Mercury in Sediments of San Francisco Bay

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Introduction

San Francisco Bay is a complex ecosystem that is under much stress due to the vast industrial, agricultural and municipal activities around the Bay and along the rivers that discharge into it. Heavy metals that are released into the ecosystem are of particular concern because of their toxicity to wildlife and the subsequent effects on humans. Mercury (Hg) is a heavy metal pollutant that is known to be highly toxic, although its effects on San Francisco Bay are not yet well understood. The toxicological impact of mercury on sensitive ecosystems, such as the wetlands around the Bay, is of special significance.

Wetlands extend along the shore of most parts of San Francisco Bay (Fig. 1) and support a wide variety of species. Elevated concentrations of heavy metals can perturb the ecological equilibrium of the wetlands by accumulating in organisms populating the wetlands (Kennish, 1992). A change in the balance of these areas can lead to long-term changes in the whole Bay ecosystem.

In order to evaluate the importance of mercury contamination in San Francisco Bay, it is important to consider two variables, total mercury content and rates of transformation between the different species of mercury, for which analysis of sediments in or near sensitive areas is a useful technique. Considering the higher toxicity of organic mercury than elemental mercury, I can use the results from experiments conducted under laboratory conditions regarding the chemical speciation of mercury by Compeau and Bartha (1984) to evaluate where in San Francisco Bay and under what conditions the concentration of organic mercury might be highest, and therefore might have the most severe effects on the ecosystem.

Using this information, along with measurements of mercury levels in sediment cores from the Bay, I can determine the geographic regions of San Francisco Bay where the rate of transformation from inorganic to organic mercury (methylation) is potentially the highest. These are the areas that are most endangered by the mercury pollution.

