

## **San Francisco Bay Mercury TMDL: Implementation Plan for Atmospheric Deposition**

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## **SAN FRANCISCO BAY MERCURY TMDL: IMPLEMENTATION PLAN FOR ATMOSPHERIC DEPOSITION**

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The goal of this report is to provide technical support for the development of an implementation plan for controlling atmospheric deposition. There are three parts to this report that correspond to the subtasks identified in the Scope of Work for the Clean Estuaries Partnership Study on Technical Support of Mercury TMDL Implementation Plan:

### **Subtask 1a. Identify key uncertainties in atmospheric emissions, deposition, and bioaccumulation.**

- A brief summary of existing knowledge on the atmospheric cycle of mercury, atmospheric deposition in San Francisco Bay, and emissions of mercury in the vicinity of the Bay and in the U.S. is presented. This summary of information is essential to understanding the significance of identified uncertainties.
- Key uncertainties in emission, deposition and bioaccumulation are identified

### **Subtask 1b. Propose studies to resolve key uncertainties and suggest mechanisms for funding and implementing needed studies**

- Available data show that atmospheric deposition of mercury is responsible for approximately 10 % of the total mercury entering San Francisco Bay. It is not known how much of this deposition originates in emission sources near the bay. Additional work needs to be performed to quantify emissions more accurately and to relate to deposition in the San Francisco Bay Region.
- However, the most important data gap is the quantification of the bioavailability of Hg from all sources. It is possible that the mercury entering the bay from the atmosphere is as significant a factor in determining the Hg content of fish tissue as anthropogenic sources of mercury in sediments.

### **Subtask 1c. Evaluate feasibility, potential load reduction, and existing regulatory tools for reduction of local and long-range air emissions**

- Model-derived estimates of atmospheric concentration of Hg contributed by anthropogenic emission sources are described. The dominant fraction of the total air concentration in the vicinity of San Francisco Bay appears to originate in the global background. If this modeled result is verified

through localized field studies, it follows that local emission controls will have little, if any, effects on deposition in the Bay region.

- Amendments to the Clean Air Act to significantly reduce mercury emissions from electric utility boilers over the next two decades have been proposed by EPA, but the majority of these sources are downwind of San Francisco Bay. The benefits to deposition in the bay from these emission reductions will be indirect and perhaps marginal.

## **SUBTASK 1A. IDENTIFY KEY UNCERTAINTIES IN ATMOSPHERIC EMISSIONS, DEPOSITION, AND BIOACCUMULATION.**

In this section we summarize our knowledge of the atmospheric cycling of mercury, the magnitude and uncertainty of estimated atmospheric loads to San Francisco Bay, the significance of local sources of mercury emission, and identify key uncertainties in emission, deposition, and bioaccumulation.

### **1A. 1. The atmospheric cycle of mercury**

As a naturally occurring element with several volatile forms, there has always been a natural cycle of mercury in the environment. The global mercury cycle involves passive emission (evaporation) from the oceans and earth's crust, transport through the atmosphere, deposition and perhaps multiple cycles of re-emission and redeposition before being bound-up again in geological sinks. However, it is estimated that approximately 80 percent of today's global mercury budget is ultimately derived from anthropogenic sources, primarily the result of mining and smelting of mineral ores, burning of fossil fuels (principally coal), and the mining, smelting, use and disposal of mercury. The sources of mercury contributing to atmospheric deposition are water-soluble gases and fine particulate matter, which are transported to aquatic systems by wind and rain. In terms of its influence on deposition, the most important chemical forms of mercury in the atmosphere is the ionic form of gaseous mercury, or reactive gaseous mercury (RGM), which comprises only a few percent of total gaseous mercury in the atmosphere (Schroeder and Munthe, 1998). Although extremely low in concentration, it is understood that RGM is the chemical form of mercury that is dominant in deposition.

Mercury in the atmosphere exerts its effects on three spatial scales, governed by the chemical and physical properties of the various forms:

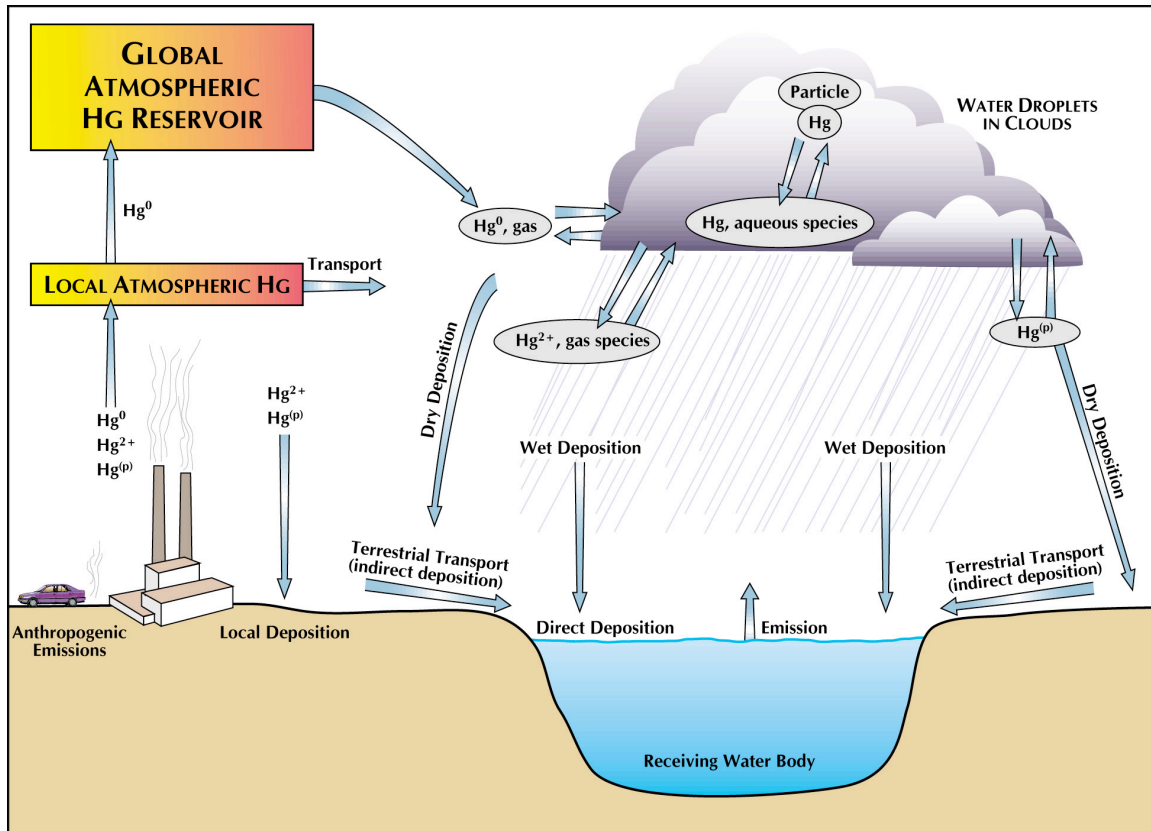
Elemental mercury vapor ( $Hg_0$ ) is the dominant form of mercury in the atmosphere and exhibits an atmospheric half-life of one to two years. Elemental mercury is relatively inert and interacts only weakly with the earth's surface, resulting in even background concentrations ( $\sim 1.6 \text{ ng/m}^3$ ) and shallow gradients near population centers.

