

San Francisco Estuary Regional Monitoring Program for Trace Substances

San Francisco Bay Atmospheric Deposition Pilot Study Part 1: Mercury

**Pam Tsai
Rainer Hoenicke**

SFEI Contribution 72
July 2001

San Francisco Estuary Institute



San Francisco Bay Atmospheric Deposition Pilot Study

Part 1: Mercury

Submitted by:
Pam Tsai, Principal Investigator
Rainer Hoenicke, RMP Program Manager
San Francisco Estuary Institute
1325 South 46th Street
Richmond, CA 94804

July 2001

ACKNOWLEDGEMENT

Funding Sources

Funding was provided by participants of the Regional Monitoring Program for Trace Substances in the San Francisco Bay Area, the Bay Area Clean Water Agencies, the California Regional Water Quality Control Board, the City of San Jose, and the U.S. Environmental Protection Agency.

Collaborating Agencies

Central Contra Costa Sanitary District
City and County of San Francisco
City of San Jose
San Francisco Estuary Institute
San Francisco Estuary Project

Science Review Group Members

Carol Bohnenkamp, US Environmental Protection Agency, Region IX
Charles Blanchard, Envir Environmental Consulting Company, Albany, CA
Bhupinder Dhaliwal, Central Contra Costa Sanitary District, Martinez, CA
Eric Hansen, City of San Jose, San Jose, CA
Rainer Hoenicke, San Francisco Estuary Institute, Richmond, CA
Lynn Hildemann, Stanford University, Palo Alto, CA
Guy Kumar, City and County of San Francisco, San Francisco, CA
Joel Pedersen, U.S. Environmental Protection Agency, Region IX
James Pederson, California Air Resources Board, Sacramento, CA
James Salerno, City and County of San Francisco, San Francisco, CA
David Tucker, City of San Jose, San Jose, CA
Donald Yee, San Francisco Estuary Institute, Richmond, CA

Site Operations

South Bay Site:	Charles Allen, City of San Jose Peter Chen, City of San Jose Eric Hansen, City of San Jose Kenneth Lee, City of San Jose Kobin Lee, NASA Ames Research Center
Central Bay Site:	Arlene Giordano, City and County of San Francisco Guy Kumar, City and County of San Francisco
North Bay Site:	Mary Lou Esparza, Central Contra Costa Sanitary District Susan Hasselwander, Central Contra Costa Sanitary District Pedro Mendoza, Central Contra Costa Sanitary District

Quality Assurance Officer

Donald Yee, San Francisco Estuary Institute, Richmond, CA

Instrumentation Loans

California Air Resources Board, Sacramento, CA

Bay Area Air Quality Management District, Richmond/San Pablo Station, Richmond, CA

ACKNOWLEDGEMENT (CONTINUED)

Meteorological Information

Bay Area Air Quality Management District, San Francisco, CA

Central Contra Costa Sanitary District, Martinez, CA

Technical Editor

Patricia Chambers, San Francisco Estuary Institute, Richmond, CA

Peer Reviewers

Don Birrer/Chuck Weir, East Bay Dischargers Authority, San Lorenzo, CA

Geoff Brosseau, Bay Area Stormwater Management Agencies Association, Oakland, CA

Terry Cooke/John Koehler, URS Corporation, Oakland, CA

Eric Hansen, City of San Jose, San Jose, CA

Lynn Hildemann, Stanford University, Palo Alto, CA

Andy Jahn, Port of Oakland, Oakland, CA

James Kuwabara, US Geological Survey, Menlo Park, CA

Robert P. Mason, Chesapeake Biological Laboratory, University of Maryland, Solomons,
MD

Lester McKee, San Francisco Estuary Institute, Richmond, CA

Doug Steading, University of California at Santa Cruz, CA

Clyde Sweet, Illinois State Water Survey, Champaign, IL

Donald Yee, San Francisco Estuary Institute, Richmond, CA

Other Contributors

Jon Leatherbarrow, San Francisco Estuary Institute, Richmond, CA

Robert P. Mason, Chesapeake Biological Laboratory, Solomons, MD

Lester McKee, San Francisco Estuary Institute, Richmond, CA

Clyde Sweet, Illinois State Water Survey, Champaign, IL

Victor Tsai, California Institute of Technology, Pasadena, CA

TABLE OF CONTENTS

ABSTRACT	8
1.0 INTRODUCTION	10
2.0 OBJECTIVES OF THE STUDY	12
3.0 METHODOLOGY	
3.1 General Methodology for Atmospheric Deposition Study	14
3.2 San Francisco Bay Atmospheric Deposition Pilot Study.....	14
3.2.1 Dry Deposition	6
3.2.2 Wet Deposition.....	17
3.2.3 Quality Assurance and Quality Control.....	18
4.0 RESULTS AND DISCUSSION	
4.1 Dry Deposition	20
4.1.1 Ambient Air Concentration.....	20
4.1.2 Estimate Deposition Loading: Modeling Equations.....	20
4.1.3 Evaluation of Modeling Input Parameters	22
4.1.4 Loading of Mercury from Atmospheric Deposition.....	24
4.2 Wet Deposition.....	24
4.3 Total Loading from Direct Atmospheric Deposition.....	26
4.4 Loading from Tributaries That is Atmospheric in Origin.....	26
4.5 Comparison of Loading from Different Sources and Pathways.....	27
4.6 Uncertainties in the Loading Estimates	29
5.0 CONCLUSIONS	31
6.0 REFERENCES	32

LIST OF FIGURES

- Figure 1. General Methodology for Atmospheric Deposition Study
- Figure 2. Monitoring Sites Included in the San Francisco Bay Atmospheric Deposition Pilot Study
- Figure 3. Mercury Concentration in the Ambient Air – San Francisco Bay Area (Year 2000)
- Figure 4. Hydrologic Areas in the San Francisco Bay Region

LIST OF TABLES

Table 1.	Chemicals Selected for monitoring in the Pilot Study
Table 2.	Sampling Schedule for Trace Elements
Table 3.	Average Mercury Concentration in the Ambient Air
Table 4.	Parameters Used in Estimating Dry Deposition of Atmospheric Mercury
Table 5.	Dry Deposition of Atmospheric Mercury to the San Francisco Estuary
Table 6.	Estimated Volume-Weighted Average Mercury Concentration from Precipitation Collected at Sites in the San Francisco Bay Area
Table 7.	Wet Deposition of Mercury to the San Francisco Estuary
Table 8.	Concentration of Mercury in Precipitation and Estimated Deposition Flux Reported in the Literature
Table 9.	Summary of Mercury Loading from Direct Atmospheric Deposition to the San Francisco Estuary
Table 10.	Comparison of Mercury Loading to the San Francisco Estuary from Different Sources/Pathways
Table 11.	Assessment of Uncertainty Level in the Mercury Loading Estimates

ACRONYMS AND ABBREVIATIONS

BAAQMD	Bay Area Air Quality Management District
CARB	California Air Resources Board
CSJ	City of San Jose
CVAFS	Cold vapor atomic fluorescence spectrometry
DDW	Double deionized water
FOF	Field-observation Form
HAL	Hg Analytical Laboratory
Hg(II)	Divalent mercury (organic and inorganic species)
Hg(g)	Mercury in gaseous phase
Hg(0)	Elemental mercury
Hg(p)	Mercury in particulate phase (organic and inorganic species)
IPR	Initial precision and recovery
MDN	Mercury Deposition Network
MDL	Method-detection limit
MOF	Mercury Observer Form
NADP	National Atmospheric Deposition Program
OPR	Ongoing precision and recovery
POTW	Publicly Owned Treatment Works
PQL	Practical quantification level
RMP	Regional Monitoring Program for Trace Substances
SFBRWQCB	San Francisco Bay Region, California Regional Water Quality Control Board
SFEI	San Francisco Estuary Institute
SOP	Standard operating procedures
SRM	Standard Reference Material
TMDL	Total Maximum Daily Load
U.S.EPA	United States Environmental Protection Agency
V_d	Deposition velocity

ABSTRACT

This report is the first in a three-part series presenting a Pilot Study that was conducted from August 1999 through November 2000. The objective was to estimate the inputs of selected trace metals and trace organic pollutants from the atmosphere to the San Francisco Estuary in California. Ambient air samples and precipitation samples were collected at three sites strategically located around the Bay Area. This report covers the mercury component of the Pilot Study.

The Pilot Study evaluated deposition of atmospheric mercury to the San Francisco Estuary through dry and wet deposition. Analysis of total mercury in the ambient air and precipitation provided results for estimating mercury loading from dry and wet deposition, respectively. Direct atmospheric deposition of mercury to the Estuary includes loading from dry deposition and wet deposition. Indirect deposition of mercury from atmosphere to the Estuary is derived from the chemical being initially deposited to the watershed and then transported to the Estuary through runoff and tributaries, and constitutes the loading from this pathway that is atmospheric in origin. This report provides an estimate of the indirect atmospheric deposition through runoff and tributaries from the local watersheds in the San Francisco Bay Region, but excludes coastal areas that drain water directly to the Pacific Ocean. Estimate of indirect atmospheric loading through more remote watersheds such as the Sacramento River-San Joaquin River drainage areas is not included in the assessment.

Total mercury was detected in ambient air samples at concentrations of 1.5 to 4.2 ng/m³, with an average concentration of 2.1 ng/m³. Although this concentration is within the range detected in other areas of the U.S. and similar to those detected around the Chesapeake Bay area, it is about twice the concentration considered to be the global background. Flux of mercury to the Estuary from dry deposition was rather uniform with a mean of approximately 19 µg·m⁻²·yr⁻¹ and a range of 18 to 21 µg·m⁻²·yr⁻¹ estimated for different segments of the Estuary. Volume-weighted average mercury concentration in precipitation was 8.0 ng/L, ranging from 6.6 to 9.7 ng/L, within the range detected in other areas around the U.S. The average concentration detected in the San Francisco Bay Area is lower than the concentration of 11 to 15 ng/L found around the Chesapeake Bay area, but twice as high as those measured at some background locations along the U.S. west coast. Flux from wet deposition to the entire Estuary was estimated at 4.2 µg·m⁻²·yr⁻¹, ranging from 3.5 µg·m⁻²·yr⁻¹ at the South Bay site to 4.5 µg·m⁻²·yr⁻¹ at the Central Bay site, attributable to the differences in the amount of rainfall observed at different segments of the Estuary.

On an annual basis, it was estimated that direct atmospheric deposition, via both dry deposition and wet deposition, contributed approximately 27 kg of total mercury to the Estuary. Direct wet deposition constitutes about 18% of the total atmospheric deposition. Indirect inputs via deposition and runoff from the watersheds in the San Francisco Bay Region that drain water directly to the Estuary were estimated to contribute another 55 kg/yr of mercury loading to the Estuary. To put air-deposition loading into perspective, we compared mass loadings of mercury among the various major conveyances or pathways. Any comparison of loading estimates presented in this

report only serves as the first-level screening purposes, because these loading estimates are derived from different reports with various degree of uncertainty.

The uncertainty level in the estimates derived from this study is low (with an error of within $\pm 25\%$) for wet deposition, moderate-high (with an error of two to five folds) for dry deposition, and moderate-high for indirect deposition to surrounding land surfaces and subsequent tributary inputs attributable to atmospheric deposition. This results in a moderate-high uncertainty for overall estimates. It is very difficult to assess the uncertainty associated with mercury loadings estimated by other authors because the level of documentation differs, and different data sources, calculation approaches, and assumptions may have been used. It is believed that the mass-loading estimate of mercury from point-source discharges is fairly accurate due to recent implementation of clean-sampling, handling, and processing techniques, as well as the advanced technology in detecting mercury at ultra-low levels. The uncertainty associated with estimates of mercury inputs from watersheds and sediment remobilization is unknown and is likely very high in comparison.

Combining loading from atmospheric deposition of mercury directly to the Estuary and indirectly through runoff was estimated to contribute almost seven (7) times of the loading from wastewater discharges, an external point source. Results and evaluation presented in this report indicate that loading of mercury from wastewater discharges to the San Francisco Estuary likely constituted less than 2% of the total load from all sources and pathways, and less than 15% of the load from atmospheric deposition. Atmospheric deposition contributes a sufficient enough load of mercury to the Estuary to warrant further evaluation. Similar to the loading from watersheds, atmospheric deposition is an external loading conveyor of pollutants to the Estuary that is more feasible to manage than those from internal pollutant redistributing mechanisms like remobilization of buried sediment. In addition, pollutant loading from watershed runoff includes a component that is atmospheric in origin. Exploring a suitable strategy for minimizing mercury loading to the San Francisco Estuary should include an investigation of measures that can mitigate the sources and pathways that contribute to the releases of mercury to the atmosphere.

