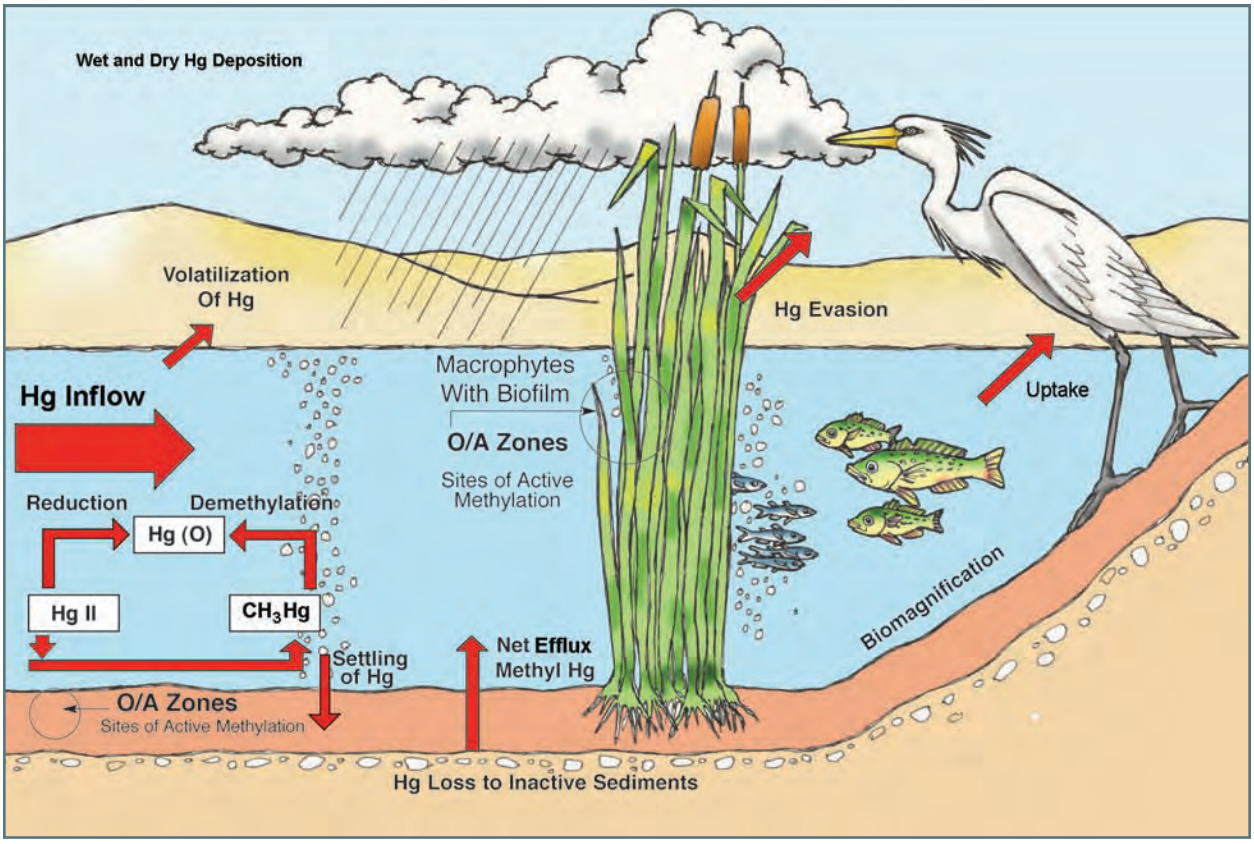
Conceptual Model of
Mercury in San Francisco Bay

January 16, 2006



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EXECUTIVE SUMMARY

The watershed of San Francisco Bay has a legacy of mercury mining and the use of liquid mercury for gold mining going back 150 years. Mercury contamination exists in San Francisco Bay as a result of this legacy as well as the presence of more modern sources, such as runoff from urban areas and atmospheric deposition. 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.

The Regional Board has 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).

The conceptual model for mercury presented in this document has been funded by the Clean Estuary Partnership (CEP) and 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). The document presents an overview of mercury transformation processes of relevance to San Francisco Bay and the processes of uptake by biota (Figure ES-1). It addresses five management questions identified as important by the CEP:

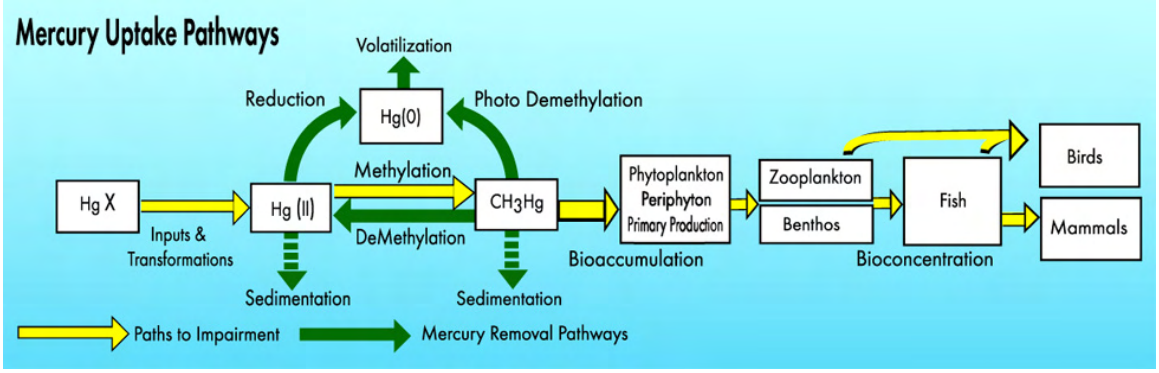

Figure ES-1. Mercury uptake pathways.

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

Available data and current understanding pertaining to each of these questions are evaluated, and recommendations 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 s
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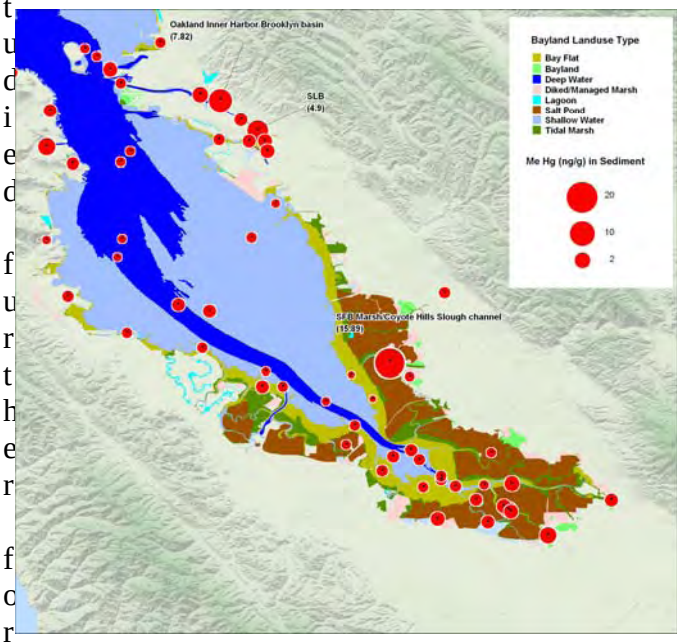

Figure ES-2. Methylmercury concentrations in the waters of South San Francisco Bay. Also shown on the map are principal habitat types in the bay. Habitat data from San Francisco Estuary Institute's EcoAtlas Information System http://www.ecoatlas.org/).

their bay-wide impacts and their potential for remediation (Figure ES-2).

Data on wetlands around the bay show that wetlands are highly effective at producing methylmercury and 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 mercury-related behavior, it is reasonable to expect changes to occur over much shorter durations. Further, some metrics, such as shallow sediments and benthic invertebrates are also expected to exhibit changes over shorter time frames (Figure ES-3). Work needs to be done to delineate these habitats and metrics 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 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. Tissue concentrations need to reflect organisms with short life spans and with significant site fidelity, such as bivalves or small fish. Data from such organisms can be associated with mercury behavior at specific locations and over short durations.

