

San Francisco Estuary Regional Monitoring Program for Trace Substances

San Francisco Bay Atmospheric Deposition Pilot Study Part 2: Trace Metals

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Part 2: Trace Metals

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ACRONYMS AND ABBREVIATIONS

BAAQMD	Bay Area Air Quality Management District
CARB	California Air Resources Board
CCCSD	Central Contra Costa Sanitary District
Cd	Cadmium
Cr	Chromium
CSJ	City of San Jose
Cu	Copper
DQO	Data quality objectives
FOF	Field observation form
HCl	Hydrochloric acid
IADN	Integrated Atmospheric Deposition Network
ICP-MS	Inductively coupled plasma mass spectrometry
IPR	Initial precision and recovery
MDN	Mercury Deposition Network
MDL	Method detection limit
NADP	National Atmospheric Deposition Program
Ni	Nickel
NWS	National Weather Services
OST	Oakland Sewage Treatment Plant
Pb	Lead
POTW	Publicly Owned Treatment Works
QA/QC	Quality assurance and quality control
RMP	Regional Monitoring Program for Trace Substances
RPD	Relative percent difference
SFEI	San Francisco Estuary Institute
SOP	Standard operating procedures
SRM	Standard reference material
TMDL	Total Maximum Daily Load
UPM	Urban particulate matter
USEPA	United States Environmental Protection Agency

ABSTRACT

This report is the second in a three-part series covering a Pilot Study conducted from August 1999 through August 2000. The objective was to estimate the inputs of selected trace metals and trace organic pollutants from the atmosphere to the San Francisco Estuary in California. Particulates in the ambient air and precipitation samples were collected at three sites strategically located in close proximity to the Estuary. This report covers the trace-metal component of the Pilot Study, measuring copper, nickel, cadmium, and chromium. Atmospheric deposition of mercury to the San Francisco Estuary is the subject of the first report presented in this series. The third report will address dry deposition of trace organic pollutants, namely PAHs and PCBs, from the atmosphere.

Dry deposition fluxes of copper, nickel, cadmium, and chromium from the atmosphere to the Estuary was approximately $1,100 \pm 730$, 600 ± 350 , 22 ± 15 , and $1,300 \pm 900 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$, respectively. The volume-weighted average concentrations of these trace metals detected in the precipitation were 1.2, 0.42, 0.11, and $0.23 \mu\text{g/L}$, respectively. The wet deposition fluxes were 630, 230, 60, and $120 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ for copper, nickel, cadmium, and chromium, respectively.

On an annual basis, it was estimated that direct atmospheric deposition, via both dry deposition and wet deposition, contributed approximately 1,900, 930, 93, and 1,600 kg of copper, nickel, cadmium, and chromium, respectively, to the Estuary. Depending on chemical species, wet deposition constituted between 10 and 70% of the total atmospheric deposition. Indirect inputs via runoff from the local watersheds surrounding the Estuary were estimated to contribute approximately twice as much as the loading from direct atmospheric deposition. To put air-deposition loading into perspective, we compared mass loadings of these metals among the various major conveyances or pathways, each with various degrees of uncertainty associated with them. Direct atmospheric deposition may contribute as much loading of certain trace metals as the loading from wastewater discharges. Although atmospheric deposition appears to be a minor contributing pathway, compared to the inputs from watersheds, it is premature to draw any conclusions before load estimates from stormwater runoff are further refined.

The uncertainty associated with the loading estimates presented in this report is assessed qualitatively. Low uncertainty indicates that the estimate has an error range of within $\pm 25\%$; a moderate uncertainty indicates that the error range could be up to two-fold; a moderate-high uncertainty presents an estimate that has an error range of up to five-fold; and an estimate with high uncertainty may have an error range of up to ten-fold. The uncertainty for the loading estimate is low for wet deposition, moderate-high for dry deposition, and moderate-high for indirect inputs via runoff attributable to atmospheric deposition, resulting in a moderate uncertainty for the overall estimate. The uncertainty is low (copper, nickel, chromium) to moderate-high (cadmium) for estimates of loading from wastewater discharges. Loading from various sources and pathways could not be fairly compared unless all load estimates have the same level of low uncertainty.

1.0 INTRODUCTION

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

Several attempts have been made to assess the contribution of the air deposition pathway to the total pollutant load to the San Francisco Estuary. Gross calculations based on ambient air monitoring results of the California Air Resources Board (CARB) and the Bay Area Air Quality Management District (BAAQMD) (Kirschmann and Grovhoug 1996, Hauri 1998a, Hauri 1998b) and a preliminary study conducted by the City of San Jose in 1996 (Eric Hansen, personal communication) suggested that the contribution of atmospheric deposition to the total pollutant load ranged from less than 1% up to 20% for certain pollutants. No definitive conclusions could be drawn from these retroactive calculations and preliminary results, but these exercises indicated that better estimates of load from this pollutant transport pathway to the Estuary should be obtained prior to evaluating the relative benefits of various alternatives in reducing pollutant load.

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

Established methods were used in monitoring concentrations of trace metals in the ambient air (Holsen et al. 1993, Yi et al. 1997a, Yi et al. 1997b, Paode et al. 1998) and in precipitation (Vermette et al. 1995b). Reasonable assumptions and parameters were incorporated into estimating deposition loading of trace metals from the air directly to the surface of the San Francisco Estuary. Estimates of trace metals deposition from the atmosphere onto land surfaces surrounding the Estuary and subsequent input through runoff from tributaries were also presented. Uncertainty associated with each estimated loading was assessed qualitatively.

This report describes the methodology used in the San Francisco Atmospheric Deposition Pilot Study (hereafter simply referred to as the Pilot Study) and presents the results obtained from monitoring certain selected particle-associated trace metals, namely copper (Cu), nickel (Ni), cadmium (Cd), and chromium (Cr), in dry particle deposition and precipitation. This report also estimated amount of these trace metals that could

potentially be deposited from the atmosphere to the surface of the San Francisco Estuary¹ (the Estuary). Estimates of trace-metal loading from atmospheric deposition were also compared with estimated mass inputs from other major sources or pathways.

¹ In this report, San Francisco Estuary encompasses San Francisco Bay, San Pablo Bay, Suisun Bay, and the Sacramento/San Joaquin River Delta.

2.0 OBJECTIVES OF THE STUDY

Section 303(d) of the Clean Water Act requires states to identify impaired water bodies and the pollutants causing the impairment. States are also required to establish a Total Maximum Daily Load (TMDL) of the pollutant to the water body that will eliminate the impairment. Copper and nickel are two of the pollutants that have been listed as possibly impairing the beneficial uses of the Estuary. Copper and nickel were detected in water samples at concentrations that exceeded their respective criteria under the California Toxics Rule.

In addition to identifying pollutants that cause the impairment of water bodies, the state must identify pollutant sources and allocate the allowable pollutant load from those sources. An implementation plan must also be established, and the TMDL allocation and implementation plan must be incorporated into the state's basin plans. Estimating the magnitude of loading contributed from each potential source and pathway is one of the first steps toward implementing a TMDL or anti-degradation plan for trace metals.

Five primary sources or pathways were previously identified to contribute pollutant loading to the Lower and Central South San Francisco Bay (TetraTech & URS 1998, TetraTech 1999). External sources and pathways that contribute pollutant loads to the entire San Francisco Estuary include the following:

- a. Non-point sources associated with runoff and erosion (load from tributaries and storm drains), including contribution from atmospheric deposition
- b. Direct atmospheric deposition
- c. Point-source wastewater effluent discharges from municipal (Publicly-Owned Treatment Works, POTWs) and industrial facilities, which may include contribution from indirect atmospheric deposition through stormwater drainage to some treatment plants

Primary objectives of the Pilot Study are: 1) estimating loading of trace metals from atmospheric deposition directly to the Estuary surface; 2) estimating loading of trace metals from atmospheric deposition to other surfaces and potentially indirect loading to the Estuary (atmospherically-derived tributary load); and 3) comparing loading from atmospheric deposition to loadings from other major quantifiable or semi-quantifiable sources and pathways. Results from this Pilot Study provided the first set of data collected in this region for deposition of particle-associated trace metals, as well as metal concentrations in precipitation samples. Results from the Pilot Study can be used to further investigate sources of trace metals and explore potential mechanisms that can be used to reduce total loading of these chemicals to the Estuary.

3.0 METHODOLOGY

Deposition of air pollutants to the Estuary surface water can occur by several processes, including rain scavenging of gases and particles, dry deposition of particles, deposition associated with cloud and fog-water, and air-water exchange processes. Methodology used for this study of atmospheric deposition of air pollutants consisted of sample collection during rain events for wet deposition and during non-rainy days for dry deposition. Air-water exchange process does not occur for the non-volatile trace metals addressed in this report, and deposition through cloud and fog-water is outside the scope of this study.

3.1 General Methodology for Atmospheric Deposition Study

A summary of the general atmospheric deposition study methodology is presented in Figure 1. The wet deposition study measures pollutant concentrations in the rainfall, captured by specific precipitation collectors. Other investigators have used both direct and indirect methods to study dry deposition of trace metals. The direct method measures pollutant concentration in particles depositing on a surrogate surface or deposition plate (surrogate plate) during non-rainy days. The indirect method collects pollutants from the ambient air and performs inferential calculations using relevant equations, and pertinent constants and assumptions. The method chosen for this study is the direct method, using surrogate surface plates. The rationale for selecting this method will be further discussed in Section 3.2.1.

3.2 San Francisco Bay Atmospheric Deposition Pilot Study

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

Monitoring Parameters

The Pilot Study was designed to obtain estimates of dry deposition during non-rainy days as well as wet deposition from precipitation. To facilitate timely implementation, the Pilot Study was divided into two phases (Table 1): Phase 1 monitored trace metals, and Phase 2 addressed trace organic compounds. Because of the differences in sampling protocol and data evaluation, results from mercury monitoring are the main topic of another report (Tsai & Hoenicke 2001), and Phase 2 of the study addressed trace organic compounds (Tsai et al. 2001). Deposition of copper and nickel was evaluated because these chemicals have been implicated in impairing the beneficial uses of the San Francisco Estuary. At the request of the Central Contra Costa Sanitary District (CCCSD), cadmium and chromium were also included in the analysis, since their inclusion had minimal impact on the overall project budget or schedule.

Brief information on the environmental effects of Cu, Ni, Cd, and Cr (USEPA 2001) is presented below. Copper is not biodegraded or transformed. Exposure routes for aquatic organisms to Cu include ingestion, gill uptake, and dermal absorption. In aquatic organisms, exposures to Cu are associated with developmental abnormalities. Copper bioconcentrates in aquatic organisms, however, biomagnification does not occur. Exposure routes for ecological mammalian species include ingestion, inhalation, and dermal absorption. Copper does not bioaccumulate in mammals. Copper is associated with adverse hematological, hepatic, developmental, immunological, and renal effects in mammals.

Nickel does not appear to accumulate in plants or small animals and it is not expected to accumulate in fish. Nickel can persist in natural waters indefinitely and its adverse effects of nickel on aquatic organisms include reduced survival time.

Exposure routes for aquatic organisms to cadmium include ingestion and gill uptake. Freshwater biota is most sensitive to the toxicity of Cd, followed by marine organisms, birds, and mammals. Toxicity to Cd is inversely proportional to water hardness. Cd bioaccumulates in both aquatic and terrestrial animals, with higher bioconcentration in aquatic organisms. Primary exposure routes for ecological mammalian species include ingestion and inhalation. Cd interferes with the absorption and distribution of other metals and causes renal toxicity in vertebrates. Chronic effects of Cd on aquatic organisms include decreased reproduction rates.

Exposure routes for aquatic organisms to chromium include ingestion, gill uptake, and dermal absorption. Bioaccumulation of Cr occurs in aquatic receptors. Biomagnification does not occur in aquatic food chains. Exposure routes for ecological mammalian species include ingestion, inhalation, and dermal absorption. Cr is not truly metabolized, but undergoes various changes in valence states and binding with ligands and reducing agents in vivo. Elimination of Cr is slow. Certain soils with a relative high content of Cr (0.2 to 0.4%) were found to be infertile. Plants growing in acidic sandy soil with low organic content seemed to have the greatest risk of toxicity.