1.0 INTRODUCTION

Toxic pollutants are routinely emitted into the atmosphere either naturally or by human activities such as industrial discharges (stationary sources) and driving motor vehicles (mobile sources). Toxic pollutants can also be emitted from non-point sources such as soils, waste dumps, or agricultural fields. The distance and the pathway air pollutants can be carried depend on several factors: weather conditions, type of pollutant, the phase of the pollutant (solid, liquid, condensed vapor, or gas), and the size of the particle the pollutant is adsorbed. These factors also affect the removal of a pollutant from the atmosphere. Deposition of pollutants from the atmosphere to surface water can occur by several processes, including rain or snow-scrubbing of gases and particles, dry deposition of particles, deposition associated with cloud and fog water, and air-water exchange processes.

Mercury cycles through the atmosphere continuously and is deposited worldwide, making it hard to track. The U.S. EPA (2001) estimates that combustion of mercury-containing material accounts for 86% of the atmospheric mercury emissions in the U.S. and is broken down as follows:

- Coal-fired electric utility boilers-----33%
- Municipal waste combustion-----19%
- Coal- and oil-fired commercial/industrial boilers -----18%
- Medical waste incinerators -----10%
- Hazardous waste combustion -----4%
- Residential boilers -----2%

Another 10% of the total emissions come from industrial sources such as chlor-alkali, Portland cement, and pulp and paper manufacturing. The remaining 3% comes from laboratory uses, dental preparations, landfills, oil-fired electric utilities, sewage sludge incineration, wood-fired boilers, and miscellaneous sources such as geothermal power plants. Mercury can deposit from the air to the water and then re-volatilize to the atmosphere in a continuous cycle. In addition to emissions from domestic sources, a significant amount of mercury enters the United States from other countries as a result of the global transport. Worldwide, it is believed that approximately 34% of the mercury emitted into the atmosphere comes from coal combustion (USEPA 2001).

The most significant ongoing source of mercury to the San Francisco Estuary¹ (the Estuary) is the erosion of mercury-laden soils and drainage from abandoned mines, and moderate to low level of inputs comes from point sources (SWRCB 2001). In the Mercury TMDL Report to the U.S. EPA, the San Francisco Bay Region of the California Regional Water Quality Control Board (SFBRWQCB) has evaluated three general categories of sources that release mercury to the atmosphere in the Bay Area and provides the following estimates of mercury being released from these sources (Abu-Saba and Tang 2000):

a. Stationary combustion sources (incineration, calcination, and manufacturing

¹ In this report, San Francisco Estuary encompasses San Francisco Bay, San Pablo Bay, Carquinez Strait, and Suisun Bay.

- activities): 250 kg per year
- b. Mobile combustion sources (combustion of fuels from cars, trucks, and ships): 10-20 kg per year
- c. Area-wide non-combustion sources (breakage of fluorescent lamps; erosion and runoff from abandoned mines): 10 to 130 kg per year

It has been estimated that anthropogenic mercury emissions have tripled the mercury concentration in the air and in the surface of the ocean since 1900 (Mason et al. 1994). Atmospheric deposition may play a major role in influencing the water quality of the Great Lakes and other surface water bodies. The amount of direct deposition to the surface of the Great Lakes was estimated to be 83% of the total mercury load to the Lakes (Shannon and Voldner 1995), and 50% of the mercury in the Chesapeake Bay was estimated to come directly from air deposition (Mason et al. 1997).

This report describes the methodology used in the San Francisco Atmospheric Pilot Study (hereafter simply referred to as the Pilot Study) and presents the results of monitoring mercury in the ambient air and precipitation. It also provides estimates of mercury atmospheric deposition and the associated uncertainties. These estimates were compared with mass inputs from other major sources or pathways.

2.0 OBJECTIVES OF THE STUDY

Section 303(d) of the Clean Water Act requires States to identify impaired water bodies and the pollutants causing the impairment, and to establish a Total Maximum Daily Load (TMDL) of the pollutant to the water body allowable to eliminate the impairment. Mercury is one of the chemicals that have impaired all segments of the San Francisco Estuary and some of the rivers, creeks, and reservoirs surrounding it. Total recoverable mercury detected in the water in Lower San Francisco and South San Francisco Bay exceeded the Basin Plan numeric objective established by the SFBRWQCB. In addition, fish caught from the Estuary have shown mercury concentrations at levels that may pose a threat to human health, if consumed.

In addition to identifying pollutants that cause the impairment of water bodies, the state must identify pollutant sources and allocate the allowable pollutant load from those sources. An implementation plan must also be established, and the TMDL allocation and implementation plan must be incorporated into the state's basin plans.

The determination of the impairment caused by some chemicals is often based on limited or poor quality data. In such cases, there is a compelling need to conduct a more complete assessment to confirm or refine the impairment listing. The problem concerning mercury is well defined by the SFBRWQCB (Abu-Saba and Tang 2000), but the sources and pathways for mercury inputs are not well understood. Estimating relative magnitude of loading contributed from each potential source and pathway is one of the first steps toward implementing the TMDL workplan for mercury.

Five primary sources or pathways were identified to contribute pollutant loading to the Lower and Central South San Francisco Bay (TetraTech 1999). These sources and pathways are also the primary contributors of pollutant loading to the entire San Francisco Estuary.

- a. Non-point sources associated with runoff and erosion (load from tributaries and storm drains)
- b. Exchange with the sediments (net particulate flux from buried sediment) or benthic remobilization: an internal process that redistribute pollutants to different compartments within the Estuary
- c. Direct atmospheric deposition
- d. Point-source wastewater effluent discharges from municipal (Publicly-Owned Treatment Works, POTWs) and industrial facilities.
- e. Net exchange within the water column and bed-load transport (diffusive flux): an internal process within the Estuary

Among the five primary sources or pathways of pollutant loading, benthic particulate remobilization and diffusive flux within the water column are internal processes that redistribute pollutants to different compartments within the Estuary, and they may be less feasible to manage. On the other hand, loadings from point source wastewater discharges, tributaries, and direct atmospheric deposition are external sources that may be more manageable. It is worthwhile to note that loading from tributaries includes a

component that is atmospheric in origin, and in some cases it includes a secondary input from mine drainage, or erosion from natural geological sources.

Williston (1968) reported atmospheric mercury concentrations of 0.5 to 25 ng/m³ in the winter and 1.0 to 50 ng/m³ in the summer from samples collected in Los Altos, CA. Los Altos lies 15 miles from the Pacific Ocean on the southwestern side of the San Francisco Estuary, and about 25 miles from the New Almaden Mercury Mine. The New Almaden Mercury Mine operated from 1845 until its closure in 1975, and was once the largest producer of mercury in North America (Abu-Saba and Tang 2000). The New Almaden Mercury Mine has since been closed; instrumentation for monitoring and analyzing mercury has been vastly improved; and clean sample-handling techniques have been implemented. Results from Williston's study may represent an overestimate and are unlikely indicative of the current atmospheric concentrations of mercury in the Bay Area.

This Pilot Study was initiated and funded by organizations that participate in the Regional Monitoring Program for Trace Substances (RMP), a long-term environmental monitoring program implemented in the region. The San Francisco Estuary Institute (SFEI), a scientific institute located in Richmond, CA, served to coordinate and manage the Pilot Study under the umbrella of the RMP.

Established methods were used in monitoring concentrations of mercury in the ambient air (Pirrone et al. 1995, USEPA 1997) and in precipitation (Vermette et al. 1995b). Reasonable assumptions and parameters were incorporated into estimating deposition loading of mercury from the air directly to the surface of the San Francisco Estuary. Estimates of mercury deposition from the atmosphere onto land surfaces surrounding the Estuary and subsequent input through runoff from tributaries are also presented. Uncertainty level associated with each estimated loading was assessed semi-quantitatively.

Results from this Pilot Study provide the first set of atmospheric mercury data collected and publicly released in the San Francisco Bay Area since the late 1960s. Primary objectives of the Pilot Study were to:

- a. estimate the loading of mercury from atmospheric deposition directly to the Estuary surface;
- b. estimate the loading of mercury from atmospheric deposition to other surfaces and potentially indirect loading to the Estuary (atmospherically-derived tributary load); and
- c. compare the loading from atmospheric deposition to loadings from other major quantifiable or semi-quantifiable sources and pathways.

Results from the Pilot Study can be used to further investigate sources of mercury and explore potential mechanisms that can be used to reduce total loading of mercury to the Estuary.

3.0 METHODOLOGY

Deposition of air pollutants to the Estuary surface water can occur by several processes, including rain scavenging of gases and particles, dry deposition of particles, deposition associated with cloud and fog-water, and air-water exchange processes. The methodology used for this study to measure atmospheric deposition of air pollutants consisted of sample collection during rain events for wet deposition and during non-rainy days for dry deposition. Air-water exchange processes were included in the estimate of dry deposition, but deposition through cloud and fog-water was not addressed in this study.

3.1 General Methodology for Atmospheric Deposition Study

A summary of the general atmospheric deposition study methodology is presented in Figure 1. The wet deposition study measures pollutant concentrations in the rainfall, captured by specific precipitation collectors.

Other investigators have used both direct and indirect methods to study dry deposition. The direct method measures concentration in particles depositing on a surrogate surface or deposition plate (surrogate plate) during non-rainy days. The indirect method monitors pollutants from the ambient air, and performs inferential calculations to determine depositional rates. Direct method using surrogate plate is not suitable for monitoring chemicals such as mercury in the atmosphere that exist predominately in the gaseous phase. Therefore, indirect method was used in this study.

3.2 San Francisco Bay Atmospheric Deposition Pilot Study

An initial conceptual study design for the Pilot Study (CSJ 1998) was further evaluated and refined into the Final 1999 Workplan (SFEI 1998) and 2000 Workplan (SFEI 1999). The 1999 Workplan considers the study objectives and specific issues that are relevant to San Francisco Bay in developing protocols for the Pilot Study. Key components include chemicals of concern, ancillary measurements, monitoring duration and frequency, and sampling site selection. The 1999 and 2000 Workplans provide details of the study design. Detailed sampling procedures are presented in the Standard Operating Procedures pertinent to each specific field operation and laboratory analysis. A brief discussion of the methodologies used in the Pilot Study is presented below.

Monitoring Parameters

The Pilot Study was designed to obtain estimates of dry deposition during non-rainy days as well as wet deposition from precipitation. To facilitate timely implementation, the Pilot Study was divided into two phases (Table 1): Phase 1 monitored trace metals, including mercury that is the main topic of this report, and Phase 2 addressed trace organic compounds.

Monitoring Duration and Frequency

The California Air Resources Board (CARB) and the Bay Area Air Quality Management District (BAAQMD) are maintaining an extensive network to monitor ambient air quality in the San Francisco Bay Area. The original intent of the Pilot Study was to collocate Pilot Study sites with the existing air monitoring sites managed by

CARB or BAAQMD. During planning stages of the Pilot Study, it became apparent that it was not feasible to collocate sampling sites at existing stations because of economic and logistical considerations. For similar reasons, monitoring frequency for the Pilot Study was set on a 14-day schedule, unlike the CARB/BAAQMD schedule of sampling every 6 or 12 days. Sampling every 14 days was more feasible for the local organizations that contributed in-kind services to maintain and operate the monitoring sites. Sampling of precipitation was implemented in August 1999 for a total of 12 months (Table 2). Due to some technical difficulties, ambient air sampling for mercury analysis did not provide reliable results until April 2000, and the sampling was concluded before the annual wet season began in the Bay Area in November 2000.

Monitoring Stations

The Bay Area is densely urbanized with a mix of residential, commercial, industrial (mostly electronics/high technology and other light industries), agricultural, and undeveloped (open space) land uses. There are many congested major highways surrounding the Estuary. Several petroleum refineries in the region are located primarily in the North Bay. The Central Bay has two major airports and seaports. The South Bay is the hub for electronic industries and has an expanding major airport. Loading of mercury in the South Bay has also been influenced by ten abandoned mines located between 15 to 30 miles southeast of the Estuary (Abu-Saba and Tang 2000).