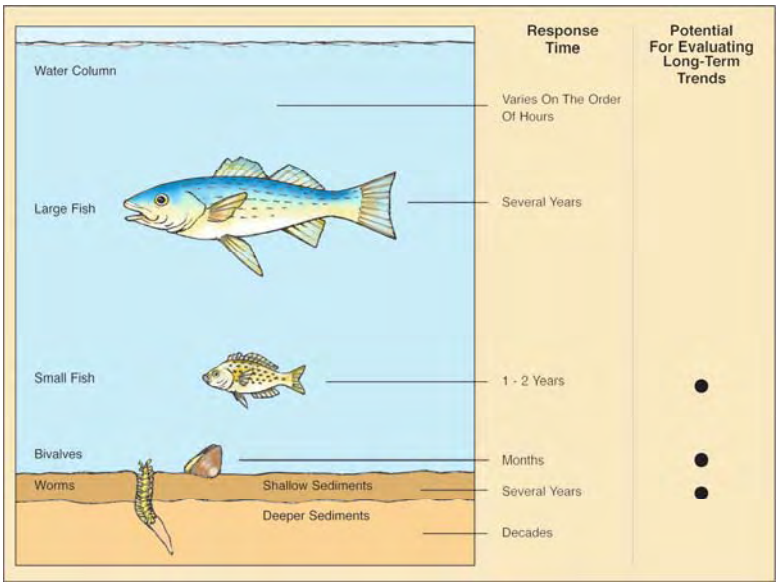

Figure ES-3. Response times for different metrics in the bay. Shallow sediments, benthic invertebrates, and small fish are appropriate for evaluating changes over the time frame of years.

CHAPTER 1. INTRODUCTION

The watershed of San Francisco Bay has a legacy of mercury mining and the use of liquid mercury for gold mining going back 150 years. Mercury contamination exists in San Francisco Bay as a result of this legacy as well as the presence of more modern sources, such as runoff from urban areas and atmospheric deposition. To a very limited extent, municipal and industrial point sources also contribute a mercury load to the bay. The effects of the mercury are seen in the biota of the bay, especially in bird eggs and in fish. Elevated mercury concentrations, greater than 0.3 mg/kg wet weight, limit the consumption of bay-caught fish, and the eggs of several bird species contain mercury at levels above 0.5 mg/kg, a level that is thought to affect the survival rate.

The San Francisco Bay Regional Water Quality Control Board (SFBRWQCB) has 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 process. The process began in 2000 with the publication of the first Project Report by Regional Water Board Staff (SFBRWQCB, 2000). This report presented the first estimates of sources, mass loads from point and non-point sources, expected rates of change in mercury concentrations and impairment with load reductions using a simple model of sediments in the bay. This work was the basis for subsequent reports (SFBRWQCB, 2003; SFBRWQCB, 2004) with small modifications to individual load estimates, although the general format was followed. Most recently, analyses of mercury in the bay were used to develop a Basin Plan Amendment, with specific load allocations for various sources (SFBRWQCB, 2004).

The development of the conceptual model of mercury in the San Francisco Bay ecosystem described in this document has been funded by the Clean Estuary Partnership. The objective of this document is to synthesize the most relevant scientific information, from San Francisco Bay and other mercury-contaminated locations worldwide, to help develop the basis for the future implementation strategy. The emphasis in this document is not on the loads of total mercury, which have been described in the Regional Board reports cited above, but on the biogeochemical processes that lead to mercury impairment in San Francisco Bay, notably methylation

and biological uptake. Toward this end, we have summarized information on mercury impairment from various Regional Board Staff reports (Chapter 2), presented an overview of mercury transformation and biological uptake in San Francisco Bay (Chapter 3), and, using the information in Chapter 3 and other published information, addressed the following set of management questions developed by the Clean Estuary Partnership:

- 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?

These questions are addressed in individual chapters that follow a consistent format (Chapters 4-8). In each chapter we present recent and ongoing relevant research and data that pertains to the specific issue, with a special emphasis on data from the bay and delta where available, and then present ideas for future research that can be used to evaluate specific decisions in response to each of the questions above. The format juxtaposes the known information and the important unknowns, and allows readers to quickly focus in on specific management issues of interest.

CHAPTER 2. MERCURY IMPAIRMENT IN SAN FRANCISCO BAY

The following water quality standards pertaining to total mercury are applicable to San Francisco Bay:

- A maximum concentration of 51 ng/l across the entire bay (California Toxics Rule Numeric Objective)
- A maximum 4-day average concentration of 25 ng/l north of the Dumbarton Bridge (Basin Plan Numeric Objective)
- A Basin Plan Narrative Objective also controls the quantity of mercury in water such that there will not be a "detrimental increase in concentrations of toxic substances found in bottom sediments or aquatic life."

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. In this chapter, we present a summary of these observations from past reports (SFBRWQCB, 2000, SFBRWQCB, 2003).

2.1 WATER COLUMN CONCENTRATIONS

Based on the numeric standards for water column concentrations, it appears that San Francisco Bay concentrations exceed the 51 ng/l standard about 10% of the time (Figure 2-1). The instantaneous concentrations also exceed the four-day average 25 ng/l standard about 20% of the time.

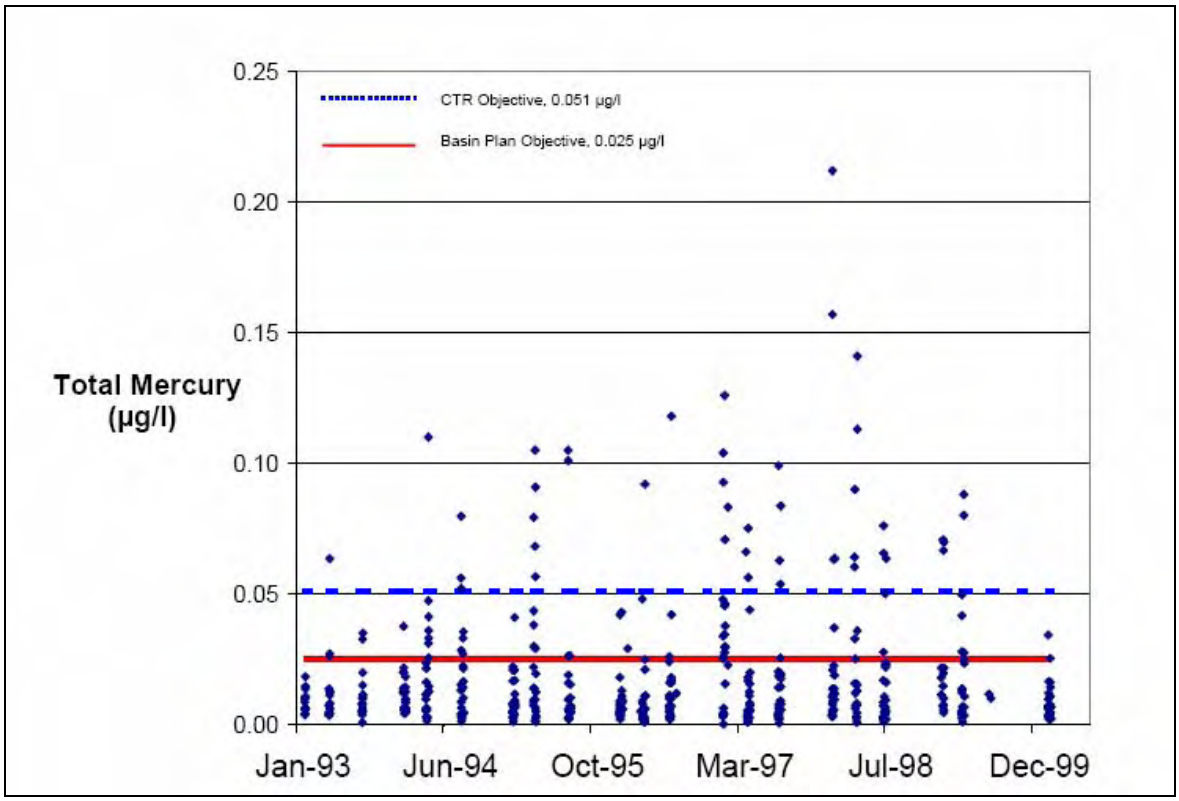

Figure 2-1. Water column mercury concentrations in San Francisco Bay (Source: SFBRWQCB, 2003)

