigation were between 0.19 and $2.57 \mu\text{g g}^{-1}$. Mercury toxicity to clapper rail embryos appears to be one of the primary causes of mortality in the population of this endangered species.

The only avian species in the Bay with observed egg mercury comparable to the clapper rail is the Caspian tern (Schwarzbach and others 1997a), an obligate piscivore that feeds on relatively large fish. Why do some clapper rails in San Francisco Bay produce eggs with elevated mercury concentrations? Rails are non-migratory, spending their entire lives in Bay marshes. In addition, during the breeding season they have a small home range of a few acres, rarely moving between marshes. Because of these small home ranges, rail eggs are highly vulnerable to local methylmercury production. A 1994 investigation of total and methylmercury in intertidal sediments of the Bay (Schwarzbach, unpublished data) found total mercury to be fairly homogenous but methylmercury to vary greatly among locations sampled.

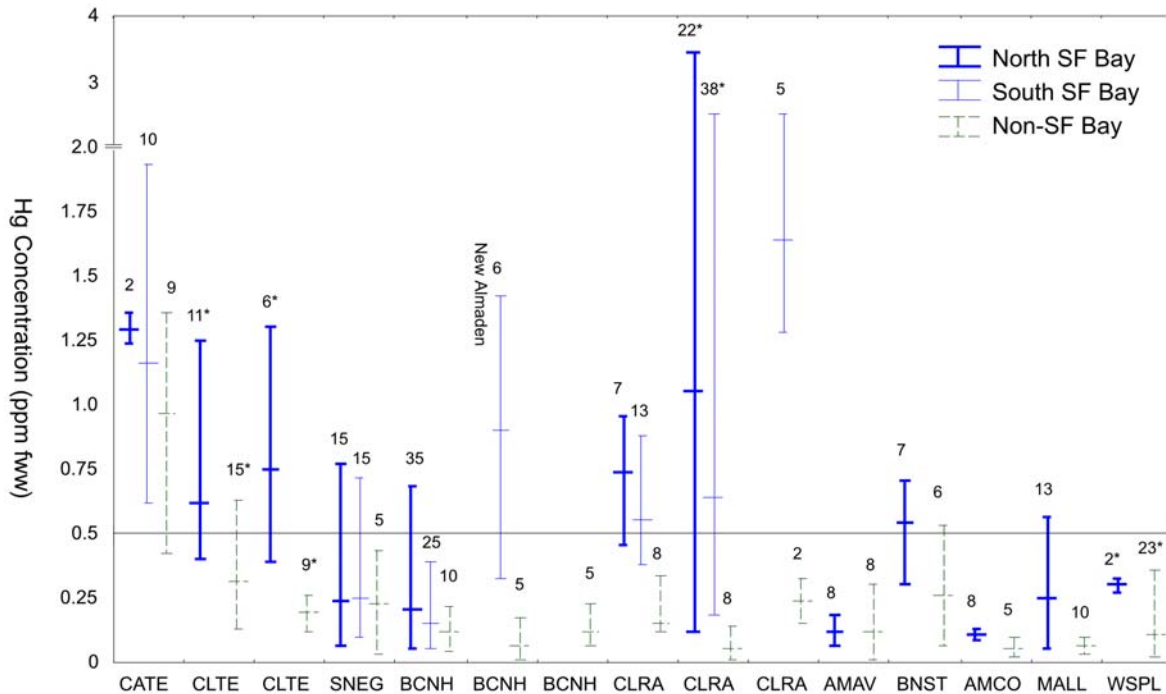


Figure 3 Comparison of mercury concentrations observed in avian eggs in California. Concentrations in avian eggs from within San Francisco Bay are consistently greater than in cohorts collected elsewhere in California. Mean concentrations and ranges of mercury in eggs from San Francisco Bay are presented for: black-crowned night-herons [BCNH] (*Nycticorax nycticorax*), snowy egrets [SNEG] (*Egretta thula*), mallards [MALL] (*Anas platyrhynchos*), American coots [AMCO] (*Fulica americana*), California clapper rails [CLRA] (*Rallus longirostris obsoletus*), black-necked stilts [BNST] (*Himantopus mexicanus*), American avocets [AMAV] (*Recurvirostra americana*), Western snowy plovers [WSPL] (*Charadrius alexandrinus nivosus*), Caspian terns [CATE] (*Sterna caspica*), and California least terns [CLTE] (*Sterna antillarum browni*). These concentrations are compared with the same or similar species from collection sites outside San Francisco Bay. Night-heron eggs from both North and South San Francisco Bay are compared with eggs from the Sacramento Valley, Tulare Basin, and Edwards Air Force Base (Mojave Desert). Snowy egret eggs from North and South bays are compared with the Tulare Basin. Eggs of two strictly piscivorous species, the California least tern and Caspian tern, from San Francisco Bay are compared with San Diego Bay and Elkhorn Slough, respectively. Eggs collected from nests of stilts and avocets at Hayward Marsh (South Bay) are compared with those from the Tulare Basin; coot eggs from Hayward Marsh are compared with those from Edwards Air Force Base. Eggs from California clapper rails from both the North and South bays are compared with Yuma clapper rails (*Rallus longirostris yumanensis*) nesting along the Colorado River and light-footed clapper rails (*Rallus longirostris levipes*) from Southern California. Numbers above bars represent number of eggs represented. Note the break in the y axis scale. Asterisk (*) indicates only fail-to-hatch eggs were collected.

Mercury Sources to Tidal Wetlands

Mercury sources, pathways, and loadings to the Estuary were reviewed by Davis and others (2000a). Mercury can enter the tidal wetland food web through local runoff from upland areas or from tidal exchange with tidal flats and open waters of the Estuary. Mercury entering through tidal exchange originates primarily from historic sediment deposits, runoff from portions of the Coast Range with abundant natural mercury deposits and historic mercury mines, and runoff from gold mining regions of the Sierra Nevada. Urban stormwater runoff may contribute significant mercury loads to the Estuary and directly to specific tidal wetlands, but these loads can only be crudely estimated using existing data. Atmospheric deposition and municipal and industrial effluents account for relatively minor loads of total mercury to the Estuary and tidal wetlands. Information on mercury loads to the Estuary in general is reviewed below, as these loads and the regional patterns they have created also impact tidal wetlands. Little reliable information is available on direct mercury inputs to tidal wetlands from local watersheds.

Historic Sediment Deposits

Fluxes of mercury from sediments can be a dominant pathway for mercury entry into the food web. Historic sediment deposits can influence mercury concentrations in the Estuary's tidal wetlands in two basic ways. First, contaminated sediment deposits may be present in existing wetlands or in the soils or sediments of areas selected for tidal wetland restoration. Second, historic deposits may be transported into wetlands from contaminated deposits upstream or within the Estuary. The geographic distribution and chemical properties of mercury-contaminated sediments must be understood so the potential detrimental impacts of these deposits on restoration projects can be minimized.

Sediment deposits contaminated with mercury are present throughout much of the Bay-Delta watershed. Two of the principal causes of this contamination were gold mining in the Sierra Nevada and mercury mining in the Coast Range.

