



Bay Area Petroleum Refinery Mercury Air Emissions, Deposition, and Fate

Prepared for:
Western States
Petroleum Association

**WSPA Member Facilities
San Francisco Bay Area, California**

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Western States Petroleum Association

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Lynn McGuire, P.E.
Principal-in-Charge

Vicki J. Hoffman
Senior Scientist

Susan Paulsen
Vice President and Senior Scientist

Environmental Resources Management

1777 Botelho Drive, Suite 260
Walnut Creek, California 94596
T: 925-946-0455 F: 925-946-9968

Flow Science Incorporated

723 East Green Street
Pasadena, California 91101
T: 626-304-1134 F: 626-304-9427

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ERM and Flow Science

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LIST OF ACRONYMS

3-D	three-dimensional
BAAQMD	San Francisco Bay Area Air Quality Management District
CAF	Combustion-AF
CARB	California Air Resources Board
CEC	California Energy Commission
cm	centimeter
CTM	chemical transport model
CVAFS	cold vapor atomic fluorescence spectrometry
DAF	Digestion-AF
DEM	Digital Elevation Model
FCCU	fluidized catalytic cracking unit
g	gram
h	hour
Hg	mercury
HgCl ₂	mercury chloride
HgS	mercury sulfide
ISCST	Industrial Source Complex Short Term (Model)
kg	kilogram
km	kilometer
L	liter
LCI	Land Cover Institute (USGS)
m	meter
MDN	Mercury Deposition Network
µg	microgram

MM5	Mesoscale Meteorological 5-KM Gridded Data
Mmol	10 ³ kg-mole
MMSCF	million standard cubic feet
NADP	National Atmospheric Deposition Program
ng	nanogram
NPDES	National Pollutant Discharge Elimination System
nmole	nanomole
NTN	National Trends Network
O ³	ozone
QA/QC	quality assurance and quality control
ppb	parts per billion
RFG	refinery fuel gas
RPD	relative percent difference
RWQCB	Regional Water Quality Control Board
scm	standard cubic meter
SFB	San Francisco Bay
TMDL	total maximum daily load
TRI	Toxics Release Inventory
UNEP	United Nations Environment Programme
US	United States
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WSPA	Western States Petroleum Association
yr	year

1.0 INTRODUCTION AND SUMMARY

At the request of the Western States Petroleum Association (WSPA), ERM-West, Inc. (ERM) and Flow Science Incorporated (Flow Science) have prepared this report with mercury sampling results obtained by Brown and Caldwell, to respond to Regional Water Control Board (RWQCB) requests to the five Bay Area refineries to complete a technical report on the fate of mercury in crude oil in the San Francisco Bay (SFB) Area Petroleum Refineries.

Various analyses have been performed to comply with the RWQCB requests. These analyses are listed below and are discussed in detail throughout the report.

- Measured airborne emissions of mercury from the combustion of refinery fuel gas and from process vent stacks;
- Conducted atmospheric dispersion modeling for calculating mercury deposition;
- Prepared Synthesis of Results;
- Estimated the mercury mass balance from refinery operations; and
- Performed literature review of mercury emissions and relevant studies in the SFB Area and the United States (US) for context.

Mercury occurs naturally in the environment from enriched soil, forest fires, oceans, volcanoes, and geothermal areas. It is also released from human activities such as mining, industrial activities including cement production, municipal waste incineration, chlor-alkali production, and fuel combustion. Model-based estimates indicate that human induced recycling, natural emissions, and new point-sources each account for approximately one-third of total inputs of atmospheric mercury (Lindberg et al. 2007). Tables 1-1 and 1-2 compare mercury contributions to the SFB by source type, and through direct deposition and from watershed transport, respectively.

Table 1-1 summarizes mercury contributions from various source types in the SFB Area. The primary contributors are the erosion of buried sediments and runoff from the Central Valley watersheds. These sources account for 36% and 38%, respectively.

Table 1-1 *Estimated Annual Mercury Contribution (in kg/yr) from Various Sources to the San Francisco Bay and Contributions from the Bay Area Refineries*

Contributing Sources	Contribution (kg/yr) ¹	Percent of Total Mercury Contribution
Mercury Contributions – Bay Area Refineries		
SFB Area Refineries	1	< 0.1%
Mercury Contribution from Area Wide Source Types		
Wastewater (municipal & industrial) Discharges	18	2%
Non-urban Storm Water Runoff	25	2%
Direct Atmospheric Deposition into the SFB	27	2%
Guadalupe River Watershed (mining legacy)	92	8%
Urban Storm Water Runoff	160	13%
Central Valley Watershed	440	36%
Erosion of buried sediments	460	38%
Total	1220	100%

¹ Source: San Francisco Bay RWQCB total maximum daily load (TMDL), 2006.

Table 1-2 provides a comparison of mercury contributions from SFB Area refineries estimated by this study via direct atmospheric deposition to watersheds and urban runoff for both the total and from the SFB Area refineries.

Table 1-2 *Estimated Annual Mercury Contribution (kg/yr) from Direct and Indirect Atmospheric Deposition into the San Francisco Bay*

Source	Contribution (kg/yr)	SFB Area Refinery Percent Contribution
Direct Deposition		
Direct Atmospheric Deposition into the SFB (total) ¹	27.00	-
<i>Direct Atmospheric Deposition into Bay Waters from SFB Area Refineries</i>	0.19	0.7%
Indirect Mercury Contributions		
Non-Urban Storm Water Runoff (total) ¹	25.00	-
Urban Storm Water Runoff (total) ¹	160.00	-
<i>Contribution from Surrounding Watersheds from Refineries</i>	0.82	0.44%

¹ Source: San Francisco Bay RWQCB total maximum daily load (TMDL), 2006.

Conclusions from the mercury fate and transport analysis indicate that the SFB Area refineries contribute minimal mercury to the Bay. Modeled mercury deposition rates from SFB Area refineries, when compared with reported estimates of mercury deposition at locations within and around the SFB Area, are equivalent to approximately 0.5% to 5% of both wet and dry deposition flux estimates.

Assuming all of the mercury from SFB Area refineries that is deposited to the watershed area draining directly to the SFB reaches the Bay, the contribution from the SFB Area refineries is estimated to be equivalent to approximately 5.6% of the mercury contributed to the SFB by

municipal and industrial discharges, approximately 3.7% of the mercury deposited directly from atmospheric deposition occurring over the SFB, and approximately 0.2% of the mercury contributed to the SFB by the Central Valley Watershed (see Section 3, Table 3-3). Thus, estimated mercury loadings from atmospheric deposition of mercury emitted by SFB Area refineries are a small fraction of total mercury loadings from other sources in the SFB region.

2.0 ATMOSPHERIC DISPERSION AND DEPOSITION MODELING

An atmospheric dispersion and deposition modeling analysis was performed to simulate the downwind transport and deposition rate of mercury due to airborne emissions of mercury from the five SFB Area refineries.

2.1 Modeling Emissions

Mercury mass emission rates used in the atmospheric dispersion and deposition modeling were derived from direct measurement of mercury in refinery fuel gas and in process vent stacks. A final review of data quality on all sample results was conducted; the review confirmed the validity of the data for modeling and reporting. A discussion of the measurements and emissions calculation methodology used to determine the mercury mass emission rates is included in Appendix A.

Emissions from the combustion of fuel gas (combustible gas generated during petroleum refining) were calculated assuming that 100% of the mass of mercury contained in the refinery fuel gas burned will be emitted into the atmosphere. Emissions from each of the refineries were calculated using refinery-specific fuel gas usage from April 2007 through March 2008. Mercury emissions due to the combustion of refinery fuel gas were distributed between various stack locations based upon:

- Specific refinery operations and information provided by refinery staff;
- Combustion source size and permitted limits found in Title V Permits; and
- Source type.

Depending on this refinery-specific information, ERM minimized the number of stacks or point sources by co-locating stacks that may have similar release characteristics since this would not significantly impact total mercury deposition rates on a regional scale. Total calculated mercury emissions from combustion of fuel gas at the five SFB Area refineries are 1.14 kg/yr.

In addition, process vent stacks were directly measured for mercury content and the average stack mercury mass rate that was attributed to the process stacks at each refinery. Total calculated mercury emissions from process stacks at the five SFB Area refineries are 17.96 kg/yr.

2.2 Modeling Methodology

2.2.1 Model Selection

After the consideration of various dispersion and deposition models, it was determined that the CALPUFF modeling system would be most appropriate for the analysis of the SFB and surrounding watersheds, which encompass a large area. The modeled area, or modeling domain, was based on the drainage basins located within the SFB Area, which drain into the SFB. The modeling domain for this analysis is illustrated in Figure 2-1. CALPUFF was chosen because (1) it is a regulatory agency-approved model; (2) it can incorporate both wet and dry deposition; (3) it uses a regional meteorological data set; and (4) it is capable of predicting pollutant concentrations and deposition rates on both a local and regional scale. The United States Environmental Protection Agency (USEPA)-approved CALPUFF modeling system is the

state-of-the-art system that has been used by the CARB for modeling exercises in the Bay Area and throughout the state.

The components of the CALPUFF modeling system include:

- CALMET;
- CALPUFF; and
- CALPOST.

The CALPUFF modeling system can simulate dispersion in multiple layers with space-varying, three-dimensional (3-D) meteorological data fields, (created by CALMET) to more accurately simulate pollution dispersion. This is especially true in locations such as the SFB Area, where the terrain varies and there are many microclimates. CALPUFF also utilizes mixing height, surface characteristics such as land use and land cover, and dispersion properties that are also included as part of the CALMET output file. The CALMET processing also accounts for the land/water interface the meteorological changes that occur between water and land surfaces through the development of independent dispersive parameters of the wind and atmospheric data. It does so by using the land use data, and overwater and overland characteristics to define specific surface roughness, albedo, and bowan ratio, which are used to define dispersive conditions within the wind field.

Using ERM internal software similar to CALPOST, post-processing was performed to compile specific results tables and summary reports of the deposition values created by the CALPUFF model.

2.2.2 Meteorological Data Development

A meteorological data set was developed using CALMET. Recently, the California Air Resources Board (CARB) completed a modeling analysis to assess whether sources of air pollutants potentially contributing to regional haze may impact visibility in Federal Class I Areas (National Parks, Wilderness Areas, National Monuments, etc.). This "Regional Haze" analysis was performed using the CALPUFF modeling system and a 3-D wind field data set created by CALMET. ERM requested and received the various CALMET input and output files from CARB and has reviewed the specific characteristics, inputs, and output computer files. The primary datasets used for preprocessing included Mesoscale Meteorological 5-KM Gridded Data (MM5), United States Geological Survey (USGS) Land Cover Institute (USGS-LCI) digitized regional land-use data, and USGS Digital Elevation Model (DEM) terrain data. The MM5 data have wind vectors, speeds, temperatures, precipitation, and boundary layer heights at 5-kilometer (km) intervals. The CALMET preprocessor was first used by CARB to regrid the data to user specified grid spacing (in this case 4 km) by interpolating the MM5 data at each 4 km grid point. This "regridded" MM5 data was then incorporated with data from 279 surface stations, the digitized surface and terrain data, and the digitized land use data to modify the flow vectors (both speed and direction) based upon the angle and height of the opposing terrain.

Due to the extremely large size of the raw MM5 data sets, CARB supplied ERM with the initial "regrid" of the MM5 data at intervals of 4 km for 2002. CARB also provided ERM with the preprocessed land use and terrain data, and the preprocessed surface station data and a CALMET input file. The combined file size is over 500 gigabytes.

ERM's initial review of the final data set (files used by CARB as input to CALPUFF) revealed that the processed CALMET data set did not include the precipitation data, which are required

for calculating the wet deposition of mercury. Therefore, the data were reprocessed to include the missing precipitation data.

2.2.3 Modeling Assumptions and Input Parameters

Numerous model inputs and control parameters were used for the air dispersion and deposition modeling. Tables 2-1 through 2-3 provide information on the specific parameters and model input assumptions used in the analysis. Table 2-1 provides the general technical model inputs. Table 2-2 provides specific mercury speciation information and Table 2-3 provides chemical parameters used by the CALPUFF model for calculating deposition velocities.

Table 2-1 CALPUFF Technical Modeling Inputs

Model Input Description	Default Input used?	Model Input Used?
Length of run	No-Default	8760 hours
Technical Options		
Vertical distribution	Yes	Gaussian
Terrain adjustment method	Yes	Partial plume path adjustment
Subgrid-scale complex terrain flag	Yes	Not modeled
Near-field puffs modeled as elongated slugs	Yes	No
Transitional plume rise modeled	Yes	Yes, transitional rise computed
Stack tip downwash	Yes	Yes, use stack tip downwash
Method used to simulate building downwash	Yes	ISC method
Vertical wind shear modeled above stack top	Yes	No, vertical wind shear not modeled
Puff splitting allowed	Yes	No, puffs are not split
Chemical mechanism flag	Yes	Chemical transformation not modeled
Wet removal modeled	No	Yes
Dry deposition modeled	Yes	Yes
Gravitational settling (plume tilt) modeled	Yes	No
Method used to compute dispersion coefficients	Yes	PG dispersion coefficients for rural areas (computed using the ISCST multi-segmented approximation) and MP coefficients in urban areas
Sigma-v/sigma-theta, sigma-w measurements used	Yes	Use both sigma-(v/theta) and sigma-w from PROFILE.DAT to compute sigma-y and sigma-z (valid for METFM - 1, 2, 3, 4, 5)
Back-up method used to compute dispersion when measured turbulence data are missing	Yes	PG dispersion coefficients for rural areas (computed using ISCST multi-segment approximation) and MP coefficients in urban areas
Method for Lagrangian timescale for Sigma-y (used only if MDISP=1,2 or MDISP2=1,2)	Yes	617.284 (s)
Method used for Advective-Decay timescale for Turbulence (used only if MDISP=2 or MDISP2=2)	Yes	No turbulence advection
Method used to compute turbulence sigma-v & sigma-w using micrometeorological variables (Used only if MDISP = 2 or MDISP2=2)	Yes	Standard CALPUFF subroutines
PG sigma-y, z adj. for roughness	Yes	No
Partial plume penetration of elevated inversion	Yes	Yes
Strength of temperature inversion	Yes	No
Map Projections and Grid Control Parameters		
Projection	No	LCC: Lambert Conformal Conic
DATUM-region for output coordinates	No-Default	WGS-84, Global Coverage
Project origin (decimal degrees) latitude	No-Default	37 N
Project origin (decimal degrees) longitude	No-Default	120.5 W
Project parallels (decimal degrees) latitude	No-Default	30 N
Project parallels (decimal degrees) latitude	No-Default	60 N

Model Input Description	Default Input used?	Model Input Used?
No of X grid cells (NX) (kilometers) ¹	No-Default	333
No of Y grid cells (NY) (kilometers) ¹	No-Default	333
No of vertical layers (NZ)	No-Default	12
Cell face heights	No-Default	0., 20.0, 40.0, 80.0 160.0, 300.0, 600.0, 1000.0, 1500.0, 2200.0, 3000.0, 4000.0, 5000.0
Grid origin (kilometers) (X)	No-Default	-497.2
Grid origin (kilometers) (Y)	No-Default	-544.9
Miscellaneous Dry Deposition Parameters		
Reference cuticle resistance	Yes	30.0 s/cm
Reference ground resistance	No	5.0 s/cm
Reference pollutant reactivity	Yes	8
Number of particle size intervals used to evaluate particle size deposition velocities	Yes	9
Vegetation state in un-irrigated areas	Yes	1
Miscellaneous Dispersion and Computational Parameters		
Horizontal size of puff (m) beyond which time-dependent dispersion equations (Heffter) are used to determine sigma-y and sigma z	Yes	550
Stability class used to determine plume growth rates for puffs above the boundary later	Yes	5
Vertical dispersion constant for stable conditions	Yes	0.01
Factor for determining transition-point from Schulman-Scire to Huber-Snyder Building downwash scheme	Yes	0.5
Range of land use categories for which urban dispersion is assumed	Yes	10, 19
Maximum travel distance of puff/slug (in grid units) during one sampling step	Yes	1.0
Maximum number of slugs/puffs release from one source during on time step	No	1
Maximum number of sampling steps for one puff/slug during on time step	No	1
Number of iterations using when computing the transport wind for a sampling step that includes gradual rise	Default	2
Minimum sigma y for a new puff/slug (m)	Default	1.0
Minimum sigma z for a new puff/slug (m)	Default	1.0
Minimum wind speed (m/s) allowed for non-calm conditions.	Default	0.5
Maximum mixing height (m)	Default	3000
Minimum mixing height (m)	No	20
Wind speed classes	Default	1.54, 3.09, 5.14, 8.23, 10.8 ISC Rural Values
Wind speed profile power-law exponents for stability classes 1-6	Default	A, B, C, D, E, F 0.07 ,0.07, 0.10, 0.15, 0.35, 0.55

Model Input Description	Default Input used?	Model Input Used?
Potential temperature gradients for Stable Classes E and F (deg/km)	Default	0.02, 0.035
Plume path coefficients for each stability class (used when MCTADJ=3)	Default	A, B, C, D, E, F 0.5, 0.5, 0.5, 0.5, 0.35, 0.35

¹ Number of grid cells exceeds maximum number allowed in USEPA Version of the CALMET model. The executable code was revised to accommodate this large number of cells and recompiled to complete the meteorological modeling.

Mercury Speciation. Releases of Mercury to the atmosphere typically occur in three forms: elemental [Hg(0)], reactive (RGM), and particulate [Hg(p)], or any combination of these. Each mercury species exhibits different depositional characteristics. RGM deposition occurs more quickly than Hg(0) because it is more soluble and adsorbs to most surfaces. It is widely accepted that this form of mercury has the highest deposition rate (Vijayaraghavan et al. 2008). Mercury speciation data are not available specifically for the combustion of refinery fuel gas; however, there are data available for combustion emissions from coal-fired power plants. Table 2-2 summarizes Hg speciation fractions that have been compiled using emissions data from 30 coal-fired power plants located in the eastern United States (Vijayaraghavan et al. 2008). The 30 power plants referenced above represent facilities with the highest percentage of RGM emissions (Vijayaraghavan et al. 2008) and would subsequently provide a conservative basis (or upper bound) for the deposition modeling. Total mercury emissions from each of the five Bay Area Refineries were multiplied by the fractions for each of the three mercury species as indicated in Table 2-2.

Table 2-2 Mercury Speciation

Mercury Species	Speciation Description	Percent of Emitted Mercury
Hg(0)	Elemental	39%
Hg(p)	Particulate	4%
RGM	Reactive	57%

Source: Plume-in-grid modeling of atmospheric mercury (Vijayaraghavan et al. 2008)

Deposition Velocities. The CALPUFF model is capable of using site-specific atmospheric conditions and land-use data provided in the meteorological data set for calculating representative deposition velocities. In addition to land-use data, specific chemical parameters are input and used by CALPUFF to calculate site-specific deposition velocities for Hg(0), Hg(p), and RGM as discussed below. For the best representation of specific conditions in the San Francisco Bay Area, this analysis has been performed utilizing the CALPUFF-derived deposition velocities. For each of the mercury phases, both dry and wet deposition were calculated.

For the deposition of particulates, the CALPUFF modeling input parameters include mass mean diameter, the associated standard deviation, and scavenging as summarized in Table 2-3. These default values are provided by the CALPUFF model and represent default values for a non-reactive set of pollutants (nitrate-NO₃), and would provide maximum deposition rates.

For the elemental and reactive mercury phases, input parameters include diffusivity, reactivity and mesoscale resistance, and Henry's Law coefficients. The wet deposition of these more reactive mercury phases are only affected by scavenging from liquid (not frozen) precipitation

(see Table 2-3). Except for the Henry's Law coefficients, default values producing the highest deposition rates of reactive pollutants were used (nitric acid – HNO₃).

Table 2-3 Chemical Parameters

Dry Deposition Parameters (Particulate)					
Species Name	Geometric Mass Mean Diameter (microns)			Geometric Standard Deviation (microns)	
Mercury particulate (Hg(p))	0.48			2.0	
Dry Deposition Parameters (Gas)					
Species Name	Diffusivity	Alpha Star	Reactivity	Meso. Resist.	Henry's Law Coef.
Hg(0)	0.1628	1.0	18.0	0.0	1.00E-07
RGM	0.1628	1.0	18.0	0.0	1.00E-07
Wet Deposition Parameters					
Species Name	Scavenging Coefficient (sec ⁻¹)				
	Liquid Precipitation		Frozen Precipitation		
Hg(0)	6.00E-05		0.00E+00		
Hg(p)	1.00E-04		3.00E-05		
RGM	6.00E-05		0.00E+00		

Source: CALPUFF Modeling System.