In the summer, northwest winds from the Pacific Ocean are drawn landward through the Golden Gate and over the lower portions of the San Francisco Peninsula (**BAAQMD 1998**). Wind speeds may be locally strong in regions where air is channeled through narrow openings such as the Carquinez Strait, the Golden Gate, or the San Bruno Gap (Figure 2). In the winter, the Bay Area experiences storm periods with moderate-to-strong winds (>5 m/sec) and periods of stagnation with very light winds (<1 m/sec). Winter stagnation episodes are characterized by air mass outflow from the Central Valley, nighttime drainage airflows in coastal valleys, weak onshore airflows in the afternoon, and other light and variable winds. Analogous to a Mediterranean climate, the Bay Area wet season between November and April and the remaining dry season are hydrologically distinct (Trujillo et al. 1991). To the extent feasible, specific sampling locations were selected to comply with the siting criteria prescribed in the National Atmospheric Deposition Program (Bigelow 1984). Criteria used to select specific sampling locations for the Pilot Study were as follows:

- a. The site is accessible and secured, with adequate power supply
- b. The site is as close to the Estuary as possible
- c. The site is located up-wind (prevailing winds) from local major stationary sources in the immediate vicinity
- d. The site is convenient to the participating site operators

Three study sites were chosen using these criteria to represent different segments of the Estuary: North Bay, Central Bay, and South Bay (Figure 2). The South Bay site is located at the northwest corner of the Moffett Federal Airfield/NASA Ames Research Center. The Central Bay site is located at the northern end of Treasure Island. The North

Bay site is located in Martinez within the property boundary of the Central Contra Costa Sanitary District's Wastewater Treatment Plant. In addition to being part of the Pilot Study, the South Bay site also became one of the Mercury Deposition Network (MDN) stations under the National Atmospheric Deposition Program (NADP). Collocation of mercury wet deposition sampling under the MDN/NADP with the Pilot Study at the South Bay site began in January 2000 and resulted in ten replicate field precipitation samples.

3.2.1 Dry Deposition

Mercury in the atmosphere exists predominately in the gaseous phase in the form of elemental mercury, Hg(0), with a trace amount of divalent mercury, Hg(II) (Lindberg and Stratton 1998). Mercury has not been detected in routine air toxics monitoring conducted by CARB in the Bay Area. Ambient air samples in that program were collected on filters and analyzed by X-ray fluorescent spectrometry. The detection limit of 2-4 ng/m³ provided by these analyses is much higher than the global background concentration of about 1 ng/m³ (Shannon and Voldner 1995). In addition, atmospheric mercury exists predominately in gaseous phase and, therefore, would not be captured in the filtered samples. Using more refined and sensitive methodology, instrumentation, and analyses became an essential part of the strategy in monitoring mercury in the ambient air for the Pilot Study.

The methodology used in the sampling and Cold Vapor Atomic Fluorescence Spectrometry (CVAFS) analysis of total mercury in the ambient air was adapted from a U.S. EPA report (1997). A gold trap/cartridge device (Brooks Rand Ltd.², Seattle, WA) was used to collect mercury from the air (dry deposition, indirect method). Initially, the Pilot Study intended to quantify mercury in particulate and gaseous phases separately, by inserting a pre-filter in front of the gold traps. Results from the first-month sampling at a flow rate of 1 L/min showed unexpected high levels of mercury being detected on the pre-filters, suggesting that the pre-filters might have trapped mercury species other than those in the particulate phase. Further testing of the pre-filters was then conducted to investigate their trapping efficiency, using elemental mercury and mercuric chloride as the surrogates for gaseous mercury. Results from this preliminary testing showed that both glass-fiber and Teflon® filters adsorbed a significant fraction (>40%) of mercuric chloride, albeit at different rates. The efficacy of the sampling set-up for particulate mercury described in U.S. EPA Compendium Method IO-5, adjusted to accommodate a much lower flow rate, was questionable because reactive-gaseous mercury, such as mercuric chloride, in the air samples could be trapped in the pre-filters and misinterpreted as part of the particulate phase. Given the overall objectives of the Pilot Study, it was considered more important to ascertain accurate measurements of total mercury than to investigate appropriate methodologies for proper separation of mercury species. Therefore, two gold-coated sand traps in series (without pre-filters) were used to collect total mercury from the ambient air; measurements from the two traps were combined.

² Quoting names of a commercial product or laboratory does not constitute an endorsement from the authors or from their affiliated organizations.

3.2.1.1 Field Operation

The mercury air sampler consists of a vacuum pump and an air mass-flow controller. Pumps were allowed to warm up for at least 30 minutes prior to use. The airflow was set at 0.6 L/min and calibrated with a Bios Dry Cal® DC-1 Flow Calibrator. The airflow rate was rechecked with a Riteflow® 150 mm glass flow meter, and recorded at the beginning and at the end of each sampling event. All air samples were collected continuously for 24 hours every 14 days at each site. In addition, a duplicate sample was collected at each site on a rotational basis.

3.2.1.2 Laboratory Analysis

No sample preparation was necessary. Ambient air samples were analyzed for total mercury by EPA Method 1631, using isothermal desorption and CVAFS detection. Sample results were not blank subtracted because sample preparation prior to analysis was not required.

3.2.2 Wet Deposition

An automatic collector specifically designed for the National Atmospheric Deposition Program/Mercury Deposition Network (NADP/MDN) was used to collect precipitation samples. The device has been described in detail and evaluated by other investigators (Vermette et al. 1995a). A sampler (Aerochem Metrics, Inc., Bushnell, FL) modified by the Illinois State Water Survey was used that had two sampling bottles for collecting samples of mercury and other trace metals simultaneously. A precipitation sensor activated the lid to expose the funnels during a precipitation event. At the end of the precipitation event, the sensor dried off closing the lid. Procedures for the preparation of the bottles, funnels and capillary tubes used in collecting precipitation are presented below.

3.2.2.1 Preparation of Sampling Trains and Site Operation

Precipitation samples were collected with 2-liter borosilicate glass bottles with Teflon®-lined phenolic resin caps. The bottles were initially cleaned by heating to 70°C for 48 hrs in 4 N HCl, followed by thorough rinsing in low-mercury (<1 ng/L) double deionized water (DDW). The caps were cleaned by soaking for 48 hours in 0.1 N HCl at room temperature. After this and before each subsequent use, the bottles were filled with low-mercury DDW, to which 5 mL of BrCl in concentrated HCl was added, the caps replaced, and the bottles placed in a low mercury Class-100 clean air station to soak for 24 hours. Bottles were then emptied, thoroughly rinsed with low-mercury DDW, and allowed to dry for several hours in a low-mercury clean air station. To each bottle, 20±0.5 mL of 0.12 N HCl (<0.5 ng/L) was added and the lids were tightly fastened. The bottles were then enclosed in new polyethylene bags and packed into polyethylene foam lined shipping containers.

The funnel and capillary tube were initially cleaned by a thorough rinse in HNO₃, followed by a low-mercury DDW rinse. The openings of the funnel and capillary tube were wrapped in aluminum foil and immediately placed in a muffle furnace to be baked at 950°F for a minimum of 4 hours. Upon removal, the funnel and capillary tube were

placed in separate new polyethylene bags. All chemicals used in the preparation and sampling phases (BrCl, HCl, and HNO₃) were low-mercury reagent grade. Composite precipitation samples were collected once every 14 days for the Pilot Study, while samples were collected once every 7 days for the collocated MDN site in the South Bay.

3.2.2.2 Chemical Analysis

Frontier Geosciences Inc., NADP/MDN's Hg Analytical Laboratory (HAL), was chosen to perform analysis of total mercury because of their experience with the national monitoring program. After collection, samples were returned to HAL via two-day delivery. Upon arrival, the bottles were unpacked in the Class-100 air station and 1 mL of 0.2 N BrCl in HCl was added to each bottle to oxidize all mercury compounds to Hg(II). Following the addition of BrCl, the caps were replaced and the bottles were shaken several times over a period of at least 4 hours to remove any adsorbed mercury from the bottle walls and to allow leaching of mercury from suspended matter.

Aliquots of each sample were then transferred gravimetrically to 125 mL Teflon® bottles prior to analysis. The aliquot to be analyzed was first pre-reduced with 200 µL of NH₂OH-HCl to eliminate free halogens, and poured into a purge vessel. Then 300 µL of 25% SnCl₂ was added to reduce all mercury to Hg⁰. The sample was then purged for 20 minutes with N₂ (400 mL/min) onto a gold-coated silica trap. The traps were analyzed for mercury by thermal desorption, dual gold amalgamation, and CVAFS (Bloom and Fitzgerald 1988).

3.2.3 Quality Assurance and Quality Control

Sampling techniques used in the Pilot Study closely followed the general clean technique principles as described in U.S. EPA Method 1669 (USEPA 1996), the Quality Assurance Plan implemented for the NADP/MDN (Welker 1997), and the Quality Assurance Project Plan prepared for the Pilot Study (SFEI 2000). Site operators followed the procedures described in the Standard Operating Procedures (SOPs) for the specific sampling method. Information pertaining to sample installation, operating conditions, and sample conditions were recorded on the MDN Observer Form (MOF) supplied by HAL, or the Field Observation Form (FOF) specifically designed for the Pilot Study. Original MOFs and FOFs were included in the shipment of samples to the designated analytical laboratories. Copies of the MOF and FOFs were also forwarded to SFEI for evaluation and record keeping.

All equipment and supplies used in sampling were rigorously cleaned (see 3.2.2 Wet Deposition). Additionally, clean sample bottles were double bagged. Gold sand traps were repeatedly heated at 500°C until thoroughly blanked, i.e. no response was recorded of mercury desorption. Blanked gold sand traps were plugged with Teflon® end-plugs and bagged in clean polyethylene bags before shipment. Powder-free gloves were worn when handling samples.

For ambient air samples, the instrumentation was calibrated on each analytical batch, using five calibration points from 50 pg to 10,000 pg. The method detection limit (MDL) was 20 pg per sample and the practical quantification limit (PQL) was 50 pg per

sample. An initial precision and recovery (IPR) standard at a concentration of 500 pg, and an IPR blank were analyzed. Each analytical batch was closed with an ongoing precision and recovery (OPR) standard at a concentration of 500 pg and an OPR blank. The criteria for the calibration were an average response factor with relative standard deviation of <15%, and a recovery of 75 to 125%. Initial and continuing calibration verifications were required at the beginning and at the end of each analytical sequence. Calibration, reagent, and bubbler blanks were analyzed with the samples to assess potential contamination during the analytical sequence. Trip blanks were collected during each sampling event at each monitoring site. Trip blanks were taken by placing capped clean gold traps in the same housing compartment as the sampling traps. Ninety-four percent (94%) of the trip blanks showed concentrations below the MDL. An average of 11 pg per trap, <1% of the total mercury detected in each sampling trap, was detected in trip blanks. The relative percent differences between replicate field samples were $14 \pm 12\%$ (mean \pm standard deviation).

For precipitation sampling, the Pilot Study specifically followed the quality assurance protocol as described in the NADP/MDN Quality Assurance Plan (Welker 1997). Field blanks were collected during non-rainy periods to assess any contamination resulting from field operations. Mercury was detected at 0.065 ± 0.028 ng/bottle in the field blanks, slightly higher than the level of 0.040 ± 0.039 ng/bottle detected in the bottle blanks. Because one of the Pilot Study and the MDN samplers were collocated at the South Bay Site, 10 duplicate field samples were generated that allowed us to estimate any bias introduced by the sampling process. The average relative percent difference (RPD) for the precipitation volume collected was $3.6 \pm 3.5\%$, and that for the mercury concentration was $16.4 \pm 15.8\%$.

In the laboratory, at least 10% of the precipitation samples were analyzed in duplicate and 10% of all samples were analyzed for recovery with a matrix spike. A standard reference material (SRM) DORM-2 was analyzed with each batch of samples. Reagent blanks were measured once for each batch of reagents. The reagent blank value represents contamination introduced by the analytical method, and thus is subtracted from the sample concentration.

MDN reported an instrument detection limit of approximately 0.5 pg mercury and a method detection limit for a 100 mL aliquot of about 0.1 ng/L (MDN 2001). During the first three quarters in 2000, bottle blanks were reported at 0.040 ± 0.039 ng per bottle with average sample spike recoveries of $100.3 \pm 9.4\%$ and SRM recoveries of $94.8 \pm 3.6\%$. The average relative percent difference from sample replicate analysis was $6.3 \pm 15.4\%$.

Results of the chemical analyses were first reviewed by the analytical laboratories and then by the staff at SFEI. Field operating conditions recorded on the MOFs and FOFs were used to further evaluate sample integrity and data quality.

