CHAPTER 5. MANAGEMENT QUESTION: AT WHAT LOCATIONS ARE CURRENT METHYLATION RATES AND METHYLMERCURY FLUX HIGHEST?

Beginning with a general overview of mercury methylation in the environment, this section presents a discussion of existing knowledge on methylmercury in the bay, as well as necessary studies to more fully understand conditions and locations within the bay that are likely to contribute most to the methylmercury supply. For the purpose of this discussion, the bay is treated not as a single unit but as a heterogeneous mix of habitats with different effects on mercury methylation.

5.1 BACKGROUND ON MERCURY METHYLATION

Of the commonly observed species of mercury in the environment, methylmercury is widely understood to be the form that causes the greatest toxicity to wildlife and humans, principally because of its ability to bind strongly to sulfur atoms in biological tissue. For this reason, a great deal of research attention in the past two decades has been devoted to understanding the processes that lead to the formation of methylmercury in aquatic ecosystems. It is commonly understood now that mercury methylation is a bacterially mediated process, where sulfate reducing bacteria co-metabolize inorganic mercury to produce methylmercury. For mercury methylation to be significant, aquatic chemistry conditions must enable both the dissolution of mercury from solid or suspended forms and the bacterial reduction of sulfate.

Inorganic mercury as the free mercuric ion (Hg^{2+}) is found at very low levels in natural waters, although it can exist at higher concentrations as dissolved aqueous complexes with various organic and inorganic ligands. These ligands include natural organic acids, sulfide, and chloride (e.g., Ravichandran et al., 1999; Benoit et al., 1999). Both organic acids and sulfides have been demonstrated to significantly enhance the dissolution of mercury. The presence of sulfides is of particular significance because it hypothesized that the HgS aqueous complex can penetrate bacterial cell walls and, among the dissolved species, is more amenable to methylation (Benoit et al., 2001).

Sulfate reducing bacteria are most active in low-oxygen environments in the presence of an organic substrate; it follows that if a source of dissolved inorganic mercury is present under these conditions, mercury methylation is also likely to be enhanced. In the aquatic environment, conditions with low oxygen and with sufficient organic carbon typically occur in poorly mixed productive water bodies, and in sediment porewaters. Shallow-water zones, such as wetlands, because of their high primary productivity and resulting low oxygen conditions in sediment porewaters, are known to be significant producers of methylmercury.

In this report when we speak of methylation we generally refer to net methylation, although at any given time, it is known that both methylation and demethylation occur simultaneously, with the residual of these reactions resulting in measurable quantities of methylmercury. Demethylation can be a biotic as well as an abiotic process, and conditions where demethylation is active can reduce observed methylmercury concentrations. Demethylation has been studied less intensively than methylation, although the data that do exist, indicate that it is somewhat less sensitive to aquatic chemistry conditions that methylation, possibly because many more bacterial groups are responsible for demethylation than for methylation (Marvin-DiPasquale and Agee, 2003). For most practical purposes, it may be noted that measured methylmercury concentrations reflect a dynamic balance between methylation and demethylation.

Following production and accumulation of methylmercury, the next most important step is its advection or dispersion to that portion of the water body where it may enter the food web. This is especially important if the methylmercury has been produced in the sediments or if it is produced in the water column of only a portion of the water body. Transfer of methylmercury to the food web may happen by ingestion of methylmercury containing sediments by benthic-dwelling organisms, by the diffusion of methylmercury into the water column where it enters the food web through uptake by plankton, or by suspension of bay sediments by currents. The net impact of methylmercury production in any part of the water body is a function of the net rate of methylation and the quantity of mercury methylated as well as the efficiency with which it is transferred into the food web.

5.2 EXISTING DATA ON MERCURY AND METHYLMERCURY IN THE BAY

Mercury and methylmercury concentrations have been measured in the sediments and waters of San Francisco Bay in the past 10 years for different research and monitoring programs. The studies and sampling time frames are:

- Regional Monitoring Program (RMP) conducted by San Francisco Estuary Institute, with total mercury measurements from 1994 to the present, and methylmercury measurements from 2001 to the present.

- Wet and dry season measurements of total mercury and methylmercury in water in 2001 and 2002 reported by Gill et al. (2003) as part of CALFED-supported research.
- Sediment total and methylmercury in 2001 by Moss Landing Marine Laboratories as part of CALFED-supported research (Heim et al., 2003).
- Water column total mercury and methylmercury monitoring by the University of California at Santa Cruz between 1999 and 2002 reported by Conaway et al. (2003).

Figures 5-1 to 5-6 present a consolidation of these reported results for total mercury in water and sediment for the entire bay, and for methylmercury in water and sediment for the North Bay and the South Bay. These plots show data for multiple years, and where replicate measurements were made at the same station over several years, the average values are plotted. (Inter-year variation in concentration is discussed in Chapter 7.) Because of the potential role of habitat in methylation of mercury, the methylmercury values for both water and sediment are overlaid on a map of the bay habitats obtained from the San Francisco Estuary Institutes EcoAtlas Information System (http://www.ecoatlas.org/). The following general observations about the distribution of mercury and methylmercury in San Francisco Bay are notable:

- High concentrations of total mercury in water are observed in the shallow southern and northern portions of bay; four of the five highest concentrations occur in the South Bay. The Central Bay has the lowest total mercury concentrations.

- The highest sediment total mercury concentrations occur in the shoreline portion of the bay near Oakland Harbor. Concentrations in much of the rest of the bay appear to be at relatively uniform levels.

- Water-column methylmercury concentrations are generally higher in the South Bay than in the North Bay. The five highest reported concentrations all occur in the South Bay. It is also observed that concentrations are higher in the shallow extremities of the bay than in the deeper portions. Water column methylmercury concentrations showed a relationship with total mercury over the entire range of concentrations when plotted on a log-log scale (Figure 5-7). However, in the range where most stations fell, i.e., total mercury concentrations between 5 and 30 ng/l, the relationship to methylmercury was weak, and could vary by an order of magnitude for a specific total mercury concentration.

- Sediment methylmercury concentrations are higher in the shallow and coastal regions of the bay. The highest concentrations occur in Coyote Hills Slough Channel and in the central, coastal portions of the bay near Oakland and Richmond. Similar to the water column concentrations, sediment methylmercury concentrations showed a weak relationship with total sediment mercury concentrations on a log-log scale (Figure 5-8). This relationship is influenced by stations at the high and low end; in the range with the greatest number of data points, between 100 and 1,000 ng/g, the relationship to methylmercury was weak.

- Most of the data collection in water is concentrated in the deeper portions of the bay, although plots of the data show significant elevated spots of methylmercury in the shallower regions. There are few co-located measurements of sediment and water column mercury concentrations.

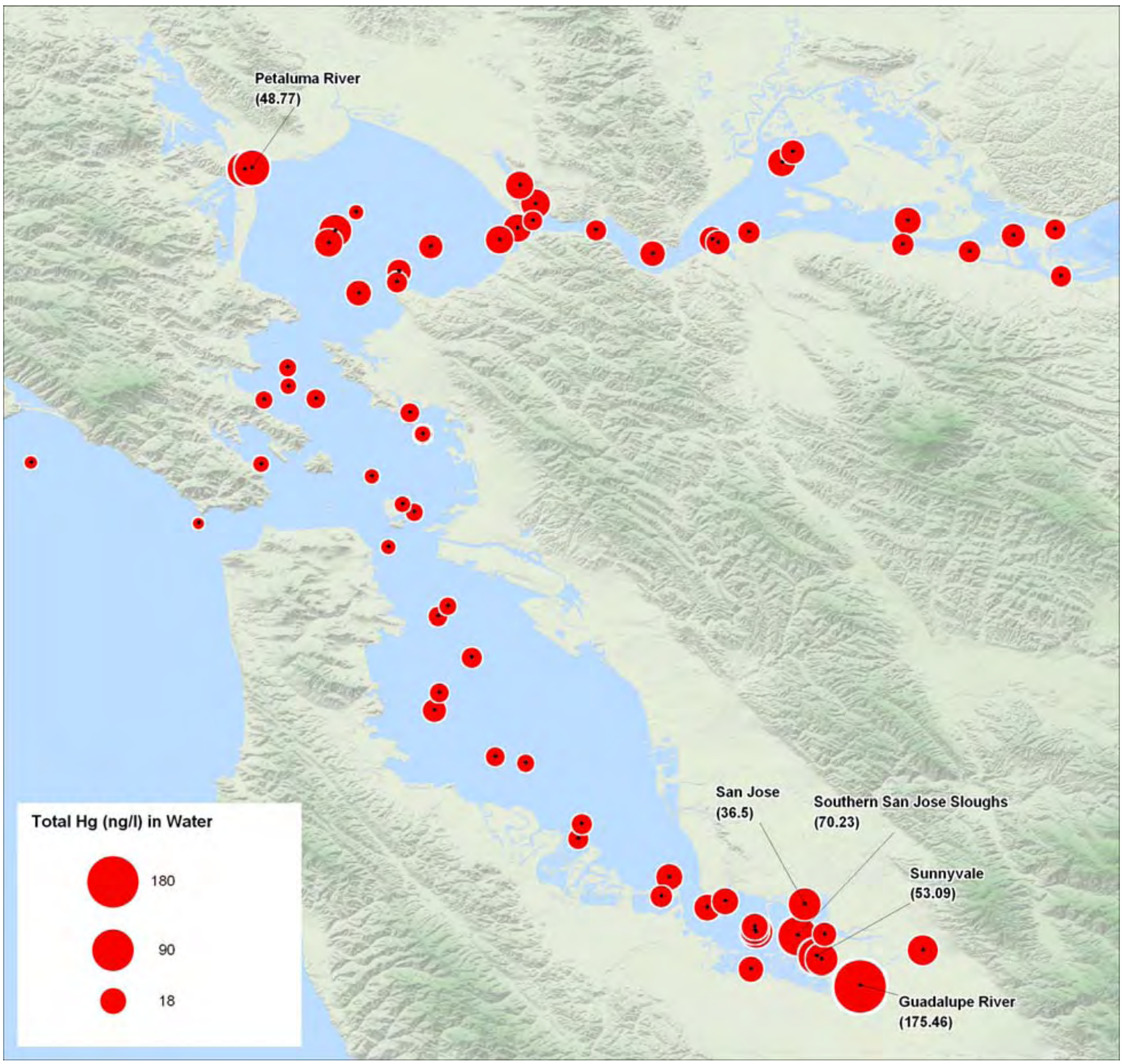

Figure 5-1. Total mercury concentrations in the waters of San Francisco Bay. The five highest data points are highlighted.

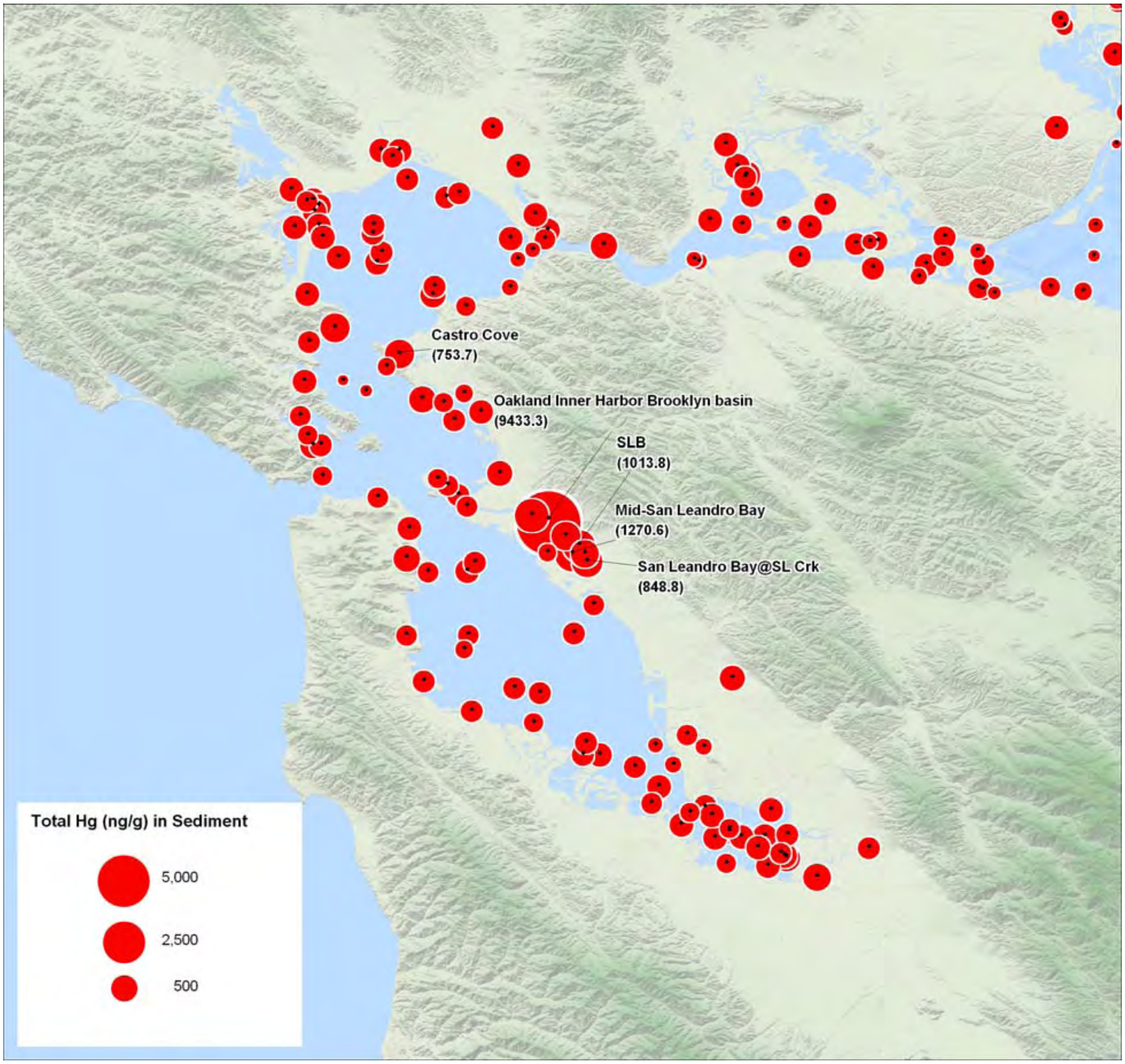

Figure 5-2. Total mercury concentrations in the sediments of San Francisco Bay. The five highest data points are highlighted.