Table 2-3 shows the values assumed for this analysis. As stated above, the parameters selected have the highest potential for deposition and, therefore, provide a conservative basis of deposition for this assessment. In addition, it should be noted that, for the particulate phase, the default mass mean diameter are for diameters of 10 microns or less as established by the USEPA. Particulates from the use of combustion sources are typically in the range of less than one micron, thus providing additional conservative estimates for deposition.

The CALPUFF dispersion modeling requires the input of source-specific parameters. The mercury modeling analysis was performed using a series of point sources. Point-source inputs include:

- Source location;
- Stack emissions;
- Stack gas exit temperature;
- Stack gas exit velocity;
- Stack inner diameter; and
- Stack base elevation.

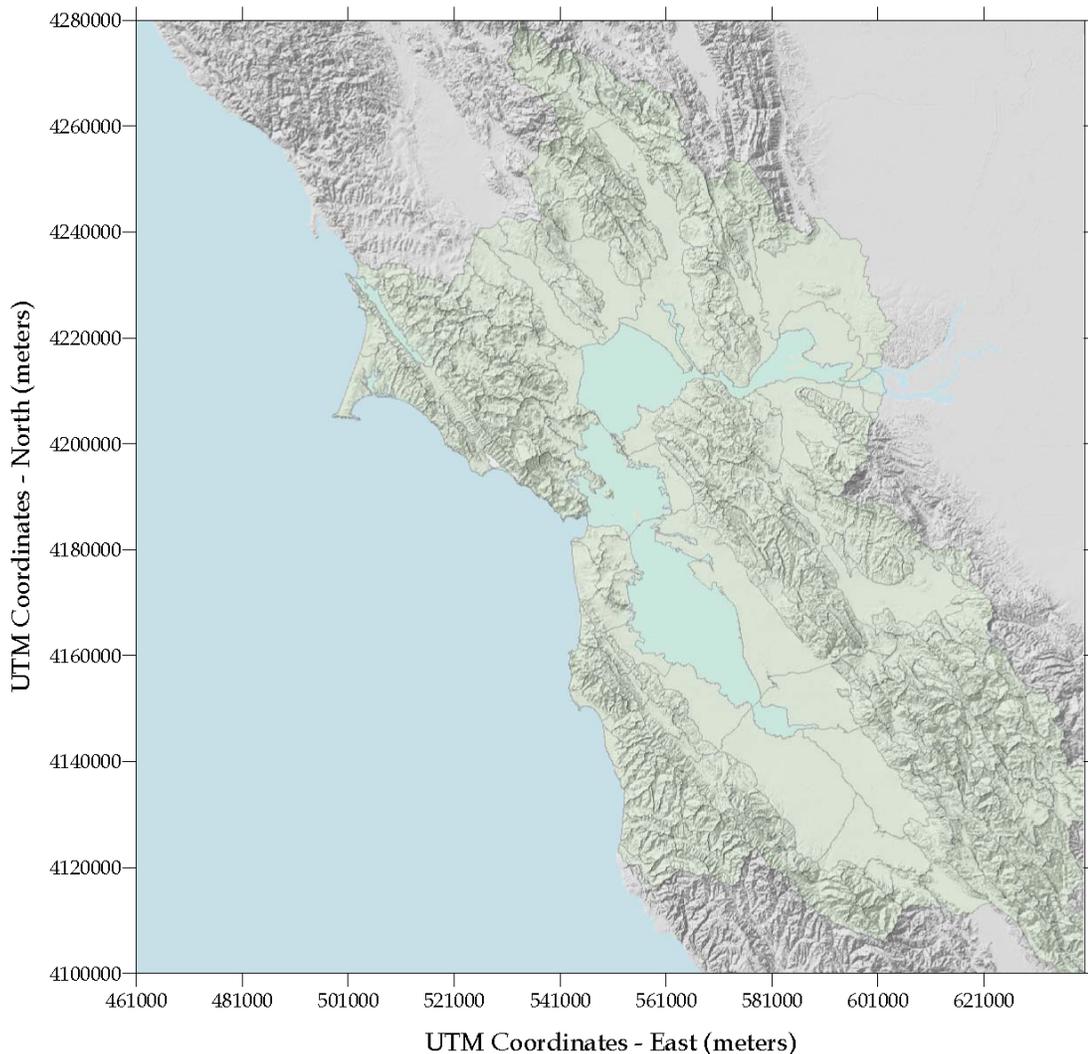
For each refinery, the modeling was performed assuming the mercury emissions are emitted from several representative stacks (between five and eight depending on the refinery). This minimized the number of modeled emission points. The stack emissions were co-located, or combined to best represent source type, size (based on Title V permits), and location. The stack release parameters were dependent on specific refinery processes and representative source-release parameters. Modeled source locations were unique for each of the refineries, in order to best represent the specific combustion sources at each site. Because this analysis is meant to calculate the transport of mercury throughout the Bay Area, the co-location of sources should

not significantly impact the overall modeled mercury concentrations and deposition within the drainage basins throughout the modeling domain.

2.2.4 Modeling Domain and Deposition Calculation Locations

The modeling analysis included the identification of numerous grid point locations for use in the calculation of deposition rates. In order to represent the regional nature of this analysis, a Cartesian grid was used, and points were placed every one and one half kilometers throughout the modeling domain. The modeling domain includes the rectangular area as illustrated in Figure 2-1 and covers the SFB and its surrounding water shed. Elevations for each of the gridded points were obtained from USGS DEMs. The CALPUFF dispersion model utilizes the model inputs, including mercury emissions, source release parameters, and regional meteorological conditions to calculate mercury deposition rates at each of the gridded point locations.

Figure 2-1 Modeling Domain



2.3 Atmospheric Dispersion Modeling Results

Air dispersion modeling was conducted for the refineries using the source parameters, which include a representative set of sources for each of the five SFB Area Refineries. Mercury deposition was calculated assuming emissions were in the particulate phase. Deposition rates within the modeling domain are dependant on many variables, including, but not limited to distance from a source, meteorology, land use and terrain features.

A review of the modeling results reveal that the majority of the deposition occurs to the north of the refinery sources, with a lesser amount depositing to the east and northwest. The lateral extent of the deposition is caused by a combination of the predominant wind characteristics in the SFB Area and local and regional terrain. CARB has illustrated seven general wind flow patterns that occur in the SFB Area as shown in Figure 2-2. Table 2-3 summarizes the percentages of directional airflow patterns (illustrated in Figure 2-2) that typically occur at four periods of the day (as well as daily average) by season. Most commonly, winds travel from the

west through the Golden Gate and from the northwest through the Cheleno and Luca Valleys. As illustrated, many are combination wind patterns, moving from one direction and changing due the interaction of local terrain. As seen in Figure 2-2 wind flow patterns labeled Northwesterly, Southerly, Bay Inflow, and Bay Outflow (flow patterns 1a, II, V, and VI) are likely to pick up mercury emissions from the refineries. These wind conditions occur approximately 51% of the time and are the most common wind patterns in this area, which are consistent with the modeling results. To a lesser extent, the modeling results show deposition occurring to the northwest of the refinery sources. This is also consistent with the wind flow patterns (III, IV, and VI) showing a frequency of 19% toward the northwest.

Upon further review of the modeling, the results showed that wet deposition dominates over dry deposition. It also reveals that a majority of the wet deposition occurs toward the north and that dry deposition occurs most often to the east. Based upon the wind flow patterns during winter months, when most of the wet weather patterns occur, southerly flows are generated by storm fronts and then move across the SFB Area. Table 2-3 shows a predominance of southerly and southeasterly winds that occur during winter months (32% during the rainy season) and would account for the dominance of the wet deposition to the north. During the summer and autumn months when rainfall is least, winds are dominated by the northwesterly wind flow regime, ranging from 78 to 54 percent, respectively.

The modeled deposition rates at each of the gridded points can also be used to calculate the total annual mercury deposition within a modeling region due to SFB Area Refineries. An analysis of the total deposition has been completed and is discussed in Section 3.

Table 2-4

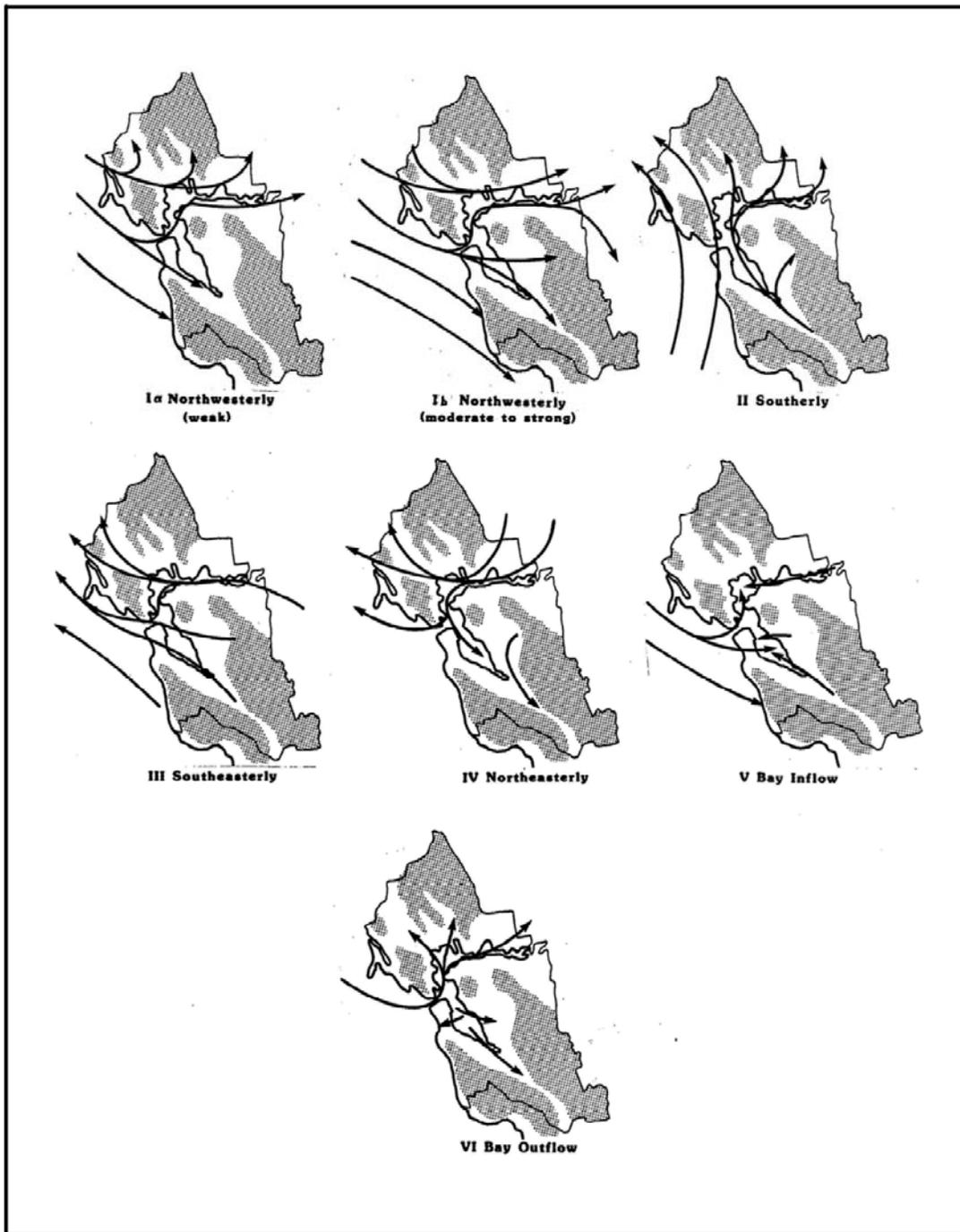
San Francisco Bay Area Air Basin Surface Airflow Types Seasonal and Diurnal Percentage of Occurrence (1977-1981 Data)

Types	la	lb	II	III	IV	V	VI	VII
	North-westerly (Weak)	North-westerly (Moderate to Strong)	Southerly	South-easterly	North-easterly	Bay Inflow	Bay Outflow	Calm
Time - PST	P e r c e n t o f t h e T i m e							
Winter								
4 a.m.	3	4	19	14	8	21	5	24
10 a.m.	4	5	19	20	10	11	19	9
4 p.m.	16	16	16	12	13	3	22	1
10 p.m.	6	9	14	14	10	20	3	21
All Times	7	9	17	15	10	14	12	14
Spring								
4 a.m.	27	25	11	2	4	21	5	12
10 a.m.	29	25	14	6	5	3	17	1
4 p.m.	22	60	7	4	4	2	2	---- ¹
10 p.m.	40	34	8	2	4	5	3	5
All Times	29	36	10	3	4	6	7	5
Summer								
4 a.m.	40	37	4	---- ¹	0	6	2	10
10 a.m.	37	44	4	---- ¹	1	1	13	0
4 p.m.	20	77	2	0	1	0	---- ¹	0
10 p.m.	39	55	2	0	---- ¹	1	1	1
All Times	34	53	3	0	1	2	4	3
Fall								
4 a.m.	25	13	7	6	3	22	3	19
10 a.m.	28	15	6	11	6	7	23	4
4 p.m.	31	46	5	2	6	2	7	---- ¹
10 p.m.	37	24	6	4	3	13	1	12
All Times	30	24	6	6	4	11	9	9
Annual								
4 a.m.	24	20	10	6	4	16	4	16
10 a.m.	25	22	11	9	6	6	18	4
4 p.m.	22	50	8	5	6	2	7	---- ¹
10 p.m.	31	30	8	5	4	10	2	10
All Times	26	30	9	6	5	8	8	8

¹ < 0.5 percent

Source: California Air Resources Board, Aerometric Data Division, 1984. Reprinted January 1992. California Surface Wind Climatology, June.

Figure 2-2 San Francisco Bay Area Airflow Pattern Types



Source: California Air Resources Board. Aerometric Data Division. 1984.
Reprinted January 1992. California Surface Wind Climatology. June.

2.4 Analysis Limitations

Simulation of dispersion and the predictions of concentration and deposition related to mercury emissions from point sources by their very nature may include limitations in the accuracy of model predictions. Modeling for the SFB Area refineries is no different. Dispersion models calculate a wide variety of concentrations/deposition over a series of specific locations, which represent an ensemble average of specific events. Events can include “known” meteorological parameters (wind speed, wind direction, mixing height, etc.) or source-specific characteristics (point source, area source, volume source, etc.). Variations in these collective events reveal both inherent and controlled limitations of dispersion models. Inherent deviations are the variability of uncontrolled parameters in the events, such as the repeatability of identical wind speeds over numerous observations. In theory, the inherent deviations can create a difference in modeled vs. measured concentrations of $\pm 50\%$ (USEPA 2005). Controlled (or reducible) variances are associated with parameters within the event that can be more easily managed or reproduced, such as a constant emission rate. Typically, these can be designed to minimize the variation. Model variations are considered reducible as opposed to inherent.

Studies for examining model accuracy have confirmed that dispersion models are more reliable in estimating long-term averaged concentrations than they are in estimating short-term averages at specific locations. Models are reasonably reliable for calculating the magnitude of highest concentration occurring within an area; however, not necessarily at a given point in time or space of that predicted concentration. Model accuracies for the highest derived concentrations typically range from ± 10 to $\pm 40\%$.

Studies have shown that the CALPUFF modeling system provides the technical basis and has the capabilities for addressing both long-range transport and complex wind situations. Studies have also shown that model accuracies are sufficient for use in the 50 km – 200 km range, and in some instances up to 300 km. Although scientific advancements continue to emerge, the CALPUFF model has been found to be scientifically accepted for use in regulatory applications by both state and federal agencies and for simulating long-range transport.

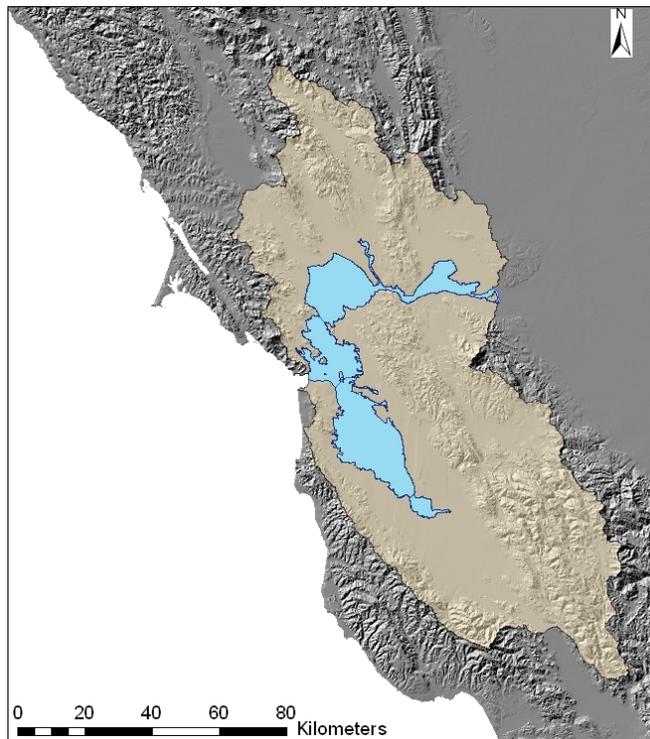
Mercury can be emitted in various phases (i.e., elemental, particulate, and reactive gas phase), or in combination. Therefore, inherent uncertainties can occur depending on the assumptions made regarding the amount of each phase being emitted. In addition, reactive gas phase mercury is highly dependent upon outside ambient conditions and, thus, would provide a greater rate of uncertainty within the dispersion and deposition in the model. However, specific mercury emissions speciation was not available for this analysis. Therefore, in order to minimize the uncertainty and increase the reliability of the modeled results, the mercury emissions were assumed to be in the particulate phase.

3.0 SYNTHESIS OF RESULTS – MERCURY TRANSPORT & FATE

Estimates of atmospheric deposition rates of mercury resulting solely from emissions from the SFB Area refineries were presented in Section 2. These deposition rates from the SFB Area refineries (at individual model grid points) were used to estimate the resulting total atmospheric deposition in the watershed area draining directly into the SFB. These model-based estimates of atmospheric deposition in the watershed area were compared with reported rates of atmospheric deposition of mercury in the SFB Area and other regions of the US.

The watersheds draining directly into the SFB (see Figure 3-1) were identified using the California Interagency Watershed Map of 1999 (updated May 2004, “calw221”) ([CalWater 2.2.1, http://gis.ca.gov/catalog/BrowseRecord.epl?id=22175](http://gis.ca.gov/catalog/BrowseRecord.epl?id=22175)), which is the State of California’s working definition of watershed boundaries. Note that the drainage area indicated in Figure 3-1 does not include the drainage area associated with streams flowing into SFB through the Sacramento-San Joaquin Delta (such as the Sacramento and San Joaquin Rivers). Thus, the area identified in Figure 3-1 is consistent with the modeling domain chosen in Section 2. The SFB watershed area in CalWater 2.2.1 also includes watersheds that drain directly into the Pacific Ocean, but these watersheds were also excluded from this analysis.

Figure 3-1 Watershed Area Draining Directly into the San Francisco Bay



Notes:

- Identified from the California Interagency Watershed Map of 1999.
- Note that the above area does not include the (indirect) contributing area of streams flowing into the San Francisco Bay through the Sacramento-San Joaquin Delta.

The modeled atmospheric deposition at individual modeled grid points, as described in Section 2, were interpolated to obtain average total deposition rates from the SFB Area refineries over the areas identified in Figure 3-1. Spatial averaging was performed using a commercial Geographic Information System software package called ArcGIS®. For this analysis, the point-based model deposition rates were interpolated to a fine grid mesh (0.1 km x 0.1 km) and aggregated over these fine grids to obtain spatially averaged deposition rates for the entire area shown in Figure 3-1. Over the SFB Area, the average annual total deposition rate of mercury resulting from the SFB Area refineries was estimated to be 0.1 µg/m²/yr (see Table 3-1).