RGM, whether from primary emissions or secondarily formed by atmospheric reactions, exhibits a primarily localized effect. Ambient RGM concentrations range from 5 to 200 picograms/ $\text{m}^3$  ( $\text{pg/m}^3$ ). Because of its high solubility and

high dry deposition velocity from the gas phase, RGM emitted into or produced within the planetary boundary layer has a half-life measured in hours. Emissions of RGM from all but the tallest emission stacks are likely deposited by wet or dry processes within about 100 km of its origin.

Particulate-associated mercury, Hg(p), consists of primary emissions or secondary interactions between RGM and particulate matter. The transport properties of particulate matter are inversely proportional to particle size, with atmospheric half-lives of minutes to days.

The key interactions of mercury in the atmosphere are shown in conceptual form in Figure 1. Emissions from anthropogenic sources typically comprise a mix of the three major forms of mercury: particulate, ionic and elemental. The particulates and the Hg<sup>2+</sup> forms in the emissions are thought to deposit near the sources (~100 km), whereas Hg<sup>0</sup> enters the global reservoir, and may eventually deposit anywhere on earth. The atmospheric deposition of mercury, therefore, in some cases may be a local pollution problem, but in most cases is a continental or global-scale problem. Of note is the significant role played by particles and water droplets in clouds in converting elemental mercury to more reactive forms that can deposit, either during rain or dry conditions as shown in Figure 1. Wet and dry deposition can occur directly on the waterbody of interest, or may occur on land and be transported to the waterbody by runoff (indirect deposition). As indicated in Figure 1, the conversion of gaseous elemental mercury to forms that are more likely to deposit to the earth's surface can occur at a location distant from emission sources; there may be regional hot spots of deposition that have more to do with the cloud chemistry that favors formation of RGM than the proximity of emission sources.



**Figure 1. Atmospheric cycling of mercury.** Depending on the nature of the source, emissions include different proportions of elemental, particulate, and ionic mercury. Of these forms, ionic and particulate mercury is more likely to deposit near the source, and elemental mercury is more likely to enter the global atmospheric reservoir, where it has a half-life of 1-2 years. Clouds play an important role in converting elemental mercury to forms that are more likely to deposit. Volatile forms of mercury may also be released back to the atmosphere from water surfaces.

Deposition can occur directly to a water body of interest, or may occur at some distance and be transported to the water body via run off. The latter mode of deposition is called indirect deposition, and in many cases can be a more important route than direct deposition.

## 1A. 2. Atmospheric Deposition in San Francisco Bay

A recent pilot study performed by the San Francisco Estuary Institute has estimated the input of atmospherically deposited mercury into the bay (SFEI, 2001). This work was performed from August 1999 to November 2000 at three stations located in and around the bay. Wet deposition was estimated using measured rainfall Hg concentrations and total rainfall to the bay. The estimation of dry deposition involved several steps: the total atmospheric concentration of mercury in air was measured and divided into the three major fractions based on literature values ( $Hg^0$ , 95%;  $Hg^{2+}$ , 2%; and Hg, particulate, 3%); the concentration of each species was multiplied by a literature-estimated deposition velocity to obtain a total dry deposition flux for mercury. The nature of the dry deposition calculations makes it clear that there is a greater uncertainty associated with it.

This is typical: in most atmospheric deposition estimates, dry deposition inputs are much harder to estimate than wet deposition inputs. The estimated direct wet and dry deposition to the bay, and indirect deposition, calculated assuming that 32% of the land-deposited mercury reaches the bay, are shown in Table 1. The calculated values show that dry deposition is the dominant component of the total deposition, as is indirect deposition. The deposition estimates in Table 1 do not include indirect atmospheric deposition that occurs in the Central Valley watershed.

**Table 1. Estimated atmospheric deposition to San Francisco Bay (Source: SFEI, 2001)**

Parameter	Value	
Area of Bay (km <sup>2</sup> )	1133	
Area of Watershed (km <sup>2</sup> )	7261	
Wet Deposition (microgram/m <sup>2</sup> /yr)	4.2	
Hg total air concentration (ng/m <sup>3</sup> )	2.1	
Hg <sup>0</sup> fraction	0.95	
Hgp fraction	0.03	
Hg <sup>2+</sup> fraction	0.02	
Deposition Velocity, Hg <sup>0</sup> cm/s	0.0035	
Deposition Velocity, Hgp cm/s	0.20	
Deposition Velocity, Hg <sup>2+</sup> cm/s	1.00	
Runoff Coefficient	0.32	
<b>Deposition Estimates</b>	Wet	Dry
Direct Deposition (kg)	4.8	22.0
Indirect Deposition (kg)	9.8	45.1
<b>Total Deposition (Wet + Dry) (kg)</b>	<b>81.7</b>	

Table 1 also shows highlighted a group of parameters that are used to calculate the deposition, but are inferred or literature determined. Of these parameters, the fraction of Hg<sup>0</sup>, Hg<sup>2+</sup>, and particulate Hg are amenable to direct measurement, but due to technical constraints, were not measured directly in the SFEI study. The product of the deposition velocity and gas phase concentration is the deposition flux. The estimated deposition velocity of Hg<sup>2+</sup> species and particulate Hg are much greater than that for elemental mercury, and these two species are a major portion of the deposition flux, even though they are a small fraction of the air phase concentration.

