ATMOSPHERIC DEPOSITION OF TRACE METALS IN THE SAN FRANCISCO BAY AREA

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ABSTRACT

A pilot Study was conducted from August 1999 through August 2000 to estimate the loading of selected pollutants from the atmosphere to the San Francisco Estuary. Particulate in the ambient air and precipitation samples were collected at three locations. Dry deposition flux of copper, nickel, cadmium, and chromium was approximately 1100±73, 600±35, 22±15, and 1300±90 $\mu g/m^2$/year, respectively. The volume-weighted average concentrations of these trace metals in the precipitation were 1.2, 0.4, 0.1, and 0.2 µg/L, respectively. Direct atmospheric deposition, via both dry deposition and wet deposition, contributed approximately 1900, 930, 93, and 1600 kg/year of copper, nickel, cadmium, and chromium, respectively, to the Estuary. Indirect inputs via runoff from the local watersheds contributed approximately twice as much as the loading from direct atmospheric deposition. Direct atmospheric deposition contributes less than 10% of the total loading from stormwater runoff, and, therefore, represents a minor contributor to the total load.

KEYWORDS

trace metals, atmospheric deposition, dry deposition, wet deposition, pollutant load

INTRODUCTION

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 allowable to eliminate the impairment. 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.

Copper and nickel are two of the pollutants that have been listed as possibly impairing the beneficial uses of the San Francisco Estuary. These two trace metals were detected in water samples at concentrations that exceeded their respective criteria under the California Toxics Rule. The likelihood of impairment due to copper and nickel is becoming better understood. However, there are still significant remaining questions with regard to some sources and pathways for trace metal inputs. 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.

Several attempts, based on retroactive calculation, have been made to assess the contribution of the air deposition pathway to the total pollutant load to the 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,b) 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 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 of monitoring certain selected particle-associated trace metals, namely copper (Cu), nickel (Ni), cadmium (Cd), and chromium (Cr) in the ambient air and precipitation. This report also estimates amount of these trace metals that could potentially be deposited from the atmosphere to the surface of the San Francisco Estuary[1] (the Estuary). Estimates of trace-metal loading from atmospheric deposition were also compared with estimated mass inputs from other major sources or pathways.

METHODOLOGY

Sample Collection

The Bay Area is densely urbanized with a mix of residential, commercial, industrial (mostly electronics/high technology and other light industries), agricultural, and undeveloped (open space) land uses. There are many congested major highways surrounding the Estuary. Several petroleum refineries in the region are located primarily in the North Bay. The Central Bay has two major airports and seaports. The South Bay is the hub for electronic industries and an expanding major airport.

Three study sites were chosen to represent different segments of the Estuary: North Bay, Central Bay, and South Bay (Figure 1). The South Bay site is located at the northwest corner of the Moffett Federal Airfield/NASA Ames Research Center. The Central Bay site is located at the northern end of Treasure Island. The North Bay site is located in Martinez within the property boundary of the Central Contra Costa Sanitary District's Wastewater Treatment Plant. Samples were collected every 14 days for a total of 12 months, from August 1999 through August 2000.