Table 3-1 Total Deposition of Mercury to the SFB Area Obtained by Interpolation of Point-Based Model Estimates Presented in Section 2

Location	Area (km²)	Total Deposition (g/yr)	Average Deposition (g/km²/yr or µg/m²/yr)
SF Bay Water	1121	190	0.17
SF Bay Land	9035	820	0.1
SF Bay Area Total	10156	1010	0.1

Estimated deposition fluxes of mercury from the SFB Area refineries were compared with reported estimates of atmospheric mercury deposition fluxes at locations within and around the SFB in Table 3-2. Table 3-2 illustrates that the modeled total deposition flux of mercury from the SFB Area refineries varies from 0.5% to 5% of both the wet and dry deposition flux estimates reported in the literature. The observed and model-based estimates of deposition fluxes presented in Table 3-2 are within the range of deposition fluxes reported from other parts of the US (see Table B-8).

Table 3-2 Comparison of Estimated Total Mercury Deposition Fluxes ($\mu\text{g}/\text{m}^2/\text{yr}$) From SFB Area Refineries with Measured and Modeled Atmospheric Mercury Deposition Fluxes Reported in the Literature

Geographical area	Wet/dry	Flux ($\mu\text{g}/\text{m}^2/\text{yr}$)	Estimate from this study as a fraction of literature value	Data Source
San Francisco Bay and the watersheds draining directly into it (Figure 3-1)	wet+dry	0.1	-	Model-based estimates from this study
Covelo, CA (MDN Site CA 97)	wet	3.8-4.8	2.1% - 2.6%	Measurements from MDN, see Table B-5
San Jose, CA (MDN Site CA 72)	wet	2.1-3.1	3.2% - 4.7%	Measurements from MDN, see Table B-5
Entire San Francisco Estuary	wet	4.2	2.4%	Measurements from Tsai and Hoenicke (2001), see Table B-6
Moffett Field, Central CA	wet	4.4	2.3%	Measurements from Steding and Flegal (2002), see Table B-7
Long Marine Lab, Central CA	wet	4	2.5%	Measurements from Steding and Flegal (2002), see Table B-7
San Francisco Bay Area ^a	wet	5-15	0.7% - 2%	Model-based estimates from Seigneur et al. (2004)
San Francisco Bay Area ^b	wet	2-4	2.5% - 5%	Model-based estimates from Selin and Jacob (2008)
Entire San Francisco Estuary	dry	19	0.5%	Model-based estimates from Tsai and Hoenicke (2001), see Table B-6
San Francisco Bay Area ^a	dry	2-5	2% - 5%	Model-based estimates from Seigneur et al. (2004)

Notes:

^a Based on a visual inspection of the maps presented by Seigneur et al. (2004), the values corresponding to two grid cells (100 km x 100 km grid resolution) approximately overlapping with the San Francisco Bay Area were used.

^b Based on a visual inspection of the maps (grid resolution of 400 km x 500 km) presented by Selin and Jacob (2008), the values associated with the area generally corresponding to the San Francisco Bay Area were used.

The model-based estimate of total annual deposition of mercury from the SFB Area refineries to the region shown in Figure 3-1 (1.0 kg/yr, see Table 3-1) was compared with the contributions of mercury from various sources to the SFB (see Table 3-3). If it is assumed that all of the mercury deposited to the watershed region shown in Figure 3-1 reaches the Bay, the modeled contribution of atmospheric deposition from the SFB Area refineries, is approximately:

- 5.6% of the mercury contributed to the SFB by municipal and industrial discharges
- 3.7% of the mercury deposited directly from atmospheric deposition to the SFB water surface, and
- 0.2% of the mercury contributed to the SFB by the Central Valley Watershed.

It is unlikely that 100% of the mercury deposited to the watershed by atmospheric deposition is transported in storm water to SFB. Therefore these results are likely overestimates.

Table 3-3 Comparison of Annual Total Mercury Deposition (kg/yr) from SFB Area Refineries to the San Francisco Bay Area (model-based) with Annual Mercury Contribution from Various Sources Listed in the SFBRWQCB TMDL (2006)

Source	contribution (kg/yr)	SFB Area Refinery atmospheric contribution (as a fraction of other Hg sources to the SFB)
Maximum WSPA member facilities (model-based estimate from this study) ^a	1	-
Wastewater (municipal & industrial) Discharges	18	< 5.6%
Non-urban Storm Water Runoff	25	< 4%
Direct Atmospheric Deposition	27	< 3.7%
Guadalupe River Watershed (mining legacy)	92	< 1.1%
Urban Storm Water Runoff	160	< 0.6%
Central Valley Watershed	440	< 0.2%
Erosion of Buried Sediments	460	< 0.2%

^a This estimate, from Table 3-1, assumes that all mercury deposited to watersheds surrounding SFB reaches the Bay in storm water, and is thus a highly conservative estimate.

3.1 Conclusions

This analysis indicates that the SFB Area refineries contribute minimal mercury to the Bay. Modeled mercury deposition rates from SFB Area refineries are equivalent to approximately 0.5% to 5% of both wet and dry deposition flux estimates (as presented in Table 3-2) when compared with reported estimates of mercury deposition at locations within and around the SFB Area.

Assuming that all of the mercury from SFB Area refineries deposited to the watershed area draining directly to the SFB reaches the Bay, the contribution from the SFB Area refineries is estimated to be approximately:

- 5.6% of the mercury contributed to the SFB by municipal and industrial discharges,
- 3.7% of the mercury deposited directly from atmospheric deposition occurring over the SFB Area, and
- 0.2% of the mercury contributed to the SFB by the Central Valley Watershed.

Thus, estimated mercury loadings from atmospheric deposition of mercury emitted by SFB Area refineries are a small fraction (less than 6%) of total mercury loadings from other sources in the SFB region.

The calculation of the mercury emissions, dispersion and deposition modeling and the predictions of mercury transport and fate include component features that may over-predict or under-predict. Overall, the predicted mercury deposition and transport to the SFB is likely to be over-predicted due to the conservative emission calculation assumptions, as well as assumptions used in the transport.

3.2 Analysis Limitations

Predicting the fate of mercury deposition related to the SFB Area Refineries may be affected by laboratory and analysis methodologies, as well as the need to simplify some aspects of the dispersion and deposition process for maintaining a manageable computational effort and the conservative assumptions, and thus, the overestimation for mercury contributions to the SFB.

3.2.1 Mass Emissions

Refinery fuel gas (RFG) testing follows a rigorous QA/QC protocol during the first quarter of the study period. In general, the sampling results differed from the duplicate results by an average of 16%, which is in the expected range for this analysis. This could be either an over estimate or under estimate of mercury concentrations. However, the mercury emissions from the RFG combustion were calculated assuming that 100% are emitted into the atmosphere. This is most likely an overestimate of emissions.

The accuracy of stack testing results and the resultant emission calculations, which are based on the source testing of the Fluidized Catalytic Cracking Unit (FCCU) stacks, could also be marginally in error due to testing frequency, laboratory methodologies, and from variations in operating conditions. The scheduled stack tests were to be spread out over a one-year period to best represent annual average conditions. This again could be the estimated 10%-20% error range toward an over estimation or an underestimation of stack mercury concentrations. Again, the emissions calculated from the combustion of refinery fuel gas assumed 100% of the mercury content is emitted into the atmosphere which would lead to an over prediction of mercury concentrations and depositions rates.

3.2.2 Dispersion Modeling

In general, USEPA-approved dispersion models, including CALPUFF, have been found to have an accuracy factor of two from observations. These variations can either over-predict or under-predict pollutant concentrations and deposition rates. However, studies have shown that dispersion models are more reliable when estimating long-term average concentrations and deposition rates than short-term at specific locations. Since the modeling for this analysis only involves the predictions of annual-average concentrations, the accuracy of the results are expected to be less than a factor of two in variation, increasing the overall reliability in the assessment.

Mercury can be emitted in various phases, or in combination (i.e., elemental, particulate, and reactive gas phase.) There are no mercury speciation data available for refinery fuel combustion. However, there are data available from coal-fired power plants. The mercury speciation used in the modeling analysis was compiled using emissions data from 30 coal-fired power plants located in the eastern United States. These 30 facilities were chosen at the request of the RWQCB as conservative parameters to define the speciation due to their high percentage of RGM emissions. It is widely accepted that RGM has a higher deposition rate than the other emitted species (Vijayaraghavan et al. 2008). The use of speciation data from the coal-fired power plants would most likely result in conservative deposition modeling results.

3.2.3 Transport and Fate

The assumptions used in the transport and fate analysis were conservative and over-predictive. The analysis assumed that 100% of the mercury deposited within the San Francisco Bay Watershed would eventually drain into the Bay. This assumption will overstate transport because it does not account for soil absorption and the root and leaf uptake of plants.

Although this mercury transport and fate analysis includes both component features that overestimate and underestimate impacts, on balance, total Bay Area mercury deposition are likely overestimated.

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Appendix A
Mercury Mass Balance

APPENDIX A MERCURY MASS BALANCE

Information on levels of mercury in refinery processes and discharges include some recent compilations of mercury in crude samples, refined products, and estimates by the refineries reported to the USEPA and local agencies. WSPA member refineries conducted additional sampling and analysis as requested by the RWQCB. Sampling and analytical data collected during the course of this study, data provided by the refineries, and publicly available information were used to develop a simplified mercury mass balance estimate around the five SFB Area refineries. Sampling and analytical data were used to estimate mercury concentrations of refinery fuel gas, process vent stacks, crude oils, and petroleum coke. Information on the refined products, the refinery production rates, and material properties obtained from the individual refineries were used to determine annualized mass rates. Publicly available information reported by the refineries was used to estimate the amount of mercury being removed in waste sent to landfills outside of the Bay Area and in permitted water discharges. WSPA performed the mercury material balance to comply with the request from the RWQCB but the level of accuracy is different for each source and this makes it infeasible to close the mercury material balance. This section presents a summary of the mercury in the various refinery streams, contains a discussion regarding the methodologies used to obtain the data, and its relative accuracy. The variation in the regulatory mandated calculations of many streams restricts any statistical method to “balance” the data.

A.1 Summary of Mercury Mass Findings

The simplified mercury mass balance that was developed for this study is based on the estimated amounts of mercury entering the five SFB refineries in crude oil, the amount of mercury exiting in the combustion of refinery fuel gas, petroleum coke, process stacks, refined products, refinery waste, and in permitted water discharges. This is a simplified approach, because it does not attempt to quantify the effect of accumulation of mercury that can occur in process equipment, introducing a time-dependent fluctuation, in mercury quantities that may influence waste quantities generated in future years. The results are also dependent on the level of accuracy of the sources used to calculate mercury mass rates. These factors should be considered when evaluating the result of the mercury mass balance calculation. The calculated mass of mercury contained in the refinery streams used to develop the mass balance is provided in Table A-1 below.

Table A-1 Simplified Mass Balance Summary

	Media	Basis of Calculation	Mercury Mass Rate (kg/year)	Analytical Variability (kg/year)	Observed Variability (kg/year)
Input	Crude	Analytical Data and Crude Processing Rates.	224	+/-58	+/-62
Output	Refinery Fuel Gas	Analytical Data and Refinery Fuel Gas Consumption Rates	1.14+/-	+/-0.18	+/-0.44
	Process Stacks	Process Stack Test Results	17.96	+/-3.59	6.82
	Petroleum Coke	Analytical Data and Coke Production Rates	3.18	+/-0.22	--
	Water Discharges	NPDES Permit Limitation	0.91	--	--
	Refined Products	Literature Review	26.0	--	--
	Refinery Waste	TRI Reports for 2000 through 2007	221 to 650	--	--
	Total Output		270 to 699		

The result of the mass balance suggests that there is a difference between the amount of mercury entering the facilities (224 kg/yr) and the amount exiting the facility (270 to 699 kg/yr). This inherent variation was predictable due to inherent differences in the governmental mandated methods used to calculate the various waste streams, and in the differing timeframes for each of the media data reported. Statistically, the analysis necessarily uses unlike data sets, particularly the TRI data and the Water Discharge Data. These data sets were not intended for comparison nor designed to be used in a mass balance exercise. Therefore, there is inherent variation in the level of accuracy in comparing any of this source data. The sources of information and the relative level of accuracy for each data set is discussed in the following sections.

A.2 Mercury in Crude Feedstock

Mercury enters the refining process as a trace component of crude oil feedstocks. Samples of crude oils were collected and analyzed on a monthly basis. These analytical data were used along with throughput volumes to calculate the mercury mass. The 9-month sampling period for the crude was from October 2007 through June 2008.

A.2.1 Crude Mercury Sampling Results

For each of the refineries, approximately three crude samples were collected during each of the first 6 months of the sampling period and a single sample was collected during each of the final 3 months. Representative samples were obtained at the inlet to each crude unit at each refinery and represented the mix of crudes being processed at that time. The crude samples were sent to either Frontier Geosciences or CEBAM Analytical for analysis. Both laboratories analyzed for total mercury by cold vapor atomic fluorescence spectrometry (CVAFS). However, samples analyzed by CEBAM were prepared according to the Combustion-AF (CAF) Method and samples analyzed by Frontier Geosciences (Frontier) were prepared using the Digestion-AF (DAF) Method. Both are USEPA-approved methods and have adequate detection limits for the purposes of this study (0.5 parts per billion [ppb]).

Laboratory procedures were modified to improve consistency of results between the two laboratories. Frontier addressed the potential of volatile mercury loss that was reported in previous studies (Wilhelm, 2007) by withdrawing the sample from the container with a gas-

tight syringe and injecting the sample below the surface of the nitric acid used for digestion. Both laboratories used sonication to homogenize the crude samples prior to sample preparation.

To evaluate the potential impact from using different analytical methods, ERM submitted duplicate samples from the seven crude units to the two laboratories. The difference between the Frontier and CEBAM results ranged from between 0.4 ppb and 13.29 ppb. The largest differences were reported for the samples with the highest mercury content. Similar comparative studies indicate that the standard deviation of these analytical results is proportional to the mercury concentration (Hwang, 2007). That is, the largest variations were found in the samples with the highest mercury concentrations. The relative percent difference (RPD), which is the difference of the duplicate means as a percentage of the inter-laboratory mean, ranged from 2-56% with an average of 27%. A similar study conducted for these two laboratories found that the inter-laboratory results varied by an average of 24%, with a range of 0.1-94% (Wilhelm 2007).

The average mercury concentrations found in the crude at the different refineries ranged from 1.52 to 14.69 ppb. Table A-2 provides the average mercury concentration for the crudes at each of the refineries. Good agreement was found with other recent and independent studies of mercury concentrations in the crude refined in North America (Wilhelm, 2007). The quality assurance/quality control (QA/QC) results for the crude samples show that the results are within the expected range.

Table A-2 *Mercury Concentrations in Crude*

Refinery Crudes	Minimum Mercury Concentration (ng/g)	Maximum Mercury Concentration (ng/g)	Average Mercury Concentration (ng/g)
1	<0.36	14.30	6.19
2	2.26	9.05	5.23
3	3.32	21.63	10.30
4	5.10	41.29	19.07
5	<0.42	8.69	1.52
6	0.50	10.80	2.87
7	<0.32	2.91	1.51

A.2.2 Crude Processing Rate and Properties

Annual throughput of processed crude and the crude properties were provided by each of the refineries. For the purposes of this analysis, throughputs from July 2007 through June 2008 were used. These 12 months include the 9-month sampling period. The throughput from the refineries for this time period was approximately 278,155,288 barrels. During the sampling period, the density of the crude ranged from 308 to 342 pounds per barrel.

A.2.3 Mass of Mercury in the Crude

Based on the average mercury concentration in the crudes at each crude unit and annual crude throughputs, the estimated amount of total mercury in the crude is approximately 224 kg/year. This estimate may vary by ± 58 kg/yr (24%) to account for limitations in the analytical results as discussed above in Section A.2.1. Inherent variability in the process data may also cause the estimate to vary by an additional ± 62 kg/yr (26%).

Measurement "uncertainty" is intrinsic in any sampling and calculation method of this scale. Because the mercury mass in the crude was estimated as the product of the crude processing

rate and the corresponding mercury concentration in the crude, the inherent variability of these parameters will generate uncertainty in the total mercury mass estimated. A statistical analysis was conducted on the sampling data for each refinery discussed in A.2.1 and A.2.2 to estimate the standard error of the sample mean and the percent variability around the mean at the 95 percent confidence level. The variability of the mercury concentration in the various crude stocks ranged from 19.3% to 47.9% (depending upon the refinery), with a mean standard error variability of 24.5%. The variability of the crude processing rate is much less, ranging from 2.3% to 17.1% and a mean standard variability of 7.7%. The standard error variability of the product of the mercury concentrations and the crude processing rate ranged from 19.2% to 58.1%, with a mean standard error variability of 26.6%. This compares well with the average variability of the two individual parameters (26.3% standard error variability).

A.2.4 Crude Representativeness

Detailed crude representativeness data for the study period and the 5 years prior to the study was provided to the RWQCB in a Confidential Business Information binder. This information was used to assess whether the crude sampled during this study was similar to the crude that had historically been processed at these facilities. Table A-3 below shows that the average percent of SJV crude processed during the study period and the historical percent processed. In general, the average percent lies within the range of the historical data.

Table A-3 *Percent of SJV Crude in Mercury*

Refinery Crudes	Percent of SJV Crude					Study Period
	2003	2004	2005	2006	2007	
1	20%	24%	27%	33%	33%	25%
2	91%	78%	77%	77%	79%	76%
3/4	28%	23%	23%	23%	25%	27%
5	0%	0%	0%	0%	0%	0%
6/7	66%	65%	68%	74%	76%	69%

A.3 Refinery Fuel Mercury Content

Samples of mercury in refinery fuel gas (RFG) were collected by Brown & Caldwell from the five SFB Area refineries to estimate potential emissions resulting from its combustion. For most of the refineries, RFG mercury sample collection began in May 2007 and lasted until January 2008. Each of the refineries had unique testing dates and completion dates. Samples were obtained at seven locations (i.e., two of the refineries had two independent fuel gas systems requiring additional sets of samples).

A.3.1 Refinery Fuel Gas and Sampling Methodology and Results

The mercury sampling in RFG was performed by Brown & Caldwell using USEPA's Modified Method 30b. The sample collection method is consistent with the ASTM and ISO methods for the measurement of mercury in natural gas. The efficacy of this method was proven during a pilot test that also resulted in approved design specifications for sampling equipment handling combustible gas in a refinery environment. During the first quarter of sampling, monthly testing followed a rigorous QA/QC process, which included:

- Two simultaneous tests (using two blank sorbent traps) at two separate locations to provide critical precision measures (four measurements);
- Two sorbent traps spiked with known mercury concentrations – laboratory spikes to verify analytical methodologies are correct and consistent; and
- At least one sorbent trap spiked with a known mercury concentration – field spike to verify collection techniques are correct and consistent.

During the first quarter, seven to nine samples were obtained from each location: two duplicates for 3 months plus at least one field blank. The sampling results must meet the following QA/QC requirements:

- Field duplicate results fall <25% relative percent difference (RPD) for each monthly sampling;
- Breakthrough to “B” trap must be < 10% of “A” trap; and
- Spike recovery must fall within 75%-125% recovery.

If these criteria were met, the sampling efforts were relaxed to one sample per monthly sampling event, per sampling location, with spiked duplicates and a field blank collected once per quarter. If criteria were not met, then the sampling continued with the collection of duplicates and/or spikes.

The average mercury content for the different refineries ranged from 0.023 microgram per standard cubic meter ($\mu\text{g}/\text{scm}$) to 0.83 $\mu\text{g}/\text{scm}$. The average mercury concentration in the refinery fuel gas across all of the refineries was 0.294 $\mu\text{g}/\text{scm}$. Table A-3 provides the average, mercury concentration in the seven types of refinery fuel gas used at the refineries. The QA/QC analysis shows that most of the data were within acceptable limits. The following is a summary of the QA/QC results:

- Forty-one of the 58 samples met all of the QA/QC criteria.
- Five samples had an RPD value greater than 25%.
- Breakthrough to “B” trap was reported for one sample.
- Spike recovery did not meet the QA/QC criteria for 15 samples. Most of these samples were collected at one location. Subsequent sampling indicates that the issue at this location was addressed.