Hydraulic mining for gold, in particular, was responsible for the widespread distribution of mercury-contaminated sediment throughout the watershed. Hydraulic mining mobilized 1.2 billion m³ (Gilbert 1917) of alluvial deposits from ancient river beds in the Sierra Nevada from its beginning in 1856 (Evans 1883) to its curtailment in 1884 due to a court decision. Miners passed this material through various types of conduits containing a layer of elemental mercury at the bottom that would trap and form an amalgam with the gold present in the gravel. Much of the mercury used for this purpose was lost along with the sediment debris that was discharged to downstream waterways. Preliminary data suggest that 2.4 to 4.8 million kg of mercury were released to Sierra Nevada waterways along with hydraulic mining debris (Churchill, personal communication, see "Notes").

Mercury-contaminated hydraulic mining debris poured out of the hydraulic mining districts in Plumas, Butte, Sierra, Yuba, Nevada, Placer, El Dorado, and Amador counties

(Clark 1970) and settled in the lower reaches of the Sierran rivers, in the Sacramento River, in the Delta, and in the Bay. Increased flooding, shoaling of the navigable waters of the Sacramento River, and deposition of hydraulic mining debris (referred to as “slickens” at the time) on vast expanses of valuable agricultural lands led to the demise of hydraulic mining (Evans 1883).

The limited information available indicates that significant deposits of hydraulic mining debris remain in the watershed. For example, extensive deposits, up to 5 m deep and 2 to 3 km across, have been documented in the floodplain of the Bear River, where they are largely protected from erosion by levees (Figure 4) (James 1991). Vast supplies of easily transported sediment still dominate the channels of Sierran rivers downstream of the mining districts (James, personal communication, see “Notes”). Of the 194 m³ (254 million yd³) of debris released to the Bear River, 106 m³ (139 million yd³) remain in the lower Bear River Basin (Hunerlach and others 1999).

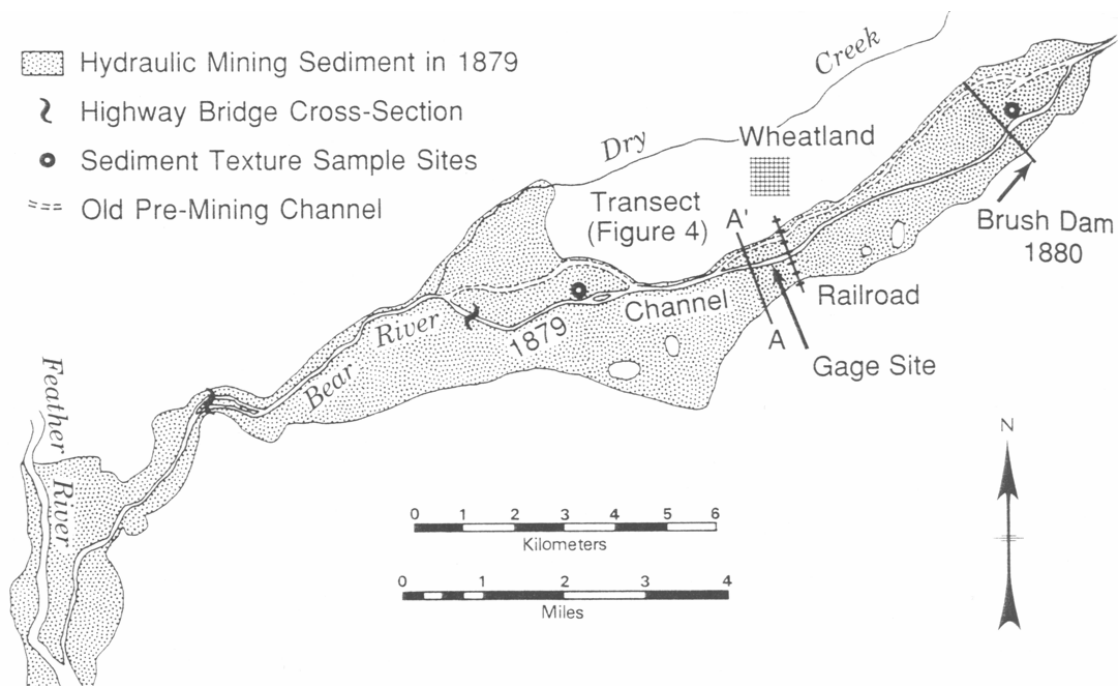


Figure 4 Distribution of hydraulic mining sediment in the lower Bear River, 1879. A transect from points labeled A-A' on the map showed much of the hydraulic mining sediment to still be in place. From James (1991).

Recent studies have also documented extensive deposits of hydraulic mining debris that remain in San Francisco Bay (Bouse and others 1999; Jaffe and others 1999). About 400 million m³ of hydraulic mining debris, or one-third of the total volume produced, deposited in northern San Francisco Bay. Jaffe and others (1999) estimated that about

half of this material remains in the Bay. Furthermore, much of this remaining material is currently being exposed due to the net erosion of sediment occurring in the North Bay. Mercury concentrations in this material obtained from a core in San Pablo Bay ranged from 0.3 to 0.4 $\mu\text{g g}^{-1}$ dry weight, about seven times higher than natural background concentrations (Hornberger and others 1999), but mercury concentrations have only been determined in two deposits of hydraulic mining debris in the Bay-Delta watershed. A more recent study (Marvin-DiPasquale and others 2003) also found mercury concentrations in the 0.3 to 0.4 $\mu\text{g g}^{-1}$ dry weight range in San Pablo Bay sediments from three open water sampling locations, and that an isotopic tracer indicated a similar degree of influence of hydraulic mining debris among the three locations. Deposits of hydraulic mining debris also appear to be present in tidal marshes in the Estuary, as suggested by the presence of a layer with relatively high mineral content deposited in the late 1800s in cores from many North Bay marshes. It is likely that some, but not all, diked historic wetlands in the Delta and Bay also contain deposits of hydraulic mining debris. In summary, available information suggests that deposits of hydraulic mining debris contaminated with mercury are likely present in many subtidal portions of the Bay-Delta, in some tidal wetlands and diked wetlands, and in the lower reaches of the attending watersheds.

Other mining activities also contributed to the presence of contaminated sediment deposits throughout the watershed. Processing of lode gold ore, primarily in the Sierra Nevada, led to the release of approximately 1.2 million kg of mercury to the environment (Churchill, personal communication, see "Notes"). In combination, hydraulic mining (2.4 to 4.8 million kg) and lode gold mining (1.2 million kg) combined to release a total of 3.6 to 6.0 million kg of mercury to the environment.

Extensive mercury mining took place in the Coast Range between 1846 and 1981. Approximately 103.6 million kg of mercury were produced in California (Churchill, personal communication, see "Notes"), accounting for 88% of the mercury extracted in the entire United States during this period (Foe and Croyle 1998), and much of this production was from northern California Coast Range counties. Mercury losses to the environment during ore processing ("furnace losses") averaged about 25% in the late 1800s and early 1900s, suggesting that losses from mercury processing could have been on the order of 34 million kg (Churchill, personal communication, see "Notes"). Contaminated tailings, soils, and drainage from abandoned mercury mine sites have caused mercury contamination of downstream waterbodies in the past and continue to supply contaminated sediments to the Bay-Delta today.