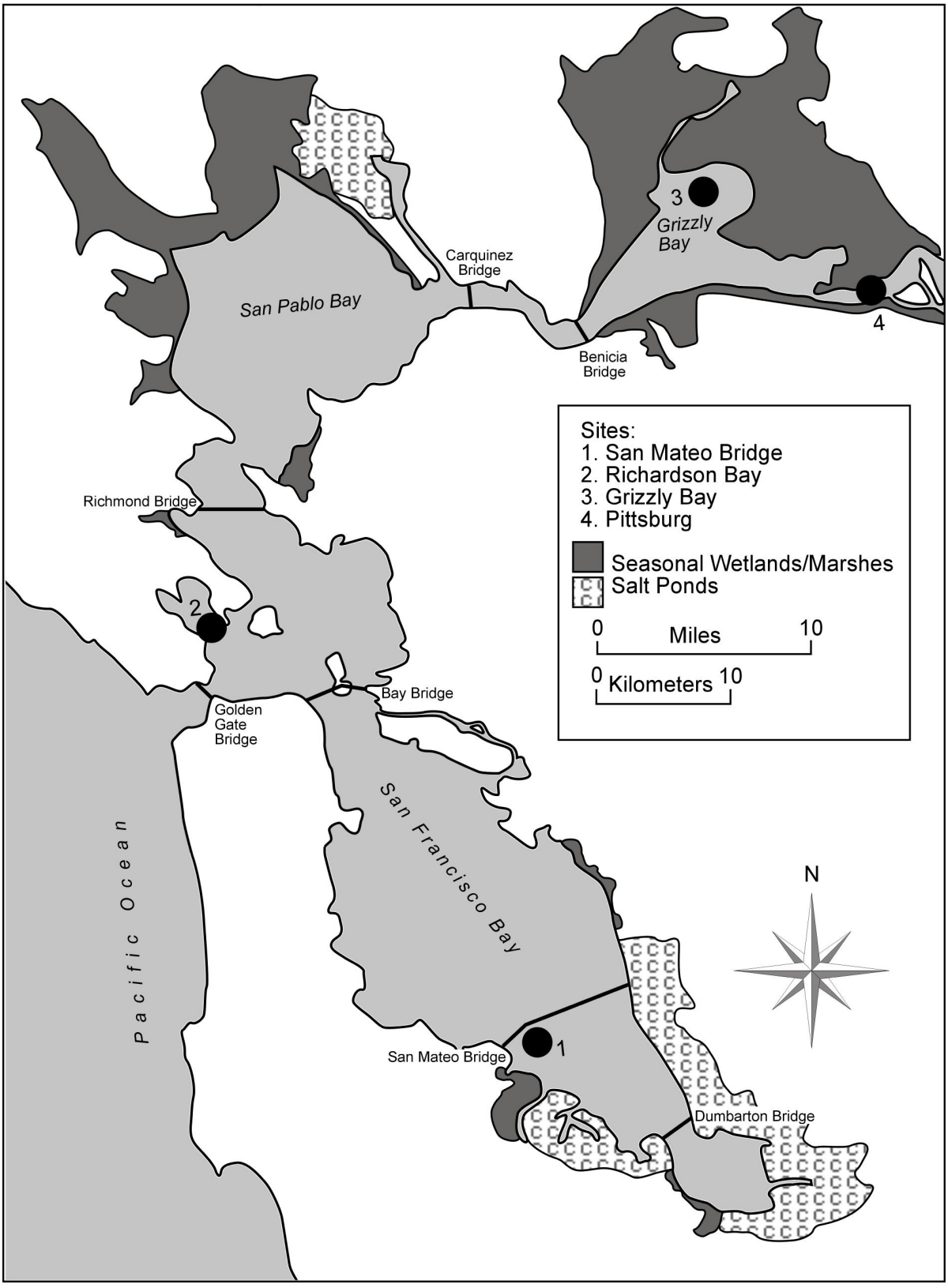

Figure 1. Wetlands of San Francisco Bay and sites of sediment sampling (based on Bain, 1995).

Past Studies

Most studies on heavy metals in San Francisco Bay usually focus on trace elements that are found in high concentrations, such as copper and zinc. Mercury, on the other hand, has been analyzed to a lesser extent because of the low concentrations of mercury in the ecosystem and the difficult analytical procedure (Taylor, 1994, pers. comm.). Luoma and Philips (1988) studied the distribution and fate of various trace metals, including mercury, in San Francisco Bay. They linked high metal concentrations to anthropogenic inputs, but they did not assess the broad-scale effect of metal pollution on the ecosystem. Gunther and others (1987) identified major sources of heavy metals in San Francisco Bay and determined the extent of inputs for different trace metals. The largest amounts enter the Bay from the Sacramento-San Joaquin River systems, although deposition of dredged sediments in the northern part of the Estuary is also of concern.

Other studies have assessed heavy metals in Bay Area wetlands. In 1992 the San Francisco Regional Water Quality Control Board (RWQCB) conducted a pilot study on critical habitats surrounding the Bay to determine whether there were regions with exceptionally high levels of contamination in the marshes, creeks and mudflats (Taberski *et al*., 1992). They studied bioaccumulation of mercury in oysters and mussels to compare mercury levels in organisms from different regions of the Bay. The RWQCB set maximum tolerable concentrations of trace metal contamination for sediments used in wetland restoration in the Bay Area (Wolfenden and Carlin, 1992). Sediments used for other purposes than wetland restoration may contain more mercury. Depending on the use of the sediments, the threshold level of mercury content may vary by about two orders of magnitude.

Background

Mercury is a silver-colored heavy metal that is liquid under standard conditions. Its molecular mass is 200.61 grams per mole (Miall, 1961), and its density is 13.6 grams per cubic centimeter. Mercury can occur in an inorganic form or as complex organic compounds.

Chemical Transformations of Mercury: In the environment mercury is readily converted from its inorganic form to the more toxic organic compounds (Fig. 2). Mercury compounds are especially chemically complex in aquatic ecosystems (Boudou and Ribeyre, 1983). Methylmercury is the most toxic compound because of its high stability and solubility in organic solutions (Beijer and Jernelov, 1979). Its ionic character enables methylmercury to penetrate membranes of organisms and accumulate in their fatty tissue.