4.0 RESULTS AND DISCUSSION

This section presents results of the monitoring and loading estimates of mercury from the atmosphere to the Estuary surface. These estimates are further compared with mercury loading estimates from wastewater effluent dischargers, primarily POTWs.

4.1 Dry Deposition

4.1.1 Ambient Air Concentrations

Although sampling for the Pilot Study was started in August 1999, sampling of total mercury in the ambient air was not fully implemented until the end of April 2000, after methodological problems had been resolved (Section 3.2.1 above). Results from late April 2000 through the end of November 2000 indicated that total mercury concentrations in the ambient air ranged from approximately 1.5 to 4.2 ng/m³ (Figure 3). Average concentrations during the seven-month sampling period were 2.2, 1.9, 2.3 ng/m³ in South Bay, Central Bay, and North Bay, respectively (Table 3). The average concentration from all three sites combined was 2.1 ng/m³, compared to the global background concentration of 1.0 ng/m³ (Shannon and Voldner 1995). Mercury concentrations at the North Bay site were significantly higher than those at the Central Bay Site (p value = 0.008). The North Bay site is situated in an industrial corridor, while the Central Bay Site has the prevailing wind coming from the Pacific Ocean through the Golden Gate. Mercury concentrations measured at the South Bay Site were not statistically different from those observed at either the Central Bay Site or the North Bay Site.

Atmospheric mercury concentrations detected in the Bay Area were similar to those detected around the Chesapeake Bay (Sheu et al. 2001), and within the range reported in studies conducted at other locations within the U.S. Mercury concentration detected in the continental U.S. ranged from 0.50 to 50 ng/m³ (Williston 1968, Johnson and Braman 1974, Fitzgerald et al. 1991, Seigneur et al. 1994, Burke et al. 1995, Keeler et al. 1995, Pirrone et al. 1995, Shannon and Voldner 1995, Lindberg and Stratton 1998). In these studies, lower mercury concentrations were detected in rural areas and at higher altitude; and higher concentrations were detected in the industrial areas or in areas that were near mines or point sources.

4.1.2 Estimate Deposition Loading: Modeling Equations

To estimate deposition loading of chemicals from the ambient air to the Estuary, a series of calculation need to be performed. The methodology defined in the Quality Assurance Project Plan established for the Integrated Atmospheric Deposition Network was used to estimate the atmospheric deposition of toxic chemicals to the Great Lakes (Hoff et al. 1996). That methodology was applied to derive estimates of dry deposition of mercury from the ambient air to the estuary surface. Five equations used in the calculation are shown below. Appropriate conversion factors have been applied to all calculations to adjust for the units in different magnitude (e.g., day vs. year, ng vs. _g, m³ vs. L, etc.).

$$L = F_t \emptyset_t C_t \text{ (atmospheric-tributary)} + C_p R_p A \text{ (wet deposition)} \quad (1)$$

$$+ AK_{0L}(1-\varnothing_a)C_a(RT/H) \text{ (gas absorption)}$$

$$+ \varnothing_a AC_a V_d \text{ (dry deposition)}$$

$$V = AK_{0L} (1 - \varnothing_w) C_w \text{ (volatilization/evasion)} \quad (2)$$

$$1/K_{0L} = (1/k_w) + (RT/Hk_a) \quad (3)$$

$$k_{w,x} = k_{w,CO_2} (Sc_x/Sc_{CO_2})^{-0.5} \quad k_{w,CO_2} = 0.45(u_{10})^{1.64} \quad (4)$$

$$k_{a,x} = k_{a,H_2O} (D_{a,x}/D_{a,H_2O})^{0.61} \quad k_{a,H_2O} = 0.2 u_{10} + 0.3 \quad (5)$$

Where: A = area of Estuary, m²
C_a= concentration of total mercury in air, ng/m³
C_p= concentration in precipitation, µg/L
C_w= concentration in water, µg/L
C_t= concentration in tributary, µg/L
D_{a,x}= diffusivity, cm²/s
F_t= tributary flow, 10³m³/yr
H= Henry's law coefficient, Pa m³/mol
K_{0L}= air-water mass transfer coefficient, m/yr in equations (1) and (2),
m/day in equation (3)
k_{w,x}= water-side mass transfer coefficient, m/d, of the gas x
k_{a,x}= air-side mass transfer coefficient, m/d, of the gas x
L = total atmospheric load to the estuary, g/yr
R= gas constant, Pa m³/mol °K
R_p= rate of precipitation, m/yr
Sc= Schmidt number
T= temperature, degrees Kelvin (°K)
u₁₀= wind speed at 10 m height, m/s
V= loss from volatilization/evasion
V_d= particulate deposition velocity, m/yr
ϕ_a= particulate fraction of the concentration in air
ϕ_t= fraction of tributary loading that is atmospheric in origin
ϕ_w= particulate fraction of the concentration in water

An alternate approach (equation 6) can be used to calculate the first term in equation (1) for the loading from tributaries that is atmospheric in origin. This alternative approach was used in this report to calculate the mercury loading from indirect atmospheric deposition through runoff and tributaries.

$$L_t = (L_d + L_p)\varnothing_r \quad (6)$$

Where: L_t = loading from tributaries that is atmospheric in origin
L_d = loading from dry deposition to the watershed
L_p = loading from wet deposition to the watershed

\varnothing_r = fraction of the material deposited in the watershed that reaches the Estuary (or the percentage of incident precipitation that is manifested as runoff (the runoff coefficient))

4.1.3 Evaluation of Modeling Input Parameters

Deposition of particulates from ambient air to the Estuary surface depends on their deposition velocity (V_d), while deposition of chemicals in vapor phase occurs through an air-water exchange mechanism. In general, atmospheric mercury exists primarily in vapor phase (>90%) as elemental mercury, Hg(0), and divalent mercury, Hg(II), and a minor component of total atmospheric mercury exists in particulate phase (<10%) (Lindberg and Stratton 1998, Lin and Pehkonen 1999). In the literature, about 1-11% of the total gaseous mercury in the ambient air was reported to be Hg(II) (Lindberg and Stratton 1998, Sheu et al. 2001). In urban/industrial areas, however, particulate mercury was found at concentrations that were ten times as high as those found in rural areas (Keeler et al. 1995) and more likely to be associated with particles greater than 2.5 μm . In industrialized regions, Lin and Pehkonen (1999) suggested that Hg(p) can be up to 40% of the total gaseous mercury.

Divalent gaseous mercury, Hg(II), is a highly surface-reactive species, and its behavior mirrors other “sticky” gases such as HNO_3 . This species of mercury would be efficiently absorbed by cloud droplets during formation of rain. Hg(II) could dry deposit over 100 times more readily than Hg(0) (Lindberg and Stratton 1998). Therefore, even concentrations of reactive gaseous mercury, e.g. Hg(II), at a few percent of total gaseous mercury could be important to mercury dry deposition. Lindberg and Stratton (1998) used a deposition velocity (V_d) of 0.1, 0.09, and 2.0 cm/s in calculating dry deposition of Hg(p), Hg(0), and reactive gaseous mercury, respectively, to the forest canopy.

Dry deposition velocity (V_d) strongly depends on particle size, meteorology (atmospheric stability, relative humidity, and wind speed), and characteristics of the deposition surface (Caffrey et al. 1998). Employing mathematical models, Caffrey et al. (1998) predicted a minimum average deposition velocity of 0.006 cm/s for particles composed of various elements with equivalent spherical diameters between 0.09 to 0.53 μm under a mean wind speed of 4.0 m/s and stable meteorological conditions. A V_d of 0.02 cm/s was predicted for a particle size of 2.5 μm , and the V_d increased to 11 cm/s for a particle size of 60 μm .

Although it was generally believed that particulate mercury is typically sub-micron in size, Keeler et al. (1995) reported mercury being present in both fine mode (average size of 0.68 μm) and coarse mode (average size of 3.78 μm). Flux of mercury on coarse particles was 4-5 times greater than the flux of fine particles. A V_d of 0.2 cm/s was chosen by Hoff et al. (1996) to estimate deposition of toxic chemicals, including mercury, in particulate phase, while Fitzgerald et al. (1991) used a V_d of 0.5 cm/s to estimate dry deposition flux of particulate mercury, and a V_d of 5.0 cm/s was reported for PCBs (Holsen et al. 1991). The higher V_d is applicable to chemicals trapped on “giant” particles, those of greater than 30 μm in diameter. Such large particles might be more often seen very near urban areas.

Based on the 1994 to 1998 data collected in the Bay Area, the fraction of coarse particulate matter (particle size of between 2.5 μm and 10 μm) constitutes 45 to 57% of the total particulate matter in the 0 to 10 μm size range, excluding particles larger than 10 μm (CARB 1999). It is unknown how much the size fraction greater than 10 μm contributes to the total particle mass suspended in the air. The distribution of mercury in each fraction of the particulate matter is also unknown, and mercury entrapped in the larger particles conceivably could be relatively high, especially if particles greater than 10 μm are included. Because only total mercury concentrations were measured, and mercury species were not identified in this Pilot Study, certain assumptions must be made in calculating the dry deposition flux of mercury from the atmosphere to the Estuary surface. Parameters used in estimating direct dry deposition of atmospheric mercury to the Estuary surface are presented in Table 4.

Sheu et al. (2001) reported that atmospheric mercury from areas over the Northern Chesapeake Bay consisted of 1 to 9% Hg(p) and 1 to 11 % Hg(II). In the absence of site-specific data on mercury speciation, it was assumed in this report that atmospheric mercury in the Bay Area had the following components: 95% in elemental form, 3% in particulate phase, and 2% in Hg(II). These assumptions incorporated data reported by Sheu et al. (2001) for samples collected at three sites in Baltimore, and the land-use data reported for the Bay Area (Davis et al. 2000). Based on the evaluation of the values presented in the literature (Fitzgerald et al. 1991, Holsen et al. 1991, Hoff et al. 1996, Lindberg and Stratton 1998) and the consideration of the environmental characteristics of the Bay Area, deposition velocity, V_d , was assumed to be 0.2 and 1.0 cm/s for Hg(p) and Hg(II), respectively. It should be noted that loading from dry deposition is directly proportional to the concentration of Hg(p) or Hg(II) in the air. Likewise, the value of V_d also affects loading estimates in a linear fashion. Since this Pilot Study was conducted in the highly urbanized Bay Area with mixed industries and abandoned mines, the parameters and assumptions used in calculating load estimate of dry deposition, although representing our best professional judgment, might result in underestimates.

Segmentation and areas of the Estuary used in this report were similar, but not identical to those used in other reports. For example, the 2000 TMDL Mercury Report to U.S. EPA divided the Estuary into six segments: South Bay, Lower Bay, Central Bay, San Pablo Bay, Carquinez Strait, and Suisun Bay (Abu-Saba and Tang 2000). In the present report, the South Bay (485 km^2) consists of the area south of the San Francisco-Oakland Bay Bridge. The Central Bay (214 km^2) consists of the area between the San Francisco-Oakland Bay Bridge, the Golden Gate Bridge and the Richmond-San Rafael Bridge. The North Bay (434 km^2) consists of the area between north of the Richmond-San Rafael Bridge and east to Sherman Island (Figure 4). Surface area for the Estuary and for different segments of the Bay is derived from the information presented in the Bay Area EcoAtlas (Monroe and Olofson 1999) and includes modern (ca. 1988) habitats of the deep bay/channel, shallow bay/channel, tidal flat, young low-medium tidal marsh, and beaches. The North Bay encompasses both the North Bay and Suisun Bay sub-regions.

4.1.4 Loading of Mercury from Atmospheric Deposition

Using the data provided in Table 4 and the equations presented in Section 4.1.2, the loading of mercury to the Estuary via the dry deposition pathway was estimated (Table 5). It was estimated that approximately 4.6 kg of particulate mercury and 15 kg of Hg(II) were deposited annually to the Estuary surface. Dry deposition of Hg(II) to the South Bay, Central Bay, and North Bay was estimated at 6.6, 2.6, and 6.4 kg/yr, respectively. Dry deposition of particulate mercury, Hg(p) to the South Bay, Central Bay, and North Bay was estimated to be 2.0, 0.8, and 1.9 kg/yr, respectively. The spatial variations in the deposition loading were driven by the differences in surface area. Absorption of gaseous Hg(0) was about 2.2 kg/yr. Estuary-wide deposition flux via dry deposition was approximately $19 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, and very similar among estuary segments. The above deposition estimates assume that dry deposition occurs during dry as well as wet weather. Rain events recorded were 291 hours (in South Bay) to 393 hours (in Central Bay) during the one-year sampling period. Because dry deposition theoretically does not occur during rainy periods, including rainy hours in calculating loading from dry deposition could potentially contribute to an overestimate of up to 5%.