In general, the sample results were similar to the duplicate results. Even with the five samples that exceeded the RPD criteria, the average RPD was 16%, which is within the expected range for this analysis.

Table A-4 Mercury in Refinery Fuel Gas

Refinery Fuel Gases	Minimum Mercury Concentration ($\mu\text{g}/\text{scm}$)	Maximum Mercury Concentration ($\mu\text{g}/\text{scm}$)	Average Mercury Concentration ($\mu\text{g}/\text{scm}$)
1	0.064	1.119	0.398
2	0.011	0.102	0.041
3	0.027	0.499	0.144
4	0.060	0.162	0.109
5	0.041	2.386	0.786
6	0.001	0.052	0.021
7	0.002	2.404	0.812

A.3.2 Refinery Fuel Gas Combustion Rates

The volume of RFG that was combusted during the 12-month period (April 2007 through March 2008) was approximately 178,000 million standard cubic feet (MMSCF). The volume of RFG combusted by sources that vent to process stacks was not included in this total. Combustion emissions from those sources were captured by the sources tests. Information regarding the RFG usage was provided by the individual refineries.

A.3.3 Mercury Emissions Rates from Refinery Fuel Gas Combustion

The aggregate annual mercury emission rate of 1.14 kg/year was calculated using RFG combustion rates and the measured concentrations of mercury. This estimate may vary by ± 0.18 kg/yr to account for the potential error in the analytical results (16%) and an additional ± 0.44 kg/yr (39%) for the inherent uncertainty in the process data.

Statistical analyses were conducted to assess the inherent variability of the refinery fuel gas combustion rate and the mercury concentration data used to estimate the overall mercury emissions for each of the refineries. The 95th-percentile standard error for the mercury concentrations in fuel gas sampling at the five refineries (which contain a total of seven fuel gas systems), ranged from 16.2% to 54.1%, with a mean standard error percentage variability of 40.2%. Similar to the crude measurements, the standard error was much lower within each refinery, ranging from 2.3% to 10.2% around the individual means (averaging 3.9%). The average standard error percent variability for the product of the refinery gas combustion rate and the corresponding mercury concentration (used to calculate mass mercury emission rates) ranged from 21.5% to 52.7%, with a mean value of 39.3%. Again, this is in good agreement with the average variability of the individual refinery fuel gas combustion rates and mercury concentrations (40.2%).

A.4 Mercury Emissions from Process Stacks

A.4.1 Process Stack Source Testing Methodologies and Results

The RWQCB requested that each of the four refineries with a fluidized catalytic cracking unit (FCCU) perform three sampling events. The sampling events were scheduled such that they would provide an adequate representation of normal annual operating conditions. This was accomplished by scheduling the stack testing events during different times of the year.

The stack testing was performed by the Avogadro Group, LLC (Avogadro). The sampling techniques employed for all but one of these stack tests were consistent with USEPA Method 101A, which tests only for mercury in the exhaust gas. For one of the tests, Avogadro used techniques consistent with USEPA Method 29, which is used to determine concentrations of multiple trace metals at the exhaust stack.

The process stack test results were reviewed for quality and validity by Avogadro through a rigorous QA program. Avogadro's review procedure includes review of each source test report by a project QA officer, including review of laboratory and fieldwork, data sheets, data inputs, calculation and averages, and the preparation of report text. In addition, the equipment used to conduct the emission measurements are maintained according to the manufacturer's instructions and calibrations are performed according to the schedule outlined by the CARB. All this work is completed to produce the most accurate results possible with the methods that were used. However, Avogadro does acknowledge that, with isokinetic tests such as these, there is an inherent error of approximately 10% (Avogadro, 2009). There is also a potential 10% error margin from the laboratory analysis for values that are above the reporting limit. Due to the conservative nature of the detection limit, values below the detection limit are not expected to have any significant error. Stack test results are summarized in Table A-5.

Table A-5 Mercury Concentration from Process Stacks (FCCUs)

Refinery Stacks	Test Date	Minimum Hg Concentration @ 7% O ₂ (µg/m ³)	Maximum Hg Concentration @ 7% O ₂ (µg/m ³)	Average Hg Concentration @ 7% O ₂ (µg/m ³)
1	Feb. 7-8, 2008	<0.11	0.71	<0.45
	Oct. 8-10, 2008	<0.12	<0.13	<0.13
	Dec. 16-17, 2008	<0.11	<0.11	<0.11
2	Jun. 6-8, 2006	2.38	3.35	2.92
	Feb. 7, 2008 ¹	2.32	2.50	2.39
	Feb. 23, 2009	1.90	2.03	1.96
3	Feb. 7-8, 2008	<0.13	<0.14	<0.13
	Aug. 27-28, 2008	<0.12	<0.13	<0.13
	Oct. 30-31 2008	<0.09	<0.12	<0.10
4	Mar. 19-20, 2008	<0.57	1.75	<1.09
	Sept. 16-17, 2008	0.104	0.286	0.186
	Nov. 11-12, 2008	0.26	<0.38	<0.32

Notes:

1. Four runs were performed for this test. The first run is not considered in these results because the test was performed while the unit was not operating at the proper load.

The inherent uncertainty of the mercury concentration from the process stacks were estimated from the standard error around the means for the mercury concentration data from the four refineries with FCCUs. The 95th-percentile standard error for the mercury concentrations ranged from 10.7% to 68.1%, with a mean standard error percentage variability of 38.0%.

A.4.2 Mercury Emissions

The stack testing results indicate that 17.96 kg Hg/yr are emitted into the atmosphere from the SFB Area refinery FCCU stacks. For each of the four refineries, the estimated annual mercury emissions exceed 0.1 kg Hg/yr, which was the minimum detection limit specified for the testing. The mass estimate may vary by plus or minus 11.28 kg/yr to account for the potential error from the sampling and analytical methods (10% for non-detect values and 20% for values reported above the detection limit) and an additional 38% from the inherent variability of the sampled data.

A.5 Mercury Content in Petroleum Coke Sample

A.5.1 Petroleum Coke Sampling and Results

Samples of the petroleum coke were collected to determine annual quantities of mercury removed from the site via coke production. Petroleum coke samples were gathered from the four refineries with a total of five coke production units. The coke samples were composites of daily samples that had been collected throughout the week. The composite samples were delivered to the laboratory (Frontier Geosciences) where they are prepared by a hydrofluoric/nitric/hydrochloric bomb digest according to Method FGS-111. The digested samples were then analyzed for total mercury by CVAFS according to Method FGS-069. The results from the five different types of coke analyzed are summarized in Table A-6.

Table A-6 *Mercury in Petroleum Coke*

Coke	Average Mercury Concentration (ng/g)
1	1.22
2	1.70
3	2.40
4	4.37
5	0.63
Average	2.07

Frontier indicated that the data were within the set control limits and they provided statistical information to assess the relative accuracy of the coke analytical data. The data show that the average laboratory control sample RPD is 6.8% with a 2 sigma value of 18.3%.

A.5.2 Mass of Mercury

The analytical data and the amount of crude processed indicate that approximately 3.18 kg of mercury leaves the refineries in coke. According to Frontier, the precision of the mass mercury estimates may vary by about ± 0.22 kg/yr (6.8%).

Due to the limited amount of data relating to the coke production and the corresponding mercury emissions, no statistical analyses could be conducted to assess the inherent variability of the process data with any confidence in the results. Since the overall magnitude of the emissions is small relative to the overall emissions, the inherent variability would not have a significant change to the overall results of this study.

A.6 Mercury in Waste Materials Transported Off-site

The refineries provide annual Toxics Release Inventory (TRI) reports per criteria established by USEPA. Each TRI submittal includes estimates of mercury in waste materials transported off-site to appropriate waste management facilities using these criteria. Readily available reports show that from 2000 through 2007, the five SFB area refineries generated aggregate amounts of mercury that ranged from 220.72 kg/yr in 2007 to 648.75 kg/yr in 2002 and averaged 417.27 kg annually. Table A-7 summarizes the mass of mercury removed off-site and presents the main waste stream types for each facility. The "main waste streams" reflected in Table A-7 contain at least 90% of the mercury removed off-site.

Table A-7 TRI Waste Discharge Data [table not formatted to show the boxes]

Refinery	Main Waste Stream Types	Off-Site Mercury Waste Discharge (Kg)							
		2000	2001	2002	2003	2004	2005	2006	2007
1	1. Lab Waste/Packs								
	2. Soil/Dirt	11.93	3.48	17.56	4.74	9.24	31.64	61.02	29.57
	3. Sludge								
	4. Spent Caustic								
2	1. Equipment Cleanout								
	2. Filter Waste	388.28	567.84	299.93	306.77	351.63	158.75	165.81	31.05
	3. Biosolids								
	4. Lab Waste/Packs								
3	1. Sludge								
	2. Soil/Dirt	188.74	5.90	52.07	55.70	8.35	25.17	19.50	24.18
	3. Tank Bottoms								
	4. Industrial Debris								
4	1. Metal Cake								
	2. Diesel & Catacarb Filters	0.23	14.52	0.14	3.18	0.01	0.01	1.36	26.31
	3. Biosludge								
	4. Tank Bottoms								
	5. Lab Waste								
5	1. Biological Sludge								
	2. Tank Bottoms	2.84	57.02	99.68	32.55	40.78	66.94	64.08	109.62
	3. Soil/Dirt								
	4. Primary Sludge								
Total		592.02	648.75	469.37	402.94	410.01	282.51	311.77	220.72

There are a number of issues that limit the accuracy of TRI data toward developing mass estimates that account for mercury in all refinery waste streams. The most common of these include changes in waste classification, profiles, and time. The mandated calculations might be useful in comparing year-to-year data, but cannot be used as an accurate measurement of mercury where it was not directly monitored, sampled, and measured.

A.6.1 Classification

Waste classification sampling is typically based on grab samples. It is prohibitively difficult to cost effectively conduct a rigorous and representative sampling protocol that is designed to collect representative samples from high and low volumes, solid and/or liquid, and from homogenous and combined waste streams. Waste classifications are based on concentration thresholds independently set by federal, state, and local regulations. The analytical reporting limits provided by the laboratories are typically set at these regulatory thresholds to simplify lab reporting and to provide the refinery a straight-forward (i.e., yes or no) way to classify each waste stream constituent. If the concentration of mercury in the waste stream varies significantly, the estimate of mercury has the potential to be greater than, less than, or approximately equal to the actual mercury total mass.

A.6.2 Profiles

Waste stream profiles are "recertified" by the disposal site each year. Once a profile has been established, the waste profile remains "certified" unless the process(es) that generate the waste(s) have changed. Complex and changing refinery operations (often on a day-to-day basis) such as new projects, variations in feedstock, market-driven changes in product

formulations and demand, and product additives can create the need for “recertification.” In addition, multi-year maintenance turnaround schedules, unplanned upsets, and unit downtime may introduce variable waste streams that may not fully reflect the current certified waste profile.

A.6.3 Time

The timeframe chosen for assessing mercury in waste streams should account for data types, process, sampling and measurement variability, maintenance and turnaround activities, and raw material inputs, products, by-products, and waste products that occur or are consumed or produced over a specific time span. Raw material inputs vary over time based on availability, price, and production requirements. Products and by-products vary according to market, and regulatory demand and requirements. Waste streams may require 5 to 10 years or longer between scheduled maintenance activities to capture the majority of the disposed mass for a given constituent.

Considering the process and requirements for assessing refinery waste streams, the analytical profile methodology for quantifying constituent content, and the time duration of waste stream generation as compared to this quantification, it would be reasonable to find that the TRI reports reflect greater mercury mass than what might be found in the annual estimates of mercury in the crude.

A.7 Mercury Content of Refined Products

A literature search was conducted to assess published information available that would characterize the mercury content in the most commonly produced products produced by the Bay Area refineries. The most commonly produced products include gasoline (both California and non-California blends), diesel fuel, aviation fuel, and fuel oil. The annual mercury mass for these streams from the five SFB Area refineries in aggregate is estimated to be 26 kg/yr.

The literature survey produced nine studies that are detailed Section 4. Of note are two literature sources specific to the Bay Area:

- “Estimate of mercury emission from gasoline and diesel fuel consumption, San Francisco Bay area, California” (Conaway et al., 2005).
- “Trace Element and PAH of Jet Engine Fuels” (US Navy, 2000).

Table A-8 below provides a summary of the mercury content in the most commonly produced, refined products. The mercury content from the literature was combined with associated product volumes for the five SFB Area refineries obtained from the California Energy Commission (CEC) to produce mass estimates.

Table A-8 Average Mercury in Refined Products

Product	kg/year
Aviation Fuel	02.4
Diesel	02.0
Fuel Oil	13.0
Gasoline, CA	07.7
Gasoline, non-CA	00.99
Total	26.0

The most common products accounted for 85 to 92% of all product categories from the SFB Area refineries. The refineries were polled to determine categories of less or least common, including lube oils, bunker fuel, asphalt, propane, and butane. As much as the individual percent of each non-predominant product can vary from week to week, in aggregate they ranged from 8 to 15%.

Data were obtained from the CEC reflecting annual volumes of the five predominant products from the SFB Area refineries, and are shown in Table A-9 below.

Table A-9 CEC Product Volumes

Predominant Product	Volume (barrels/year)
Aviation Fuel	38,098,000
Diesel	42,183,000
Fuel Oil	16,627,000
Gasoline, CA	139,998,000
Gasoline, non-CA	18,043,000

To produce mercury mass estimates, most common product densities were obtained from literature references and a conversion calculation was performed. It was assumed that the density of non-California gasoline was equivalent to that of California gasoline.

Table A-10 below provides a more detailed overview of mercury in refined products, with values rounded to two significant figures here and in Table A-6. Mercury content was combined with associated product volumes to produce mercury mass estimates. Based on the range of results, the average provides a suitable estimate for the SFB Area refineries. Mercury content values for gasoline and diesel in the literature were produced from studies in the SFB region, and those for aviation fuel from a California study conducted by the US Navy.

Table A-10 Detailed Mercury in Refined Products

Predominant Product	Low Hg (kg/year)	High Hg (kg/year)	Average Hg (kg/year)
Aviation Fuel	0.01	04.9	02.4
Diesel	0.29	05.7	02.0
Fuel Oil	1.60	21.0	13.0
Gasoline, CA	1.30	22.0	07.7
Gasoline, non-CA	0.16	02.8	0.99
Total	3.40	56.0	26.0

The amount of mercury in predominantly refined products is estimated to be 26 kg/yr. These products make up approximately 85 to 92% of product streams in the refineries, where the non-predominant products mentioned above make up the remaining 8 to 15%.

A.8 Mercury Content in Water Discharges

The amount of mercury allocated to each facility by the respective National Pollutant Discharge Elimination System (NPDES) permits was used to calculate an estimate of the amount of mercury in the wastewater discharge. The aggregate amount of mercury that can be emitted according to the NPDES permits is 0.91 kg/yr. This represents a conservative estimate of the mass of mercury because the refineries typically operate below the respective limits to stay in compliance with the permit.

A.9 References

- Avogadro Group. (2009). Telephone conversation between Dan Duncan of Avogadro Group and Eric Rivero-Montes of ERM. 15 January.
- Conaway CH, Mason RP, Steding DJ, Russell Flegal A. (2005) Estimate of mercury emission from gasoline and diesel fuel consumption, San Francisco Bay area, California. *Atmospheric Environment* 39: 101-105.
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Appendix B
Literature Review

APPENDIX B LITERATURE REVIEW

Flow Science conducted a review of relevant literature to evaluate natural and anthropogenic emissions of mercury and rates of atmospheric deposition of mercury in the SFB Area and the US, and to assess the overall mercury budget of the SFB. In the remainder of this document, the terms SFB and San Francisco Estuary are used interchangeably. Considering the focus of this report on evaluating emissions of mercury from SFB Area refineries, the following literature review emphasizes studies dealing with atmospheric deposition and emission of mercury in the SFB Area.

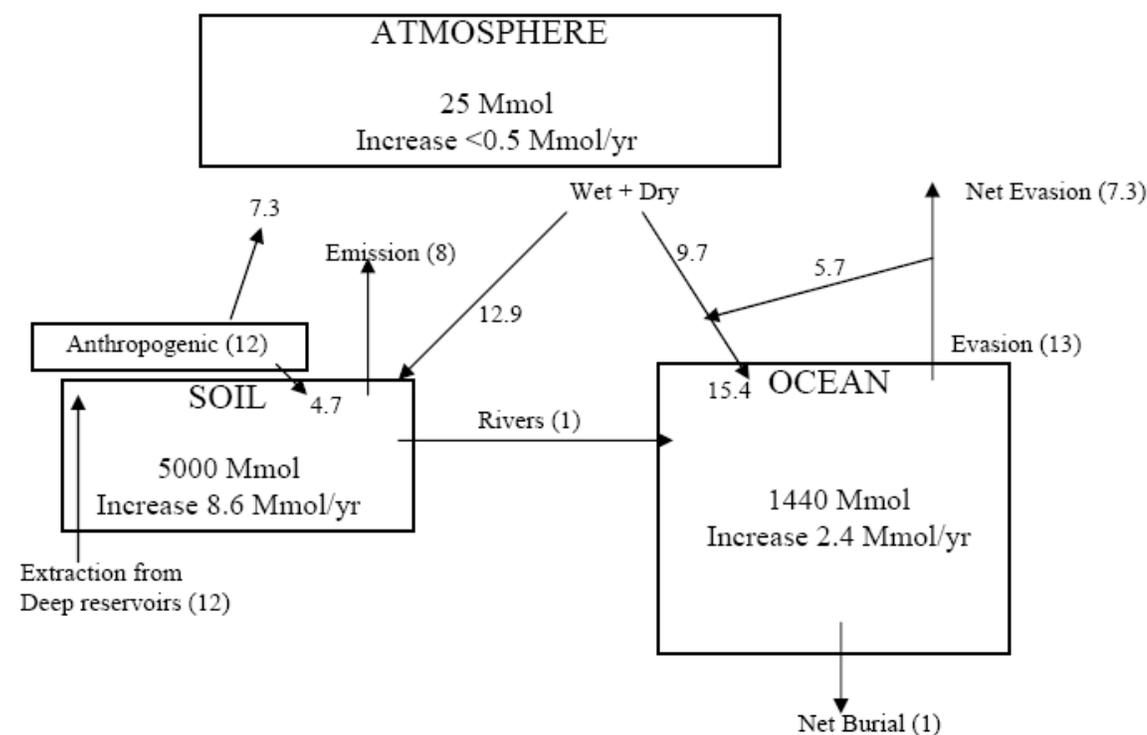
B.1 Overview of the Global Mercury Cycle

The study of Lindberg et al. (2007) and the report by United Nations Environment Programme (UNEP 2002) provide a comprehensive overview of the scientific literature on the sources, sinks, and transformations of mercury in the environment. The following material is drawn from these studies.

Mercury occurs naturally in the environment with some of the sources of atmospheric mercury being naturally enriched soils, forest fires, oceans, volcanoes, and geothermal areas. Mercury is also released to the environment due to human activities such as mining (including legacy mining) and industrial activities such as cement production, municipal waste incineration, chlor-alkali production, and fuel combustion. Mercury is rarely found in the nature as the pure, liquid metal, but rather within inorganic compounds (such as mercury sulfide [HgS] and mercury chloride [HgCl₂]) and as organic mercury compounds (such as methylmercury). The most common organic mercury compound that microorganisms and natural processes generate from other forms is methylmercury, which can accumulate in aquatic animals to levels that are thousands of times greater than levels in the surrounding water. Mercury has a long retention time in soils (up to hundreds of years) and mercury accumulated in soil could be released from soils and/or sediments to surface waters and other media for prolonged periods.

Model-based estimates indicate that global mercury deposition increased by two to four times in modern times compared to the pre-industrial times. Model-based estimates also indicate that human-induced recycling, natural emissions (from land and oceans), and new point-source releases each account for about a third of the total present-day atmospheric inputs of mercury (see Figure B-1). Although current emissions from North America and Europe are decreasing, there has been no discernible net change in the size of the atmospheric pool of mercury in the Northern Hemisphere since the mid-1970s.