2.2 FISH TISSUE CONCENTRATIONS

The fish tissue criterion is based on risks due to human consumption. Using an average body weight of 70 kg, and an allowable consumption of 0.0001 mg/day of mercury per kg of body weight, and assuming a fish consumption rate of 32 g/day for people who regularly consume bay fish, it was estimated that the allowable mercury concentration in fish would be 0.2 mg/kg. It should be noted that the fish tissue target was calculated to protect 99% of the Bay Area Population. 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, and 95% of these individuals eat less than 32 g of fish per day.

This fish tissue concentration target is exceeded by several species of fish caught in the bay, notably sturgeon, striped bass, and leopard shark (Figure 2-2). Although the allowable concentration is sensitive to the quantity of fish that is assumed to be consumed by humans, based on values used by the Regional Water Board, the bay is impaired with respect to fish tissue concentrations. Surveys have determined that of the species with median concentrations greater than 0.2 mg/kg, striped bass are most commonly consumed by fishermen in the bay, and the Regional Water Board has proposed a target of 0.2 mg/kg in the tissues of this species.

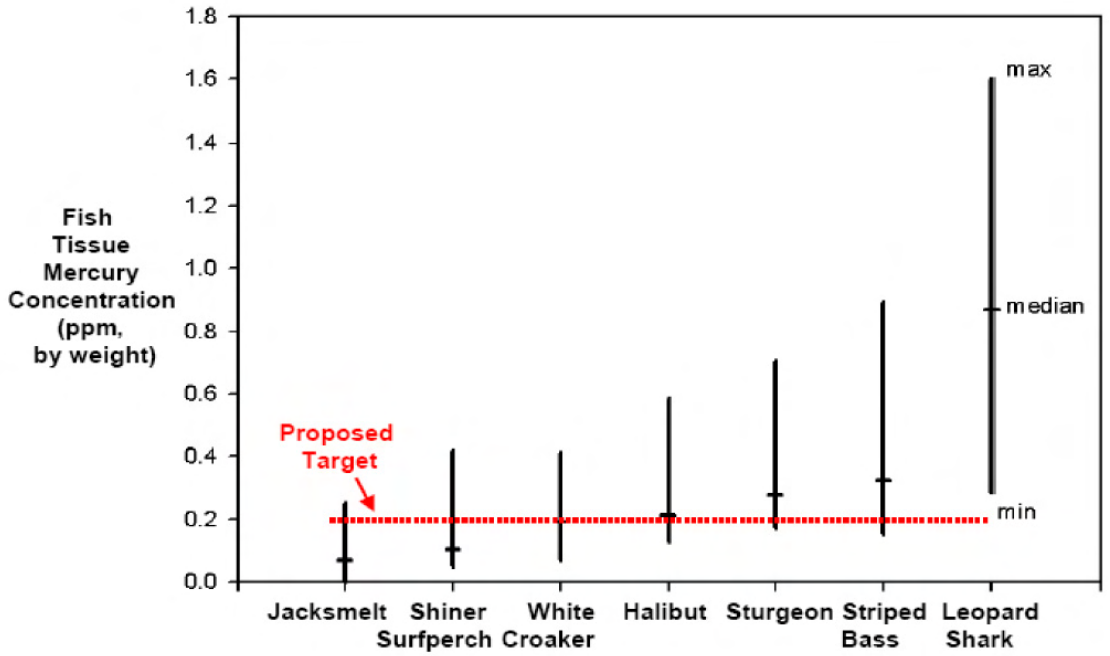

Figure 2-2. Tissue concentrations in different species of fish collected in San Francisco Bay (Source: SFBRWQCB, 2003).

2.3 BIRD EGG CONCENTRATIONS

Egg concentrations above 0.5 mg/kg have been associated with adverse effects in birds based on various studies that involved dosing birds or eggs with mercury. Mercury concentrations in bird eggs collected from North and South San Francisco Bay as part of a large Fish and Wildlife Service study (reported in Davis et al., 2003a) show elevated concentrations compared to similar populations in other parts of California (Figure 2-3). Species for which the median concentrations were higher than the 0.5 mg/kg level were Caspian Terns, California Least Terns, Black-crowned Night-herons, California Clapper Rails, and Black-necked Stilts. California Clapper Rails in particular, a federally protected species, have median egg concentrations slightly in excess of 1 mg/kg and a 50% reduction in these concentrations has been proposed by the Regional Water Board to address this impairment.

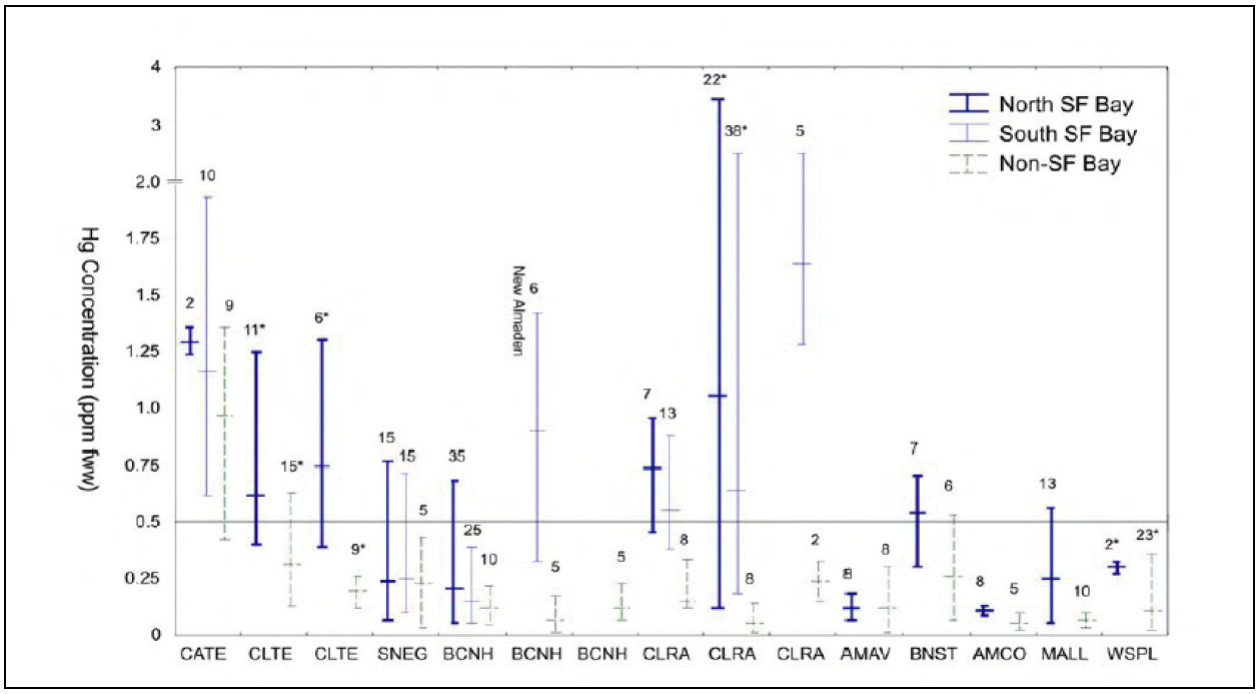

Figure 2-3 Mean concentrations and ranges of mercury in eggs from San Francisco Bay are presented for: Black-crowned Night-herons [BCNH] (*Nycticorax nycticorax*), Snowy Egrets [SNEG] (*Egretta thula*), Mallards [MALL] (*Anas platyrhynchos*), American Coots [AMCO] (*Fulica americana*), California Clapper Rails [CLRA] (*Rallus longirostris obsoletus*), Black-necked Stilts [BNST] (*Himantopus mexicanus*), American Avocets [AMAV] (*Recurvirostra americana*), Western Snowy Plovers [WSPL] (*Charadrius alexandrinus nivosus*), Caspian Terns [CATE] (*Sterna caspica*), and California Least Terns [CLTE] (Sterna antillarum browni). Source: Davis et al., 2003a.