Mercury-flux estimates provided in this report represent atmospheric fluxes into the Estuary water column rather a net flux. For example, this report does not address any volatilization (evasion or degassing) of mercury from the Estuary water, soils, or plants. Volatilization of mercury to the ambient air would be predominately driven by gaseous Hg(0). Evasion of Hg(II) from the Estuary water to the atmosphere is likely negligible due to its high solubility in water and low vapor pressure, relative to Hg(0). The RMP routinely monitors total mercury and dissolved mercury in surface water samples in the Estuary. Based on three sampling events in 1999, Estuary-wide average concentration for total mercury and dissolved mercury was 19 and 3.3 ng/L, respectively (SFEI 2001). Assuming that 95% of the total atmospheric mercury concentration is gaseous Hg(0), it was estimated that at equilibrium, Hg(0) concentration in the Estuary water would be approximately 6.7 pg/L, which is approximately 0.2% of the total dissolved mercury detected Estuary-wide in 1999. If Hg(0) concentration in the Estuary water exceeds 6.7 pg/L, then there would be evasion (out-gassing) of Hg(0) from the Estuary water to the atmosphere. Monitoring Hg(0) concentration in the water from the Estuary is needed to assess whether there is an evasion of Hg(0) from the water to the atmosphere. Investigating volatilization of mercury from soils or plants warrants a separate effort.

4.2 Wet Deposition

The volume-weighted average mercury concentration in precipitation from the 59 samples collected at all sites in the Bay Area was 8.0 ng/L. The volume-weighted average concentration was essentially driven by six sampling events of greater than 1,000 ml (Table 6); excluding data from small-volume samples did not change the average concentration significantly. Therefore, all data from each site were used in calculating site-specific average mercury concentration. The volume-weighted average concentrations for the South Bay, Central Bay, and North Bay Site, were 9.7, 6.6, and 7.4 ng/L, respectively.

Loading of mercury from precipitation (wet deposition) was calculated by using equation (7). Rainfall in the Bay Area exhibits high inter-annual and spatial variation (BAAQMD 1998, NWS 2001a). Annual average rainfall in the Bay Area ranges from under 38 cm (15 inches) to more than 106 cm (40 inches). In this report, precipitation rate at each sampling site was obtained from the data recorded during September 1, 1999 through August 31, 2000, the same period as the sample collections, at the weather station closest to each site: the National Weather Service (NWS) station at the Moffett Airfield for South Bay (NWS 2001a); the BAAQMD station at the Oakland Sewage Treatment Plant (OST) for Central Bay; and the CCCSD station for North Bay. Annual precipitation of 36 cm (14.3 inches), 68 cm (26.8 inches), and 58 cm (22.8 inches) was recorded at the South Bay, Central Bay, and North Bay sites, respectively. For the Estuary-wide calculation, the 30-year annual average precipitation rate of 21 inches (53 cm) was estimated from NWS' precipitation contour depicted for the San Francisco Bay Area. Mercury loading from precipitation (L_p) was determined using the following expression:

$$L_p = C_p R_p A_p \quad (7)$$

Where L_p = loading from precipitation

C_p = concentration of mercury in precipitation, ng/L

R_p = rate of precipitation, m/yr

A_p = area of the Estuary that is covered by precipitation, m^2

The wet deposition rate of mercury directly to segments of the Estuary ranged from 3.5 to 4.5 $\mu g \cdot m^{-2} \cdot yr^{-1}$ with an overall deposition rate of 4.2 $\mu g \cdot m^{-2} \cdot yr^{-1}$ for the entire Estuary (Table 7). Approximately 4.8 kg of mercury was deposited annually from the atmosphere through rainfall directly to the surface of the entire San Francisco Estuary. Annual loading of mercury from rainfall was 1.7, 0.96, and 1.8 kg at the South Bay, Central Bay, and North Bay Site, respectively. The loading estimate does not include wet deposition to the watershed that subsequently drained to the Estuary through surface runoff and tributaries.

The volume-weighted average mercury concentration of 8.0 ng/L in precipitation measured in the Bay Area sites is within the range of the values observed in studies conducted in other areas of the U.S. (Table 8). In 1999, the volume-weighted average concentration of mercury in the precipitation detected at the 33 sites that participated in the MDN ranged from 4.5 to 17.0 ng/L (MDN 2001). The lowest concentration was observed at Covelo, CA, which is a rural site about 180 miles north of the Bay Area, and the highest concentration was found at Camp Ripley, MN. Mercury concentrations found in the Bay Area were similar to the concentrations detected in Lake Champlain, VT (Burke et al. 1995) and the Northeast Pacific Ocean (Fitzgerald et al. 1991), but were about twice as high as the concentration detected at Covelo, CA and the Pacific Northwest coast of Washington. On the other hand, mercury concentration found in the Bay Area was substantially lower than that reported in Seattle, WA and Chesapeake Estuary, MD (Mason and Fitzgerald 1996, Mason et al. 2000) that had potential influence from local point sources such as power plants and waste incinerators.

Annual wet deposition flux is a function of the chemical concentration in precipitation and the annual rainfall amount. As a result of the relatively low annual rainfall volume observed in the Bay Area, the average annual wet deposition flux of $4.2 \mu\text{g}/\text{m}^2$ estimated for the Bay Area sites is in the low end of the flux range of 3.9 to $17.7 \mu\text{g}/\text{m}^2$ reported for other sites that participated in the MDN in 1999, and especially low for an urbanized area.

4.3 Total Loading from Direct Atmospheric Deposition

Combining load estimates from dry deposition and wet deposition, the Estuary received a total of approximately 27 kg per year of mercury directly from the atmosphere (Table 9). These results suggest that in the Bay Area, wet deposition constitutes approximately 18% of the total direct loading of mercury from atmosphere, compared to 50% or greater reported in other areas. As shown in Table 9, the estimated fraction of loading from wet deposition to different segments of the Estuary ranges from 16% to 20%, and the variation is related to the annual rainfall amount.

4.4 Loading from Tributaries That is Atmospheric in Origin

Assessment of the relative contribution of atmospheric deposition to the total pollutant load to the Estuary would not be complete without taking into account its contribution through indirect routes. Loadings initially deposited on the surface of the land, streets, structures, vegetation, etc. could be eventually transported to the Estuary through surface runoff and tributaries. Contribution from atmospheric deposition indirectly through runoff and tributaries might be much greater than what could be deposited directly to the Estuary. Loading via atmospheric deposition is proportional to the receiving surface area; surface areas of the entire watershed for indirect deposition are much larger than the Estuary surface.

Flow regime, weather/climate conditions, and watershed and landscape characteristics are the most important factors that have impact on pollutant flux from surface runoff and potential transport to aquatic systems. Based on a modeling analysis, Tsiros (1999) reported that total annual mercury surface runoff flux varied from 2 to 60% of the atmospheric deposition to the watershed. The extent of the surface runoff flux reflects the collective influence and interaction of the various meteorological, soil, land use/land cover and scale characteristics of the watershed (Tsiros 1999). In the mercury budget study for the St. Lawrence River, it was estimated that less than 12% of the mercury atmospherically deposited on the watershed consisting of either forested or agricultural land was transported to the surface water (Quemerais et al. 1999). Estimates from studies of atmospheric deposition to some lakes in Sweden and mid-continental North America suggested that up to 30% of the atmospheric deposition to the watershed reaches the lake (Mason et al. 1994). Based on the rates of deposition of lead, Hg, and PCBs to the Lake Superior watershed, Dolan et al. (1993) estimated that roughly 10% of the material which is derived from wet and dry deposition in the watershed reaches the lakes by fluvial transport, and this runoff coefficient has been used by Hoff et al. (1996) in their estimates of atmospheric deposition of toxic chemicals to the Great Lakes.

Average runoff coefficients for different land uses vary from <10% in undeveloped areas with few impervious surfaces to 95% in business districts dominated by impervious surfaces (Dunne and Leopold 1978). Runoff coefficients are also influenced by antecedent rainfall conditions, and increase with increasing soil saturation even in forested watersheds. In estimating an appropriate runoff coefficient for the Bay Area, land use data provided by the Association of Bay Area Governments (ABAG 1995) was combined with runoff coefficients presented by Dunne and Leopold (1978) for the five broad land-use categories (residential, commercial, industrial, agricultural, and open space). A number of hydrologic areas were delineated for the San Francisco Bay Region on the CALWATER map (WITS 1999) (Figure 4). Excluding coastal areas that drain water directly to the Pacific Ocean, the total watershed area immediately surrounding the San Francisco Estuary is estimated to be 7,261 km². This estimate does not include the Sacramento River-San Joaquin River drainage area.

Based on the size of each hydrologic area, its land-use characteristics, and runoff coefficients ($\bar{\phi}_r$) obtained from the literature for various land-uses, an area-weighted average of $\bar{\phi}_r$ for the Bay Area was estimated to be about 0.32 (32% of incident rainfall). The runoff coefficient is a measure of the fraction of the total rainfall that is transported to the Estuary. A runoff coefficient of 32% means that 68% of the rainfall does not reach the Estuary due to evaporation and net retention by the soil. However, the loss mechanisms for rainfall (in terms of its availability to the Estuary) may not be applicable to the transport of mercury that is deposited to the watersheds. The majority of the atmospherically deposited mercury is either adsorbed onto particulates or present in a form that is not as readily subject to volatilization. In the absence of any empirical data, this report uses the estimated $\bar{\phi}_r$ as a surrogate for the fraction of mercury deposited in the watersheds that actually reaches the Estuary. The fraction could conceivably be substantially greater than the 32% assumed in this report.

Using equation (6) presented earlier, loading estimates of dry deposition (L_d) (Section 4.1.2), loading estimates of wet depositions (L_p) (Section 4.2), and a runoff coefficient ($\bar{\phi}_r$) of 0.32, approximately 55 kg per year of atmospheric mercury was estimated to be deposited to the Estuary indirectly through run-off and tributaries, approximately twice the direct deposition.

4.5 Comparison of Loading from Different Sources and Pathways

Before mitigation measures can be explored to reduce pollutant loading to the Estuary, relative contributions from various sources and pathways and their significance must be evaluated. Therefore, estimate of mercury loading to the Estuary from atmospheric deposition is compared with loadings from other sources/pathways, and presented in Table 10. It is important to note that these estimates were derived from three different sources that may use very different databases, and apply different approaches and assumptions. Thus, these estimates have various degrees of uncertainties that will be discussed in more details in Section 4.6 below. No conclusions should be drawn without careful evaluation of each variable that was incorporated into the calculations. Information presented below serves as a first-level screening and should not be construed as an accurate comparison of loading from all sources and pathways.

Among the primary sources and pathways that contribute to total loading of chemicals, the most complete and reliable empirical data are available from monitoring of wastewater discharges. Wastewater discharges accounted for approximately 12 kg⁽³⁾ of mercury loading to the Estuary in 2000 (Ellgas 2001) while the Pilot Study estimated atmospheric deposition contributed 27 kg directly and another 55 kg indirectly through surface runoff or tributaries. Thus, total loading of mercury from direct atmospheric deposition was estimated to be about twice the contribution by wastewater discharges from POTWs and industrial facilities. Compared to direct atmospheric deposition, indirect atmospheric deposition (through runoff and tributaries) was estimated to contribute at least twice as much of the mercury loading to the Estuary. Combining direct and indirect routes, atmospheric deposition contribute almost seven (7) times as much as the inputs from wastewater discharges.

In addition to the loadings from atmospheric deposition and wastewater discharges presented above, sediment remobilization and diffusive flux contribute pollutant loads to the estuary water column. However, they are internal processes that redistribute pollutants within the Estuary, and not truly contributors of new pollutant loads to the Estuary. On the other hand, runoff through tributaries from watersheds contributes external pollutant loads to the Estuary. Watersheds that drain water to the Estuary include local drainage areas in San Francisco Bay Region and the more remote drainage areas in the Sacramento River-San Joaquin River Region, which drains water from about 160,000 km² land area, about 37% of the State (Calfed 2001). Runoff from watersheds could be an important contributor to the total pollutant load to the Estuary. The SFBRWQCB (Abu-Saba and Tang 2000)⁴ provided estimates of mercury load from the two watersheds that contribute pollutant loading to the Estuary, and the potential redistribution of mercury to the water column from sediment remobilization within the Estuary. Estimates from the SFBRWQCB are as follows:

- a. “Within-basin Watershed” (San Francisco Bay Region), including loading that is atmospheric in origin: 168 kg per year
- b. Sediment remobilization within the Estuary: 500 kg per year
- c. Central Valley Watershed⁵, including loading that is atmospheric in origin: 607 kg per year

It is worthy to note that sediment transported from the Guadalupe River hydrologic drainage area, which covers the land area where abandoned mines were located, contributed an estimated 49 kg per year of mercury (Abu-Saba and Tang 2000), almost 30% of the total loading from the entire “within-basin watershed.” The aforementioned estimates of loading from watersheds include loadings that are atmospheric in origin (evaluated by the Pilot Study) as well as those that are derived from non-atmospheric sources or pathways (not evaluated by the Pilot Study). This Pilot

³ This value is extrapolated from data submitted by about 83% of all Publicly-Owned Treatment Plants.