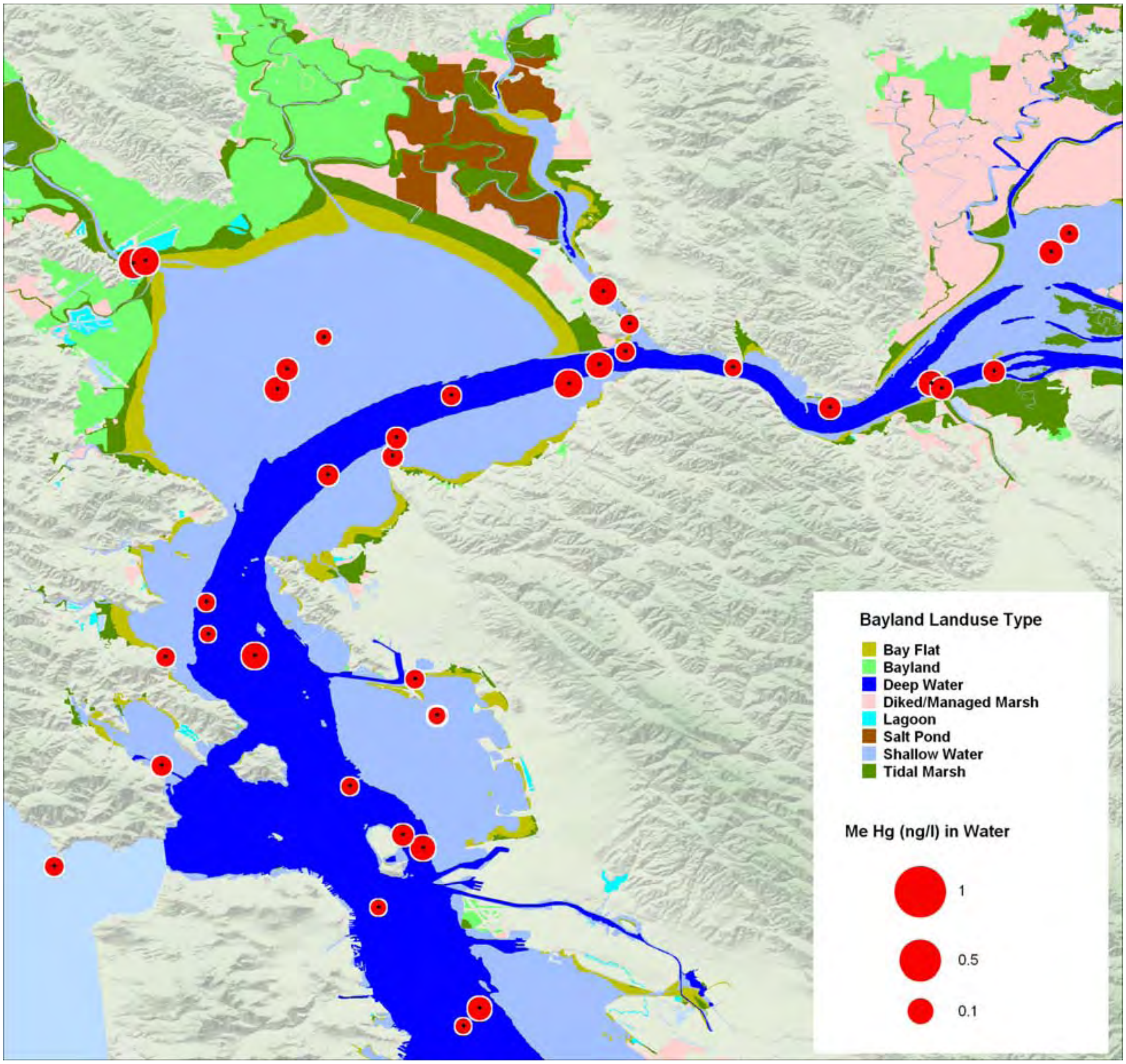

Figure 5-3. Methylmercury concentrations in the waters of North San Francisco Bay. Also shown on the map are principal habitat types in the bay. Habitat data from San Francisco Estuary Institute's EcoAtlas Information System (http://www.ecoatlas.org/).

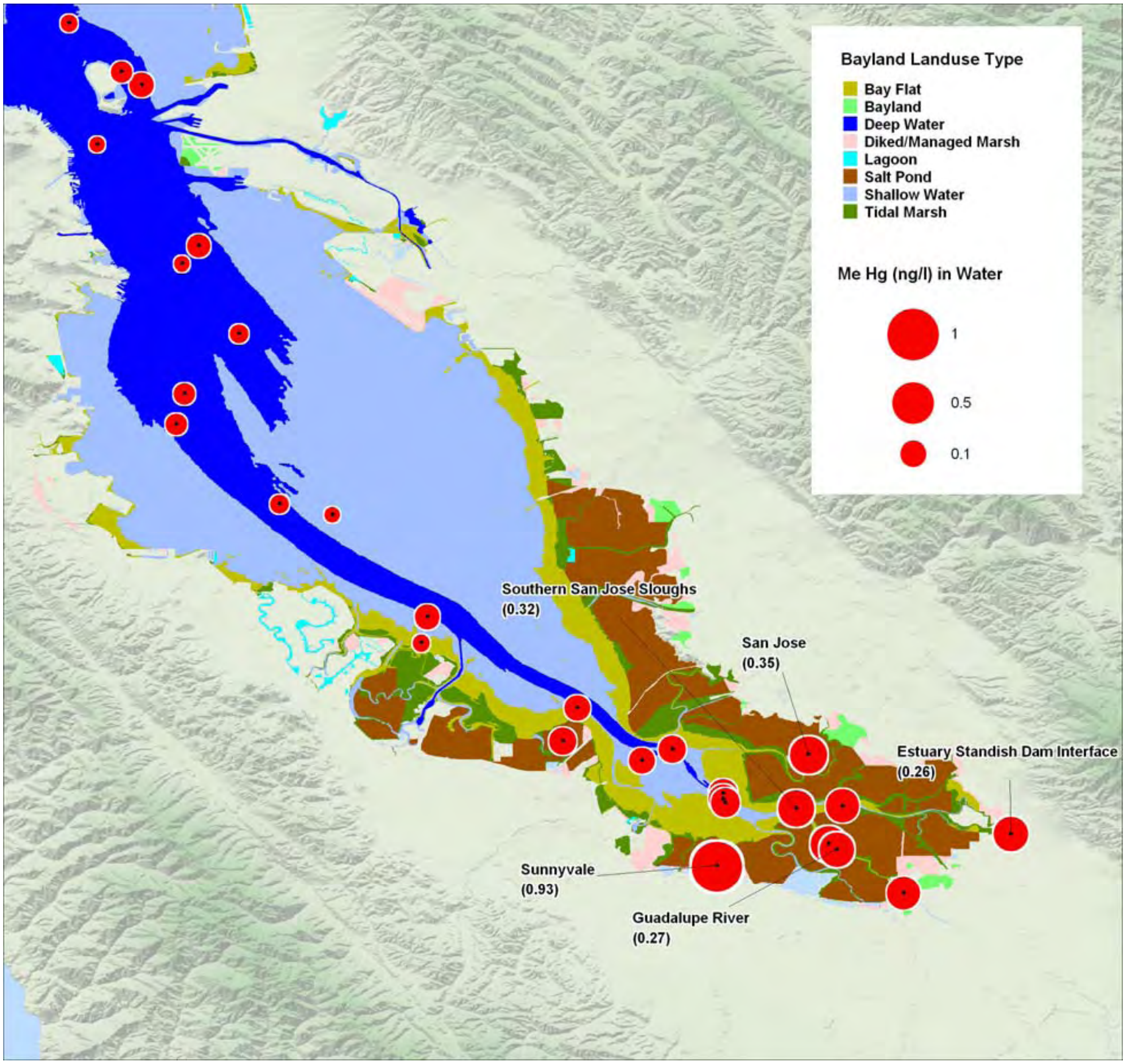

Figure 5-4. Methylmercury concentrations in the waters of South San Francisco Bay. Also shown on the map are principal habitat types in the bay. Habitat data from San Francisco Estuary Institute's EcoAtlas Information System (http://www.ecoatlas.org/).

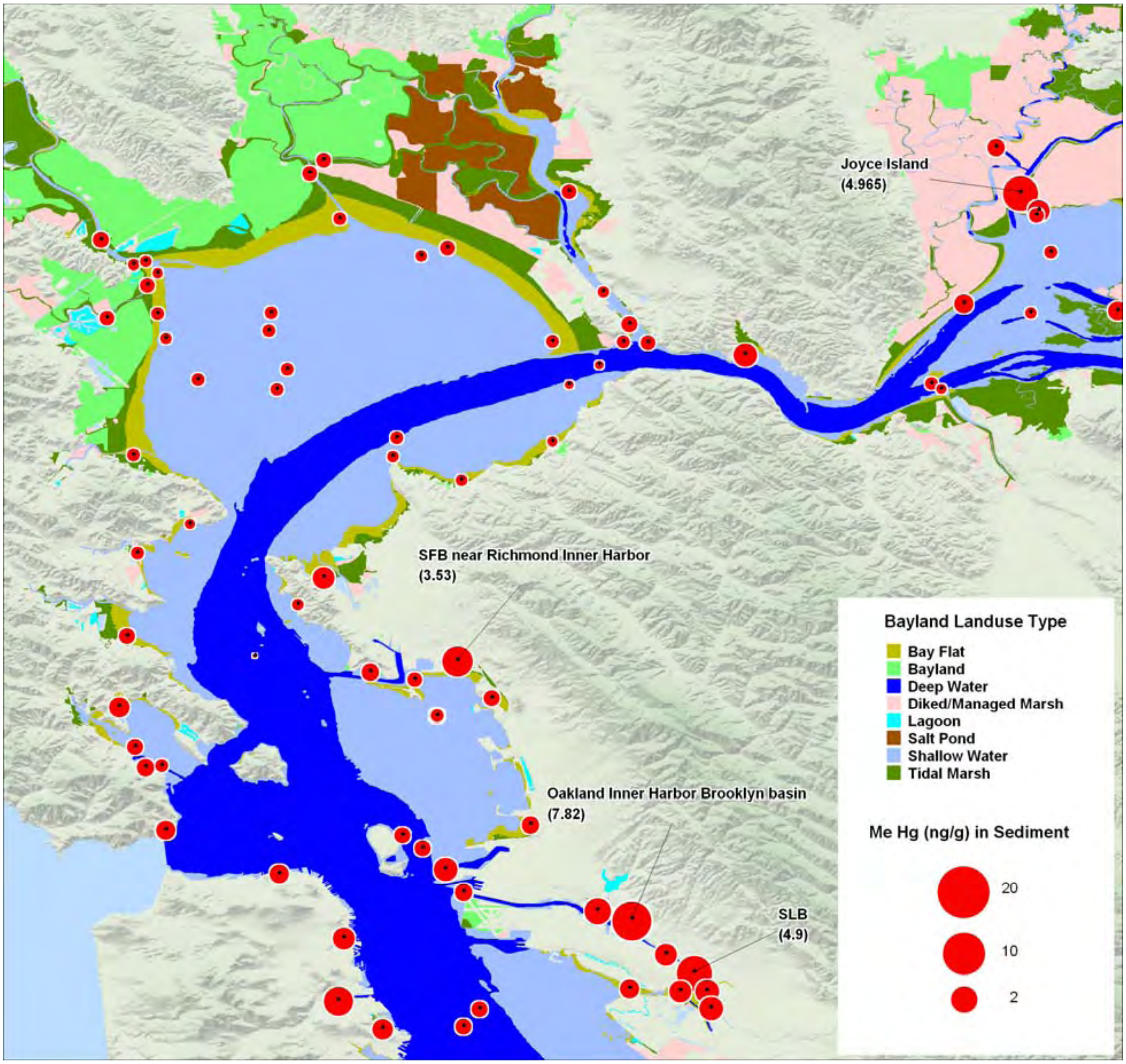

Figure 5-6. Methylmercury concentrations in the sediments of North San Francisco Bay. Also shown on the map are principal habitat types in the bay. Habitat data from San Francisco Estuary Institute's EcoAtlas Information System (http://www.ecoatlas.org/).

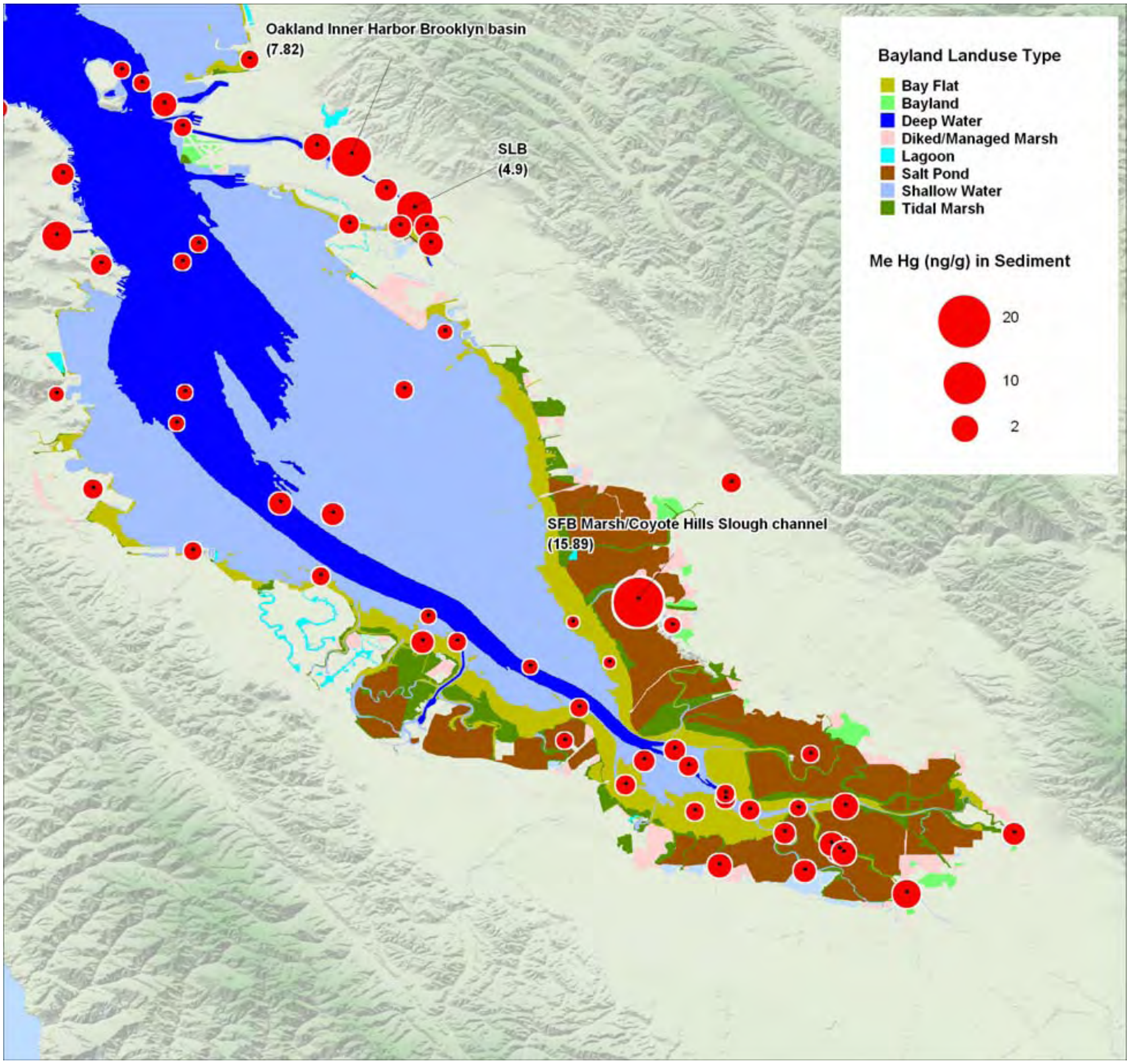

Figure 5-6. Methylmercury concentrations in the sediments of South San Francisco Bay. Also shown on the map are principal habitat types in the bay. Habitat data from San Francisco Estuary Institute's EcoAtlas Information System (http://www.ecoatlas.org/).