CHAPTER 3. OVERVIEW OF MERCURY TRANSFORMATION AND UPTAKE PROCESSES IN SAN FRANCISCO BAY

The toxicity of mercury to humans and wildlife is closely tied to its transformation into methylmercury and uptake through the food chain. To manage the mercury contamination in San Francisco Bay, it is therefore important to understand the processes that convert mercury in water and sediments into more biologically active forms. Our best current understanding of the reactions of mercury in water and sediment and uptake by biota is summarized in this section. Although a great deal of work on mercury has been conducted in San Francisco Bay, important data gaps, relevant to the management of mercury in the bay, still remain. These data gaps are also addressed in this chapter. The discussion in this chapter lays the groundwork for the evaluation of specific management questions in Chapters 4 through 8.

3.1 WATER COLUMN

Inorganic mercury, and to a lesser extent methylmercury, enters the bay as dissolved and particulate phases from numerous sources. In shallow estuaries, such as San Francisco Bay, the water column is thought to be less important as a site of mercury methylation than the sediments. However, processes in the water column influence both the transport and the fate of the incoming mercury, depending on the mercury species and the water quality conditions.

3.1.1 IMPORTANT PROCESSES AND FACTORS

Mercury enters the bay from a number of sources including direct deposition, point sources from sewage treatment plants and industries, and non-point sources such as urban runoff. The magnitude of the non-point sources varies by season, with the wet months being significant in transporting large quantities of mercury from the watershed into the bay. The mercury in these sources exists in the dissolved and adsorbed phases in different chemical forms: various dissolved Hg(II) species, adsorbed Hg(II) on suspended solids, and solid-phase HgS particles mixed in the

sediment. Methylmercury can also enter the bay from the above sources, but is generally at much lower concentrations.

Once in the water column, mercury undergoes a variety of transformations, depending on its chemical form. The larger, denser HgS particles will settle out soon after entering the bay. As salinity increases from the inflowing rivers to the bay, the smaller suspended solids clump together and settle. The dissolved Hg(II) species are involved in a variety of reactions depending on the salinity of the water, pH, organic carbon content, and the concentrations of other ions such as sulfide. Elemental mercury can also exist in the water column, however, any elemental mercury will volatilize readily to the atmosphere. Legacy sources due to past mercury and gold mining, and natural sources are more likely to have mercury in solid phases, such as cinnabar, which can be present in sediment entering the bay. Cinnabar can also be formed in the sediment, given the necessary redox conditions and sulfide concentrations.

Methylation occurs most readily near the oxic-anoxic boundary. Since the bay is relatively shallow, this zone is more likely to exist in the sediment, rather than the water column. But this oxic-anoxic boundary zone can move up into the water column in response to changes in redox conditions. This zone is where the activity of sulfate-reducing bacteria is highest. Sulfate reducing bacteria are the primary agent that transforms dissolved Hg(II) into its organic form, CH_3Hg, or methyl mercury, as demonstrated for saline systems by Compeau and Bartha (1985) and others. Field research and experiments have shown that neutral, dissolved Hg(II) species are more readily methylated than charged species (Benoit et al, 1999). Methyl mercury species are quickly taken up by biota, but can exist in the dissolved form or be adsorbed to suspended solids or organic matter. Methyl mercury in the water column can undergo other processes including photodegradation resulting in Hg(0), which is then volatilized back to the atmosphere. Dimethylmercury has been found in oceanic waters, but is rarely detected in estuarine waters. Thus, it is not likely to be important in the bay, and has not been included in the water column diagram.

The uptake of methyl mercury in the water column by phytoplankton is an important first step for bioaccumulation in the estuary. This step represents the highest bioaccumulation factor for methyl mercury, e.g. 300,000 in freshwater systems (Mason et al, 1996). The remaining steps are factors of about 6 to 6.5 from phytoplankton to zooplankton and then to fish.

3.1.2 UNCERTAINTIES AND DATA GAPS

More accurate estimates of the effect of decreasing the mercury load can be made by considering the actual mercury species present in the different sources to the bay, instead of considering all species to be equally available for methylation and subsequent uptake by biota. A distinction between dissolved and sorbed forms of mercury would be helpful in evaluating the initial fate of the mercury in the various sources.

Additional water quality data as depth profiles for the bay are necessary to confirm that the water column is not a primary site for Hg methylation (Table 3-1). The methylmercury concentration in the water column is probably the best indicator of bioaccumulation in the system. The existing data for dissolved methyl mercury in the water column range from 0.009 ng/L to 0.109 ng/L with the highest concentration in the South Bay especially in the near shore areas. Further monitoring of the bay is needed to determine if any "hot spots" exist in the nearshore areas. The monitoring data with chemical calculations could be used to refine the estimate of evasion of mercury from the bay surface, which is currently thought to be small, but may be larger.

Table 3-1
Uncertainties and Data Needs Related to Water Column Mercury

Information Need	Proposed Data	Existing Level of Uncertainty	Importance for Decision-Making
Mercury Chemical Forms in Different Sources	Particulate and dissolved mercury and methylmercury in inflows	High	High
Bay Water Quality Characteristics	Profiles of salinity, TSS, DO, DOC, SO_4, S^2, and methyl mercury	Moderate	High
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

3.2 SEDIMENT

The sediment is likely to be the primary zone where methylation occurs in San Francisco Bay, as has been shown for San Francisco Bay and other mercury-contaminated coastal areas (Marvin-DiPasquale and Agee, 2003; Tomiyasu et al., 2000; Covelli et al., 1999; Hammerschmidt and Fitzgerald, 2004; Bloom et al., 2004). Understanding mercury transformation processes in sediments will help estimate the response of the ecosystem to changes in mercury loads and the time frame of the responses.

The primary location for Hg methylation in the San Francisco Bay Estuary is considered to be in the sediment within the upper layers at the oxic-anoxic interface (Figure 3-1). The reactions in porewater are basically identical to those described in the water column as described above; however, porewater chemistry and the supply of mercury in sediments may favor greater methylation than the water column. In the bay muds, the active zone of methylation is expected to be found in the upper 4 to 6 cm, with the maximum methylation occurring in the top 2 cm, where sulfate-reducing bacteria are the most active. It is essential to understand the processes in this zone to predict the methylation rate in the bay. The methyl mercury produced in the sediment can be taken up by benthic organisms or diffused upward into the water column for uptake by epibenthic or pelagic biota. Predicting the effect of decreasing mercury loads to the bay requires understanding the portion of incoming load that is available

for methylation and buried below the active zone that is not returned to the water column. Aside from mercury methylation and diffusion, another factor that must be considered in San Francisco Bay is the significant erosion of deeper mercury-rich sediments, some of which were deposited during an era of greatly enhanced mining activity in the watershed of the bay.