The highest concentrations of mercury, approaching 1 $\mu\text{g g}^{-1}$, found by the USGS in their analysis of several sediment cores from the Bay were from sediments deposited after 1950 in Grizzly Bay (Hornberger and others 1999). The origin of this contamination is unknown, but the timing of the elevated concentrations, as determined by ^{210}Pb and ^{137}Cs dating, may suggest an industrial source or mechanized mercury mining. Sport fish collected near Pittsburg around 1970 showed high concentrations that appeared to be associated with industrial activity (CDPH 1971). California had two mercury cell chlor-

alkali plants. This type of facility was historically one of the major sources of mercury to waterways. One of these chlor-alkali plants, located in the Pittsburgh area, modified their production process to eliminate the need for mercury cells in April 1970 (CDPH 1971). Mechanized mercury mining, which replaced earlier methods, may also have caused the high mercury concentrations in Grizzly Bay sediment. Accelerated mercury releases in Clear Lake have been attributed to mechanized mercury mining (Richerson, personal communication, see "Notes"). The mercury-enriched horizon also contains hydraulic mining debris (Bouse and others 1999).

It is not known how widespread such mercury peaks are. The difficulty in attributing sources in this instance of high mercury concentrations and in understanding the frequency of such occurrences underscores that study of mercury in the watershed has been very limited. Wastewater discharges and runoff from urban and industrial areas have probably also created localized deposits of mercury-contaminated sediment throughout the watershed.

Coast Range Runoff

There are hundreds of abandoned mercury mine sites in the Coast Range, and these sites and downstream sediment deposits originating from these sites are continuing sources of mercury to areas further downstream. Mercury from these sites is predominantly in the form of solid phase cinnabar (mercury sulfide ore). Although cinnabar is extremely insoluble, the process of mining and roasting tends to increase the availability of mercury in waste-rock (Slotton and others 1998).

In a recent study, Cache Creek, which receives water flowing out of Clear Lake and runoff from many sites with inactive mercury mines, was found to transport large masses of mercury (Foe and Croyle 1998). The total mercury load from Cache Creek for water year 1995 was estimated to be 980 kg. (A water year begins October 1 of that year and ends September 31 of the following year.) About half of this load was trapped in a settling basin near Woodland. The mass of mercury exported by Cache Creek in that year was of a similar magnitude as the total estimated load (800 kg) exported into the Estuary by the Sacramento River and Yolo Bypass from May 1, 1994 to April 30, 1995 (Foe and Croyle 1998). Mercury loads during storms were on the order of 5 to 100 kg d⁻¹, accounting for most of the annual load. Sediment mercury loading studies along one small tributary to Cache Creek (Davis Creek, Davis Creek Reservoir) have routinely found annual loads of 100 to 250 kg (D.G. Slotton, personal communication, see "Notes"). Mercury loads from Cache Creek and other Coast Range watersheds are therefore a significant source of mercury-contaminated sediment to the Bay-Delta and its wetlands.

Runoff from a large inactive mine (New Almaden) in part of the Coast Range that is tributary to the Guadalupe River and South Bay has also been shown to be a significant source of mercury to the Bay. Total mercury loads to the Bay from the Guadalupe River watershed have been estimated at 4 to 30 kg yr⁻¹ (Thomas and others 2002). This

mercury input has been shown to have a large influence on the water quality of south San Francisco Bay (Leatherbarrow and others 2002).

Sierra Nevada Runoff

The Sierra Nevada contains hundreds of abandoned gold mining sites, and these sites and downstream sediment deposits originating from these sites are continuing sources of mercury. Elemental mercury is the predominant form present in Sierra Nevada streams. Reservoirs in the Sierra Nevada foothills appear to trap mercury from upstream (Slotton and others 1997; Larry Walker Associates 1997). Downstream of reservoirs, however, deposits of hydraulic mining debris and other mercury-contaminated sediments in channels and floodplains are subject to sustained re-mobilization (James 1991), which leads to continuing transport of mercury-contaminated sediment into the Bay-Delta.

Recent studies of mercury bioaccumulation have detected relatively high concentrations in the lower reaches of several Sierra Nevada rivers. Suchanek and others (1999) found elevated concentrations of mercury in crayfish and small fish at sites on and downstream of the lower Cosumnes River. Surveys of sport fish have detected elevated mercury concentrations in the lower Feather River and the lower Stanislaus River (see Figure 1).

Other Mercury Inputs

Although the information available to support estimation of mercury inputs to the Estuary from urban runoff is limited, it does suggest that this pathway is a significant component of the mercury budget. The current crude estimate for stormwater loading from small tributaries to the Bay, based on land use data and a limited number of mercury measurements, is 200 to 400 kg yr⁻¹ (Davis and others 2000a). Measurements using better sampling methodologies are needed to quantify this pathway more accurately. Urban runoff inputs to the Delta were not included in this estimate. This load is similar in magnitude to the loads from the Sacramento River and Yolo Bypass. In addition to affecting mercury concentrations in the Bay-Delta on a regional level, urban runoff would have a particularly strong influence on tidal wetlands that directly receive runoff from urban areas.

Other mercury inputs for which quantitative estimates exist include atmospheric deposition and municipal and industrial effluents, but these inputs are a relatively minor part of the mercury budget for the Estuary. Direct atmospheric deposition to the Bay accounts for an estimated 5 to 15 kg yr⁻¹. Atmospheric deposition to the land surface is substantial, but this loading is accounted for in the estimates for inputs from large and small tributaries. Other studies have estimated that less than 10% of the amount deposited on land is eventually transported to water (Mason and Sullivan 1998). A mercury budget for the North Bay calculated inputs of 31 kg yr⁻¹ from municipal and industrial effluents (SFBRWQCB 1998), approximately an order of magnitude lower than

inputs from the Sacramento River and urban runoff. As for urban runoff, municipal and industrial effluent discharges may play a significant role in mercury cycling in tidal wetlands that directly receive these flows.

Comparisons of mercury sources should be made with caution due to probable differences in bioavailability. As an example, mercury in treatment plant effluents is probably mostly in a dissolved form and more readily bioavailable than the particulate mercury that dominates inputs from the rivers and urban runoff. Similarly, elemental mercury from Sierra Nevada gold mining appears to have higher bioavailability than cinnabar from Coast Range mercury mining (Domagalski and others 2002).

Mercury Cycling in Tidal Wetlands

General Features of the Mercury Cycle

Mercury exists in the environment in a variety of forms and has a complex biogeochemical cycle. A simplified description of this cycle is provided in Figure 5. The most important forms of mercury in the Bay-Delta watershed are elemental or metallic mercury (Hg^0), mercuric mercury (Hg^{2+}), cinnabar or mineral mercury (HgS , which is one form of mercuric mercury), and monomethylmercury (CH_3Hg^+ , commonly referred to as “methylmercury”). The term “total mercury” is used to refer to the sum total of these major forms and other minor ones.