### 1A. 3. Emissions of Mercury in the Vicinity of the Bay and in the US

To determine the importance of local sources, we evaluated the total emissions of mercury from the 9 counties that surround the bay: San Francisco, San Mateo, Santa Clara, Alameda, Contra Costa, Sonoma, Napa, Marin, and Solano (Group 1). We also considered emissions from 8 other counties near the bay region: Mendocino, Lake, Colusa, Yolo, Sacramento, San Joaquin, Stanislaus, and Santa Cruz (Group 2). For comparison we looked at emissions from northern California and the entire state of

California. Mercury emission data for all US states is collected and assessed at the county level every three years by the National Toxics Inventory. The most recently available data are for 1996 (USEPA, 2002a).

Emission data grouped by industrial/commercial activity are shown in Table 2. The dominant contribution of medical waste incinerators in the areas near San Francisco Bay shows clearly in the data. In the counties near the bay region, municipal waste combustors, cement manufacturing, and carbon black production are also important sources. Major sources of mercury emissions in the US overall, such as coal-fired boilers, are not significant in California.

**Table 2. Total mercury emissions summarized by industries and commercial activities, by groups of counties**

<b>Industrial/Commercial Activity</b>	<b>All State (lbs/yr)</b>	<b>Northern California (lbs/yr)</b>	<b>Counties Near Bay Group 1+2 (lbs/yr)</b>	<b>Counties Adjacent to Bay Group 1 (lbs/yr)</b>
Medical Waste Incinerators	7,017	2,882	2,285	1,666
Portland Cement Manufacturing	2,378	1,441	314	1
Municipal Waste Combustors	1,874	586	586	0
Industrial/Commercial/ Institutional Boilers & Process Heaters	362	118	66	54
Off-Site Waste And Recovery Operations	189	89	78	0
Miscellaneous Organic Chemical Processes	171	16	4	0
Carbon Black Production	169	169	169	169
Other Solid Waste Incineration - Crematories	154	58	47	35
Hazardous Waste Incineration	123	106	28	8
Miscellaneous Metal Parts & Products (Surface Coating)	123	2	2	2
Utility Boilers: Natural Gas	93	0	0	0
Municipal Landfills	91	22	15	10
Secondary Lead Smelting	64	0	0	0
Petroleum Refineries - Catalytic Cracking, Catalytic Reforming, & Sulfur Plant Units	61	14	14	14
Oil & Natural Gas Production	36	33	0	0
Pulp And Paper Production	27	27		0
Utility Boilers: Oil	25	5	0	0
Solvent Extraction For Vegetable Oil Production	25	25	0	0
Asphalt Roofing And Processing	22	2	2	2
Utility Boilers: Coal	20	9	9	0
Pulp & Paper Production - Combustion (Kraft, Soda, Sulfitte, & Semi-Chemical)	18	18	0	0
Stationary Reciprocal Internal Combustion Engines	7	0	0	0

Plywood And Composite Wood Products	2	2	2	0
Steel Foundries	1	1	1	1
Printing/Publishing (Surface Coating)	1	1	1	0
<b>Total</b>	<b>13,053</b>	<b>5,626</b>	<b>3,623</b>	<b>1,962</b>
<b>Group 1:</b> San Francisco, San Mateo, Santa Clara, Alameda, Contra Costa, Sonoma, Napa, Marin, and Solano				
<b>Group 2:</b> Mendocino, Lake, Colusa, Yolo, Sacramento, San Joaquin, Stanislaus, and Santa Cruz				

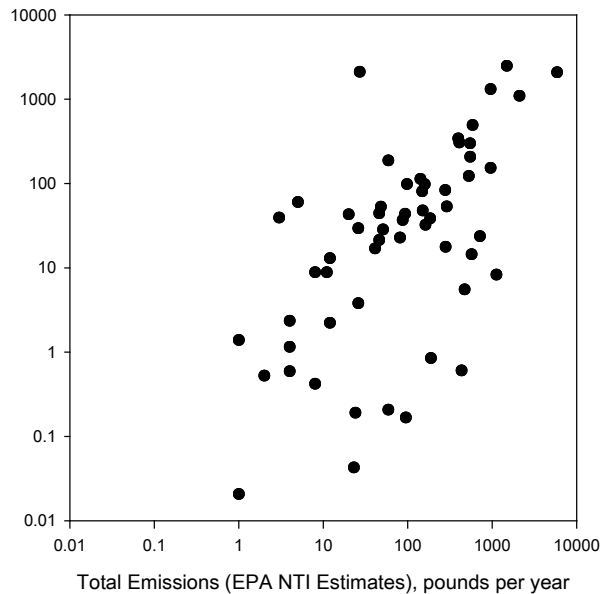
Total emissions from all types of sources are also estimated by EPA as part of the National Air Toxics Assessment (USEPA 2002) and by the California Air Resources Board. These estimates include the emission sources in Table 2, as well as other area-wide and mobile sources. Estimates from EPA and CARB are shown for comparison for the 9 Bay Area counties in Tables 3 and 4. The emission estimates from the two agencies differ substantially. In Figure 2, emission estimates for all 58 California counties by USEPA and CARB are compared on a log-log scale. The tables and the plot show that in some cases, the estimates can vary by more than an order of magnitude. The reasons underlying this large discrepancy were not explored in detail for this document, but must be considered if mercury emission controls are to be proposed.

