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Clean Estuary Partnership

North of Dumbarton Bridge Copper and Nickel Conceptual Model and Impairment Assessment Report

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GLOSSARY OF ACRONYMS

µg/L	Micrograms per liter, or parts per billion
ABAG	Association of Bay Area Governments
ACCWP	Alameda Countywide Clean Water Program
ACR	Acute-to-Chronic Ratio
AMEL	Average Monthly Effluent Limit
ASARCO	American Smelting and Refining Company
Ave.	Average
BACWA	Bay Area Clean Water Agencies
BAPPG	Bay Area Pollution Prevention Group
BASMAA	Bay Area Stormwater Management Agencies Association
BM&M	Bay Modeling and Monitoring
BMP	Best Management Practice
BOD	Biological Oxygen Demand
BPP	Brake Pad Partnership
CAP	Copper Action Plan
CB	Copper Baseline
CCC	Criterion Continuous Concentration (chronic)
CCCWP	Contra Costa Clean Water Program
CEP	Clean Estuary Program
CFR	Code of Federal Regulations
cm	Centimeter
CMC	Criterion Maximum Concentration (acute)
CMR	Conceptual Model Report
CMIA	Conceptual Model Impairment Assessment
COMM	Ocean, Commercial, and Sportsfishing Beneficial Use
CTR	California Toxics Rule
Cu	Copper
Cu^{2+}	Copper ion
CV	Coefficient of variation
CWA	Clean Water Act
CWF	Clean Water Fund
DHS	Department of Health Services
DTSC	Department of Toxic Substances Control
EC	Environmental Clearinghouse
ECA	Effluent Concentration Allowance
EMP	Environmental Monitoring Program
EOA	Eisenberg, Olivieri, and Associates
ERL	Effects Range-Low
ERM	Effects Range-Medium
ERS	Electronic Reporting System
EST	Estuarine Habitat Beneficial Use
FACR	Final Acute-to-Chronic Ratio
FAV	Final Acute Value
FSURMP	Fairfield Suisun Urban Runoff Management Program
ft	Feet
g/day	Grams per day
GAC	Granular Activated Carbon
HNO_3	Nitric Acid
IA	Impairment Assessment
IAR	Impairment Assessment Report
ICS	Industrial Control Strategies
IEP	Interagency Ecological Program
IPBL	Interim performance-based effluent limits
IQR	Inter-quartile Range

Kd	Partition coefficient
kg	Kilogram
L1, L2	Ligands
LC50	50% Lethal Concentration (concentration with kills half of the test species)
LGVSD	Las Gallinas Valley Sanitary District
LSB	Lower South Bay
LSSFB	Lower South San Francisco Bay
LTA	Long-term Average
LWA	Larry Walker Associates
M	Molar
m^3/s	Cubic meters per second
MAR	Marine Habitat Beneficial Use
MCSTOPPP	Marin County Stormwater Pollution Prevention Program
MDEL	Maximum Daily Effluent Limit
MEC	Maximum Effluent Concentration
MEP	Maximum Extent Practicable
mg/kg	Milligrams per kilogram
mg/L	Milligram per Liter
MGD	Million Gallons per Day
mi^2	Square miles
MIGR	Fish Migration Beneficial Use
MLML	Moss Landing Marine Laboratories
mm	Millimeter
MMWD	Marin Municipal Water District
MOA	Memorandum of Agreement
NAP	Nickel Action Plan
NDB	North of Dumbarton Bridge
Ni	Nickel
nM	Nano Molar
NOAA	National Oceanic and Atmospheric Administration
NPDES	National Pollutant Discharge Elimination System
OAL	Office of Administrative Law
P2	Pollution Prevention
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
POTW	Publicly Owned Treatment Works
ppb	Parts per billion
psu	Practical salinity units
RMP	Regional Monitoring Program
RO	Reverse Osmosis
RWQCB	Regional Water Quality Control Board
SA	Salicylaldoxime
SCVURPPP	Santa Clara Valley Urban Runoff Pollution Prevention Program
SD	Sanitary District
SF	San Francisco
SFEI	San Francisco Estuary Institute
SFO	San Francisco Airport
SFSU	San Francisco state University
SHELL	Shellfish Harvesting Beneficial Use
SIP	Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California; aka State Implementation Policy
SMAV	Species Mean Acute Value
SPWN	Fish Spawning Beneficial Use
SSO	Site-Specific Objective
STOPPP	San Mateo Stormwater Pollution Prevention Program
SWMP	Storm Water Management Plan

SWRCB	State Water Resources Control Board
TDC	Environmental Consulting Firm
TIE	Toxicity Identification Evaluation
TMDL	Total Maximum Daily Load
TOC	Total Organic Carbon
TSS	Total Suspended Solids
TWG	Technical Work Group
ug/g	Microgram per gram
US EPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WER	Water-Effects Ratio
WMI	Watershed Management Initiative
WQO	Water Quality Objective
WSPA	Western States Petroleum Agencies
WWTP	Wastewater Treatment Plant

EXECUTIVE SUMMARY

Introduction

This report includes an impairment assessment and a conceptual model for copper and nickel in San Francisco Bay:

- The impairment assessment summarizes existing data on copper and nickel in water, sediment, and biota and compares them to environmental standards. The assessment also documents ongoing and proposed source control measures for copper and nickel.
- The conceptual model describes the sources of copper and nickel to the Bay and the processes that determine concentrations and fate of these metals in the ecosystem. It uses available information to predict how the ecosystem would respond to management actions that reduce ongoing inputs of copper and nickel.

Copper and nickel were on the 1998 Clean Water Act Section 303(d) ”impaired waters” list for San Francisco Bay. In the recently approved 2002 303(d) list, copper was removed and nickel was retained, with qualification. Copper and nickel have been of ongoing environmental concern in San Francisco Bay since the mid-1980’s, because elevated water column concentrations may impair aquatic uses in the Bay by producing either acute or chronic toxicity in sensitive aquatic organisms.

San Francisco Bay is a dynamic tidal system. Water and sediment circulation patterns are especially complex as a result of the Bay’s elongated shape, the large volume of fresh water (Delta outflow) that passes through its northern reach, its narrow connection to the Pacific Ocean at the Golden Gate, and the relatively low freshwater inputs from local tributaries, especially those in South San Francisco Bay. Ocean tides enter and leave the Bay twice a day. The volume between tidal elevations is called the *tidal prism*, approximately 25 percent of the total volume of the Bay. The Sacramento and San Joaquin Rivers convey the freshwater inflows to the North Bay and transport wet and dry weather runoff from the Central Valley to the Bay.

The toxicity of copper and nickel to aquatic organisms is dependent on site-specific factors such as pH, hardness, suspended solids, dissolved oxygen, dissolved carbon compounds, salinity, and concentrations of other organic and inorganic constituents. Additionally, new toxicity data has become available that should affect the national aquatic life criteria values. Because the national aquatic life criteria for copper and nickel that were adopted as water quality standards in the California Toxics Rule (CTR) may not be directly applicable to San Francisco Bay, USEPA has provided guidance outlining procedures that may be used to develop site-specific criteria for these metals [USEPA, 1994]. An abundance of work has been performed in San Francisco Bay in accordance with this USEPA guidance which can be used to justify the adoption of site-specific water quality objectives for copper and nickel. The original work on such objectives was performed in Lower South Bay, south of the Dumbarton Bridge (see Section 1 of the *Copper & Nickel North of the Dumbarton Bridge Step 1: Impairment Assessment Report, July 2002* for a summary of LSB work). In May 2002, the Regional Board adopted a Basin Plan amendment to establish site-specific objectives for copper and nickel in Lower South Bay, based on that work.

Additional technical work has been performed North of the Dumbarton Bridge (NDB), following the same technical approach and procedures used in the Lower South Bay. Results from that work indicates that site-specific objectives for copper and nickel are appropriate in the Bay NDB. That technical work and the resulting site-specific objectives for copper and nickel are summarized in this document and described in detail in a separate document (*North of Dumbarton Bridge, Copper and Nickel, Development of Site-specific Objectives*, [LWA/EOA, 2004]).

The following management questions have been raised by interested parties in the consideration of adoption of these site-specific objectives. These questions are addressed in the impairment assessment and conceptual model described in this document.

1. Will the adoption of site-specific objectives lead to increased loadings from point sources that will have a measurable impact on dissolved water column copper and nickel concentrations in SF Bay?
2. What implementation measures are needed to ensure that existing copper and nickel concentrations in the water column and surface sediments of the Bay will not increase significantly?
3. Does copper toxicity to sensitive invertebrates (as measured by a Water Effects Ratio) vary significantly over space or time in the Bay?
4. Do existing copper or nickel concentrations in surface sediments cause sediment toxicity in the Bay?
5. Will additional loadings of copper and nickel from point sources produce significant changes in sediment concentrations or sediment toxicity in the Bay?
6. Do existing dissolved copper or nickel concentrations cause phytoplankton toxicity in the Bay?

Impairment Assessment

In February 1989, the State Board designated the Lower South Bay as an impaired water body under Section 304(l) of the Clean Water Act, due to evidence of water quality impacts associated with seven metals based on total recoverable fractions: cadmium, copper, lead, mercury, nickel, selenium, and silver. The State Board identified the three municipal wastewater treatment plants and stormwater discharges into the Lower South Bay as point sources contributing to this impairment.

The 1996 San Francisco Bay Impaired Water Body (Clean Water Act Section 303(d)) listing identified the entire Bay as a high priority impaired water body. "Metals" (as a broad category) were noted as the pollutant of concern and municipal point sources, urban and storm runoff and surface mining were identified as the sources of metals.

In 1998, the RWQCB staff refined the broad listing of "metals" on the 1996 303(d) list to specifically identify mercury, copper, nickel and selenium as the metals of concern. The specific rationale used to support the listing for copper and nickel was "exceedance of the California Toxics Rule {draft at that time} dissolved criteria and National Toxic Rules total criteria, and elevated water and sediment tissue levels." The list identified sources as municipal point sources, urban runoff/storm sewers, atmospheric deposition, and other and was approved by USEPA in May 12, 1999.

Dissolved water quality objectives for copper and nickel in San Francisco Bay were adopted in the May 2000 California Toxics Rule [USEPA, 2000]. The CTR established each of these objectives as a specific numeric value times a WER value. If site-specific studies were not performed to establish a WER value, a default value of 1.0 was to be assumed.

Information was submitted by RWQCB staff to the SWRCB by memorandum dated February 26, 2002 citing the available Step 1 NDB copper water effect ratio (WER) data as support for a recommendation to de-list copper. Available ambient dissolved copper concentrations in the estuary never exceeded the most conservative copper objectives derived from the NDB site-specific WER values.

Based in part on the Step 1 NDB WER and related ambient concentration information for copper and nickel, the SWRCB approved on February 4, 2003 the 2002 303(d) list. The SWRCB list included the delisting of copper throughout the Bay and nickel throughout the Bay, except for nickel in the area around the mouth of the Petaluma River.

However, USEPA did not approve delisting nickel for Lower San Francisco Bay, San Pablo Bay, Suisun Bay, and the Sacramento/San Joaquin Delta because USEPA asserted that the applicable WQO was the Basin Plan 7.1 µg/L total metals nickel objective. The nickel total metals objective was exceeded 102 times since 1993 in those segments while the CTR 8.2 µg/L dissolved metals objective was only exceeded four times and only at the mouth of the Petaluma River. USEPA noted that "the State is in the process of developing site-specific water quality standards for nickel that will likely be attained. Therefore it is most reasonable to proceed with water quality standards modifications that will likely obviate the need to complete a nickel TMDL for the Bay."

Site-Specific Objectives

For copper the geometric mean final WERs (FWERs) were 2.670, 2.876, and 3.535, respectively, for the Dumbarton North, Dumbarton South and Coyote Creek stations in Lower South Bay (LSB). The range of chronic SSOs for the lower South Bay resulting from the Impairment Assessment was 5 to 12 µg/L dissolved copper. EPA reviewed this work and found that the species used were appropriate, the data valid and the conclusions reasonable [USEPA July 27, 1998].

Copper WER studies performed in San Francisco Bay North of Dumbarton Bridge have measured dissolved WER values ranging from 1.6 to 5.3. The mean WER value measured in all NDB samples was 2.7. A range of chronic copper SSOs of 6.8 to 8.4 µg/L was developed from the observed WER values NDB.

The nickel SSO adopted for the LSB is based on recalculation of the national criterion and is therefore a value applicable Bay-wide. Candidate nickel SSOs range from 11.9 µg/L to 20.9 µg/L.

The results of SSO studies and ambient water column monitoring NDB have established that aquatic life impairment due to water column levels of dissolved copper and nickel in San Francisco Bay is unlikely. Results of studies regarding phytoplankton and sediment quality indicate that copper and/or nickel are not likely to be causing impairment of phytoplankton or benthic communities in the Bay. Studies are ongoing to resolve uncertainties, regarding sediment toxicity, phytoplankton toxicity, and the impact of loadings on sediment concentrations. Additional studies are proposed to resolve uncertainties regarding the impact of load management alternatives on ambient copper and nickel levels in the Bay.

Conceptual Model

Available information regarding the sources, loadings, fate and transport, toxicity and ambient levels of copper and nickel in San Francisco Bay are summarized in the conceptual model portion of this document.

Sources and Pathways

The major sources and pathways of copper and nickel to San Francisco Bay are remobilization from in-Bay sediments, riverine inputs, urban and non-urban runoff, POTWs and industrial effluents, and atmospheric wet and dry deposition. Municipalities and industries have invested significant resources in the determination of sources of copper and nickel to wastewater and runoff. Those sources, and associated control measures, are identified in this document.

Loadings

Numerous estimates of loadings of copper and nickel to the Bay have been made. SFEI made the most recent estimate in 2000, which estimated local loads to the Bay of 74 tons per year for copper and 64 tons per year for nickel. SFEI estimated external loads from the Central Valley to be 270 and 410 tons per year for copper and nickel, respectively. The SFEI estimates do not account for re-mobilization of copper and nickel from Bay sediments, which is estimated to be an even larger source than Delta outflow from the Central Valley.

Mass loadings to San Pablo Bay and Lower South Bay were estimated by Rivera-Duarte and Flegal in 1997. SFEI summarized results from that study in its report on the Sources, Pathways and Loadings Workgroup published in 2001. The mass loading estimates indicated that benthic remobilization was a dominant source of loadings of both copper and nickel to the Bay, with riverine loadings next most important. For copper in San Pablo Bay, benthic remobilization is estimated to be 72% of the total loading, riverine and runoff is 26%, and POTWs and atmospheric deposition are each 1%. For nickel in San Pablo Bay, the respective loading percentages are 77%, 21%, 2% and <1%.

Fate and Transport

Copper and nickel partition between the dissolved and particulate phase in San Francisco Bay. Processes of sorption and desorption impact this partitioning. The ratio of adsorption to desorption is referred to as the partition coefficient (Kd). This coefficient depends on metal chemistry and site-specific factors, including salinity, suspended solids, and dissolved organic carbon.

Dissolved copper and nickel exist as inorganic complexes, organic complexes, colloids and free cationic species. The ionic forms of copper and nickel are most toxic to aquatic organisms, as they are the forms which most readily diffuse or are taken up across cell membranes. The complexation of dissolved copper has a direct effect on copper toxicity in San Francisco Bay. Complexation of nickel does not demonstrate a similar effect on nickel toxicity. Neither copper nor nickel bioaccumulate in organisms to a significant degree.

In the northern reach of the estuary, dissolved copper and nickel both have non-conservative excesses (in Bay sources). Copper excesses in the northern reach are relatively consistent during both wet and dry seasons, whereas dissolved nickel excesses are as much as ten-fold greater during the wet season. This difference is due to several coupled processes. These may include weathering of nickel-enriched serpentines, formation of soluble nickel-sulfide complexes, and episodic flushing of adjacent wetlands.

Ambient Conditions

Water column and sediment monitoring has been performed at numerous sites in San Francisco Bay NDB by the Regional Monitoring Program (RMP) since 1993. Plots and tables of these RMP ambient results are provided in this document.

Uncertainty in Conceptual Model that can be Addressed through Water Quality Modeling

The following areas of important ongoing uncertainty have been identified that can be significantly reduced through the use of mathematical hydrodynamic and water quality models of San Francisco Bay.

a. Incremental water quality impacts that may result at various locations in San Francisco Bay due to changes in (1) concentrations and/or (2) mass loadings from existing POTW and Industrial discharges of treated wastewater.