⁴ Numbers shown here represent the best estimates provided in the report by Abu-Saba and Tang (2000).

⁵ Although the Central Valley Watershed is not included in the San Francisco Bay Region, it contributes pollutant loading to the North Bay.

Study does not include assessment of contribution from the Central Valley Watershed that appears to be the largest contributor of mercury loading to the Estuary, according to the evaluation presented by the SFBRWQCB (Abu-Saba and Tang 2000).

4.6 Uncertainties in the Loading Estimates

Uncertainty levels associated with the various loading estimates presented in this report and those of others have been assessed in a semi-quantitative manner (Table 10). In this report, low level of uncertainty indicates that the estimate is accurate within 50%; a moderate level of uncertainty indicates that the estimate may vary up to 2-fold; a moderate-high uncertainty presents an estimate that has an error of up to 5-fold; and an estimate with a high level of uncertainty may vary up to ten-fold.

Estimates of mercury loading to the San Francisco Estuary were based on site-specific measurements and some assumptions derived from literature when site-specific data were not available. Uncertainty in mercury measurements from analysis of field samples is low because of strict quality control and quality assurance procedures implemented for the study. On the other hand, uncertainty arising from parameters that were not derived from site-specific measurements is higher. Assumptions used in estimating mercury loading in this report are believed to be reasonable for the Bay Area environment. Nevertheless, these assumptions impose a certain degree of uncertainty, which varies with the specific source or pathway being assessed.

Various loading estimates have different level of uncertainty associated with the sources of input parameters (Table 11). Among the estimates of atmospheric deposition addressed in this report, loadings from direct wet deposition have the lowest uncertainty and the highest confidence level, because the loadings were based on site-specific environmental monitoring data and pertinent geographic as well as meteorological data. Propagation of errors due to sampling and analytical variation, and instrumental precision is believed to be within 50%. On the other hand, estimates of direct dry deposition used some parameter inputs that were not site-specific. As shown in Table 5, deposition of particulate and reactive mercury constitutes approximately 90% of the estimated total loading from dry deposition. Consequently, assumptions used in estimating deposition of particulate mercury and reactive mercury are critical contributors to the overall uncertainty. The two largest uncertainties arise from the assumptions regarding percentage of atmospheric mercury in the particulate phase, Hg(p), and reactive mercury, Hg(II), and their deposition velocity, V_d . If Hg(p) or Hg(II) is less than the 3 or 2% of the total atmospheric mercury assumed in the calculation, the true loading estimates for dry deposition would be proportionally lower. Similarly, if V_d for particulate mercury or reactive mercury is lower than its respective value used in the calculation, then the loading estimate would be lower correspondingly. Conversely, if the fraction of Hg(p) and Hg(II), or the V_d is higher than what was assumed, then the loading estimates would be higher. In order to reduce the uncertainty level in estimating mercury load from dry deposition, it is necessary to obtain accurate measurements of the speciation of atmospheric mercury as well as its particle size distribution in the particulate phase.

Deposition load contributed from runoff or tributaries that is atmospheric in origin includes both dry and wet deposition. Because dry deposition contributes a larger load than wet deposition, estimate of loading from runoff or tributaries that is atmospheric in origin inherits the same uncertainty as the direct dry deposition estimate. In addition, it uses a runoff coefficient of 0.32 as the surrogate for the fraction of mercury transported from watersheds. It is believed that this runoff coefficient may underestimate the true fraction of mercury deposited onto the watershed that is eventually transported to the Estuary through runoff and tributaries. The overall uncertainty is believed to be moderate-high for the estimate of indirect loading of atmospheric mercury to the Estuary.

The uncertainty level in the estimates is low for wet deposition, moderate-high for dry deposition, and moderate-high for atmospheric deposition to tributaries, resulting in a moderate-high uncertainty level for the overall load estimates (Table 10). It is difficult to evaluate the uncertainty level of the estimates presented in other reports that have different level of documentation and may have used different data sources, calculation approach, and assumptions. The confidence level is high for the estimated loading from POTW by Ellgas (2001) because site-specific analytical data with low uncertainty were used in the estimate. This report did not assess the input parameters and assumptions used in the estimates of loading from watersheds or from sediment remobilization as reported by Abu-Saba and Tang (2000).

5.0 CONCLUSIONS

The atmospheric mercury concentration of 2.1 ng/m^3 detected in the Bay Area is about two times the global background concentration. This is within the range of the concentrations detected in other areas in the continental USA. Volume-weighted average mercury concentration of 8.0 ng/L detected in precipitation is also within the range found in other locations that participated in the national Mercury Deposition Network. These measurements found in the Bay Area are twice those detected at sites that might be considered “background” locations on the western U.S. coast, and they are substantially lower than those at other locations with local influence from point sources or those potentially situated in the path of long-range transport of polluted air masses.

Annually, direct atmospheric deposition contributes approximately 27 kg and indirect deposition (via runoff and tributaries but excluding Central Valley drainage area) contributes approximately 55 kg. In the Bay Area, wet deposition constitutes approximately 18% of the total direct loading of mercury from atmosphere, compared to 50% or greater reported in other areas. Comparing to other sources and pathways, loading of mercury from atmospheric deposition (combine direct and indirect routes) contributes almost seven (7) times as much as the loading from wastewater discharges. Based on the results of this Pilot Study for indirect atmospheric deposition and the estimates provided by Abu-Saba and Tang (2000) for loading from watersheds, mercury loading from the San Francisco Bay Region Watershed comprises of about 30% that is atmospheric in origin.

Although comparison of loading estimates is presented in this report, it is important to note that there are different degrees of uncertainty associated with those estimates: low (with an error of within $\pm 25\%$) for wastewater discharges, and moderate-high (with an error of two to five-fold) for atmospheric deposition. Uncertainty level associated with loading estimates for watersheds, and that attributable to benthic remobilization within the Estuary, is unknown but likely very high (with an error of ten-fold or greater). Information presented in this report serves as the first-level screening and should not be construed as an accurate comparison of loading from all sources and pathways.

Results and evaluation presented in this report indicate that loading of mercury from wastewater discharges to the San Francisco Estuary likely constituted less than 2% of the total load from all sources and pathways, and less than 15% of the load from atmospheric deposition. Atmospheric deposition contributes sufficient load of mercury through direct deposition to the Estuary and indirect deposition through runoff from watersheds. Similar to the loading from watersheds, atmospheric deposition is an external loading conveyor of pollutants to the Estuary that is more feasible to manage than those from internal pollutant redistributing processes like remobilization of buried sediments. In addition, pollutant loading from watershed runoff includes a component that is atmospheric in origin. Exploring suitable strategy for minimizing mercury load to the San Francisco Estuary should include the investigation of measures that can mitigate the sources and pathways that contribute to the releases of mercury to the atmosphere.

6.0 REFERENCES

- ABAG. 1995.** Description of land use classification categories. Association of Bay Area Governments (ABAG), Oakland, CA.
- Abu-Saba, K.E. and L.W. Tang. 2000.** Watershed Management of Mercury in the San Francisco Bay: Total Maximum Daily Load - Report to U.S. EPA. California Regional Water Quality Control Board, San Francisco Bay Region, Oakland.
- BAAQMD. 1998.** Particulate Matter Monitoring Network: Description for the Bay Area Air Quality Management District Planning Area. Bay Area Air Quality Management District. , San Francisco.
- Bigelow, D.S. 1984.** Instruction Manual: NADP/NTN Site Selection and Installation. National Atmospheric Deposition Program, Program Office, Illinois State Water Survey, Champaign, IL 61820.
- Bloom, N.S. and W.F. Fitzgerald. 1988.** Determination of volatile mercury species at the picogram level by low temperature gas chromatography with cold vapour atomic fluorescence detection. *Analytica Chim. Acta* 209: 151-161.
- Burke, J., M. Hoyer, G. Keeler and T. Scherbatskoy. 1995.** Wet deposition of mercury and ambient mercury concentrations at a site in the Lake Champlain Basin. *Water, Air, and Soil Pollution* 80: 353-362.
- Caffrey, P.F., J.M. Ondov, M.J. Zufall and C.I. Davidson. 1998.** Determination of size-dependent dry particle deposition velocities with multiple intrinsic elemental tracers. *Environ. Sci. Technol.* 32: 1615-1622.
- Calfed. 2001.** Facts about the Bay-Delta, Calfed Bay-Delta Program.
- CARB. 1999.** California Ambient Air Quality Data 1980-1998. Air Resources Board, California Environmental Protection Agency, Sacramento, CA.
- CSJ. 1998.** Work Plan for RMP Pilot Study on Aerial Deposition: Determining the extent of pollutant loadings on the surface of the San Francisco Estuary from Atmospheric Deposition. City of San Jose, San Jose, CA.
- Davis, J.A., L.J. McKee, J.E. Leatherbarrow and T.H. Daum. 2000.** Contaminant loads from stormwater to coastal waters in the San Francisco Bay region: Comparison to other pathways and recommended approach for future evaluation (draft internal document). San Francisco Estuary Institute, Richmond, CA.
- Dunne, T. and L.B. Leopold. 1978.** *Water in Environmental Planning*. W. H. Freeman and Company, San Francisco, USA. 300 pp.

Ellgas, B. 2001. Comparison of 1999-2000 POTW Hg Data, Methods & Special Studies CWEA/BADA Mercury Workshop, San Jose, CA.

Fitzgerald, W.F., R.P. Mason and G.M. Vandal. 1991. Atmospheric cycling and air-water exchange of mercury over mid-continental lacustrine regions. *Water, Air, and Soil Pollution* 56: 745-767.

Hoff, R.M., W.M.J. Strachan, C.W. Sweet, C.H. Chan, M. Shackleton, T.F. Bidleman, K.A. Brice, D.A. Burniston, S. Cussion, D.F. Gatz, K. Harlin and W.H. Schroeder. 1996. Atmospheric deposition of toxic chemicals to the Great Lakes: A review of data through 1994. *Atmospheric Environment* 30: 3505-3527.

Holsen, T.M., K.E. Noll, S.P. Liu and W.J. Lee. 1991. Dry deposition of polychlorinated biphenyls in urban areas. *Environ. Sci. Technol.* 25: 1075-1081.

Johnson, D.L. and R.S. Braman. 1974. Distribution of atmospheric mercury species near ground. *Environ. Sci. Technol.* 8: 1003-1009.

Keeler, G., G. Glinsorn and N. Pirrone. 1995. Particulate mercury in the atmosphere: Its significance, transport, transformation and sources. *Water, Air, and Soil Pollution* 80: 159-168.

Lin, C.J. and S.O. Pehkonen. 1999. The chemistry of atmospheric mercury: a review. *Atmospheric Environment* 33: 2067-2079.

Lindberg, S.E. and W.J. Stratton. 1998. Atmospheric mercury speciation: concentrations and behavior of reactive gaseous mercury in ambient air. *Environ. Sci. Technol.* 32: 49-57.

Mason, R.P. and W.F. Fitzgerald. 1996. Sources, sinks and biogeochemical cycling of mercury in the ocean. pp. 249-272. *In: W.B.e. al. (ed.) Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances*, Kluwer Academic Publishers, Netherlands.

Mason, R.P., W.F. Fitzgerald and F.M.M. Morel. 1994. The biogeochemical cycling of elemental mercury: Anthropogenic influences. *Geochim. et Cosmochim. Acta* 58: 3191-3198.

Mason, R.P., N.M. Lawson and G.R. Sheu. 2000. Annual and seasonal trends in mercury deposition in Maryland. *Atmospheric Environment* (in progress).

Mason, R.P., N.M. Lawson and K.A. Sullivan. 1997. Atmospheric deposition to the Chesapeake Bay watershed - Regional and local sources. *Atmospheric Environment* 31: 3531-3540.