**Table 3. Emissions of mercury in 1996 from Bay Area Counties (USEPA, National Air Toxics Assessment)**

County	Major Source Emissions (lbs/y)	Area & Other Emissions (lbs/y)	On-Road Emissions (lbs/y)	Non-Road Emissions (lbs/y)	Total Emissions (lbs/y)
Alameda	3.6	398.0	1.5	67.9	<b>471.0</b>
Contra Costa	281.0	221.0	1.0	45.1	<b>547.0</b>
Marin	0.0	47.0	0.3	11.6	<b>59.0</b>
Napa	0.0	89.0	0.1	5.8	<b>95.0</b>
San Francisco	1.2	396.0	0.8	36.3	<b>434.0</b>
San Mateo	1.3	152.0	0.8	34.0	<b>188.0</b>
Santa Clara	0.0	488.0	1.8	78.7	<b>569.0</b>
Solano	25.6	118.0	0.4	18.2	<b>162.0</b>
Sonoma	1.6	2076.0	0.5	20.9	<b>2099.0</b>

**Table 4. Emissions of mercury in 1996 from Bay Area Counties (California Air Resources Board)**

County	Stationary Sources (lbs/yr)	Area Sources (lbs/yr)	Natural Sources (lbs/yr)	Total (lbs/yr)
Alameda	4.4	1.1	0.1	5.6
Contra Costa	299.3	0.6	0.1	300.0
Marin	0.0	0.2		0.2
Napa	0.0	0.1	0.0	0.2
San Francisco	0.1	0.6		0.6
San Mateo	0.3	0.5	0.0	0.9
Santa Clara	13.0	1.2	0.3	14.5
Solano	27.3	4.9	0.1	32.4
Sonoma	1097.9	1.5	0.2	1099.6



**Figure 2. Comparison of mercury emission from USEPA NTI and CARB datasets. Emissions are for 1996 in both cases. Data are shown for 58 counties in California. For some counties, estimates of total emissions can vary by more than one order of magnitude.**

In addition to the estimates developed by EPA and CARB, Abu-Saba and Tang (2000) also developed mercury emission estimates for the San Francisco Bay area. Three major source categories of emission were assessed: stationary sources (~250 kg), mobile sources (~20 kg), and area-wide non-combustion sources such as breakage of fluorescent lights (~100 kg/yr). These emissions are significantly below what has been estimated by EPA for the 9 counties in the San Francisco Bay region, and highlight the uncertainty underlying all mercury emission estimates.

California emissions account for 5.5% of the total US emissions of 187 tons annually (US EPA, 2002a). In the US in general, the principal sources of mercury emissions are electric utility and other commercial/industrial boilers, municipal waste combustors, and medical waste incinerators. The mix of sources is shown in Figure 3.

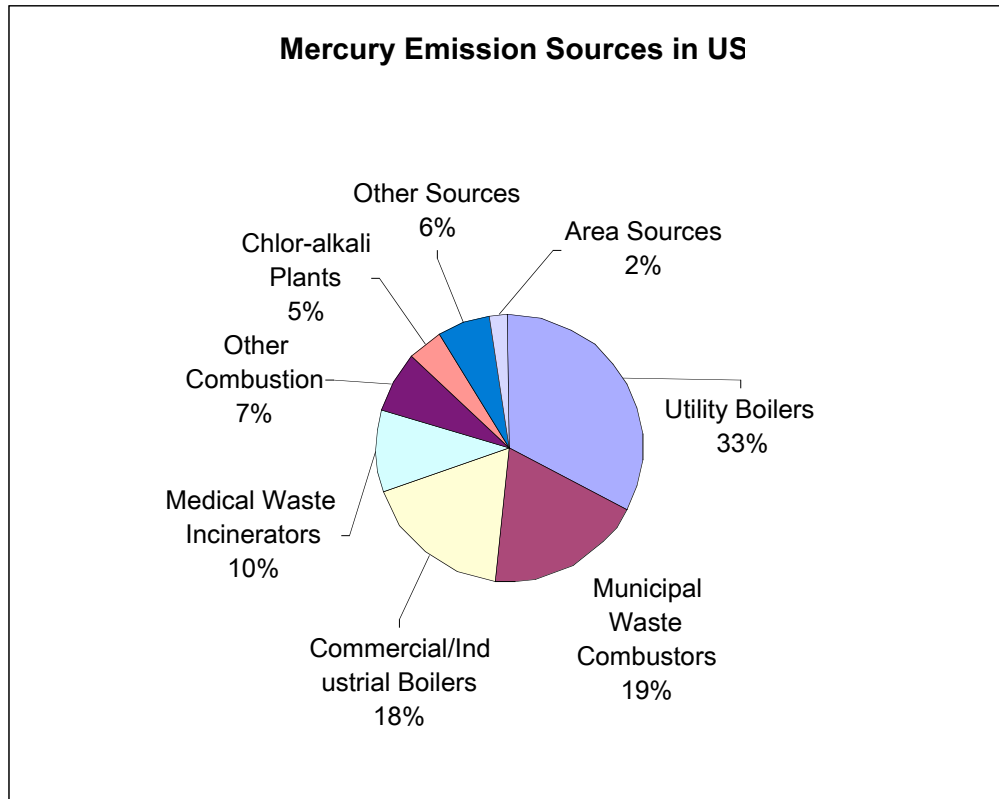


Figure 3. Distribution of mercury emission sources in the US by industrial category. Data from 1997 US EPA Report to Congress (USEPA 1997a).

#### 1A. 4. Key Uncertainties in Emission, Deposition and Bioaccumulation

Using detailed estimates of emissions of mercury from point sources and area sources published by two agencies, US EPA and CARB, we find that there are substantial differences between the two estimates, in many cases by more than a factor of two, sometimes by more than an order of magnitude. These differences exist both for point sources and for other, more diffuse sources. Methods used in developing the estimates were not evaluated in enough detail to explain the differences. Although it is reasonable to first use the data from CARB for load calculations relating to San Francisco Bay because they are based on local information, the wide differences in the emission estimates between the two agencies nonetheless underscore the point that all emission estimates need to be treated with caution. Should control of mercury emissions become necessary for reasons outlined here, more refined emission estimates will be required. Based on the data shown in Table 2, the role of medical waste incinerators in overall mercury emissions must be reliably estimated, because they are a large and potentially

controllable source in the vicinity of the bay. As the attached Appendix discusses, control of emissions from medical waste incinerators in Florida may have contributed to the decline in observed mercury concentrations in biota.

The greatest uncertainty in deposition calculation arises from methods used to estimate dry deposition, which constitutes more than three-quarters of the deposition input to the bay. Because different gas-phase forms of mercury have very different deposition velocities, it is essential to determine the gas-phase speciation of mercury directly. This was not done in the SFEI study because of sampling equipment problems. Speciation of total gas-phase mercury was performed based on literature-reported values, most of which pertained to the north-eastern US (95%  $\text{Hg}^0$ ; 2%  $\text{Hg}^{2+}$  and 3%  $\text{Hg}$ , particulate). Should the measured fraction of  $\text{Hg}^0$  differ from the estimated value by a relatively small amount (e.g., from 95% to 90%) there will be a change of almost a factor of two in the calculated dry deposition of mercury. With all other parameters remaining constant, the estimate of total deposition input will increase to ~160 kg. For this reason, it is highly recommended that region-specific gas-phase species data be obtained in subsequent work.