Methylmercury is the most important form of mercury in the aquatic environment with regard to accumulation by biota and transfer through the food web. Methylmercury is produced through addition of a methyl group to Hg^{2+} , a process referred to as methylation. Methylation is performed primarily by sulfate-reducing bacteria (Compeau and Bartha 1985; Regnell and others 1996; Gilmour and others 1998), which are found at zones of transition from oxic to anoxic conditions in the water column or sediment (Watras and others 1994; Slotton and others 1995; Choi and Bartha 1994; Devereux and others 1996; Gilmour and others 1998; Bloom and others 1999). Other types of bacteria appear to be important methylators in some cases (Macalady and others 2000). Abiotic methylation can also occur in the presence of humic substances (Compeau and Bartha 1985). Methylmercury can be converted back into Hg^{2+} and/or Hg^0 , primarily via bacterial degradation (Robinson and Touvinen 1984; Summers 1986; Summers and Barkay 1991; Oremland and others 1991, 1995; Marvin-DiPasquale and Oremland 1998). Net methylmercury production, or methylmercury production in excess of degradation, is the critical quantity that leads to food web accumulation.

Hg^{2+} is the primary form that can be converted to methylmercury. Hg^{2+} exists in many states, including dissolved, colloidal, organically and inorganically complexed, and bound to particles. Hg^{2+} is most susceptible to methylation when it is in a dissolved state, and least susceptible to methylation in the particulate state. Recent studies suggest that a dissolved, neutrally charged Hg^{2+} -sulfide complex may be important in mercury uptake by

methylating bacteria (Benoit and others 1999a, 1999b). Dissolved Hg^{2+} can also be converted to Hg^0 by photoreduction (Amyot and others 1997).

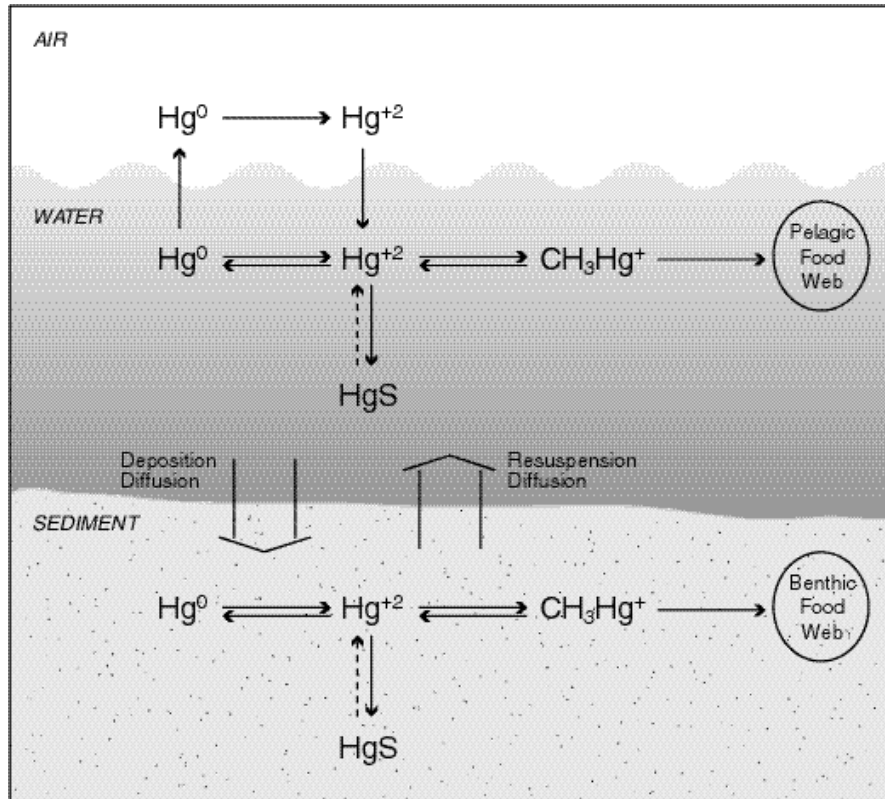


Figure 5 Mercury cycle in tidal wetlands

HgS (solid phase cinnabar) is the predominant form present in runoff from the mercury mining regions of the Coast Range. HgS must be transformed to dissolved Hg^{2+} or a dissolved Hg -sulfide complex before it can be converted to methylmercury. This is a slow process because HgS is extremely insoluble, although the process of mining and roasting mercury ore increases its solubility. Dissolved organic carbon also increases the solubility of HgS (Ravichandran and others 1999).

Hg^0 (elemental mercury) is the predominant form contaminating the gold mining regions of the Sierra Nevada. Hg^0 must be oxidized to Hg^{2+} before it can be converted to methylmercury. Hg^0 also has low solubility in water, which limits its rate of conversion to Hg^{2+} . Hg^0 appears to be relatively non-reactive in water (Watras and others 1994). Hg^0 is volatile and can leave the aquatic environment in the vapor phase where it becomes part of a large atmospheric global background pool. Atmospheric Hg^0 slowly

photooxidizes to Hg^{2+} , which readily binds to particles or dissolves in water and is deposited back to land or water surfaces via rainfall.

Mercury Accumulation in Food Chains

The precise mechanism for entry of methylmercury to the food chain is unknown. However, this initial step is critical, because concentrations of mercury in plankton are about 10,000-fold higher than in water (Krabbenhoft 1996). In a well-studied Wisconsin Lake, for example, a 30,000-fold increase in methylmercury was observed from the concentration dissolved in water (0.9 parts per trillion) to the concentration in seston (25,000 parts per trillion) (Watras and others 1994).

After this initial step, methylmercury concentrations increase approximately three-fold with each additional step in the food chain (Watras and others 1994), in a process known as biomagnification. In this process consumers retain and further concentrate much of the methylmercury of their prey and subsequently pass this on to the next trophic level. Species at high trophic positions in the aquatic food web, such as predatory fish, attain concentrations that are approximately a million times higher than concentrations in water. Because methylmercury biomagnifies, trophic position is one of the primary factors influencing observed tissue concentrations.

No systematic study exists of mercury distributions in the food web of the Bay. High mercury concentrations have been identified in some species of sport fish (e.g., leopard shark) and not others, and the reasons for this variation are not clear. Whether mercury threatens restoration of certain fish species and how that threat would change if exposures change because of restoration actions are simply not known and will not be clear until the food web dynamics of this element are better characterized in this specific ecosystem. Several research groups are currently addressing mercury accumulation in the Delta food web.

Factors Influencing Methylmercury Production

Methylmercury production appears to be the most important step in the mercury cycle with regard to food web accumulation. Intensive studies in the Everglades found that the spatial pattern of net methylmercury production in Everglades sediments generally matched the spatial patterns of sediment methylmercury concentration and methylmercury accumulation in biota (Gilmour and others 1998). Detailed studies in Wisconsin lakes similarly concluded that methylmercury production within the lakes was a major source to these ecosystems, and methylmercury was rapidly taken up into the food chain (Watras and others 1994). These studies suggest that net methylmercury production may generally determine the degree of contamination of aquatic food chains.