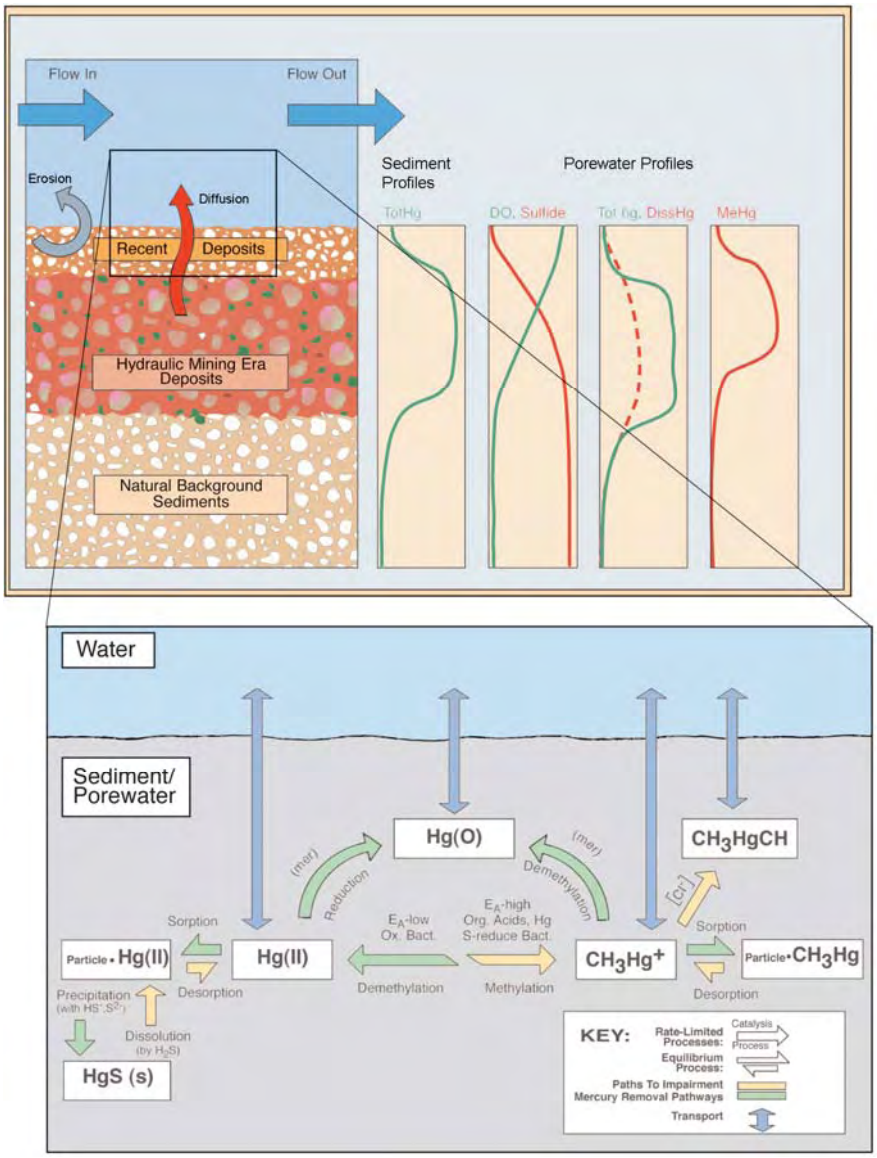

Figure 3-1. Mercury transformation in the sediments of San Francisco Bay. Although much of the mercury transformation and diffusion into the water column occurs in the upper few centimeters of sediment, San Francisco Bay sediments at actively eroding at some locations that may contain a deeper layer of mercury-rich sediment, a legacy of the mercury and gold mining era of the 19th century.

3.2.1 IMPORTANT PROCESSES AND FACTORS

The mercury species present in sediment depend partly on whether the sediment is oxic or anoxic. Field investigations in saline mudflats have shown there can be a thin oxic layer in the upper 0.5 cm, which is maintained by oxygen in the flowing water

above the sediment. In sandy sediments, the oxic layer can be thicker than in silt or clay. In the oxic layer, most of the mercury is likely to be adsorbed to organic matter, sulfur compounds, or iron or manganese oxides (Gagnon et al., 1997). Dissolved mercury in the porewater in this zone can diffuse up into the water column.

The deeper sediments are usually anoxic. The inorganic mercury in anoxic sediments is likely to be adsorbed to organic matter, sulfhydryl groups, or sulfides or to be present as solid-phase precipitates such as cinnabar (HgS). The upper zone near the oxic-anoxic interface is the active zone for methylation by sulfate-reducing bacteria (SRB). In saltmarsh and estuarine sediments investigated in the field, the highest methylation rates were typically in the upper 1-2 cm of sediment (King et al., 2001). The active zone for SRB can extend to a depth of 4 to 6 cm. Mercury in deeper sediment below the bioturbation and resuspension zone is unavailable for methylation and becomes buried by more recent sediment, and thus is effectively sequestered.

The dissolved Hg(II) species in the porewater are the forms converted to methyl mercury by the SRB. The methyl mercury can then move by diffusion into the oxic layer. In this layer, some of the methyl mercury can be demethylated to Hg(II) and then converted to Hg(0). Some of the remaining methyl mercury can be diffused into the water column. The methyl mercury can be taken up by biota in the sediment or water column or be adsorbed onto organic matter or sulfhydryl groups. In the presence of high sulfide concentrations, dimethylmercury can be generated, which is more volatile than methyl mercury and can be lost to the atmosphere. However, dimethylmercury has not been found in sediment or the water column at most field sites. Thus, the formation of this species with subsequent loss to the atmosphere is not considered an important process for San Francisco Bay sediments. There are other microbially-enhanced degradation processes such as the oxidative demethylation pathway in anoxic sediments and the mer-operon pathway under anoxic conditions that can occur when mercury is present at relatively high concentrations. The amount of methylmercury available for uptake by biota is the resultant of both sets of processes – methylation and demethylation. There are several factors that affect the bioavailability of sediment Hg. Lawrence and Mason (2001) showed that the accumulation of inorganic and methyl mercury by benthic estuarine organisms cannot be predicted using only total mercury concentrations in sediments. They concluded that sediment characteristics and the concentration of Hg in organisms at the base of the food chain were important. The recent results of a nation-wide synoptic survey of Hg contamination of lakes and streams also showed that there was no correlation between Hg in fish and total Hg in sediment (Krabbenhoft et al., 1999). Both studies highlight the importance of understanding the processes and factors that affect net methylation.

3.2.2 UNCERTAINTIES AND DATA GAPS

Rates of mercury methylation, including seasonal variation and relationship to sediment/porewater chemistry, have been evaluated at a limited number of sites in San Pablo Bay (Marvin-DiPasquale et al., 2003) and the Delta (Gill et al., 2003; Marvin-DiPasquale and Agee, 2003). Additional shallow sediment data from the bay

are needed to better characterize the existing methyl mercury pool in sediment and to determine if "hot spots" are present. Measurements of key factors affecting the methylation rate at the same time such as DO, TOC, sulfate, sulfide, and chloride will identify areas where high methylation rates are more likely (Table 3-2). These data can be then used to estimate the net methylation rate of the present shallow sediment using rates from the literature that have similar conditions. These estimates can be checked using the measured methyl mercury in the sediment and overlying water column. If bay conditions differ substantially from those where rates are available, mesocosm experiments could be conducted to refine the methylation rates in the bay.

The depth of resuspension, erosion, and bioturbation in the bay muds is unknown. The present estimate of this active zone is 15 cm, but this may be too deep. In addition, only a portion of this zone is where most methylation occurs. Determining the depth of the methylation zone and active zone is necessary to determine the portion of the existing sediment pool that is available for methylation and resuspension into the water column. Appropriate depths for these zones would improve the loading estimates from sediment. Mercury found below the active depth could be considered permanently sequestered.