Effects of Mercury on Organisms: Mercury has very toxic effects on both plants and animals. The organic compounds of mercury, including methylmercury, are more toxic than the inorganic compounds (Eisler, 1987). Lethal concentrations of total mercury for mammals are 0.1 to 0.5ppmw (parts per million by weight) daily dose and 1.0 to 5.0ppmw dietary intake. These levels vary because different animals have different ways of processing the accumulated mercury metabolically. Sublethal doses in organisms impact the nervous system, inducing apathy, loss of coordination of movements, and brain damage (Armstrong, 1979; Hudson *et al*., 1984; Clarkson and Marsh; 1982).

Effects of metal-induced stress on organisms inhabiting the aquatic ecosystems of the Bay are apparent in the most contaminated sites (Kennish, 1992). However, although symptoms of mercury poisoning occur in certain benthic species, it does not mean that this trend can be generalized for other species (Luoma and Philips, 1988). The difficulty of generalizing the response of organisms to mercury surfaces with oysters and mussels from different regions of the Bay (Taberski *et al*., 1992). Significant differences occur in the amount of mercury accumulated in benthic species between populations that were exposed to high concentrations of mercury from polluted sites in the Bay and control populations that were

not exposed to mercury. Tests were conducted to determine variations of mercury uptake over space and time. However, there were no apparent trends governing the distribution of mercury accumulation with respect to the variables studied.

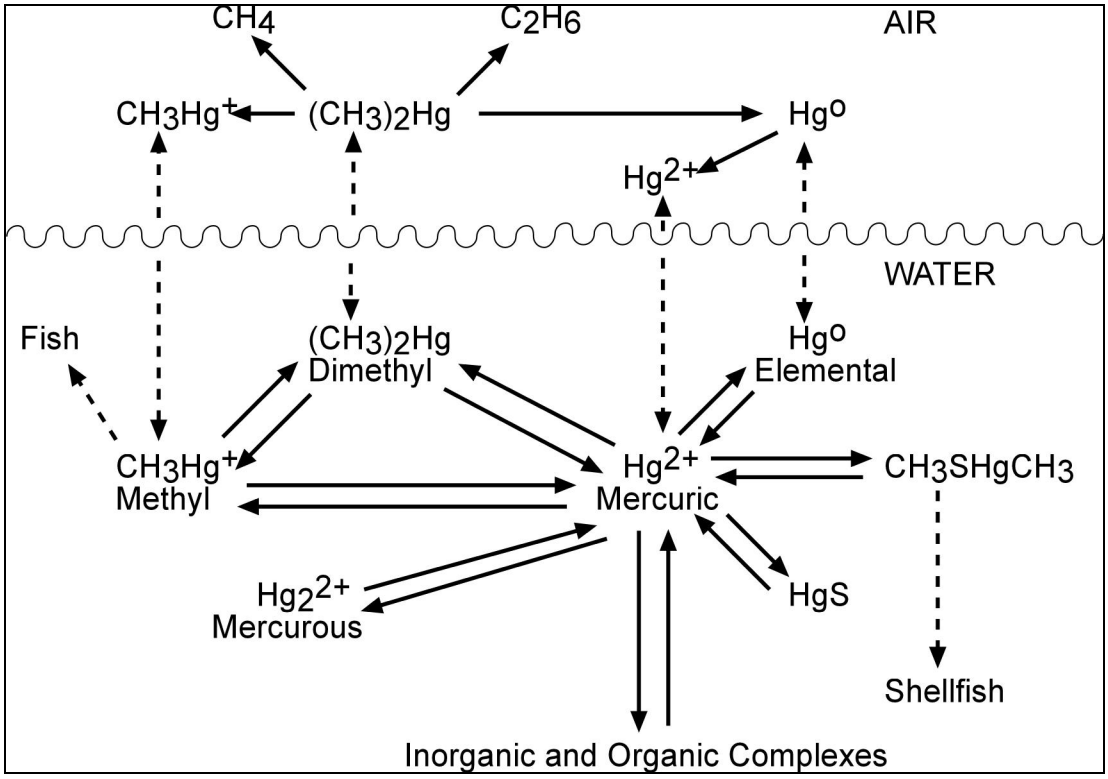

Figure 2. Transformations of mercury in the environment (adapted from Eisler, 1987).