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

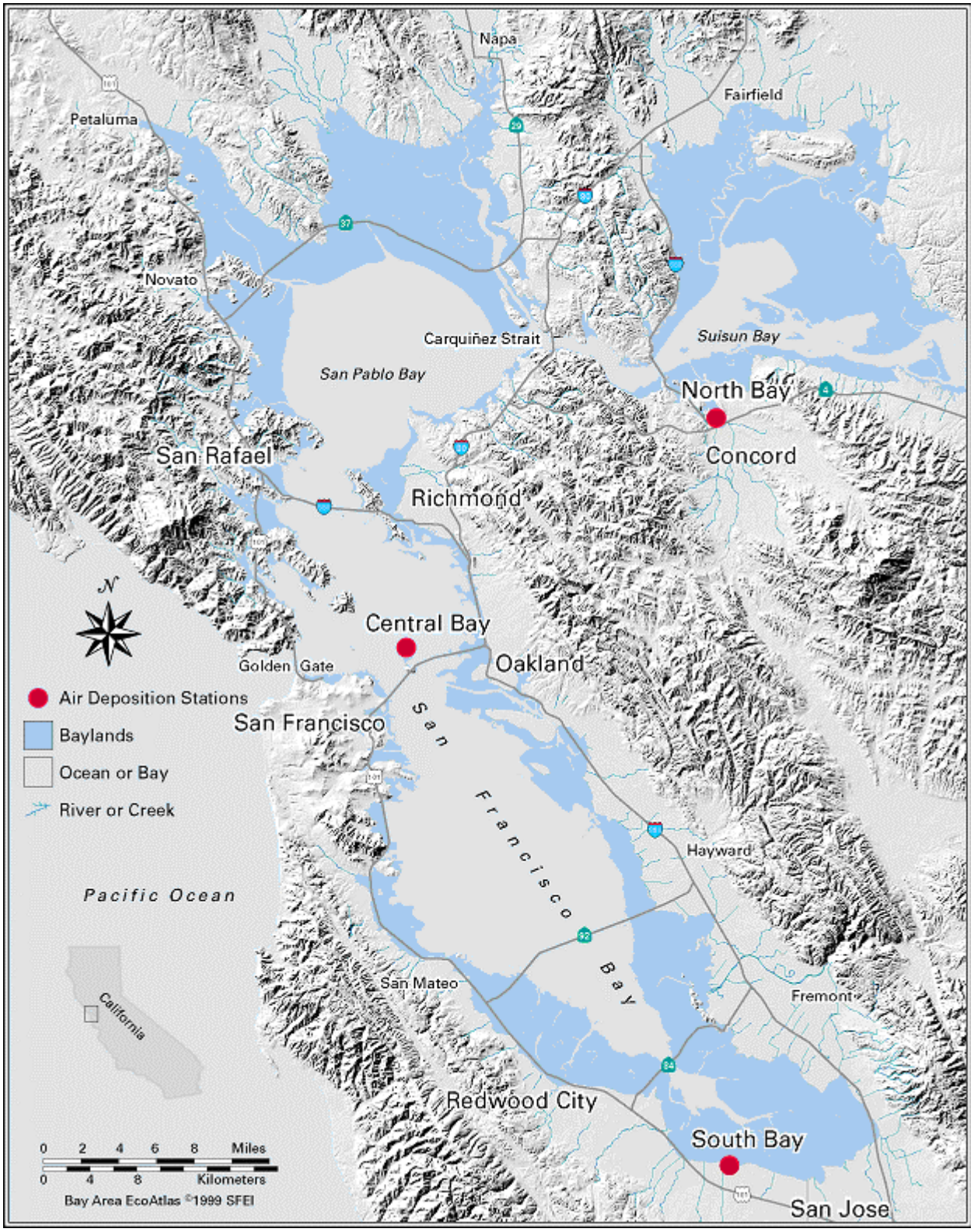

Figure 1. Monitoring Sites Included in the San Francisco Bay Atmospheric Deposition Pilot Study

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) modeled flux using airborne concentration data and modeled deposition velocity, and (2) directly measured flux using surrogate surfaces. When using surrogate surfaces, the geometry of the surface, surface roughness, and substrate all influence the wind profile and local turbulence above the sampling surface, which in part controls the measured flux. In general, these surfaces are designed to minimize disruption of the flow field so that minimum fluxes are measured. In the modeling approach, the size distribution of the particles, which is critical in determining the flux, may be altered by the measurement device or not measured at all. This lack of information about size distribution of particles often requires the use of an overall deposition velocity that is assumed to be appropriate for the chemical 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 and 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 ≥ 2 µm. Shahin et al. (2000) asserted that large particles are not sampled efficiently by most samplers, and are therefore not included in most modeling estimates. 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 in 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; Pirrone et al., 1995a; Yi et al., 1997a; Yi et al., 1997b; Paode et al., 1998).

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,b), and evaluated by other investigators (Holsen et al., 1993; Pirrone et al., 1995a; 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.

Egret I, constructed with metal-free materials, was designed to simulate, as closely as possible, the natural flow and deposition of air particles onto the water surface. It had two pivoting windvanes that responded to wind direction. Particles from the ambient air deposited 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. The cartridge plate was pointed into the wind with a leading knife-edge ($<10^o$) 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 grease, non-volatile and free of interfering contaminants to the Pilot Study, was pre-weighed to ensure consistency in the sample collection. 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” (U.S. EPA 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.

Wet Deposition

An automatic collector specifically designed for the National Atmospheric Deposition Program/Mercury Deposition Network (NADP/MDN) was used to collect one cumulative composite precipitation sample every 14 days. The device has been described in detail and evaluated by other investigators (Vermette et al., 1995). A sampler (Aerochem Metrics, Inc., Bushnell, FL) modified by the Illinois State Water Survey was used to provide two orifices 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 was again activated to close the lid.

High-density polyethylene plastic 1-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.

Sample Preparation and Analysis

Dry Deposition. 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 the 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, the urban particulate matter (UPM) from NIST was used as the standard reference material (SRM).