   Mathematical models can be used to address this issue by assessing the incremental effect of increased loadings from some or all sources on water quality at various locations in the Bay.

b. Incremental changes in surface sediment concentrations of copper and nickel that may result from increased loadings of copper and nickel from NPDES discharges.

   Mathematical models can be used to predict the change in surface sediment concentrations under the existing NPDES loading condition and various other loading scenarios.

c. The impact of the erosion of bedded sediments or exposed ore slag with high copper or nickel concentrations on Bay water quality.

   Mathematical models can be employed to assess the effect of significantly elevated areas of surface sediment concentration on dissolved copper and nickel concentrations around the Bay.

d. The relative magnitude and importance of different copper and nickel sources to Bay water quality.

Mathematical models can be used to calculate source loadings from all significant sources. The results from the ongoing Brake Pad Partnership modeling effort will assist greatly in the quantification of urban runoff loadings to the Bay.

1. INTRODUCTION

Section 303(d) of the federal Clean Water Act (CWA) requires states to compile lists of water bodies that do not meet water quality standards and to develop plans for achieving the standards. Copper and nickel were on the 1998 CWA 303(d) List for San Francisco Bay because of elevated water column concentrations. Copper was removed from the 303(d) list for San Francisco Bay in 2002 based on consideration of Water Effect Ratio-adjusted dissolved copper objectives and ambient data on dissolved copper levels in the Bay NDB. Nickel was retained on the 2002 303(d) list for the Bay NDB pending adoption of dissolved CTR objectives in the Basin Plan.

This report includes an impairment assessment and a conceptual model for copper and nickel in San Francisco Bay NDB:

- The impairment assessment summarizes existing data on copper and nickel in water, sediment, and biota and compares them to indicators of impairment.
- The conceptual model describes the sources of copper and nickel to the Bay and the processes that determine concentrations and fate of these metals in the ecosystem. It uses available information to predict how the ecosystem would respond to management actions that reduce ongoing inputs of copper and nickel and addresses uncertainties in these predictions.

This Introduction presents the regulatory background, describes San Francisco Bay and its beneficial uses, introduces the pollutants of concern, and presents the rationale for the current 303(d) listing.

1.1 Regulatory Background

The Clean Water Act provides protection to the surface waters of the United States. Section 101(a)(2) of the Act establishes a national goal of “water quality, which provides for the protection and propagation of fish, shellfish, and wildlife, and recreation in and on the water, wherever attainable.” Section 303(c)(2)(a) requires that states develop water quality standards to protect human health and the aquatic environment, and Section 303(d) requires that states develop lists of waterbodies that do not meet those standards. U.S. Environmental Protection Agency (USEPA) regulations require that 303(d) lists be compiled every two years.

In California, Section 13001 of the California Water Code identifies the California State Water Resources Control Board (SWRCB) and Regional Water Quality Control Boards (RWQCBs) as the principal agencies responsible for controlling water quality. These boards are responsible for compiling the 303(d) list of impaired waterbodies. The lists are to be determined using state policy and USEPA guidelines and are subject to approval by USEPA.

1.2 San Francisco Bay and Beneficial Uses

1.2.1 Bay Description

The Bay/Delta estuary is one of the largest estuaries in North America. It comprises two distinct regions, San Francisco Bay and the Sacramento-San Joaquin Delta, and has a surface area of some 1,620 square miles.

The San Francisco Bay system is the largest coastal embayment on the Pacific Coast of the United States [Nichols and Pamatmat, 1988]. The watershed encompasses about 60,000 mi^2, or 40% of California [STB et al., 2000]. Its waters have a surface area of 470 mi^2 and are divided into several segments: Suisun Bay (including Grizzly and Honker Bays), Carquinez Strait, San Pablo Bay, and San Francisco Bay. As shown in **Table 1.1** below, the area, depth, and volume of each of these segments varies considerably.

Table 1.1. Bathymetric Data for San Francisco Bay

Region	Surface Area (mi^2)	Mean Depth (ft)	Mean Volume (acre-ft)
Suisun Bay	36	14	323,000
Carquinez Strait	12	29	223,000
San Pablo Bay	105	9	605,000
Central Bay	103	35	2,307,000
South Bay	214	11	1,507,000
Total >>>	*470*	*17*	*4,965,000*

Suisun Bay is a shallow embayment between Chipps Island, at the western boundary of the Delta, and the Benicia-Martinez Bridge; adjacent is Suisun Marsh, the largest brackish marsh in the United States. The narrow, 12-mile-long Carquinez Strait joins Suisun Bay with San Pablo Bay. San Pablo Bay is a large, open bay that extends from the Carquinez Strait to the San Pablo Strait near the Richmond-San Rafael Bridge. Adjacent to San Pablo Bay lies the northern part of San Francisco Bay, known informally as Central Bay; it is bounded by the San Pablo Strait to the north, the Golden Gate Bridge to the west, and the Oakland-San Francisco Bay Bridge to the south. The southern part of San Francisco Bay, known informally as South Bay, includes all Bay waters south of the Oakland-San Francisco Bay Bridge.

1.2.2 Tributaries

The Sacramento-San Joaquin Delta is a 1,150-square-mile, triangular-shaped region of land and water at the confluence of the Sacramento and San Joaquin rivers. Bounded by the city of Sacramento to the north, Vernalis to the south, and Chipps Island to the west, the Delta is divided into several segments [Gunther, 1987]. The northern Delta is dominated by waters of the Sacramento River, the southern Delta by waters of the San Joaquin River, and the eastern Delta by waters of the Cosumnes and Mokelumne rivers. The Delta's western segment is subject to the greatest tidal effects. The central Delta, surrounded by the other segments, includes many channels where waters from all four rivers mix. The Delta's rivers, sloughs, and excavated channels comprise a surface area of about 75 square miles.

Large volumes of freshwater are episodically introduced into the Bay through the Delta from the

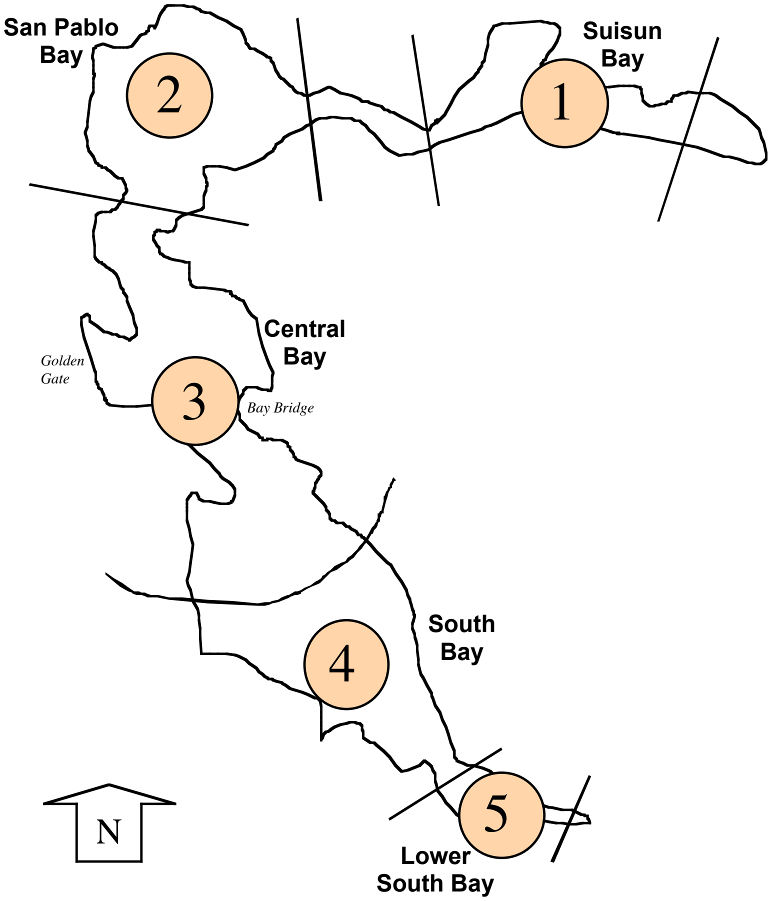
Sacramento and San Joaquin Rivers, at discharge rates ranging from less than 1,000 cubic meters per second (m^3/s) to greater than 10,000 m^3/s [Tetra Tech, 1999; DWR, 1998].

1.2.3 Tidal influence

San Francisco Bay is a dynamic tidal system. Water and sediment circulation patterns are especially complex as a result of the Bay's elongated shape, the large volume of water that passes through its northern reach, its narrow connection to the Pacific Ocean at the Golden Gate, and the relatively low freshwater inputs from local tributaries, especially those in South San Francisco Bay. Ocean tides enter and leave the Bay twice a day. Between high and low tides, changes in the surface of the water may be as much as 9 feet. The average range, 4 to 4-1/2 feet, moves 390 billion gallons of salt water through the Golden Gate. This volume between tidal elevations is called the *tidal prism* [US Army Corps of Engineers, 2001].

Also affecting the Bay's tidal system is the water flowing into the Bay from rivers and other sources. Runoff following rainstorms and snowmelt from the Sierras, travel through either the Sacramento or San Joaquin River to their final destination in the Bay.

Figure 1.1. Regions of San Francisco Bay Defined by Revised Regional Monitoring Program



1.2.4 Current and projected land uses and population

The San Francisco Bay area is bordered by nine counties (**Figure 1.2**). The project area includes portions of all nine counties (except for Santa Clara County) north of the Dumbarton Bridge and whose watersheds drain to San Francisco Bay. Information on land use and populations was gathered from the Regional Board's "Watershed Management Initiative Integrated Plan Chapter" [SWRCB, 2002] and ABAG's "Projections 2002" [ABAG, 2001]. A summary of this information is provided below.

The local drainage area to San Francisco Bay (i.e., exclusive of the Central Valley) encompasses 8550 square kilometers. Land uses in the drainage area are as follows: open space (56%), residential (21%), agricultural (13%), commercial (5%) and industrial (4%) [Davis *et al.*, 2000].

1.2.5 Projections for the Overall San Francisco Bay Area

1.2.5.1 Population

By 2025, the population of the San Francisco Bay area will exceed 8.22 million people, an increase of over 1.44 million from its current level of 6.78 million [ABAG, 2000]. Alameda County will grow by 270,500 people to 1.71 million, Contra Costa County will grow by 261,100 people to 1.18 million and Solano County will grow by 176,800 people to 571,000. In percentage terms, Solano and Napa Counties will see the highest growth during the forecast period. Solano County will add more than 45% and Napa County will add more than 32%, respectively.

1.2.5.2 Job Growth

It is estimated that the San Francisco Bay area will add approximately 1,180,000 jobs during the next twenty-five years. Alameda County will add over 262,500 jobs during this period, an increase of 37%. As a city, San Francisco will add the most jobs over the next 25 years, more than 162,000. In percentage terms, Solano and Sonoma Counties will see the highest growth during the forecast period. Both counties will add approximately 52%, respectively.

1.2.5.3 Land Available for Development

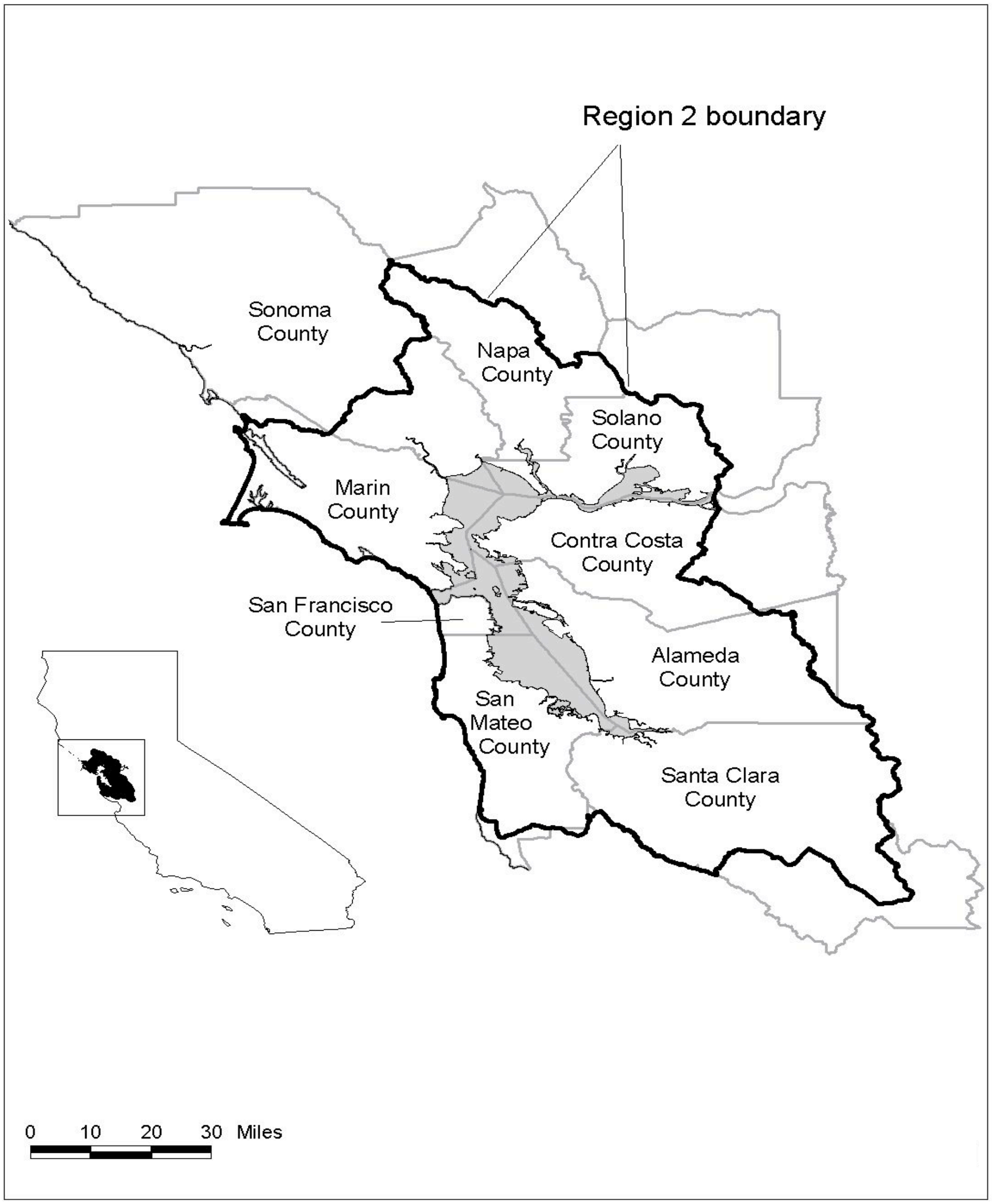
In 2000, about 17% of the region's total acreage was developed, or 752,000 acres. There are approximately 252,800 acres of land available for development in the San Francisco Bay area over the next twenty-five years. This is approximately 5.7% of the region's total area. About 192,700 acres are available for residential development and 57,400 for commercial or industrial development. The largest amount of land available for development is in Sonoma, Contra Costa, Alameda, and Santa Clara Counties. In percentage terms, San Francisco has the most with 52.6%, but only 15,700 acres. Contra Costa and Alameda Counties have the second and third most with 9.1% and 7.8%, respectively.

ABAG notes that the impact of potential growth is difficult to characterize because the nature of urban development is constantly changing. If for example the movement towards "smart growth" continues, ABAG's projections could be realized by developing or redeveloping fewer acres with higher densities than what is now planned.

1.2.6 Beneficial Uses

Chapter 2 of the 1995 Basin Plan lists designated beneficial uses for San Francisco Bay. The beneficial uses potentially impacted by copper or nickel toxicity to aquatic organisms in San Francisco Bay are estuarine habitat (EST), marine habitat (MAR), ocean, commercial and sportfishing (COMM), fish migration (MIGR), fish spawning (SPWN) and shellfish harvesting (SHELL). Detailed descriptions of these uses are provided in the Basin Plan.

Figure 1.2. San Francisco Bay Region



1.3 Copper and Nickel

Concern for copper and nickel toxicity in San Francisco Bay has existed since the mid-1980's, when USEPA aquatic life criteria for trace metals were promulgated and those numeric criteria were adopted as water quality objectives in the San Francisco Basin Plan. At the time of adoption, the USEPA criteria were interpreted as total recoverable values. Limited sampling in San Francisco Bay indicated that ambient levels of total recoverable copper and nickel exceeded the newly adopted Basin Plan objectives. Although the 1993 USEPA metals policy contained the recommendation to apply USEPA aquatic life criteria for trace metals, including copper and nickel, as dissolved values, reliable information on dissolved levels of metals in the Bay was just emerging, various parties were reluctant to accept the change from the total recoverable interpretation of objectives, and residual concern for these metals continued to exist.