Based on the mercury species that are dominant in wet and dry deposition ( $\text{Hg}^{2+}$  species, fine mercury containing particles, gaseous elemental mercury), two hypotheses regarding atmospherically deposited mercury are possible: (1) a large fraction of the mercury that deposits atmospherically is in a form that is relatively bioavailable, and when transported to the sites of bacterial methylation, may become chemically available to sulfate reducing bacteria that produce methylmercury, (2) the mercury that deposits is reactive enough that a significant fraction of it is re-emitted to the atmosphere. If the first hypothesis were true, it follows that even though atmospherically deposited mercury forms only ~10% of the total mercury load to the bay, it may be a much larger fraction of the *bioavailable* mercury that finds its way up the food chain. If the second hypothesis were true, atmospheric deposition would be a relatively insignificant additional source of mercury to the bay. Determining which of these two hypotheses is more applicable to the bay is essential to fully evaluate the importance of mercury deposition to bioaccumulation in the biota.

### **SUBTASK 1B: PROPOSE STUDIES TO RESOLVE KEY UNCERTAINTIES AND SUGGEST MECHANISMS FOR FUNDING AND IMPLEMENTING NEEDED STUDIES**

In this section we discuss approaches to improve our knowledge of mercury emissions, deposition, and bioaccumulation. Because of the global nature of atmospheric mercury cycling, studies to resolve uncertainties with respect to the nature and magnitudes of sources in the San Francisco Bay region will involve local data collection and monitoring as well as partnerships with other research groups across the US and the world. The experience of management of mercury problems in other large water bodies, such as Chesapeake Bay (Mason et al, 1999) and the Florida Everglades (SFWMD, 2002), must also be considered in designing and obtaining funding for needed monitoring and research. We discuss at some length in Appendix A the regulatory and scientific activities to reduce mercury levels in biota in the Everglades of South Florida because of

the major role of atmospheric deposition in mercury contamination in this region. Efforts to reduce mercury in the Everglades began in the early 1990s and continue to date. Knowledge of the South Florida experience may be helpful as the Clean Estuaries Partnership considers plans to reduce atmospheric mercury loads into San Francisco Bay.

### **1B. 1. Emissions**

A reliable inventory of mercury emission sources near the bay is needed. The differences in the estimates of emissions from EPA and CARB (shown in Table 3 and 4, and Figure 2) are large enough that the accuracy of the data may be questioned, especially when the emissions database are used as a basis to control emissions. This is not to imply that the CARB and NTI estimates are flawed, but these estimates were performed with other goals in mind, and looked at a large number of other toxic air pollutants in addition to mercury. An emission inventory targeted only at mercury may provide more robust and accurate information on the amount and nature of mercury that is being released in the counties near the bay. This detailed emission inventory should be coupled with more spatially detailed deposition estimates (see below) to identify which sources are more important in local deposition. Funding for such a study may be obtained from EPA and cities and municipalities around the bay.

### **1B. 2. Deposition**

Although the SFEI deposition study (SFEI, 2001) provides a good first-order estimate of the atmospheric contribution of mercury to overall loads in the bay, for the purpose of planning atmospheric load reductions, further data are needed. We recommend a more detailed sampling network of about 6-8 stations including locations in the bay and also near urban point sources of mercury emission. The stations should measure wet deposition of mercury, and speciate the gas phases of mercury for calculation of dry deposition. Techniques for gas-phase mercury speciation have been widely published (Munthe et al., 2001; Stratton et al., 2001). Furthermore, some of the deposition monitoring stations should be designed to be permanent so that they can be used to develop a long term monitoring record of atmospheric loads to the bay, and possibly become a part of the national mercury deposition network (MDN). Funding and technical assistance for this study may be obtained from agencies such as the US Geological Survey, Electric Power Research Institute, Regional Monitoring Program, and the US Environmental Protection Agency.

Using information in wet deposition samples on the abundance of other trace and major ions, it is possible to try to explain the source of the deposition. Such methods were used in Florida to associate mercury deposition to specific sources such as medical waste incinerators (Dvonch et al., 1999). Although the results of these analyses are not without controversy, such studies could be attempted in the San Francisco Bay region to link specific source types to deposition. The data could also show that there is no local source signal, and the deposition is controlled by the global background pool as suggested by the RELMAP modeling discussed above.

### 1B. 3. Bioavailability of Deposition

Over the long term, the bioavailability of atmospherically deposited mercury should serve as the principal basis of regulatory efforts to control mercury in San Francisco Bay. If this mercury is more bioavailable and can methylate more rapidly than mercury from other, land-based sources, it may be appropriate to fund efforts to control atmospheric inputs, as opposed to larger, but less bioavailable, sources. From initial reports of studies in the Florida Everglades, it appears that newly added mercury in mesocosms is taken up more readily by biota than existing sediment-bound mercury. Studies in the Everglades involve the use of small mesocosms to which radio-labeled mercury is added as an external spike, in a manner analogous to wet deposition. Addition in a radio-labeled form allows scientists to track the added mercury separately from what is naturally present in the mesocosm. The subsequent methylation and uptake of the radio-labeled mercury by the biota provides information on the potential rates of uptake of atmospherically deposited mercury. Although results from the Florida mesocosm experiments are preliminary, if the experiments consistently result in preferential methylation and uptake of newly deposited mercury versus mercury associated with resident sediments or bound in geologic materials, they could provide a strong basis for cutting emission and deposition of new mercury even when there are other significant mass sources of mercury present in a water body. This research, being conducted by the USGS, is pertinent to San Francisco Bay. Reduction of atmospheric loads will be warranted if it is conclusively demonstrated that newly deposited mercury in the bay is more bioavailable than the large existing reservoir of mercury in sediments. It is recommended that the research now being conducted in Florida be followed closely by members of the Clean Estuaries Partnership over the next 12-18 months.