Many factors influence methylmercury production. Total mercury concentration is one important factor. In many ecosystems, however, total mercury concentration alone is a poor predictor of methylmercury production and food web contamination. Some ecosystems with low total mercury concentrations in water and sediment, such as the lakes in northern Wisconsin and the Everglades, have high concentrations in piscivorous fish due to high rates of methylmercury production (Watras and others 1994; Wiener and Spry 1996; Gilmour and others 1998). Other ecosystems with high concentrations of total Hg may have low or moderate concentrations of methylmercury and bioaccumulation (e.g., Gill and Bruland 1990; Suchanek and others 1998; Bonzongo and others 1996).

Other factors that influence methylmercury production can have an overriding influence on the degree of food web accumulation. Methylmercury production rates depend on the level of activity of methylating bacteria and the speciation of the mercury present, which determines the rate of mercury uptake by methylating bacteria. Mercury speciation and methylating bacteria activity in turn are influenced by several environmental factors, including redox potential, pH, salinity, dissolved organic carbon, concentrations of sulfur compounds, and temperature. Spatial patterns in these factors will determine spatial patterns in methylmercury production and accumulation in tidal wetlands.

Mercury Cycling in Tidal Wetlands

Tidal wetlands are retentive environments that tend to trap particulate Hg. The storage of particulate Hg and the high levels of sulfate-reducing bacteria activity in the often saturated, organic-rich, and anaerobic environments of tidal wetlands suggest that they may be important sites of methylmercury production. Positive correlations of methylmercury concentrations in biota to water color (Westcott and Kalff 1996), sediment organic matter (Benoit and others 1998) and dissolved organic carbon (Watras and others 1995; Krabbenhoft and others 1995; Driscoll and others 1995) may also reflect effects of methylating bacterial activity often found in such circumstances. A number of studies have found correlations between the percentage of wetlands in a watershed and concentrations of methylmercury in waters leaving the watershed (St. Louis and others 1994; Hurley and others 1995; Krabbenhoft and others 1999).

The limited amount of local data presently available also suggests that wetlands can be sites of relatively high rates of net methylation. Krabbenhoft and others (1999) found methylmercury in sediments of five tributaries to the Delta ranged between 0.55 ng g^{-1} to 2.84 ng g^{-1} , with methylmercury accounting for 0.1% to 2.2% of total mercury. The average percent methylmercury for these five sites (1%) was the lowest observed in 21 study basins across the U.S. In contrast, in a 1994 investigation of tidal marsh sediments in the Bay, Schwarzbach (unpublished data) found methylmercury concentrations between 0.41 ng g^{-1} and 25.2 ng g^{-1} , with percent methylmercury ranging between 0.1% and 6.6%. The maximum value (6.6%) falls above the 80th percentile of mean percent methylmercury from the 21 USGS study basins. Marvin-DiPasquale and others (2003)

found a methylmercury concentration of 5.4 ng g^{-1} and 1.9% methylmercury at a tidal marsh in San Pablo Bay; these values were much higher than those measured for three samples from the open waters of San Pablo Bay. Because free methylmercury is short-lived, percent methylmercury is considered an indicator of the rate of methylmercury production (Gilmour and others 1998). The relatively high maximum percent methylmercury measured in Bay tidal wetlands indicates the potential for high net methylation rates in these ecosystems.

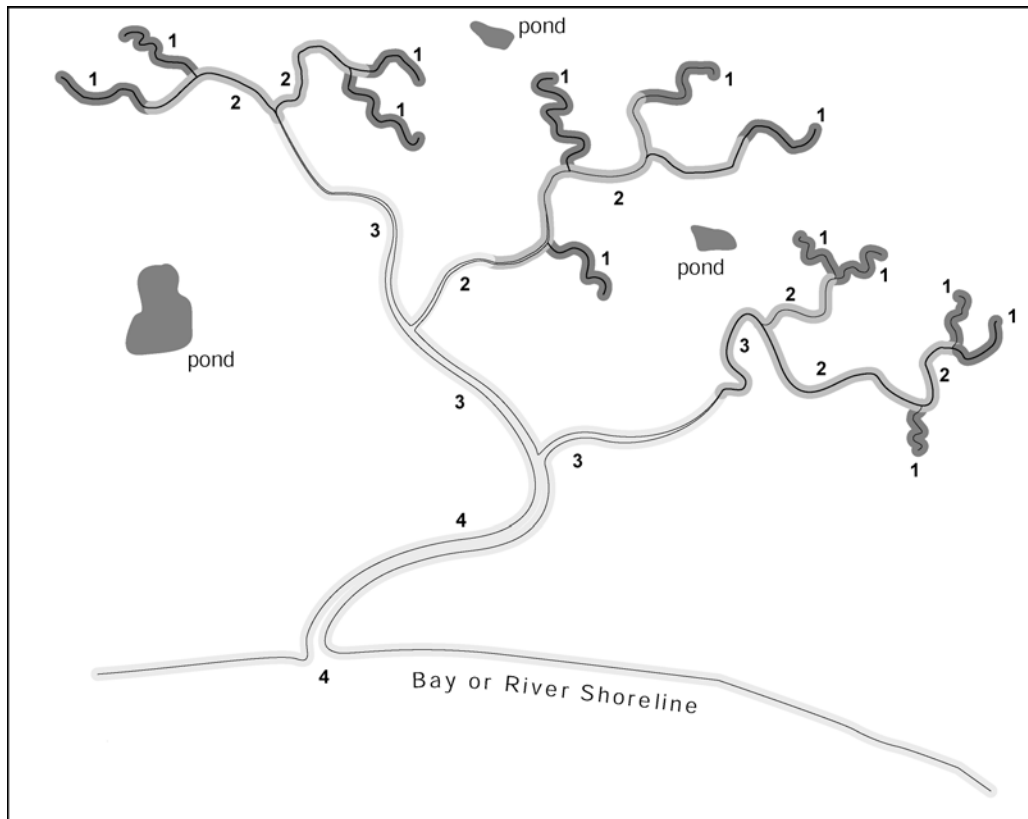
It is likely that distinct spatial variation in methylmercury production in Bay-Delta tidal wetlands will be found on multiple spatial scales, including variation within each tidal wetland, among tidal wetlands in the same region, and among tidal wetlands in different regions. Understanding this spatial variation and its underlying causes will allow environmental managers to minimize the impacts of restoration activities on mercury bioaccumulation. Some hypotheses on spatial patterns in mercury bioaccumulation that may exist on these different spatial scales are presented below. While the complexity of the mercury cycle makes it difficult to predict what these patterns may be, the systematic and predictable variation of other environmental variables at these spatial scales implies that such patterns will be found.