Figure B-1 Estimates of Present Day Global Mercury Reservoirs (Mmol) and Fluxes (Mmol/yr) from these Reservoirs



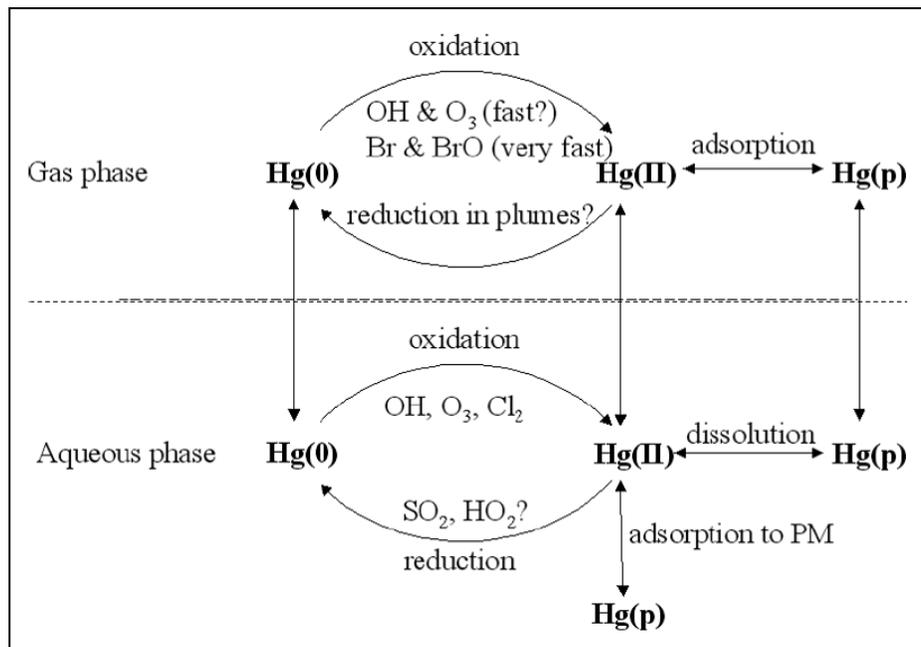
Notes:

- Flux of volatile mercury from water to air is termed "Evasion" in the above figure.
- Modified from Lindberg et al. (2007)
- Mmol = 10^3 kg-mole

Mercury can exist in the atmosphere in elemental (Hg(0)), divalent (Hg(II)), and particulate (Hg(p)) forms. Elemental mercury in the atmosphere can undergo transformation into inorganic mercury forms, providing a significant pathway for deposition of emitted elemental mercury (see Figure B-2). Among the three predominant species of mercury, Hg(0) is removed slowly from the atmosphere via wet and dry deposition, and Hg(II) species are removed rapidly because of their high solubility and reactivity. Thus, chemical transformation between Hg(0) and Hg(II) can affect the atmospheric lifetime of mercury.

The primary mechanisms for wet deposition of mercury are oxidation of Hg(0) by ozone (O_3) in clouds and the gas-phase oxidation of Hg(0) by OH and O_3 followed by an uptake of cloud droplets. Wet deposition of mercury occurs predominantly as dissolved and particulate Hg(II), with methylmercury occurring in minimal concentrations (~0.5-2.5% of total). Dry deposition of mercury mainly occurs by direct deposition of gas-phase Hg(0) and Hg(II) and, to a lesser extent, by deposition of atmospheric particles containing mercury. Measurement or model estimation of dry deposition is complicated by the fact that dry deposition processes are a complex function of meteorological factors (temperature, wind speed, etc.), surface wetness, and surface geomorphology. Estimates of dry deposition in forested catchments in the northern hemisphere were found to equal or exceed estimates of wet deposition.

Figure B-2 Schematic Illustrating the Atmospheric Chemical Transformations Between Elemental ($Hg(0)$), Divalent ($Hg(II)$) and Particulate ($Hg(p)$) Mercury in Gaseous and Aqueous Phases



Notes:

- “?” indicates uncertainties in these processes.
- Source: Lindberg et al. (2007).

B.2 Mercury Emissions from Anthropogenic and Natural Sources

B.2.1 Mercury Emissions Reported by the California Air Resources Board

The California Toxics Inventory, from the CARB, provides estimates of mercury emissions (and emissions of other toxic substances) from stationary, area-wide (associated with human activity and emissions taking place over a wide geographic area, such as unpaved road dust, wildfires, etc.), mobile (both off-road and on-road), and natural sources. The total emissions of mercury from the above sources for each of the nine counties comprising the San Francisco Bay Area Air Quality Management District (BAAQMD), for the year 2004 and 2006, are presented in Table B-1. Compared to the statewide average annual emission values of 44.6 and 37.1 micrograms per square meter per year ($\mu g/m^2/yr$), the average annual emissions from the SFB were 79.7 and 81.7 $\mu g/m^2/yr$, for the years 2004 and 2006, respectively.

Table B-1 *Reported Total Emissions of Mercury (tons/yr) from the Nine Counties Comprising the BAAQMD for the Years 2006 and 2004*

Region	area ^a (km ²)	2006 Emissions		2004 Emissions	
		tons/yr	µg/m ² /yr	tons/yr	µg/m ² /yr
BAAQMD					
Alameda County	1910	0.29	153.2	0.22	113.9
Contra Costa County	1865	0.32	169.3	0.30	160.1
Marin County	1346	0.05	33.5	0.04	32.9
Napa County	1952	0.04	21.3	0.04	21.6
San Francisco County	121	0.09	734.8	0.08	664.7
San Mateo County	1163	0.12	106.5	0.12	103.3
Santa Clara County	3343	0.39	115.7	0.45	133.6
Solano County	2148	0.10	45.6	0.11	50.9
Sonoma County	4081	0.07	17.7	0.07	17.3
Area-weighted average	-	-	81.7	-	79.7
Entire California	403928	15	37.1	18	44.6

Notes:

- a - Areas were obtained from <http://quickfacts.census.gov/qfd/index.html>
- b - Area-weighted average emissions were computed in units of µg/m²/yr, consistent with the units of other estimates presented in this report.
- Source of the data is <http://www.arb.ca.gov/toxics/cti/cti.htm>.

B.2.2 Mercury Emissions from Anthropogenic Sources in the United States

In 1990, more than half of the emissions of mercury from the US were from coal-fired power plants, municipal solid waste combustors, and medical waste incinerators (USEPA 2006). Due to increased regulation, overall mercury emissions to the atmosphere from the US have decreased by about 45% from 1990 (199 tons) to 1999 (102 tons) (see Table B-2).

Table B-2 *Estimated Emissions of Mercury (tons/yr)^a in the US from Various Anthropogenic Sources*

Source	1990	1994-95	1999
Utility Coal Boilers	46.3	47.2	43.4
Industrial Boilers	10.9	-	10.9
Medical Waste Incinerators	45.1	14.6	1.5
Municipal Waste Combustion	51.4	26.9	4.4
Hazardous Waste Incinerators	6.0	-	6.0
Chlorine Production	9.1	6.5	5.9
Electric Arc Furnaces	6.3	-	NA
Gold Mining	3.1	-	10.4
Other	21.3	-	19.6
Total	199.4	144.0	102.1

Notes:

- a - Original data for 1990 and 1999 were converted to metric tons per year (1000 kilograms [kg]/year [yr]) and presented here.
- Source of the data for 1990 and 1999 is USEPA (2006) and for 1994-95 is USEPA (1997).

B.2.3 Mercury Emissions from Fuel Consumption in the San Francisco Bay Area

Conaway et al. (2005) collected gasoline and diesel samples from refineries and service stations in the SFB Area and found that mercury concentrations in gasoline ranged from 0.08 to 1.4 nanograms per gram (ng/g) and those in diesel ranged from 0.05 to 0.34 ng/g. On average, combustion of these fuels in the SFB Area was estimated to contribute 5 kg/yr (range of 0.7 to 13 kg/yr) of mercury to the environment (see Table B-3). The authors estimated that the total flux from the combustion of these fuels, assuming that all of the resulting emissions reach the atmosphere, represents less than 3% of the total atmospheric emissions (including those from medical waste incinerators, cement manufacturing and geothermal power production) in the SFB Area. Considering that reported concentrations of mercury in crude oil are generally much higher than those found in the study samples, the authors suggested that there is little evidence that mercury is enriched into these fuels from the refining process.

Table B-3 Gasoline Consumption and the Corresponding Estimated Mercury Emissions to the Environment (kg/yr) in the San Francisco Bay Area for a Range of Mercury Concentrations Measured in Gasoline Samples

year	Gasoline consumption (x 10 ⁹ liters)	Total emission (kg/yr) ^a			emission flux ^b (µg/m ² /yr)
		Low concentration (0.08 ng/g)	average concentration (0.50 ng/g)	High concentration (1.4 ng/g)	
1993	11	0.6	4	10	0.03-0.56
1994	11	0.6	4	10	0.03-0.56
1995	11	0.6	4	10	0.03-0.56
1996	11	0.6	4	11	0.03-0.61
1997	12	0.7	4	11	0.04-0.61
1998	12	0.7	4	12	0.04-0.67
1999	12	0.7	4	12	0.04-0.67
2000	13	0.7	5	12	0.04-0.67
2001	13	0.7	5	13	0.04-0.73

Notes:

- a - Total emission was estimated by the authors after converting the consumption volume to a mass (by multiplying with a density of 0.7 g/cm³) and multiplying it by the corresponding concentration.
- b - Average emission flux, in units of µg/m²/yr, consistent with the units of other estimates presented in this report, was obtained by dividing the emissions (in kg/yr) by the total area of the nine counties mentioned above (17929 kilometers [km]²).
- San Francisco Bay Area comprises the counties of Alameda, Contra Costa, Marin, Napa, San Francisco, San Mateo, Santa Clara, Solano, and Sonoma.
- Source: Conaway et al. (2005).

B.2.4 Mercury Emissions from Wildfires

Although vegetation and soil are sinks for atmospheric mercury, mercury contained in vegetation and soil can be released to the environment during wildfires. Wiedinmyer and Friedli (2007) estimated that annual average emissions of mercury from fires were about 30% of the total anthropogenic emissions in the US, with the highest monthly averages in western states such as California (see Table B-4). The authors indicated that, on an annual basis, mercury emissions from forest fires dominate the inventory of fire emissions and that agricultural fire emissions are relatively insignificant.

Table B-4 Average Monthly Emission of Mercury (kg/month) from Fires in California and the US for the Period 2002-2006

Month	Emissions (kg/month)	
	California	United States
JAN	17	800
FEB	37	900
MAR	58	2600
APR	68	2800
MAY	73	1500
JUN	160	4800
JUL	513	8000
AUG	600	11100
SEP	974	4800
OCT	709	3800
NOV	173	1800
DEC	56	800
Total (kg/yr)	3438	43700

Source: Wiedinmyer and Friedli (2007).

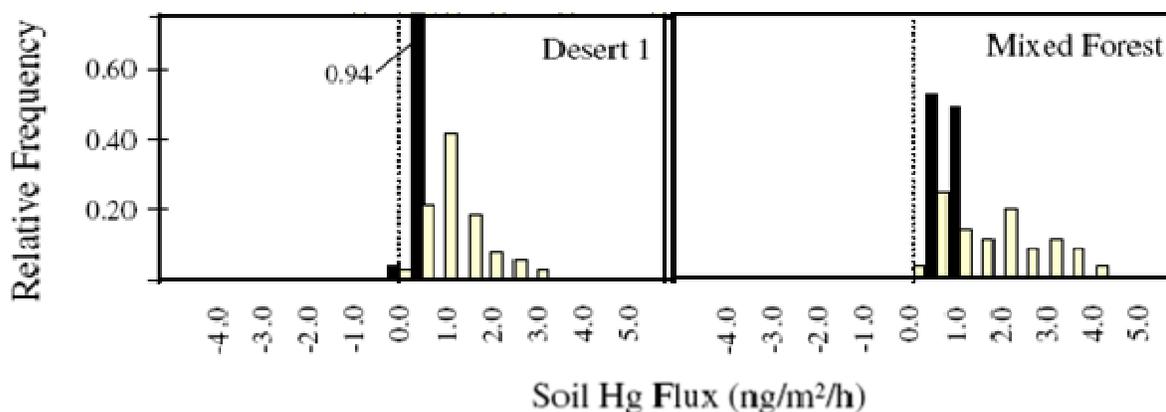
Friedli et al. (2003) measured mercury concentrations in a wildfire (177 hectares of final burn area) plume in the Ontario region of Canada and found that most of the emitted mercury was elemental mercury in the gaseous form (0.56 ng/m³ of Hg(0), compared to less than 0.083 ng/m³ of Hg(p)). Artaxo et al. (2000) measured mercury and trace metal concentrations in ambient air over the Amazon Basin in Brazil from August to September 1995, a time period coinciding with the peak biomass burning season. The authors found that, over areas that are heavily impacted by mining or biomass burning, mercury concentrations ranged from 5 to 14 ng/m³, whereas the concentrations over pristine areas and areas not downwind of mining activities ranged from 0.5 to 2 ng/m³. The authors estimated that biomass burning contributed to about 31% of the measured mercury concentration. Adsorption of gaseous mercury on existing biomass burning particles, direct release of mercury from the vegetation to the atmosphere, and evaporation of mercury from soil were suggested as some of the mechanisms by which mercury is released during forest fires.

B.2.5 Mercury Emissions from Natural and Other Sources

Nacht et al. (2004) estimated the mean flux of mercury from the Sulphur Bank Mercury Mine Superfund site located in the Sonoma-Clear Lake area, about 110 km northwest of Sacramento (total study area of 3.8 km²), an area of extensive mercury enrichment due to historical mining and geothermal activity. The authors found that the mean flux of mercury (only the elemental form, Hg(0)) from this site ranged from 14 to 11,000 nanograms per square meter per hour (ng/m²/h), and that the estimated total annual emission flux of mercury was 17 kg/yr. This estimate of annual flux reported by the authors is equivalent to an emission flux of 4473 µg/m²/yr, and is two orders of magnitude higher than the reported estimates of average atmospheric deposition flux at several locations in the US (see Section B.3.4). The authors estimated that about 47% of the total emissions originated from anthropogenically disturbed material (mine waste, ore, etc.) and the remainder from the undisturbed naturally enriched substrate.

Ericksen et al. (2006) measured mercury fluxes from bare soils with low mercury concentrations (<0.1 mg/kg) at 11 sites (situated in varying ecosystem types) across the US. Two of the 11 sampling sites were in California, including a site in Northern California (in the foothills of the Sierra Nevada, about 100 km north of Sacramento) situated in a mixed forest ecosystem, and a site in Southern California (in the Mojave Desert) situated in a desert ecosystem. The authors observed that, for most of the sites, soil fluxes during dark conditions (<1 W/m²) were significantly lower than those during light conditions (>1 W/m²) (see Figure B-3). The authors indicated that there were significant differences in the soil fluxes between the sampling sites and that no consistent trends of soil flux as a function of the ecosystem type were identified. However, based on limited data available from one semiarid site in Nevada, the authors found significant correlation between soil moisture content and soil mercury flux. The mean soil flux at the Southern California and the Northern California sites was found to be 0.6 ± 0.6 ng/m²/h and 1.1 ± 1.0 ng/m²/h, respectively. Soil fluxes at the Southern California site (a very arid desert ecosystem) were found to be significantly different from those at a semiarid desert site in Nevada, although the two sites had similar air and soil mercury concentrations, possibly due to differences in the soil moisture content at these sites. The authors estimated that the soil flux averaged across all the sites and averaged over light and dark conditions was 0.9 ± 0.7 ng/m²/h (equivalent to 1.8 to 14 μ g/m²/yr). Thus, the “background” flux of mercury from bare soils is comparable to the reported estimates of average atmospheric deposition flux at several locations in the US (see Section B.3.4). By scaling up their measurements and making other simplifying assumptions, the authors estimated the background mercury flux from soils in the contiguous US to be approximately 100 tons/yr.

Figure B-3 Histograms of Relative Frequency of Soil Mercury Flux



Notes:

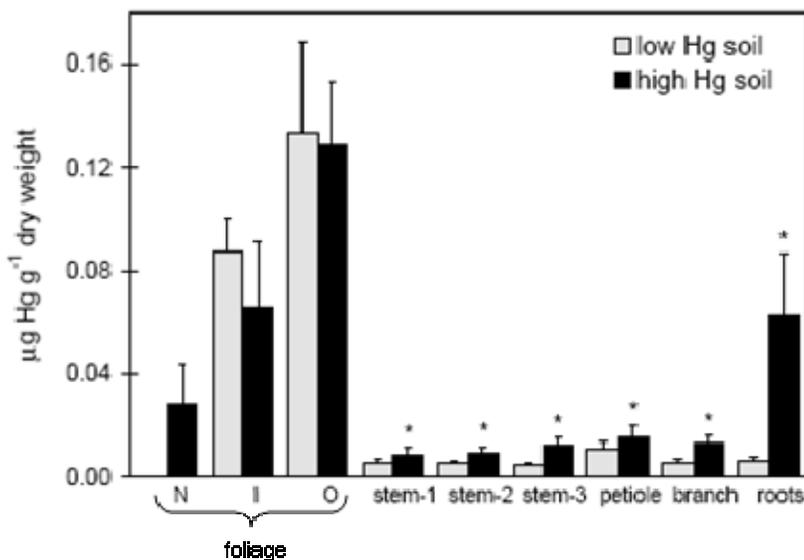
- Soil mercury conditions shown as dark (dark shaded bars) and light (light shaded bars).
- Southern California sites are labeled “Desert 1.”
- Northern California sites are labeled “Mixed Forest.”
- Negative flux indicates deposition.
- Modified from Ericksen et al. (2006).

B.2.6 Mercury Exchange between Vegetation and the Atmosphere

In a controlled experimental environment, Ericksen et al. (2003) measured exchange of mercury between air and vegetative surfaces of aspen stands (including foliage, stems, branches and roots) grown in soils with high (12 μ g/g) and low (0.03 μ g/g) mercury concentrations. The authors indicated that foliar mercury concentrations increased as a function of leaf age and that the concentration of mercury in foliage grown in low mercury soil was similar to the concentration in those grown in high mercury soil (see Figure B-4). Thus, uptake of gaseous

Hg(0) was the predominant pathway by which mercury accumulated in the foliage. However, mercury concentration in other plant compartments (stems, branches, roots, etc.) was higher in the aspen grown in high mercury soil than in the aspen grown in low mercury soil. The authors indicated that because of leaf senescence, approximately 80% of mercury in the aboveground biomass was found in the litterfall by the end of their experiment. Thus, litterfall would serve as an input of mercury to terrestrial ecosystems. Moreover, the authors suggested that litterfall measurements could be useful in estimating mercury deposition rates in deciduous forests, since incident precipitation, the other route by which mercury could be removed, removes less than 3% of the mercury deposited on the foliage.

Figure B-4 Foliar and Non-foliar Mercury Concentrations in Aspen Grown in Low Hg Soil ($0.03 \mu\text{g/g}$, grey bars) and High Hg Soil ($12 \mu\text{g/g}$, black bars) in 2001



Notes:

- Foliar Hg concentrations are shown for new ("N", <21 days old), intermediate ("I," 22-35 days old) and old ("O," >35 days old) leaves.
- Stems were sampled from the top 1/3 ("stem-1"), middle 1/3 ("stem-2") and bottom 1/3 ("stem-3") portions of the aspen stand.
- The "*" indicates that Hg content was statistically different between samples from low and high Hg soils.
- Modified from Ericksen et al. (2003).

B.3 Estimates of Atmospheric Deposition of Mercury

B.3.1 Wet Deposition Estimates from the Mercury Deposition Network

The Mercury Deposition Network (MDN) is a national database of routine mercury measurements that is maintained by National Atmospheric Deposition Program/National Trends Network (NADP/NTN) and is available online. The MDN reports weekly concentrations of total mercury in precipitation and the seasonal and annual flux of total mercury in wet deposition at selected locations throughout the US and Canada. The annual wet deposition flux for the period 1997 through 2007, estimated from event-based flux measurements within each calendar year, at two sites (CA 97, which is located in Covelo, about 270 km north of San Francisco, and CA 72, which is located in San Jose, about 70 km south of San Francisco), is presented in Table B-5. As expected, the annual wet deposition flux is correlated with the annual precipitation amount at both these sites.