Figures 1.3 and 1.4 depict the conceptual models of copper and nickel in San Francisco Bay. Sources of copper and nickel range from industrial, POTW, urban runoff, atmospheric deposition, tributaries, and the sediment bed, to name a few. The processes involving the sedment bed include resuspension and dissolution, erosion of buried sediments, and benthic flux of dissolved copper and nickel. Resuspension and dissolution occur as a function of the movement of the water over the sediments, which lifts the sediments and mixes them with the water column [Kimmer, 2003]. Erosion of buried sediments results when the water movement wears away rock, which may contain serpentinite formations or other metal containing geological structures. Benthic flux (sometimes referred to as internal recycling) represents the transport of dissolved chemical species between the water column and the underlying sediment. This transport is affected by oxidation reduction reactions, complexation and repartitioning, among other chemical processes [Topping *et al*, 2001].

Figure 1.3. Conceptual Model of Copper for San Francisco Bay

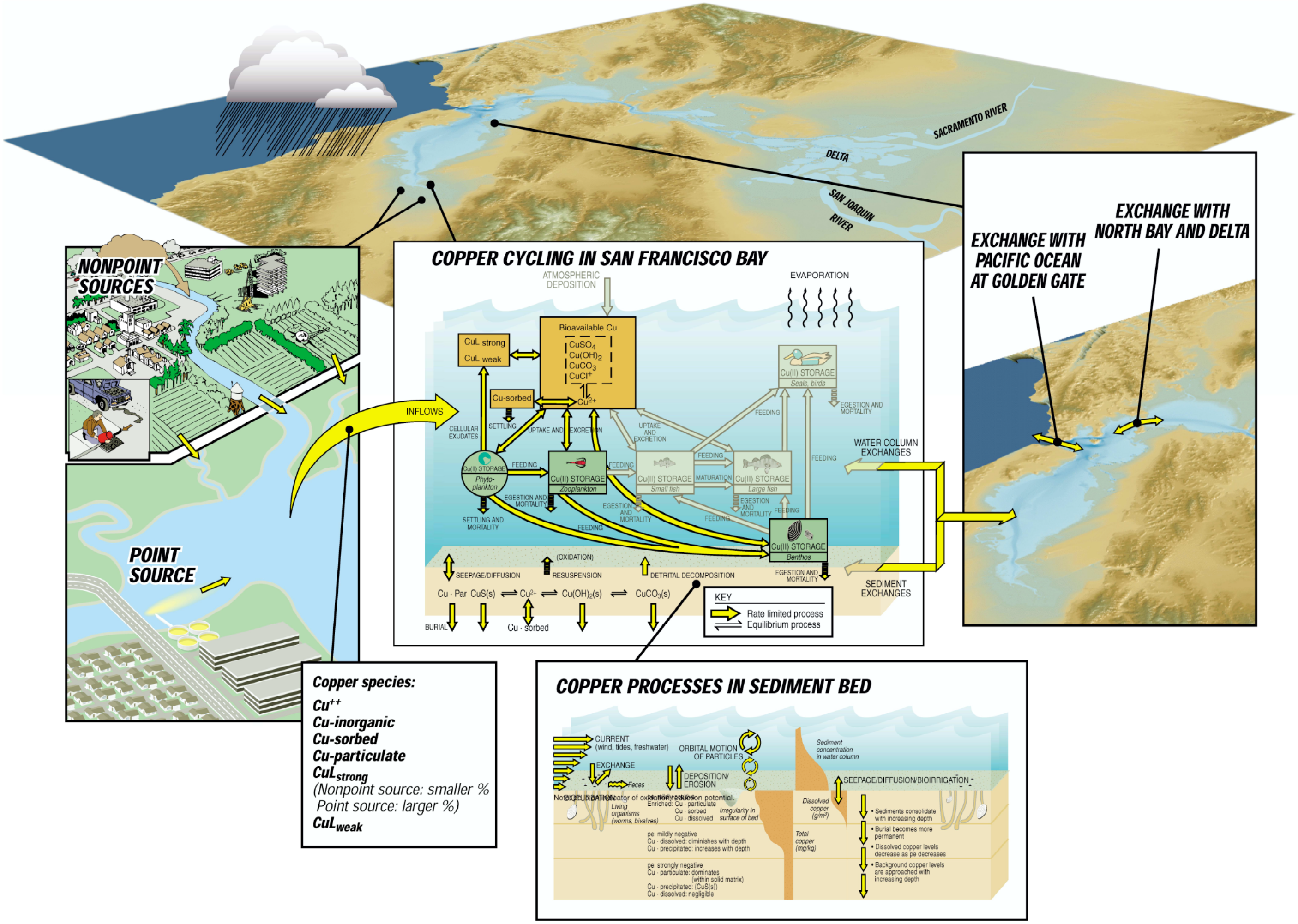


Figure derived from *Conceptual Model Report for Copper and Nickel in Lower South San Francisco Bay* (Tetra Tech, 1999)

Figure 1.4. Conceptual Model of Nickel for San Francisco Bay

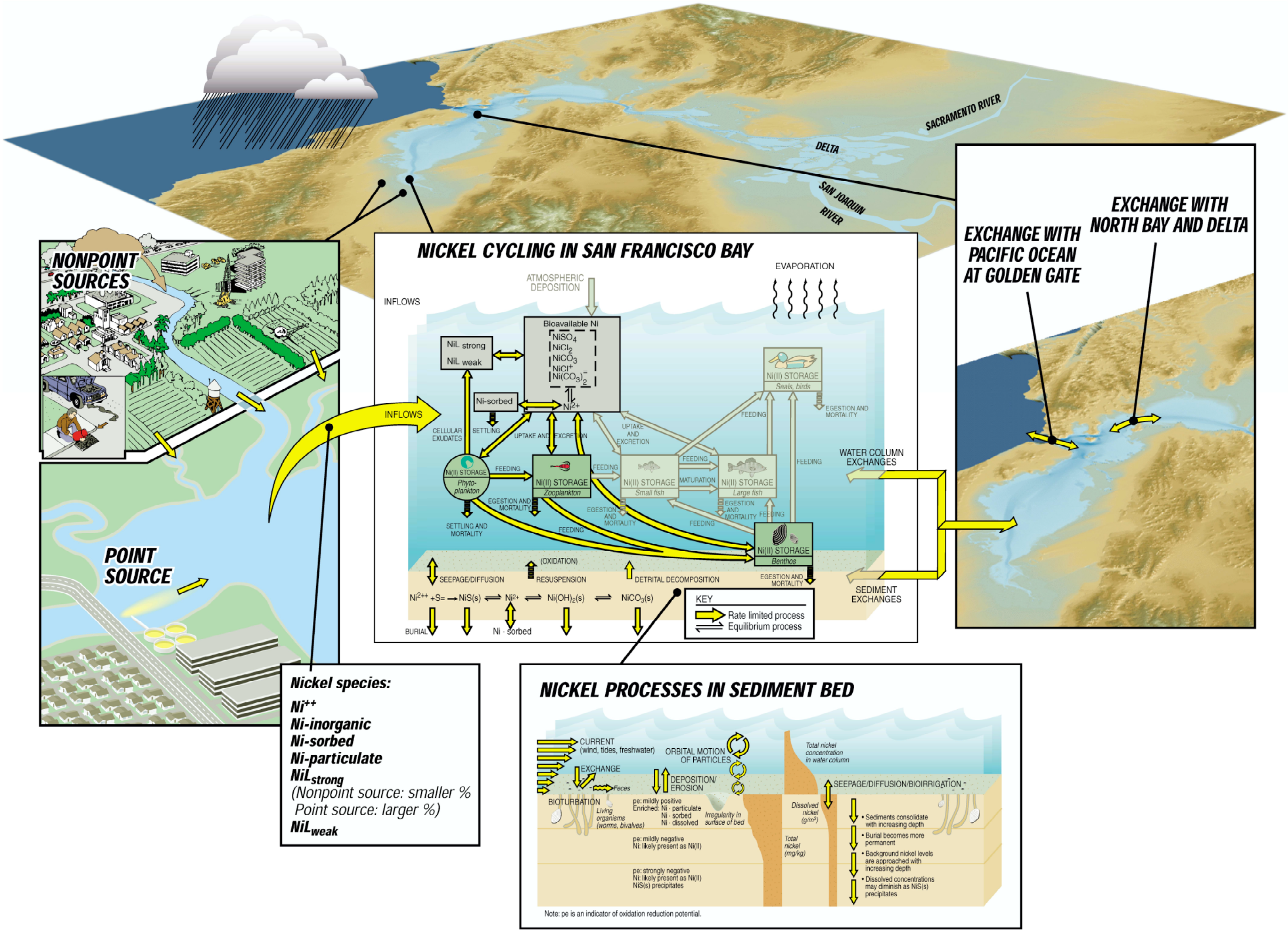


Figure derived from *Conceptual Model Report for Copper and Nickel in Lower South San Francisco Bay* (Tetra Tech, 1999)

1.4 Basis for the Impairment Listing

Section 304(l) of the federal Clean Water Act (as amended in 1987) required States to develop lists of water bodies impaired by toxic pollutant discharges, identify point sources and pollutants causing toxic impacts, and develop individual control strategies (ICS) for each point source identified. In February 1989, the State Board designated the Lower South Bay as an impaired water body under Section 304(l), due to evidence of water quality impacts associated with seven metals based on total recoverable fractions: cadmium, copper, lead, mercury, nickel, selenium, and silver. The State Board identified the three municipal wastewater treatment plants and stormwater discharges into the Lower South Bay as point sources contributing to this impairment. In June 1989, EPA Region IX approved the State's inclusion of the Lower South Bay and conditionally approved the three NPDES permits as ICSs for the municipal discharges.

The 1996 San Francisco Bay Impaired Water Body listing identified the Bay as a high priority impaired water body. Metals were noted as the pollutant of concern and municipal point sources, urban and storm runoff and surface mining were identified as the sources of pollutants. A detailed scientific analysis of the available data to support the listing was not conducted. The listing was essentially based on the analysis contained in the State Board's 304(l) listing.

An ad hoc workgroup made up of staff from the RWQCBs, the SWRCB, and USEPA developed and released guidelines (August 11, 1997) for use in California for conducting the 1998 listing to meet Section 303(d) requirements of the Clean Water Act. An updated listing for the Bay was prepared in early 1998 by the RWQCB staff. The RWQCB staff refined the broad listing of pollutant of concern noted as "metals" on the 1996 303(d) list to specifically identify mercury, copper, nickel and selenium as the metals of concern. The specific rationale used to support the listing for copper and nickel was "exceedance of the California Toxics Rule {draft at that time} dissolved criteria and National Toxic Rules total criteria, and elevated water and sediment tissue levels." The list identified sources as municipal point sources, urban runoff/storm sewers, atmospheric deposition, and other. The 1998 list was approved by USEPA May 12, 1999.

Regional Board staff began the process to update the 1998 list in early 2000 and issued a formal request for available information supporting changes to the list. At the time of this public solicitation of water quality information, the Step 1 water quality monitoring study of copper and nickel north of Dumbarton Bridge (NDB) conducted by the Bay Area Clean Water Agencies (BACWA), Bay Area Stormwater Management Agencies Association (BASMAA), and Western States Petroleum Association (WSPA) was underway.

On November 28, 2001, the Regional Board adopted a resolution allowing the Executive Officer to transmit the staff recommendations for changes to the 303(d) list of impaired waterbodies. The staff recommendations, documented in a staff report dated November 14, 2001, were based on water quality information readily available, including information solicited from individuals, organizations, and agencies on or before May 15, 2001. Data from the first two events of the NDB study were submitted to the RWQCB for use in this update on May 15, 2001. Information after May 15 could be used if a study was underway and staff was notified by May 15 of pending NDB information.

The RWQCB staff recommendations of November 14, 2001 included a recommendation to de-list copper in San Francisco Bay segments north of the Dumbarton Bridge. This was based on evaluation of ambient dissolved copper concentrations compared to the California Toxics Rule (CTR) water quality objective of 3.1 µg/L and a default WER of 1.0. The data evaluated spanned from 1993 to April 2001 and were collected by both the Regional Monitoring Program (RMP) and the NDB study.

Review of these data indicated that the CTR water quality objective for copper was consistently achieved except at the mouth of the Petaluma River. The staff report noted on page 32 "Regional Board staff recommends that targeted monitoring for copper and nickel continue to ensure that beneficial uses are protected, and to document any other sites in the estuary that may be exhibiting exceedances similar to the mouth of the Petaluma River. Based on the consistently high levels documented at the Petaluma River mouth, the RMP and special study spatial coverage is not adequate to conclude that unmonitored freshwater/saltwater interfaces or actively dredged river channels are meeting the water quality standards for copper and nickel." New information bore out this statement, since shoal monitoring in San Pablo Bay showed exceedances of 3.1 µg/L at two monitoring stations in June 2001. However, no exceedances of the criterion maximum concentration (CMC or acute criterion), which is 4.8 µg/L for dissolved copper, have been recorded in 466 samples since the RMP began in 1993.

Additional information was submitted by RWQCB staff to the SWRCB by memorandum dated February 26, 2002 citing the available Step 1 NDB water effect ratio (WER) data as further support for the original recommendation to de-list copper. That memo noted that both shallow and deep-water locations WERs were higher than 1.5 and usually above 2. The CTR allows the national criterion of 3.1 µg/L to be multiplied by the WERs developed in accordance with USEPA guidance to generate applicable thresholds of impairment. Accordingly, a site-specific objective for copper based on WERs does not have to be adopted in the Basin Plan before the State Board can de-list based on the available information and the CTR at 40 CFR 131.38 (b)(1), footnote i, and (c)(4)(i) and (iii).

Available ambient dissolved copper concentrations in the estuary never exceeded the most conservative WER-based objectives. This statement was also true for the mouth of the Petaluma River, and as such, RWQCB staff recommended that it also <u>not</u> be listed for copper. The two new data points from the San Pablo Bay shoals did not exceed the WER-based chronic objective, nor the acute objective of 4.8 µg/L, the latter of which should not be exceeded more than once in three years, according to USEPA guidance.

The WERs demonstrated that Bay waters consistently render copper less toxic than in clean laboratory waters, and justify a site-specific objective(s) for copper in San Francisco Bay segments that have concentrations close to or intermittently above 3.1 µg/L. Since the information was available to support a finding that the WER adjusted water quality standard for copper was met in the San Francisco Estuary north of the Dumbarton Bridge, but that numeric site-specific objectives were not established, the de-listing recommendation was accompanied by a recommendation to establish one or more site-specific objectives based on the latest scientific information. Also, as stated in the November 14, 2001 staff report, de-listing needed to be accompanied by commitments by dischargers to copper pollution prevention to meet the anti-degradation portion of the water quality standard.

Based in part on the Step 1 NDB WER and related ambient concentration information submitted to the RWQCB and SWRCB staff in 2002 as part of the 2002 303(d) list update process, the SWRCB approved on February 4, 2003 the 2002 303(d) list. The SWRCB list included the de-listing of copper throughout the Bay and nickel throughout the Bay, except for nickel in the area around the mouth of the Petaluma River. USEPA gave final approval on July 25, 2003 to the SWRCB 2002 303(d) list, including de-listing copper for the Bay north (and south) of the Dumbarton Bridge.

However, USEPA did not approve de-listing nickel for Lower San Francisco Bay, San Pablo Bay, Suisun Bay, and the Sacramento/San Joaquin Delta because USEPA asserted that the applicable WQO was the Basin Plan 7.1 µg/L total metals nickel objective. The nickel total metals objective was exceeded 102 times since 1993 in those segments while the CTR 8.2 µg/L dissolved metals objective was only exceeded four times and only at the mouth of the Petaluma River. USEPA established a low priority ranking for the nickel listing noting that "the State is in the process of developing site-specific water quality standards for nickel that will likely be attained. Therefore it is most reasonable to proceed with water quality standards modifications that will likely obviate the need to complete a nickel TMDL for the Bay."

On January 21, 2004, the RWQCB approved amendments to the Basin Plan that replaced the total metals water quality objectives with the CTR dissolved metals objectives. Once these amendments are deemed in effect (following SWRCB, OAL, and USEPA approval), USEPA could proceed with de-listing the Bay for nickel, except for the Petaluma River mouth, unless a NDB SSO has been adopted by then. The nickel SSO adopted for the LSB is based on recalculation of the national copper criterion and is therefore a value technically applicable Bay-wide.