Monitoring Duration and Frequency

CARB and BAAQMD are maintaining an extensive network for monitoring ambient air quality in the Bay Area. The original intent of the Pilot Study was to collocate Pilot Study sites with the existing air monitoring sites managed by CARB or BAAQMD. During planning stages of the Pilot Study, it became apparent that it was not feasible to collocate sampling sites at existing stations because of economic and logistical considerations. For similar reasons, monitoring frequency for the Pilot Study was set on a 14-day schedule, unlike the CARB/BAAQMD schedule of sampling every 6 or 12 days. Sampling every 14 days was more feasible for the local organizations that contributed in-kind services to maintain and operate the monitoring sites. Sampling was started in August 1999 for a total of 12 months (Table 2).

Monitoring Stations

The Bay Area is densely urbanized with a mix of residential, commercial, industrial (mostly electronics/high technology and other light industries), agricultural, and undeveloped (open space) land uses. There are many congested major highways surrounding the Estuary. Several petroleum refineries in the region are located primarily in the North Bay. The Central Bay has two major airports, seaports, and some metal-plating facilities. The South Bay is the hub for electronic industries and an expanding major airport. One each of the inoperative chromite-mine and copper-mine are located in the South Bay (Abu-Saba & Tang 2000). Another inoperative copper-mine is located on the west of the North Bay.

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

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

Three study sites were chosen using these criteria to represent different segments of the Estuary: North Bay, Central Bay, and South Bay (Figure 2). The South Bay site is located at the northwest corner of the Moffett Federal Airfield/NASA Ames Research Center within one mile south of the Estuary. The Central Bay site is located within _ mile of the Estuary at the northern end of Treasure Island. The North Bay site is located in Martinez within the property boundary of the Central Contra Costa Sanitary District's Wastewater Treatment Plant, which is about 3 miles south of the North Estuary. Sampling instruments were installed on the ground level at the South and North Bay sites, and on the roof of a 15-foot tall building at the Central Bay site.

3.2.1 Dry Deposition

Dry atmospheric deposition of toxic air pollutants has been the subject of numerous research projects in the last three decades. A number of different techniques have been used in an effort to make reliable flux estimates. These approaches can be

divided into two categories: 1) directly measure deposition fluxes using surrogate surfaces (direct method), and 2i) calculate deposition fluxes using airborne concentration data and modeled or assumed deposition velocity (indirect method). When using direct method, the geometry of the surrogate surface, surface roughness, and the substrate used all influence the wind profile and local turbulence above the sampling surface, which in part controls the measured deposition flux. In general, these surfaces are designed to minimize disruption of the flow field so that minimum fluxes are measured. In the indirect modeling approach, the size distribution of the particles present in the ambient air is critical in determining deposition velocity and the resulting deposition fluxes. Yet the information on the particle size distribution is often not measured in the study. This lack of information about particle size distribution often requires the use of an overall deposition velocity that is assumed to be appropriate for the species in question. Several investigators have shown that large particles are responsible for a large proportion of the deposition flux, although they may account for only a small fraction of the total airborne mass (Holsen & Noll 1992, Holsen et al. 1993, Shahin et al. 2000). This is due to the large increase in the deposition velocity for a small increase in the particle diameter for particles $\geq 2 \mu\text{m}$. Shahin et al. (2000) asserted that large particles are not sampled efficiently by most samplers and are therefore not included in most estimates using indirect modeling approach. This omission makes modeling estimates generally lower than the deposition flux measurements using surrogate surfaces.

Due to the reasons described above, a direct method, employing surrogate surface plates, was used in this Pilot Study to collect samples of trace metals associated with particulate matter during the non-rainy days. Although this method is not suitable for collecting volatile chemicals, such as mercury, PAHs, and PCBs that are predominately present in gaseous phase in the atmosphere, it has been used successfully in collecting non-volatile trace metals in particulates (Holsen et al. 1993, Yi et al. 1997a, Yi et al. 1997b, Paode et al. 1998).

3.2.1.1 Field Operations

The direct method employed in this study used surrogate plates to collect dry deposition samples of trace metals in particles from the air. The sampler “Egret I” used in this Pilot Study was an adaptation of the prototype developed by other investigators (Holsen et al. 1991). The original sampling device, with greased Mylar films mounted on a knife-edge plate, has been described by Yi and associates (Yi et al. 1997a, Yi et al. 1997b), and evaluated by other investigators (Holsen et al. 1993, Pirrone et al. 1995, Paode et al. 1998). The prototype was further modified for this study. The total exposed surface area was enlarged from 123 cm^2 to 500 cm^2 , and all components of the device were made with metal-free materials.

Egret I had two wind-vanes pivoting according to the wind direction (Figure 3). Particles from the ambient air deposit directly onto a 20 X 25 cm Mylar film coated with a thin-layer of L-Apiezon grease. The Mylar film was placed on a surrogate surface plate, which in turn was mounted and secured to the wind-vane with plastic clips (Figure 4). The cartridge plate was pointed into the wind with a leading knife-edge to provide a laminar or non-turbulent flow of air over the surface of the Mylar film. The L-Apiezon

grease applied to the Mylar film provided a sticky surface to capture particles, and prevent particle bounce (Noll et al. 1990). The non-volatile grease was free of the chemicals being monitored in the Pilot Study.

Metal-free materials were used to construct the frame and various parts of Egret I: cartridges, wind-vanes, and the surrogate surface plates. In addition, transparent materials were used whenever possible to reduce thermal microclimates induced from blackbody radiation. When installing or retrieving samples, ultra-clean field techniques adapted from EPA Method 1669 “Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels” (USEPA 1996) were practiced to minimize contamination from field operations.

Greased Mylar film was exposed to the ambient air for 24 hours. Actual exposure duration, along with other pertinent field operating information and sample conditions, was recorded on a field observation form (FOF). Duplicate samples as well as one field blank sample were collected at each site once every 14 days. During sample installation and retrieval, field blanks were removed from the plastic containers for instantaneous exposure and returned to the containers immediately.

3.2.1.2 Sample Preparation and Analysis

Mylar film was cleaned sequentially with methanol, 2% nitric acid, and deionized distilled water. After the Mylar film was air-dried, approximately 150 mg of L-Apiezon grease was evenly applied. The Mylar film was weighed before and after the grease was applied to ensure that same amount of grease was applied. After sample retrieval, particles collected on the greased Mylar film were recovered by rinsing with 50 mL hexane. The samples were then dried under vacuum before they were digested in 20 mL of 10% ultra-pure HNO_3 for 30 minutes in a microwave oven. Samples were subsequently analyzed with a Thermo Jarrell Poems II inductively coupled plasma-mass spectrometer (ICP-MS) (Paode et al. 1998). EPA Method 200.8 was used for analysis. For quality assurance and quality control purposes, urban particulate matter (UPM) from NIST was used as the standard reference material (SRM).

3.2.2 Wet Deposition

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

3.2.2.1 Field Operation

High-density polyethylene one-liter bottles and funnels with adaptors were used to collect samples. Bottles and funnels were cleaned to reduce metal contamination. The cleaning protocol for the bottles and funnels included: alkaline detergent, nitric acid bath, HCl bath, and multiple rinses with distilled water between each solution. Finally, the bottles were filled with distilled water and topped off with a small drop of trace-metal grade HCl. The acidified distilled water in the bottle was emptied right before installation at the sample collection site. The adaptors used to connect the funnel and sample bottle did not have direct contact with the precipitation samples and required less stringent cleaning procedures. Adaptors were soaked overnight in a HCl bath, rinsed with distilled water, and air dried prior to each use.

3.2.2.2 Chemical Analysis

Precipitation samples were weighed and acidified with trace-metal grade nitric acid to an acid concentration of 0.2%. The samples were equilibrated for more than 48 hours before being analyzed. For samples containing less than 10 mL of precipitation, 20.0 mL of reagent water was added, and the sample was acidified to 0.2%.

Before analysis, concentrated HNO_3 was added to 10 mL of the sample until it contained 2% nitric acid. The sample was then digested at 85°C for 2 hours. The digested samples were then analyzed on either a Perkin Elmer model 5000 or 6100 ICP-MS, using external calibration and indium as an internal standard as described in either USEPA method 1638 or 6020. The calibrations and blanks met the data quality objectives of the method.

3.2.3 Quality Assurance and Quality Control

Sampling techniques used in the Pilot Study closely followed the general clean technique principles as described in USEPA Method 1669 (USEPA 1996) and the Quality Assurance Project Plan prepared for the Pilot Study (SFEI 2000). Site operators followed the procedures described in the standard operating procedures (SOPs) for the specific sampling method. Information pertaining to sample installation, operating conditions, and sample conditions was recorded on the FOF specifically designed for the Pilot Study. Original FOFs were included in the shipment of samples to the designated analytical laboratories. Copies of the FOFs were also forwarded to SFEI for evaluation and record keeping.

All equipment and supplies that had direct contact with the samples were rigorously cleaned (see above). Additionally, clean sample bottles and funnels were double bagged. Surrogate surface plates with greased Mylar films were placed in polyethylene containers before being enclosed in clean plastic bags. Powder-free gloves were worn when handling samples.

3.2.3.1 Dry Deposition

Results of all quality assurance and quality control (QA/QC) parameters are presented in Table 3. The overall data quality objectives (DQO) for the laboratory analyses were met, although low recovery of Cr (an average of 47% with a range of 21 to 167%) was observed in analysis of the UPM reference material. The low recovery of Cr

from the UPM was likely related to the incomplete digestion of particles using 10% HNO₃ digestion procedures, instead of complete digestion using hydrofluoric acid. Hydrofluoric acid was not used a digestion agent because of the related safety risks.

Method detection limits (MDL), defined as three times the standard deviation of the preparation blank values, were estimated to be 0.01, 0.007, 0.002, and 0.04 µg/sample for Cu, Ni, Cd, and Cr, respectively (Table 3). The MDLs were calculated from 24 analyses performed throughout the study. The average values of the field blanks for Cu, Ni, and Cd were below their MDLs, and that for Cr was about the same as the MDL. Overall, Cu, Ni, and Cr were detected in about 6%, 15%, and 43%, of the field blanks, respectively. No detectable concentrations of Cd were found in the field blanks. The high frequency of Cr detected in the field blanks might be related to the wide range of recovery reported by the laboratory. Data presented in this report were not blank-corrected.

Field samples collected at the Central Bay Site on September 28, 2000 and October 12, 2000 were excluded from further evaluation due to documented mistakes in sample installation. Sample spike recovery ranged from 73% for Cd, 87% for Cu and Cr, and 88% for Ni. It should be noted that about 40% of the samples had Cd concentrations below the MDL, while less than 3% of the samples had Ni or Cr concentration below the MDL. All samples had detectable concentrations of Cu. Replicate samples were collected at each site during each sampling event. Among the four trace metals measured, only Cu met the DQO of less than 30% relative percent difference (RPD)² set for this study. Overall average RPD for Ni and Cr was approximately 34%, slightly above the DQO, and that for Cd was about 83%, far from the DQO. Results of the replicate analyses indicated that measurements for Cd were highly variable. This high variability may be due to the fact that most of the detectable measurements for Cd were only slightly above its MDL. The averaged RPD was about 20% (Table 3), meeting the DQO, when the RPD was calculated only for those replicate field samples with analyte concentrations greater than three times their respective MDLs.