Table 3-2
Uncertainties and Data Needs Related to Water Column and Sediment Mercury

Information Need	Proposed Data	Existing Level of Uncertainty	Importance for Decision-Making
Characterization of Existing Bay Sediments	Profiles of salinity, DO, TOC, SO_4, S^2, and methyl mercury	High	Essential
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
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	Essential

3.3 BIOTA

Mercury contamination is a concern in the San Francisco Bay estuary because of the human health risks from dietary exposure to methylmercury, the primary form of mercury in the edible flesh of fish, as well as the threat to wildlife that rely on fish as a large part of their diet. It is essential to understand the factors affecting mercury uptake by biota and the existing levels of bioaccumulation in the estuary. It is also necessary to establish an effective means to measure change in the level of Hg bioaccumulation in the system.

3.3.1 FACTORS AFFECTING HG UPTAKE BY BIOTA

The mercury uptake pathway diagram (Figure 3-2) provides a broad summary of the factors that affect Hg uptake in biota. The right-hand portion of this figure identifies the central importance of methylmercury. Methylmercury typically constitutes a minuscule fraction of the total mercury in aquatic ecosystems (< 1% in estuarine sediments and the water column), but it is the critical form or species of Hg that is incorporated into and magnified in the food chain. The greatest bioconcentration occurs between the water and phytoplankton (Mason et al., 1996). The bioconcentration factor for phytoplankton[1] can be on the order of 5.5 (phytoplankton concentrations ~ 300,000 times water concentrations), the corresponding BCFs for zooplankton or benthos and fish could be on the order of 6 and 6.5. As a rule of thumb, the BCF values for methylmercury increase by ~ 0.5 log units per trophic level after the initial uptake by phytoplankton.

Dietary uptake is the dominant pathway for methylmercury accumulation in fish. The bioavailability of methylmercury has been shown to be controlled by digestive processes of fish rather than due to the limitation of transfer across the gills, skin or intestinal epithelium (Leaner and Mason, 2002). Fish have been estimated to assimilate from 65 to 80% of the methylmercury present in the food they eat (Wiener et al, 2002). Not only is mercury readily assimilated, but it is slowly eliminated resulting in increasing methylmercury in fish as a function of age, size and trophic level. The assimilated mercury is distributed throughout the tissues and organs of the fish, but a large portion of the Methylmercury eventually relocates to skeletal muscle where it becomes bound to the muscle protein.

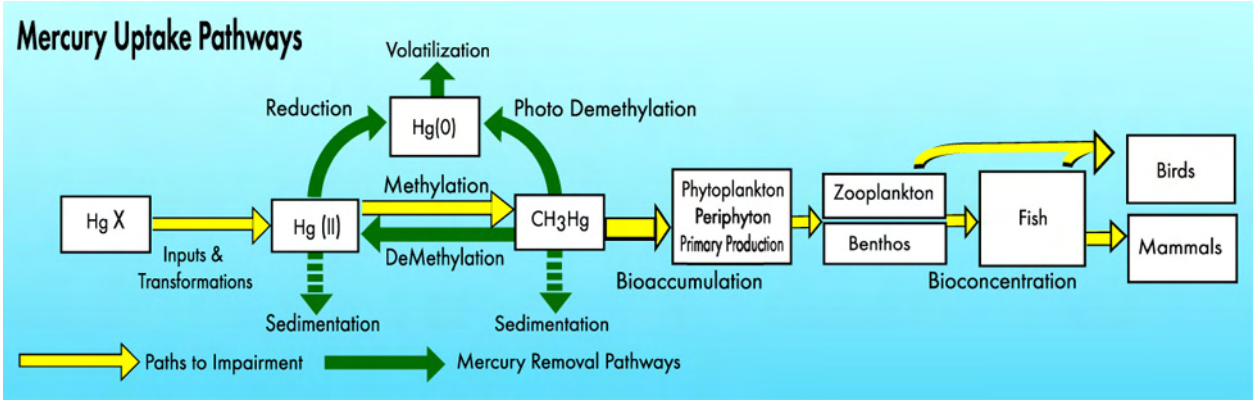

Figure 3-2. Mercury uptake pathways.

The bioaccumulation of fish from San Francisco Bay is demonstrated by the monitoring data collected in 1994, 1997 and 2000 as part of the Regional Monitoring Program. Figure 3-3 shows the relationship between the size (average length) and mercury concentration of muscle tissue from White croaker, Leopard shark, and Striped bass collected from 10 locations within the bay. The highest Hg

[1] $BCF_{plankton} = \log(C_{plankton}/C_w)$, where $C_{plankton}$ and C_w are Hg concentrations in phytoplankton and water

concentrations were measured in Leopard sharks (Figure 3-3b). Sharks are near the top of the food chain, and elevated concentrations of Hg are found worldwide in shark populations.

The bioaccumulation of methylmercury in aquatic organisms, in particular fish, is known to be primarily a function of three interacting factors: the amount of mercury introduced to the system (Hg loading), the net mercury methylation rates (methylation efficiency), and food chain length and the level of interactions. Maximum methylmercury concentrations will be observed in fish when there is an ample inventory of bioavailable Hg [i.e., Hg(II)], sediment and/or water-column conditions promote methylation by sulfate reducing bacteria (e.g., in wetlands), and a multi-step food-web structure exists. Complete information on any single factor is not sufficient to predict methylmercury concentrations in fish.

The food-web structure in the estuary may be less important than these other factors in determining the level of bioaccumulation potential. There are many food-web factors, such as decreases of phytoplankton standing crop in the estuary that could affect the expected or maximum level of Hg accumulation in fish tissue. A detailed understanding of the existing food-web structure would provide information on the potential level of bioaccumulation given different source levels or changes in the food web structure. A detailed understanding of the following phenomena is required to assess the effects of alternative biological transport pathways: 1) standing crops of various organisms and their affinity for methylmercury, 2) the bioenergetics of carbon transfer and energy transfer efficiencies between trophic levels.

Although potential human-health effects from the ingestion of fish contaminated with methylmercury is a primary concern in the estuary, there are also significant ecological risks associated with the uptake of methylmercury by birds and mammals from the ingestion of fish (Figure 3-2). Methylmercury is readily passed to developing eggs or embryos, and these early developmental stages are more sensitive than the adult to methylmercury exposure. Recent work by Schwarzbach and Adelsbach (2002) indicates that a number of birds that nest or feed in the estuary may be affected by mercury bioaccumulation. They showed that the eggs of both piscivorous and non-piscivorous birds had elevated mercury concentrations, and that some of the egg-mercury concentrations were elevated above the known toxic threshold limits.