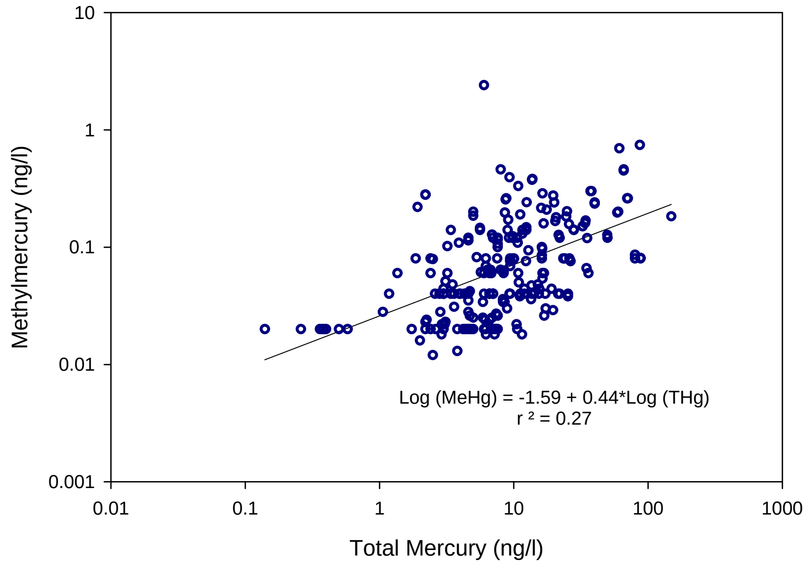

Figure 5-7. Unfiltered methylmercury in water as function of co-located total mercury concentrations. Data sources include the RMP, Gill et al., 2003, and Conaway et al., 2003.

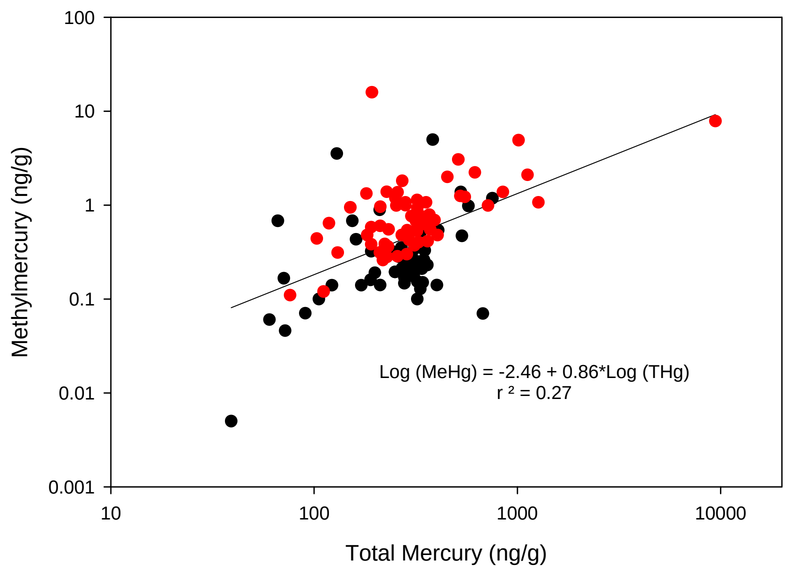

Figure 5-8. Methylmercury in sediments as function of co-located total mercury concentrations in sediment. Red circles are stations in the South Bay, and black circles are stations in the North Bay. Data from Heim et al., 2003.

In addition to the bay-wide monitoring data reported above, the San Francisco Bay and Delta has been the subject of detailed process studies to identify sediment-water fluxes of dissolved mercury and methylmercury (Gill et al., 2003). Direct experimental measurements were made of mercury fluxes in benthic chambers on selected dates at several locations in the Delta. The measured rates show significant temporal and spatial variability, ranging from high negative to positive values (-300 to +520 ng/m^2/day for total mercury; -18 to +170 ng/m^2/day for methylmercury), although most values were positive. A further complication is that there is no meaningful correlation between the dissolved and methylmercury flux rates from the same sampling stations. At several locations, fluxes were also estimated using measurements of porewater mercury species concentrations and overlying water concentrations. Where porewater-estimated and benthic chamber rates were both measured, the measured rates in the benthic chambers were substantially higher, often by more than an order of magnitude. Most sites indicated peaks of methylmercury in 1-2 cm depth of sediment. Dissolved mercury fluxes, although highly variable, did not show a distinct elevated level at any particular station. Methylmercury at a marsh site, on the other hand, showed a large peak in an October sample. This value was significantly higher than observed for any other station during the entire period of the study. It was also found that surface water methylmercury concentrations were elevated near a marsh stations but decreased to background levels in the Delta within a short distance.

Detailed process studies using radiolabeled mercury isotopes to measure mercury methylation and demethylation in relation to environmental variables have been conducted at a few locations in the Bay and Delta (Marvin-DiPasquale and Agee, 2003; Marvin-DiPasquale et al., 2003). Data from marsh and open water locations in San Pablo Bay indicated substantially elevated methylation rates and methylmercury concentrations in porewater from a marsh location, compared to three open water locations, in spite of all stations having similar total mercury concentrations in sediments (Marvin-DiPasquale et al., 2003). Methylmercury concentrations in the open water zones were about a tenth of the levels at the marsh site. A similar study at three sites in the Delta showed strong temporal and spatial variations in mercury methylation and demethylation (Marvin-DiPasquale and Agee, 2003). Methylmercury production was highest during late winter (February/March) when it was positively correlated with sulfate reduction rates. At other times, in May and October, although sulfate reduction rates were much higher, there was no relationship with methylation rates. It has been proposed that higher levels of sulfide buildup during periods of high sulfate reduction are responsible for inhibiting methylation by making the mercury less bioavailable. It should be pointed out that these findings are not fully supported by the methylmercury flux measurements of Gill et al. (2003), who did not report unusually high fluxes during measurements in February in the same sampling areas.

In general, the results discussed above support the idea that sediments can be a source of dissolved and methylmercury to overlying waters, and some locations, principally marshes, are consistently higher in methylmercury than other locations. Although wetlands in the saline portion of the bay have not been studied as intensively as freshwater wetlands in the Delta, the monitoring data do appear to indicate an elevation of methylmercury in the shorelines of the main stem bay. In this respect, wetlands in the San Francisco Bay and Delta transform mercury in a manner similar to what has been reported in the literature for wetlands in general. However, current data make it difficult to estimate quantitatively the contribution of the methylmercury from sediments at different locations to the overall supply to the bay, which include other watershed and atmospheric sources. Detailed process studies, especially of flux, have a great potential for developing quantitative estimates. As performed, though, the experimental data are notable for the high seasonal and spatial variability they exhibit. In the absence of sufficiently replicated studies at a selected number of locations, robust estimation of Delta or Bay-wide methylmercury sediment-water fluxes is a very difficult task.

5.3 Hypotheses and Data Requirements to Advance Understanding of Mercury Methylation in the Bay

Although relatively limited process studies have been conducted in the bay where the mercury transformations and fluxes are explored directly for us to conduct a bay-wide estimate of mercury fluxes, the data shown in Figures 5-1 to 5-6 provide some insight into the behavior and methylation of mercury across the bay. A possible interpretation that emerges is that mercury is methylated primarily in the coastal zones from where it is transferred to the rest of the bay, and is gradually lost from the water column due to biological uptake, dilution and demethylation. An alternative interpretation is that methylmercury fluxes from sediments in different habitats are similar, only that dilution by the water column results in lower values in the deeper water zones. Each of these interpretations calls for specific actions to reduce mercury methylation and to reduce net impairment to biota. However, before any management actions are planned, additional study is needed using a set of hypotheses on mercury methylation in the bay as a starting point. We have identified several hypotheses that need to be tested, their significance to the overall management issues, and the monitoring and experimental studies that may be used to test the hypotheses. The goal of this approach is to build a sound scientific footing upon which to base management actions to reduce mercury impairment in the bay.

Hypothesis 1: Sediments are the primary sites of mercury methylation

It is probable that most of the methylmercury produced in San Francisco Bay is produced in the sediments, with the water column providing a small fraction. If confirmed to be true, this can be the basis for identifying interventions to limit fluxes of methylmercury from sediments to the water column, particularly if the zones of significant methylation are localized. If, on the other hand, the water column is a significant generator of methylmercury, such interventions are likely to have little benefit.

Proposed Experiments. Evaluate the production of methylmercury in the water column in different locations of the bay. This may be done using transparent chambers suspended in water where inorganic mercury labeled with stable isotopes has been introduced. The experiments need to be conducted in water of different depths and in anoxic or hypoxic zones. The net formation of methylmercury (of the same isotope that is introduced) in these chambers provides evidence of the significance of water column methylation or lack thereof. Rates of net methylation from these studies may be compared with net methylation and flux from sediments (discussed under Hypothesis 2). Weighting the two rates by their respective areas in the bay, the relative significance of water column methylation may be evaluated.

Hypothesis 2: Of the different habitats in the bay, wetlands, mudflats, shallow water zones (less than 1 m deep), and tributaries are significant contributors of methylmercury to the bay

A significant volume of published literature (e.g., St. Louis et al., 1994, 1996), as well as the data from San Francisco Bay discussed above, provide support for the significance of enhanced methylation in sediments of wetlands, mudflats, and other shallow water zones. However, the flux of this mercury to the rest of the bay, relative to the methylmercury flux from other, deeper water zones is not known. If it turns out that a significant quantity of the methylmercury entering the bay waters originates in these zones, interventions in these areas are likely to have benefits on impairment. In particular, it may require further, mercury-related investigation of the proposed creation of salt marshes in the South Bay at the locations of existing salt ponds. If, on the other hand, these sources, once weighted by their areas, are not the major source of methylmercury to the wider bay, the concern regarding the mercury impacts of salt pond restoration may be partially alleviated.

Proposed Experiments and Field Monitoring. It is proposed that flux chamber experiments be performed to estimate the magnitude of the methylmercury fluxes from the different habitats in the North and South Bay, such as salt marshes, mud flats, shallow water zones and tributary areas, as well as deeper water zones. These experiments will complement measurements reported for locations in the Delta (Gill et al., 2003). For the results to have any utility for planning management actions, the variability shown in existing data must be considered in planning future experiments; measurements must be made across different seasons and with at least two replicate measurements at location. In the presence of budget constraints, greater replication at a smaller number of stations is preferable to a larger number of un-replicated measurements. The flux chamber experiments should be supplemented by more spatially intensive sampling of methylmercury in surface waters in the vicinity of known sources of methylmercury to evaluate their impact on the wider bay. Together, the experiments and the monitoring will allow for a more robust estimate of the methylmercury contribution of the coastal shallow water areas to the main bay.

Hypothesis 3:For a certain type of habitat, methylation is controlled by the quantity of total mercury in the sediment

The current plan to reduce mercury impairment in the bay calls for a reduction of total mercury concentrations in bay sediments. However, total mercury concentration is only one of several factors that may affect the quantity of methylmercury produced, as discussed above. Other factors relate to the solubilization of mercury and the methylation rate of the dissolved mercury. Thus, a simple relationship between total and methylmercury was not observed in the Bay-Delta region as shown in Figure 5-7. We need to understand better what controls mercury methylation in different parts of the bay. If it is true that methylmercury concentrations are correlated to the total mercury concentrations, at least in portions of the bay, there is reason to believe that total load reductions will reduce methylmercury production and thus biological impairment in the bay. If, however, other factors are found to be more important, even at smaller spatial scales, or that the methylmercury production is insensitive to the total mercury in sediments, total mercury load reductions may cause no meaningful change in the impairment status.

Proposed Monitoring, Experiments, and Pilot Study. This hypothesis needs to be tested using field monitoring, experiments using sediment cores, and pilot field studies. Monitoring locations reported in Figure 5-1 are an adequate starting point. At a subset of these locations that have similar total mercury concentrations, but with significant differences in methylmercury concentrations, additional monitoring of ancillary parameters is proposed (such as sulfide, dissolved oxygen, organic carbon, water depth, etc.) such that the differences can be explained given current knowledge of mercury transformation. It is proposed that cores of bay sediments from these locations be used to conduct experiments with introduced stable mercury isotopes. These experiments will confirm whether the rates of mercury methylation are naturally greater in some locations than others. Following these experiments, an important field-scale pilot study that should be conducted is to cover the sediments at one or more stations with elevated methylmercury with lower total mercury sediments from a different location in the bay, and after allowing for the site to attain steady state, evaluate resulting methylmercury concentrations. Statistically significant decreases in methylmercury provide support for capping as an intervention strategy and also for the idea of methylmercury decreasing as total mercury in the system decreases.

Hypothesis 4: Point sources of mercury discharge have localized effects on methylmercury production

Some point sources of mercury discharge to the bay are thought to be more bioavailable than non-point sources such as the Central Valley and Guadalupe Watershed loads. If this is true, it may be reflected in higher concentrations of dissolved and methylmercury in the vicinity of such discharges. In this case, the reduction of point source loads may provide a localized benefit even though the quantity of load reduced is small relative to the total mercury loads in the bay.

Proposed Monitoring/Experiments. This hypothesis needs to be tested using field monitoring in the proximity of discharge locations. Total, dissolved and methylmercury concentrations need to be measured to identify whether these values are significantly different from what is observed in other locations in the bay.

5.4 SUMMARY

Methylmercury, rather than total mercury, is the species of greatest concern when the environmental impacts of mercury are being evaluated. An improved understanding of mercury methylation in San Francisco Bay is therefore central to evaluating future strategies to reducing the current level of mercury impairment. Monitoring data in water and sediments, as well as more detailed process-oriented measurements, indicate that shoreline zones are elevated in methylmercury, and that total mercury concentrations, in water, sediments, or both, cannot explain methylmercury concentrations. A set of hypotheses, targeted toward developing management strategies to reduce the impairment level, are proposed. These include comparative measurements of methylmercury production in water and sediments, estimation of fluxes from coastal zones to the main stem of San Francisco Bay, the relationship between total mercury and methylation, and the effect of point sources of specific portions of the bay. It is hoped that these studies will help define the available options for controlling mercury impairment in the bay with reasonable time frames.

CHAPTER 6. MANAGEMENT QUESTION: CAN EXISTING WETLANDS BE MANAGED OR NEW WETLANDS BE DESIGNED TO MINIMIZE NET METHYLATION RATES, OR LIMIT EXPOSURE TO METHYLMERCURY THAT IS PRODUCED?