Wet Deposition. Precipitation samples were weighed and acidified with trace-metal grade nitric acid to an acid concentration of 0.2%. The samples were stored 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, 10 mL of the sample was acidified to 2% nitric acid, and the sample was digested at 85°C for two hours to dissolve trace metals in particulates. 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 EPA method 1638 or 6020.

Quality Control

Sampling techniques used in the Pilot Study closely followed the general clean technique principles as described in U.S. EPA Method 1669 (U.S. EPA 1996), the Quality Assurance Plan implemented for the NADP/MDN (Welker 1997), and the Quality Assurance Project Plan prepared for the Pilot Study (SFEI 2000). 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.

All equipment and supplies that had direct contact with the samples were rigorously cleaned (see above, "Wet Deposition"). 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.

Dry Deposition. The overall data quality objectives (DQO) for the laboratory analyses were met, although recovery of Cr as low as 30% 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% HNO_3 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. 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.

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. Recovery of trace metals from the greased Mylar films ranged from 73% for Cd, 87% for Cu and Cr, and 88% for nickel. 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 concentration of Cu. Replicate samples were collected at each site during each sampling event. Among the four trace metals assessed, only Cu met the DQO of less than 30% relative percent difference (RPD) 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 might 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%, meeting the DQO, when

the RPD was calculated only for those replicate field samples with analyte concentrations greater than three times their respective MDLs.

Wet Deposition. The detection limits, estimated from the preparation blank values, for Cu, Ni, Cd, and Cr were 0.02, 0.01, 0.005, and 0.03 µg/L, respectively. 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. 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, primarily attributable to the amount of 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, 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 found at the amount four times or greater 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-subtracted 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.

RESULTS AND DISCUSSION

Dry Deposition

A total of 67 samples were collected among 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 1440 minutes; the actual exposure duration was recorded on the FOFs for each sampling event. Results were calculated based on actual exposure durations.

Dry deposition rates (µg/m^2/day) and deposition fluxes (kg/year) of trace metals to different segments of the Estuary were calculated using the following formulas:

Deposition flux rate (µg/m^2/day) = µg/day ÷ 500 cm^2 × 10,000 cm^2/m^2

Deposition loading (kg/year) = deposition flux rate (µg/m^2/day) x surface area of the Estuary (m^2) x 365 days/year

Figures 2 to 5 show that dry deposition fluxes of all trace metals varied between sampling events at all three locations. Deposition fluxes were consistently lower during the wet season (November through March). However, a data set encompassing a one-year period is too limited to draw any conclusion regarding long-term seasonal variations. Average dry deposition fluxes

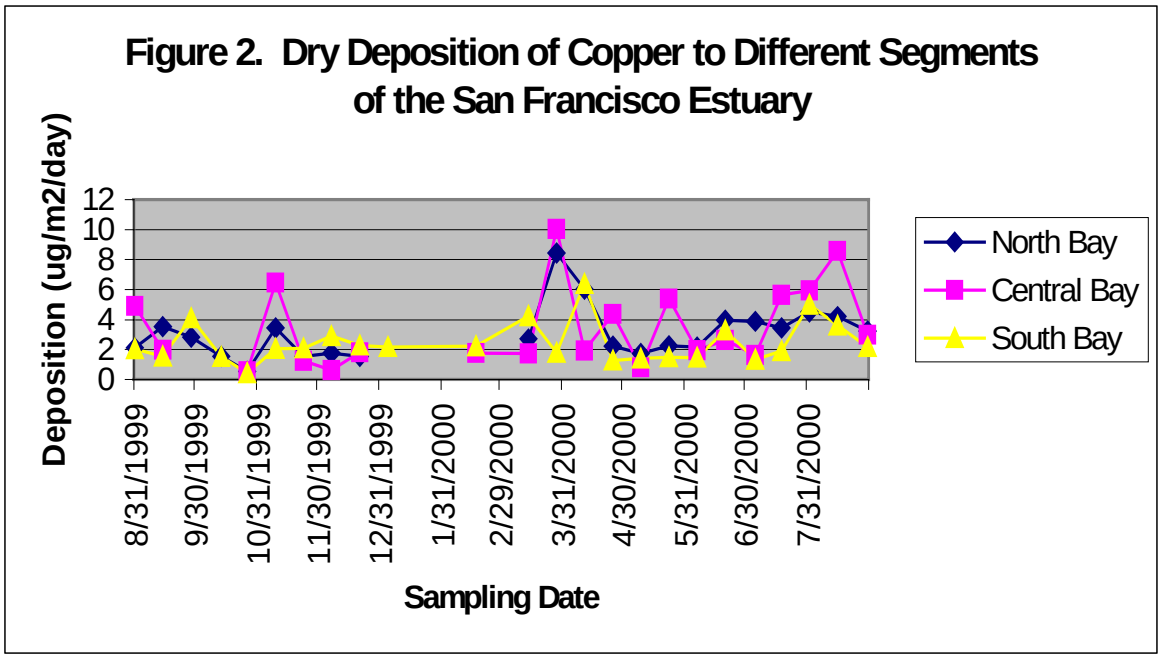
Figure 2. Dry Deposition of Copper to Different Segments of the San Francisco Estuary
Deposition (ug/m2/day)
12
10
8
6
4
2
0
8/31/1999
9/30/1999
10/31/1999
11/30/1999
12/31/1999
1/31/2000
2/29/2000
3/31/2000
4/30/2000
5/31/2000
6/30/2000
7/31/2000
Sampling Date
North Bay
Central Bay
South Bay