Variation Within Tidal Wetlands

Mercury methylation is primarily performed by sulfate-reducing bacteria, which reside at the oxic-anoxic interface in sediments or water. The location of methylation at the oxic-anoxic interface is a critical part of the picture of mercury cycling in tidal wetlands, because it begins to suggest a relationship between methylation and tidal marsh physiography and hydro-geomorphology. Tidal wetlands share a common physiographic template and set of geomorphic features and processes (Figure 6). Although environmental conditions tend to vary considerably at very small scales within this template, there is nevertheless a great deal of similarity in tidal wetland structure throughout the Estuary. Methylmercury production is most likely to occur in a few areas within the recognizable template. Furthermore, significant food web accumulation of methylmercury is most likely to occur mostly in only two of the potential areas of methylmercury production, as described below.

There is a very large and almost continuous oxic-anoxic interface in the sediments of a tidal wetland. This interface can be envisioned to extend from the base of the unconsolidated sediment at the centerline of any channel outward along the drawdown curves of the seepage faces of the channel banks, and further outward along the surface of the water table that in some places emerges on the drainage divides as tidal marsh ponds or pans (Figure 6). The oxic-anoxic interface is very near the surface (1 to 10 cm deep) along the channel bottom, and much further from the vertical surfaces of the channel banks. The drawdown curve typically extends from the channel bed at the base of the bank to the marsh surface 5 to 10 m away from the bank, and is generally too deep within the bank to be invaded by burrowing animals, although it may be invaded by plant roots. The sediment composition at the oxic-anoxic interface varies from very fine silts and

clays and organic detritus in the channels, to mostly fine clays in the banks, to mostly fibrous organic peat on the drainage divides furthest from the channels. The substrate of the ponds is typically an organic mix of diatoms, bacteria, fine organic detritus, and a scant amount of fine silts. An organically-rich oxic-anoxic interface therefore occurs near the surface in three places: in the channels, on the drainage divides, and in the ponds.






Most likely exposure of biota to anoxic/oxic horizon 
 Less likely exposure 
 Least likely exposure 

Figure 6 Schematic diagram of the hypothesized distribution of food web accumulation of mercury in tidal wetlands. Numbers indicate order of channels (1 = 1st order, 2 = 2nd order, etc.).

The poor hydraulic conductivity of the bank sediments tends to trap water on the drainage divides. Little or none of the water that reaches the drainage divides or the ponds between the channels (during over-bank flood tides, river inputs, or rainfall) and that percolates into the sediments ever returns to a channel. The water table on the drainage divide and the depth of water in the ponds is regulated by evapotranspiration, rather than

by sub-surface drainage to a channel. As a result, the near-surface watertable across the drainage divides and in the ponds is seldom flushed. It tends to be more saline and mineral-rich than the near-surface watertable elsewhere in the tidal wetland. In many ways, the vegetated drainage divides of tidal wetlands are very harsh environments. They support few plant species, compared to areas near channels, and almost no infauna. Some ponds, however, support abundant aquatic insects and micro-crustaceans that feed at the oxic-anoxic boundary. Most of the invertebrate and vertebrate wildlife of tidal wetlands is restricted to the ponds, the channel beds, and the channel banks.

The depth of the anoxic-oxic boundary varies within the channel network of a tidal marsh. In the larger channels that do not empty at low tide, there can be a regular flux of fine sediment at the channel bed surface during each tide, but the oxic-anoxic interface tends to be deeper than this material in flux, and is probably deeper than the burrowing depth of most infauna. In contrast, the smaller, more headward channels have a thin layer of material in flux that coats the bed, and the oxic-anoxic interface is very near the surface. During the flood phases of a neap tide cycle, these headward channels can be re-filled with water that does not leave the drainage network during ebb phase. In this way, there is an increase in residence time of water in the smaller channels. These channels are the preferred habitat of many species and life stages of fishes, birds, small mammals, and macroinvertebrates.

Based on these considerations, we hypothesize that the unconsolidated, fine grain sediment layers at the oxic-anoxic interface of the smallest channels and in the ponds are the most likely places of heightened methylmercury production and food web accumulation. Methylmercury produced in these places would be available for accumulation in a multi-step food web. For example, clapper rails, which have been shown to accumulate high concentrations of mercury, forage on the banks and beds of the smallest channels, as do many estuarine fishes, passerine birds, shorebirds, and raptors. Shorebirds also forage in the ponds.

Hypotheses such as this one should be developed and evaluated with field studies. If predictable spatial variation does exist within marshes, it will be important to take this into account in any studies investigating mercury accumulation. Studies comparing wetlands should employ stratified sampling designs that will allow for meaningful comparisons.

Variation Among Tidal Wetlands in the Same Local Area

Significant variation in mercury accumulation can also be expected among tidal wetlands in the same local area of the Bay-Delta. Sediment mercury concentrations are probably very heterogeneous in space due to the heterogeneous nature of sediment deposition and erosion. A deposit of hydraulic mining debris might be present in one wetland and absent in another wetland nearby. Present or historic local sources of mercury contamination, such as industrial discharges or urban runoff, may impact one wetland and not another. The speciation of mercury inputs to tidal wetlands may also vary

on a local scale. In the Delta, runoff from mercury mining regions of the Coast Range, dominated by cinnabar, and gold mining regions of the Sierra Nevada, dominated by elemental mercury, mix with runoff from other regions of the State within a relatively small area. Mercury cycling in neighboring wetlands may be quite different if they receive water from different sources. Methylmercury production may also vary on a local scale, either due to variation in mercury speciation or in the activity of methylating bacteria. There may be significant variation in methylmercury production along salinity gradients from one wetland to another along the tidal reaches of rivers and streams and along the main estuarine gradient. USFWS (1994) data indicate that methylmercury concentrations in tidal wetland sediment are more heterogeneous than total mercury concentrations, suggesting the importance of variation in methylmercury production. Mercury concentrations, speciation, and accumulation may therefore vary significantly among neighboring wetlands.

Variation at this local spatial scale must be understood to predict and minimize the impacts of restoration activities. Concentrations and speciation of mercury in sediments and the water supply should be evaluated prior to initiation of wetland or floodplain restoration projects. Variation in mercury methylation on a local scale needs to be understood so that net methylmercury production can be minimized.

Variation Among Tidal Wetlands in Different Regions

Numerous factors could cause significant variation in mercury bioaccumulation on a regional basis. Many studies have correlated spatial patterns in mercury bioaccumulation with variation in water quality variables, including salinity, sulfate and sulfide concentrations, oxygen, dissolved organic carbon, temperature, and pH (Table 1). Mercury sources and environmental conditions are quite different on the eastern and western sides of the Central Valley, and could lead to different degrees of accumulation. Considerable differences also exist between environmental conditions in the freshwater portions of the estuary (the Delta) and the saline portions (the Bay). Differences in other factors such as wetland morphology, species distributions, and food web structure may also cause regional differences in mercury bioaccumulation.