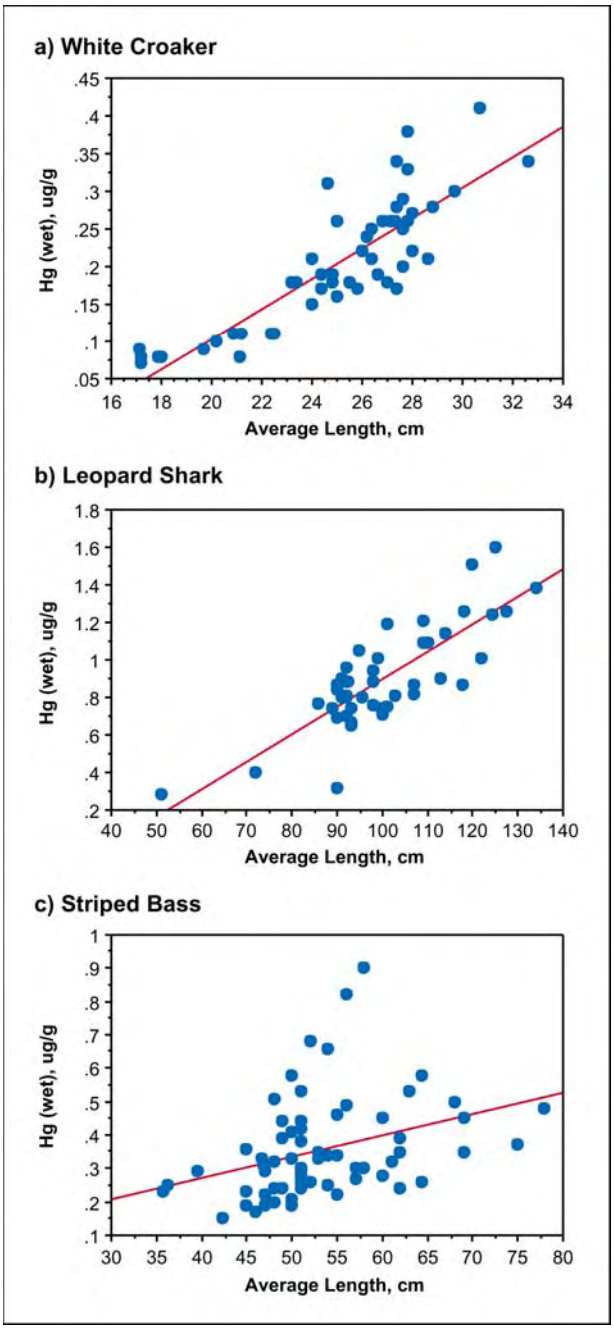

Figure 3-3. Relationship between size and Hg concentration of muscle tissue in three fish species sampled by SFEI between 1994 and 2000.

3.3.2 CHANGES IN THE LEVEL OF BIOACCUMULATION

With the development and implementation of plans to reduce Hg loading to the estuary, it is necessary to be able to detect changes in the levels of Hg in fish tissue. One of the objectives of the fish-monitoring program should be the detection of a specified level of change in Hg concentration in fish tissue within a fixed period of time. The monitoring program should focus on the sampling of resident species within targeted size ranges. There is also a need to examine the levels of Hg at other levels in the food web in order to build a predictive model of Hg accumulation in fish

tissue in San Francisco Bay. Identified uncertainties and data needs are presented in Table 3-3.

Table 3-3
Uncertainties and Data Needs Related to Biota

Information Need	Proposed Data	Level of Existing Uncertainty	Importance for Decision-Making
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
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

CHAPTER 4. MANAGEMENT QUESTION: WHAT IS THE RELATIVE BIOAVAILABILITY OF MERCURY FROM DIFFERENT SOURCES TO SAN FRANCISCO BAY?

As discussed in Chapter 3, the bioavailability of mercury is strongly dependent on its speciation and even its physical form. Thus, the impact of mercury from a particular source depends not just on the magnitude of the load but also on the chemical and physical form of the mercury in it. In general, the dissolved methylmercury is the form most available to biota. Dissolved Hg(II) compounds are the second-most available form, because they must first be methylated. Sorbed mercury is less available than the dissolved forms because it has to be desorbed to the dissolved phase and then methylated before it can be taken up by biota. Solid-phase inorganic mercury compounds, especially particles containing cinnabar, are the least available because they first have to first be dissolved before they can be methylated. Finally, solid-phase mercury containing particles are less available with increasing size because of resistance to weathering and dissolution. In general, bioavailability cannot be assessed directly, except through mesocosm-type experiments that reflect natural environmental conditions. More commonly, speciation of mercury (into methyl-, dissolved, or particulate forms) or leaching with extractants for solid phases (e.g., sequential extractions with acids and bases, Bloom et al., 2003) is used to define bioavailability operationally.

San Francisco Bay receives mercury loading from a variety of natural and anthropogenic sources. The identified source categories of mercury to the San Francisco Bay include the following:

- Legacy mercury inputs – from past mercury and gold mining including modern riverine transport of these sources
- Direct atmospheric deposition
- Urban runoff (includes indirect atmospheric deposition on the watershed of the bay)
- Resuspension of previously-deposited bed sediment in the Bay
- Point sources – sewage treatment plants, industries
- Other non-point sources

Current knowledge regarding the relative bioavailability of these sources is discussed below, followed by a presentation of additional hypotheses that need to be confirmed.

Legacy Mining

Contributions from legacy mining at both mercury and gold mines influence the mercury load from the Central Valley, Guadalupe River Watershed, and resuspension of previously deposited sediment from the bay bottom. Small mines or mercury deposits in other parts of the bay watershed can also contribute to runoff in either urban or non-urban areas. The predominant form of mercury from mining sources is in the particulate phase, particularly during high flows with mercury present as cinnabar or metacinnabar (Domagalski et al., 2003; Tetra Tech, 2004, 2005). These compounds are mercury sulfide minerals, with very low solubility. Cinnabar weathers less readily than metacinnabar, although there is evidence that both minerals may dissolve more readily in the presence of elevated levels of hydrogen sulfide (Paquette and Helz, 1997 and Benoit et al., 1999).

Atmospheric Deposition

Atmospheric deposition that falls directly on the water surface of the bay may consist predominantly of dissolved-phase or reactive species species. The wet deposition can include dissolved Hg(II) species and methylmercury, while the dry deposition is mostly reactive gaseous mercury (RGM) and Hg(II) sorbed to particulates (SFEI, 2001). Typically, the largest reservoir of mercury in any water body will be in the sediments, and generally, directly deposited mercury from the atmosphere is considered to be more bioavailable than mercury present in sediments. Based on work done in a wetland environment (Gilmour et al., 2003), it has been suggested that "new" atmospherically deposited mercury is more bioavailable than "old" mercury already existing within water bodies. This conclusion has not been extensively tested.

Urban Runoff

Urban runoff and erosion of mercury-containing soils contains dissolved mercury compounds as well as sorbed mercury on suspended solids. An extensive amount of data storm drains has been collected at various locations around the bay in recent years (data collected by the Santa Clara Valley Urban Runoff Pollution Prevention Program and the Joint Stormwater Agency Project, Kinnetic Laboratories and EOA,

Inc., 2002, and by Alameda Countywide Clean Water Program, Salop et al., 2002). All of the reported data on urban runoff loads have been in total mercury form. Although the data show that stromwater runoff from urban areas is a large contributor of total mercury loads to the Bay (more than an order of magnitude greater than the wastewater sources), not much is known about the chemical forms of mercury in runoff and how their bioavailability compares with other related sources such as legacy mining and wastewater discharge. The magnitude of the urban stormwater loads provide support for the need to better understand the potential of this mercury to become bioavailable.

Resuspended Sediment Mercury

A substantial source of mercury to the bay waters is resuspension of mercury from sediments. Based on evaluation of bay bathymetry, it has been shown that portions of the bay show substantial erosion in the past few years (Jaffe et al., 1998; Capiella et al., 1999; Foxgrover et al., 2004). The net erosion is the result of long-term processes: the vast amount of sediments deposited during the hydraulic mining era of the 19th century, followed be a depletion of sediment supply due to reservoir construction in the 20th century. An example of the deposition and erosion magnitudes in South San Francisco Bay is shown in Figure 4-1. Existing data provide a good estimate of the locations of erosion throughout San Francisco Bay. At present little is known about the form of the mercury that enters the bay waters via resuspension, although the total mercury can be inferred from existing sediment mercury data.