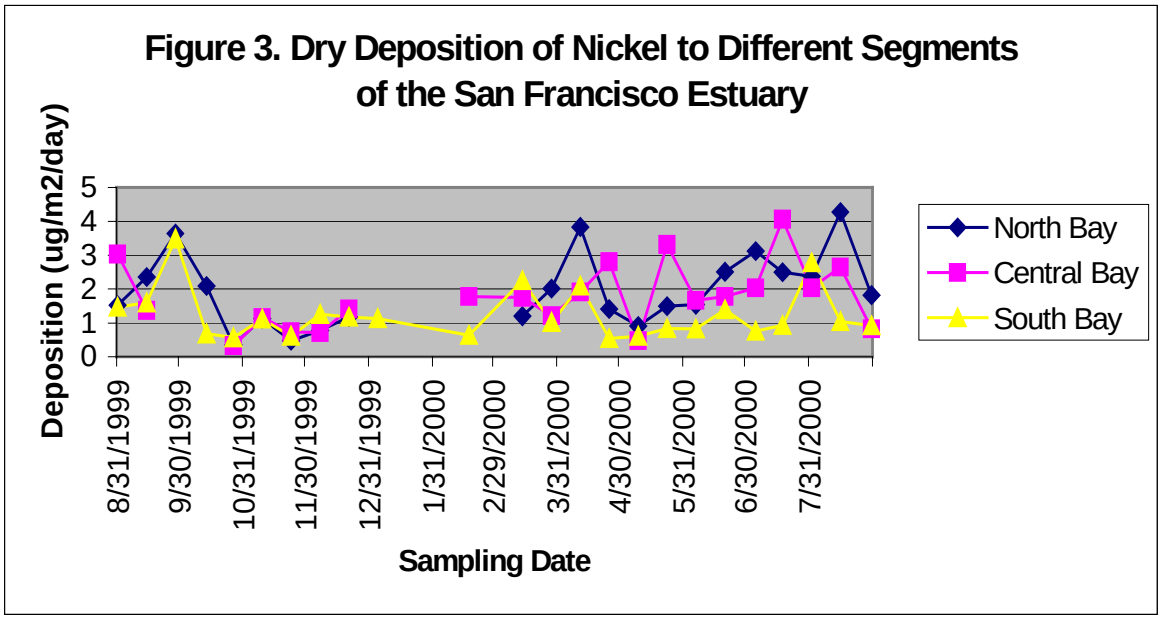
Figure 3. Dry Deposition of Nickel to Different Segments of the San Francisco Estuary
Deposition (ug/m2/day)
5
4
3
2
1
0
8/31/1999
9/30/1999
10/31/1999
11/30/1999
12/31/1999
1/31/2000
2/29/2000
3/31/2000
4/30/2000
5/31/2000
6/30/2000
7/31/2000
Sampling Date
North Bay
Central Bay
South Bay