1.5 Clean Estuary Partnership

This work is being performed under the direction and review of the Clean Estuary Partnership. The Clean Estuary Partnership (CEP) is a cooperative partnership, including three official partners:

- San Francisco Bay Regional Water Quality Control Board (RWQCB)
- Bay Area Stormwater Management Agencies Association (BASMAA)
- Bay Area Clean Water Agencies (BACWA)

The goal of the CEP is to facilitate efforts to improve water quality in San Francisco Bay. The CEP is working towards developing water quality management strategies, including TMDLs, which identify pollutant sources, assess impacts, and set forth actions that will lead to solutions. This report on copper and nickel is one of a series of impairment assessment and conceptual model reports being developed by the CEP. The impairment assessment reexamines the question of whether the Bay is impaired by copper and nickel. The conceptual model examines what we know about the inputs and fates of copper and nickel in the ecosystem. Together, the impairment assessment and conceptual model will be used to determine management actions that should be taken to maintain or lower the concentrations of copper and nickel in the Bay and additional data that are needed to make that decision.

2. IMPAIRMENT ASSESSMENT

The assessment of the degree to which uses of the San Francisco Bay north of the Dumbarton Bridge are impaired by levels of dissolved copper or nickel in the aquatic environment is presented in this section. The aquatic environmental compartments considered in this assessment include the water column and the surface sediments of San Francisco Bay.

From considerations of the impairment assessment work on copper and nickel in the Lower South Bay and from meetings and communications from interested parties NDB, the following set of management questions have emerged which form the basis for the impairment assessment for San Francisco Bay NDB are described in this section.

1. Will the adoption of site-specific objectives lead to increased loadings from point sources that will have a measurable impact on dissolved water column copper and nickel concentrations in SF Bay?
2. What implementation measures are needed to ensure that existing copper and nickel concentrations in the water column and surface sediments of the Bay will not increase significantly?
3. Does copper toxicity to sensitive invertebrates (as measured by a Water Effects Ratio) vary significantly over space or time in the Bay?
4. Do existing copper or nickel concentrations in surface sediments cause sediment toxicity in the Bay?
5. Will additional loadings of copper and nickel from point sources produce significant changes in sediment concentrations or sediment toxicity in the Bay?
6. Do existing dissolved copper or nickel concentrations cause phytoplankton toxicity in the Bay?

2.1 Water Quality

Copper and nickel toxicities are directly proportional to their free ionic concentrations. Free ionic concentrations of these metals are dependent on site-specific factors such as pH, hardness, suspended solids, dissolved oxygen (i.e., Redox state), dissolved carbon compounds, salinity, and other constituents. Because of the potential for spatial inaccuracies in the national aquatic-life criterion, USEPA has provided guidance concerning three procedures that may be used to convert a national water quality criterion into a site-specific criterion [USEPA, 1994]. One of these, the Indicator Species procedure, is based on the assumption that characteristics of ambient water may influence the bioavailability and toxicity of a pollutant. Under this procedure, acute toxicity in site water and laboratory water is determined in concurrent toxicity tests using either resident species or acceptable sensitive non-resident species, which can be used as surrogates for the resident species. The ratio of the ambient to the laboratory water toxicity values, deemed a water effects ratio (WER), can be used to convert a national concentration criterion for a pollutant to a site-specific concentration criterion (or site-specific objective (SSO) in California terminology).

Findings from prior SSO related studies in Lower South Bay identified in the San Jose WER report (p. 4-43) [City of San Jose, 1998] include:

- The toxicity of copper and nickel in Lower South Bay is less in ambient site-water than the national water quality criteria predict (i.e., Water Effect Ratio[1] values are significantly greater than 1.0);
- The amount of bioavailable copper and nickel in San Francisco Bay is reduced by the presence of water quality components, which make up the apparent complexing capacity of Lower South San Francisco Bay. These components can bind with copper and nickel, making them biologically unavailable (i.e., natural or anthropogenic organic ligands) or may compete for receptor sites on, or in, the organism (i.e., manganese and iron);
- The apparent complexing capacity is greatest in the extreme northern and southern portions of San Francisco Bay;
- The amount of bioavailable copper decreases from north to south in the Lower South Bay (i.e., mean WER values increase in the South Bay in a southward direction);
- Existing toxicological data indicate that the USEPA national aquatic life criteria for copper and nickel are over-protective of the beneficial uses of Lower San Francisco Bay; and
- The Lower South Bay results could justify multiple WER values (i.e., one for the northern end, one for the southern most reaches).

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[1] A WER is the ratio of toxicity of a given pollutant in site water to toxicity in laboratory water. If the value of the water effect ratio exceeds 1.0, the site water reduces the toxic effects of the pollutant being tested.

2.1.1 USEPA Criteria Methodology

Because a national aquatic life criterion might be more or less protective than intended for the aquatic life in most bodies of water, EPA has provided guidance concerning three procedures that may be used to derive a site-specific criterion [USEPA, 1994]:

2.1.1.1 Recalculation Procedure

The Recalculation Procedure is intended to take into account relevant differences between the sensitivities of the aquatic organisms in the national dataset and the sensitivities of organisms that occur at the site. This procedure involves eliminating non-resident species from the national data set of aquatic species whose toxicity test results are used to compute the water quality criterion, and then recalculating a site-specific objective with the modified set of species.

2.1.1.2 Indicator Species Procedure

The Indicator Species procedure is based on the assumption that characteristics of ambient water may influence the bioavailability and toxicity of a pollutant. Acute toxicity in site water and laboratory water is determined in side-by-side toxicity tests using either resident species or acceptable sensitive non-resident species which are used as surrogates for the resident species. The Indicator Species Procedure allows for modification of the national criterion by using a site-specific multiplier that accounts for ambient water quality characteristics that may affect the bioavailability of the pollutant in question. As part of this procedure, a water effects ratio (WER) is determined using results from toxicity tests performed in ambient water and laboratory water.

A WER is the ratio of toxicity of a compound to an aquatic organism when the tests are performed using standard laboratory water versus the toxicity when the tests are performed using ambient water. A WER is expected to appropriately take into account the (a) site-specific toxicity of a compound and (b) interactions with other constituents of the site water that may either reduce or increase the toxicity of the compound in question. If the value of the water effect ratio exceeds 1.0, the pollutant is less toxic in the site water than in laboratory water. The difference in toxicity values, expressed as a WER, is used to convert a national water quality criterion for a pollutant to a site-specific water quality criterion.

2.1.1.3 Resident Species Procedure

This procedure is used to account for differences in resident species' sensitivity and differences in bioavailability and toxicity of a material due to the physical and chemical characteristics of the ambient water. The Resident Species Procedure allows for modification of the national criterion by concurrently testing resident species for chronic and acute toxicity in ambient site water.

2.1.2 Water Column-based Site-Specific Objectives for Copper and Nickel

2.1.2.1 Copper

For copper, the City of San Jose used the Indicator Species Procedure in its Impairment Assessment. The range of adjusted WERs for the two Dumbarton stations used to derive a LSB final dissolved copper WER and SSO was 2.2 to 4.5. The range of chronic SSOs for the lower South Bay resulting from the Impairment Assessment was 5 to 12 µg/L dissolved copper. EPA reviewed this work and found that the species used were appropriate, the data valid and the conclusions reasonable [USEPA July 27, 1998].

Copper WER studies performed in San Francisco Bay North of Dumbarton Bridge have measured dissolved WER values ranging from 1.6 to 5.3. The mean WER value measured in all NDB samples was 2.7. A range of chronic copper SSOs of 6.0 to 8.6 µg/L NDB was derived from the observed WER values using the pooled data for Regions 1, 2, 3 and for Regions 4 & 5 multiplied by either 3.1 µg/L (the CTR WQO) or 2.5 µg/L (the San Jose recalculated national WQO) [EOA/LWA, 2004].

2.1.2.2 Nickel

For nickel, a combination of the Recalculation procedure and modification of the EPA recommended Acute-to-Chronic Ratio (ACR) was used by San Jose to develop site-specific modifications to the national water quality criterion. In 1995, Watson, et al. (1996) recalculated the numeric nickel national water quality criterion using the procedure outlined by the USEPA (Carlson, et al. 1984). The corrections, additions, and deletions resulted in a proposed criterion of 10.2 µg/L using the most conservative approach. During this recalculation process, it became obvious that there were no recent chronic data that could be used to recalculate the Final Acute-to-Chronic Ratio (FACR).

The FACR derived in 1986 (17.99) was based on two freshwater and one marine species. There was a large difference between the freshwater and saltwater ACR values that contributed to the FACR. The ACR for the freshwater minnow, *Pimephales promelas*, was 35.58 and that for the waterflea, *Daphnia magna*, was 29.86. Only one marine species, the mysid shrimp, *Mysidopsis bahia* (since reclassified as *Americamysis bahia*), had verifiable chronic data which resulted in a single marine ACR value of 5.48.

In 1997, Watson, et al. (1999) designed and conducted acute and chronic flow-through bioassay tests on three marine species (topsmelt fish, *Atherinops affinis*; red abalone, *Haliotes rufescens*; and the mysid shrimp, *Mysidopsis intii*). The topsmelt is a native to Lower South San Francisco Bay, while the other two species are West Coast natives and commonly used surrogate resident species. Abalone and mysids were found to be far more sensitive to nickel than was topsmelt. Chronic values for abalone and mysids were similar (26.43 and 22.09 µg/L, respectively), and were lower than available literature values. The chronic value for the topsmelt was 4,270 µg/L.

The resultant acute-to-chronic ratios for all three marine species tested by San Jose were remarkably similar, ranging from 5.50 to 6.73. These values were in turn comparable to the ACR value previously reported for *M. bahia* of 5.48 (USEPA 1986). A FACR derived solely from a geometric mean of these four marine species ACRs would be 5.959. An alternative FACR of 10.50 was also developed, using a combination of the four marine ACRs plus two freshwater ACRs.

Watson, et al (1996, 1999) updated the national data-set by deleting non-native species, eliminating questionable data from the data set, adding additional saltwater acute and chronic test data to the dataset, and recalculating both new "proposed" national and site-specific criteria for nickel.

Since abalone is a commercially important species, the calculated Final Acute Value (FAV) that would normally be used for criteria derivation was replaced in the national dataset by the lower (more conservative) abalone Species Mean Acute Value (145.5 µg/L) in order to protect this species. Thus, the recalculated potential national and "South San Francisco Bay" site-specific FAVs were 145.5 µg/L and 124.8 µg/L, respectively. While the San Jose reports used the terminology "South San Francisco Bay " SSOs, the approach taken resulted in a range of SSO values applicable throughout the Bay and potentially to the West Coast. This report will use the "Resident Species" terminology for this SSO approach.

Using the two updated FACRs (marine and combined freshwater plus marine) and the two recalculated FAVs (national and resident species), four alternative SSOs can be derived using the Formula: FAV ÷ ACR = CCC

1) Recalculated National Criterion/Combined Freshwater and Marine ACR;
145.5 µg/L ÷ 10.50 = 13.86 µg/L

2) Recalculated National Criterion/Marine ACR
145.5 µg/L ÷ 5.959 = 24.42 µg/L

3) SF Bay Resident Species/Combined Freshwater and Marine ACR; and
124.8 µg/L ÷ 10.50 = 11.89 µg/L

4) SF Bay Resident Species/Marine ACR;
124.8 µg/L ÷ 5.959 = 20.94 µg/L

The chronic values of 22.09 and 26.43 ug /L for mysids and abalone, respectively indicate that all but option 2) (24.42 µg/L) of the above four potential nickel SSOs would be protective (in clean laboratory water) of the more sensitive mysid (and abalone) and, as such, be protective of the Beneficial Uses San Francisco Bay and North and South of the Dumbarton Bridge. It should be noted, however, that these SSO values are based on clean laboratory toxicity test results and do not include any of the ambient "apparent complexing capacity" present in the Bay that may be responsible for making nickel even less bioavailable to aquatic organisms.

EPA reviewed this San Jose work and found that the species and methodologies used were appropriate for developing site-specific modifications to the national water quality criterion for nickel. As such, no additional toxicity testing is required to derive a nickel SSO for other regions of the Bay. Use of the resident species dataset, while more conservative, would appear appropriate for establishing a NDB SSO, versus use of the recalculated national dataset.

Decisions are required as to whether it is more technically appropriate to use the four species marine ACR versus the combined freshwater/marine (used for the LSB) given the relative robustness of the marine ACR dataset.

2.1.3 Impairment Assessment using Site-Specific Objectives

Comparison of ambient dissolved copper and nickel concentrations in San Francisco Bay NDB with the ranges of site-specific objectives noted above indicates that the Bay would be in consistent compliance with those objectives. Using the site-specific objectives as indicators of the condition of aquatic life uses, the conclusion would be that such uses in the Bay NDB are not likely to be impaired by either copper or nickel. This finding would be consistent with the finding of the copper and nickel impairment assessment report and Basin Plan amendment for the Lower South Bay.

2.1.4 Uncertainty

The following areas of uncertainty were identified in the Lower South Bay studies and are applicable to the use of site-specific objectives as the basis for the impairment assessment in the Bay NDB.

- Use of single sensitive organisms (early life stage) in lab water
- Use of surrogate sensitive fish and invertebrate species to indicate toxicity to native species
- Phytoplankton toxicity
- Length of toxicity tests versus full life exposure
- Limited number of Nickel ACR values

Each of these areas of uncertainty were previously addressed in the impairment assessment report prepared for the Lower South Bay. That information is incorporated herein by reference. Additional information to resolve uncertainty regarding phytoplankton toxicity is provided in Section 2.5 of this document.

2.2 Sediment Quality

2.2.1 Sediment Concentrations

Average surface (top 5 cm) sediment copper concentrations for San Francisco Bay range from approximately 16 to 63 mg/kg dry weight, based on data collected by the Regional Monitoring Program over the period from 1993 through 2001. Highest copper levels in surface sediment (55 to 63 µg/L) occur in the northern areas (Napa River, Petaluma River, Grizzly Bay and Honker Bay) where the percent fines (< 63 um) are highest (greater than 90% fines). By contrast, lowest levels of copper in surface sediment (16 to 20 µg/L) have been measured at non-depositional sites (Sacramento River, Pacheco Creek, etc) where coarse sediments prevail (less than 20% fines) (see **Tables 3.5 & 3.6**).

Average surface sediment concentrations for nickel for the Bay range from 65 to 110 mg/kg dry weight (RMP data for 1993-2001). Nickel levels follow the pattern exhibited by copper, with highest concentrations in the same areas where fines exceed 90%. Nickel is strongly enriched in some geologic components of the northern Bay. Analysis of sediment cores by Hornberger *et al.*, 1999 and Luoma *et al.*, 1998 indicates that elevated concentrations of nickel in surface sediments in North San Francisco Bay were originated from natural geologic outputs, likely from nickel deposits in ultramafic rocks.

The ambient copper and nickel concentrations in surface sediments of San Francisco Bay are not at levels of concern. While no enforceable sediment quality objectives have been adopted in California, one common frame of reference for sediment quality evaluation is the effects-range numerical values produced by Long *et al.* for NOAA. Sediment quality guidelines [Long *et al.*, 1995; Long and Morgan, 1990] were used to evaluate if sediment concentrations were within ranges that have been previously associated with biological effects. Those guidelines were derived from a large national database and are currently the most widely used and accepted sediment effects guidelines available. In interpreting the guidelines, concentrations below the Effects Range-Low (ERL) are not typically associated with adverse effects, concentrations between the ERL and Effects Range-Median (ERM) are occasionally associated with adverse effects, and concentrations above the ERM are frequently associated with adverse effects [Long *et al.*, 1995].

The ERL and ERM values developed by Long, *et al.* for copper are 34 and 270. Comparing these values with observed surface sediment concentrations in San Francisco Bay NDB, approximately half of the sites sampled showed copper concentrations that exceeded the ERL value. The highest copper levels in surface sediments in the Bay NDB were in Honker Bay, where levels reached 63 mg/kg. This value was far below the ERM value of 270 mg/kg, a level at which effects are expected.

Effects-Range values for nickel are not considered to be very accurate predictors of effects [Long *et al.*, 1995] because of limited data. Therefore, similar comparisons of observed nickel data with Effects-Range values for nickel is not deemed to be useful.