Wetlands are highly valued because they provide unique habitat for biota, particularly for wading birds, and are a nursery ground for many species. Wetlands surrounding San Francisco Bay are an important part of the Pacific Flyway. Because of their shallow depths, large areas, and aquatic vegetation, wetlands attenuate flood flows and are also highly efficient in removing water-borne pollutants, including total mercury. Unfortunately, wetlands are generally very efficient at producing methylmercury, and in most cases that have been studied, methylmercury increases in concentration in wetlands (e.g. St. Louis et al. 1994, 1996, Driscoll et al. 1995, Gill et al., 2003; Heim et al., 2003). Aside from the role of mercury methylation in existing wetlands around the bay, the understanding of wetland mercury behavior takes on greater importance because of the proposed creation of additional wetlands by restoration of former salt ponds in San Francisco Bay (Beutel and Abu-Saba, 2004).

This section provides an overview of mercury transformations in wetlands, and describes possible studies that may be used to better understand mercury behavior in the San Francisco Bay region. The eventual goal of such studies would be the identification of means to reduce methylmercury production and/or to limit the transfer of methylmercury from wetlands to the wider bay.

6.1 MERCURY CYCLING PROCESSES IN WETLANDS

Many of the mercury cycling processes in wetlands are similar to those occurring in aquatic systems generally and are discussed elsewhere in this document (Chapter 3). We will focus here mostly those aspects of wetlands that distinguish them from other water bodies. A schematic showing the most important mercury transformations in wetlands is shown in Figure 6-1.

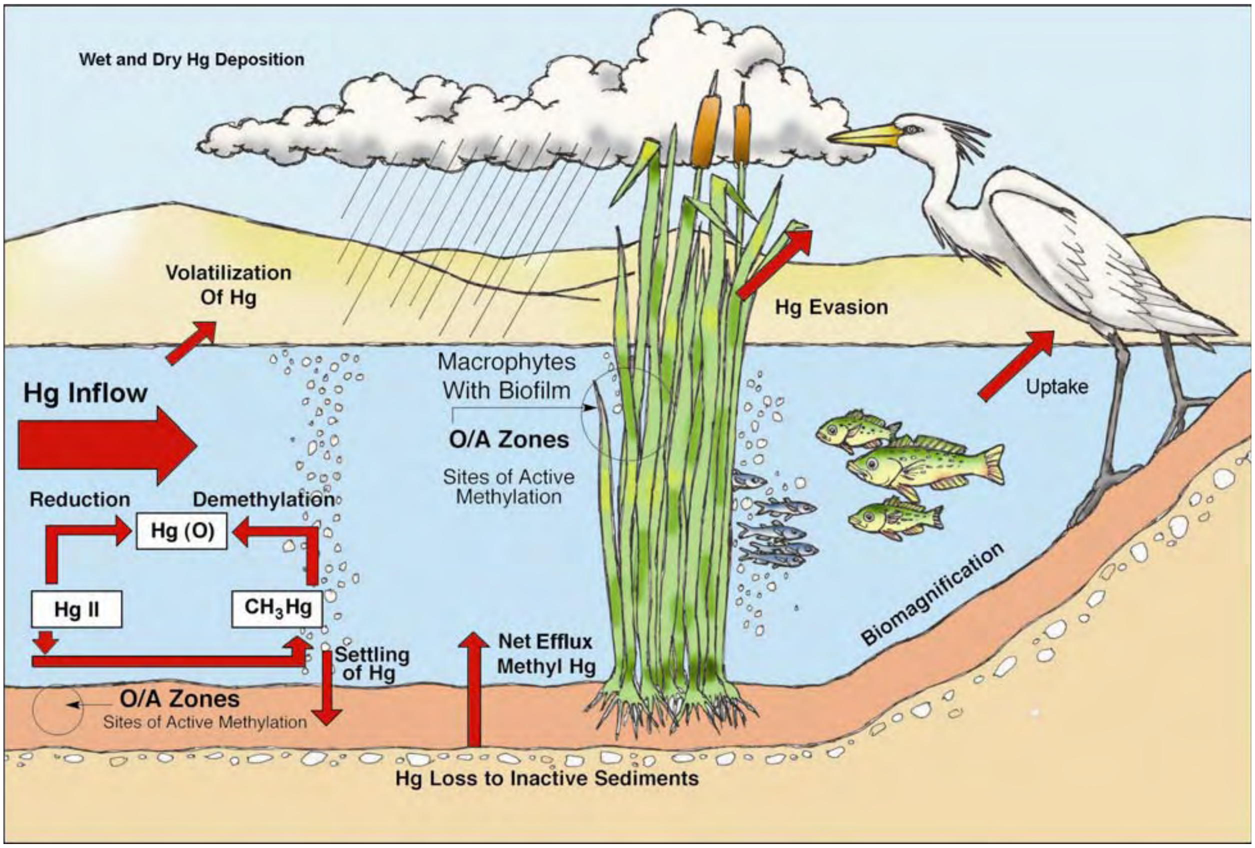

Figure 6-1. Mercury cycling and biotic uptake in wetlands along the edge of the bay.

Mercury methylation in wetlands is influenced by their shallow gradients, high organic matter production, and warmer water column temperatures. Unlike upland watersheds, almost all of the water that flows into wetlands moves laterally through them. Wetlands experience relatively little infiltration into their sediments. In upland catchments, infiltration through soils typically removes over 90 percent of the input mercury (Meili, et al. 1991, 1997; Hurley, et al. 1995; Driscoll, et al. 1994). Even the poorest mercury adsorbing soils, for example, sands, can remove over 80 percent of applied dissolved mercury after infiltration through less than 1 meter of soil. Wetlands, lacking strong vertical gradients, do not benefit from this soil filtration. Instead, much of the methyl mercury precursor, dissolved or complexed aqueous mercury, remains in the water. Relative to other surface waters, wetlands exhibit very high biofilm surface area to water volume ratios. Waters in wetlands are shallow and typically contain macrophytes that provide additional surface area beyond that of the sediment. On these surfaces, oxic-anoxic (A/O) interfaces are readily established in microbial films. The sulfate and iron reducing bacteria responsible for mercury methylation thrive in these interfaces. The reducing agent necessary for their metabolism, labile organic mater, is readily available in wetland waters. It is also important to note that, not only are these A/O zones abundant in wetlands, they occur very near the bulk water, and not at depth in sediments, where diffusion limits the input of reactants for the methylation, and also limits the release of any methyl mercury produced. The typical low velocity flow through wetlands keeps these oxic-anoxic interfaces near the water column. The slower flowing water does not replenish dissolved oxygen as quickly as commonly occurs in streams and rivers. Another reason for enhanced methylation in wetlands is the typical occurrence of warmer temperatures than deeper water bodies; methylation rates are generally greater at higher temperatures.

Recent studies have documented the substantial evasion of elemental mercury to the atmosphere by wetland macrophytes, a natural process that is likely to reduce the buildup of mercury in wetlands. Most natural waters appear to be supersaturated with elemental mercury, and at any given time are releasing elemental mercury to the atmosphere. The release is mainly a physical-chemical process. In wetlands, those aquatic plants with portions of their structure above the water surface, have been shown to release significant amounts of elemental mercury directly to the atmosphere (Lindberg et al., 2002). Whether this is a detoxifying process, or occurs incidentally through plant respiration, is unknown. However the mercury efflux rates can be large.

The factors that influence the relative amount of methylmercury that is produced in wetlands and accumulates in biota is less well understood. We do know the following: other things being equal, oligotrophic wetlands (those with low nutrient content) tend to produce higher mercury concentrations in fish than wetlands with abundant nutrients. Apart from biodilution in nutrient enriched wetlands, it is also thought that the additional productivity increases the amount of detritus that settles from the water column, taking mercury with it. Some of the mercury from the detrital rain is not recycled, but instead becomes buried in the sediments, and is not available to biota. This phenomenon has been noted in wetlands where atmospheric sources of mercury are dominant, and may be less applicable to conditions where the sediment is the major source of mercury. Microcosm experiments also indicate that the biodilution associated with higher productivity and biomass is influential in maintaining lower mercury concentrations in biota (Pickhardt, et al., 2002). Sulfate, at low aqueous concentrations, also appears to influence methylation rate (Hudson et al., 1994, Benoit et al., 1999). Addition of sulfate to waters with little sulfate has been shown to accelerate methylation. But further additions do not appear to further accelerate the reaction. Some researchers have hypothesized that at higher concentrations of sulfate, more sulfide is produced, and the latter, by binding the dissolved mercury, slows the reaction (Benoit et al., 1999). There is some evidence supporting this hypothesized inhibition in natural systems (e.g., Marvin-DiPasquale et al., 2003), although the sulfide levels at which inhibition occurs vary.

6.2 EXISTING DATA ON MERCURY METHYLATION IN THE SAN FRANCISCO BAY-DELTA

Several recent field studies in the San Francisco Bay and Delta have documented methylmercury concentrations in and around marshes, and the extent of methylation in marsh sediments. Of greatest relevance to San Francisco Bay are mercury data from former salt ponds collected as part of the South Bay Salt Pond Restoration Project (reported in Beutel and Abu-Saba, 2004). These data show that sediment total mercury concentrations exceed bay-wide averages in ponds near Alviso Slough in South San San Francisco Bay (values of 0.2 to 2 mg/kg versus open water concentrations in the bay of 0.3 to 0.5 mg/kg). Methylmercury concentrations in the ponds range from 2 to 11 ng/g, i.e., some locations are well in excess of typical bay sediment concentrations of 1 ng/g. However, methylmercury and total mercury concentrations in the ponds are not correlated, in a manner similar to the weak correlation observed between total and methylmercury at various locations in the bay (Figure 5-8). Studies conducted on biota in the ponds show substantial elevations in the eggs of fish-eating birds (1.2 to 1.6 mg/kg), although concentrations in invertebrate tissues were similar to those observed elsewhere. In some ponds, fish mercury data exceed the 0.3 mg/kg EPA human health criterion. Although the data are limited, it was also reported that fish and bird mercury concentrations were not correlated with sediment methylmercury concentrations.

A marsh area in the delta that has been monitored for mercury methylation and demethylation rates si the Frank’s Tract in the San Francisco Bay-Delta as shown in Figure 6-2. Methylmercury fluxes at the marsh site were observed to be more than one hundred times higher than a non-marsh location during a sampling event in October, 2001 (Gill et al., 2003). At other times, the marsh methylmercury fluxes were not substantially higher. Another useful set of measurements was made by Gill et al (2003) by monitoring total and methylmercury in the vicinity of Franks Track Marsh. These measurements show a rapid drop-off of methylmercury concentrations from within the marsh (0.3 ng/l) to open waters (<0.06 ng/l) (Figure 6-4). Measurements of mercury methylation and demethylation by means of introduced stable isotopes of mercury also confirmed the role of marshes in promoting methylation in San Francisco Bay (Marvin-DiPasquale et al., 2003). This study showed that during a single sampling event in March, 2000, methylmercury concentrations in top 4 cm of marsh sediments were nearly 10 times higher than in open water sediments, even though the total mercury content in the samples was similar (Figure 6-5). In the same depth zone (0-4 cm), the methylation rates were about 40 times higher in the marsh sediments than in open water sediments. Methylation rates were higher in deeper zones in open water sediments, reaching about a third of the value of rates in marsh sediments. The flux of this deeper methylmercury into overlying waters was not studied by Marvin-DiPasquale et al. (2003). Finally, sediment methylmercury data collected across the bay different research groups (an summarized in Chapter 5), show higher concentrations in coastal margins of the bay, some of which are near marshes.

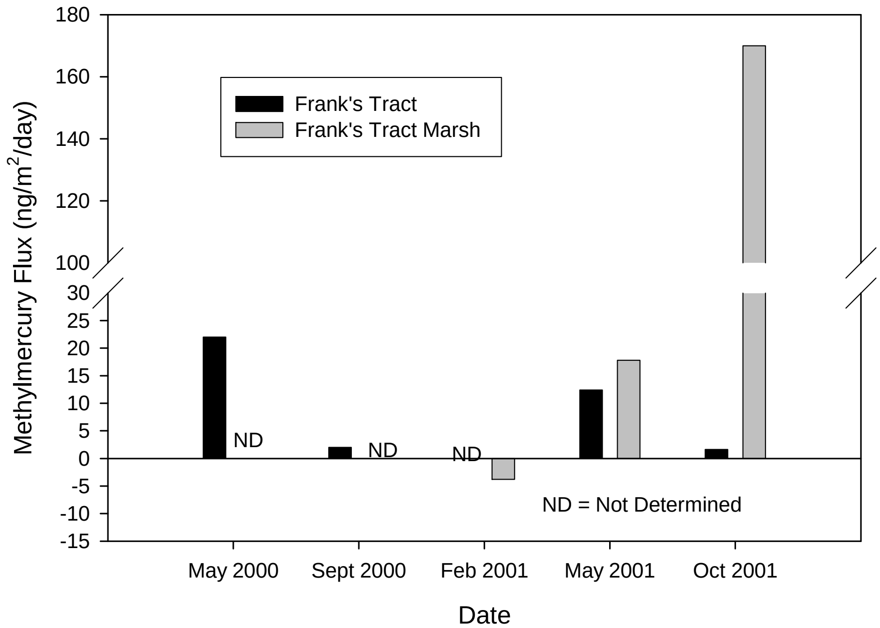

Figure 6-2. Mercury cycling in Frank's Tract in the San Francisco Bay Delta. Grey bars indicate the methylmercury flux from a wetland site compared to an open water site (black bars). The flux from the marsh site in October, 2001 was substantially greater than measured at the open water site during the different sampling periods. Based on data from Gill et al., 2003.

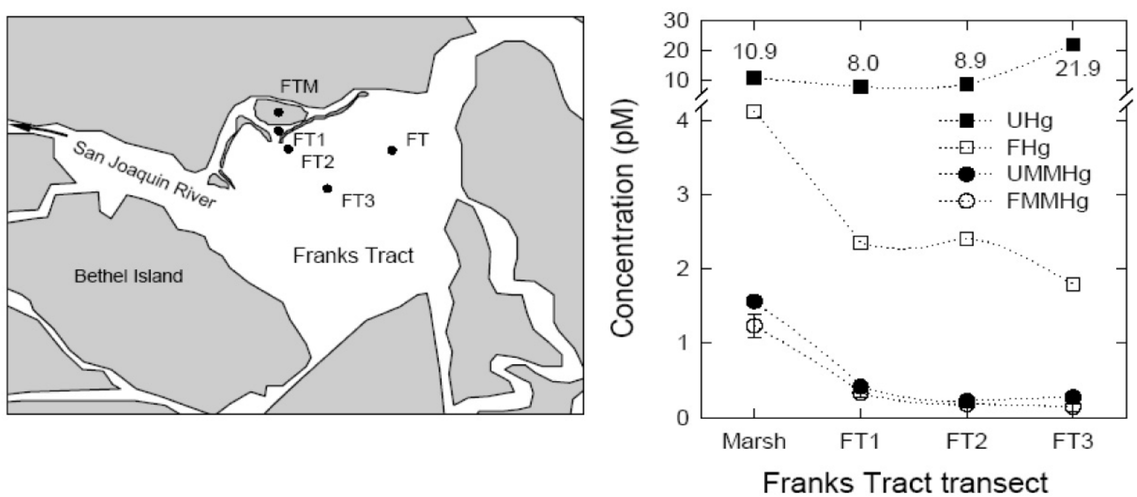

Figure 6-3. Concentration of methylmercury in the vicinity of a wetland (Frank's Tract Marsh, shown as FTM in the figures above. Source: Gill et al., 2003.