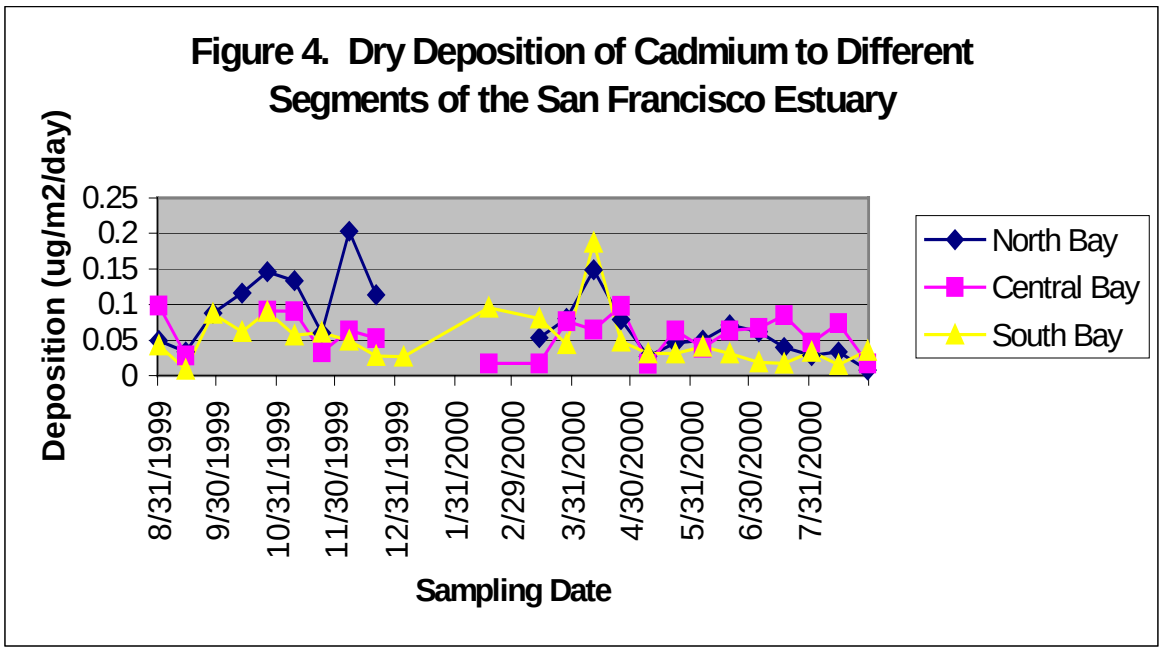
Figure 4. Dry Deposition of Cadmium to Different Segments of the San Francisco Estuary
Deposition (ug/m2/day)
0.25
0.2
0.15
0.1
0.05
0
8/31/1999
9/30/1999
10/31/1999
11/30/1999
12/31/1999
1/31/2000
2/29/2000
3/31/2000
4/30/2000
5/31/2000
6/30/2000
7/31/2000
Sampling Date
North Bay
Central Bay
South Bay

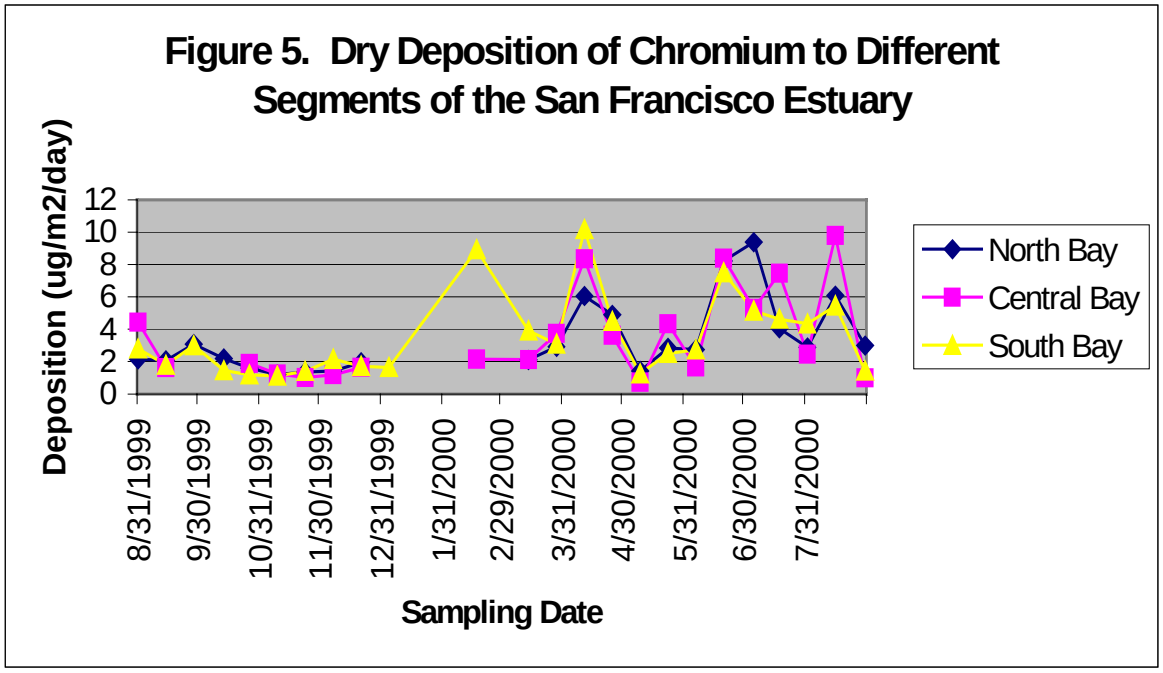
Figure 5. Dry Deposition of Chromium to Different Segments of the San Francisco Estuary
Deposition (ug/m2/day)
12
10
8
6
4
2
0
8/31/1999
9/30/1999
10/31/1999
11/30/1999
12/31/1999
1/31/2000
2/29/2000
3/31/2000
4/30/2000
5/31/2000
6/30/2000
7/31/2000
Sampling Date
North Bay
Central Bay
South Bay

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) $\mu g/m^2$/day for Cu, Ni, Cd, and Cr, respectively (Table 1).