2.2.2 Sediment Toxicity

Sediment toxicity is an area of uncertainty, based on the fact that average surficial sediment concentrations in San Francisco Bay NDB can range from 2 to 3 times higher than an average background concentration of 20 mg/kg. As stated in the Impairment Assessment Report (IAR) for Lower South Bay:

> *"There are currently no definitive methods that can be used to determine whether any observed sediment toxicity is caused by the presence of copper. Sediments are extremely complex and even though many of the components that make up the sediment are fairly well known, interactions between those components remain unclear at this time."*

No sediment special studies were recommended by the IAR for Lower South Bay because of the lack of any methodology that can be used to definitively assess the specific role that copper plays in any observed sediment toxicity.

Surface sediment samples have exhibited toxicity to test organisms at a number of sites throughout the Estuary. Since 1993, the RMP has seasonally evaluated the toxicity of sediments to mussel embryos and amphipods. For each seasonal sampling period since 1993, the proportion of sediment samples that were toxic to at least one test organism ranged from 33% to 100%, with no clear overall trend, but with clear seasonal differences. As with water toxicity, sediment toxicity is more frequent in the Estuary during the wet season than in the dry season, suggesting stormwater runoff may be an important source of constituents that cause sediment toxicity. This pattern is particularly clear for amphipods. For example, 51% of the winter samples tested between 1993 and 1999 were toxic to amphipods, while only 16% of the summer samples were toxic during this period.

Sediment from specific locations in the Estuary has been most frequently toxic to amphipods and mussel embryos. Samples from Grizzly Bay, the mouth of the Napa River, Redwood Creek, and the South Bay have often been toxic to amphipods. Samples collected in the northern Estuary (Grizzly Bay and the Sacramento and San Joaquin Rivers) have often been toxic to mussel embryos. Grizzly Bay sediment is contaminated by a complex mixture of moderate concentrations of trace metals and trace organic compounds.

Initial analyses to identify the causes of observed sediment toxicity have yielded a variety of answers, in large part due to the complex mixtures of chemicals involved. Comparisons of the chemical data to toxicity test data indicated that amphipod mortality and reductions in normal mussel embryo development may have been related to various chemicals in sediments [Thompson *et al.*, 1999; Anderson *et al.*, 2001; Phillips *et al.*, 2000].

Causes of sediment toxicity have been further investigated using toxicity identification evaluations (TIEs). TIEs are laboratory procedures designed to characterize the class of chemicals causing toxicity, then identify and confirm specific chemicals responsible for toxicity. TIE procedures developed by the U.S. EPA and novel techniques developed as part of RMP special studies have shown that divalent metals may have contributed to inhibited bivalve embryo development and caused amphipod mortality in sediment samples from the Grizzly Bay station [Phillips *et al.*, 2000, Anderson *et al.*, 2001]. However, the TIE findings were not conclusive regarding the contribution of copper to observed sediment toxicity effects. (See City of San Jose comments on the Phillips *et al.* (2000) paper in Attachment 1 to their May 18, 2004 comment letter included in **Appendix A**.)

The source of toxicity in Grizzly Bay sediment samples is clearly unknown. There are a number of issues that would require more investigation to link observed toxicity to copper, if such a link exists. It is therefore recommended that the results from TIE testing should only be used to develop a more definitive test procedure to confirm the suggested toxicant. Chemical specific data must also be used to verify the source of toxicity conclusively. Pollutants should be positively identified using statistical testing of biological endpoints that can be compared to chemical specific toxicological data (taken from EPA criteria documents or other sources) for the pollutant believed to be associated with observed toxicity.

2.2.3 Plans to Resolve Uncertainty

Sediment toxicity is likely to persist for many years to come, considering the continuing toxicity observed in the RMP. Additional special studies are planned to further examine whether water and sediment toxicity tests used in the RMP are accurate predictors of impacts on the Estuary's aquatic and benthic communities. Because the amphipod (*Eohaustorius estuarius*) used in the

RMP is not a resident of the Estuary, there has been some debate regarding its ecological relevance. Sensitivity of selected resident organisms to key chemicals of concern will be compared to sensitivity of this amphipod species. Similar tests are planned to evaluate the water test species. Information from these experiments will confirm whether the current species employed are adequately sensitive to represent and ensure the protection of the Estuary ecosystem. Determination of the causes of sediment toxicity observed in monitoring will ultimately require evidence from numerical analysis of monitoring data and manipulative experiments. Such experiments will include continued toxicity identification evaluations (TIEs), laboratory and/or *in situ* sediment spiking and dose-response tests at concentrations shown to be associated with toxicity [SFEI, 2003].

2.3 Benthic Macroinvertebrates

Community analysis of benthic macroinvertebrates is a useful indicator for overall ecosystem health, but is typically not a valuable indicator for assessment of impairment by single stressors. Many of the stressors and pollutants in the Bay co-vary – as a result, it is difficult to attribute or identify an impact to a single pollutant or stressor. The best use of this indicator would be to confirm impacts that were predicted by indicators that had a tighter linkage to copper and nickel. The IAR for Lower South Bay concluded that community analysis of benthic macroinvertebrates was not a useful indicator for the assessment of copper and nickel impairment.

The USEPA aquatic life criteria are calculated to be protective of sensitive invertebrates and fish. Therefore, as described elsewhere in this report, the water column-based site-specific objectives for copper and nickel directly account for toxicity to sensitive benthic invertebrate species (e.g. copper sensitivity to *Mytilus edulis* and nickel sensitivity to mysids).

2.4 Fish and Shellfish

The USEPA water column-based aquatic life criteria for copper and nickel directly account for toxicity to sensitive fish and shellfish species. Of the four most sensitive species to copper (which govern the copper criteria value), one (summer flounder, *Paralichthys dentatus*) is a fish species: This sensitive fish species has an acute LC50 value of 12.7 µg/L dissolved copper, while the most sensitive fish (chronic) has a chronic toxicity value of 5.9 µg/L. By comparison, the acute toxicity value for the most sensitive invertebrate species (mussel, *Mytilus edulis*) is roughly 8 µg/L. Maximum ambient levels of dissolved copper NDB are four-fold and two-fold lower than the acute and chronic toxicity values for these sensitive fish in clean laboratory water, respectively. At these ambient levels, impairment of fish species in San Francisco Bay by copper is unlikely.

For nickel, none of the four most sensitive species in the USEPA criteria toxicological data set are fish. In fact, the most sensitive fish species in the USEPA data set (Atlantic silverside, *Menidia menidia*) has an acute LC50 value of 7958 µg/L nickel. With ambient levels of dissolved nickel NDB typically less than 4 µg/L, no impairment of fish species by nickel is likely in San Francisco Bay.

2.5 Copper Toxicity to Phytoplankton

Certain phytoplankton species are very sensitive to concentrations of free ionic copper. Therefore, phytoplankton have been an important consideration in prior copper impairment assessments (IA) of Lower South San Francisco Bay (LSB). Many of the IA conclusions, findings, and uncertainties associated with phytoplankton toxicity in the LSB are applicable to the Bay north of Dumbarton Bridge (NDB). This section summarizes the findings of the prior IA regarding phytoplankton and the results of studies undertaken to address the issue of whether phytoplankton are being adversely impacted by ambient levels of copper in the Bay.

2.5.1 San Jose SSO Report (Lower South Bay)

The City of San Jose, in their report "*Development of a Site-Specific Water Quality Criterion for Copper in South San Francisco* Bay" [City of San Jose, 1998] summarized the available toxicity values for various nationally and locally present phytoplankton. The report described the limitations of currently available phytoplankton laboratory toxicity testing methods and the rationale why phytoplankton were not used for developing the LSB Water Effect Ratios (pp. 50-53 Protection of South Bay Plant Life).

2.5.2 Draft Impairment Assessment Report (Lower South Bay)

In July 1999, the Copper Nickel TMDL Work Group (TWG) of the Santa Clara Basin Watershed Management Initiative (WMI) provided initial comments on the draft *Impairment Assessment Report for Copper and Nickel in Lower South San Francisco Bay* [May 1999] (IAR). Comments on phytoplankton toxicity were the most numerous, with 21 out of 57 comments were either directly or indirectly (i.e., copper speciation and phytoplankton community structure) related to phytoplankton toxicity.

In response to these concerns, additional literature was compiled and the available data re-evaluated in an issue paper in July 1999. The Assessment Team compared the findings of this re-evaluation to the project's established Indicator Evaluation Criteria (Table 2-1, IAR, May 1999). These criteria were developed early in the South Bay impairment assessment process to evaluate the applicability of individual environmental measurements as indicators of beneficial use impairment. Based on several factors, ranging from feasibility issues to the ability to interpret test results, phytoplankton were judged not to be an acceptable indicator for the impairment assessment.

Special studies were proposed in the draft IAR to address some of the uncertainties that affect the ability to interpret phytoplankton study results (as well as other relevant laboratory and field results).

2.5.3 Conceptual Model Report (Lower South Bay)

The "*Conceptual Model Report for Copper and Nickel in Lower South San Francisco Bay*" [Tetra Tech, 1999] (CMR) stated that additional data should be collected to further assess the speciation of copper and nickel in the Bay. The presence of ionic forms of these metals was deemed to be important to the assessment of potential impacts on phytoplankton.

At the time the CMR and IAR were being prepared, there were relatively few measurements in San Francisco Bay of free ionic copper and complexing ligand types and concentrations. Work by Bruland *et al.* [1992] provided initial information to indicate that significant complexation occurs in the Bay. The recommendation was to conduct additional speciation measurements and to compare the free ionic copper concentrations to the known threshold toxicity levels (10^{-11} M or 6 x 10^{-5} µg/L) of sensitive phytoplankton in seawater having little or no complexing capacity and low concentrations of competing ions (i.e. zinc, manganese, and iron). Free ionic copper concentrations at or above these levels would be an indication that the potential for impairment to phytoplankton productivity exists.

2.5.4 Final Impairment Assessment Report (Lower South Bay)

The final "*Impairment Assessment Report for Copper and Nickel in Lower South San Francisco Bay*" [Tetra Tech, 2000a] (IAR) found that the weight of available evidence supported the conclusion that impairment of beneficial uses due to copper and nickel was unlikely. The IAR also found that uncertainties remained regarding the scientific information upon which that conclusion was based. The IAR summarized the key uncertainties and potential special studies to reduce the associated level of uncertainty (Section 5.3 Uncertainties and Special Studies). Two of the three areas of uncertainty cited in the IAR were similar to those identified in the CMR and included 1) toxicity of copper to phytoplankton and 2) biogeochemical processes influencing copper and nickel speciation relative to bioavailability.

The Final IAR included information on phytoplankton community structure, species abundance, the feasibility of conducting laboratory bioassays to directly measure copper toxicity, and whether existing dissolved copper levels were toxic to phytoplankton. Articles were cited which indicated that certain marine species of phytoplankton, in particular species of cyanobacteria, were highly sensitive to copper. Additionally, some studies in San Francisco Bay had suggested that cyanobacteria were not commonly found in the Bay. Based on these studies, some South Bay stakeholders had questioned whether existing dissolved copper concentrations were causing toxicity to these species.

Prior to the release of the final South Bay Impairment Assessment Report, two papers regarding the occurrence of the cyanobacteria *Synechococcus* sp. in San Francisco Bay were published. Both papers[2], which were included in the South Bay Impairment Assessment Report Appendices, showed that cyanobacteria were a "persistent component of the San Francisco Bay phytoplankton in all the estuarine habitats" in 1998 and 1999.

After receiving this information, the Copper and Nickel TMDL Work Group requested the Technical Review Committee to examine the information and comment on its significance to findings of the South Bay Impairment Assessment Report. The Technical Review Committee's response lent additional support to the overall finding that impairment to the beneficial uses due to ambient copper concentrations is unlikely.

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[2] Ning, X., J. E. Cloern and B. E. Cole. 2000. Spatial and temporal variability of picocyanobacteria *Synechococcus* sp. in San Francisco Bay. Limnology and Oceanography; Palenik, B. and A. R. Flegal,1999. Cyanobacterial populations in San Francisco Bay. Regional Monitoring Program for Trace Substances, Technical Report. (http://www.sfei.org/rmp/reports/cyanobacterial.html)

The final conclusion reached in the South Bay IAR was that ambient levels of dissolved copper in South Bay (which are the highest levels in the Bay) were not adversely affecting phytoplankton populations in the South Bay. The South Bay IAR was reviewed by SWRCB peer reviewers, Dr. Alex Horne and Dr. David Jenkins. Dr. Horne concluded that the IAR "reflects good science and a thorough external reviewing of the complex physical, chemical, biological and regulatory problems of assessing impairment of beneficial uses…". Professor Horne strongly supported the recommendation of the IAR that the 303(d) list should be updated to de-list copper and nickel as stressors for Lower South San Francisco Bay.

2.5.5 San Jose Phytoplankton Study

Issues identified in the South Bay Impairment Assessment study included (a) whether copper-sensitive phytoplankton species are important to the San Francisco Bay ecosystem, (b) whether copper-sensitive species are present in the Bay; and (c) the fact that USEPA criteria development is not driven by the consideration of phytoplankton toxicity. These issues are also relevant to the consideration of copper and nickel impairment in San Francisco Bay north of the Dumbarton Bridge.

The City of San Jose agreed to pursue additional studies of phytoplankton distribution and abundance. In cooperation with the Regional Board and local scientific experts, the City designed a project to develop bioassessment techniques for South San Francisco Bay's plankton community.

In 2001 San Jose began a project to develop and conduct a pilot monitoring program of the plankton of the South San Francisco Bay (i.e., south of the San Mateo Bridge) to provide guidelines for long-term monitoring, and recommendations of indicators of ecosystem condition. The project had two phases: (a) development of a monitoring plan including potential indicators of ecosystem condition; and (b) field work to test and further refine the monitoring plan and proposed indicators. The biological, physical, and habitat information collected in this study were intended to aid in the understanding of the effects of natural variability on plankton community composition in the South Bay.

In physically dynamic environments such as San Francisco Bay, the effects of natural variability (i.e., physical changes in the environment, such as salinity, temperature, seasonal runoff, etc.) on phytoplankton community structure must be understood in order to appropriately evaluate effects from other sources.

Results were presented in a report titled "*Plankton Communities in South San Francisco Bay: Historical Data Analysis and Pilot Monitoring, Phase I Draft Report"* prepared by the Romberg Tiburon Center for Environmental Studies, San Francisco State University dated May 1, 2003. A brief summary of the report's findings and conclusions are presented below.

The Phase I monitoring found nutrient and chlorophyll levels in South San Francisco Bay compared well with USGS data for Station 36 sampled five times between 1992 and 1999. Picocyanobacteria (among the most sensitive phytoplankton to copper) were still present and varied a great deal. For example, average cyanobacteria measured by the study in August 2002 (0.40E07 and 0.38E07 cells/L) were an order of magnitude lower than previously published values of Ning *et al.* [2000] for August 1998. However, May 2002 abundance values for cyanobacteria (15.5E07 & 13.1E07 cells/L) were consistent with those reported for May 1998 for South S.F. Bay (15.4E07 cells/L) by Ning *et al.* [2000]. Enumeration of phytoplankton samples collected seven times from August 2001 to February 2003 indicated the usual presence of diatoms, large and small (5 mm) flagellates, dinoflagellates, and cyanobacteria.

The Phase I study confirmed the presence of sensitive phytoplankton species in South San Francisco Bay. This study found that "Regardless of site or season, the [Cu^{2+}] values throughout San Francisco Bay did not exceed $1E^{-13}$ M, suitably below the toxicity limit for sensitive aquatic organisms [Buck & Bruland, 2003].

The study review of extant data was not able to further develop or link any of the proposed variables to specific indicators of ecosystem health. Further, the study did not link pollutant data to ecosystem health, a major project objective. The merits of the study were discussed among the interested parties (Regional Board, City, SFSU). That discussion concluded that it was not likely that indicators of ecosystem health could be linked to anthropogenic effects or to specific pollutant data in the foreseeable future. Therefore, the study was concluded.

2.5.6 CALFED Open Water Processes White Paper

One of the investigators in the San Jose/RTC project, Dr. Wim Kimmerer prepared a draft White Paper for the CALFED Ecosystem Restoration Program titled "*Open Water Processes of the San Francisco Estuary"* [Kimmer, 2003]. The document contains a comprehensive literature review and discussion of phytoplankton, particularly in the context of primary productivity in the Bay. It covers the multitude of complex factors that affect phytoplankton growth, species composition, and the timing and location of blooms. These include light and nutrient limitation, grazing, hydrodynamic effects, and the impact of the Delta and the Pacific Ocean. Copper is not mentioned as a factor influencing phytoplankton dynamics in the Bay. The White Paper lists the following eight key uncertainties regarding phytoplankton primary production, none of which include copper toxicity:

- How do phytoplankton and higher plants interact, especially in the Delta?
- How will changes in sediment supplies to the water column affect primary production?
- How have biomass and primary production changed as a result of *P. amurensis* and *Corbicula fluminea*?
- How do stratification and shoal-channel exchange influence bloom dynamics in Suisun, San Pablo, and Central Bays?
- What is the effect of losses to export pumping and agricultural diversions on phytoplankton?
- What are the effects of barriers in the Delta on phytoplankton?
- What is the influence of the coastal ocean on phytoplankton?
- What is the role of benthic microalgae in estuarine primary production?