Source	Input (kg/day)
Municipal and industrial point sources	0.8
Urban runoff	0.2
River systems	3.0

Table 1. Input of mercury to San Francisco Bay from various sources (Gunther *et al*., 1987).

Sources of Mercury in San Francisco Bay: Gunther and others (1987) identify the mercury that is transported through the Sacramento-San Joaquin river system as the most important source of mercury in San Francisco Bay. Input from other sources is of less importance (Tab. 1). The larger inputs from the rivers are a result of mining operations along the Sacramento and San Joaquin rivers (Kinkel *et al*., 1956).

Direct releases of large amounts of mercury still have an influence on concentrations in areas downstream of the mercury additions, but it is not yet clear whether present inputs to the Estuary exceed the historic levels (Luoma and Philips, 1988). Background concentrations of mercury are about 0.05ppmw in San Francisco Bay (Hornberger, 1995, pers. comm.). These are mercury concentrations found in areas in which anthropogenic additions can be ruled out. Background concentrations are part of the undisturbed natural environment, which contains heavy metal concentrations that are not considered to be dangerous.

Environmental Standards for Mercury: It is important to maintain mercury contamination in sediments at the lowest possible level and to minimize exposure of organisms. The RWQCB has established the maximum allowed concentrations for sediments depending on their use (Wolfenden and Carlin, 1992). Sediments used for wetland creation as cover may not exceed 0.35ppmw mercury concentration. For non-cover use the concentration may not be higher than 1.3ppmw. On the other hand, sediments exceeding 40ppmw must be disposed of in an appropriate landfill. To put these limits into perspective, Wolfenden and Carlin (1992) also determined mean concentrations of mercury contamination in different areas (Tab. 2).

Area	Mean (ppmw)	Range (ppmw)
Western United States	0.065	< 0.01 – 4.6
Coterminous United States	0.089	< 0.01 – 4.6
San Francisco Bay Basins	0.45	< 0.01 – 4.6

Table 2. Levels of mercury in sediments in the United States and San Francisco Bay (Wolfenden and Carlin, 1992).

Redox potential	Salinity	Effect on methylation rate
low (-220 mV	low (0.4%)	highest methylation rate
low (-220 mV)	high (2.5%)	methylation rate 38% lower
high (+110 mV)	low (0.4%)	sharply reduced rate
high (+110 mV)	high (2.5%)	lowest methylation rate

Table 3. Variation of mercury methylation with salinity and redox potential (Compeau and Bartha, 1984).

Redox potential (mV)	Salinity (%)	Removal of methylmercury (%)
-220	0.4	25
-220	2.5	55
+110	2.5	60
+110	0.4	65

Table 4. Demethylation of 1 ppm monomethylmercuric chloride in relation to redox potential and salinity (Compeau and Bartha, 1984).

Influence of Salinity and Redox Potential on Methylation of Mercury: Compeau and Bartha (1984) simulated the processes in wetlands that are important in methylation and demethylation of mercury at pH = 6.8, the natural pH of salt marsh wetlands, under conditions of varying redox potential and salinity. They found that mercury is most readily transformed to its most toxic form if the salinity and the redox potential of the system are low (Tab. 3). Increased amounts of sea water, on the other hand, suppress the methylation of elemental mercury. Mercury transforms continuously in the environment. The different mercury species that form from a given amount of total mercury reach a dynamic equilibrium. Continuous inflow of additional inorganic mercury results in a steady increase in the absolute concentration of methylmercury, provided that the produced organic mercury is removed by stream flow. Compeau and Bartha (1984) found that microbial demethylation also depends on the above parameters. They monitored the demethylation of a fixed amount of methylmercury over a period of seven days with no further input of methylmercury. Demethylation is highest if the redox potential is high (Tab. 4), whereas the effect of salinity is of less importance in this case. However, microbial demethylation does not remove all of the accumulated organic mercury.