Table 1. Dry Deposition of Trace Metals to Different Segments of the San Francisco Estuary

Monitoring Sites	Copper	Nickel	Cadmium	Chromium
Average Deposition Flux ($\mu g/m^2$/day)				
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)
All Sites	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

* Significant different from the South Bay Site at p=0.01
** Significant different from the South Bay Site at p=0.02
*** Estimates by Kirschmann and Grovhoug (1996)

Average deposition fluxes of Ni observed at the North Bay and Central Bay Sites were statistically significantly higher than the average flux observed at the South Bay Site, with p-value at 0.01 and 0.02, respectively. Deposition fluxes of Cu, Cd, and Cr did not show statistically significant differences among the three sites.

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 2 shows that the dry deposition fluxes of Cu, Ni, Cd, and Cr at 1100±730, 600±350, 22±15, and 1300±900 $\mu g/m^2$/year 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 may use different types of air samplers and/or analytical methods. For some chemical species, using direct methods with 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 was demonstrated by the results reported by Golomb et al. (1997), Paode et al. (1998), Sweet et al. (1998), and Shahin et al. (2000) (Table 2).

Table 2. Estimated Dry Deposition Flux of Trace Metals Reported in the Literature*

Sampling Site	Sampling Method	Copper	Nickel	Cadmium	Chromium	Citation
Lake Michigan	Auto D	3650	2555	73	365	Shahin et al., 2000
Urban Chicago	D	21900	NA	NA	NA	Paode et al., 1998
Lake Michigan	D	3650	NA	NA	NA	Paode et al., 1998
South Haven, MI	D	2555	NA	NA	NA	Paode et al., 1998
Lake Superior	I	2400	570	380	130	Sweet et al., 1998
Lake Michigan	I	1300	320	380	130	Sweet et al., 1998
Lake Erie	I	3300	460	400	1000	Sweet et al., 1998
Southern Lake Michigan	D	2000	NA	NA	NA	Zufall et al., 1998
Massachusetts Bay	D	2000	930	130	1200	Golomb et al., 1997
Massachusetts Bay	I	NA	NA	NA	466	Golomb et al., 1997
Chesapeake Bay	I	NA	NA	NA	110-300	Wu et al., 1994
San Francisco Estuary	**D**	**1100±730**	**600±350**	**22±15**	**1300±900**	**This study**

* All data is presented in $\mu g/m^2/year$
Auto D – Direct method using surrogate surface plates equipped with automatic rain sensor and cover
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

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 $\mu g/m^2/day$ (corresponding to 3650, 2555, 73, and 365 $\mu g/m^2/year$) for copper, nickel, cadmium, and chromium, respectively (Shahin et al., 2000). Indirect sampling using dichotomous sampler during 1993 and 1994 around Lake Michigan as one of the IADN monitoring stations yielded dry deposition fluxes of 1300, 320, 380, 130 $\mu g/m^2/year$ for copper, nickel, cadmium, and chromium respectively (Sweet et al., 1998). Golomb et al. (1997) used both direct and indirect methods to measure dry deposition of certain trace metals to the Massachusetts Bay, and found that deposition flux of chromium varied by a factor greater than two, 1200 $\mu g/m^2/year$ from the direct method versus 466 $\mu g/m^2/year$ 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 dry deposition loading to each segments of the San Francisco Estuary are presented in Table 1. Loading of Cu, Ni, Cd, and Cr to the entire Estuary was approximately 1200±830, 680±400, 25±17, and 1400±1000 kg/year, respectively. Loading to the South Bay was about 430±240, 220±130, 9±7, 620±440 kg/year, to the Central Bay about 270±210, 140±76, 4±2, and 280±220 kg/year, and to the North Bay about 490±280, 300±170, 12±8, and 530±360 kg/year for Cu, Ni, Cd, and Cr, respectively. Table 1 also shows that estimates of Ni and Cd loads to the South Bay obtained by 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 data and the methodologies used in estimating the loading as presented in this Pilot Study are very different from those used by Kirschmann and Grovhoug (1996). Estimates by Kirschmann and Grovhoug (1996) 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 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 minimize direct influence from localized sources.