The bioavailability of mercury in Sierra Nevada streams may be different from that of Coast Range watersheds, because the two regions have different aquatic environments and different forms of historic mercury contamination. Sierra Nevada streams contain elemental mercury (Hg^0), which must be oxidized to mercuric mercury (Hg^{2+}) before methylation can occur. Sierra streams originate from snowmelt in granitic watersheds. They are colder, more oligotrophic, and have lower alkalinity and hardness than Coast Range runoff, which drains from uplifted, low elevation, marine sedimentary material (Foe and Croyle 1998). Sierra Nevada streams are also impounded by reservoirs, which appear to block the export of methylmercury and sediment-bound mercury (Slotton and others 1997). In contrast, the Coast Range watersheds are mostly impacted by cinnabar. There, the rate-limiting step prior to methylation is cinnabar dissolution rather than reduction. Mining activities have accelerated this process, dramatically increasing the

availability of Coast Range mercury (Slotton and others 1998). Coast Range watersheds are also more heavily influenced by wetlands, which are known areas of methylation. These regional differences in mercury forms and environmental conditions could result in significant variation in mercury bioaccumulation in tidal wetlands.

Table 1 Factors that may influence spatial patterns in mercury bioaccumulation in Bay-Delta tidal wetlands

<i>Variable</i>	<i>Relationship with methylmercury production</i>	<i>References</i>
Oxygen	Sulfate reducing bacteria are the primary methylators and require anaerobic conditions	Compeau and Bartha 1985; Regnell and others 1996; Gilmour and others 1998; Choi and Bartha 1994
pH	Low pH associated with increased methylation	Xun and others 1987; Westcott and Kalff 1996; Rose and others 1999
Sulfate	In low sulfate waters, increased sulfate increases methylation.	Chen and others 1997
Sulfate	In high sulfate waters (e.g., estuaries) increased sulfate increases demethylation. Increased sulfide decreases methylation.	Oremland and others 1995; Benoit and others 1998
Dissolved organic carbon	High DOC in the water column may indicate high organic loading leading to high bacterial activity and anoxic sediments.	Watras and others 1995; Krabbenhoft and others 1995; Driscoll and others 1995
Dissolved organic carbon	Complexation of Hg species by DOC may increase dissolved concentrations without appreciably increasing biological uptake.	Barkay and others 1997
Temperature	In general, higher temperatures (up to 35 to 40 °C) result in higher bacterial activity.	Choi and Bartha 1994
Salinity	Bacterial and algal mercury uptake related to concentration of neutral species (HgCl ₂ , MeHgCl)	Barkay and others 1997; Mason and others 1995

Differences between salt marshes and freshwater marshes in water chemistry may lead to differences in mercury bioaccumulation. The ratio of methylmercury to total mercury, which is an index of methylmercury production, is relatively low in estuaries (Benoit and others 1998), and this may be due to the high sulfate concentrations present in seawater. Benoit and others (1998) found an inverse correlation of mercury methylation with sediment sulfide concentrations along a salinity gradient in the Patuxent River estuary. These high sulfide concentrations in sediment result from anaerobic reduction of the high sulfate concentrations in seawater. Benoit and others (1999a, 1999b) have proposed a mechanism by which high sulfide concentrations may limit mercury bioavailability to sulfate reducing bacteria. Other research has suggested that complexation of mercury with chloride ions to form negatively charged species may also inhibit uptake by sulfate-reducing bacteria in estuarine and marine environments (Barkay

and others 1997). The many differences in conditions between seawater and freshwater and the complexity of the mercury cycle make it difficult to predict whether salt marshes or freshwater marshes would be more prone to mercury bioaccumulation. However, the studies conducted to date have suggested mechanisms that could lead to regional differences. If these differences exist, this would be one factor to consider in selecting locations for restoration. It should be noted that, despite the hypothesized existence of mechanisms that would result in differences between salt- and freshwater habitats, available bioaccumulation data, including mercury concentrations in clapper rail eggs from salt marshes and in sport fish from freshwater regions, indicate that mercury production and accumulation is sufficient to result in potentially hazardous concentrations in both saltwater and freshwater portions of the Estuary, as discussed previously.

Potential Effects of Restoration on Mercury Accumulation in Food Webs

Overview of Anticipated Restoration Activities

The number and size of proposed tidal wetlands restoration projects are increasing. The variety of engineering approaches to restoration is also increasing, as is the complexity of habitat components designed into restoration projects. The approaches range from the simple breaching of a levee to the engineered partial fill of subsided sites with dredged sediments with careful contouring of the sediment surface to achieve desired tidal elevations.

There is a set of initial considerations for all tidal wetland projects with regard to mercury. Existing mercury levels on the site must be quantified, as well as the existing template of channels and water storage compartments, which may relate to the existing distribution of mercury. The historical channel system may provide a template for mercury sampling. We recommend that the potential distribution of small channels should be analyzed relative to the existing mercury distribution. In the case of wetlands where dredged sediments might be deposited, the mercury load of these deposits must be analyzed, and the channel design in plan view and cross section must be considered in relation to the mercury loads.

The very large scale of many proposed tidal wetlands projects raises questions about regional and subregional effects on tidal circulation and residence times that cannot be answered without predictive modeling and monitoring as projects are developed. Large-scale tidal wetlands restoration could have regional effects on mercury levels; however, any deleterious effects might be minimized or avoided by careful project design.

Possible Effects on Methylmercury Production, Movement, and Entry into the Food Web

Restoration activities may lead to increased concentrations of methylmercury in the estuarine food web and exacerbate the existing mercury problem. Restoration activities may affect mercury bioaccumulation on both a local and regional scale.

Effects on a Local Scale

Tidal wetland restoration will create conditions within the wetlands that favor mercury methylation by sulfate-reducing bacteria. The characteristics of wetlands that favor methylation were described above. These restoration efforts could obviously impact food webs on a local scale.

Creation of tidal wetlands through flooding of diked farmlands or floodplains would very likely result in particularly high rates of mercury bioaccumulation. It is well established that mercury present in soils and vegetation is released into the aquatic environment after flooding and transformed into methylmercury, with resulting increases in fish tissue concentrations (Bodaly and others 1984, 1997; Hecky and others 1987; Kelly and others 1997; Paterson and others 1998). This has been observed in subarctic, temperate, and tropical reservoirs, although most research has been conducted in subarctic regions (Bodaly and others 1997). Methylmercury production is particularly intense in flooded wetlands, due to the large quantities of organic carbon present (Kelly and others 1997). In subarctic reservoirs fish mercury concentrations remain elevated for 20 to 30 years after flooding (Bodaly and others 1997). However, some examinations of Hg concentrations in fish tissues from impounded lakes (French and others 1998) and restored wetlands (Suchanek and others 1999) have not shown significant patterns with respect to the age of the lake or wetland.

Creation of tidal wetlands through placement of dredged material may also result in increased methylmercury production if the dredged material contains mercury in substantial concentrations or in forms that are readily converted to methylmercury, and if the material is placed in an environment that favors methylation. The use of dredged material may also result in low methylmercury concentrations if the material is low in organic content, microbial activity, or total mercury. The potential for increased methylmercury production associated with dredged material reuse should be evaluated before these projects are initiated.