Influence of Oxygen Availability: In laboratory experiments Bisogni and Lawrence (1975) found that rates of methylation of mercury were approximately twice as high under aerobic conditions as under anaerobic conditions. However, an analysis of marine sediments from San Francisco Bay by Olson and Cooper (1976) reveals that methylation rates are higher and methylmercury is more persistent under anaerobic conditions. The opposing findings suggest that the effect that oxygen availability has on the methylation rate of mercury is influenced by another factor in San Francisco Bay. Methylation of mercury in the environment depends on many factors that are closely interwoven. The combination of all factors involved in mercury methylation seems to override the effect of oxygen availability on the methylation rate under a controlled environment.

Methodology

This project consists of two separate parts. The first part deals with San Francisco Bay specifically. Analyses of sediments from cores taken at several sites in San Francisco Bay yield information about the distribution and speciation of mercury in the Bay. In the second part of the project I attempted to compare the levels of mercury contamination of San Francisco Bay wetlands with mercury concentrations in wetlands of other areas in the United States. I contacted researchers in Washington, Georgia, Florida and Maryland. This attempt, however, proved to be unsuccessful. No institution was able to give me any data on total mercury content of wetlands in their area. There are hardly any monitoring programs for mercury in estuarine wetlands. Some institutions recently have started monitoring mercury in wetlands, but studies are not yet completed and consequently no data are available now.

Analysis of Sediment Samples: The U.S. Geological Survey (USGS) obtained samples of San Francisco Bay sediments from a core drilled by Cal-Trans near the San Mateo Bridge. A core near Pittsburg was drilled in 1995 for a seismic study that is being conducted by Lawrence Berkeley Laboratory (Williams, 1995, pers. comm.). I sampled bag samples from the San Mateo Bridge core at 15m (50ft) and 30m (100ft) below the sediment surface and bag samples from the Pittsburg core from 22 to 23.5m (72 to 77ft), 25 to 26.5m (82 to 87ft) and 55 to 56.5m (179 to 185ft) below the boat deck, which was 15m (49ft) above the sediment surface. The Pittsburg samples were obtained from the top part of the respective sedimentary layers in the recovered core. All samples taken consisted of 15 to 20g of sediment. They were analyzed for mercury content using EPA method #7471 (Determination of mercury in soils and sediments) by Sequoia Analytical Laboratory, Redwood City, CA.

Because mercury is present in the Bay in very low concentrations, the methods of determining mercury levels are complicated. In order to determine small concentrations of heavy metals, gas chromatography is not the method of choice. Accurate results are more properly obtained by using atomic absorption. The drawback of this method is that it only detects the total amount of mercury present in the sample, but it is unable to distinguish between different species of mercury.

Spatial Distribution of Mercury: The information necessary to determine trends in the spatial distribution of high organic mercury concentrations in San Francisco Bay was obtained through library research. Using these trends and the data from the sediment samples, I can draw conclusions about the possibility of adverse effects on the different regions of San Francisco Bay that are related to exposure to mercury.

Data

The analysis of core samples from Pittsburg and the San Mateo Bridge shows mercury concentrations in the sediments that are at most very slightly above the natural background concentration of 0.05ppmw (Tab. 5). Mercury concentrations ranged from <0.01ppmw to 0.07ppmw in the Pittsburg samples and from 0.033ppmw to 0.052ppmw in the samples from San Mateo Bridge. Increased levels of mercury occur only in the top layers of sediment directly under the water column (Hornberger, 1995, pers. comm.). Mercury concentrations in Richardson Bay and Grizzly Bay were determined by the USGS. Enriched concentrations ranging from 0.2ppmw to 0.9ppmw that are significantly different from the background concentrations are only found in the upper three feet of sediment.

Site	Depth (ft)	Hg concentration (ppmw)
Pittsburg	72 – 77	n. d.
Pittsburg	82 – 87	0.01
Pittsburg	179 – 185	0.07
San Mateo Bridge	50	0.052
San Mateo Bridge	100	0.033
Richardson Bay	0 – 3	0.2 – 0.4
Richardson Bay	3 – 5	0.05
Grizzly Bay	0 – 3	0.2 – 0.9
Grizzly Bay	3 – 6	0.05

Table 5. Mercury concentrations in San Francisco Bay sediments; Grizzly Bay and Richardson Bay (data from Hornberger, 1995).