3.2.3.2 Wet Deposition

For wet deposition, two types of sampling trains were deployed, and two different analytical laboratories were used. The change of laboratory began with samples collected on February 1, 2000. Results of all the parameters assessed for QA/QC purposes are presented in Table 4. Laboratory #1 is the laboratory used prior to February 1, 2000, and laboratory #2 is the laboratory used after February 1, 2000. Analyses at both laboratories, as reflected by the percent recoveries and RPDs, met the DQOs established for the Pilot Study (Table 4). MDLs for Cu and Cd had some variations that were considered inconsequential. The detection limits, defined as three times the standard deviation of the preparation blank values, for Cu, Ni, Cd, and Cr were 0.03, 0.01, 0.004, and 0.03 µg/L at Laboratory #1, respectively, and 0.02, 0.01, 0.005, and 0.03 µg/L, respectively, at Laboratory #2.

² Relative percent difference was calculated by dividing the difference with the mean.

Only Cu was detected in bottle blanks and procedural blanks at concentrations greater than the MDL, with average concentrations of 20 ng/L and 13 ng/L, respectively. Field blanks and system blanks were also collected during non-rainy periods to assess any contamination resulting from field operations. A system blank is defined as a “simulated rainfall event,” in which double-distilled water was rinsed through the sampling funnel, tubing, and collected in the sample bottle to determine the amount of contamination of the sampling train during non-rain periods. A field blank is collected without rinsing with double-distilled water. Table 4 also presents analytical results of the field blanks, system blanks, and the distilled water used to collect system blanks as previously described. Trace metals were detected in the system blanks at amounts comparable to those detected in the distilled water. Chromium was found at approximately 74 ng/bottle in the system blank, slightly greater than the 63 ng/bottle detected in the distilled water. Other trace metals were below their respective detection limits. A total of 18 field blanks (six field blanks from each site) were collected, and the average concentrations of Cu, Ni, Cd, and Cr from the three sites were 5 ± 6 (mean \pm standard deviation), 2 ± 3 , 0.1 ± 0.1 , and 3 ± 3 ng/bottle, respectively. There were no statistically significant differences in the amount of Ni, Cd, and Cr detected in the field blanks among the three sites. The average 10 ng/bottle of Cu found in the field blanks from the Central Bay Site was statistically significantly higher than those from the other two sites. With the exception of two samples, all samples with detectable trace-metal concentrations were four times or more than the amount detected in the field blanks. The remaining two samples had Cr measurements that were two to three times the amounts detected in the field blanks. Data presented in this report were not blank-corrected because field blanks were collected at different sampling events under different conditions than the field samples, and contaminations in the field blanks were not consistently observed.

4.0 RESULTS AND DISCUSSION

This section presents results of the monitoring and loading estimates of the selected trace metals from the atmosphere to the Estuary surface. These estimates are further compared with estimates of trace metal loading from other major sources and pathways outlined in Section 2.0. Among the other major sources and pathways for trace metal loading to the Estuary, reliable empirical data are available only from effluent monitoring conducted by wastewater dischargers, primarily POTWs.

4.1 Dry Deposition

A total of 67 samples were collected from the three monitoring stations. During each sampling event, duplicate samples and a field blank were collected at each station. The targeted exposure duration was 24 hours or 1,440 minutes; the actual exposure duration was recorded on the FOFs for each sampling event. Results were calculated based on actual exposure times.

The dry deposition rates ($\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$) and deposition fluxes (kg/year) of the trace metals to different segments of the Estuary were calculated using the following formulas:

$$\text{Deposition flux rate } (\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}) = \mu\text{g/day} \div 500 \text{ cm}^2 \times 10,000 \text{ cm}^2/\text{m}^2$$

$$\text{Deposition loading (kg/year)} = \text{deposition flux rate } (\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}) \times \text{surface area of the Estuary segment (m}^2) \times 365 \text{ days/year}$$

Dry deposition fluxes of all trace metals varied between sampling events at all three locations (Figures 5 to 8). Deposition fluxes were consistently lower during the wet season (November through March). However, the data set encompasses only a one-year period, and is too limited to draw any conclusions regarding long-term seasonal variations. Average dry deposition fluxes from all sites combined were approximately 3.0 (2.5 to 3.5), 1.6 (1.2 to 1.9), 0.061 (0.051 to 0.076), and 3.5 (3.3 to 3.5) $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ for Cu, Ni, Cd, and Cr, respectively (Table 5). Results from the Wilcoxon's signed-ranks test (non-parametric paired sample comparison) indicated that deposition fluxes of Ni and Cd at the North Bay site were significantly higher than that measured at the South Bay site, with p-value at 0.004 and 0.007, respectively. It should be noted that about 40% of the samples had Cd measurements below its MDL.

Other investigators have studied dry deposition of trace metals at various locations around the U.S. (Holsen et al. 1993, Wu et al. 1994, Golomb et al. 1997, Paode et al. 1998, Sweet et al. 1998, Zufall et al. 1998, Shahin et al. 2000). Table 6 shows that dry deposition fluxes of Cu, Ni, Cd, and Cr at $1,100\pm 730$, 600 ± 350 , 22 ± 15 , and $1,300\pm 900$ $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ measured in the San Francisco Estuary fell within the range of those observed around other lakes and bays in the USA. However, one should be cautious in comparing estimates among various studies that use different types of air samplers and/or analytical methods. For some chemical species, using direct methods such as surrogate surface plates may yield measurements that are substantially higher than using indirect methods with dichotomous air samplers. This discrepancy in measurements due to the deployment of different sampling methods is seen in Table 6, as

demonstrated by the results reported by Golomb et al. (1997), Paode et al. (1998), Sweet et al. (1998), and Shahin et al. (2000).

The dry deposition fluxes measured around Lake Michigan from December 1993 to October 1995, using an automated dry deposition sampler with knife-edge surrogate surfaces, were approximately 10, 7, 0.2, and 1.0 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ (corresponding to 3,650, 2,555, 73, and 365 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) for copper, nickel, cadmium, and chromium, respectively (Shahin et al. 2000). Indirect estimates made using dichotomous sampler during 1993 and 1994 and an estimated overall deposition velocity around Lake Michigan as one of the IADN monitoring stations yielded dry deposition fluxes of 1,300, 320, 380, 130 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ for copper, nickel, cadmium, and chromium respectively (Sweet et al. 1998). Golomb et al. (1997) used both direct and indirect methods to measure the dry deposition of trace metals to the Massachusetts Bay, and found that the deposition flux of chromium varied by a factor greater than two, 1,200 $\mu\text{g}/\text{m}^2/\text{year}$ from the direct method versus 466 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ from the indirect method. Possible factors contributing to the difference include: 1) the dichotomous sampler under-collects some particles, especially those that are larger than 10 μm ; 2) the deposition velocities used to calculate deposition flux in the indirect method are too small for some chemical species; 3) differences in the sampling duration; and 4) differences in the analytical methods (Golomb et al. 1997).

Estimates of the dry deposition loading to each segments of the San Francisco Estuary are presented in Table 5. Loading of Cu, Ni, Cd, and Cr to the entire Estuary was 1,200 \pm 830, 680 \pm 400, 25 \pm 17, and 1,400 \pm 1,000 kg/year, respectively. Loading to the South Bay was 430 \pm 240, 220 \pm 130, 9 \pm 7, 620 \pm 440 kg/year, to the Central Bay 270 \pm 210, 140 \pm 76, 4 \pm 2, and 280 \pm 220 kg/year, and to the North Bay 490 \pm 280, 300 \pm 170, 12 \pm 8, and 530 \pm 360 kg/year for Cu, Ni, Cd, and Cr, respectively. Table 5 also shows that estimates of Ni and Cd loads to the South Bay obtained in this Pilot Study were comparable to the values estimated by Kirschmann and Grovhoug (1996) that were based on ambient air concentration data and assumed deposition velocities derived from the literature. On the other hand, loads to the South Bay estimated by this Pilot Study for Cu and Cr were 50% and 200%, respectively, of that estimated by Kirschmann and Grovhoug. It should be noted that the monitoring strategy and the methodologies used in estimating the loadings presented in this Pilot Study are very different from those used by Kirschmann and Grovhoug (1996). Their estimates were obtained using the “indirect method” that was based on the ambient air concentration data, and assumed deposition velocities of 0.28, 0.29, 0.26, and 0.47 cm/sec for Cu, Ni, Cd, and Cr, respectively. The ambient air concentration data were obtained by CARB from January 1994 through June 1996, using samplers with no particle size cut-points for collecting total suspended particulates, at the monitoring sites in San Jose, Fremont, and San Francisco. On the other hand, estimates of the loading presented in this Pilot Study were determined by a “direct method” of measuring particulates deposited on surrogate surface plates. The Pilot Study data were collected from August 1999 through August 2000 at three stations located in the South Bay, Central Bay, and North Bay. These three stations were strategically sited to be as close to the Estuary as possible, and to minimize direct influence from localized sources. The estimated loadings presented in this study may not represent the worst-case scenario.

Based on the air quality monitoring data collected by CARB (CARB 1999), the average concentrations of Cu, Ni, Cd, and Cr in the Bay Area showed some temporal variation over the years (Figures 9 and 10). Concentrations of these trace metals detected in the ambient air also varied between different areas of the Bay Area³ (Figures 11 through 14). These variations in ambient air concentrations will have an effect on the estimated deposition flux and loading.

4.2 Wet Deposition

A total of 42 precipitation samples were successfully collected and analyzed from the three monitoring stations: 12 from South Bay, 15 from Central Bay, and 15 from North Bay. Precipitation volumes of each sample ranged from less than 10 mL (one sample) to greater than 1000 mL (one sample). A portion of the samples collected on February 15, 2000 at all three sites was lost because the collecting funnels were blown away due to unusual high winds within one day after deployment of the sampling train.

Concentrations of the selected trace metals in precipitation varied among sampling events at each site and among the three sites. Statistical analyses were performed using Wilcoxon's signed-ranks test (non-parametric paired sample comparison). The only significant finding was that the Cd concentration measured at the North Bay site was statistically significant than that found at the Central Bay site (p-value 0.02). The volume-weighted average concentration of the trace metals detected in the precipitation from the 42 samples collected at all sites in the Bay Area was 1.2, 0.42, 0.11, and 0.23 µg/L for Cu, Ni, Cd, and Cr, respectively (Table 7). Excluding results from small-volume samples did not affect the volume-weighted average concentrations. Therefore, results from all samples were included in further evaluation.

Deposition fluxes ($\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) and loadings (kg/year) were calculated by using equation (1) and equation (2) shown below, respectively.

$$F_p = C_p R_p \quad (1)$$

Where F_p = Wet deposition flux

C_p = Concentration of trace metals in precipitation

R_p = Rate of precipitation.

$$L_p = F_p A_p \quad (2)$$

Where L_p = Loading from precipitation

F_p = Wet deposition flux of trace metals

A_p = Area of the Estuary that is covered by precipitation

³ Ambient air samples in the South Bay were collected at San Jose 4th Street and Fremont stations; Central Bay samples were collected at the San Francisco Arkansas Street station; North Bay samples were collected at the Richmond and Concord stations.

Rainfall in the Bay Area exhibits high inter-annual and spatial variation (BAAQMD 1998, NWS 2001a). Annual average rainfall in the Bay Area ranges from under 38 cm (15 inches) to more than 106 cm (40 inches). In this report, the precipitation rate at each sampling site was measured during September 1, 1999 through August 31, 2000, during the same period as the sample collections, at the weather station closest to each site: the National Weather Service (NWS) station at the Moffett Airfield for South Bay (NWS 2001a); the BAAQMD station at the Oakland Sewage Treatment Plant (OST) for Central Bay; and the CCCSD station for North Bay. Annual precipitation rates of 36 cm (14.3 inches), 68 cm (26.8 inches), and 58 cm (22.8 inches) were recorded at the South Bay, Central Bay, and North Bay sites, respectively. For the Estuary-wide loading calculation, the 30-year annual average precipitation rate of 53 cm (21 inches) was estimated from NWS' precipitation contour depicted for the San Francisco Bay Area. This amount of rainfall was believed to be the best available data that reasonably represents the rainfall amount during the sampling period of this study.