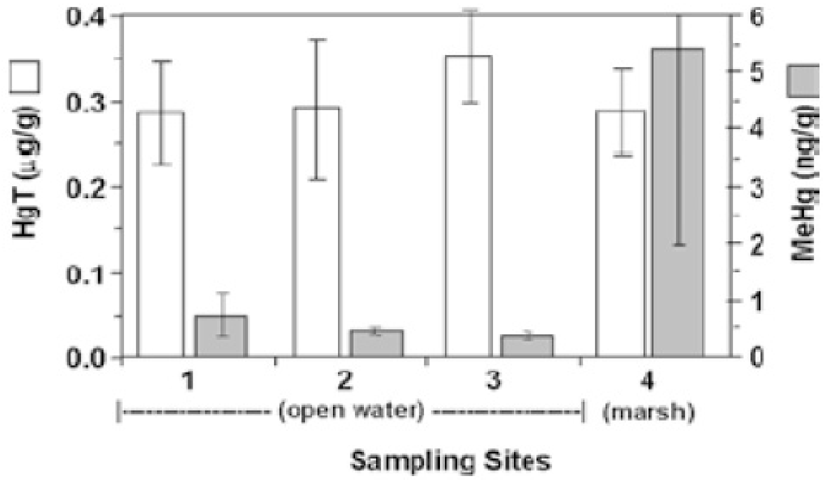

Figure 6-4. Methylmercury concentrations in open water and marsh sediments at sites in San Pablo Bay. Source: Marvin-DiPasquale et al., 2003.

Overall, these results provide strong support for a contribution of methylmercury from marsh areas, although the seasonal nature of methylmercury production, and the limited number of data points limits our ability to quantify the magnitude of the exports.

6.3 HYPOTHESES TO BE TESTED TO IDENTIFY STEPS FOR MINIMIZING METHYLMERCURY PRODUCTION AND EXPOSURE IN WETLANDS

Available information for the San Francisco Bay and other systems is not adequate to make *a priori* judgments about processes that will successfully limit mercury methylation or limit the exposure of the methylmercury that is produced. It is proposed that a series of process-oriented studies be conducted in wetlands to better understand the factors that may be used to control mercury methylation and flux. While controlling factors can generally not be modified for existing wetlands, knowledge about them may be useful in the design of new wetlands from restored salt ponds. The Salt Pond Restoration Project has developed a wide range of management options that may be used to control mercury loads, mercury methylation, and bioaccumulation during the design and construction phase and during the operation of the wetlands (Beutel and Abu-Saba, 2004). These management strategies are based on existing literature reports and may or may not be specifically applicable to the ponds. This chapter complements the work previously done by the Salt Pond Restoration Project by suggesting proposed studies within a framework of testable hypotheses. The need for quantification of flux of methylmercury from wetlands to the wider bay has been previously discussed in Chapter 5 and is not repeated here.

Hypothesis 1. Net mercury methylation is related to factors such as water depth, vegetation, hydroperiod, and other design parameters of wetlands

The biochemical reactions that result in the accumulation of methylmercury in wetland water and sediments are strongly influenced by a suite of water chemistry variables. Important variables that have been identified in other studies include organic matter content, pH, sulfate, sulfide, and chloride levels. These variables are in turn affected by controllable factors such as water depth, vegetation, and hydroperiod, and freshwater/saltwater ratio. The goal of these studies would be to obtain an estimate of conditions that are least likely to produce methylmercury.

Proposed Monitoring: A suite of methylmercury, total mercury and ancillary parameters such as sulfate, sulfide, salinity, organic carbon, chloride, and pH need to be measured in water about three to four times a year across a set of wetlands that represent a range of vegetation, water depths, and hydroperiod. The wetlands chosen for this monitoring should reflect the types of habitats that are being considered for restoration in San Francisco Bay, and also span a range of total mercury concentrations in sediments as understood from current data summarized in Chapter 5. The database that will result form this monitoring may be used to infer the conditions that most favorable from the mercury methylation standpoint.

Hypothesis 2. Nutrient loads indirectly affect methylmercury uptake in higher trophic level organisms by increasing the detrital rain

Methylmercury exposure to biota in wetlands is a result not just of net methylation, but also of burial processes due to sediment accretion. In most wetlands, because of the high primary productivity, there is a substantial amount of biomass that is produced, which after senescence falls as detritus and forms sediment over time. This detrital rain contains a large fraction of organic matter and has the ability to absorb and remove the mercury (both dissolved and methylmercury) from the water column and sequester it in sediment layers. Methylmercury in sediments is less available to the food web than is methylmercury in water. Higher productivity also results in the greater biomass production which tends to dilute the concentration of methylmercury in the food sources of the next higher trophic level. Hence any process that enhances biological production, such as the addition of nutrients, has the potential to reduce the mercury uptake by higher trophic level organisms, even though it may not change the rates of methylation. Understanding the role of nutrients is important in evaluating management actions to reduce the impacts of methylmercury to biota because water sources at different nutrient levels (especially municipal wastewater discharge) may be used in wetlands to minimize the transfer to higher trophic levels.

Proposed Experiments: Mesocosm experiments, where a portion of a wetland is walled off with a rigid plastic wall, have been used with some success in the wetlands of the Florida Everglades and are also appropriate for use here. The isolated portions of the marsh inside the mesocoms can then be subject to modified chemical conditions, with other factors remaining constant. In this instance, additional nutrients (nitrogen, phosphorus, or both) can be added to mesocosms to observe changes in methylmercury concentrations in small fish, with no additions of total mercury. The experiments need to be conducted at several nutrient levels across different representative marshes, with different vegetation and salinity to determine if, for a given level of total mercury, there are nutrient levels that reduce methylmercury uptake by higher trophic levels.

6.4 SUMMARY

An extensive body of scientific literature supports the concept of wetlands being zones of efficient mercury methylation. Given that San Francisco Bay is likely to see the creation of additional wetlands following salt pond restoration, the primary goal of the studies described here is to develop a better understanding of methylmercury production and uptake by the higher food web such that both may be minimized. This may be done through appropriate design of wetlands, by controlling water depth, vegetation, and hydroperiod and by adapting the chemistry of water entering the wetlands, principally by controlling nutrient and salinity levels.

CHAPTER 7. MANAGEMENT QUESTION: GIVEN VARIOUS SCENARIOS FOR MANAGEMENT ACTIONS, WHEN WILL WE LIKELY SEE IMPROVEMENTS IN SEDIMENT AND TISSUE CONCENTRATIONS?

Treating San Francisco Bay as a well-mixed box, the Regional Water Board has estimated that the mercury impairment in the bay will be reduced below current standards in 120 years. The major mechanism through which this decline is expected to occur is the deposition of new sediment, at lower total mercury concentrations, over the existing sediments. Model estimates indicate small changes (on the order of 10%) in total mercury concentrations over the next 20 years (see Figure 7-1). Given that mercury concentrations from portions of the bay, as currently measured, vary by a factor of at least 500% even after excluding contaminated hot spots (see plots in Chapter 5 and Figure 7-2), it would seem than the model-predicted change will be completely swamped by natural variability over decade-long time-frames.

If the one-box model were indeed a full representation of the mercury processes in the bay, including a representation of the heterogeneities within it, this would imply that there is little to be learned from more temporally intensive monitoring of the bay, say on the order of 3-5 years. Some support for this argument could be presented in the form of fish tissue data for striped bass which have been collected since the 1970s to the present and have shown no statistically significant change over this period (Figure 7-3). However, these measurements were made during a period when there were no significant management interventions to reduce mercury in the system. In contrast, going forward, specific actions have been recommended by the Regional Water Board, to reduce mercury loads from a variety of point and non-point sources that may begin to show results in one to two decades. In this section, we argue that it is too early to draw the conclusion that observable changes will only occur several decades, and focus on the merits of conducting further studies to identify locations and processes in the bay where changes are anticipated to occur over time frames much shorter than the multi-decade time frames calculated by the model. Unlike past chapters, there is little past data to discuss on this topic, particularly on long-term temporal trends in mercury in water and sediments in the bay. Therefore, this section directly describes studies that will help to identify time frames of change of pertinent indicator variables. As in previous chapters these studies are framed in the context of hypotheses to be verified through field monitoring and experiments.

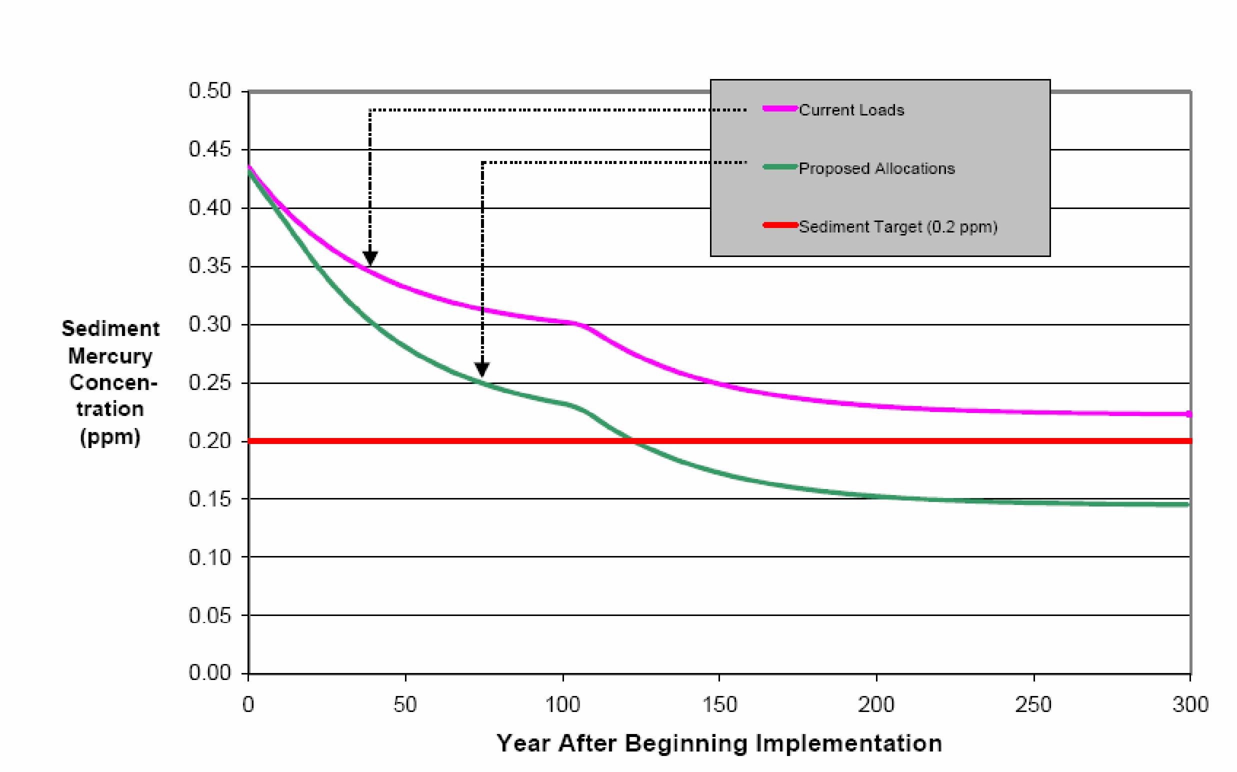

Figure 7-1. Model predicted average sediment concentrations of total mercury as a function of time. Source: SFBRWQCB, 2003.

7.1 HYPOTHESES TO BE TESTED TO IDENTIFY TIME FRAMES OF IMPROVEMENT

Hypothesis 1. Sediment Concentrations in Selected locations are expected to show changes on the time frame of 5-10 years

On a volumetric basis, San Francisco Bay has been shown in recent years to be eroding, with the South Bay losing a greater volume of sediment than the North Bay. South Bay sediment loss is estimated to be $3x10^6$ m^3 per year (Foxgrover et al., 2004) whereas North Bay sediment loss is about 1.25 $x10^6$ m^3/yr, representing the sum of data from Suisun Bay and San Pablo Bay (Capiella et al., 1999; Jaffe et al., 1998). Given the total area of the bay of about $l.24x10^9$ m^2, this corresponds to an average depth change of about 0.3 cm per year over the entire area of the bay, although there are specific zones of deposition and erosion in the bay, where the depth change will be larger. It is thus reasonable to assume that over time scales of 5-10 years, the sediment in the upper few centimeters at many locations will have changed, either through erosion or through deposition. The corresponding change in mercury concentrations will depend on the location. At some erosional locations in the North Bay, current knowledge of the depth profile of mercury suggests that the newly exposed sediment layers are expected to be higher in concentration. Other locations may exhibit weaker increasing trends in concentration, and in other locations concentrations may decrease.

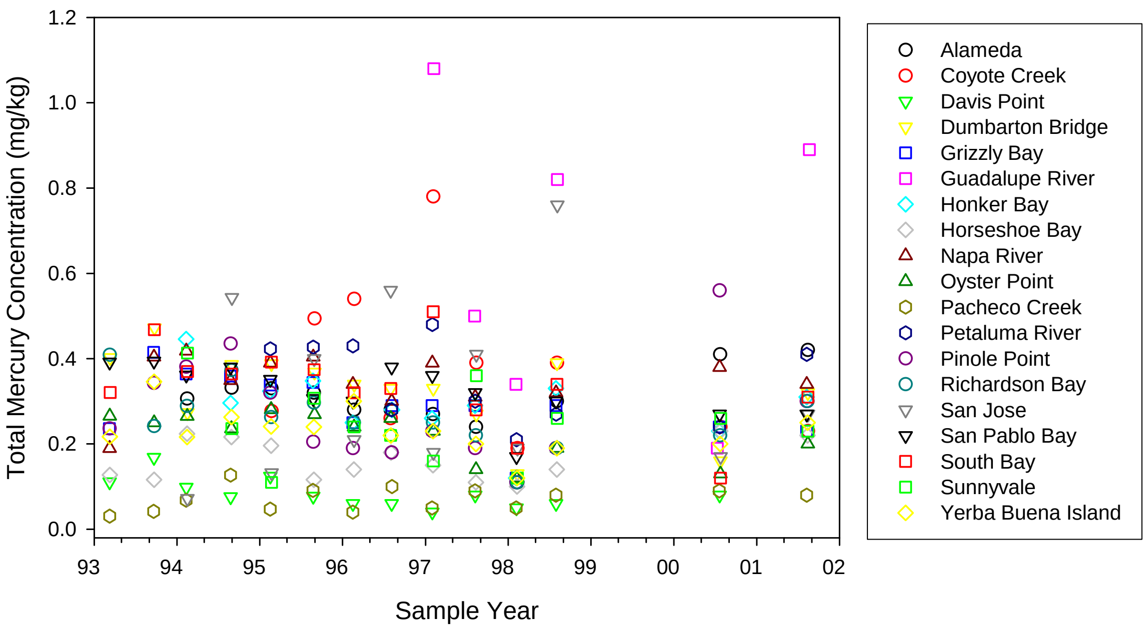

Figure 7-2. Sediment concentrations at different locations in San Francisco Bay. RMP Data.