Table B-5 Annual Wet Deposition Flux^a of Mercury ($\mu\text{g}/\text{m}^2/\text{yr}$) and Corresponding Annual Precipitation Total^b (in mm/yr) at Two MDN Sites (CA 97 in Covelo and CA 72 in San Jose) in Central California

year	CA 97		CA 72	
	Flux ($\mu\text{g}/\text{m}^2/\text{yr}$)	Precip. (mm/yr).	Flux ($\mu\text{g}/\text{m}^2/\text{yr}$)	Precip. (mm/yr).
1997	-	-	-	-
1998	4.8	1211	-	-
1999	4.3	837	-	-
2000	3.8	639	3.1	318
2001	-	-	2.9	289
2002	-	-	2.2	242
2003	-	-	2.2	279
2004	-	-	2.3	255
2005	-	-	2.1	431
2006	-	-	2.5	310
2007	-	-	-	-

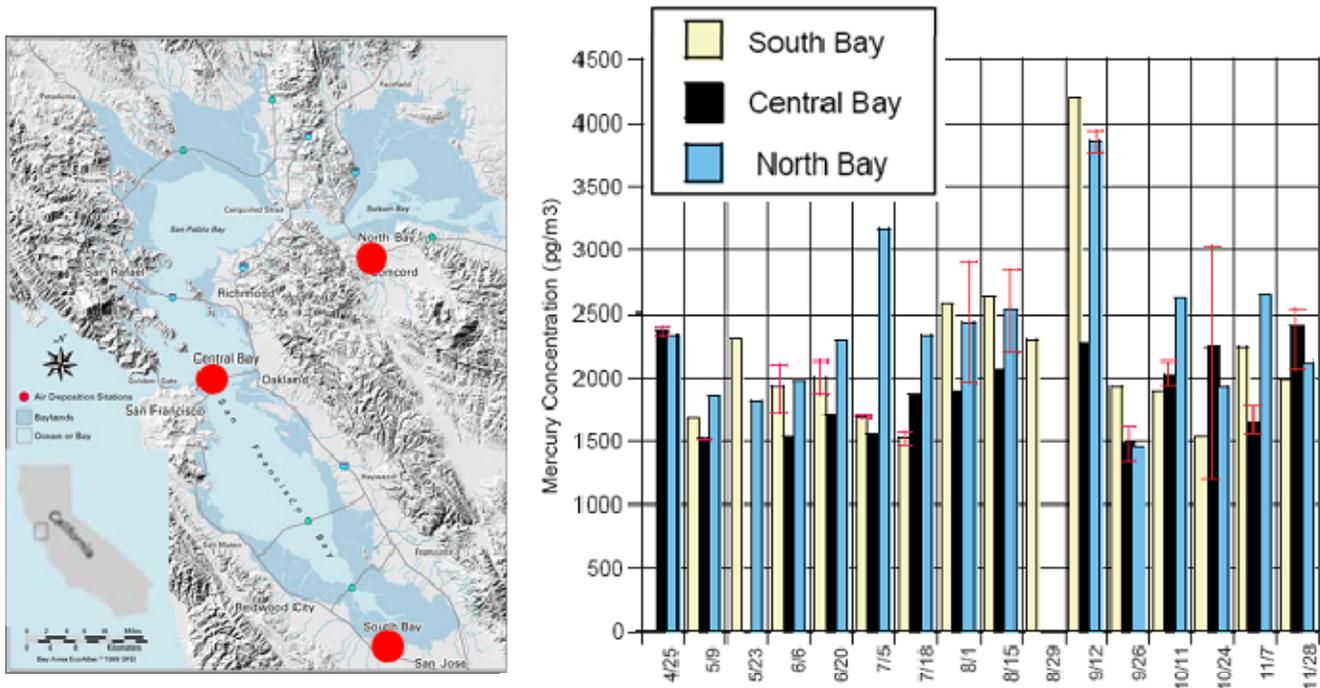
Notes:

- a - Annual wet deposition flux was assumed to be the sum of event-based estimates within the calendar year. Only those years for which event-based estimates spanned the complete calendar year were used.
- b - Event-based precipitation totals, corresponding to only those events for which flux estimates were available, were summed to obtain the annual total.
- Raw data are from <http://nadp.sws.uiuc.edu/mdn/>

B.3.2 San Francisco Bay Atmospheric Deposition Pilot Study (Tsai and Hoenicke 2001)

Tsai and Hoenicke (2001) used measurements of mercury concentration to estimate the deposition flux of mercury at three locations in the San Francisco Estuary (North Bay, Central Bay, and South Bay in Figure B-5) for the period August 1999 through November 2000. The North Bay site was situated in an industrial corridor, near several petroleum refineries, the Central Bay site was close to two major airports and seaports, and the South Bay site was downstream of several abandoned mines. The South Bay site also coincided with the MDN site (CA 72, see Section B.3.1) in San Jose.

Figure B-5 Modeling Sites in the San Francisco Bay Area

**Notes:**

- Left panel: Modeling sites (indicated by red circles) in the San Francisco Bay Area.
- Right panel: Mercury concentration (pg/m³) in the ambient air in the San Francisco Bay Area in the year 2000 at the three study sites.
- Red whiskers on the bars indicate the range in these measurements.
- Source: Tsai and Hoenicke (2001).

The authors found that mercury concentrations in the ambient air at the North Bay site were statistically higher than those at the Central Bay site (see Figure B-5), but concentrations at the South Bay site were not statistically different from either the Central Bay or the North Bay sites. Using a flux deposition model, the authors estimated that the average annual dry deposition flux at North Bay, Central Bay and South Bay sites to be 21, 18 and 19 $\mu\text{g}/\text{m}^2/\text{yr}$, respectively (see Table B-6). From measurements of mercury concentrations in precipitation, the authors estimated that the wet deposition flux of mercury ranged from 3.5 to 4.5 $\mu\text{g}/\text{m}^2/\text{yr}$, with an overall estimated wet deposition rate of 4.2 $\mu\text{g}/\text{m}^2/\text{yr}$ for the entire estuary. The authors indicated that uncertainties in some of the parameters used in the dry deposition flux model could be within 200% (of the values used within the model), and uncertainties in measurement of mercury concentration in precipitation could be within 25%. The authors suggested a 2- to 5-fold uncertainty in the estimates of overall atmospheric loading to the estuary (estimated as the sum of direct atmospheric deposition and indirect loading through inputs from upstream watersheds).

Table B-6 *Estimated Flux ($\mu\text{g}/\text{m}^2/\text{yr}$) of dry and Wet Deposition of Mercury and the Associated Direct Atmospheric Loading (kg/yr) at the Three Study Sites of Figure B-5*

	Direct Atmospheric Loading (kg/yr)				Flux ($\mu\text{g}/\text{m}^2/\text{yr}$)
	Hg(p)	Hg(II)	Hg(0)	Total	
Dry Deposition					
South Bay	2	6.6	0.57	9.2	19
Central Bay	0.8	2.6	0.38	3.8	18
North Bay	1.9	6.4	0.7	9	21
Entire Estuary	4.6	15	2.2	22	19
Wet Deposition					
	Precip. (mm/yr)				
South Bay	360	-	-	1.7	3.5
Central Bay	680	-	-	0.96	4.5
North Bay	580	-	-	1.8	4.3
Entire Estuary	530	-	-	4.8	4.2

Source: Tsai and Hoenicke (2001).

B.3.3 Mercury Concentrations in Coastal California Precipitation

Steding and Flegal (2002) used a model of air mass trajectory to identify the sources of mercury in rainwater samples collected from an urban site (Moffett Field) and a rural site (Long Marine Lab) in Central California. The authors suggested that a combination of Hg(0) emissions from Asia, a series of reduction-oxidation reactions resulting in increased production of atmospheric Hg(II), and the subsequent trans-Pacific transport of Hg(0) and Hg(II) result in higher mercury concentrations, compared to baseline concentrations from the equatorial Pacific, observed in the rainwater samples. The authors also argued that local sources of mercury result in elevated concentrations at the urban site (Moffett Field) relative to the rural site (Long Marine Lab). Estimated wet mercury deposition at these two sites is shown in Table B-7.

Table B-7 *Estimated Annual Wet Deposition Flux of Mercury ($\mu\text{g}/\text{m}^2/\text{yr}$) at Long Marine Lab (rural site) and Moffett Field (urban site) in Central California Based on Data Collected During 2000-2001*

Site	Precip. (mm)	Flux ($\mu\text{g}/\text{m}^2/\text{yr}$)
Moffett Field	350	4.4
Long Marine Lab	740	4.0

Notes:

- a - Although not all the events during the study period were sampled, the authors indicated that it did not result in biased estimates, as verified by comparisons with independent observations.
- b - Deposition values were converted from nanomoles ($\text{nmol}/\text{m}^2/\text{yr}$) to $\mu\text{g}/\text{m}^2/\text{yr}$.
- Source: Steding and Flegal (2002)b.

B.3.4 Mercury Deposition Estimates from Across the United States

A summary of reported mercury deposition estimates from locations across the US is presented below (see Table B-8). The overall range of wet deposition estimates is 1.48 to 30 $\mu\text{g}/\text{m}^2/\text{yr}$ and the overall range of dry deposition estimates is 0.4 to 15.8 $\mu\text{g}/\text{m}^2/\text{yr}$.

Table B-8 *Estimates of Wet and Dry Deposition Flux of Mercury ($\mu\text{g}/\text{m}^2/\text{yr}$) at Locations Across the US*

Geographical Area	Time Period	Wet/Dry	Flux ($\mu\text{g}/\text{m}^2/\text{yr}$)	Source
Chesapeake Bay, MD	1997-1998	wet	14-30	Mason et al. (2000)
Lake Champlain basin, VT	1993	wet	9.26	Burke et al. (1995)
Sturgeon Point, NY ^a	Sep-Oct 1993	wet	9.7 (2.2-18.6)	Vermette et al. (1995)
Little Rock Lake, WI	----	wet	6.8 \pm 2	Fitzgerald et al. (1991)
MDN Site NV99, NV ^b	2005-2006	wet	2.28-7.2	Lyman et al. (2007)
MDN Site NV02, NV ^b	2005-2006	wet	1.48-3.32	Lyman et al. (2007)
overall range (wet)		wet	1.48-30	
Everglades, FL ^d	Feb-Mar 1999	dry	4.85 \pm 1.46	Marsik et al. (2007)
Everglades, FL ^d	June 2000	dry	2.15 \pm 1.02	Marsik et al. (2007)
MDN Site NV99, NV ^c	2005-2006	dry	1.44-10.8	Lyman et al. (2007)
MDN Site NV02, NV ^b	2005-2006	dry	0.4-15.8	Lyman et al. (2007)
Little Rock Lake, WI	----	dry	3.5 \pm 3	Fitzgerald et al. (1991)
Overall range (dry)		dry	0.4-15.8	----

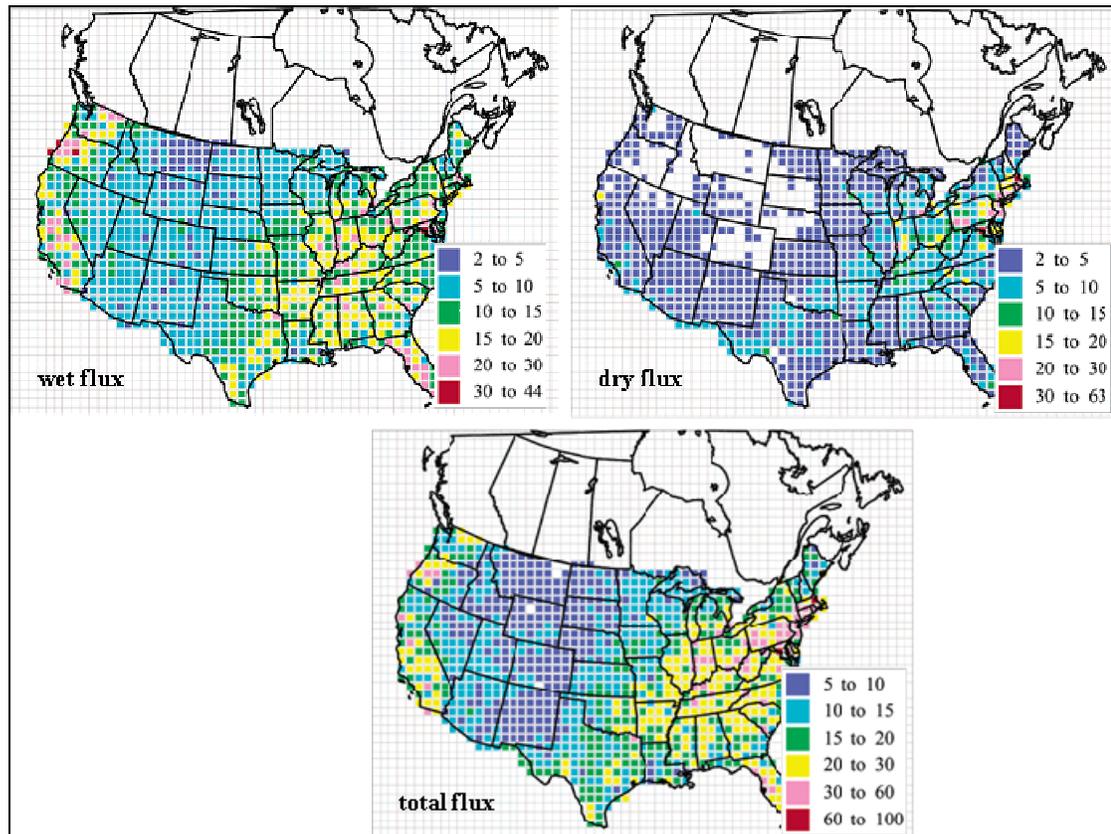
Notes:

- a - Reported weekly flux was converted to an annual flux.
- b - Seasonal estimates for spring, summer, fall and winter were converted to annual estimates, and the complete range of these annual estimates is presented.
- c - Seasonal estimates for spring, summer and fall were converted to annual estimates, and the complete range of these annual estimates is presented.
- d - Reported daily flux was converted to an annual flux.

B.3.5 Recent Large-Scale Modeling Estimates of Atmospheric Mercury Deposition

Seigneur et al. (2004) used a continental-scale, 3-D chemical transport model (CTM), nested within a global CTM, to simulate the global atmospheric fate and transport of mercury and the resulting deposition in the contiguous US. The spatial distribution of simulated total fluxes generally reflected the distribution of local/regional emission sources, precipitation patterns and prescribed upwind boundary conditions in the CTM. However, a comparison of simulated wet deposition fluxes for the year 1998 with observations from the NADP network indicated only a moderate agreement (coefficient of determination, r^2 , was 0.50). Simulated wet deposition fluxes (see Figure B-6) were highest in eastern US and in the coastal western US. The authors noted that the high wet deposition fluxes on the West Coast are due to the prescribed upwind boundary conditions of global Hg(II) concentrations in the continental CTM (i.e., transport of mercury across the Pacific) and the high precipitation along the mountain ranges of the Cascades and Sierra Nevada. The high dry deposition flux of 15-20 $\mu\text{g}/\text{m}^2/\text{yr}$ in northern California corresponds to the location of geothermal geysers, which were assumed to have relatively high emissions in the CTM. The authors also estimated that, on average, North American anthropogenic emissions contribute to 30% of the total mercury deposition in the contiguous US, while natural emissions and other regions account for 33% and 37%, respectively.

Figure B-6 Simulated Annual Wet, Dry, and Total Deposition Flux of Mercury ($\mu\text{g}/\text{m}^2/\text{yr}$) over the Contiguous US for Each 100 km by 100 km Grid Cell for the Year 1998

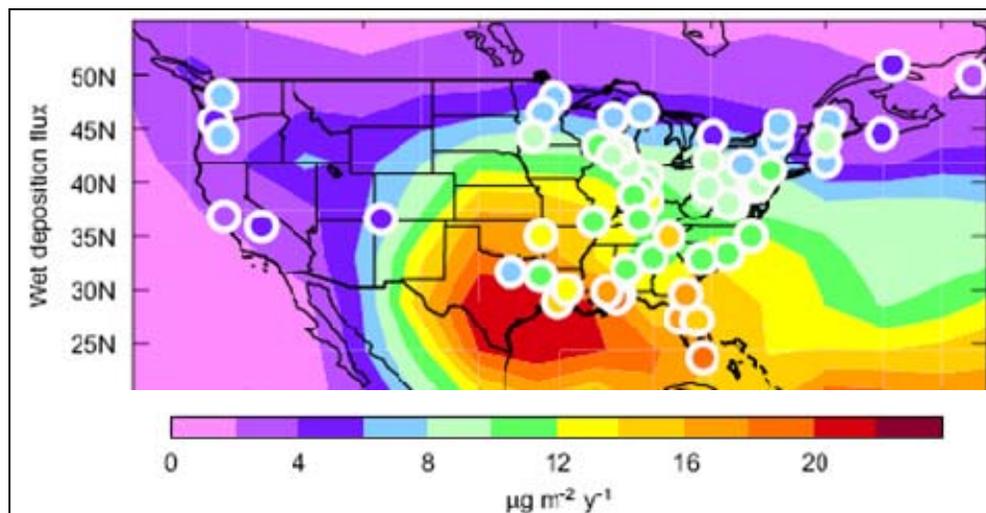


Notes:

- Simulated annual wet deposition flux of mercury shown in top left panel.
- Simulated dry deposition flux of mercury shown in top right panel.
- Simulated total deposition flux of mercury shown in bottom panel.
- Source: Seigneur et al. (2004).

Using a global 3-D CTM (GEOS-Chem), Selin and Jacob (2008) simulated wet and dry deposition fluxes of mercury for the contiguous US. Comparison of simulated wet fluxes for the period 2004-2005 with observations from the NADP network (see Figure B-7) indicated a reasonable agreement (coefficient of determination, r^2 , was 0.73). The authors indicated that GEOS-Chem also reasonably captured the observed latitudinal gradient and seasonal phase as well as the variation of seasonal amplitude with latitude. North American anthropogenic emissions were estimated to contribute 20% of the simulated total mercury deposition in the contiguous US, and dry deposition fluxes were estimated to account for 70% of the simulated total deposition.

Figure B-7 Simulated Annual Mean Wet Deposition Flux of Mercury ($\mu\text{g}/\text{m}^2/\text{yr}$) for the Period 2004-2005 (model grid resolution of 400 km x 500 km)



Notes:

- The circles show the 57 NADP sites where simulations were evaluated against observations.
- Source: Selin and Jacob (2008).

B.3.6 Comparison of Pre- and Post-Industrial Atmospheric Deposition

Sanders et al. (2008) measured total mercury concentration in sediment cores from four lakes in California that were considered to be devoid of any present or historical anthropogenic activity. The four lakes selected by the authors were the Castle Lake in Shasta-Trinity National Forest, Wildcat Lake in Point Reyes National Seashore, Island Lake in Tahoe National Forest and Emerald Lake in Sequoia and Kings Canyon National Park. The authors found that sediment mercury concentrations for the 1970-2004 (modern) time period are higher by a factor of 10 (Castle Lake), 5 (Emerald Lake), 4 (Island Lake), and 2 (Wildcat Lake) than those for the pre-1850 (pre-industrial) period. The authors suggested that increased atmospheric mercury deposition, increased atmospheric nitrogen inputs resulting in elevated primary productivity, and increased carbon inputs are the possible mechanisms to explain the enrichment of mercury in the modern lake sediments. The authors found statistically significant correlations between mercury concentrations and percentage organic material in only two of the four lakes. Thus, the source of the enriched mercury in modern sediments could not be determined. Nonetheless, the authors indicated that mercury enrichment in modern sediments found in this study is generally higher than the 3-time increase in modern atmospheric deposition rate found in lake sediments of northern Alaska by Fitzgerald et al. (2005) and the 2- to 4-time increase in modern atmospheric deposition reported by Lindberg et al. (2007).