Table 8 presents values of the parameters that are pertinent to the calculation and the resulting estimates of deposition fluxes and loading. The estimated wet deposition fluxes of Cu, Ni, and Cd to the Central Bay (1300, 390, and 160 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively), were substantially higher than those to the South Bay (140, 110, and 6 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively) or North Bay (550, 190, and 7 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively). The deposition flux of Cr (240 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) to the North Bay was the highest measured in the three segments of the Estuary. Deposition flux of Cr to the South Bay and Central Bay was 46 and 120 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively. Wet deposition loadings of Cu, Ni, Cd, and Cr to the entire Estuary were estimated to be 710, 260, 68, and 140 kg/year, respectively. The loading estimates did not include wet deposition to the watershed that subsequently drains to the Estuary through surface runoff and tributaries.

Trace metal concentrations detected in precipitation collected around the San Francisco Estuary were similar to those detected in the precipitation collected in the Great Lakes area by Sweet et al. (1998) (Table 9). Deposition fluxes of trace metals to San Francisco Estuary estimated in this Pilot Study were also within the range of the fluxes reported for Great Lakes (Sweet et al. 1998), the Massachusetts Bay (Golomb et al. 1997), and Chesapeake Bay (Scudlark et al. 1994).

4.3 Sources of Copper and Nickel

The ratio of Cu to Ni found in environmental samples might be indicative of the origin of their sources. In this Pilot Study, the Cu/Ni ratio was about 3 in the precipitation samples, which was similar to the ratio of 3 to 4 found in the UPM that was used in this study as the SRM for analyzing dry deposition samples. The Cu/Ni ratio from the dry deposition samples was approximately 2:1. Data reported by CARB from the air quality monitoring program from 1990 to 1998 indicated that the Bay Area's ambient air samples had an average Cu/Ni ratio of about 7:1. As shown in Table 10, the Cu/Ni ratio found in CARB's ambient air samples varied with locations, ranging from 4:1 in San Jose to 11:1 in Concord, suggesting that the origin of these trace metals in the ambient air may vary from one location to another, and Cu and Ni detected in different environmental samples may come from different sources.

4.4 Total Loading from Direct Atmospheric Deposition

The total deposition fluxes (dry and wet deposition) of Cu, Ni, and Cr to the San Francisco Estuary were estimated to be 1,700, 820, and 1,400 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively. These estimated deposition fluxes are within the range of those found in Southern Quebec (Gelinass et al. 2000) and in the Great Lakes region (Sweet et al. 1998), but are substantially lower than those estimated around Massachusetts Bay (Golomb et al. 1997) and Commencement Bay in Washington State (Crecelius 1991) (Table 9). The total atmospheric deposition flux for Cd at 82 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ found in this study was less than 30% of that found at other locations. In addition to possible influences from localized sources, some of the differences observed in the estimates might be attributable to the differences in the sample collection methods deployed in various studies. Gelinass et al. (2000) and Crecelius (1991) used a “bulk” sampling techniques collecting dry and wet deposition samples simultaneously in the same bottle or apparatus. Sweet et al. (1998) and Golomb et al. (1997) used either a dichotomous air sampler to measure air concentrations from which a flux estimate was made, or used a surrogate surface plate to directly measure the flux. For wet deposition, an automatic precipitation collector, similar to the approach in this study, was used.

Combining load estimates from dry deposition and wet deposition, the Estuary received a total of approximately 1,900, 930, 93, and 1,600 kg/year of Cu, Ni, Cd, and Cr, respectively, directly from the atmosphere (Table 11).

4.5 Loading from Tributaries that is Atmospheric in Origin

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

The most important factors that have impact on pollutant flux from surface runoff and potential transport to aquatic systems include flow regime, weather/climate conditions, and watershed and landscape characteristics. The extent of the surface runoff flux reflects the collective influence and interaction of the various meteorological, soil, land use/land cover and scale characteristics of the watershed (Tsiros 1999). For example, based on a modeling analysis, Tsiros (1999) reported that total annual mercury surface runoff flux varied from 2 to 60% of the atmospheric deposition to the watershed. In the mercury budget study for the St. Lawrence River, it was estimated that less than 12% of the mercury atmospherically deposited on the watershed consisting of either forested or agricultural land was transported to the surface water (Quemerais et al. 1999). Estimates from studies of atmospheric deposition to some lakes in Sweden and mid-continental North America suggested that up to 30% of the atmospheric deposition to the watershed reaches the receiving water bodies (Mason et al. 1994). Based on the rates of

deposition of Pb, Hg, and PCBs to the Lake Superior watershed, Dolan et al. (1993) estimated that roughly 10% of the material which is derived from wet and dry deposition in the watershed reaches the lakes by fluvial transport. This runoff coefficient has been used by Hoff et al. (1996) in their estimates of atmospheric deposition of toxic chemicals to the Great Lakes.

Average runoff coefficients for different land uses vary from <10% in undeveloped areas with few impervious surfaces to 95% in business districts dominated by impervious surfaces (Dunne & Leopold 1978). Runoff coefficients are also influenced by antecedent rainfall conditions, and increase with increasing soil saturation even in forested watersheds. In estimating an appropriate runoff coefficient for the Bay Area, land use data provided by the Association of Bay Area Governments (ABAG 1995) was combined with runoff coefficients presented by Dunne and Leopold (1978) for the five broad land-use categories (residential, commercial, industrial, agricultural, and open space). A number of hydrologic areas were delineated for the San Francisco Bay Region on the CALWATER map (WITS 1999) (Figure 15). Excluding coastal areas that drain water directly to the Pacific Ocean, the total watershed area immediately surrounding the San Francisco Estuary was estimated to be 7,261 km². This estimate does not include the Sacramento River-San Joaquin River drainage area.

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

Using equation (3) presented below, loading estimates of dry deposition (L_d) (Section 4.1), loading estimates of wet deposition (L_p) (Section 4.2), and the estimated run-off coefficient (ϕ_r) of 0.32, approximately 4,000, 1,900, 190, and 3,200 kg/year of Cu, Ni, Cd, and Cr, respectively, were deposited to the Estuary surface indirectly through surface run-off and tributaries (Table 12).

$$L_t = (L_d + L_p)\phi_r \quad (3)$$

Where: L_t = Loading from tributaries that is atmospheric in origin

L_d = Loading from dry deposition to the watershed

L_p = Loading from wet deposition to the watershed

ϕ_r = Fraction of the material deposited in the watershed that reaches the Estuary (or runoff coefficient)

4.6 Comparison of Loading from Different Sources and Pathways

Before mitigation measures can be explored to reduce pollutant loads to the Estuary, relative contributions from various sources and pathways must be evaluated. Therefore, estimates of trace metal loading to the Estuary from atmospheric deposition are compared with loadings from other sources/pathways (Table 12). It is important to note that these estimates were derived from two sources that may use very different databases and apply different approaches and assumptions. No conclusions should be drawn without careful evaluation of each variable that was incorporated into the calculations. Information presented below serves as a first-level screening, and should not be construed as an accurate comparison of loadings from all sources and pathways.

Among the external sources and pathways that contribute total loadings of trace metals, the most complete and reliable empirical data are available from the monitoring of wastewater effluent discharges. Estimated loadings of trace metals from wastewater discharges to the Estuary are shown in Table 12. These estimates were extrapolated from the loading data available to SFEI for 85% of the effluent sources (Davis et al. 2000)⁴. Loadings of Cu and Ni from direct atmospheric deposition were less than 30% of that contributed by effluent discharges, however, loadings of Cd and Cr from these two pathways might be similar.

Atmospheric deposition also contributes pollutants indirectly to the Estuary through runoff and tributaries. Indirect atmospheric deposition contributes at least twice as much of the trace metal loadings as does direct atmospheric deposition. Combining both the direct and indirect routes, atmospheric deposition contributes similar amounts of Cu, half the amount of Ni, and may be up to three times as much of Cd and Cr as loads from wastewater discharges. Since some wastewater treatment plants in the Bay Area have combined sewers that receive stormwater runoff during the rain events, some unknown fraction of the loads from the wastewater discharges is attributable to indirect atmospheric deposition.

In addition to the loadings from atmospheric deposition and wastewater discharges presented above, runoff through tributaries from watersheds contributes external pollutant loads to the Estuary. Watersheds that drain water to the Estuary include local drainage areas in San Francisco Bay Region and the more remote drainage areas in the Central Valley Region. This region drains water from about 160,000 km² land area, about 37% of the State (Calfed 2001). The Central Valley drains through the Sacramento-San Joaquin Rivers, which in turn empty into the North Bay of the Estuary. Runoff from watersheds could be an important contributor to the total pollutant load to the Estuary, especially if loads from the Central Valley watersheds are included.

⁴ Davis et al. (2000) reported loading based on approximately 85% of the effluent discharges in the Bay Area. For comparison purposes, values reported by Davis et al. (2000) were extrapolated to represent 100% of the effluent discharges.

Loading estimates of some trace metals from stormwater runoff to the Estuary were reported by Davis et al. (2000) and are shown in Table 12. Estimates of stormwater runoff include loadings that are derived from atmospheric deposition (evaluated by the Pilot Study) as well as those that are derived from non-atmospheric sources or pathways (not evaluated by the Pilot Study). Depending on the trace metal of interest, atmospheric deposition contributed 4 to 8% of the trace metal loading in the stormwater runoff from the San Francisco Bay Region (Table 12). Although the Central Valley Watershed is not included in the San Francisco Bay Region, it also contributes pollutant loading to the North Bay. Compared to the runoff from San Francisco Bay Region, loadings from the Central Valley Region contributed much greater input (up to 14 times) of the trace metals to the Estuary, likely related to the relative sizes of their drainage areas. The drainage area in the Central Valley Region is approximately 20 times the drainage area in the San Francisco Bay Region.

4.7 Uncertainties in the Loading Estimates

Uncertainty associated with the various loading estimates presented in this report and those of others have been assessed qualitatively, based on best professional judgment of the available data and information (Table 13). In this report, low uncertainty indicates that the estimate has an error range of within $\pm 25\%$; a moderate uncertainty indicates that the error range is up to two-fold; a moderate-high uncertainty presents an estimate that has an error range of up to five-fold; and an estimate with a high uncertainty may have an error range of up to ten-fold.

Estimates of trace metal loading to the San Francisco Estuary were based on site-specific measurements as well as some assumptions derived from the literature when site-specific data were not available. Uncertainty derived from field measurements is low because of the strict quality control and quality assurance procedures implemented for the study. On the other hand, uncertainty arising from using values that were not derived from site-specific measurements would generally be higher. Assumptions used in estimating trace metal loading in this report are believed to be reasonable for the Bay Area environment. Nevertheless, these assumptions impose a certain degree of uncertainty, and the degree of uncertainty varies with the specific source or pathway being assessed. Assignment of an uncertainty to estimates reported by Davis et al. (2000) is based on the best judgment of the authors of this Pilot Study and does not reflect the evaluation presented in the original report by Davis et al.

Among the various sources and pathways addressed in this report, loadings from direct wet deposition have the lowest uncertainty, thus the highest confidence, because the loadings were based on volume-weighted average concentrations and pertinent geographic as well as meteorological data that were site-specific and well characterized. Estimates of dry deposition had a greater degree of uncertainty because measurements of trace metals in some of the dry deposition samples had a standard deviation that was almost as large as the average value, resulting in a moderate uncertainty.

Loads contributed from runoff or tributaries that are atmospheric in origin include both dry and wet deposition from the indirect direct route, therefore, it inherits the same

uncertainties as these two components. In addition, it assumes a runoff coefficient of 0.32 that was based on the land-use characteristics in the Bay Area. It is believed that this runoff coefficient represents an underestimate. Nevertheless, it adds another level of uncertainty or potential bias.