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

Wet Deposition

A total of 42 precipitation samples were successfully collected and analyzed among the three monitoring stations: 12 from South Bay, 15 from Central Bay, and 15 from North Bay. Concentrations of the selected trace metals in precipitation varied among sampling events at each site and among the three sites. Paired two-tailed T-tests were performed, and no statistically significant differences (p-value >0.1) were observed in the concentrations of any trace metals in the precipitation collected among the three monitoring stations. The volume-weighted average concentration was 1.2, 0.42, 0.11, and 0.23 µg/L for Cu, Ni, Cd, and Cr, respectively (Table 3).

Table 3. Wet Deposition of Trace Metals to the San Francisco Estuary

Parameter	South Bay	Central Bay	North Bay	Entire Estuary
Annual Rainfall (in)	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 (µg/L)				
Number of Samples	12	15	15	42
Copper	0.38	1.8	0.90	1.2
Nickel	0.29	0.57	0.33	0.42
Cadmium	0.016	0.24	0.012	0.11
Chromium	0.13	0.18	0.42	0.23
Wet Deposition Flux (µg/m^2/yr)				
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

Deposition fluxes (µg/m^2/year) and loadings (kg/year) were calculated by using equation (1) and equation (2) shown below, respectively.

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

Where F_p = Wet deposition flux
C_p = Concentration of trace metals in precipitation
R_p = Rate of precipitation.

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

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

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 in) to more than 106 cm (40 in). In this report, precipitation rate at each sampling site was obtained from the data recorded 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 2001); 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 in), 68 cm (26.8 in), and 58 cm (22.8 in) 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 in) was estimated from NWS' precipitation contour depicted for the San Francisco Bay Area (NWS 2001).

Table 3 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 at 1300, 390, and 160 $\mu g/m^2$/year were substantially higher than those to the South Bay or North Bay. Deposition flux of Cr at 240 $\mu g/m^2$/year to the North Bay was the highest among the three segments of the Estuary. 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 4). Wet 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), Massachusetts Bay (Golomb et al., 1997), and Chesapeake Bay (Scudlark et al., 1994).

Total Loading from Direct Atmospheric Deposition

Combining dry and wet deposition, total deposition fluxes of Cu, Ni, and Cr to the San Francisco Estuary were 1700, 820, and 1400 $\mu g/m^2$/year, respectively. These estimated deposition fluxes are within the range of those found in Southern Quebec (Gelinas et al., 2000) and in 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 the State of Washington (Crecelius 1991) (Table 4). A total atmospheric deposition flux for Cd at 82 $\mu g/m^2$/year 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-collecting methods deployed in various studies. Gelinas et al., (2000) and Crecelius (1991) used a "bulk" sampling techniques collecting dry and wet deposition samples together at the same time. Sweet et al. (1998) and Golomb et al. (1997) used either a dichotomous air sampler or surrogate surface plate for dry deposition, and for wet deposition, they used an automatic precipitation collector, similar to the approach in this study.

Combining load estimates from dry deposition and wet deposition, the Estuary received a total of approximately 1900, 930, 93, and 1600 kg/year of Cu, Ni, Cd, and Cr, respectively, directly from the atmosphere.

Table 4. 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 (µg/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 (µg/m^2/year)					
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	626	226	60	124	This study
Total (Dry+Wet) Atmospheric Deposition Flux (µg/m^2/year)					
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

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. The Cu/Ni ratio found in CARB's ambient air samples (CARB 1999) varied with the locality, 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.

Loading from Tributaries that is Atmospheric in Origin

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

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). 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, and this runoff coefficient has been used by Hoff et al. (1996) in their estimates of atmospheric deposition of toxic chemicals to the Great Lakes.

Average runoff coefficients for different land uses vary from <10% in undeveloped areas with few impervious surfaces to 95% in business districts dominated by impervious surfaces (Dunne and Leopold 1978). Runoff coefficients are also influenced by antecedent rainfall conditions, and increase with increasing soil saturation even in forested watersheds. In estimating an appropriate runoff coefficient for the Bay Area, land use data provided by the Association of Bay Area Governments (ABAG 1995) was combined with runoff coefficients presented by Dunne and

Leopold (1978) for the five broad land-use categories (residential, commercial, industrial, agricultural, and open space). A number of hydrologic areas were delineated for the San Francisco Bay Region on the CALWATER map (WITS 1999) (Figure 6). 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 km^2. 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 ($Ø_r$) obtained from the literature for various land-uses, an area-weighted average of $Ø_r$ 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 $Ø_r$ 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), loading estimates of wet depositions (L_p), and the estimated run-off coefficient ($Ø_r$) of 0.32, approximately 4000, 1900, 190, and 3200 kg per year of Cu, Ni, Cd, and Cr, respectively, were deposited to the Estuary surface indirectly through surface run-off and tributaries (Table 5).

$$L_t = (L_d + L_p)Ø_r \qquad (3)$$

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

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 5). 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.