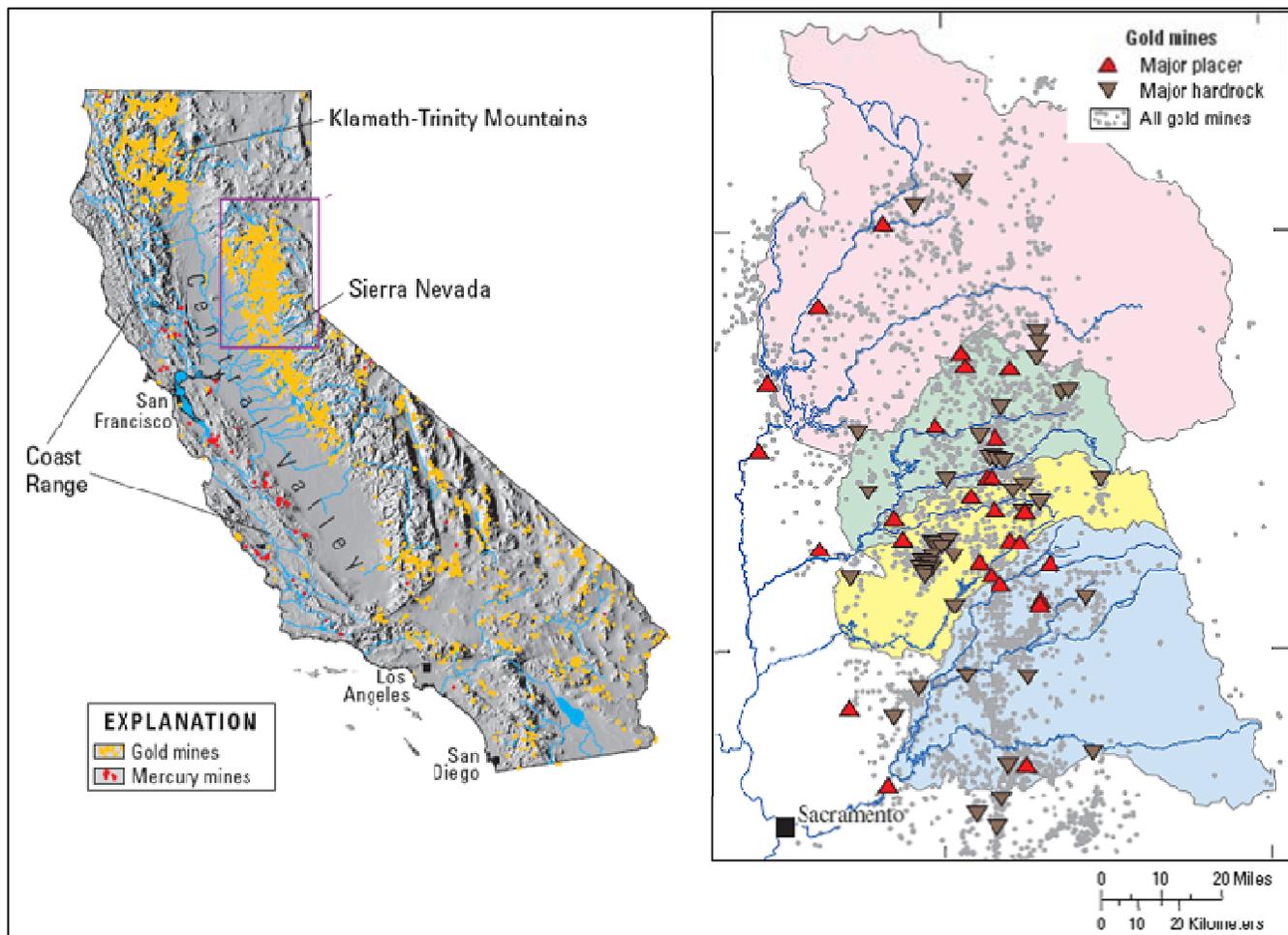
B.4 Mercury Concentrations in Sediments

Numerous studies in the scientific literature have addressed mercury contamination in the SFB and other related issues. For instance, see Conaway et al. (2007), McKee et al. (2005), Hornberger et al. (1999) and the references therein. In this section, only selected studies from the literature that are directly relevant to the broader scope of this report are discussed.

The SFB is affected not only by natural weathering of highly mercury-mineralized rocks in the upstream watersheds, but also by historical gold and mercury mining in the upstream watersheds (see Figure B-8). Between 1850 and 1900, most of the mercury mining in the world

occurred in the upstream watersheds of the SFB. Mercury was used to enhance gold recovery in the gold mining operations that occurred extensively in the mid to late 19th Century, and mercury-contaminated sediments from the Sierra Nevada were largely deposited to the northern reach of the SFB. Seasonal variability of mercury concentrations in water and sediment of the estuary are strongly dependent on the freshwater discharges from the watersheds draining into the estuary. Long-term (decadal) variability in sediment mercury concentration is a function of sediment deposition from the Central Valley, erosion of buried sediments resulting in enhanced active sediment layer, and mixing processes.

Figure B-8 Locations of Historical Gold and Mercury Mines in California



Notes:

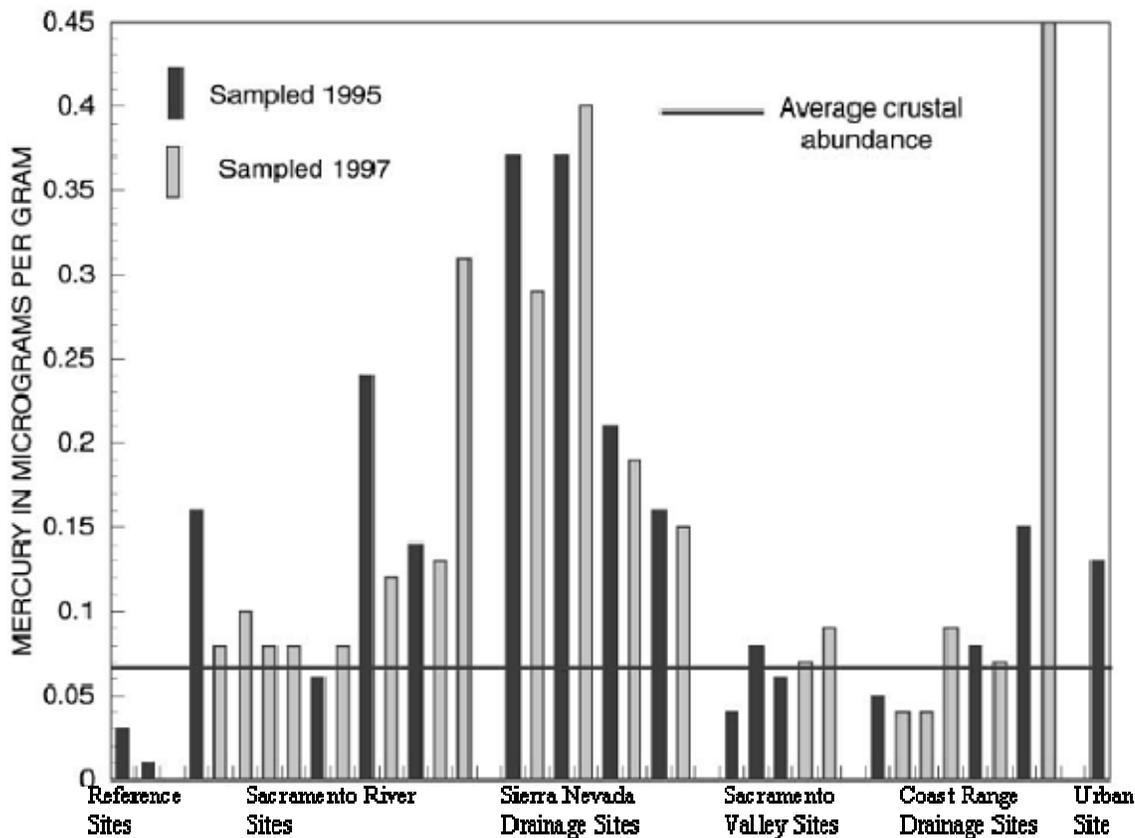
- Inset shows historical gold mines and major placer and hardrock gold mines in the northwestern Sierra Nevada.
- Source: Alpers et al. (2005).

B.4.1 Mercury in Water and Sediments of the Sacramento River Basin and the Sacramento-San Joaquin River Delta

Domagalski (2001) measured mercury and methylmercury concentrations in water and streambed sediments at 27 locations within the Sacramento River Basin. Compared to the global crustal abundance of mercury of $0.067 \mu\text{g/g}$, the author found elevated mercury

concentrations in streambed sediments from areas downstream of historical mining activity (such as Sierra Nevada sites, see Figure B-9). Methylmercury concentrations in streambed sediments ranged from 0.27 to 2.84 ng/g, and the highest concentration measured at the Sacramento Slough was attributed to the longer water residence times (about a few months), anoxic conditions in sediments, and the availability of organic material for microbial processes, all of which are ideal conditions for mercury methylation. Mercury and suspended sediment concentrations in unfiltered water followed the seasonal rainfall patterns, with the highest concentrations in winter (wet season) and relatively lower concentrations in late spring and fall (dry season). The highest loading of mercury to the SFB was attributed to sources within the Cache Creek watershed, which are downstream of historical mines, and to a possible volcanic source. The author also indicated that although mercury concentrations in Cache Creek could be as high as 2,248 nanograms per liter (ng/L) during storm water runoff events, the transported mercury was found to have a low potential for geochemical transformations, as the transported mercury was largely not present in a free ion form or in a form that could easily be reduced to elemental mercury. The author observed that it was only during high streamflow conditions that mercury in unfiltered water exceeded the federal and state recommended criterion for protection of aquatic life (as of 2001, 50 ng/L as total Hg in unfiltered water). The author estimated that the total amount of mercury transported from the Sacramento River Basin to the SFB to be 487 kg for the winter of 1996-97 and to be 169 kg for the winter of 1997-98.

Figure B-9 Concentrations of Mercury ($\mu\text{g/g}$) in Streambed Sediment of the Sacramento River Basin



Notes:

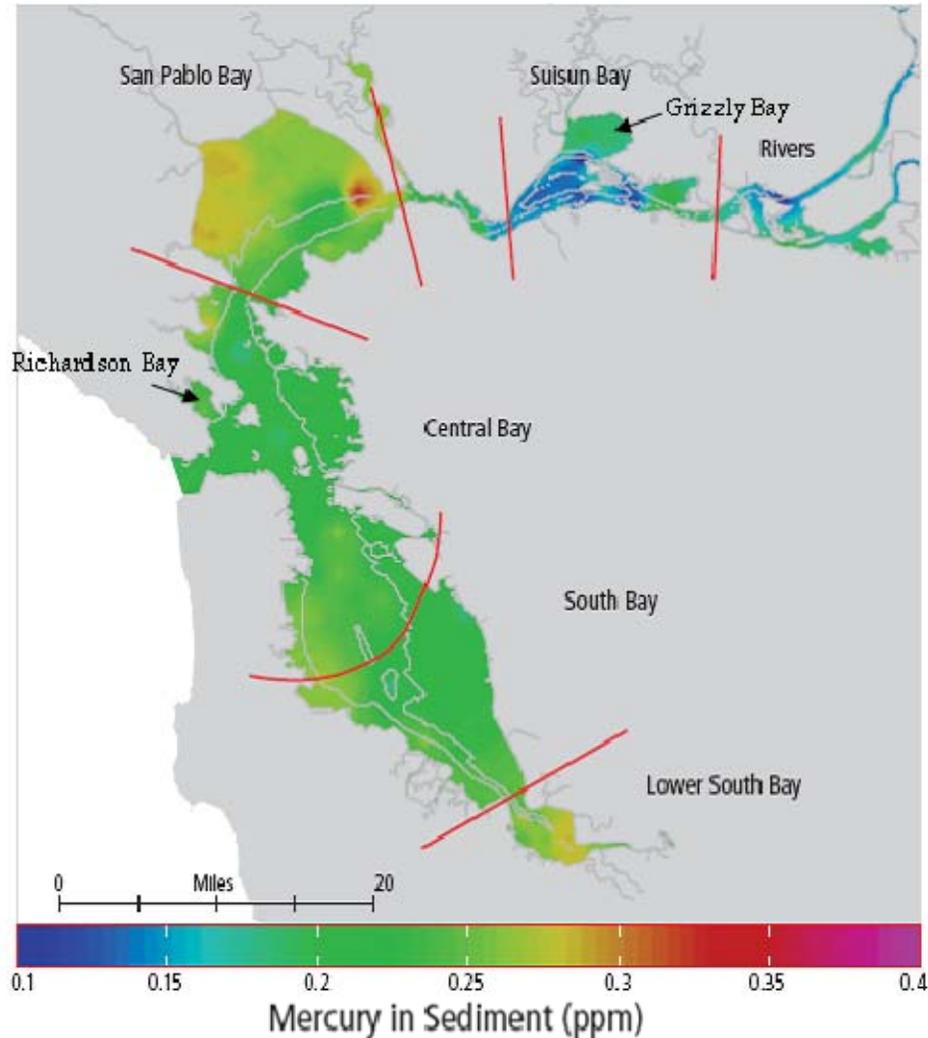
- Sampled during 1995 (black bars) and 1997 (grey bars) at 27 locations within the Basin.

- Modified from Domagalski (2001).

McKee et al. (2005) measured total mercury concentrations in water samples collected during 2002 and 2003 at Mallard Island in the Sacramento-San Joaquin Delta, about 8 km downstream of the confluence of Sacramento and San Joaquin Rivers. The authors observed that total mercury concentrations ranged from 4 to 14 ng/L and dissolved mercury concentrations ranged from 0.8 to 1.6 ng/L. The authors indicated that the Delta exhibits a “first flush” phenomenon for mercury indicated by greater mercury concentrations during the first flood of a season, despite the subsequent floods having a greater flow rates. Similar to Domagalski (2001), the authors found a relationship between suspended sediment concentration and total mercury concentration. Using this relationship and adjusting for the tidal effects on water transport (and hence mercury) within the Delta, the authors estimated that daily total mercury loads varied from 3 to 1,803 g/day and that the annual total mercury load was 58 ± 20 and 97 ± 33 kg/yr for water years 2002 and 2003, respectively. The authors extended their estimates to obtain a long-term average annual mercury load of 201 ± 68 kg/yr.

B.4.2 Mercury in Sediments and Fish of the San Francisco Bay

Figure B-10 Mercury Concentration in Sediments (ppm) of the San Francisco Bay Based on Data Collected by the San Francisco Estuary Institute from 2002 to 2007

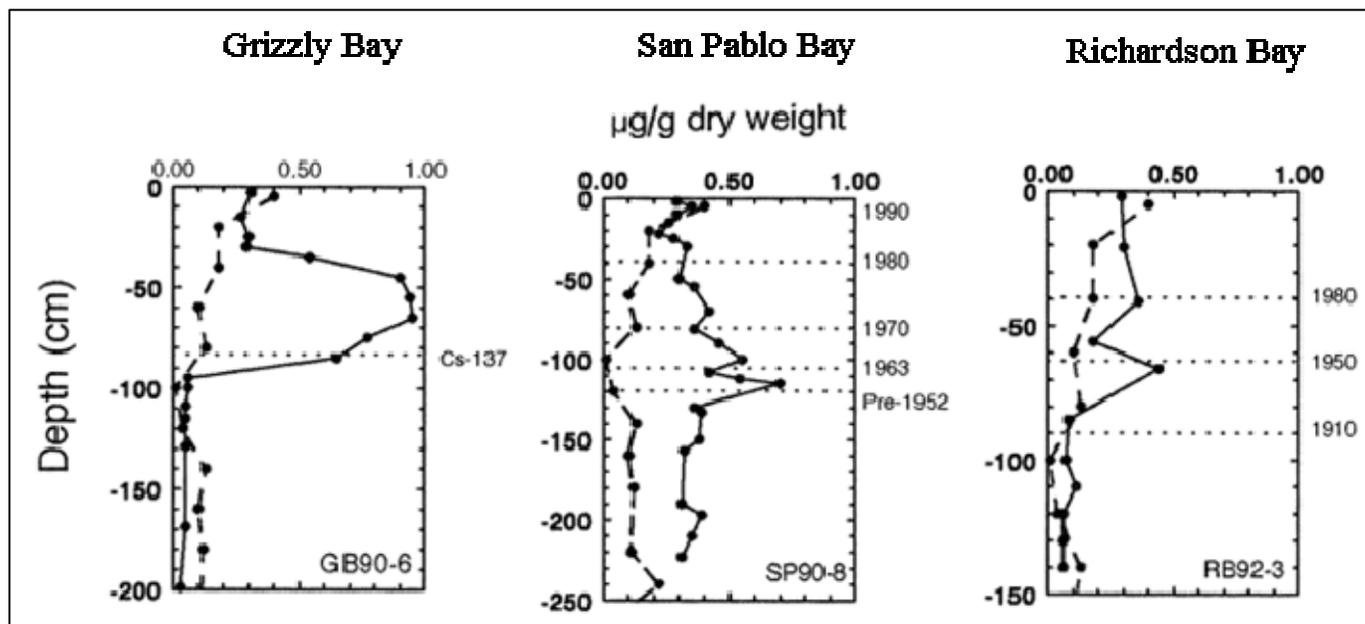


Source: SFEI (2008).

Hornberger et al. (1999) measured concentrations of mercury and other metals in six sediment cores from various parts of the SFB. These concentrations were compared to those in a sediment core from Tomales Bay (located about 45 km north of the SFB, not shown in Figure B-10), considered to be a uncontaminated reference because of a lack of industrialization and urbanization. The authors found that concentrations in the deepest horizons of the SFB cores were comparable to those in the reference core ($0.06 \pm 0.01 \mu\text{g/g}$) from Tomales Bay (see Figure B-11) and that the maximum concentrations of mercury in the cores were found to be about 20 times the reference baseline concentration. The authors also indicated that the earliest anthropogenic influence on metal concentrations appeared as mercury contamination (concentration of $0.3\text{-}0.4 \mu\text{g/g}$) in sediments deposited at San Pablo Bay between 1850 and 1880. Due to the presence of mercury mines in the upstream watersheds, concentrations of mercury

were higher in sediments of San Pablo and Grizzly Bay (both in the northern part of the SFB, see Figure B-10 for the location of these sites), compared to those in Richardson Bay (which is affected by both the northern and the less contaminated southern portions of the SFB).

Figure B-11 Mercury Concentrations ($\mu\text{g/g}$, dry weight) in Sediment Cores from Grizzly Bay, San Pablo Bay, and Richardson Bay Compared to those in the Reference Sediment Core from Tomales Bay

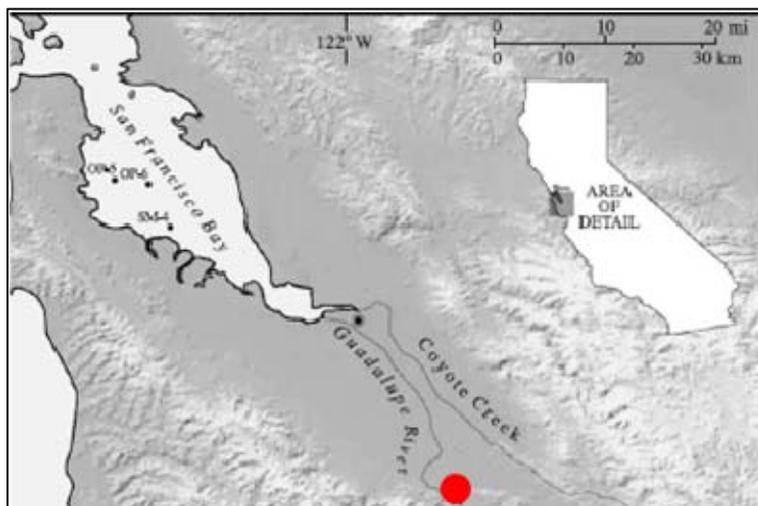


Notes:

- Sediment core from Tomales Bay shown as broken vertical line.
- The horizontal dotted lines denote the minimum age of sediment horizon as determined by an age dating model.
- Source: Hornberger et al. (1999).

Conaway et al. (2004) measured mercury concentrations in sediment cores collected from a southern SFB tidal marsh, which is downstream of the New Almaden mining district (see Figure B-12), formerly the largest mercury mining district in North America. The mercury concentrations at various depths of the sediment core and the estimated mercury accumulation rate in the sediments are presented in Table B-9. The authors observed that sediment mercury concentrations began to increase in the later part of the 19th century and reached a maximum in the mid-20th century, consistent with the temporal trends in mercury production at that mine. The authors indicated that concentrations observed in the pre-mining sediment record (prior to 1850s, 0.40 ± 0.15 nmol/g, or 0.08 ± 0.03 $\mu\text{g/g}$), are similar to those reported in the literature from deep-cores from the northern reach of the SFB and to river sediments from the northern California Coast Range (with no known mercury mineral deposits). Thus, the authors argued that natural weathering of mercury-rich deposits is not a substantial contribution to the southern SFB and that the principal source of mercury contamination in the southern SFB is anthropogenic activity (erosion of mercury mine wastes).