Discussion

The highest levels of total mercury in surface sediments occur in the northern areas of the Estuary. The data indicate that peak concentrations in the northern part of the Estuary (0.9ppmw) are much higher than those in the central area of the Bay (0.4ppmw), although the lower end of the range is the same (0.2ppmw) in both areas. This is to be expected since mercury is mostly added to the Bay from the riverine system (Gunther *et al*., 1987). Peak concentrations should be even lower further south, e.g. near the San Mateo Bridge since mercury is fairly immobile due to its high elemental weight and since it does not easily disperse throughout the Bay. Inputs of mercury have increased dramatically with the beginning of hydraulic mining (Kinkel, 1956). Mercury related to anthropogenic input can be readily distinguished from the background concentrations. Taking the sedimentation rates at different areas of the Bay into account, the accumulation of mercury from human activities appears to be limited to the upper three feet of sediment.

In sediment layers that lie below the upper meter, mercury concentrations are fairly stable, not exceeding 0.07ppmw. These concentrations are of much less danger to the environment, not only because of the lesser extent of contamination but also because of the depth at which they occur. Very few organisms ever get exposed to this mercury, and then the measured concentrations do not impose an immediate danger to such organisms (Eisler, 1987). Areas with low oxygen content tend to have a higher methylation rate of mercury (Olson and Cooper, 1976) and bottom sediments with less exposure to dissolved oxygen in water therefore have a higher relative abundance of organic mercury. However, the danger of exposure to the mercury is low because of the inaccessibility of the sedimentary layers. This pattern of distribution applies to undisturbed areas. Anthropogenic activities such as dredging can alter the pattern of mercury distribution significantly.

Areas with high total mercury concentrations are likely to produce more methylmercury. Since the concentrations of methylmercury depend on the total availability of mercury as well as the local conditions of the ecosystem, an assessment of consequences is very complex. Because of the heterogeneous distribution of mercuric compounds within a given wetland area, it is difficult to estimate the exact impact the mercury contamination has on the surrounding area. Within a given area transformation does not only occur at the interface between the sediments and the water column. Although mercury transformation occurs throughout the water column, the transformation rates into the more toxic methylmercury are higher under anaerobic conditions in lower sedimentary layers.

Mixing effects are higher in areas with larger fluxes of water, and measured concentrations of methylmercury may not reflect the amount of mercury actually converted. Due to the large volume of water passing from the Sacramento/San Joaquin Rivers, methylmercury concentrations measured in San Pablo and Suisun bays are less certain than in other areas of the Bay.

The general trend indicates that the relative amount of methylmercury should be lower in the southern region of San Francisco Bay, where demethylation is more favored and less methylation is likely. However, the absolute amount of mercury in sediments of the central and southern parts of the Bay may be higher than in the North Bay because of additional input from point sources. Examples of such areas with high contaminant input in the central Bay are Sausalito and Alameda Naval Air Station (Luoma and Philips, 1988). The additional input produces localized areas of high mercury contamination, but most of the mercury tends to remain in its inorganic form because of unfavorable conditions for conversion.

Conclusion

Mercury contamination has reached significant levels in the upper sedimentary layers directly below the water column. These concentrations can be harmful to organisms exposed to the mercury due to long term accumulation of organic mercury. Sediments at greater depths show hardly any mercury contamination and are no immediate danger to the ecosystems around the Bay.

However, the actual impacts of mercury on the ecosystem of the Estuary are not well understood. Mercury levels in sediments follow predictable patterns, but many of them have been altered by anthropogenic activities. Further studies, especially of areas with disturbed sedimentary profiles, are necessary in order to examine the effect of these alterations on the formation of organic mercury.

Most of the remaining sensitive wetland areas are in the northern region of San Francisco Bay. The uncertainties associated with methylmercury concentrations are highest in these areas. In order to identify a prevalent trend in the distribution of the different mercury species and to decrease the uncertainty in the data, it is necessary to obtain more samples from that area in proximity of wetlands. With those data it is then possible to assess the actual effect of this heavy metal on San Francisco Bay more precisely.

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