Over the next year or two, it is proposed that some lab-scale studies be conducted to evaluate the relative bioavailability of atmospheric deposition and other sources of mercury in San Francisco Bay. A possible technique to conduct such a study would be to look at the rates of methylation of mercury in vials with mercury-containing sediment from San Francisco Bay. These rates could be compared to rates where in addition to the sediment, soluble ionic mercury was also added. If the methylation rates were to increase in the presence of added soluble mercury, this would be an analog for the effects of addition of a bioavailable load to the estuary (such as deposition). If the methylation rates were to remain unchanged upon addition of additional mercury, this would be indicative of other rate limitations in the methylation process (not availability of mercury). Either result would be relevant in making a policy decision to control emission sources. Scientists at the USGS Menlo Park Laboratory have a unique expertise in this area and should be called on to propose a detailed study. Funding for such a study may come from the Regional Monitoring Program, the US Geological Survey, and the US Environmental Protection Agency.

Over a longer term, two to five years, we recommend that the Clean Estuaries Partnership support and conduct field scale experiments to understand the cycling and uptake of mercury by biota in San Francisco Bay. These studies should not be directed only at atmospheric deposition, but rather at determining the major sites and mechanisms controlling the dissolution and methylation of *all* sources of mercury present in the bay, and the processes controlling uptake in the food web. The field study sites should be

placed at different locations in the bay to evaluate the importance of specific local sources (e.g., Central Valley, Guadalupe River, tidal wetlands, etc.). These studies should consist of (1) detailed monitoring of chemistry of the water column and sediment, (2) experiments with small sediment cores (i.e., few inches in diameter) to identify the rates of methylation and demethylation of mercury and (3) larger enclosed field mesocosms (i.e., a few feet in diameter) where the uptake of mercury by larger organisms can be studied. Data from such a study will provide a rationale for prioritizing source reductions, and also allow an estimate of the rapidity with which changes in the bay will be observed, e.g., years versus decades. This will be a large study and will require a long term funding commitment. Agencies such as the US Geological Survey, US Environmental Protection Agency, CalFed and dischargers to the bay should be considered potential funding sources.

### **SUBTASK 1C. EVALUATE FEASIBILITY, POTENTIAL LOAD REDUCTION, AND EXISTING REGULATORY TOOLS FOR REDUCTION OF LOCAL AND LONG-RANGE AIR EMISSIONS**

A recent modeling study conducted using the RELMAP Model was used to estimate the contribution of different types of sources to the total atmospheric concentration of mercury in different regions of the US (USEPA 2002a). The RELMAP model has been used extensively by EPA in the 1997 Report to Congress (USEPA, 1997b) to estimate the atmospheric fate and transport of mercury over the continental United States. The sources considered include point sources, area sources, and onroad and offroad mobile sources, and the background. RELMAP estimates of resultant air concentrations from different sources are shown in Table 5. In almost all of the 9 bay counties, with the exception of San Francisco and Alameda counties, the background was the single most dominant contributor to the total concentration. Wind patterns over the San Francisco Bay region indicate that the prevailing wind direction is from the Pacific Ocean towards land, thus supporting the idea that there are no major mercury sources upwind of San Francisco Bay and that background levels may dominate the mercury concentrations in the atmosphere in the vicinity of the bay.

Table 5. Estimated atmospheric concentrations of Hg by emission source

County	Average Air Conc (ng/m <sup>3</sup> )	Point Sources (ng/m <sup>3</sup> )	Area and Other Sources (ng/m <sup>3</sup> )	Onroad Mobile Sources (ng/m <sup>3</sup> )	Nonroad Mobile Sources (ng/m <sup>3</sup> )	Estimated Background (ng/m <sup>3</sup> )
<b>Sonoma</b>	2	0.002	0.493	0.00027	0.00687	1.5
<b>Napa</b>	1.7	0.00582	0.188	0.000218	0.00469	1.5
<b>Marin</b>	1.68	0.0116	0.158	0.000418	0.0132	1.5
<b>Solano</b>	1.67	0.0296	0.133	0.000368	0.0112	1.5
<b>Contra Costa</b>	1.81	0.0311	0.25	0.000718	0.0255	1.5
<b>San Francisco</b>	3.66	0.0132	2.03	0.00224	0.121	1.5
<b>Alameda</b>	2.26	0.0162	0.698	0.00118	0.0405	1.5
<b>San Mateo</b>	1.92	0.00401	0.387	0.000936	0.0295	1.5

Based on the information presented above, it appears that there is little reduction of deposition that can be achieved by control of local emission sources in the San Francisco Bay region. However, there is another pathway for atmospheric loads to the bay, that of local deposition from major sources, that is not fully considered in a continent-scale modeling study such as RELMAP. As shown in the schematic for atmospheric cycling of mercury (Figure 1), emissions in the particulate or ionic form (Hg(p) or Hg<sup>2+</sup>) may deposit near their sources. Data on local deposition effects from major point sources were not available to assess the importance of this mechanism. Should local deposition be found to be a significant influence, especially in some regions of the bay and its watershed, control of some of the larger local emission sources can be considered. For this reason, it is important that a more spatially detailed deposition study be conducted, as outlined under Subtask 1B.

Of the sources responsible for significant mercury emissions in the San Francisco Bay and surrounding region, medical waste incinerators stand out as one of the largest sources (Table 2). Emissions from medical waste incinerators can be controlled by management of the waste stream and add-on emission control technology, an approach that has been successfully applied in Florida and is discussed in Appendix A. Using a combination of pollution prevention and control technologies, emission reductions of upto 90% from 1990 levels have been achieved. US EPA has proposed emission standards for medical waste incinerators in August 2000 (0.55 mg per standard dry cubic meter). The emission inventory reported in Table 2 applies to 1996, the most recent year for which this data is available. The inventory therefore does not reflect the most recent regulations regarding mercury emissions, and current emissions may be lower than what is reflected in the recently published inventory. In addition to medical waste incinerators, US EPA has also proposed standards for municipal waste combustors in 1995 (0.08 mg per dry standard cubic meter) that may not be reflected in the 1996 inventory. The Clean Estuary Partnership needs to determine whether some of this reduction has already taken effect and how much further reduction in medical waste incinerator and municipal combustor emissions are feasible with the existing standards.