Figure B-12 Location of the New Almaden Mine

**Notes:**

- Location of the New Almaden mine shown with red circle, with reference to the San Francisco Bay
- Source: Conaway et al. (2004).

Table B-9 Mercury Accumulation Rate for Depth Intervals in a Sediment Core from a Southern San Francisco Bay tidal marsh

Depth (cm)	Period	Sedimentation Rate (cm/yr)	Bulk density (g/cm ³)	Hg conc. (µg/g) ^a	Hg accumulation rate (µg/cm ² /yr) ^b
0-8	1998-2001	2.70	0.8	0.46	1.00
8-35	1982-1998	1.80	0.7	0.48	0.62
35-40	1975-1982	0.71	0.7	0.54	0.26
40-125	1945-1975	2.80	0.6	0.84	1.40
125-140	1870-1945	0.18	0.6	0.52	0.06
140-280	1570-1870	0.33	0.7	0.08	0.02

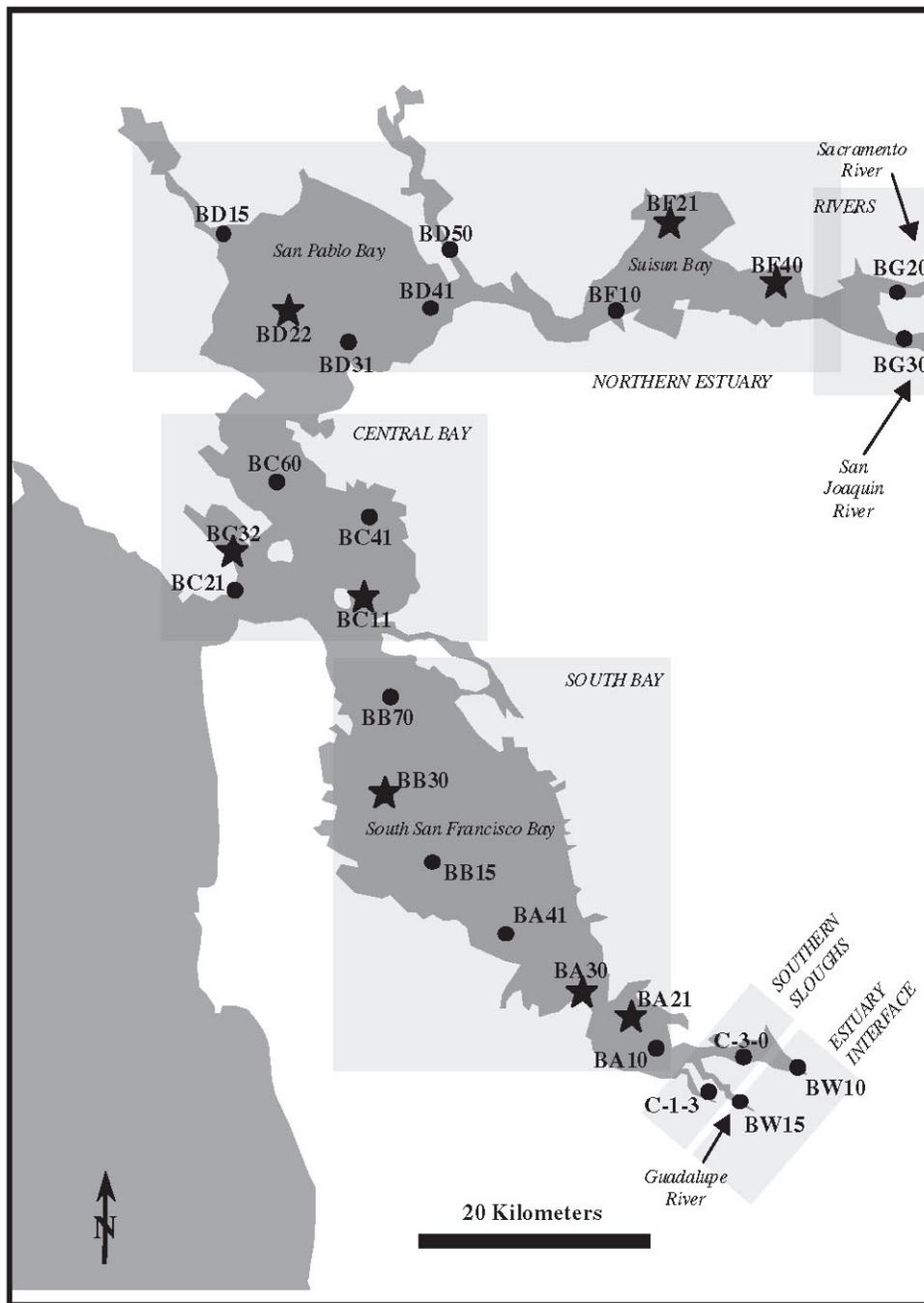
Notes:

- a - Reported concentrations were converted from nmol/g to µg/g.
- b - Reported accumulation rates were converted from nmol/cm²/yr to µg/cm²/yr.
- Source: Conaway et al. (2004).

Conaway et al. (2007) analyzed total mercury concentrations in sediments of the San Francisco Estuary for the period 1993 to 2001 at 26 sites ranging from marine to freshwater locations (see Figures B-13A and B). For analytical purposes, the 26 sampling sites were grouped into six hydrographic regions: Estuary Interface, Southern Sloughs, South Bay, Central Bay, Northern Estuary, and Rivers. The authors found that the six hydrographic regions had significantly (statistically) different sediment mercury concentrations, with the Estuary Interface region and the Rivers region having the highest (0.35 µg/g) and lowest (0.10 µg/g) median concentrations, respectively (see Figures B-13A and B). The authors indicated that sediment concentrations during the period 1993 to 2001 have decreased at few sites in the Northern Estuary region (by 22%), Central Bay region (by 17%), and South Bay region (by 32%). This decrease in sediment mercury concentrations was attributed to the transport of relatively lower concentration mercury sediment to the estuary from the Sacramento River and San Joaquin River watersheds.

Greenfield et al. (2005) analyzed seasonal, interannual, and long-term variations in mercury contamination of sport fish in the SFB. The authors indicated that interannual variation in mercury was evident in striped bass but absent in shiner surfperch, leopard shark and white croaker. Mercury concentrations in striped bass showed no evidence of a trend between 1970 and 2000, and the authors attributed this to the continuing contribution of mercury from historical mines and erosion of buried sediments. The authors indicated that variations in mercury bioavailability to fish could be a function of fish ecology, watershed loading, contaminated sediment exposure, and net methylmercury production rates.

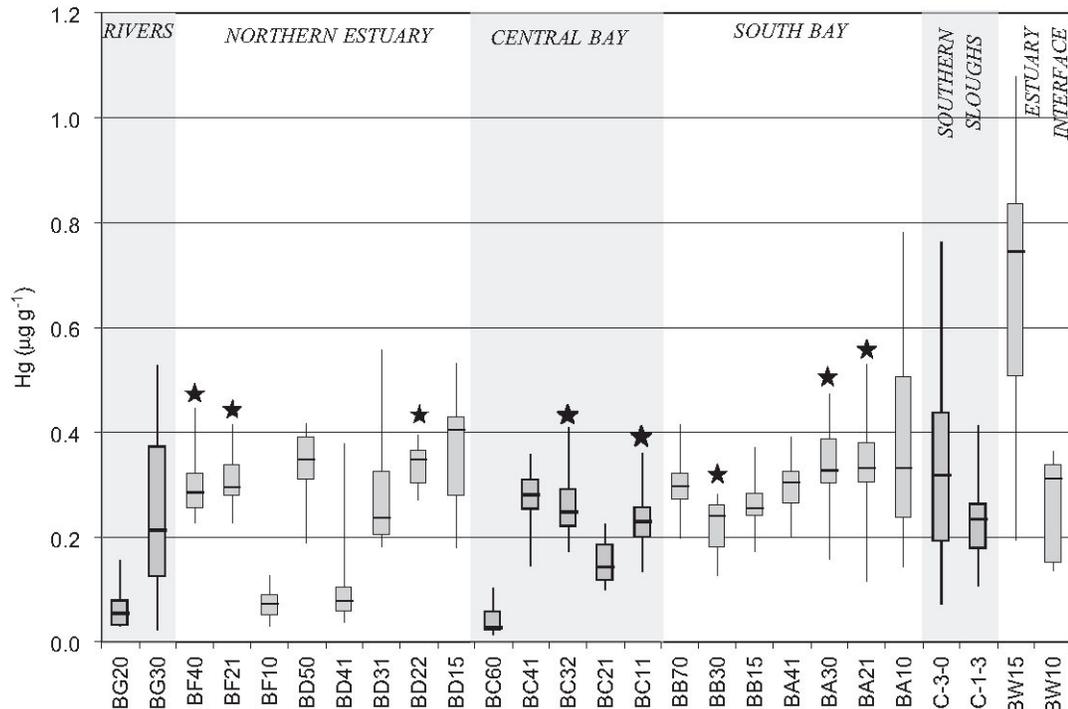
Figure B-13A Sampling Locations of Total Mercury Concentrations in Sediments of the San Francisco Estuary, 1993 to 2001



Notes:

- Sampling locations in the San Francisco Estuary, grouped into six hydrographic regions (from south to north): Estuary Interface, Southern Sloughs, South Bay, Central Bay, Northern Estuary and Rivers. Stars represent sites showing a statistically significant decrease in sediment mercury concentrations from 1993 to 2001.
- Source: Conaway et al. (2007).

Figure B-13B Total Mercury Concentrations in Sediments of the San Francisco Estuary, 1993 to 2001

**Notes:**

- Box and whisker plots showing mercury concentrations ($\mu\text{g/g}$, dry weight) for the period 1993-2001. For each station (from the bottom to the top) are shown the minimum, 25 percentile, median, 75 percentile, and maximum values.
- Source: Conaway et al. (2007).

B.5 Estimates of the San Francisco Estuary Mercury Budget

B.5.1 Estimated inputs to the San Francisco Bay from Different Sources (San Francisco Bay RWQCB 2006)

The following is a summary of estimated mercury inputs to the SFB for the year 2003 from the San Francisco Bay RWQCB. The total input to the SFB was estimated to be 1,220 kg/yr (see Table B-10) and the individual sources in decreasing order of magnitude were bed erosion (460 kg/yr), the Central Valley watershed (440 kg/yr), urban storm water runoff (160 kg/yr), the Guadalupe River watershed (92 kg/yr), direct atmospheric deposition (27 kg/yr), non-urban storm water runoff (25 kg/yr), and wastewater discharges (18 kg/yr). Based on box models that account for sediment and mercury inputs and outputs to and from the SFB, this report estimated that mercury losses for 2003 (by transport to the Pacific Ocean via the Golden Gate, plus the net result of dredging and disposal and other losses), were approximately 1,700 kg/yr. The estimated contribution of the various sources of urban storm water runoff (a total load of 160 kg/yr) is presented in Table B-11 and the major sources of mercury loading to the SFB from municipal wastewater discharge are presented in Table B-12.

Table B-10 *Estimated Annual Mercury Contribution (in kg/yr) from Various Sources to the San Francisco Bay in 2003*

Source	contribution (kg/yr)	% of total
Wastewater (municipal & industrial) Discharges	18	1.5%
Non-urban Storm Water Runoff	25	2.0%
Direct Atmospheric Deposition	27	2.2%
Guadalupe River Watershed (mining legacy)	92	7.5%
Urban Storm Water Runoff	160	13.1%
Central Valley Watershed	440	36.0%
Erosion of Buried Sediments	460	37.6%
Total	1220	100%

Source: San Francisco Bay RWQCB total maximum daily load (TMDL) 2006).

Table B-11 *Estimated Annual Mercury (in kg/yr) in urban Storm Water Flowing to the San Francisco Bay in 2003*

Urban Storm Water Source	Estimated Hg Load (kg/yr)
Santa Clara Valley Urban Runoff Pollution Prevention Program	44.0
Alameda Countywide Clean Water Program	39.0
Contra Costa Clean Water Program	22.0
San Mateo County Storm Water Pollution Prevention Program	16.4
Vallejo Sanitation and Flood Control District	3.2
Fairfield-Suisun Urban Runoff Management Program	3.1
American Canyon	0.3
Sonoma County area	3.1
Napa County area	3.1
Marin County area	6.5
Solano County area	1.6
San Francisco County area	17.2
Total ^a	159.5

Notes:

- a - The total urban storm water load of 160 kg/yr, presented in Table B-10, was obtained by San Francisco Bay RWQCB TMDL (2006) by rounding off the total presented here.
- Modified from Table 5-w of San Francisco Bay RWQCB TMDL (2006).

Table B-12 *Estimated Annual Mercury (in kg/yr) from Municipal Wastewater Discharge Flowing to the San Francisco Bay in 2003*

Municipal Wastewater Discharger	Estimated Hg Load (kg/yr)
East Bay Dischargers Authority	3.6
San Francisco, City and County of, Southeast Plant	2.7
East Bay Municipal Utilities District	2.6
Central Contra Costa Sanitary District	2.2
San Jose/Santa Clara Water Pollution Control Plant	1.0

Notes:

- Only discharges with an estimated load of at least 1 kg/yr are presented here.
- Modified from Table 2-1 of San Francisco Bay RWQCB TMDL (2006).

B.5.2 Model-based Mercury Mass Balance in the San Francisco Bay Area

McKee and Mangarella (2006) used a combination of locally available data and estimates from other regions of the US in a simple conceptual modeling framework to estimate the mercury contribution to the SFB from storm water conveyances (see Table B-13). The authors estimated that the total mercury loading to the SFB from storm water is 176 kg/yr, with atmospheric deposition and watershed surface sediment erosion contributing 48 and 59 kg/yr, respectively.

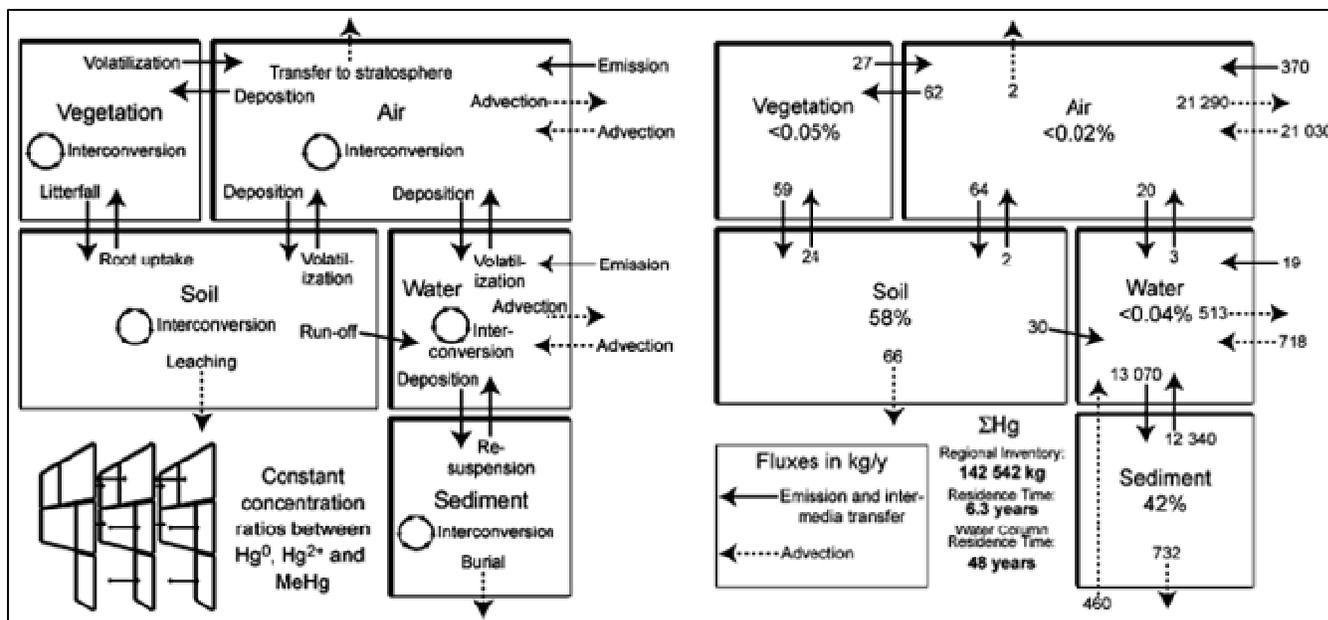
Table B-13 *Estimated Annual Mercury (in kg/yr) in San Francisco Bay Area Storm Water Conveyances*

Mercury Source	Estimated Hg Load (kg/yr)
Watershed Surface Sediment Erosion	59 (30-182)
Atmospheric Deposition (direct deposition to water surfaces)	48 (20-93)
Instruments	23 (8-28)
Bed and Bank Erosion	21 (4.1-160)
Switches and Thermostats	10 (9-11)
Fluorescent Lighting	4.1 (2.4-5.8)
Paint	2.6 (1-4)
Railway Lines	1.5 (0.09-3)
Industrial Hotspots	1.4 (0.25-7.4)
Landfill	1 (0.5-1.5)
Laboratory	1 (0.2-1.4)
Gasoline	1 (0.1-2)
Batteries	0.8 (0.15-1.5)
Auto-Recycling	0.7 (0-3)
Dental	0.4 (0.2-0.6)
Other Uses	0.09 (0.006-0.18)
Total	176 (76-504)

Source: McKee and Mangarella (2006).

Macleod et al. (2005) developed a model that simultaneously describes the fate and transport of elemental, divalent and methylated mercury species in the environment (including air, soil, vegetation, water and sediments) (see Figure B-14). The objective of this modeling study was to describe the long-term average dynamics of mercury in a generic regional environment, and hence, the model is not appropriate for describing episodic depletion or accumulation of mercury species.

Figure B-14 Steady-state Mass Balance of Total Mercury in the San Francisco Bay Area



Notes:

- Left panel: Model schematic showing conceptual transfer (straight arrows) and transformation (circular arrows) processes between the various reservoirs for Hg(0), Hg(II), and MeHg species.
- Right panel: Estimated fluxes (in kg/yr) and storages (as percentages of the total regional inventory).
- Source: Macleod et al. (2005).

The key assumption of this model is that temporally and spatially averaged ratios of concentrations of the individual mercury species are constant in each environmental medium (air, soil, vegetation, etc.). The authors indicated that this key assumption will be valid (however, it is not a requirement) when chemical reactions for inter-conversion of mercury species are fast relative to the rates of transport in and out of any medium or across media. The various parameters required by the model (such as physical properties of the media, transport velocity parameters, etc.) were obtained from the scientific literature, and the 95% confidence intervals of many of these parameters ranged from one third to three times their median values. The authors indicated that although their “lumped” modeling approach (which employs single best-estimate parameters) does not account for spatial and temporal heterogeneity observed within the SFB Area, it provides an approximate (and relatively simple) mass balance budget and enables the identification of key model parameters using uncertainty analysis. Comparison of model simulated and observed mercury concentrations and fluxes in the SFB Area indicated that the model is reasonably consistent with the observations and that the 95% confidence intervals on the model estimates overlapped with those on the observations. However, the fact that these confidence intervals spanned two orders of magnitude highlights the inability of a “lumped” modeling approach to capture the

spatial and temporal heterogeneity of the SFB Area. Nonetheless, the model provides useful estimates of the SFB mercury budget.

The estimated steady-state mass balance of total mercury in the SFB Area is shown in Figure B-14. The authors indicated that the mass balance of total mercury in the SFB Area is determined almost entirely by the dynamics of Hg(II) species, the most prevalent species in all environmental media except the atmosphere (where Hg(0) is predominant). It is evident from Figure B-14 that there is a net atmospheric deposition of total mercury to soils, water, and vegetation in the SFB Area. The residence time of total mercury in the atmosphere was estimated to be 6.3 years and the residence time of total mercury in the sediments was estimated to be 48 years.