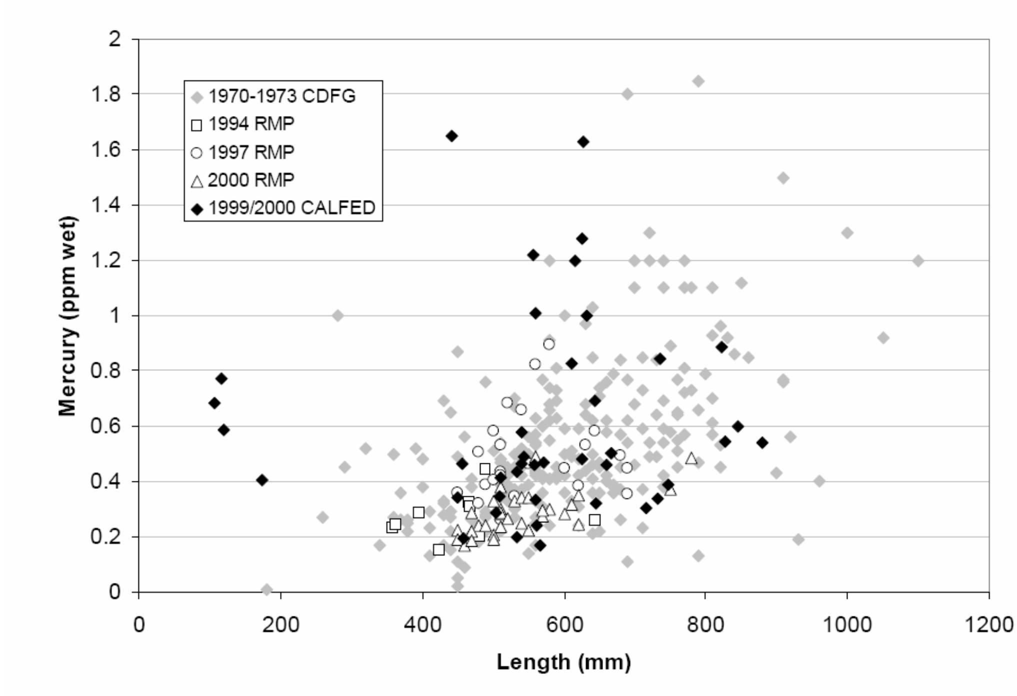

Figure 7-3. Striped bass mercury concentrations as a function of length. Concentrations observed in surveys from the 1970s are compared with more recent surveys. Source: Davis et al., 2003b.

Proposed field monitoring. Identify all major areas of erosion in the bay from existing USGS studies. In these areas, date cores using the prevalence of isotopes such as ^{210}Pb and obtain the profiles of mercury with depth. In areas where significant changes in concentration occur over depth, as measured in some locations by Hornberger et al. (1999), select a small number stations for temporal monitoring of concentration change every three to five years. Because of the variability and measurement error associated with sediment sampling, several replicate samples need to be obtained from each of these locations to identify whether statistically significant changes have occurred. The number of replicates can be determined after an initial screening effort using multiple replicate to better characterize variability at a specific location. This monitoring effort can be used to track the status of total mercury in the bay and to verify whether the assumptions used in the one-box model with respect to bed erosion are valid.

Hypothesis 2. Locations near major sources of mercury discharge will respond more rapidly than the bay in general

If the bay were well mixed, and change in the loads to the bay would be reflected relatively rapidly across the entire bay. But because that is not the case, it is possible that some sections of the bay, specifically locations that are near sources of elevated mercury input to the bay (i.e., in South San Francisco Bay near the discharges of Guadalupe River and various urban point and non-point sources) will see changes more rapidly than does the bay in general. Where the discharges are point sources, where it has been hypothesized that mercury is more bioavailable than from non-point sources, the changes could be more apparent. In general, if such changes are seen at locations near discharges, more temporally intensive sampling at these sites will be justified. If no such changes are observed, the implication would be that enough mercury at these sites, in both water and sediment, originates from general bay-wide sources, and no temporally intensive sampling at these locations is called for.

Proposed field monitoring. Identify all major points of discharge to the bay, and locate stations in close proximity of the most significant of these discharges. Some such areas are already being monitored in one or more sampling programs as shown in Chapter 5. The sampling at these stations should be continued, once every two to three years at a minimum with both water and sediments being monitored for mercury and methylmercury. These data will need to be evaluated for changes in total mercury as well as methylmercury. Because of the potential seasonality of methylmercury production, the sampling should be conducted at or near periods where it has been established that production is near a maximum. This may be done as part of studies described in Chapter 5. It is anticipated that a 10-15 year record of data at these sites will provide a sufficient basis for continuing sampling at this frequency.

Hypothesis 3. Some localized interventions to remove or cap high-mercury sediment will have local and bay-wide benefits

If it is established that mercury methylation in sediments is the major contributor of methylmercury to the bay, as opposed to external sources and methylation in water, it may be practical to focus on removing methylmercury hot-spots by removing sediments, or by capping with clean sediments. These actions can be done in the time frames of years, i.e., far more rapidly than changes can be made to non-point and most point sources. It is further anticipated that changes at these hot spots will have local effects on methylmercury production, and, depending on the scale of the intervention, may have more general bay-wide effects. Monitoring of methylmercury near remediation zones, in water, sediments, and biota, will provide a support for the efficacy of this approach. If statistically significant decreases are seen, the method may successfully be applied elsewhere, perhaps as an alternative to more difficult non-point source reductions. If no such changes are seen, especially in the vicinity of the remediation, the results will define the limits of the improvement in biological impairment by means of controlling total mercury loads.

Proposed field monitoring. Sample sediment, water, and resident biota tissue concentrations in the vicinity of a hot spot that has been selected for remediation for at least two years. Following remediation, and attainment of steady state for a year, resample water, sediment, and tissue concentrations at and around the hot spot for a period of five years. This data set will provide information on the expected benefits from remediation of methylmercury hot spots and can be used to evaluate the further use of this approach at other locations within the bay.

CHAPTER 8. MANAGEMENT QUESTION: HOW SHOULD WE BEST MONITOR TO DETECT CHANGES IN MERCURY CONCENTRATION IN SEDIMENTS AND TISSUE?

Currently the Regional Monitoring Program (RMP) conducts the most extensive sampling of mercury-related parameters in the bay. This includes yearly sampling of sediments and bivalves and triennial sampling of fish at a fixed set of locations in the bay. The data collection was begun in 1993/1994 and forms the backbone of the mercury TMDL developed by the Regional Water Board. In some areas, and in some years, other research groups have also supplemented the RMP sampling. These data have been assessed in preceding chapters; however, for the purpose of an analysis to evaluate temporal trends, we focus principally on the relatively long record presented in the RMP dataset. We review trends in data on sediments and tissue and provide suggestions for future monitoring to best capture anticipated changes from any actions to reduce mercury or methylmercury in the bay.

8.1 SEDIMENT MERCURY

Nine years of available data on mercury in the surface sediments of the bay do not demonstrate a clear trend in concentrations (Figure 8-1). This may reflect the reality of concentrations not changing significantly, or of small changes in either direction being masked by sample and/or measurement variability. The concern with variability is a far greater factor in sediment analyses than in water analyses, and can only be addressed through the measurement of a sufficiently large number of replicates. Such a dataset is not currently available for evaluating temporal sediment mercury trends in the bay.

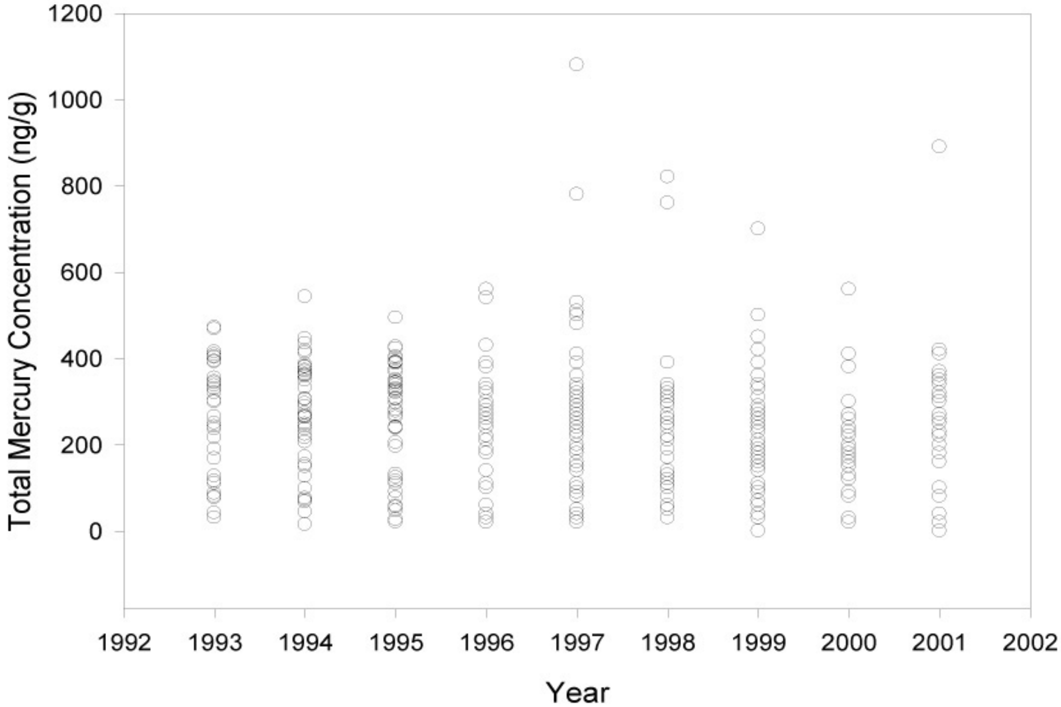

Figure 8-1. Total mercury concentrations as a function of time in San Francisco Bay. RMP data.

On a volumetric basis, San Francisco Bay has been shown in recent years to be eroding, as discussed in the previous section. South Bay sediment loss is estimated to be 3x10^6 m^3 per year (Foxgrover et al., 2004) whereas North Bay sediment loss is about 1.25 x10^6 m^3/yr (Capiella et al.,1999; Jaffe et al., 1998), corresponding to an average depth change of about 0.3 cm per year over the entire area of the bay. The resulting change in mercury concentrations will depend on the location. At some erosional locations in the North Bay, the newly exposed sediment layers are expected to be higher in concentration, whereas in other locations concentrations may decrease. Thus, monitoring of sediment mercury concentrations in shallow sediments may provide clues as to the changing mercury loads and concentrations in the bay over reasonably short time frames (say, over five years).

Beginning in 2000 the sediment analyses have included methylmercury in addition to total mercury. Methylmercury production is a seasonal feature that is linked to temperature and organic matter production in natural waters, and, at a given location, is expected to be much more variable than total mercury concentrations. To a certain extent, the relatively uniform temperatures of San Francisco Bay compared to the delta may limit seasonal differences; however, primary production maxima in the late summer, with a supply of organic carbon to deeper waters may create a significant seasonal peak in methylation. Although bay-wide data do not show a clear seasonal effect in methylmercury concentrations (Figure 8-3), this may be partly due to measurements that were made in mostly deeper waters. Sampling in shallower waters, where methylation is more significant, and where greater temperature differences are expected to occur, may be more appropriate targets for measurement.

For future sediment sampling, we recommend the following:

- Collect deep sediment cores from some locations in the South Bay. Date the sediments by depth and measure total mercury concentrations in a manner similar to what has been done in the North Bay (Hornberger et al., 1999). Depending on the depth profile of mercury, this will provide an indication of the extent of mercury concentration change that may be expected in future years.
- Collect sediment samples in shallow sediments (0.5 to 5 cm deep) every three to five years at a range of locations around the bay. Based on erosional trends in the bay, and mercury depth profiles, some locations are expected to show changes in concentrations. Triplicate measurements of cores at these locations is recommended.
- For two to three years, conduct a temporally intensive sampling to identify if there are any peaks in methylmercury production. Data from the delta show seasonal peaks as discussed in prior chapters, although data from the bay are insufficient to make this determination.
- Once peaks in methylmercury production have been identified, or the absence of such peaks in the bay has been confirmed, reduce the frequency of sampling to once in three or five years, and increase the spatial coverage, especially near major point source inflows, and near shallow margin areas where inflows. If methylmercury production peaks occur, the sampling should occur as near the peak as feasible. If no peaks are evident, the timing of sampling is not critical.
- Measure ancillary parameters such as sulfides and organic carbon at the same locations and times as mercury and total mercury. This has been done in studies conducted as part of the CALFED Program but not consistently in the RMP program.

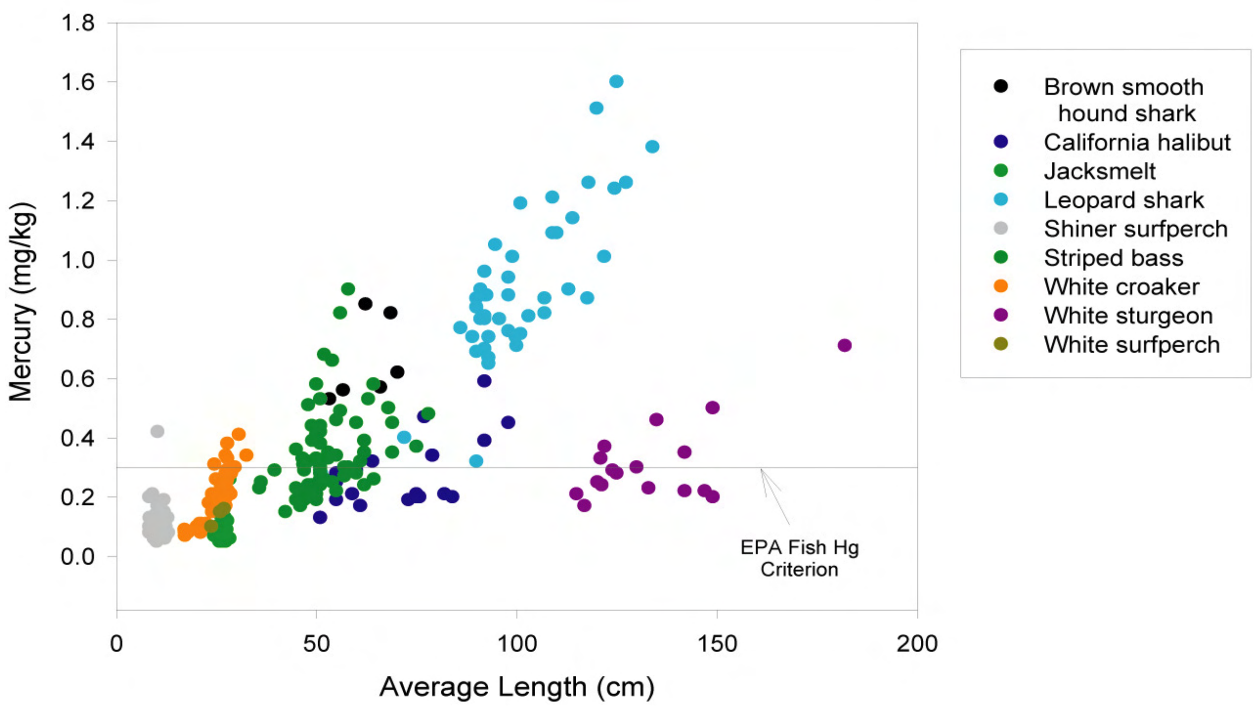

Figure 8-2. Fish tissue mercury as a function of length and species (different colored symbols). RMP data.