Nationally, there are efforts underway to reduce the emissions of mercury from major sources over the next two decades. The bulk of the mercury reductions in the recently proposed Clear Skies Initiative (USEPA, 2002b), for example, will be based on power plant emission reductions. Because most of the large coal fired power plants in the US are not in California, and because San Francisco Bay is upwind of most of the mercury emissions in the rest of the US, it is not clear if there will be any direct benefit of the mercury emission reductions. However, to the extent that these emission reductions cause a decrease, or a reduction in the rate of increase, in the global atmospheric mercury pool, there may be indirect benefits to San Francisco Bay. Note, however, that global emissions of mercury are continuing to increase and any reductions in US emissions may be outweighed by increased emissions in other parts of the globe, particularly from coal burning in Asia.

## 7. SUMMARY

Available data shows that atmospheric deposition of mercury is responsible for just over 10% of the total mercury load entering San Francisco Bay (~80 kg out of a total of ~640 kg, Abu-Saba, 2002). Programs attempting to reduce mercury levels in the sediments and biota of the bay should consider efforts to reduce mercury emissions and atmospheric deposition. Emission inventories indicate the presence of significant mercury sources in the counties in the San Francisco Bay region, although exact estimates of emissions vary, depending on the agency performing the estimate (California Air Resources Board or US EPA National Air Toxics Assessment). It does appear from EPA data that medical waste incinerators are a major source of emissions in the areas surrounding the bay. Other large sources of emissions nationally, such as coal combustion, are not important in this region of the US. Model studies conducted by EPA show that the dominant fraction of mercury in air in the San Francisco Bay area counties can be explained by background levels, thus indicating the limited ability of local sources to influence deposition. However, the large-scale regional models do not consider local deposition which may be important in some areas surrounding the bay, but for which there was no data.

For the implementation plan of the mercury TMDL as it pertains to mercury deposition, additional studies in three areas are proposed:

1. Additional work needs to be done to quantify emissions more accurately than is now available. We need a better understanding of the major sources, and a further evaluation of the significance of medical waste incineration, as indicated by the US EPA inventory.
2. Longer term and more spatially detailed deposition estimates are needed, especially speciation of gas phase mercury to better assess the contribution of dry deposition, and also the potential role of local deposition.
3. Laboratory studies need to be performed to compare the bioavailability of atmospheric deposition and the existing reservoir of sediment-associated mercury. A strong case for controlling deposition can be made if it is shown that

atmospheric inputs of mercury, although a small proportion mass-wise, are more bioavailable, and hence have greater potential to accumulate in biota.

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## Appendix A

### MERCURY IN FLORIDA

The approach followed by regulatory agencies in Florida in response to the discovery of high fish-tissue concentrations of mercury in the Everglades provides a case study of how mercury issues in San Francisco Bay might be addressed.

When the problem of mercury in the Everglades was first discovered in the late 1980s, virtually nothing was known of its causes, effects, or potential solutions. In response, the Florida Department of Environmental Protection (DEP) and the South Florida Water Management District (SFWMD) organized a multi-agency group to understand the causes of the mercury problem in Florida. Operating as the South Florida Mercury Science Program, these agencies have sponsored research and assessment that have improved the understanding of the sources, transformations and fate of mercury in the Everglades. The program has also been effective at linking local information to that at regional and global levels to better support decision making in South Florida and improve the estimation of risks to fish-eating Everglades wildlife. One of the key findings from this collaborative effort on mercury includes the determination that:

- Atmospheric deposition accounts for greater than 95 percent of the external load of mercury to the Everglades. Once deposited, the effect of newly deposited mercury is quickly felt through a burst of methylmercury production occurring over a period of hours to days. The relative proportions of local and long-range transport of mercury to the Everglades remain an open question (SFWMD, 2002).

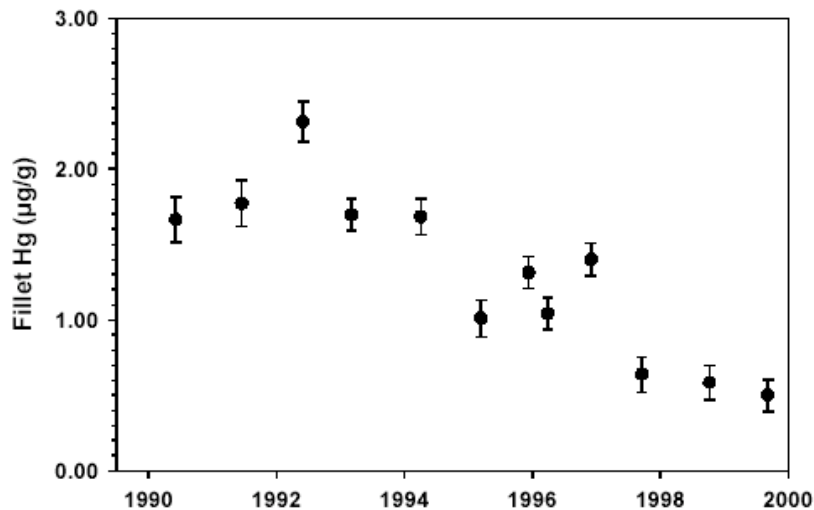
Finding remedies for the problem of excessive mercury in fish has been limited by the lack of knowledge of its causes. However, one general aspect of the solution is clear: mercury emissions to the environment should be limited where available information and technology allow. The DEP has vigorously pursued the following approaches:

- *Pollution Prevention* – The 1993 Florida Solid Waste Management Act required elimination of mercury from some commercial products and will reduce the mercury content of wastes. It bans the use of mercury in packaging materials, prohibits incineration of mercury-containing devices, promotes recycling of such products and phases out the use of mercury-containing batteries. Presently, international treaties within North America and between North America and Europe are seeking further reductions in the use of mercury.
- *Waste Disposal* – Hazardous waste regulations have been tightened to require stricter control of mercury-containing wastes. Proper disposal minimizes the long-term releases of mercury into the environment. A side effect of stricter regulation of mercury discharges has been to encourage elimination of mercury from commercial products and industrial processes.
- *Emissions Control* – A Florida emissions inventory found that the major sources of atmospheric mercury were municipal solid waste combustors, medical waste

incinerators and electric utility boilers. DEP adopted the first U.S. regulations limiting emissions of mercury from waste combustors and has adopted USEPA regulations for medical waste incinerators. Solid waste combustor emissions controls (e.g., carbon injection systems, scrubbers) are in place on most facilities in Florida, and medical waste incinerator emissions have dropped sharply as the industry has moved away from incineration in response to emissions regulations. Emissions in Florida from each of these sectors have dropped more than 90 percent since 1990 (SFWMD, 2002).