The uncertainty in the estimates is low for wet deposition, moderate-high for dry deposition, and moderate-high for atmospheric deposition contribution to tributaries, resulting in a moderate uncertainty for the overall load estimates (Table 13). It is difficult to evaluate the uncertainty of the estimates presented in other reports that may have used different data sources, calculation approaches, and assumptions. Based on the information presented in the report by Davis et al. (2000) and the data shown in Table 12, uncertainty related to the estimates of loading from wastewater discharges is low for Cu, Ni, and Cr, and moderate-high for Cd. The uncertainty associated with the loading estimates from stormwater runoff in the San Francisco Bay Region is moderate-high. Loads from stormwater were crude estimates and the uncertainty is unknown. Loading from various sources and pathways could not be fairly compared until all load estimates have the same level of low uncertainty. Uncertainty level can be reduced by improving analytical sensitivity (dry deposition), obtaining site-specific transporting coefficient of pollutants from the watershed (indirect deposition), and obtaining more accurate estimate of loads from stormwater runoff.

5.0 CONCLUSIONS

Dry deposition fluxes of copper, nickel, cadmium, and chromium at $1,100 \pm 730$, 600 ± 350 , 22 ± 15 , and $1,300 \pm 900 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively, from the atmosphere to the San Francisco Estuary were similar to those estimated in the Great Lakes area. Concentrations of 1.2, 0.42, 0.11, and 0.23 $\mu\text{g/L}$ detected in the precipitation, and the wet deposition fluxes of 630, 230, 60, and 120 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ estimated for copper, nickel, cadmium, and chromium, respectively, were also similar to those found at other locations.

Estimated loadings of copper, nickel, cadmium, and chromium from direct atmospheric deposition (include dry and wet depositions) to the San Francisco Estuary were approximately 1,900, 930, 90, and 1,600 kg/year, respectively. Depending on the type of trace metals, contributions from precipitation ranged from 10 to 70% of the total loading from atmosphere. Compared to loadings from effluent discharges, direct atmospheric deposition contributed less than 30% of the loading for copper and nickel. Loads for cadmium and chromium from these two pathways might be similar.

Total loadings of trace metals from atmospheric deposition, combining direct loads to the Estuary surface and indirect loads through stormwater runoff, could contribute as much as three times the loading from effluent discharges. Based on the information presented in this report and others, atmospheric deposition contributed only about 4 to 8% of the loadings of trace metals in stormwater runoff from watersheds in the San Francisco Bay Region, excluding stormwater runoff loading from the Central Valley Region. Although atmospheric deposition appears to be a minor contributing pathway, relative to the inputs from watersheds, it is premature to draw any conclusions before loading estimates from stormwater runoff are further refined. Loading from various sources and pathways could not be fairly compared until all load estimates have the same level of low uncertainty.

6.0 REFERENCES

ABAG. 1995. Description of land use classification categories. Association of Bay Area Governments (ABAG), Oakland, CA.

Abu-Saba, K.E. and L.W. Tang. 2000. Watershed Management of Mercury in the San Francisco Bay: Total Maximum Daily Load - Report to U.S. EPA. California Regional Water Quality Control Board, San Francisco Bay Region, Oakland.

BAAQMD. 1998. Particulate Matter Monitoring Network: Description for the Bay Area Air Quality Management District Planning Area. Bay Area Air Quality Management District, San Francisco.

Bigelow, D.S. 1984. Instruction Manual: NADP/NTN Site Selection and Installation. National Atmospheric Deposition Program, Program Office, Illinois State Water Survey, Champaign, IL 61820, Fort Collins, CO.

Calfed. 2001. Facts about the Bay-Delta, Calfed Bay-Delta Program.

CARB. 1999. California Ambient Air Quality Data 1980-1998, Air Resources Board, California Environmental Protection Agency, Sacramento, CA.

Crecelius, E.A. 1991. Estimate of the atmospheric deposition of contaminants on Commencement Bay, Washington 84th Annual Meeting & Exhibition, Air & Waste Management Association, Vancouver, British Columbia, June 16-21.

CSJ. 1998. Work Plan for RMP Pilot Study on Aerial Deposition: Determining the extent of pollutant loadings on the surface of the San Francisco Estuary from Atmospheric Deposition. City of San Jose, San Jose, CA.

Davis, J.A., L.J. McKee, J.E. Leatherbarrow and T.H. Daum. 2000. Contaminant loads from stormwater to coastal waters in the San Francisco Bay region: Comparison to other pathways and recommended approach for future evaluation (draft internal document). San Francisco Estuary Institute, Richmond, CA.

Dunne, T. and L.B. Leopold. 1978. Water in Environmental Planning. W. H. Freeman and Company, San Francisco, USA. 300 pp.

Gelinas, Y., M. Lucotte and J.P. Schmit. 2000. History of the atmospheric deposition of major and trace elements in the industrialized St. Lawrence Valley, Quebec, Canada. Atmospheric Environment 34: 1797-1810.

Golomb, D., D. Ryan, N. Eby, J. Underhill and S. Zemba. 1997. Atmospheric deposition of toxics onto Massachusetts Bay - I. Metals. Atmospheric Environment 31: 1349-1359.

- Hauri, J. 1998a.** Effect of aerial deposition of pollutants on water quality of the San Francisco Bay.
- Hauri, J. 1998b.** Scoping study of air deposition monitoring information relevant to water quality of San Francisco Bay.
- Holsen, T.M. and K.E. Noll. 1992.** Dry deposition of atmospheric particles: application to current models of ambient data. *Environ. Sci. Technol.* 26: 1807-1815.
- Holsen, T.M., K.E. Noll, G.C. Fang, W.J. Lee, J.M. Lin and G. Keeler. 1993.** Dry deposition and particle size distributions measured during the Lake Michigan Urban Air Toxics Study. *Environ. Sci. Technol.* 27: 1327-1333.
- Holsen, T.M., K.E. Noll, S.P. Liu and W.J. Lee. 1991.** Dry deposition of polychlorinated biphenyls in urban areas. *Environ. Sci. Technol.* 25: 1075-1081.
- Kirschmann, H. and T. Grovhoug. 1996.** Gross estimates of atmospheric deposition to South San Francisco Bay. City of San Jose, San Jose, CA.
- Mason, R.P., W.F. Fitzgerald and F.M.M. Morel. 1994.** The biogeochemical cycling of elemental mercury: Anthropogenic influences. *Geochim. et Cosmochim. Acta* 58: 3191-3198.
- Noll, K.E., P.F. Yuen and K.Y.P. Fang. 1990.** Atmospheric coarse particulate concentrations and dry deposition fluxes for ten metals in two urban environments. *Atmospheric Environment* 24A: 903-908.
- NWS. 2001a.** Average Annual Rainfall Maps, National Weather Services.
- Paode, R.D., S.C. Sofuoglu, J. Sivadechathep, K.E. Noll, T.M. Holsen and G.J. Keeler. 1998.** Dry deposition fluxes and mass size distributions of Pb, Cu, and Zn measured in Southern Lake Michigan during AEOLUS. *Environ. Sci. Technol.* 32: 1629-1635.
- Pirrone, N., G.J. Keeler and T.M. Holsen. 1995.** Dry deposition of trace elements to Lake Michigan: A hybrid-receptor deposition modeling approach. *Environ. Sci. Technol.* 29: 2112-2122.
- Quemerais, B., D. Cossa, B. Rondeau, T.T. Pham, P. Gagnon and B. Fortin. 1999.** Sources and fluxes of mercury in the St. Lawrence River. *Environ. Sci. Technol.* 33: 840-849.
- Scudlark, J.R., K.M. Conko and T.M. Church. 1994.** Atmospheric wet deposition of trace elements to Chesapeake Bay: CBAD Study year 1 results. *Atmospheric Environment* 28: 1487-1498.

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

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

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

Shahin, U., S.M. Yi, R.D. Paode and T.M. Holsen. 2000. Long-term elemental dry deposition fluxes measured around Lake Michigan with an automated dry deposition sampler. Environ. Sci. Technol. 34: 1887-1892.

Sweet, C.W., A. Weiss and S.J. Vermette. 1998. Atmospheric deposition of trace metals at three sites near the Great Lakes. Water, Air, and Soil Pollution 103: 423-439.

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

TetraTech, I. and G.W.C. URS. 1998. Task 2.1 Source Characterization Report - Calculation of total maximum daily loads for copper and nickel in South San Francisco Bay: Draft. City of San Jose, San Jose, CA.

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

Tsai, P. and R. Hoenicke. 2001. San Francisco Bay Atmospheric Deposition Pilot Study - Part 1: Mercury (Final Report). San Francisco Estuary Institute. Final Report. Richmond, CA.

Tsai, P., R. Hoenicke, H. Bamford and J. Baker. 2001. San Francisco Bay Atmospheric Deposition Pilot Study - Trace Organics (in preparation). San Francisco Estuary Institute, Richmond, CA.

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

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

USEPA. 2001. Screening Level Ecological Risk Assessment Protocol for Hazardous Waste Combustion Facilities - Peer Review Draft, USEPA, Office of Solid Waste.

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

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

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

Wu, Z.Y., M. Han, Z.C. Lin and J.M. Ondov. 1994. Chesapeake Bay atmospheric deposition study, year 1: sources and dry deposition of selected elements in aerosol particles. *Atmospheric Environment* 28: 1471-1486.

Yi, S.M., T.M. Holsen and K.E. Noll. 1997b. Comparison of dry deposition predicted from models and measured with a water surface sampler. *Environ. Sci. Technol.* 31: 272-278.

Yi, S.M., T.M. Holsen, X. Zhu and K.E. Noll. 1997a. Sulfate dry deposition measured with a water surface sampler: A comparison to modeled results. *Journal of Geophysical Research* 102: 19695-19705.

Zufall, M.J., C.I. Davidson, P.F. Caffrey and J.M. Ondov. 1998. Airborne concentrations and dry deposition fluxes of particulate species to surrogate surfaces deployed in Southern Lake Michigan. *Environ. Sci. Technol.* 32: 1623-1628.