MDN. 2001. NADP/MDN: Mercury Deposition Network. National Atmospheric Deposition Program/Mercury Deposition Network.

Monroe, M. and P.R. Olofson. 1999. Goals Project. Baylands Ecosystem Habitat Goals. A report of habitat recommendations prepared by the San Francisco Bay Area Wetlands Ecosystem Goals Project. U.S. Environmental Protection Agency, San Francisco, CA/SF Bay Regional Water Quality Control Board, Oakland, CA.

NWS. 2001a. Average Annual Rainfall Maps, National Weather Services.

Pirrone, N., G. Glinsorn and G.J. Keeler. 1995. Ambient levels and dry deposition fluxes of mercury to lakes Huron, Erie and St. Clair. *Water, Air, and Soil Pollution* 80: 179-188.

Quemerais, B., D. Cossa, B. Rondeau, T.T. Pham, P. Gagnon and B. Fortin. 1999. Sources and fluxes of mercury in the St. Lawrence River. *Environ. Sci. Technol.* 33: 840-849.

Seigneur, C., J. Wrobel and E. Constantinou. 1994. A chemical kinetic mechanism for atmospheric inorganic mercury. *Environ. Sci. Technol.* 28: 1589-1597.

SFEI. 1998. Final 1999 Workplan: San Francisco Bay Atmospheric Deposition Pilot Study Project. San Francisco Estuary Institute, Richmond, CA.

SFEI. 1999. 2000 Workplan: San Francisco Bay Atmospheric Deposition Pilot Study Project. San Francisco Estuary Institute, Richmond, CA.

SFEI. 2000. Quality Assurance Project Plan for the San Francisco Atmospheric Deposition Pilot Study. San Francisco Estuary Institute, Richmond, CA.

SFEI. 2001. 1999 Annual Report: Regional Monitoring Program for Trace Substances. San Francisco Estuary Institute, Richmond, CA.

Shannon, J.D. and E.C. Voldner. 1995. Modeling atmospheric concentrations of mercury and deposition to the Great Lakes. *Atmospheric Environment* 29: 1649-1661.

Sheu, G.R., R.P. Mason and N.M. Lawson. 2001. Speciation and Distribution of Atmospheric Mercury over the Northern Chesapeake Bay Chemicals in the Environment, ACS Books (in press), Washington D. C.

SWRCB. 2001. Implementation of Clean Water Act Section 303(d) Ambient Monitoring, Impaired Water Body List, and Total Maximum Daily Loads, California State Water Resources Control Board.

TetraTech. 1999. Task 1 Conceptual Model Report for Copper and Nickel in Lower South San Francisco Bay. Prepared by Tetra Tech Inc. for the City of San Jose. Final Report. San Jose, CA.

Trujillo, L.F., K.L. Markham, J.R. Palmer and M.F. FriebeL. 1991. Water Resources Data California Water Year 1991. U.S. Geological Survey. Data Report CA-91-2.

Tsiros, I.X. 1999. A modeling analysis of factors influencing mass balance components of airborne deposited mercury in terrestrial landscapes. J. Environ. Sci. Health A34: 1979-2005.

USEPA. 1996. Method 1669: Sampling ambient water for trace metals at EPA water quality criteria levels. Office of Water, Engineering and Analysis Division, U.S. Environmental Protection Agency, Washington DC.

USEPA. 1997. Compendium Method IO-5: Sampling and analysis for vapor and particulate phase mercury utilizing cold vapor atomic fluorescence spectrometry (CVAFS). U. S. EPA. EPA/625/R-96/010a.

USEPA. 2001. Air Pollution and Water Quality: Air Deposition Initiative, U.S. Environmental Protection Agency.

Vermette, S., S. Lindberg and N. Bloom. 1995a. Field tests for a regional mercury deposition network - Sampling design and preliminary test results. Atmospheric Environment 29: 1247-1251.

Vermette, S.J., M.E. Peden, T.C. Willoughby, S.E. Lindberg and A.D. Weiss. 1995b. Methodology for the sampling of metals in precipitation: results of the National Atmospheric Deposition Program (NADP) pilot network. Atmospheric Environment 29: 1221-1229.

Welker, M. 1997. Quality Assurance Plan: Mercury Deposition Network. National Atmospheric Deposition Program. Illinois State Water Survey, Champaign, IL.

Williston, S.H. 1968. Mercury in the atmosphere. J. Geophysical Res. 73: 7051-7055.

WITS. 1999. Watershed Information Technical System. California Environmental Resources Evaluation System (CERES), California Resources Agency.

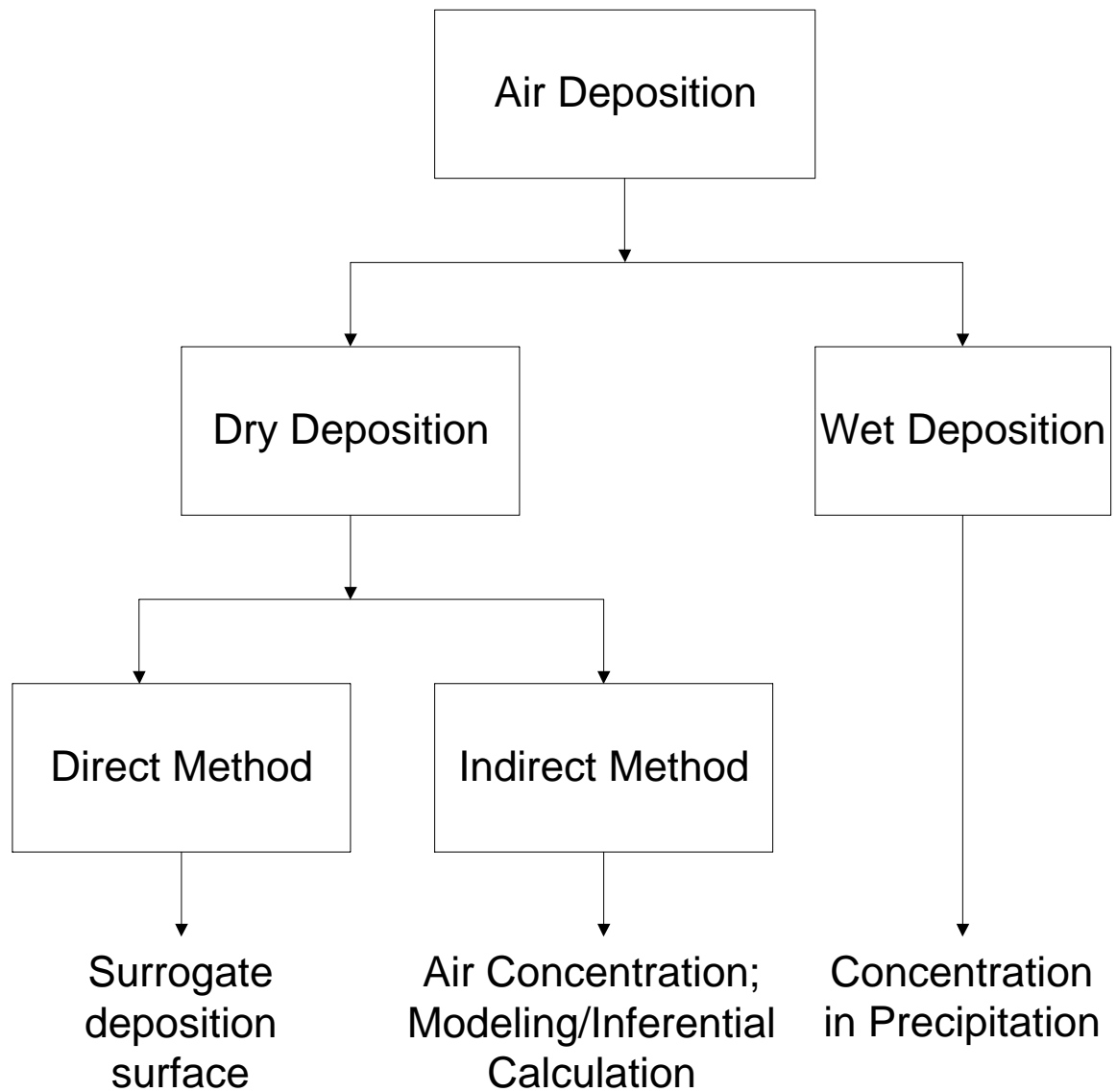


Figure 1. General Methodology for Atmospheric Deposition Study



Figure 2. Monitoring Sites Included in the San Francisco Bay Atmospheric Deposition Pilot Study

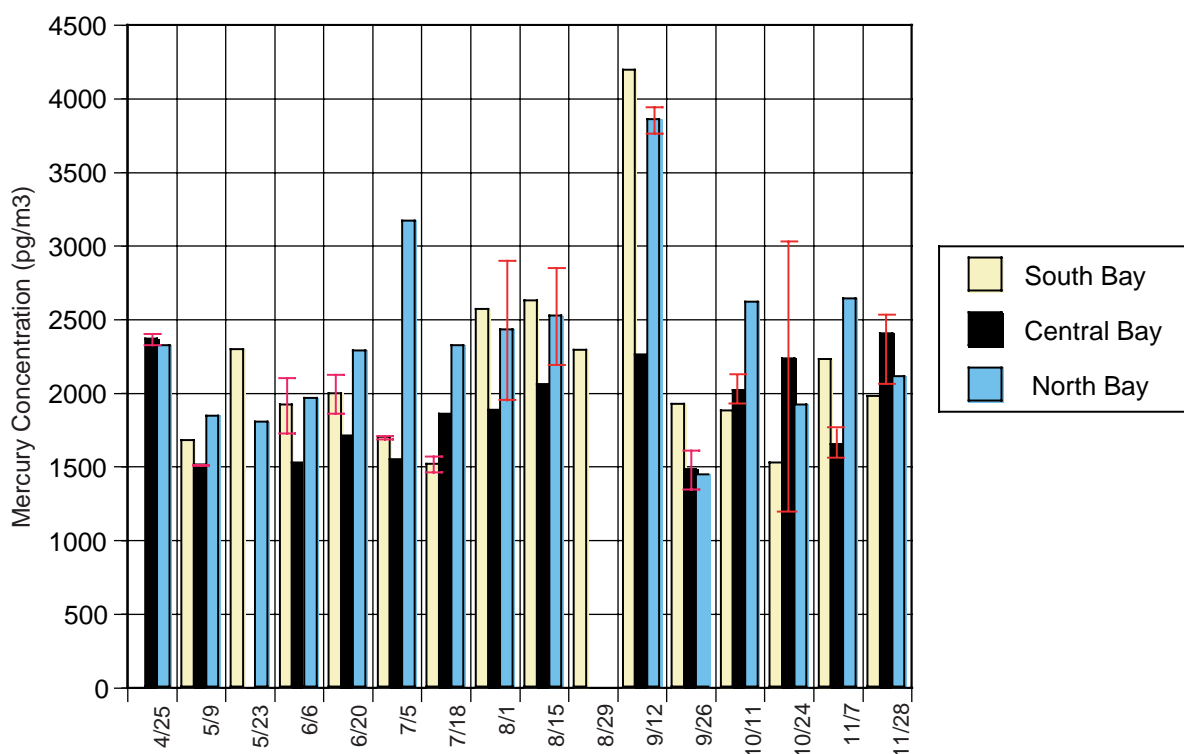


Figure 3. Mercury Concentration in the Ambient Air San Francisco Bay Area, Year 2000 (Bars indicate range of two measurements.)