Source controls have the greatest likelihood for reducing the mercury problem by decreasing the delivery of atmospheric mercury to the Everglades. Findings from both environmental monitoring and computer models suggest control of atmospheric sources of mercury can have positive benefits for the Everglades Protection Area. Monitoring over the last decade suggests that lower emissions are producing a corresponding reduction in mercury burdens of Everglades fish and wading birds.

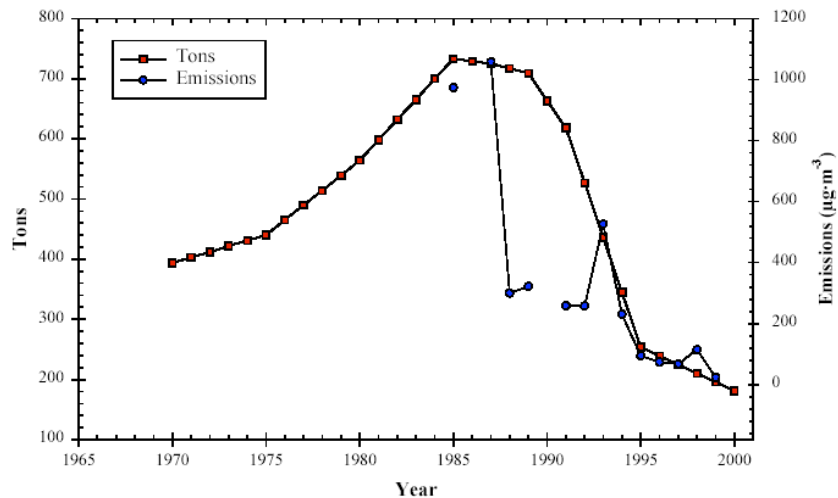
Data from about 1994 to the present suggest mercury levels are declining in Everglades biota. Figure A-1 shows a continuing, if small decline in mercury in largemouth bass. Similar declines have been observed in mercury levels in the feathers of great egret nestlings. This apparent trend is consistent with the timing and extent of a national trend in the mercury content of incinerated trash in the United States. While this evidence is preliminary, it is consistent with the time lag predicted by modeling for a decline in atmospheric deposition resulting from decreasing amounts of mercury emitted by air sources within South Florida.



**Figure A-1. Mercury concentrations in size-standardized largemouth bass in a specific location in the Everglades (L-67 canal) (SFWMD, 2002).**

How these trends in mercury in biota compare to trends in mercury load to the Everglades or to emissions trends in the United States or Florida are unknown. Figure A-2 illustrates national estimates of mercury in municipal solid waste from 1970 to 1990, as

well as projected trends to 2000. For comparison purposes, presented on a separate scale is the annual trend of Municipal Waste Combustor (MWC) (i.e., incinerator) emissions concentration of all facilities in Florida, from Tampa south. As indicated, the trends appear to be sharply downward.



**Figure A-2 Estimated trends of mercury in U.S. municipal solid waste from 1970 to 2000, and South Florida Municipal Waste Combustor emission concentrations from mid-1980s to 2000.**

Atmospheric deposition trend monitoring of rainfall mercury deposition began in South Florida, with the establishment of four monitoring sites of the Florida Atmospheric Mercury Study (FAMS) adjacent to the Everglades in 1994 and 1995 and continuing through 1996. In 1995, DEP sponsored the installation of one of the first Mercury Deposition Network (MDN, a sub-network of the National Atmospheric Deposition Program) sites at the ENP Beard Center, collocated with the FAMS site there. The sites, operated by their respective groups side-by-side for 15 months, established that comparability was excellent. After completion of the FAMS project, SFWMD assumed responsibility for the ENP MDN site and established two others (Andytown and ENRP) to ensure continuity of long-term trend monitoring of atmospheric mercury wet deposition to the Everglades. Recent meta-analysis of mercury wet deposition from both FAMS and MDN does not indicate any significant trend (Pollman and Atkeson, 2001, in prep). It is likely that emissions reductions occurred before the monitoring began in 1994, and data variability will hamper trend detection in deposition data.

The question of the importance of the global background source of mercury coming into Florida remains one of significant debate. Beginning with the FAMS observations and supplemented by additional measurements in South Florida and elsewhere, deposition has been shown to be strongly seasonal. Approximately 85 percent of rainfall mercury

deposition to the Everglades occurs during the summer months, when the easterly trade winds come from the Atlantic Ocean (Guentzel, 1997; Guentzel et al., 2001). The advection of large amounts of total mercury by trade winds over the Florida peninsula is not in dispute, but it is not known how much RGM is thereby made available to contribute to deposition.

Air-surface interactions of mercury are bidirectional. Whatever its ultimate source, mercury in water bodies, wetlands or upland soils may be chemically reduced to the volatile, elemental form and emitted to the atmosphere. With its long residence time in the atmosphere, elemental mercury emitted or re-emitted from the earth's surface enters the global atmospheric mercury cycle, becoming a source of atmospheric mercury even in regions remote from human activities. Much of the increasing energy consumption predicted for developing nations will come from the combustion of coal (a fuel with a high mercury content). Unless global controls are instituted, the global background of atmospheric mercury can be expected to rise in coming years.

Because the data are limited, this apparent continuing trend of reductions in emissions and fish and wading bird body burdens of mercury remains a working hypothesis that will be subject to data evaluation from other sites within the Everglades and Florida and to rigorous statistical analysis. Monitoring of mercury trends in atmospheric deposition, fish and wading birds will continue indefinitely. It is likely that much of the emissions reduction responsible for this apparent trend occurred prior to the initiation of mercury monitoring in wet deposition in South Florida. The time lag between emissions reduction and fish and bird reduction is consistent with the lag predicted by E-MCM modeling. Further work, consisting of hind-casting emissions and examination of new sediment cores, is underway to test this hypothesis (SFWMD, 2002).

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