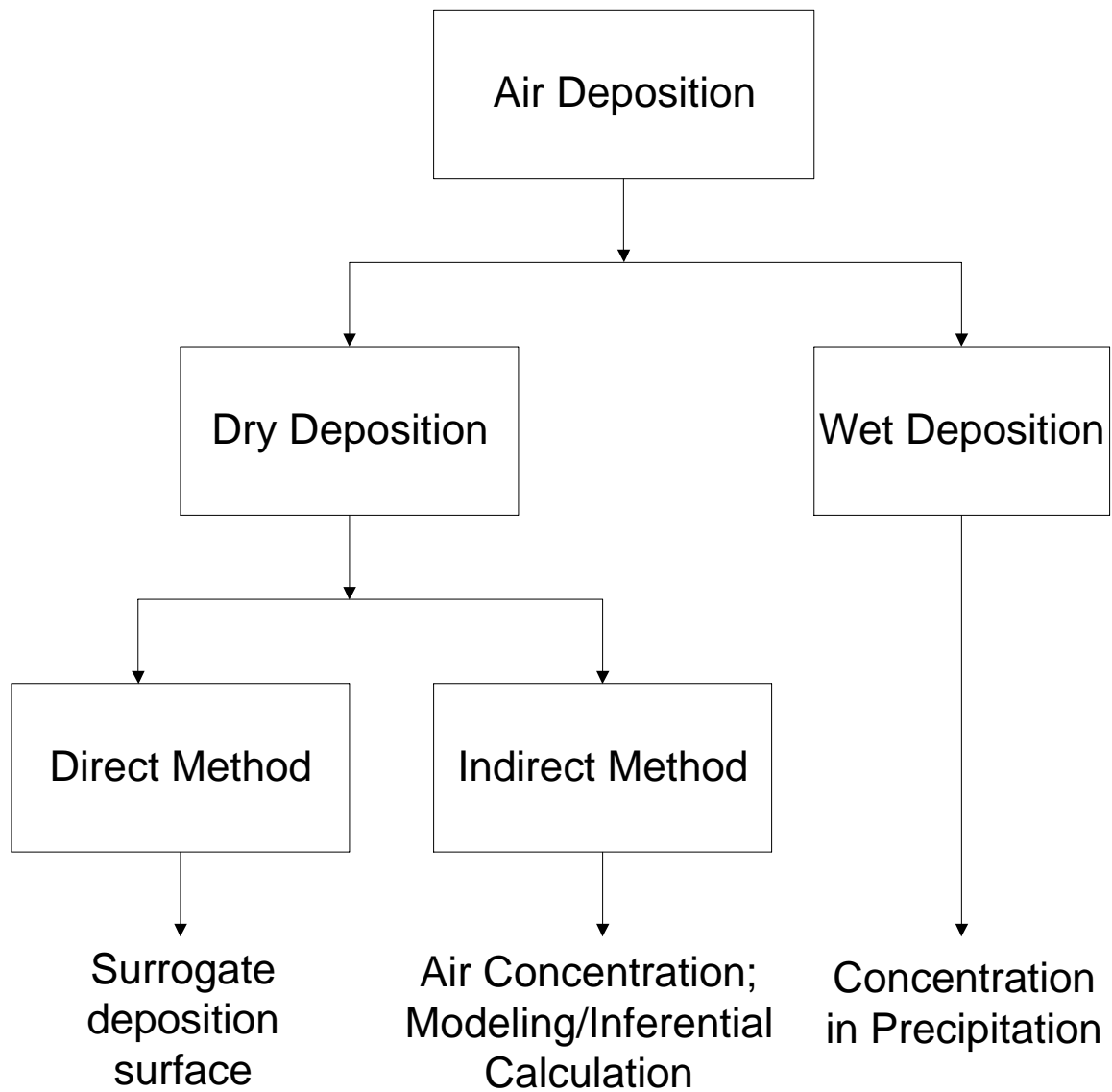


Figure 1. General Methodology for Atmospheric Deposition Study



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



Figure 3. Dry Deposition Sampling Device (Egret I)



Figure 4. Greased Surrogate Surface Plate

Figure 5. Dry Deposition of Copper to Different Segments of the San Francisco Estuary

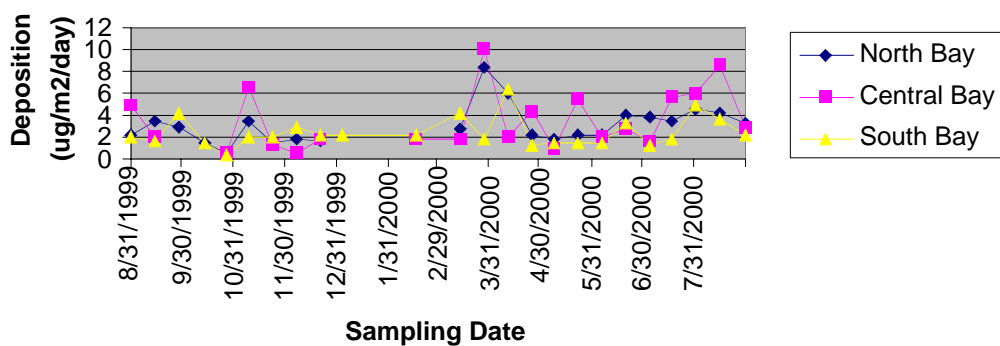


Figure 6. Dry Deposition of Nickel to Different Segments of the San Francisco Estuary

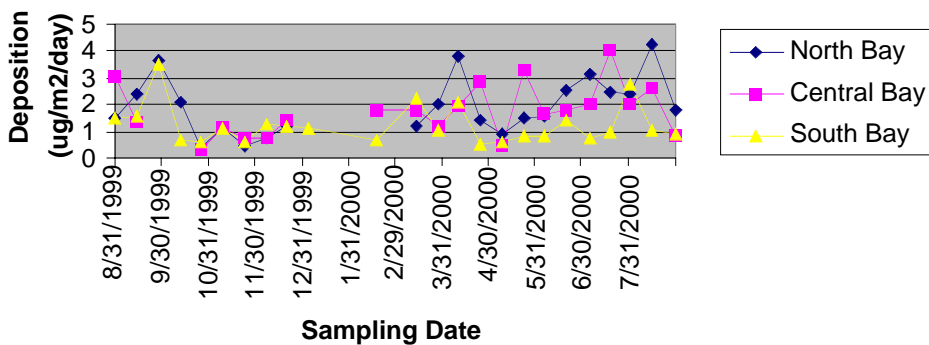


Figure 7. Dry Deposition of Cadmium to Different Segments of the San Francisco Estuary

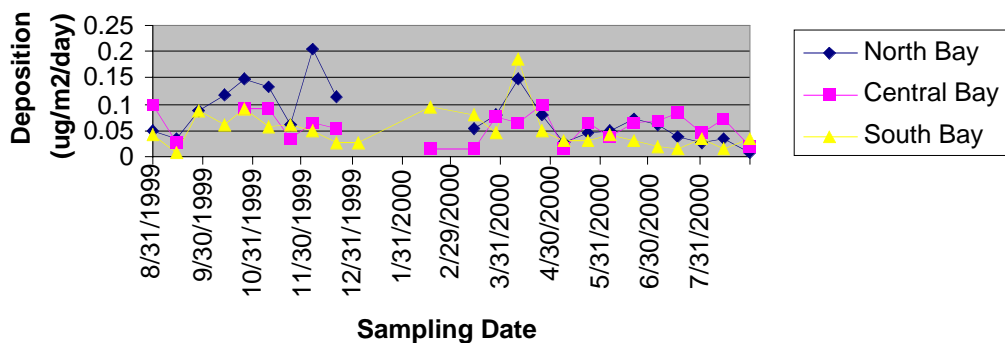
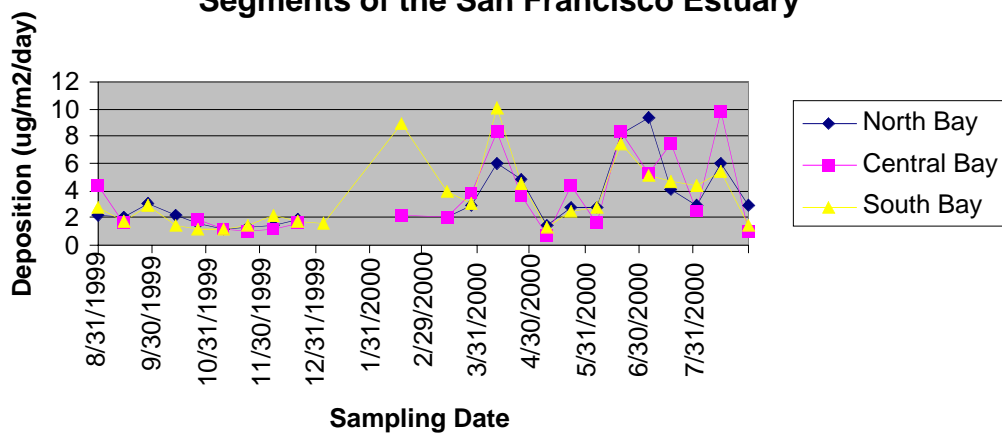
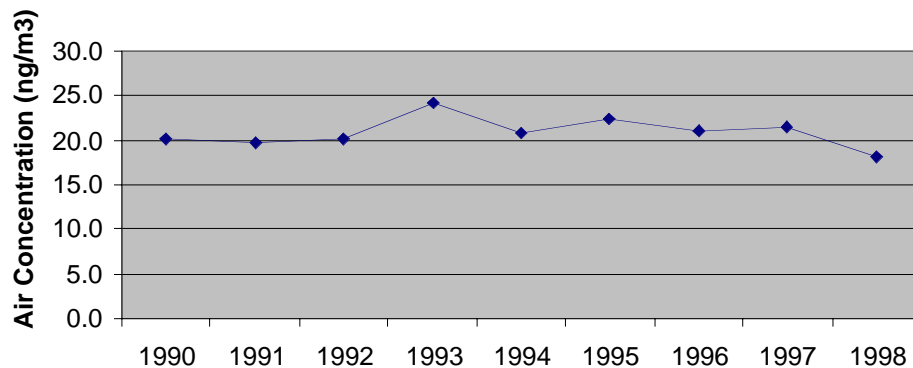


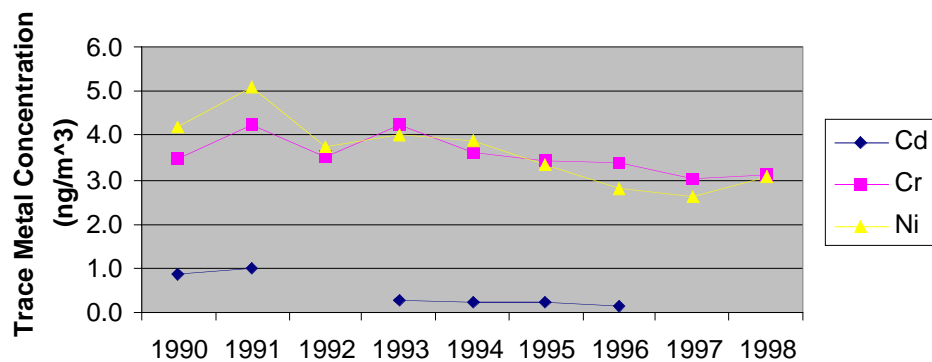
Figure 8. Dry Deposition of Chromium to Different Segments of the San Francisco Estuary



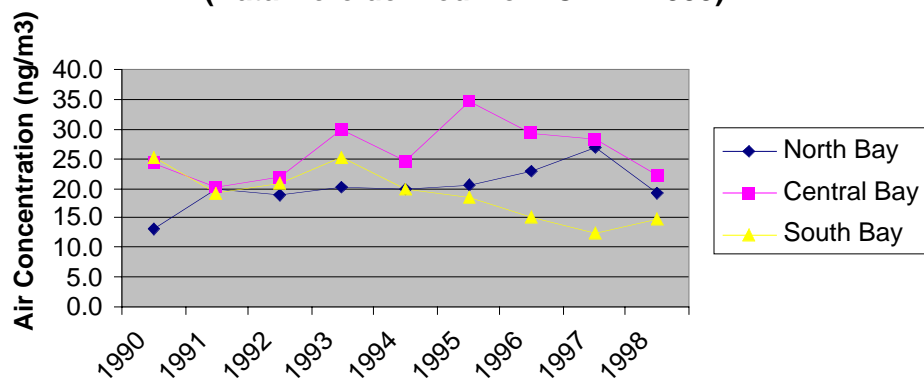
**Figure 9. Average Copper Concentration in the Ambient Air - San Francisco Bay Area
(Data were derived from CARB 1999)**



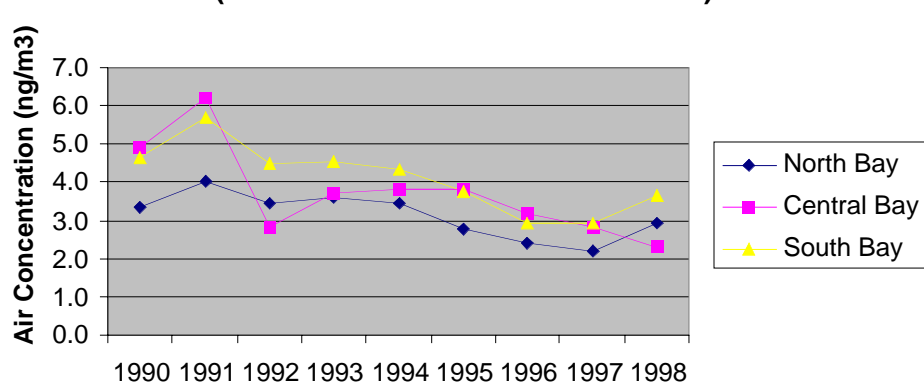
**Figure 10. Average Annual Concentrations of Trace Metals in the Ambient Air - San Francisco Bay Area
(Data were derived from CARB 1999)**