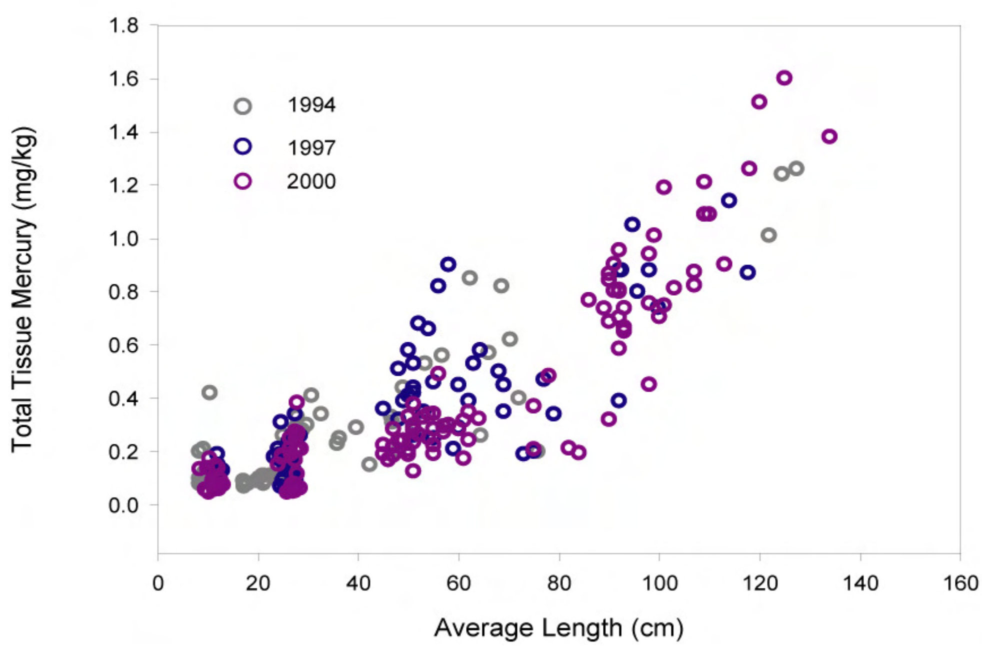

Figure 8-3. Fish tissue concentrations as a function of length and sampling year (different colored symbols). RMP data.

8.2 TISSUE MERCURY

An ideal tissue indicator species should get its mercury intake from a well-defined location and over a known period of time. The mercury in the tissue should be in a form that is bioavailable to higher trophic level organisms, assumed for most purposes to be methylmercury. Appropriate indicators could be species that feed most of their time in the bay, or are territorial and spend their time in a small portion of the bay, and can be sampled while they are still young, thus reflecting mercury concentrations over a shorter and better-defined period. Sampling of younger, and perhaps smaller organisms, allows for observation of shorter duration changes that may not be seen in larger, older fish. By focusing on species that live in the bay, we can be sure than any mercury contained in the tissue entered the organism in the bay.

Data on clams and fish in the bay meet the criteria above to a certain extent, and may be used to compare variations in the mercury at different sampling locations. Data shown in Figure 3 demonstrate that clam mercury concentrations are generally higher in the creeks leading to the bay, and are lower at locations within the bay. Clams in the North Bay and the South bay exhibit similar levels of mercury. Because fish are mobile within the bay, a similar association with specific sampling location is less useful than for clams. However, in any sampling program fish mercury concentrations are essential to consider because they are the most common pathway through which mercury impacts higher trophic levels. In addition, data worldwide show that the mercury exists in fish tissue primarily as methylmercury, which may not be the case in organisms such as clams. Fish concentrations of mercury are sensitive to species and age for which length is commonly used surrogate (Figure 8-4). Thus, larger fish are most likely to exceed the EPA tissue criterion of 0.3 mg/kg and the San Francisco Bay target of 0.2 mg/kg. Although a mercury concentration of 0.2 mg/kg in striped bass of a specific size (82 cm) has been selected as a target for the bay, for monitoring to evaluate changes in mercury loads, an appropriate indicator may be a fish of a smaller size and feeding range.

Based on the discussion above, for future biological sampling we recommend the following:

- Select one or more species that spend much of their life in the bay and can be sampled while still relatively young (perhaps young of the year for striped bass)

- Consider the use of an indicator species in experimental studies of mercury uptake as described in Chapter 6.

- Expand the spatial coverage of sampling of bivalves measuring methylmercury in them to limit contamination from sediments that have not been depurated.
- Consider placing bivalves as sentinel species in various locations, especially those that are near sources of discharge, where the total mercury

concentrations are high or where the source of mercury is thought to be more bioavailable.

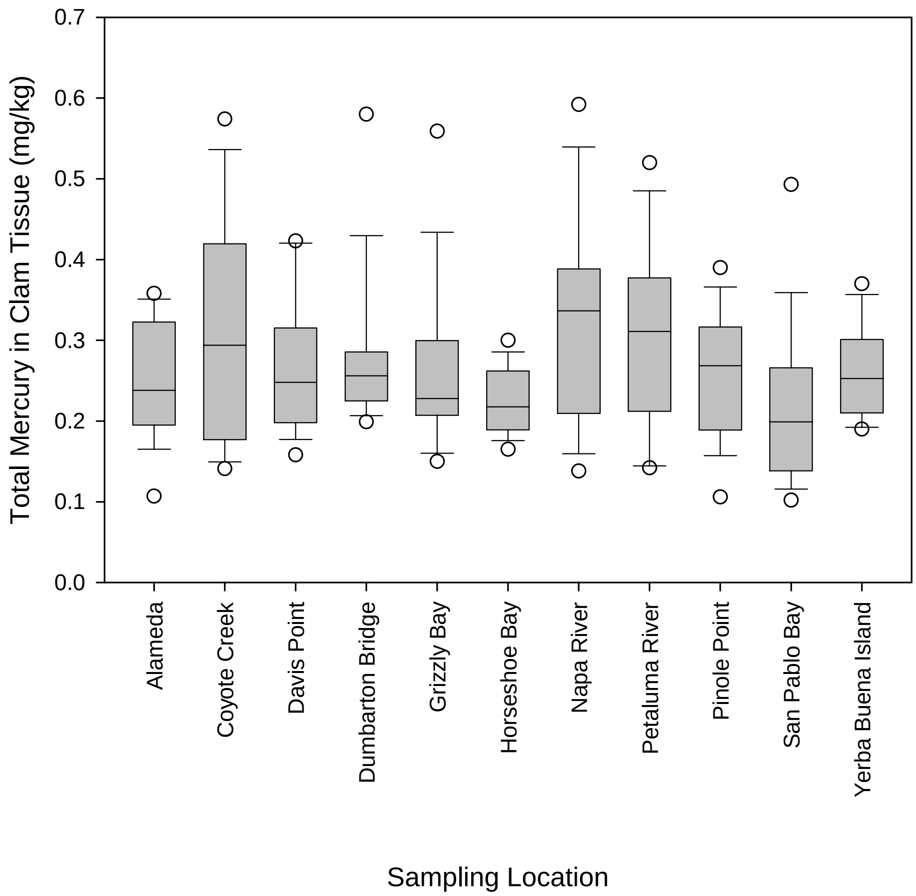

Figure 8-4. Tissue mercury in clams from different locations in San Francisco Bay. RMP Data.

8.3 SUMMARY

The potential of different media for monitoring of changing mercury concentrations in the bay is summarized in Figure 8-5. The relatively high level of erosion occurring the bay provides a means to observe changing sediment concentrations in the surface sediment, especially where profiles of mercury with depth indicate significant change. It is proposed that these processes be further characterized through a combination of routine and specialized monitoring, such as dated deep cores. The seasonality of methylmercury production the bay also needs to be documented better for a limited period of time, such that future monitoring may be limited to periods when the potential for methylation is enhanced. Future tissue monitoring must be conducted to emphasize species that are resident in the bay for most of their lives and can be sampled at a relatively young age, thus reflecting mercury inflows into the food web at a well-defined space and time.

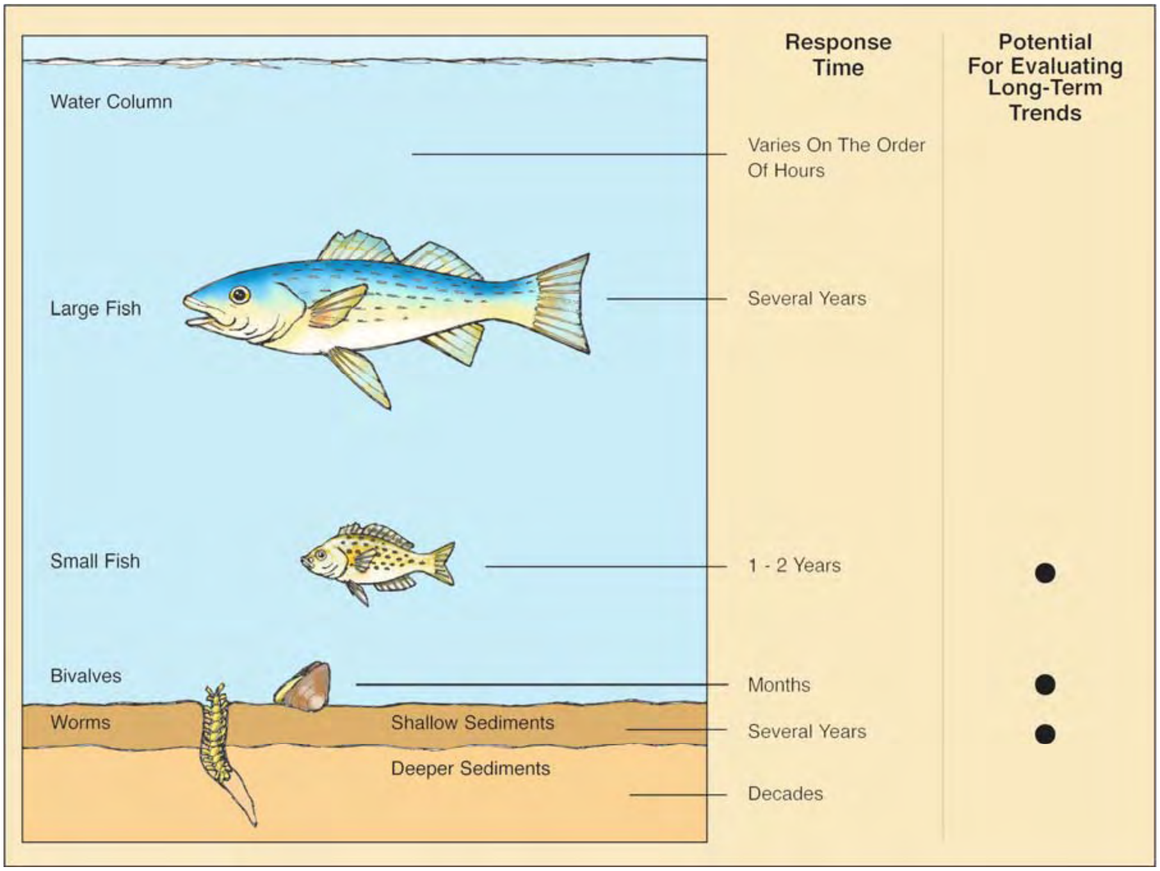

Figure 8-5. Potential for use of different environmental compartments for monitoring long-term trends of mercury in San Francisco Bay. Shallow sediments, benthic organisms, and small fish can serve as useful targets for monitoring changes over a period of a few years.

CHAPTER 9. SUMMARY AND RECOMMENDATIONS

Mercury impairment in San Francisco Bay has been determined by the San Francisco Bay Regional Water Board as a result of exceedances of mercury concentrations in water, fish tissue, and bird eggs. The Regional Board been engaged in studies to estimate current loads of mercury and allocate future loads to help reduce the impairment in the Bay as part of a Total Maximum Daily Load (TMDL) assessment and Basin Plan Amendment process (SFBRWQCB, 2003; SFBRWQCB, 2004).

This conceptual model for mercury presented in this document is intended to be a source of relevant scientific information to guide the implementation strategy to alleviate mercury impairment in the bay (through load reduction or by other means). It is specifically focused on five management questions identified to be important by the CEP:

- What is the relative bioavailability of mercury from different sources to San Francisco Bay?
- At what locations are current methylation rates and methylmercury flux highest?
- Can existing wetlands be managed or new wetlands be designed to minimize net methylation rates, or limit exposure to methylmercury that is produced?
- Given various scenarios for management actions, when will we likely see improvements in sediment and tissue concentrations?
- How should we best monitor to detect changes in mercury concentration in sediments and tissue?

Each of these questions has been addressed in this document. Available data and current understanding pertaining to each are evaluated, and recommendations have been made to conduct focused studies to fill in management-critical data gaps.

It was found that limited data exists on the bioavailability of mercury sources to San Francisco Bay, with the exception of legacy mine sources and wastewater discharges.

This is an area where mercury speciation data from each source category (e.g., urban runoff, sediment resuspension) needs to be collected. The speciation data may be supplemented by experiments to evaluate the relative bioavailability of different mercury sources, although these will be substantially more complex and resource-intensive than just the collection of speciation data.

Methylmercury data in sediments and water was reviewed from various locations in the bay. Although direct flux measurements of mercury and methylmercury to the water column are rare, and complicated by significant seasonal and site variations, the available data do indicate the presence of hot spots around the bay that need to be studied further for their bay-wide impacts and their potential for remediation.

Data on wetlands around the bay, although limited, show that the supply of methylmercury from these locations is elevated. It is not known whether the effects are localized or bay-wide. Given the addition of new wetlands to the San Francisco Bay ecosystem because of restoration of salt ponds, it is important to conduct some detailed process studies of methylmercury formation and export from wetlands. Information gathered in such work can be the basis for operational strategies to minimize methylmercury production.

If the bay is treated as a single well mixed unit, the time periods for restoration are large, and given the known variability in key metrics (e.g., sediment and fish concentrations), may not be detectable for many decades. However, if the bay is considered to consist of smaller habitats, with distinct characteristics it is reasonable to expect changes to occur over much shorter durations. Work needs to be done to delineate these habitats and set a baseline for monitoring response.

Sediment mercury concentrations need to be monitored in locations where we expect the greatest change, because of erosion or deposition. Because the areas of significant erosion or erosion are a relatively small part of the total bay area, the concentration changes will be larger and easier to detect than for the bay as a whole. Tissue concentrations need to reflect organisms with short life spans and with significant site fidelity, such as bivalves. Data from such organisms can be associated with mercury behavior at specific locations and over short durations.