In summary, different types of restoration actions may have different effects on local mercury bioaccumulation. Flooding of upland areas is known to increase net methylmercury production, altered hydrological regimes may change rates of delivery of mercury to areas where net methylmercury production is high, and use of dredged material for wetland creation may create conditions favoring enhanced net methylmercury production. For flooding of upland areas, it is highly probable that this type of action will

increase mercury bioaccumulation. The extent of the increase may be minimized through thoughtful selection of these projects. For altered hydrology and the use of dredged material, existing data are inadequate to predict general outcomes. Each of the three possible outcomes (i.e., an increase, decrease, or no change in mercury bioaccumulation) might be observed in particular projects. Further research and evaluation of these types of projects will improve our ability to predict the effects of specific projects.

Effects on a Regional Scale

Less obvious is the possibility that significantly increasing the acreage of wetland within the watershed will result in greater mercury bioaccumulation on a regional scale. Regional scale impacts may result through several mechanisms. Large-scale hydrologic alterations in the watershed may result in changes in water and sediment movement that affect mercury bioaccumulation on a regional basis, and these impacts could also affect mercury inputs to tidal wetlands. Actions that reduce sediment supply to the Estuary, for example, would be expected to increase rates of erosion of sediment from Suisun Bay and San Pablo Bay, leading to re-mobilization of contaminated sediment that was deposited in previous decades. Some of this remobilized sediment would be transported into tidal marshes. Other actions may remobilize contaminated hydraulic mining debris from floodplains behind levees.

In addition, simply increasing the amount of wetland acreage in the Estuary watershed could cause a regional increase in mercury bioaccumulation. Several studies have linked high percentages of wetland acreage in watersheds with high rates of methylmercury production and export (Zillioux 1993; Hurley and others 1995; Rudd 1995; St. Louis and others 1996; Krabbenhoft and others 1999). In a recent national study of mercury contamination by USGS, wetland density was the single most important basin-scale factor associated with methylmercury production.

The complexity of the mercury cycle and the rudimentary state of our present understanding make it impossible to confidently predict the regional impact of large scale ecosystem restoration on mercury cycling. However, given the well-established associations of net methylmercury production with flooding of uplands and with the percentage of wetlands within a watershed, it seems likely that regional increases will occur. Regional monitoring of mercury concentrations in the Estuary food web is the best way to evaluate this hypothesis.

Recommendations for Reducing Uncertainty

Despite the potentially significant human and wildlife health impacts, very little systematic study of mercury has been conducted in the Bay-Delta. The CALFED Ecosystem Restoration Program has recently funded some studies, but a comprehensive body of work will be needed to understand whether and how restoration activities will

affect mercury contamination. From a management perspective, the prudent course seems to be to minimize risk as much as possible based on existing knowledge while conducting the research needed to reduce the negative impacts of future restoration projects and the monitoring needed to assess regional and local impacts. Below we list some of the actions needed to establish the needed body of knowledge.

- A serious, multifaceted research effort on mercury should be an on-going part of tidal wetland restoration in the Estuary over the next 20 years. The complexity of the mercury cycle and the rudimentary state of current understanding limit our present ability to predict which restoration scenarios will lead to unacceptable mercury bioaccumulation. These are hard problems and it will take some time to find the necessary, creative solutions. The research program should include site-specific studies, but basic processes and broad questions must also be answered. The most creative and productive ideas for specific studies will come from researchers themselves. Annual meetings of mercury researchers with people conducting other CALFED actions are necessary for efficient integration of these efforts. A goal of the research program should be to develop numerical models that predict the extent of net mercury methylation, export to the Estuary, and food web accumulation in response to future wetland restoration projects.
- Long-term monitoring should be performed to ascertain the impact of restoration actions on mercury bioaccumulation on both a regional and local scale. This monitoring should include sampling of concentrations in sport fish as an index of human exposure and avian eggs as an index of exposure of sensitive wildlife species. Monitoring of other food web or ecosystem components may also be useful in establishing long-term trends. The utility of lower trophic level bioindicator organisms with high site fidelity in differentiating relative mercury bioavailability at fine spatial and temporal scales has been demonstrated in local studies. Long-term monitoring of individual restoration projects should be conducted until concentrations fall below thresholds of concern. Ideally, regional monitoring and assessment would be carefully coordinated with project-specific monitoring. This would be best accomplished through the establishment of a stable infrastructure to guide the monitoring that could adapt as new projects arise, management questions evolve, and scientific understanding advances.
- Detailed surveys should precede restoration projects to document existing mercury concentrations in affected areas and to evaluate the potential for increased food web accumulation of mercury. Pre-project mercury concentrations in the local food web should be established. Preliminary studies of mercury concentrations in sediments and cores of sediments, as well as determinations for the presence of hydraulic mining debris, should precede every engineering effort to restore a wetland or shallow water habitat. Such analyses should begin immediately (or as soon as feasible methods are available) to systematically sample in projects already in progress. The potential distribution of small channels in the restored wetland should be analyzed relative to the existing mercury distribution. The concentrations,

speciation, and bioavailability of mercury in the water and sediment supply of restored wetlands should also be evaluated in the planning stages of each restoration project. In the case of wetlands where dredged sediments might be deposited, the mercury concentrations and other chemical properties of these deposits must be analyzed, and the channel design in plan view and cross section must be considered in relation to the mercury burden.

- Spatial patterns in methylmercury production within tidal marshes are likely to exist and need to be understood. This will allow evaluation of the most highly impacted species, local comparisons among tidal wetlands using a stratified sampling approach, and regional comparisons among tidal wetlands. Field studies should be conducted to investigate the relationships between methylmercury production and accumulation and tidal marsh physiography and hydro-geomorphology. Once established, knowledge of these relationships can be applied to development of stratified sampling designs that would allow meaningful comparisons among tidal wetlands.
- Sources of local variation in mercury accumulation among tidal wetlands must be understood. This will enable environmental managers to minimize the impact of restoration activities. Comparative studies of existing tidal wetlands would help in developing the capability to predict mercury accumulation in restoration projects.
- An understanding of the role of tidal wetlands as net importers from or exporters to the Estuary is needed. This should include measurements of methylation and demethylation in water and sediment of different tidal wetland environments (channels, ponds, and marsh plains). Both laboratory and field measurements should be employed with an attempt to assess flux, methylation potential, and environmental covariates (e.g., total mercury concentration, sulfate reduction, suspended sediment concentrations of mercury, organic carbon content, and pH) that enhance or impair methylmercury formation on the local (i.e., wetland microhabitat) and regional (i.e., wetland export) scales.
- Criteria should be developed to guide decisions about what levels of mercury require remediation in a wetland or shallow water project. If project areas with mercury-contaminated sediments are identified, one (or a limited number) should be chosen as an experiment to evaluate the effectiveness of possible remediation approaches.
- Mercury transfer through the food web to species at risk, including humans, must be better understood. This should include an understanding of the factors controlling mercury accumulation in species involved in restoration. A study could be initiated in cooperation with the ongoing human health sampling and the IEP Bay Program to better identify the characteristics of this problem. The link between food web contamination and human exposure needs to be documented through study of fishing and fish consumption practices. This would provide information needed in development of monitoring strategies and in communicating risks to human populations with the highest mercury exposure.

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