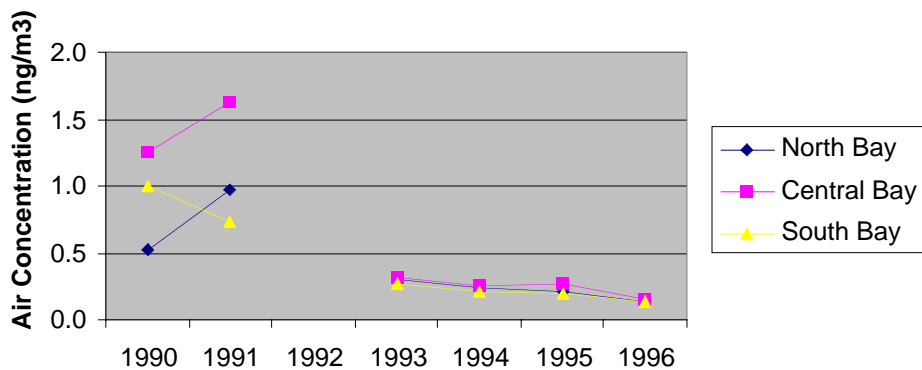
**Figure 11. Copper Concentration in the Air
Different Segments of the San Francisco Bay Area
(Data were derived from CARB 1999)**



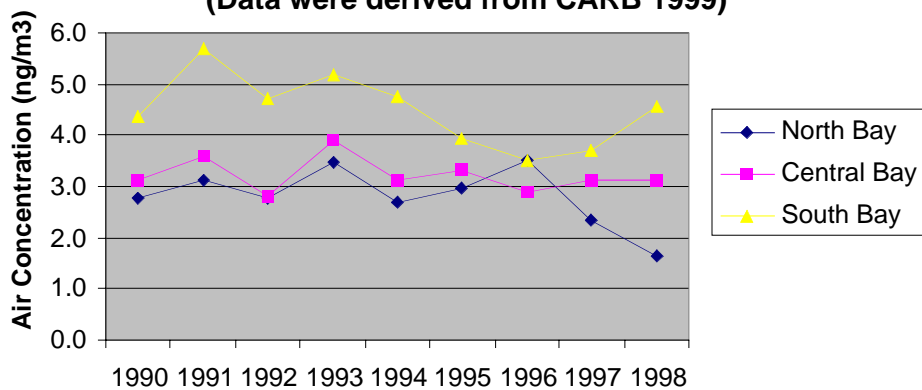
**Figure 12. Nickel Concentration in the Air
Different Segments of the San Francisco Bay Area
(Data were derived from ARB 1999)**



**Figure 13. Cadmium Concentration in the Air
Different Segments of the San Francisco Bay Area
(Data were derived from CARB 1999)**



**Figure 14. Chromium Concentration in the Air
Different Segments of the San Francisco Bay Area
(Data were derived from CARB 1999)**



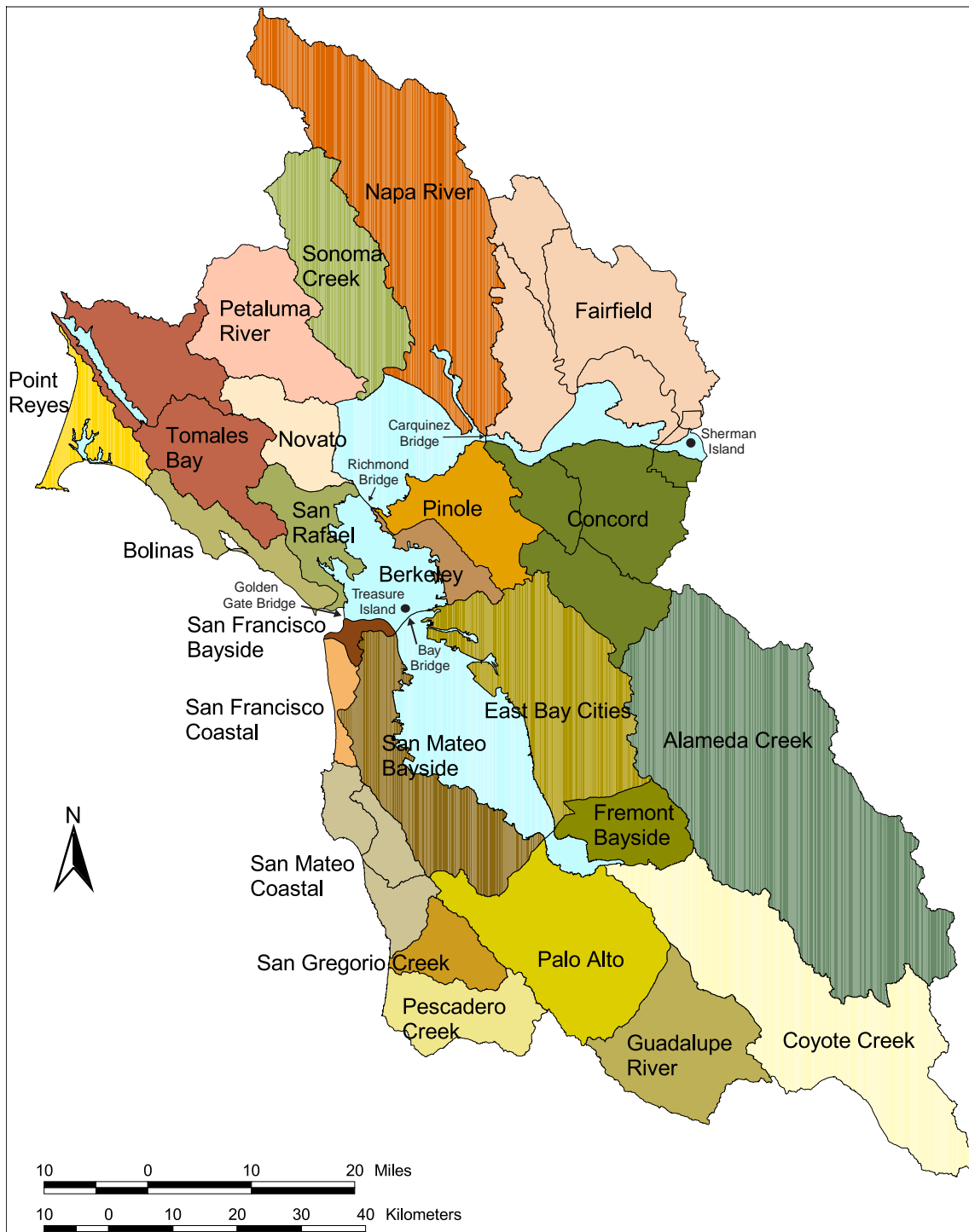


Figure 15. Hydrologic Areas in the San Francisco Bay Region
(taken from Davis et al. 2000)

Table 1. Chemicals Selected for Monitoring in the Pilot Study

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

Table 2. Sampling Schedule for Trace Elements

Samples	Sampling Duration	Sampling Frequency
Wet Deposition (Precipitation)		
Hg, Cd, Cr, Cu, and Ni	14 days	One cumulative composite sample every 14 days
Dry Deposition		
Hg, Cd, Cr, Cu, and Ni	24 hours	One sample every 14 days

Table 3. Quality Assurance and Quality Control Parameters for Dry Deposition Samples

Parameters	Copper	Nickel	Cadmium	Chromium
Laboratory Operation				
UPM Spike Recovery (%)	93±6.5 (80 to 102)	105±27 (82 to 215)	100±8.6 (79 to 119)	47±33 (21 to 167)
Sample Spike Recovery (%)	100±9.4 (85 to 119)	100±12 (81 to 120)	101±11 (79 to 118)	98±29 (77 to 227)
UPM Duplicate RPD (%)	4.7±4.7 (0.65 to 8.6)	8.9±10 (0 to 47)	6.5±6.7 (1.1 to 25)	13±12 (0.89 to 39)
Detection Limit				
Preparation Blank (µg/Sample)	0.004±0.004	0.003±0.002	0.0002±0.0008	0.03±0.01
MDL (µg/Sample)	0.01	0.007	0.002	0.04
Samples <MDL (%)	0 (0%)	4 (3%)	54 (40%)	2 (1%)
Field Blank (µg/Sample)				
Average Value (µg/Sample) All Sites	0.005±0.004	0.005±0.008	0.0005±0.0009	0.04±0.03
Field Blank >MDL				
North Bay	1 (5%)	5 (23%)	0 (0%)	7 (32%)
Central Bay	2 (10%)	1 (5%)	0 (0%)	10 (48%)
South Bay	1 (4%)	4 (17%)	0 (0%)	12 (50%)
All sites	4 (6%)	10 (15%)	0 (0%)	29 (43%)
Field Duplicate Sample RPD (%)				
North Bay	24±30 (0 to 144)	22±23 (0 to 109)	62±66 (7.8 to 243)	28±22 (1.4 to 69)
Central Bay	37±27 (0 to 96)	56±43 (2.7 to 142)	60±110 (0 to 437)	38±35 (3.5 to 85)
South Bay	25±25 (0 to 82)	27±23 (0 to 91)	157±329 (0 to 966)	37±44 (0 to 211)
All Sites (include all detectable samples)	29±28 (0 to 144)	34±34 (0 to 142)	83±176 (0 to 966)	34±35 (0 to 211)
All Sites ¹ (include sample values >3 MDL)	20±23 (0 to 143)	21±20 (0 to 97)	20±8 (9 to 25)	24±18 (3 to 93)

MDL - Method detection limit

¹ Calculated for those samples with values >3MDL

Table 4. Quality Assurance and Quality Control Parameters for Wet Deposition Samples

Parameter	Copper	Nickel	Cadmium	Chromium
Laboratory Operation (Lab 1)				
SRM Recovery (%)	105.8	101.6	94.5	102.3
MS Recovery (%)	97.2	94.7	95.4	96.7
MSD Recovery	98.7	94.1	94.1	96.7
MS/MSD RPD (%)	1.5	0.6	1.4	0.04
Sample Duplicate RPD (%)	1.1	0.8	2.6	2.5
Laboratory Operation (Lab 2)				
SRM Recovery (%)	98.0±2.4	99.9±2.2	96.4±3.8	101.8±1.9
MS Recovery (%)	107.8±3.1	107.8±2.8	108±7.2	109±4.7
MSD Recovery (%)	108±3.7	107.2±2.5	106.8±6.5	107.2±4.1
MS/MSD RPD (%)	1.6±0.5	0.6±0.9	1.4±1.1	1.6±1.5
Sample Duplicate RPD (%)	3.8±4.2	8.0±8.4	11.3±17.0	4.5±4.5
Method Detection Limit (ng/L)				
Lab 1	30	10	4	30
Lab 2	20	10	5	30
Samples <MDL (n=42)	0%	2%	10%	17%
Field Operation				
System Blank (ng/bottle) (n=3)	10±0	5±0	2.4±0.0	74±70
Distilled Water (ng/bottle) (n=3)	10±0	5±0	2.5±0.1	63±5
Field Blank (ng/bottle) North Bay (n=6)	3±2	1±0.3	0.1±0.0	3±3
Field Blank (ng/bottle) Central Bay (n=6)	10±8*	3±5	0.2±0.2	4±4
Field Blank (ng/bottle) South Bay (n=6)	3±4	1±1	0.1±0.0	3±3
Field Blank (ng/bottle) All Sites (n=18)	5±6 (MDL=0.4)	2±3 (MDL=0.2)	0.1±0.1 (=MDL)	3±3 (MDL=1)

MDL – Method detection limit

MS – Matrix spike

MSD – Matrix spike duplicate

RPD – Relative percent difference

SRM – Standard reference material NIST 1643d

* Statistically significant from the South Bay and North Bay measurements at p=0.05 and p=0.1, respectively.