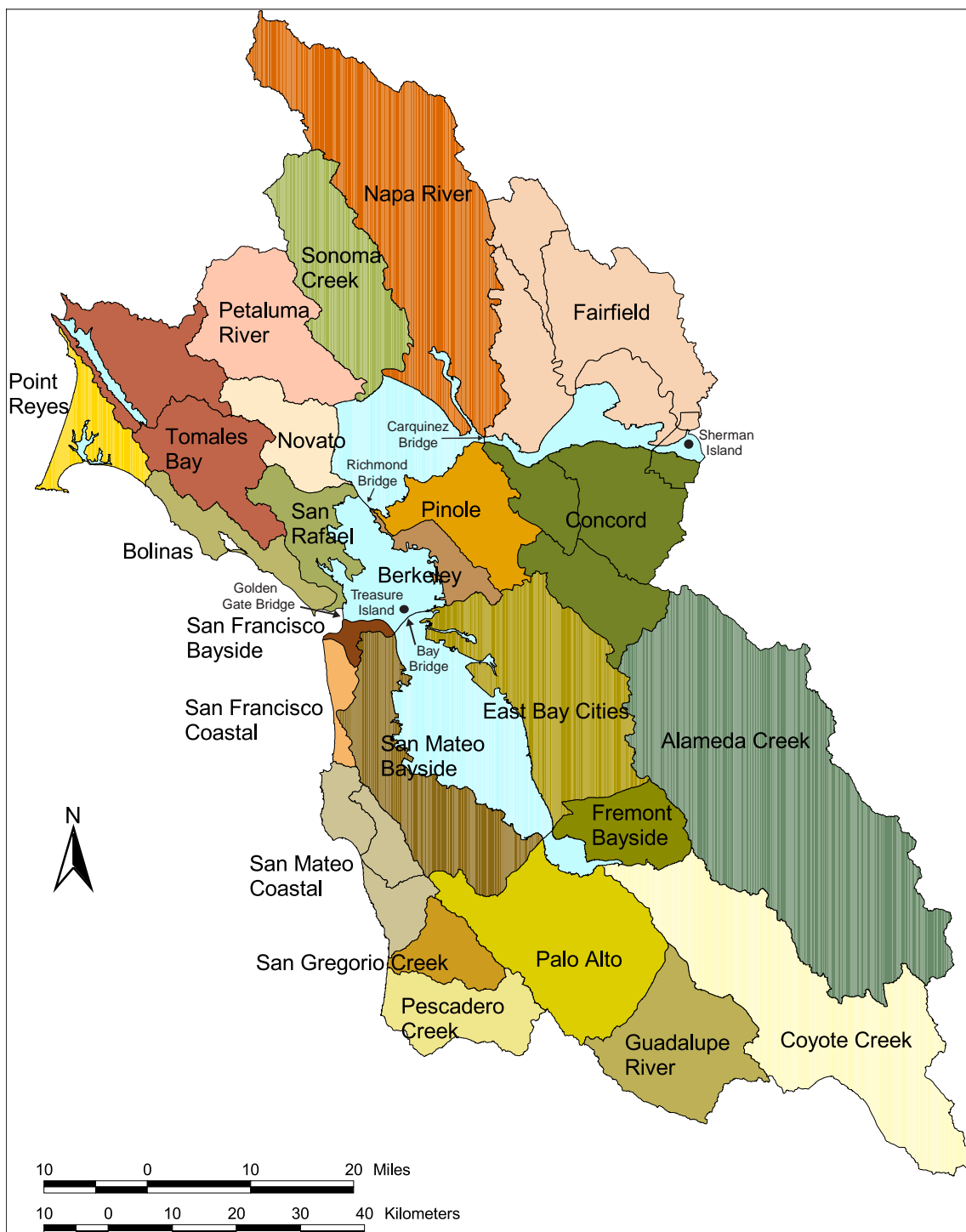


Figure 4. Hydrologic Areas in the San Francisco Bay Region
(taken from Davis et al., 2000)

Table 1. Chemicals Selected for Monitoring in the Pilot Study

Trace Elements (Phase 1)	Trace Organic Chemicals (Phase 2)
Cadmium	PAHs
Chromium	PCBs
Copper	
Mercury	
Nickel	

Table 2. Sampling Schedule for Trace Elements

Samples	Sampling Duration	Sampling Frequency
Wet Deposition (Precipitation)		
Hg and other trace metals	14 days	One cumulative composite sample every 14 days
Dry Deposition		
Hg and other trace metals	24 hours	One sample every 14 days

Table 3. Average Mercury Concentration in the Ambient Air (pg/m³)

Parameters	South Bay	Central Bay	North Bay	Entire Estuary
Average Concentration	2200	1900	2300	2100
Standard Deviation	660	330	590	570
Sample Size	15	14	15	44

Table 4. Parameters Used in Estimating Dry Deposition of Atmospheric Mercury

Parameter	Symbol	Values
Fraction of Total Mercury in Ambient Air		
Gaseous elemental Mercury	Hg(0)	0.95 (0.8-0.98) ^a
Gaseous reactive mercury	Hg(II)	0.02 (0.01 to 0.11) ^a
Particulate mercury	Hg(p)	0.03 (0.01 to 0.09) ^a
Deposition Velocity (cm/s)		
Gaseous reactive mercury	V_d	1.0 (0.1 to 5.0) ^b
Particulate mercury	V_d	0.2 (0.02 to 0.5) ^b
Air Temperature (°F)	T	60 ^c
Mean Wind Velocity (m/s)		
South Bay	u	2.5
Central Bay	u	3.5
North Bay	u	2.9
Entire Estuary	u	3.4 ^d
Surface Area (km²)		
South Bay	A	485
Central Bay	A	214
North Bay	A	434
Entire Estuary	A	1133

^a Number shown in the parenthesis presents range of the value reported by Sheu et al. (2001) for their samples taken around the Chesapeake Bay.

^b Number shown in the parenthesis presents range of the value reported in the literature.

^c Air temperature measured at Alviso (South Bay), Oakland STP (Central Bay), and CCCSD (North Bay) was 57°F, 56°F, and 63°F, respectively.

^d Wind velocity was calculated from the average annual wind velocity measured at 24 weather stations around the San Francisco Bay Area.

Table 5. Dry Deposition of Atmospheric Mercury to the San Francisco Estuary

Bay Segment	Hg(p) (kg/yr)	Hg(II) (kg/yr)	Gas Absorption of Hg(0) (kg/yr)	Total Deposition (kg/yr)	Deposition Flux ($\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$)
South Bay	2.0	6.6	0.57	9.2	19
Central Bay	0.8	2.6	0.38	3.8	18
North Bay	1.9	6.4	0.70	9.0	21
Entire Estuary	4.6	15	2.2	22	19

Hg(p) – Mercury in particulate phase

Hg(II) – Reactive gaseous mercury

Table 6. Estimated Volume-Weighted Average Mercury Concentration in Precipitation Collected at Sites in the San Francisco Bay Area

Precipitation Volume	Number of Samples	Volume-Weighted Average Concentration (ng/L)
All Data	59	7.95
>10 mL	56	7.95
>20 mL	53	7.94
>30 mL	52	7.94
>40 mL	51	7.91
>50 mL	47	7.91
>100 mL	36	7.92
>200 mL	31	7.93
>300 mL	24	7.91
>500 mL	16	7.89
>1000 mL	6	7.78

Table 7. Wet Deposition of Mercury to the San Francisco Estuary

Parameter	South Bay	Central Bay	North Bay	Entire Estuary
Annual Rainfall (inches) ^a	14.33	26.81	22.81	21
Annual Rainfall (cm)	36	68	58	53
Mercury Concentration in Rainfall (ng/L) ^b	9.7 (29) ^c	6.6 (16) ^c	7.4 (14) ^c	8.0 (59) ^c
Surface Area (km ²)	485	214	434	1133
Wet Deposition Flux ($\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$)	3.5	4.5	4.3	4.2
Loading (kg/yr)	1.7	0.96	1.8	4.8

^a Rainfall data were obtained from the weather station that was closest to the sampling site: NWS Moffett for South Bay (15.64 inches was recorded at BAAQMD's station in Alviso); Oakland STP for Central Bay; CCCSD for North Bay; NWS for the Entire Estuary.

^b Based on the volume-weighted average, using all data except one outlier.

^c Numbers in the parentheses indicate the number of samples used in calculating the volume-weighted average mercury concentration.

Table 8. Concentration of Mercury in Precipitation and Estimated Deposition Flux Reported in the Literature

Sampling Site Characteristics	Concentration (ng/L)*	Deposition Flux ($\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$)	Citation
Sites around Chesapeake Bay	11-15	14-30	Mason et al., 2000
33 MDN sites around the nation 1999	4.5-17.0	3.9-17.7	MDN 2001
6 Upper Midwest USA Sites 1990-1995		7.4	Glass and Sorensen 1999
South and equatorial Atlantic Ocean	3.56	4-7	Lamborg et al., 1999
Mid-continental N. America		6-12	cited in Lamborg et al., 1999
Lake Champlain basin, VT 1992-1994	1.5-44	7.7-9.3	Scherbatskoy 1999
Nahant, MA	10.1		Golomb 1997
17 MDN transition sites 1995-1996	5-15		Vermette et al., 1996
Pacific Ocean	2.8-17.0		cited in Mason 1996
North Atlantic Ocean	9-26		cited in Mason 1996
Chesapeake Bay	17.4		cited in Mason 1996
Chesapeake Bay	11-15	14-30	Mason et al., 2000
Pacific Northwest coast of Washington	3.2		cited in Mason 1996
Seattle, WA	15.2		cited in Mason 1996
Western NY	10	9.7	Vermette et al., 1995
Lake Champlain Basin, VT	8.3	9.3	Burke 1995
Little Rock Lake, WI		10.3	Fitzgerald et al., 1991
Northeast Pacific Ocean	9	10	Fitzgerald et al., 1991
San Francisco Bay Area	8.0	4.2	Current Pilot Study

* Most of the concentrations presented here were volume-weighted average.

Table 9. Summary of Mercury Loading from Direct Atmospheric Deposition to the San Francisco Estuary

Parameter	South Bay	Central Bay	North Bay	Entire Estuary
Dry deposition (kg/yr)	9.2 (84%)	3.8 (80%)	9.0 (83%)	22 (82%)
Hg(p)	2.0	0.8	1.9	4.6
Hg(II)	6.6	2.6	6.4	15
Hg(0)	0.57	0.38	0.70	2.2
Wet Deposition (kg/yr)	1.7 (16%)	0.96 (20%)	1.8 (17%)	4.8 (18%)
Total Direct Atmospheric Deposition (kg/yr)	11	4.7	11	27
Annual Rainfall (inches)	14.33 (36 cm)	26.81 (68 cm)	22.81 (58 cm)	21 (53 cm)

Table 10. Comparison of Mercury Loading to the San Francisco Estuary from Different Sources/Pathways

Source/Pathway	Data Source	Mercury Loading (kg/yr)	Uncertainty Level ¹
Atmospheric Deposition ²	Current Pilot Study	82	Moderate-High
Wastewater Discharges ³	Ellgas 2001	12	Low
San Francisco Bay Region Watershed ⁴	Abu-Saba and Tang 2000	168 (58-278)	Unknown
Sediment Remobilization ⁵	Abu-Saba and Tang 2000	500 (200-800)	Unknown
Central Valley Watershed ⁴	Abu-Saba and Tang 2000	607 (558-1150)	Unknown

¹ Low uncertainty: error of the estimate is within $\pm 25\%$; Moderate uncertainty: error of the estimate is up to two-fold; Moderate-high uncertainty: error of the estimate is two- to five-fold. Unknown uncertainty: level of uncertainty is unknown but possibly very high.

² Includes atmospheric deposition through direct and indirect routes.

³ Data is extrapolated from 83% of the wastewater discharges.

⁴ Estimate includes a loading component that is atmospheric in origin; Although the Central Valley Watershed is not included in the watershed area for the San Francisco Bay Region, it contributes pollutant loading to the North Bay.

⁵ Sediment remobilization is an internal process that redistributes pollutants within the Estuary, and not an external source of pollutant loading to the Estuary.

Table 11. Sources of Uncertainty Pertaining to Mercury Loading Estimates

Loading Estimate	Sources of Uncertainty	Uncertainty Level
Dry Deposition		Moderate-High
Hg Concentration in Air	Deviation in sampling and analytical operations	Within $\pm 15\%$ = Low
Hg(p) Fraction in Air	Assumed value based on measurements taken at Chesapeake Bay	Up to two-fold = Moderate
Hg(II) Fraction in Air	Assumed value based on measurements taken at Chesapeake Bay	Up to two-fold = Moderate
Deposition Velocity, cm/s	Assumed value based on literature review	Up to two-fold = Moderate
Area of the Estuary	Measuring deviation	Within $\pm 5\%$ = Low
Wet Deposition		Low
Hg Concentration in Precipitation	Deviation in sampling and analytical operations	Within $\pm 25\%$ = Low
Precipitation Amount	Instrumental precision	Within $\pm 5\%$ = Low
Atmospheric Deposition To Tributaries		Moderate-High
Area of the Watershed	Measuring deviation	Within $\pm 5\%$ = Low
Runoff Coefficient	Designation of land use categories; assumed runoff of mercury is the same as runoff of rainfall	Up to two-fold = Moderate
Parameters Related to Dry Deposition	Same as those listed under dry deposition	Two- to five-fold = Moderate-High
Parameters Related to Wet Deposition	Same as those listed under wet deposition	Within $\pm 25\%$ = Low