2.5.7 USGS

The USGS in Menlo Park is continuing a long-term study of hydrography and phytoplankton in San Francisco Bay. The Principal Investigator is Dr. Jim Cloern. The objectives of this study are

(1) to track seasonal changes in basic water quality and habitat parameters that influence biological communities and the role of phytoplankton in the distribution and reactivity of trace elements and (2) to provide a depth-integrated picture of salinity, temperature, chlorophyll and suspended sediment distribution for modeling purposes. This study continues its measurement program in support of the RMP, with monthly water sampling to map the spatial distributions of basic water quality parameters along the entire Bay-Delta system. Measurements include salinity, temperature and dissolved oxygen, which influence the chemical form and solubility of some trace contaminants, and suspended sediments and phytoplankton biomass, which influence the partitioning of reactive contaminants between dissolved and particulate forms. This basic information is required to follow the seasonal changes in water quality and estuarine habitat as they influence biological communities and the distribution-reactivity of trace contaminants.

This study has documented the presence of a highly complex and at times rapidly varying phytoplankton community throughout the Bay as measured by chlorophyll concentrations. Some species composition data are compiled but reportedly information on the small cyanobacteria such as *Synechococcus* is limited since different microscopic techniques are required. RMP staff are coordinating with Jim Cloern to identify USGS plans and schedule for compiling and reporting on historic Bay-wide species composition and abundance information.

2.5.8 Basin Plan SSO Amendment Staff Report

The RWQCB "*Staff Report on Proposed Site-Specific Water Quality Objectives and Water Quality Attainment Strategy for Copper and Nickel for San Francisco Bay South of the Dumbarton Bridge*" [RWQCB, 2002]. Response to Comments noted that "virtually all information about systems as complex as Lower South SF Bay will have associated uncertainty. This does not mean that decisions cannot be reasonably made based on the strength and weight of available evidence." The IAR, CMR, and other reports had generally identified the same basic areas of scientific uncertainty, varying slightly due to their differing focus and authorship. The Staff Report cited the following four areas of remaining uncertainty:

- Copper toxicity to phytoplankton;
- Copper and nickel cycling;
- Copper sediment toxicity; and
- Loading estimates.

The RWQCB obtained funding to have additional ambient copper speciation work conducted as this was determined to be the most direct means of addressing the copper toxicity issue (see Bruland study below).

2.5.9 Bruland Copper Speciation Study

The RWQCB contracted with Dr. Ken Bruland of the University of California, Santa Cruz during 2001 to evaluate copper speciation in San Francisco Bay. Trace metal clean techniques were employed in the collection of samples on four separate occasions from six sites throughout the Bay. The six sites sampled, from south to north, include: Dumbarton Bridge, Redwood Creek, San Bruno Shoals, Yerba Buena Island, San Pablo Bay, and Grizzly Bay. The sampling took place during June 2001, July – August 2001, January 2003 and March 2003. Results were reported in a May 2002 interim report and July 2003 draft final report.

The study found that in San Francisco Bay the total dissolved copper is strongly complexed by organic ligands. The study estimated the concentrations and conditional stability constants of two classes of ambient ligands complexing copper in the Bay: a strong L_1 class and an intermediate L_2 ligand class. These ligands complex greater than 99.9% of the total dissolved copper in San Francisco Bay and, in every case, the ligand concentrations exceed the dissolved copper concentrations. This tends to reduce copper toxicity by reducing free ionic copper concentrations.

Another factor that reduces copper toxicity is competitive uptake of other divalent cations, such as dissolved manganese(II). The highest dissolved manganese concentrations were documented in the far reaches of the Bay, at the Dumbarton Bridge and Grizzly Bay sites. The manganese values observed at the other sites were significantly lower, generally less than half the levels seen at Grizzly Bay and Dumbarton Bridge. In other waterbodies, dissolved manganese/copper ratios are good predictors of copper toxicity, so dissolved manganese needs to be considered when evaluating the potential for copper toxicity.

Ligand and dissolved copper concentrations were lowest at the Yerba Buena Island site and generally increased further away from the mouth of the Bay and into the farthest North and South Bay sites. In the January and March data, Grizzly Bay, the north-easternmost site, had significantly higher ligand concentrations than any of the remaining sites. Dumbarton Bridge, the southernmost site, had the second highest ligand concentrations.

Complimentary trends were observed for the free Cu^{2+} ion concentrations, with the highest $[Cu^{2+}]$ values at Yerba Buena Island, where there was the least excess of strong L_1 ligands. The lowest $[Cu^{2+}]$ values were observed at the Grizzly Bay site, and the second lowest at Dumbarton Bridge. Regardless, at every site sampled and over all of the different sampling periods, $[Cu^{2+}]$ never exceeded 10^{-13} M, which is low enough to be nontoxic to the residing phytoplankton community. It was extrapolated from the results that if ambient dissolved copper concentrations were to increase from the current ~3.4 µg/L range to the site-specific LSB SSO of 6.9 µg/L, or approximately 108 nM, the $[Cu^{2+}]$ (free ionic copper concentration) would reach 10^{-11} M, the previously identified toxicity threshold for sensitive phytoplankton in open oceanic type seawater [Buck & Bruland, 2003].

The report concluded that strong copper-complexing ligands dominate the chemical speciation of dissolved copper in San Francisco Bay. The concentrations of these ambient organic ligands exceeds the total dissolved copper concentrations at every site, and it is these ligands which complex greater than 99.9% of the dissolved copper. This strong organic complexation of the copper results in very low free hydrated Cu^{2+} ion concentrations. Across all sites and seasons, the $[Cu^{2+}]$ values throughout San Francisco Bay did not exceed 10^{-13} M, the reported toxicity limit for sensitive aquatic organisms in oceanic systems.

In summary, these measurements, made during 2001-2003, found free ionic copper concentrations to be a factor of 100 below the threshold toxicity values for sensitive phytoplankton.

2.5.10 CVRWQCB Algae Toxicity Study

In August 2002, the Central Valley RWQCB published results of a CALFED funded study to identify the causes of algae toxicity in the Sacramento and San Joaquin River Watersheds and the Delta titled "Algae Toxicity Study Monitoring Results: 2000-2001." As noted in the report, "the cause of toxicity to algae is infrequently identified because the laboratory control is unsuitable for comparison with ambient samples and standard toxicity identification evaluation (TIE) methods are limited for use in algae toxicity tests." The study investigated alternative TIE methods, primarily using solid phase (C8) extraction in an attempt to develop better protocols to evaluate causes of toxicity. The investigation focused on organics, since herbicides (primarily diuron) appeared to be the most prevalent source of toxicity. Work is continuing on further development of the algae TIE methodology and on how phytotoxicity relates to instream impacts. The potential relevance of this project depends on its success in developing TIE methodologies that can accurately differentiate and assess impacts of water column concentrations of copper, versus other constituents, on phytoplankton toxicity.

During the Lower South Bay SSO development process, San Jose staff evaluated the potential problems (confounding factors, extrapolation to the field, and salient endpoint to regulate) associated with algal toxicity testing. (See comments in Attachment 2 to City of San Jose letter dated May 18, 2004 in **Appendix A**).

2.5.11 SCVURPPP Copper Action Plans-Phytoplankton Uncertainties and Studies

The South Bay Copper Action Plan (CAP) (June 2000) includes several baseline activities (CB-17, CB-18) to "track and encourage" activities and research intended to reduce the scientific uncertainties associated with the impairment assessment and conceptual model reports' conclusions. These copper baseline activities from the Copper Action Plan are included among the full suite of 21 baseline CAP activities in Appendix B of the Santa Clara Valley Urban Runoff Pollution Prevention Program (SCVURPPP) NPDES Permit Number CAS029718, Order Number 01-024 dated February 21, 2001 [SCVURPPP, 2001].

Since 2001, SCVURPPP has been tracking activities and research intended to reduce the scientific uncertainties associated with the South Bay Impairment Assessment and Conceptual Models Reports' conclusions. Many of these uncertainty reduction activities are applicable to assessing potential copper impacts on a Bay-wide basis rather than just in Lower South San Francisco Bay. "Track and encourage" activities are included in the annual Copper/Nickel Work Plans prepared and submitted to the Regional Board each March 1st. Actions accomplished are summarized in the Annual Report submitted each September 15th.

The copper baseline activities relevant to phytoplankton uncertainties and studies and a brief description of their linkage to copper are described below:

- CB-17 (1): Phytoplankton species toxicity and prevalence- ambient concentrations could influence phytoplankton species composition, abundance and spatial distribution;
- CB-17 (2): Measures to assess cycling and fluxes between water column, phytoplankton, sediment and benthos - improve understanding of mechanisms and

flux rates impacting water column concentrations of total, dissolved, and free ionic copper;

- CB-17 (4): Bio-assessment tools to track presence of copper sensitive taxa in Lower South Bay- independent indicator of whether ambient concentrations are adversely impacting biota.
- CB-17 (5): Assess feasibility of phytoplankton bioassays to measure toxicity- ambient free ionic copper (not complexed with organic ligands) is form toxic to phytoplankton;
- CB-18 (3): Determine Cu-L_1 and L_2 complex concentrations (copper speciation); and
- CB-18 (4): Investigate algal uptake/toxicity with competing metals- algae may preferentially uptake substances (e.g., Manganese), which may reduce the net toxicity of ambient copper concentrations.

The San Jose/RTC study provided additional information relative to CB-17 (1) further documenting the prevalence of sensitive phytoplankton in the LSB. The on-going USGS work will continue to provide related information throughout the Bay on this topic. The San Jose/RTC study concluded that CB-17 (4) was not feasible to accomplish. The results of the Bruland copper speciation work appear to adequately address CB-18 (3) and in the process reduce, and possibly eliminate the need for additional effort on CB-17 (2), CB-17 (5), and CB-18 (4).

2.5.12 Future Tracking of CAP Uncertainty Reduction Activities

In addition to the above CAP baseline activities, SCVURPPP has initiated efforts in 2004 to help develop and implement a program to more comprehensively identify, track, and encourage investigations being conducted by others in the Bay-Delta region that will provide information useful to improving the understanding of copper/nickel impacts throughout the Bay.

The RMP itself is conducting monitoring and special studies of relevance to copper such as attempting to develop improved sediment toxicity testing methods, ambient and sediment toxicity testing, and projects conducted by their various workgroups. The RMP is a member of the Interagency Ecological Program (IEP), which in turn has members or associations with many of the agencies and researchers conducting studies in the Bay-Delta region of relevance to CAP issues such as phytoplankton monitoring. The RMP has tasks in its current workplan directed towards improved data integration from other entities, and improved data dissemination.

The IEP is undergoing a comprehensive programmatic review with a final draft synthesis report from its Science Advisory Group expected in early 2003. One recommendation was that IEP Environmental Monitoring Program (EMP) data be "more rapidly and reliably turned into more useful products through increases human intellectual investment." The Bay-Delta Science Consortium (that includes most IEP members as well as several local universities and non-profit organizations) has an overall goal to "enhance cooperation and collaboration among researchers working in the Bay-Delta." As noted in the Winter 2002 IEP Newsletter, "CALFED intends to allocate one million dollars per year for the next few years to the Consortium to help sponsor activities that will help increase collaboration and cooperation." The Consortium also indicated their intent to sponsor an on-line technical journal and to "investigate ways of sharing digital information among the many data holders and increasing its utility for synthetic analyses."

A significant amount of basic and applied research has been undertaken in the region investigating Cu/Ni processes in various segments of the Bay. Much of this work is scattered about in various reports both off-line, and on-line located at websites for particular research institutions, scientific journals, stakeholder groups, and agencies. Although many of these efforts already cite and cross-reference each other, compiling these various data sources together at one location would benefit any parties interested in research on Cu/Ni processes in the region.

To assist in the tracking of information related to the CAP baseline "uncertainty" activities, SCVURPPP in March 2004 contracted with the San Francisco Estuary Institute (SFEI) to develop a website that links organizations, research, reports, and contact people for regional "track and encourage" activities and related items of interest.

Information sought will fall under three general categories: reports supporting copper TMDL efforts, academic basic research/peer reviewed literature, and institutional research reports. For the initial design, information will be organized by topic. The general topic areas will be as follows:

- Environmental Distribution
- Sources and Loads
- Transport Processes
- Chemical Processes
- Bioavailability and Effects
- Comprehensive Studies

Within the general topics, each of the specific Uncertainty Reduction Baseline Activities included in the most recent fiscal year Copper/Nickel Action Plan Workplan will be listed. Information relevant to each baseline activity will be cited and a brief synthesis provided, and updated annually, assessing the current level of uncertainty associated with each baseline activity topic.

The FY 04-05 C/NAP Workplan includes the following uncertainty reduction baseline activities:

- CB-17 (1): Phytoplankton species toxicity and prevalence
- CB-17 (2): Measures to assess cycling and fluxes between water column, phytoplankton, sediments, and benthos
- CB-17 (3): Measures to assess wet season tributary loading and loading uncertainty
- CB-17 (4): Bioassessment tools to track presence of copper sensitive taxa
- CB-17 (5): Assess feasibility of phytoplankton bioassays to measure toxicity
- CB-18 (1): Investigate flushing time estimates for different wet weather conditions
- CB-18 (2): Investigate location of northern boundary conditions
- CB-18 (3): Determine Cu-L_1 and L_2 complex concentrations (copper speciation)
- CB-18 (4): Investigate algal uptake/toxicity with competing metals
- CB-20: Measures to revise the Conceptual Model Report

SCVURPPP is providing limited seed money and in-kind assistance to RMP/SFEI to initiate this project during calendar year 2004. Since this is a project of Bay-wide benefit, stakeholders will need to identify how to integrate this into existing RMP activities or to identify other funding sources to operate and maintain the website after 2004. While the initial SFEI website effort is focused on copper, it could serve as a template and be expanded to address other constituents of concern as a potential way to access other sources of funding.

2.6 Wildlife Health Concerns

Both copper and nickel are of concern in San Francisco Bay due to concerns regarding possible effects on early life stage aquatic organisms. Neither of these metals has a strong inclination to bioaccumulate or to biomagnify in aquatic ecosystems to levels of concern to upper trophic organisms (e.g. fish eating birds or mammals). Impacts of copper and nickel concentrations on sensitive species of birds and mammals were addressed in the Lower South San Francisco Bay Impairment Assessment Report [Tetra Tech, 2000a] and were not found to be of significant concern. Therefore, impairment of wildlife by copper or nickel is unlikely in San Francisco Bay NDB and will not be addressed in this report.

2.7 Control Programs

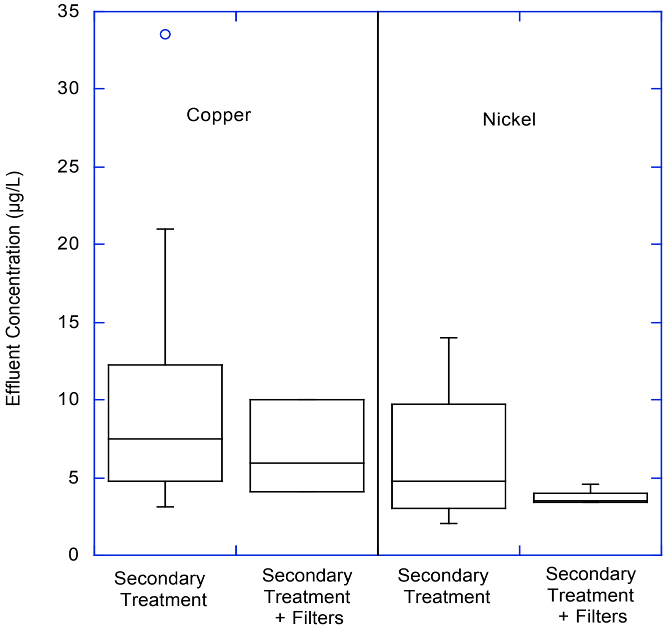
Ongoing control programs for copper and nickel from POTWs and urban stormwater are addressed in this section. These programs have been implemented in an effort to reduce effluent concentrations through source control activities. In the Lower South Bay, these control actions were a product of a working hypothesis that ambient water column concentrations will be affected by reductions in POTW and urban runoff loadings. Lower South Bay public agencies have implemented a Copper Action Plan (CAP) and a Nickel Action Plan (NAP) to ensure that control measures continue to be implemented. The benefit of these programs to ambient water quality protection is an area of uncertainty that may be addressed through use of sophisticated water quality modeling tools. (See further discussion of Action Plans in **Appendix C**).