Table 9-1 is a summary and a restatement of the major data needs outlined in Chapter 3, with characterization of mercury behavior in wetlands being the only addition (in response to the third management question above). These data needs are linked to the different hypotheses and proposed experiments and monitoring outlined in Chapters 4-8. Also shown in Table 9-1, in broad categories, are estimates of the level of effort required to obtain the data described in these sections.

Table 9-1
Summary of Data Needs

Information Need	Proposed Data	Existing Level of Uncertainty	Importance for Decision-Making	Section Discussed In	Level of Effort Required to Obtain Data
Mercury Chemical Forms in Different Sources	Particulate and dissolved mercury and methylmercury in inflows	High	High	4.1, 4.2	Medium
Bay Water Quality Characteristics	Profiles of salinity, TSS, DO, DOC, SO_4, S^2, and methyl mercury	Moderate	High	5.3	Low
Extent of Hg Evasion from Water Column	Estimate Hg(0) evasion and compare to measured Hg(II) in water column to see if feasible to generate predicted Hg(0)	High	Moderate	4.3	High
Characterization of Existing Bay Sediments	Profiles of salinity, DO, TOC, SO_4, S^2, and methyl mercury	High	Essential	5.3	Low
Extent of Sediment Erosion/Resuspension of Bay Sediments in nearshore and Mid-Bay Areas	Make estimate using grain-size information, tidal current data, and profiles of suspended solids in water column	Moderate	High	8.1	Low
Use Mesocosm to Investigate Fate of Cinnabar-Containing Sediment in Bay	Measure methyl mercury produced under similar conditions to nearshore and mid-Bay sediment, compare to observations in South Bay and use to refine load estimate	High	High	4.3	High
Characterization of mercury behavior in wetlands	Methylmercury production in wetlands of different types	High	High	6.3	High
Characterization of Hg Bioaccumulation in Resident Fish Species	Sufficiently large number of Hg measurements in resident fish species to establish level of bioaccumulation and to evaluate effectiveness of remediation efforts	Moderate	Essential	8.2	Low
Characterize Hg Concentrations at All Levels of the Food Chain, Predictive Model of Hg Accumulation in Fish	Hg measurements in plankton, benthos, forage fish, and predatory fish	High	Moderate	8.1, 8.2	Medium

APPENDIX A. COMMENTS AND RESPONSES

CEP Mercury Work Group Comments on CEP Task # 4.24
Conceptual Model of Mercury in San Francisco Bay

Tetra Tech responses are highlighted.

Larry Bahr, FSSD

Page vi, paragraph 1, line 4: You can't have an exceedance if you don't have a standard. Rewrite last sentence of paragraph to read, "The San Francisco Bay Regional Water Board has determined the San Francisco Estuary is impaired for mercury because of elevated mercury concentrations in water, sediment, fish tissue, and bird eggs."

Changed.

Page vi, paragraph 2, line 1: The regional Board **has** been engaged…

Changed.

Page vi, paragraph 3, line 1: ~~This~~ **The** conceptual model for mercury presented in this document has been ~~supported~~ **funded**…
Changed.

Page vi, paragraph 3, line 4: capitalize usage of Bay

In this document bay is capitalized when it appears as San Francisco Bay and with small letters when it is referred to as the bay.

Page vi, paragraph 3, line 6: It ~~then~~ addresses five management questions identified ~~to be~~ **as** important by the CEP:
Changed.

Page vii, paragraph 1, line 1: Available data and current understanding pertaining to each of these questions ~~have been~~ **are** evaluated, and recommendations ~~have been~~ made to conduct focused studies to fill ~~in~~ the management-critical data gaps.
Changed.

Page viii, paragraph 2, general: This paragraph assumed local reductions in Hg inputs
No change made. This issue is discussed in greater detail in the report.

Page viii, paragraph 3, general: ..significant site fidelity, such as bivalves…. (More sensitive to sediment flux such as windy periods – small fish may be better)
Sentence changed to "Tissue concentrations need to reflect organisms with short life spans and with significant site fidelity, such as bivalves or small fish."

Page viii, paragraph 3, line 3: significant erosion <u>or erosion</u>?

Changed to "Because the areas of significant erosion or deposition are a relatively small part of the total bay area, the concentration changes will be larger and easier to detect than for the bay as a whole."

Page 1-1, paragraph 1, line 4: To a **very** limited extent…
Changed.

Page 1-1, paragraph 3, line 2: …this document has been ~~supported~~ **funded** by the…
Changed.

Page 2-1, paragraph 1, bullet 1: …a maximum concentration of 51 ng/l across… (is this a daily max or monthly average?)
Daily maximum. This is clearly distinguished from the 4-day average specified in the Basin Plan, listed in the next bullet. No change made.

Page 2-1, paragraph 2: revise per comments in executive summary above, "The Regional Water Board has determined the San Francisco Estuary is impaired for mercury because of elevated mercury concentrations in water, sediment, fish tissue, and bird eggs."
Changed.

Page 3-3, paragraph 1, line 2: The ~~Methylmercury~~ **methylmercury** concentration
Changed.

Page 4-1, paragraph 2, bullet 1: …from past mercury and gold mining **including modern riverine transport of these sources**

Changed.

Page 4-2, paragraph 4, line 1: Urban runoff **and erosion of mercury-containing soils** contains…

Changed.

Page 4-3, paragraph 2, general: FSSD study on effluent discharge impacts on methylmercury concentration in Estuary as well as characterization of total / methyl concentrations in effluent.
Changed

Page 4-4, paragraph 1, general: Include discussion of FSSD study.
See above.

Page 4-4, paragraph 2, general: Air deposition of Hg may be more bioavailable than other forms.

Page 6-7, paragraph 1, general: Add DO and look at near field land management practices

Chris Sommers, BASMAA

Overall, the Conceptual Model (CM) Report is well organized and covers the general management questions that in my opinion have to begin to be addressed over the next 0-20 years. Linking the management questions to hypotheses that can be tested through studies assists the CEP and Managers to better understand what questions they will need to not only pay attention to over the next few years, but put into the mix with other (non-mercury) projects to prioritize funding. Additionally, as the first conceptual model report did, the ranking of data needs related to the importance for decision making is a must needed step.

The following paragraphs include general comments and comments specific to each chapter of the Draft CM report.

General Comments:

How are the uncertainties and data needs presented in Chapter 3, related to the MQs presented in Chapters 5-8. A better linkage needs to be made. If this document is to be used as a resource for managers to prioritize future studies, based on data needs, it would be good to have a table listing the MQs, hypotheses and importance for making management decisions.

See the newly created Table 9-1 for summary information.

Additionally, the author only provides one option for testing each of the hypotheses presented. Ideally Managers would like to have more than one option for testing hypotheses.

The proposed experimental and monitoring descriptions are a general approach to address the hypothesis. Multiple detailed sampling plans could be developed in future based on these general approaches.

Specific Comments: (Organized by Chapter, Section and Page #)

<u>Chapter 1</u>

Page 1-2. This document is intended to help Managers focus future resources on the most pertinent management questions (MQs) that need to be addressed, from a scientific point of view based on available information. However, the MQs presented here are only a subset of those developed by the CEP and therefore should be acknowledged as such. Many of the other MQs developed by CEP partners are related to the "management" of sources and better defining source loads and transport pathways. Even though these may be questions that are as important as those included in the CM report, they are not included. I am not suggesting that the CM revised to include these questions, but language should be added to ensure the reader that other MQs exist, but are not included in the CM report. I have attached the full list of MQs that the CEP developed. These can be included as an appendix if the workgroup/TC approves.

The management questions discussed in this report are those that were provided to us to at the inception of this work. We were made aware of these additional questions well after completion of this draft report and the material put together does not specifically address them. For the purpose of this revision, we have assumed that the other, more general, management questions referred to above are referenced in other CEP documents and inclusion is this report is not essential. However, if the workgroup so chooses we can include these other questions as an appendix for future reference.

<u>Chapter 2</u>

Section 2.2, Page 2-2. It would be useful if a statement or two is added to explain that the fish tissue target was calculated to protect 99% of the Bay Area Population, and:

- Roughly 170,000 sport and subsistence fishers currently choose to consume bay fish, representing about 3% of the roughly 6.5 million people who live in the Bay Area
- 95% of the 170,000 eat less than 32 g of fish per day

Changed as suggested.

Section 2.2, Page 2-2, last sentence. Change to:

"…the Regional Water Board has proposed a ~~standard~~ **target** of 0.2 mg/kg in the tissues of this species ~~as a target~~.
Changed as suggested.

Chapter 3

Good background information on mercury sources and processes is provided and is generally written in the manner that is easy individuals familiar with the subject matter to understand.

I would like to see the information needs described in the tables better linked to the management questions and hypothesis presented in Chapters 4-8. This would allow a transparent stepwise process to selecting hypotheses to test that are the most important for decision making. The table I suggest in the general comments would greatly help future discussions.

See the newly created Table 9-1 for summary information.

Chapter 4

Page 4-2, Urban Runoff. I agree with the paragraph that not much is known about the speciation of mercury in urban runoff and its bioavailability, but there are some data available on methyl and total mercury in bedded sediments collected from the storm water conveyance systems in most Bay Area counties.[1] Given this, the paragraph cites SCVURPPP data, but should probably be expanded to include other stormwater program data collection efforts.

Report now discusses all available stormwater mercury data.

Sections 4.1-4.3.

Although the text is there, these sections should follow the same format as Sections 5-8 to include a heading for "Proposed Experiments and Field Monitoring"

Sections changed.

Section 4.2.

Text should indicate that a "control" mesocosm should also be included in the study.
Changed.

Chapters 5 - 8

No major comments.

[1] KLI and EOA. 2001. Joint stormwater agency project to study urban sources of mercury and PCBs. Report prepared by Kinnetic Laboratories, Inc. and Eisenberg, Olivieri and Associates, Inc. for Santa Clara Valley Urban Runoff Pollution Prevention Program, Contra Costa Clean Water Program, San Mateo Countywide Stormwater Pollution Prevention Program, Marin County Stormwater Pollution Prevention Program, Vallejo Flood Control and Sanitation District, Fairfield-Suisun Sewer District. April. 63pp.

Richard Looker, Water Board

I read it through and my minor comments are not worth noting. I think it is a good read and is a helpful summary of current information. I do not have any serious problems with it. Overall good job.

Dan Cloak, Environmental Technical Representative

Preliminary Environmental Technical Representative comments on
Conceptual Model of Mercury in San Francisco Bay (DRAFT)
Tetra Tech, Inc., 14 March 2005

1. The report is well organized and easy to read.
2. The report contains new information and perspectives that should be useful to CEP participants and Water Board staff.
3. The report's emphasis that "directly deposited mercury from the atmosphere is considered to be more bioavailable than mercury present in sediments" (p. 4-2) is inconsistent with the following excerpt from the TMDL staff report: "Reductions in sediment mercury concentrations are assumed to result in proportional reductions in fish tissue and bird egg mercury concentrations." (Staff Report, p. 50). The latter statement is the foundation of the TMDL's linkage analysis; if it is wrong, then the load allocations and implementation plan are invalid. This inconsistency and its implications should be made prominent in the final report's executive summary and conclusions.

The role of atmospheric mercury deposition in the bay is not fully understood. The TMDL makes an **assumption** that the reduction in sediment concentrations will lead to a proportional decline in biota concentrations. This assumption does not obviate the need for specific studies to verify the potential significance of atmospheric deposition in this system. No change made.

4. Chapters 5 through 8 read like a research grant application. Was that the purpose of this report? The proposed research isn't summarized or prioritized. The CEP can't possibly pursue all of this research in the foreseeable future.

The goal of these sections was to provide managers with an estimate of the types of monitoring and/or studies that need to be done to fully address the uncertainties with regard to mercury in San Francisco Bay. Work of this nature has been performed in other water bodies, and given the long time frame for TMDL implementation, it is not unreasonable to place these ideas for discussion.

5. Rather than focusing so intensely on additional research, the next draft might also consider what control actions could be pursued now based on what is currently known and unknown. For example, based on the report's assessment that mercury deposited from the atmosphere is exceptionally bioavailable, priority should be

given to control of local air sources and actions to limit transport of deposited mercury.

The conceptual model focuses on uncertainties at present and ways to reduce those uncertainties. Control actions of the nature suggested by this reviewer may be recommended in future, although, as a first step, some additional work to characterize atmospheric deposition are recommended.

6. The report should state the extent to which current and planned research—nationally and in the Bay/Delta—may suffice in place of the projects suggested.

Published data on recent work in the region has been used in drafting the conceptual model. It is beyond the scope of this work to identify the contents of planned research where the results have not been published.

The report might benefit from incorporating some of the information and ideas (including potential adaptive management strategies) in: South Bay Salt Pond Restoration Project, *Mercury Technical Memorandum, Final Draft.* Marc Beutel, Brown and Caldwell and Khalil Abu-Saba, Larry Walker and Associates. August 2, 2004, 47 pp.

Revision addresses key issues discussed in this memorandum.

City of San Jose

General comments:

The CM is well organized and descriptive but could benefit from edits to make the technical discussion more concise.

Executive Summary:

Page vii, third paragraph should read: "Because the areas of significant erosion ~~or erosion~~ are a relatively small part of the total bay area, …"

Changed to "Because the areas of significant erosion or deposition are a relatively small part of the total bay area, the concentration changes will be larger and easier to detect than for the bay as a whole."

Chapter 4: Management question on relative bioavailability

This section should follow the format of subsequent management questions, and that format should be reflected in the TOC.

Changed.

The CM states that complexed mercury from POTWs is *likely* to be more bioavailable than particulate mercury from mining areas. Although this might be reasonably assumed, this language should be revised in light of the lack of information supporting the statement. City staff suggest: "Bioavailability of organically complexed forms of mercury in wastewater is unknown, but may be in the range between solid-phase particulate mercury present in historic mine drainage and other dissolved/particulate mercury."

Changed.

Test of hypothesis 2 (Mesocosm experiments) seems ambitious. In this section and subsequent management questions, a short table of the investigations/studies, their relative benefit and relative difficulty would be useful.

Chapter 5: Management question on methylation rates and flux

Maps in this section do not accurately reflect the location of some stations. This should be corrected in the report and the inaccuracies communicated to the source of the location information (SFEI/RMP).

Location data on these maps are from the SFEI/RMP web site, and from other CALFED sources. Could the reviewer identify which stations are not accurately placed and/or provide an accurate listing of station coordinates?

The introductory paragraph of section 5.3 does not mention the hypothesis that methylmercury may be transported from upstream/tributary sources, although hypothesis 2 does. A minor omission, but it would be good to be consistent.

Changed.

Chapter 6: Management question re: wetlands management

Wording on page 6-3, second-to-last sentence of paragraph 2 should read "Whether this is ~~done intentionally as~~ a detoxifying process, or occurs *incidentally* through plant respiration is unknown."
Changed.

In the 3rd paragraph on the same page, it should be mentioned that the productivity phenomenon is from a wetland where the primary source of mercury is thought to be atmospheric, and may not be readily comparable to processes in systems like SFB where the Hg source is primarily the sediment.
Changed.

No major comments on the remainder of the document. The City also supports the comments provided by BASMAA that were delivered via e-mail on April 7th, 2005.