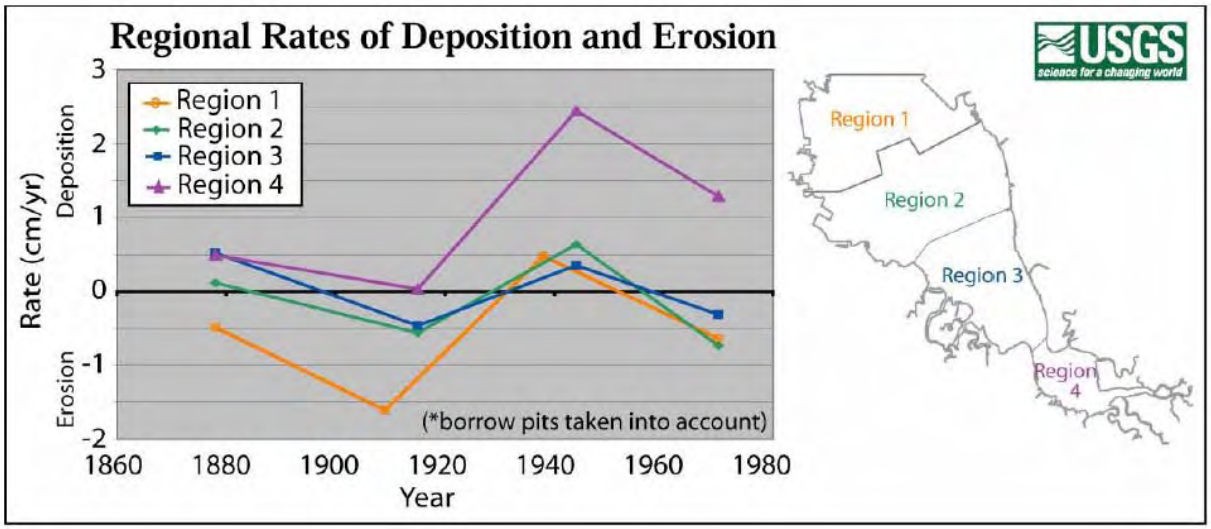

Figure 4-1. Erosion and deposition rates in different areas of South San Francisco Bay. Source: Foxgrover et al., 2004.

Point Sources

Point source data on mercury entering the bay is primarily total mercury data, with the exception of data from the San Jose/Santa Clara Water Pollution Control Plant (Hsu and Sedlak, 2003; City of San Jose, 2004) and from the Fairfield Suisun Sewer

District (Larry Bahr, personal communication). Data from the San Jose facility show that wastewater treatment removes more that 95% of the total mercury present in raw sewage. What is discharged from the treatment plant is primarily in the dissolved, and organically-complexed form, and only a small fraction is present as methylmercury (~2%). 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 However, their bioavailability compared to other dissolved and/or particulate mercury is not known. Data from the Fairfield Suisun Sewer District show that dissolved mercury is a large fraction of the total mercury (often greater than 50%), and a small fraction of the total mercury (1 to 12%) is in methylmercury form. Although there are fewer time points of data from the Fairfield Suisun Sewer District than the City of San Jose, available data show that actual concentrations of methylmercury in the former may be more than five times greater than in the latter.

4.1 HYPOTHESIS 1. SOME SOURCES OF MERCURY ARE MORE BIOAVAILABLE THAN OTHERS

Methylmercury present in a given source is more bioavailable than other forms of mercury. In addition, mercury sources may exhibit a continuum of reactivity, with variable potential rates of transformation to methylmercury

Proposed Monitoring. The first step is to determine the portion of each type of source that is methylmercury. For example, municipal sewage treatment plant discharges have been analyzed mostly for total mercury, resulting in a total load to the Bay of 14 kg/yr as listed in the Mercury TMDL (SFBRWQCB, 2004). The total mercury in treated wastewater discharges is likely to be strongly-bound complexes (Hsu, 2003) and thus, less available than dissolved soluble mercury compounds such as HgCl or $Hg(OH)_2$. Methylmercury concentrations from a recent literature survey of treated wastewater ranged from 0.1 to about 2 ng/L (Hsu, 2004). Monitoring at other sewage treatment plants and industrial discharges is needed.

Measurement of methylmercury in direct wet deposition to the Bay would provide quantification of this highly bioavailable load to the Bay. The average volume-weighted total mercury at a station in Moffett Field, Sunnyvale (South Bay) was 9.7 ng/L in a 1999-2000 pilot study (SFEI, 2001). Concentrations of methylmercury in wet deposition are likely to be small, based on literature (e.g., 0.015-0.35 ng/l, St. Louis et al, 1995), but no local data are available. Dry deposition was estimated in the SFEI pilot study using the average of the measured concentrations of total mercury in ambient air (2.2 ng/m^3), then partitioning the total by species into elemental mercury (95%), reactive gaseous mercury or RGM (2%), and particulates (3%) based on literature values. The total deposition flux was then estimated by multiplying the concentrations of each species by the appropriate deposition velocity. Of these species, the RGM would be the most available for methylation. Actual speciation of ambient mercury in the Bay area needs to be done, and the total deposition fluxes recalculated using recent total mercury data.

The methylation potential of sediment depends on the grain size distribution, the mercury species present, and other conditions such as degree of anoxia, pH, sulfate, and sulfide concentrations. For example, the bottom sediment in the Guadalupe River is fine-grained, mostly silts and clays, and was a mixture of cinnabar and more soluble compounds based on a sequential extraction procedure on sediment samples (Tetra Tech, 2004). A similar sequential extraction procedure could be used on a variety of sediment samples representing other sources to the Bay to provide an estimate of the percent of soluble compounds. These locations would be selected to include sources such as urban and non-urban runoff, smaller streams not directly affected by mining, and nearshore sediment in industrial areas around the Bay.

The next step would be to measure methylmercury in sediment cores at 1-2 cm intervals in areas of the Bay with different sources. Confirmation of in situ methylation could be obtained by extracting porewater from the core slices using centrifugation at the same location. For each of these sediment cores, the total mercury concentration would be measured and the mineralogy determined, if possible using petrologic and X-ray methods, in addition to the sequential extractions discussed above.

4.2 HYPOTHESIS 2. NEW MERCURY IS MORE BIOAVAILABLE THAN OLD MERCURY IN THE SYSTEM

This hypothesis is related to the previous one, in that if methylmercury is discharged to the Bay, it is immediately bioavailable. The question has been raised that because atmospheric deposition is discharged directly to the waterbody, partly as methylmercury, dissolved species, and RGM that it is more bioavailable than “old” mercury, which is more likely to be associated with suspended particles and the bottom sediment.

Proposed Experiments. This hypothesis could be addressed using an experiment in which the same quantity of total mercury from wet deposition and suspended solids from urban runoff, as captured from storm drains, and from the two river discharges affected by past mining (i.e., the Sacramento and Guadalupe Rivers) are added to identical mesocosms. One set of mesocosms would have bay water and wetland sediment from a location where anoxic conditions exist. The ability of the sediment to methylate mercury would be confirmed prior to the experiment by measurement of methylmercury in the top 2 cm of the sediment. A second set of mesocosms using only bay water would be used. The experiment could be continued for several months with periodic sampling of the water and sediment for methylmercury. The mesocosms would be in a controlled atmosphere, so that any mercury volatilized would also be captured and periodically tested. Additional control mesocosms would evaluate behavior under conditions where no mercury was added.

4.3 HYPOTHESIS 3. UNDER THE RIGHT CHEMICAL CONDITIONS, EVEN THE MOST TIGHTLY-BOUND FORMS OF MERCURY (E.G., CINNABAR) MAY BECOME BIOAVAILABLE

This hypothesis addresses the assumption that given enough time, all the mercury present in sediment and suspended solids, even cinnabar from former mercury mining areas, can be methylated.

Proposed Experiment. Published literature shows that cinnabar could be partly methylated, but under aggressive mixing conditions that do not represent true environmental conditions. A better test under environmental conditions is to add a known quantity of cinnabar to a series of batch reactor with wetland sediment, as discussed under Hypothesis 2. This series would include a control reactor, one with moderate and low dissolved oxygen, pH spanning the range of conditions in Bay sediment, and one with a range of sulfate and sulfide porewater concentrations. The quantity of methylmercury produced in porewater would be measured on a monthly basis for 6 to 9 months.