Copper and nickel loadings from POTWs are reduced significantly through treatment. The Action Plans for North of the Dumbarton Bridge are concerned primarily with (1) development of water quality monitoring triggers and (2) development of effective source control programs. A major difference from the LSSFB is that there is a considerably larger number of municipal, industrial, and stormwater entities contributing to copper and nickel loading to the Bay north of the Dumbarton Bridge. Another difference is that not all of the actions identified for the LSSFB are appropriate for the North Bay. Finally, the presumption is that the majority of effort will be focused on copper, with knowledge that such efforts will have a collateral benefit in reducing nickel at similar sources.

2.7.1 Municipal

Pollution prevention activities targeting copper and nickel sources have been conducted by several Bay Area POTWs beginning in the early 1990's. In some cases, these activities have resulted in reductions in influent copper concentrations. Annual average copper and nickel concentrations from 2000 shown in **Figure 2.1**, demonstrate the current range of effluent levels for several Bay Area POTWs north of the Dumbarton Bridge.

Figure 2.1. Annual Average Bay Area POTW Effluent Concentrations for 2000 (12 secondary plants & 5 secondary with filters)



To assess the range and extent of ongoing copper and nickel source control activities in the Bay Area, questionnaires were sent to pollution prevention program coordinators at 39 publicly owned treatment works (POTWs) requesting information concerning historical pretreatment and pollution prevention (P2) programs targeting copper and nickel. Respondents provided information on the sources that had been targeted, the types of programs that had been implemented for these sources, and the results of efforts to measure the effectiveness of these programs in achieving copper and nickel reductions. The POTW responses were compiled and summarized in the Activity Investigation Memo, dated January 14, 2003. This Memo was included as an appendix to the June 6, 2003 Draft "Copper & Nickel North of the Dumbarton Bridge Development of Action Plans" report. Results of the P2 work were updated in September 2003 and are summarized in **Appendix C** of this report.

2.8 Impairment Summary

Impairment of aquatic life uses is the primary concern related to copper and nickel levels in San Francisco Bay NDB. The above impairment assessment addressed three primary indicators to assess potential impairment of aquatic organisms in San Francisco Bay: (1) site-specific water column criteria based on USEPA guidance, (2) surface sediment concentrations and toxicity, and (3) phytoplankton. The overriding conclusion from the impairment assessment is that impairment of aquatic life uses NDB in San Francisco Bay is unlikely. Remaining uncertainties regarding this finding are diminishing. Mathematical modeling of San Francisco Bay using available sophisticated hydrodynamic and water quality models is recommended to assist in the development and evaluation of effectiveness of management measures and in the further reduction of remaining uncertainties.

The following areas of uncertainty in the copper and nickel impairment assessment were identified and addressed in detail in the IAR for the Lower South Bay. Further consideration of these areas of uncertainty was not performed for this assessment.

- Use of single sensitive organisms (early life stage) in lab water
- Use of surrogate sensitive fish and invertebrate species to indicate toxicity to native species
- Length of toxicity tests versus full life exposure
- Limited number of Nickel ACR values

Three areas of uncertainty that have been addressed in detail in this assessment are:

- Impact of copper and nickel on phytoplankton toxicity
- Linkage of copper and nickel to observed sediment toxicity
- Impact and need for municipal and industrial source control activities to control ambient copper and nickel levels in San Francisco Bay NDB

3. CONCEPTUAL MODEL

3.1 Background

In this section, current knowledge regarding the sources, loads, distribution, transport and behavior of copper and nickel in San Francisco Bay NDB are described. This information is important to the understanding and implementation of appropriate management activities for copper and nickel.

3.2 Regional Studies

Major regional studies of copper and nickel have been performed in San Francisco Bay. These studies include:

- Conceptual Model in Lower South Bay
- Impairment Assessment in Lower South Bay

- WER Technical Study NDB
- RMP Sources and Loadings Studies
- USGS Studies

At the national level, copper toxicity has been extensively studied. Findings from those studies have been used to support the impairment assessment and conceptual model information contained in this document.

3.3 Sources & Loads to the Bay

Numerous estimates of loadings of copper and nickel to the Bay have been made. SFEI made the most recent estimate in 2000, which estimated local loads to the Bay of 74 tons per year for copper and 64 tons per year for nickel. SFEI estimated external loads from the Central Valley to be 270 and 410 tons per year for copper and nickel, respectively. The SFEI estimates do not account for re-mobilization of copper and nickel from Bay sediments, which is estimated to be an even larger source than Delta outflow from the Central Valley.

Mass loadings to San Pablo Bay and Lower South Bay have been estimated in 1997 [Rivera-Duarte & Flegal, 1997]. SFEI summarized results from that study in its report on the Sources, Pathways and Loadings Workgroup published in 2001 [Davis *et al.*, 2001]. The mass loading estimates indicated that benthic remobilization was a dominant source of loadings of both copper and nickel to the Bay, with riverine loadings next most important. For copper in San Pablo Bay, benthic remobilization is estimated to be 72% of the total loading, riverine and runoff is 26%, and POTWs and atmospheric deposition are each 1%. For nickel in San Pablo Bay, the respective loading percentages are 77%, 21%, 2% and <1%.

3.3.1 Municipal & Industrial Point Sources

Effluent dissolved copper and nickel data and flows were obtained for 57 dischargers to San Francisco Bay North of the Dumbarton Bridge. This data was used to estimate loadings of copper and nickel to the Bay from municipal and industrial sources.

The locations of all municipal and industrial dischargers to San Francisco Bay are located on the map in **Figure 3.1**. Average daily flows and dissolved copper and nickel summary statistics for each discharger are also provided below.

Figure 3.1. San Francisco Bay Sampling Locations and Point Source Discharges

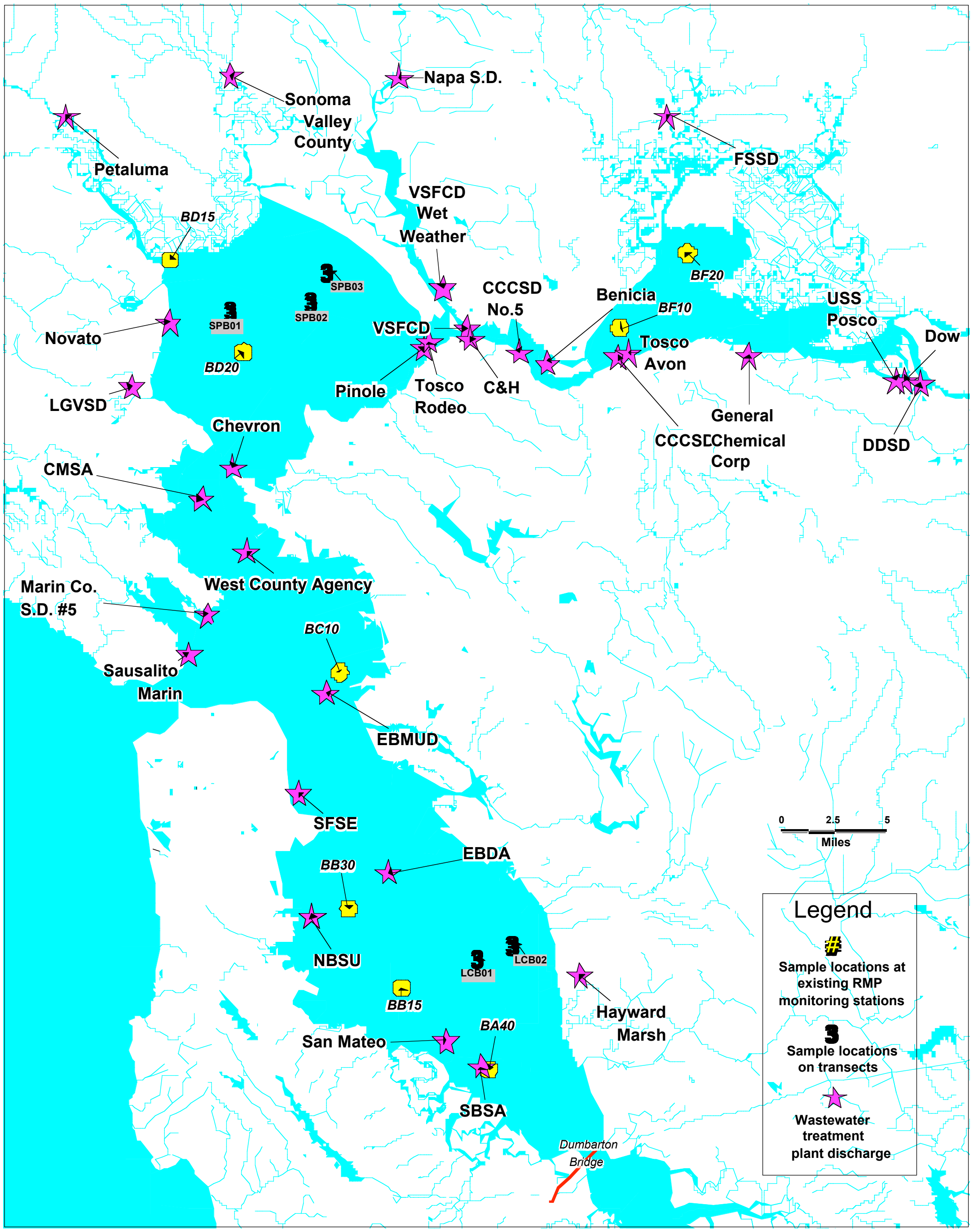


Table 3.1. Dischargers Categorized by Average Effluent Flow

Discharger	Ave. Flow MGD	Plant Size
Morton Permit	0.027	<1 MGD
GWF E 3rd St (Site I) Permit	0.043	
GWF Nichols Rd (Site V) Permit	0.047	
General Electric Company	0.052	
Rhodia Basic Chemicals Permit	0.109	
Dow Chemical Company Permit	0.26	
General Chemical Permit	0.32	
US Navy Treasure Island Permit	0.417	
S.F.Airport, Industrial	0.69	
Tiburon Treatment Plant Permit	0.706	
S.F. Airport, Water Quality Control Plant	0.75	
Rodeo Sanitary District Permit	0.76	
ConocoPhillips (at Rodeo)	1.49	1-10 MGD
Sausalito-Marin Sanitary District Permit	1.67	
SAM Permit	1.71	
Millbrae	1.86	
Mt. View Sanitary District	1.96	
Novato: Novato Plant	2.01	
Valero Benicia Refinery	2.07	
City of Benicia	3.02	
Sewerage Agency of Southern Marin Permit	3.11	
Pinole-Hercules	3.2	
Novato Sanitary District Permit: Overall	3.25	
Sonoma Valley Permit	3.32	
Las Gallinas Valley SD Permit	3.34	
Pacifica Calera Creek	3.59	
Burlingame	4.02	
Tesoro Golden Eagle Refinery	4.22	
Novato: Ignacio Plant	4.49	
EBDA: San Leandro	5.45	
Martinez Refining Company	5.98	
Chevron Richmond Refinery	6.32	
North San Mateo	6.83	
Petaluma Permit	7.3	
USS - Posco	7.6	
West County/Richmond Permit	8.87	
South San Francisco & San Bruno	9.91	
Delta Diablo Sanitation District	9.94	
Central Marin	10.43	10-30 MGD
Dublin San Ramon Services District Permit	10.52	
Sunnyvale	12.73	
San Mateo City	12.81	
EBDA: Hayward	13.07	
Vallejo San & Flood Control District	14.02	
EBDA: Castro Valley	15.37	
San Francisco Oceanside	16.38	
Fairfield-Suisun Sewer District	16.57	
South Bay System Authority	16.91	
San Francisco City & County Bayside (wet)	22.75	
Palo Alto	25.1	
EBDA: Overall	27.56	
EBDA: Union SD	29.1	
Central Contra Costa	43.89	40-75 MGD
San Francisco City & County Southeast	71.17	
EBMUD	73.49	
EBDA: E-001	74.96	
San Jose & Santa Clara	110.16	> 100 MGD

Table 3.2. Daily Maximum Effluent Copper (2001 – 2003)

	Concentration [µg/L]					
Discharger	Min	Max	Median	Mean	SD	n
City of Benicia	1.9	27.0	6.1	6.8	3.8	53
Burlingame	4.4	38.0	8.0	9.8	7.4	34
Central Contra Costa	2.0	11.0	6.7	6.6	1.7	27
Central Marin	1.4	4.5	2.7	2.8	0.8	32
Chevron Richmond Refinery	1.0	15.0	2.2	3.5	3.4	24
ConocoPhillips (at Rodeo)	1.8	20.0	6.4	6.7	4.0	32
Delta Diablo Sanitation District	2.5	16.0	7.5	7.6	2.1	65
Dow Chemical Company Permit	4.1	25.0	10.0	12.2	6.9	29
Dublin San Ramon Services District Permit	21.0	80.0	40.0	44.2	16.3	35
EBDA:	3.8	50.0	12.3	13.9	7.0	142
E-001	3.8	18.3	12.5	12.3	2.9	27
Castro Valley	3.9	19.0	9.6	9.7	3.2	28
Hayward	14.8	50.0	22.2	24.1	7.7	28
San Leandro	3.9	16.3	8.4	9.1	3.3	28
Union SD	8.1	24.7	14.5	14.3	4.0	31
EBMUD	3.0	25.9	9.0	10.1	5.0	50
Fairfield-Suisun Sewer District	2.2	9.0	4.2	4.4	1.4	57
General Chemical Permit	0.0	5.0	5.0	3.7	2.2	11
General Electric Company	5.0	10.0	10.0	8.3	2.4	8
GWF E 3rd St (Site I) Permit	12.2	32.8	21.8	21.9	4.3	40
GWF Nichols Rd (Site V) Permit	13.6	28.0	19.9	20.0	3.8	39
Las Gallinas Valley SD Permit	8.0	25.0	11.0	12.6	4.9	10
Martinez Refining Company	2.0	12.0	5.0	5.4	2.2	32
Millbrae	5.0	14.0	8.0	8.8	2.3	35
Morton Permit	1.9	30.5	5.0	10.6	13.3	4
Mt. View Sanitary District	2.5	8.3	4.7	5.0	1.4	31
North San Mateo	10.0	100.0	11.0	22.5	31.4	8
Novato Sanitary District Permit:	5.2	11.0	8.1	8.1	4.1	2
Ignacio Plant	5.2	5.2	5.2	5.2	5.2	1
Novato Plant	11.0	11.0	11.0	11.0	11.0	1
Pacifica Calera Creek	2.8	9.3	5.3	5.6	1.7	30
Palo Alto	3.3	11.5	6.3	6.4	1.4	139
Petaluma Permit	1.7	6.0	3.7	3.6	1.2	15
Pinole-Hercules	1.4	9.0	4.1	4.6	1.9	31
Rhodia Basic Chemicals Permit	1.0	22.0	11.0	10.7	6.0	30
Rodeo Sanitary District Permit	0.0	5.0	3.4	3.2	1.3	23
S.F. Airport, Water Quality Control Plant	1.2	14.8	6.7	7.0	3.6	32
S.F.Airport, Industrial	0.3	24.5	4.8	5.5	4.2	34
SAM Permit	15.3	15.3	15.3	15.3	0.0	1
San Francisco City & County Southeast	6.3	23.8	12.8	13.7	4.2	100
San Francisco City & County Bayside (wet)	28.5	64.3	50.2	48.2	13.8	10
San Francisco Oceanside	5.5	23.9	15.3	16.0	4.2	30
San Jose & Santa Clara	1.2	6.7	3.2	3.3	1.1	170
San Mateo City	3.2	14.0	5.6	6.0	2.2	30
Sausalito-Marin Sanitary District Permit	0.0	16.0	11.0	11.2	2.8	29
Sewerage Agency of Southern Marin Permit	8.3	24.0	16.0	15.5	3.6	29
Sonoma Valley Permit	2.9	12.0	7.7	7.7	1.7	57
South Bay System Authority	4.0	16.0	9.7	10.1	2.9	37
South San Francisco & San Bruno	4.6	32.7	10.3	10.6	4.8	32
Sunnyvale	0.5	4.8	1.7	1.9	1.0	121
Tesoro Golden Eagle Refinery	1.3	20.0	4.0	4.6	2.8	122
Tiburon Treatment Plant Permit	5.2	30.0	20.0	18.2	6.2	16
US Navy Treasure Island Permit	8.2	23.1	10.8	12.5	3.9	29
USS - Posco	2.0	4.7	2.5	2.7	0.8	32
Valero Benicia Refinery	1.4	13.0	8.0	7.6	2.7	68
Vallejo San & Flood Control District	3.6	11.8	6.3	6.4	1.6	40
West County/Richmond Permit	5.0	11.0	7.0	7.4	1.9	11