Table 5. Dry Deposition of Trace Metals to Different Segments of the San Francisco Estuary¹

Monitoring Sites	Copper	Nickel	Cadmium	Chromium
Average Deposition Flux ($\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$)				
North Bay	3.1±1.7 (n=22)	1.9±1.1* (n=22)	0.076±0.049* (n=22)	3.3±2.3 (n=22)
Central Bay	3.5±2.7 (n=21)	1.8±0.98** (n=21)	0.057±0.028 (n=21)	3.5±2.8 (n=21)
South Bay	2.5±1.4 (n=24)	1.2±0.74 (n=24)	0.051±0.038 (n=24)	3.5±2.5 (n=24)
Entire Estuary	3.0±2.0 (n=67)	1.6±0.97 (n=67)	0.061±0.040 (n=67)	3.5±2.5 (n=67)
MDL	0.2	0.014	0.04	0.08
Dry Deposition Load (kg/year)				
North Bay (434 Km ²)	490±280	300±170	12± 8	530±360
Central Bay (214 Km ²)	270±210	140±76	4±2	280±220
South Bay (485 Km ²)	430±240	220±130	9±7	620±440
Entire Estuary (1133 Km ²)	1200±830	680±400	25±17	1400±1000
South Bay (490 Km ²)***	903	232	9	374

¹ All values represent mean ± standard deviation of all bi-weekly measurements obtained by the current study except when it is noted.

* Significant different from the South Bay Site at p=0.01

** Significant different from the South Bay Site at p=0.02

*** Estimates provided by Kirschmann and Grovhoug (1996) with an error range of possibly up to five-fold

Table 6. Estimated Dry Deposition Flux of Trace Metals Reported in the Literature¹

Sampling Site	Sampling Method	Copper	Nickel	Cadmium	Chromium	Citation
Urban Chicago ²	D	21900	NA	NA	NA	Paode et al. 1998
Lake Michigan ²	D	3650	NA	NA	NA	Paode et al. 1998
South Haven, MI ²	D	2555	NA	NA	NA	Paode et al. 1998
Lake Superior ³	I	2400	570	380	130	Sweet et al. 1998
Lake Michigan ³	I	1300	320	380	130	Sweet et al. 1998
Lake Erie ³	I	3300	460	400	1000	Sweet et al. 1998
Southern Lake Michigan ⁴	D	2000	NA	NA	NA	Zufall et al. 1998
Massachusetts Bay ⁵	D	2000	930	130	1200	Golomb et al. 1997
Massachusetts Bay ⁶	I	NA	NA	NA	470	Golomb et al. 1997
Chesapeake Bay ⁷	I	290-810	330-910	11-32	110-300	Wu et al. 1994
San Francisco Estuary⁸	D	1100±730	600±350	22±15	1300±900	This study

¹ All data are presented in $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$.

² Average of three weekly composite samples taken in May 1994, July 1994, and January 1995.

³ Average of monthly composite samples taken between summer 1993 and summer 1994.

⁴ Average of four day measurements with two samples/day in July 1994.

⁵ Average of bi-weekly composite samples collected at two sites from September 1992 to September 1993.

⁶ Average of alternative bi-weekly composite samples collected at one site from September 1992 to September 1993.

⁷ Range of low and high estimates from weekly composite samples collected between June 1990 and July 1991.

⁸ Values represent mean \pm standard deviation from all bi-weekly two 24-hr samples collected at three sites from August 1999 to August 2000.

D – Direct method collecting particulates deposited directly on surrogate surface plates.

I – Indirect method collecting ambient air concentration and using modeling estimate.

NA – Not analyzed.

Table 7. Estimated Volume –Weighted Average Concentration of Trace Metals in Precipitation Collected at Sites in the San Francisco Bay Area

Precipitation Volume	Number of Samples	Volume-Weighted Average Concentration (ng/L)			
		Copper	Nickel	Cadmium	Chromium
All Samples	42	1174	423	112	232
>10 mL	41	1172	422	112	230
>20 mL	35	1156	417	112	213
>30 mL	31	1160	410	113	198
>40 mL	31	1160	410	113	198
>50 mL	29	1157	408	114	189
>100 mL	22	1187	416	120	185
>200 mL	16	1204	403	130	182
>500 mL	7	1550	522	186	163
>1000 mL	1	3362	1116	650	53

Table 8. Wet Deposition of Trace Metals to the San Francisco Estuary

Parameter	South Bay	Central Bay	North Bay	Entire Estuary
Annual Rainfall (inches)	14.33	26.81	22.81	21
Annual Rainfall (cm)	36	68	58	53
Surface Area (km ²)	485	214	434	1133
Trace Metal Concentration in Rainfall (ng/L)¹				
Number of Samples	12	15	15	42
Copper	380	1800	900	1200
Nickel	290	570	330	420
Cadmium	16	240	12	110
Chromium	130	180	420	230
Wet Deposition Flux (μg·m⁻²·yr⁻¹)				
Copper	140	1300	550	630
Nickel	110	390	190	230
Cadmium	6	160	7	60
Chromium	46	120	240	120
Wet Deposition Loading (kg/year)				
Copper	66	270	240	710
Nickel	51	83	82	260
Cadmium	3	35	3	68
Chromium	22	25	110	140

¹ Volume-weighted average concentrations.

Table 9. Comparison of Trace Metal Concentration in Precipitation and Estimated Deposition Flux Reported in the Literature

Sampling Site	Copper	Nickel	Cadmium	Chromium	Citation
Concentration of Trace Metals in Precipitation ($\mu\text{g/L}$)					
Lake Superior	0.9±0.5	0.3±0.3	0.1±0.1	0.1±0.1	Sweet et al. 1998
Lake Michigan	0.8±0.1	0.4±0.4	0.1±0.3	0.1±0.2	Sweet et al. 1998
Lake Erie	0.9±0.1	0.3±0.2	0.1±0.1	<0.1	Sweet et al. 1998
San Francisco Estuary*	1.2	0.4	0.1	0.2	This study
Wet Deposition Flux ($\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$)					
Lake Superior	700	230	78	78	Sweet et al. 1998
Lake Michigan	570	290	72	72	Sweet et al. 1998
Lake Erie	850	280	94	63	Sweet et al. 1998
Massachusetts Bay	500	620	140	1500	Golomb et al. 1997
Chesapeake Bay	260	257	48	88	Scudlark et al. 1994
San Francisco Estuary	630	230	60	120	This study
Total (Dry+Wet) Atmospheric Deposition Flux ($\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$)					
Southern Quebec, Canada	1190	590	270	230	Gelinas et al. 2000
Lake Superior	3100	800	458	208	Sweet et al. 1998
Lake Michigan	1870	610	452	202	Sweet et al. 1998
Lake Erie	4150	740	494	1063	Sweet et al. 1998
Massachusetts Bay	2500	1500	270	2700	Golomb et al. 1997
Commencement Bay, WA	7300-54385	3066-17885	NA	1460-6205	Crecelius 1991
San Francisco Estuary	1700	820	82	1400	This Study

* Volume-weighted average concentration

NA – Not analyzed

Table 10. Ratio of Copper to Nickel Found in the Environmental Samples

Environmental Sample	Copper/Nickel Ratio	Data Source
Urban Particulate Matter	3 to 4	NTIS standard reference material
Particulates Collected on Surrogate Surface Plate	2±1	This Study
Precipitation	3	This Study
Ambient Air Samples		
San Jose	4±1	CARB 1999
Fremont	6± 2	CARB 1999
San Francisco	8±2	CARB 1999
Richmond	5±2	CARB 1999
Concord	11±7	CARB 1999
All Bay Area Sites	7±4	CARB 1999

Table 11. Estimated Loading of Trace Metals from Direct Atmospheric Deposition to the San Francisco Estuary

Parameter	Copper	Nickel	Cadmium	Chromium
Dry Deposition (kg/year)				
North Bay	490±280	300±170	12±8	530±360
Central Bay	270±210	140±76	4±2	280±220
South Bay	430±240	220±130	9±7	620±440
Entire Estuary	1200±830	680±400	25±17	1400±1000
South Bay*	903	232	9	374
Wet Deposition (kg/year)				
North Bay	240	82	3	110
Central Bay	270	83	35	25
South Bay	66	51	3	22
Entire Estuary	710 (37%)**	260 (27%)**	68 (73%)**	140 (9%)**
Total (Dry+Wet) Direct Atmospheric Deposition (kg/year)				
North Bay	730	390	15	640
Central Bay	700	300	44	640
South Bay	340	190	7	300
Entire Estuary	1900	930	93	1600

* Estimate by Kirschmann and Grovhoug (1996) based on the average air concentration data collected by the CARB at monitoring stations located in the cities of Fremont, San Francisco, and San Jose between January 1994 and June 1996.

** Number in the parenthesis presents percentage of the total direct atmospheric deposition.

Table 12. Comparison of Trace Metal Loading to the San Francisco Estuary from Atmospheric Deposition and Other Sources/Pathways (kg/year)

Sources/Pathways	Copper	Nickel	Cadmium	Chromium	Citation
Total Atmospheric Deposition	5,900	2,800	280	4,800	This Study
Direct Atmospheric Deposition (dry and wet deposition combined)	1,900	930	90	1,600	This Study
Indirect Atmospheric Deposition ¹	4,000 (6%) ²	1,900 (4%) ²	190 (8%) ²	3,200 (8%) ²	This Study
Effluent Discharges ³	6900- 7300	5600- 6100	98-330	1500-2000	Davis et al. 2000
Stormwater Runoff from San Francisco Bay Region ⁴	66,000 (36,000 - 150,000)	49,000 (27,000 - 78,000)	2,300 (1,300 - 3,700)	40,000 (22,000 - 64,000)	Davis et al. 2000
Stormwater Runoff from Central Valley Region ^{4,5}	270,000	410,000	1,600	550,000	Davis et al. 2000

¹ Indirect atmospheric deposition is derived from runoff and tributaries that are atmospheric in origin.

² Number in the parenthesis represents percentage of the loading from stormwater runoff in the San Francisco Bay Region.

³ Data is extrapolated from the 1998 monitoring data from effluent dischargers that represented approximately 85% of the total discharges; lower number assumes zero value for non-detectable samples, and upper number uses value of detection limit for non-detectable samples.

⁴ Include loading that is atmospheric in origin

⁵ Crude estimates, according to Davis et al. (2000)

Table 13. Assessment of Uncertainty in the Trace Metal Loading Estimates

Parameters	Values Used ¹	Range of Values ²	Uncertainty
This Pilot Study			
Dry Deposition			Moderate-High
Chemical Concentration	Site-specific	Site-specific	Moderate-High
Area of the Bay	Site-specific	Site-specific	Low
Wet Deposition			Low
Chemical Concentration	Site-specific	Site-specific	Low
Precipitation Amount	Site-specific	Site-specific	Low
Atmospheric Deposition to Tributaries			Moderate-High
Chemical Concentration	Site-specific	Site-specific	Moderate-High
Area of the Watershed	Site-specific	Site-specific	Low
Runoff Coefficient	0.32	0.1 to 0.95	Moderate
Estimate from Kirschmann and Brovhoug 1996			
Dry Deposition to South Bay			Moderate-High
Chemical Concentration	Site-specific	Site-specific	Low
Area of the Bay	Site-specific	Site-specific	Low
Deposition Velocity	0.26 to 0.47	0.1 to 5.0	Moderate-High
Atmospheric Deposition to Tributaries			Moderate-High
Area of the Watershed	Site-specific	Site-specific	Low
Runoff Coefficient	0.33 to 0.74	0.1 to 0.95	Moderate
Transport Fraction	0.1	0.1 to 1.0	High
Estimates from Davis et al. 2000			
Effluent Discharges			Low: Cu, Ni, Cr Moderate-High: Cd
Stormwater Runoff from San Francisco Bay Region			Moderate-High
Stormwater Runoff from Central Valley Region			Unknown

¹ Values used in the study² Values reported in the literature

High uncertainty – estimate has an error range of up to ten-fold

Moderate-High uncertainty – estimate has an error range of two to five-fold

Moderate uncertainty – estimate has an error range of up to two-fold

Low uncertainty – estimate has an error range of within $\pm 25\%$