Figure 6. Hydrologic Areas in the San Francisco Bay Region
(taken from Davis et al., 2 000)

Table 5. 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[4,5]	66,000 (36,000 - 66,000)	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[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 from 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

Among the primary sources and pathways that contribute total loadings of trace metals, the most complete and reliable empirical data are available from monitoring of wastewater effluent discharges. Estimated loadings of trace metals from wastewater discharges to the Estuary are shown in Table 5. These estimates were extrapolated from the loading data available to SFEI for 85% of the effluent sources (Davis et al., 2000)[2]. Loadings of Cu and Ni from direct atmospheric deposition were less than 30% of that contributed by effluent discharges, and loadings of Cd and Cr might be similar for these two pathways. In addition to direct atmospheric deposition, 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 metals loading as the direct atmospheric deposition. Combining direct and indirect routes, atmospheric deposition might contribute about 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.

In addition to the loadings from atmospheric deposition and wastewater discharges presented above, sediment remobilization and diffusive flux contribute pollutant loads to the estuary water column. However, they are internal processes within the Estuary and not truly contributors of new pollutant loads to the Estuary. On the other hand, runoff through tributaries from watersheds contributes external pollutant loads to the Estuary. Watersheds that drain water to the Estuary include local drainage areas in San Francisco Bay Region and the more remote drainage areas in

[2] 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.

the Central Valley Region, which drains water from about 160,000 km^2 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.

Loading estimates of some trace metals from stormwater runoff to the Estuary were reported by Davis et al. (2000) and are shown in Table 5. 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. 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, loading from the Central Valley Region contributed much greater input (up to 14 times) of 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.

Uncertainty in the Loading Estimates

Uncertainty associated with the various loading estimates presented in this report and those of others have been assessed in a semi-quantitative manner (Table 6). In this report, low uncertainty indicates that the estimate has an error within 50%; a moderate uncertainty indicates that the estimate may vary up to 2-fold; a moderate-high uncertainty presents an estimate that has an error of up to 5-fold; and an estimate with a high uncertainty may vary 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 it is mostly controlled by 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 showed a standard deviation that was almost as large as the average value, resulting in a moderate uncertainty.

Table 6. Assessment of Uncertainty in the Trace Metal Loading Estimates

Parameters	Values Used[1]	Range of Values[2]	Uncertainty
This Pilot Study			
Dry Deposition			Moderate
Chemical Concentration	Site-specific	Site-specific	Moderate
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
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
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
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
Stormwater Runoff from San Francisco Bay Region			High
Dredged Materials			Moderate
Stormwater Runoff from Central Valley Region			High

[1] Values used in the study
[2] Values reported in the literature
High uncertainty – estimate could vary up to ten-fold
Moderate-High uncertainty – estimate could vary two to five-fold
Moderate uncertainty – estimate could vary up to two-fold
Low uncertainty – estimate varies within 50%

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 overall uncertainty is moderate-high for the estimated tributary loads that were atmospheric in origin.

The uncertainty in the estimates is low for wet deposition, moderate for dry deposition, and moderate-high for atmospheric deposition contribution to tributaries, resulting in a moderate uncertainty for the overall load estimates (Table 6). 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), it is believed that the uncertainty related to the estimates of loadings from wastewater discharges is low for Cu, Ni, and Cr, and moderate for Cd, and the uncertainty associated with the estimate of loadings from stormwater runoff is likely to be high. Loading from various sources and pathways could not be fairly compared unless all load estimates have the same level of low uncertainty.

CONCLUSIONS

Dry deposition fluxes of copper, nickel, cadmium, and chromium at 1100, 600, 22, and 1300 $\mu g/m^2$/year, respectively, from the atmosphere to the San Francisco Estuary were similar to those estimated in the Great Lakes area. Concentration of 1200, 420, 110, and 230 ng/L for copper, nickel, cadmium, and chromium, detected in precipitation were also similar to those found at other locations.

Estimated loadings of copper, nickel, cadmium, and chromium from dry deposition to the San Francisco Estuary were approximately 1200, 680, 25, and 1400 kg/year, respectively. Loadings from wet deposition were 710, 260, 68, and 140 kg/year for copper, nickel, cadmium, and chromium, 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, and could contribute as much of the loads for cadmium and chromium. 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 of 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 further refinement of the load estimates from stormwater runoff.

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