Table 3.3. Daily Maximum Effluent Nickel (2001 – 2003)

	Concentration [µg/L]					
Discharger	Min	Max	Median	Mean	SD	n
City of Benicia	2.8	8.5	4.4	4.7	1.2	51
Burlingame	0.3	6.6	3.2	3.5	1.2	34
Central Contra Costa	0.5	3.2	1.6	1.6	0.7	27
Central Marin	3.1	7.2	4.1	4.2	0.8	32
Chevron Richmond Refinery	3.0	26.0	19.1	18.9	4.7	24
ConocoPhillips (at Rodeo)	1.1	13.0	3.0	3.3	2.1	32
Delta Diablo Sanitation District	3.8	14.0	8.0	8.3	2.7	28
Dow Chemical Company Permit	2.7	40.0	10.0	17.1	16.0	29
Dublin San Ramon Services District Permit	2.0	5.1	2.8	2.9	0.8	30
EBDA:	5.0	93.0	5.4	7.5	7.9	139
E-001	5.0	19.0	5.3	6.6	2.9	27
Castro Valley	5.0	5.0	5.0	5.0	0.0	28
Hayward	5.4	93.0	8.6	12.5	16.2	28
San Leandro	5.0	9.1	5.0	5.6	1.0	28
Union SD	5.0	14.0	6.4	7.7	2.9	28
EBMUD	5.0	16.0	6.7	7.2	2.4	50
Fairfield-Suisun Sewer District	1.5	6.6	3.8	3.9	1.0	57
General Chemical Permit	2.6	5.5	5.0	4.8	0.9	8
GWF E 3rd St (Site I) Permit	7.9	58.4	15.2	16.8	7.6	48
GWF Nichols Rd (Site V) Permit	7.0	92.9	9.7	12.7	16.1	27
Las Gallinas Valley SD Permit	4.2	8.2	4.8	5.5	1.4	10
Martinez Refining Company	10.0	38.0	19.0	20.4	7.7	32
Millbrae	2.6	6.5	3.5	3.6	0.7	48
Morton Permit	1.0	13.0	10.0	8.5	5.2	4
Mt. View Sanitary District	1.7	5.9	3.9	3.7	1.1	20
North San Mateo	50.0	50.0	50.0	50.0	0.0	9
Novato Sanitary District Permit:	2.2	2.3	2.3	2.3	0.1	2
Ignacio Plant	2.2	2.2	2.2	2.2	0.0	1
Novato Plant	2.3	2.3	2.3	2.3	0.0	1
Pacifica Calera Creek	2.1	5.4	3.2	3.2	0.8	30
Palo Alto	2.8	6.0	4.0	4.2	0.8	32
Petaluma Permit	3.0	6.8	4.1	4.3	1.0	15
Pinole-Hercules	1.6	7.0	4.3	4.4	1.1	24
Rhodia Basic Chemicals Permit	7.2	37.0	20.4	20.4	10.1	10
Rodeo Sanitary District Permit	2.2	6.0	3.1	3.6	1.2	9
S.F. Airport, Water Quality Control Plant	0.3	5.4	2.3	2.5	0.9	32
S.F.Airport, Industrial	0.5	30.0	5.4	6.5	6.0	32
SAM Permit	3.1	3.1	3.1	3.1	0.0	1
San Francisco City & County Southeast	0.5	17.0	3.7	4.1	1.8	101
San Francisco City & County Bayside (wet)	2.4	6.6	5.1	4.7	1.5	10
San Francisco Oceanside	1.1	5.0	2.3	2.4	0.7	30
San Jose & Santa Clara	4.0	10.0	6.0	6.3	1.3	170
San Mateo City	2.8	17.0	4.2	5.1	3.1	30
Sausalito-Marin Sanitary District Permit	0.0	7.3	4.3	4.3	1.6	29
Sewerage Agency of Southern Marin Permit	3.0	5.2	4.3	4.3	0.6	14
Sonoma Valley Permit	1.0	6.0	2.6	3.0	1.4	9
South Bay System Authority	4.0	11.0	5.4	5.7	1.4	37
South San Francisco & San Bruno	3.7	17.1	5.2	6.7	3.5	32
Sunnyvale	1.0	5.7	2.0	2.1	0.9	83
Tesoro Golden Eagle Refinery	10.0	87.0	14.0	16.5	7.9	122
Tiburon Treatment Plant Permit	2.0	10.0	10.0	6.9	4.2	5
US Navy Treasure Island Permit	1.2	5.7	2.2	2.5	1.1	29
USS - Posco	2.0	4.7	2.5	2.7	0.8	32
Valero Benicia Refinery	3.3	100.0	10.0	12.3	9.9	135
Vallejo San & Flood Control District	2.3	3.6	2.9	2.9	0.4	38
West County/Richmond Permit	5.0	11.0	6.9	7.3	2.3	11

3.3.2 Watershed Sources

Located at the mouth of the Sacramento/San Joaquin River Delta, the San Francisco Bay watershed encompasses about 60,000 mi^2 (155,400 km^2), or 40% of California [STB *et al.*, 2000]. Copper and nickel contributions in the Central Valley watershed impact the Bay as the waters of the Sacramento and San Joaquin Rivers are conveyed into the North Bay. For this analysis, these sources to the Bay are expressed as "riverine sources". These riverine sources are comprised of component sources, which include urban and agricultural runoff, erosion of native soils, atmospheric deposition, treated wastewater discharges, and others. Analysis of these component sources in the upper watershed is not within the scope of this document.

3.3.2.1 Urban runoff estimates

Urban runoff occurs year round. However, significant loadings of most constituents, including copper and nickel, occur during wet weather urban runoff flow events. Wet weather urban runoff is a component of stormwater runoff, which has been assessed by SFEI in a report titled *Contaminant Loads from Stormwater to Coastal Waters in the San Francisco Bay Region*, [Davis *et al.*, 2000]. In that report, estimated loads to San Francisco Bay from stormwater runoff ranged from 36 to 110 tons per year for copper, with a best estimate of 66 tons per year. Estimated nickel loads were from 27 to 78 tons per year, with a best estimate of 49 tons per year. In comparison to local loads to the Bay from wastewater effluent, atmospheric deposition and dredging, storm runoff was estimated to be the dominant source of both copper (89% of total) and nickel (76% of total). For copper, the report estimated urban runoff to contribute 60% of the total storm runoff load to the Bay, indicating that urban runoff was estimated to be over half the total local load of copper to the Bay.

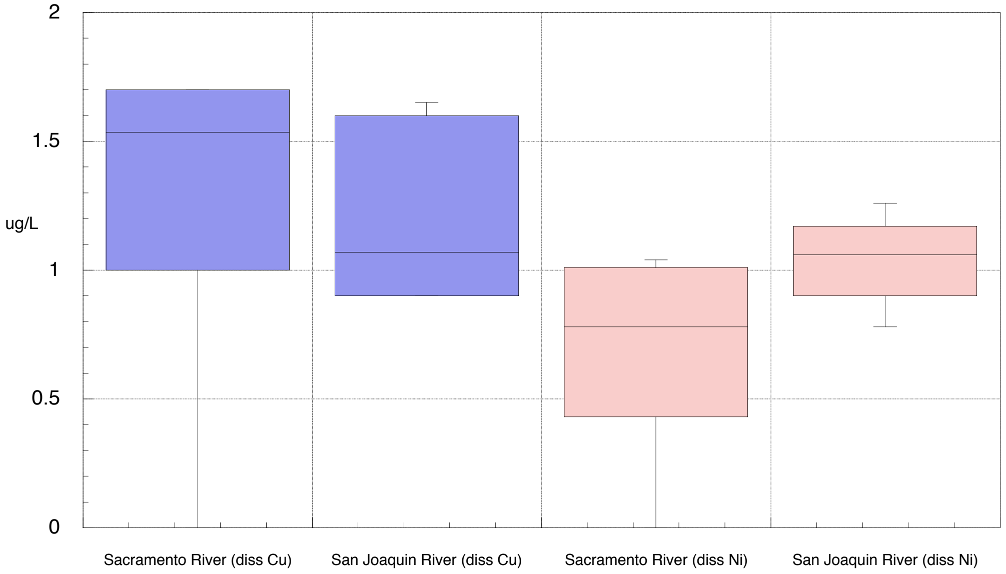
The report indicated that the estimated aggregate local loads of copper (74 tons per year) and nickel (64 tons per year) were small in comparison to loads of total copper and nickel from the Central Valley (less than 25%). Most of the load from the Central Valley is particulate bound, based on a comparison of total load estimates with estimates of dissolved copper and nickel loads to the Bay in Delta outflow.

In a March 2004 report titled *Copper Sources in Urban Runoff and Shoreline Activities* prepared by TDC Environmental, estimates for the sources of copper in urban runoff and shoreline activity inputs to San Francisco Bay were presented [TDC, 2004]. The significant sources of copper in urban runoff were estimated to be, in ranked order, vehicle brake pads, air emissions, copper-containing pesticides, soil erosion, architectural copper, industrial copper use, domestic water discharges, and vehicle fluid leaks. The significant sources of copper from shoreline activities were identified as marine antifouling coatings and copper algaecides applied to surface waters. The report noted that these estimates of source contributions had a certain degree of uncertainty associated with them.

3.3.2.2 Riverine inputs

The Sacramento and San Joaquin Rivers flow into Northern San Francisco Bay at the eastern end of Honker Bay. Concentrations of dissolved copper and nickel from these sources are presented in the box plots below (**Figure 3.2**).

Figure 3.2. Dissolved Copper and Nickel in Sacramento and San Joaquin Rivers (1993 – 1994) [SFEI, 2001]



Annual riverine loads of copper and nickel are determined by the freshwater inflow volumes from each river to San Francisco Bay. Riverine flow volumes vary significantly from year to year, depending largely on the rainfall patterns occurring in the Central Valley. Annual average flow from the Sacramento-San Joaquin Delta to the Bay is 21.1 million acre-feet (26,000 million cubic meters). In the period 1981 to 2000, maximum and minimum annual riverine flows have ranged from 4.1 to 64.9 million acre-feet per year [McKee *et al*., 2002]. The Napa River and Petaluma River contribute small increments to the total riverine flow volume.

Average annual riverine loads of dissolved copper and nickel to the Bay are approximately 107 and 71 kg/yr, respectively. During maximum observed flow years, these riverine dissolved loadings have increased to 329 kg/yr for copper and 219 kg/yr for nickel.

3.3.3 Atmospheric Deposition

The global releases of metals into the atmosphere from combustion, industry, and natural sources result in atmospheric loadings in San Francisco Bay. Pollutants released hundreds or thousands of miles away are deposited directly in the Bay during rainstorms. Load estimates from atmospheric deposition of copper and nickel to the San Francisco estuary are presented in **Table 3.4**, below.

Table 3.4. Atmospheric Deposition to North and Central San Francisco Bay (1999 – 2000) [Tsai *et al*., 2001].

	Dry Deposition		Wet Deposition	
(kg/yr)	Copper	Nickel	Copper	Nickel
North Bay	490 (±280)	300 (±170)	240	82
Central Bay	270 (±210)	140 (±76)	270	83

3.3.4 Erosion of Buried Sediment

Nickel-rich serpentinite formations in the San Francisco Bay area are eroded, transported and accumulated in estuarine sediments, providing a natural source of nickel [Topping *et al.*, 2001]. Although the relative areal coverage of these formations may not seem pronounced, the spatial distribution of serpentinite throughout the watersheds surrounding the Bay suggest the complexity and potential importance of these multiple sources.

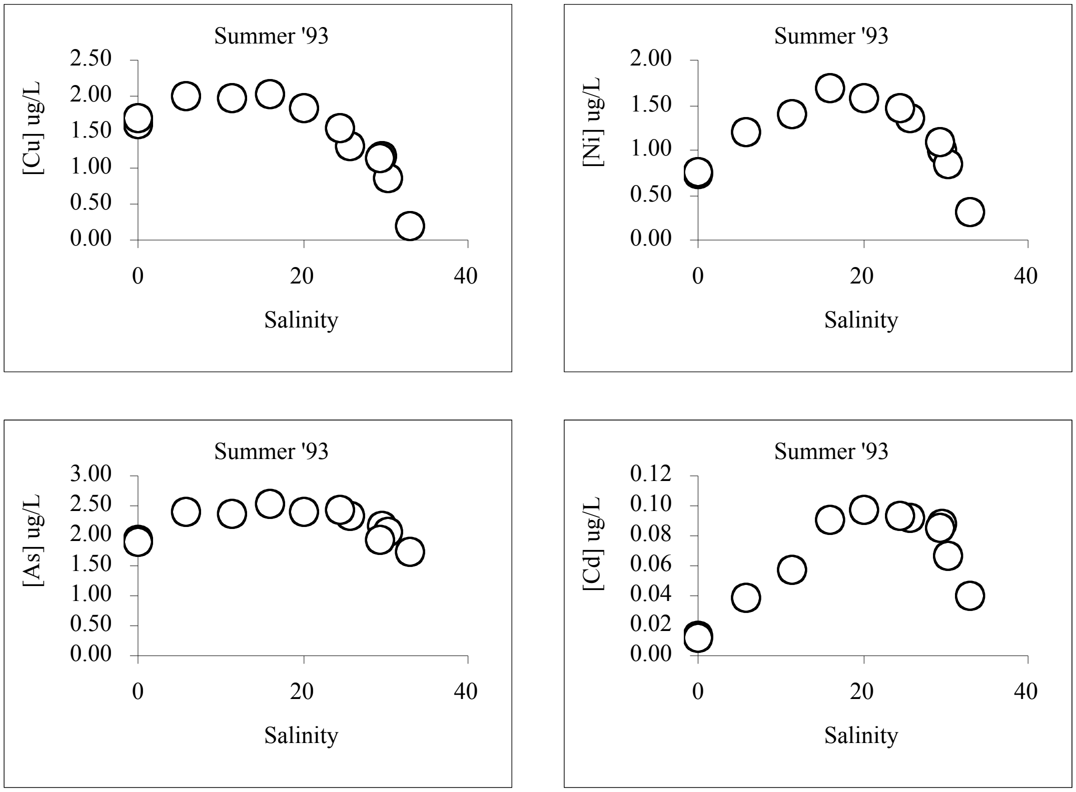
The importance of this process to ambient nickel levels in the Bay was examined in the Lower South Bay. Using data from twenty-eight unique core incubations, spanning two years and three Lower South Bay sites, the average benthic flux load was 39 kg-Ni/day, with a 95% confidence interval of 11 kg-Ni/day. This estimate is much larger than the major municipal point-source input of ~3 kg-Ni/day by the San Jose/ Santa Clara Water Pollution Control Plant for 1999 [Topping *et al.*, 2001]. The flux estimates are of similar magnitude to non-point source stormwater run-off estimates for the surrounding watersheds (~56 kg-Ni/day) [Davis *et al.*, 2000]. This value is derived by combining seven different sub-watersheds, or hydrologic units as defined by the authors. These units include significant rivers such as Guadalupe River, Coyote Creek, Alameda Creek and San Francisquito Creek. It should be noted that while other elements, such as copper, exhibited temporal variability in flux direction (both into and out of the sediment), nickel flux was consistently positive**.** That is, 27 of the 28 unique core incubations indicated a flux out of the sediment, into the overlying water column.

Since these results indicate that the magnitude of the measured benthic-flux of nickel is significant relative to major fresh-water inputs, metal remobilization from the sediment is an important consideration in determining realistic responses to future load-allocation strategies for nickel into the estuary. Data suggests that benthic interaction with the overlying water column is one of the primary processes regulating dissolved-nickel concentrations in the South Bay.

3.3.5 In-Bay Hot Spots (The Selby Smelter Site)

A smelting and refining plant, known as the Selby Smelter, operated on the shores of San Pablo Bay near Davis Point from 1886 through 1970. The plant primarily produced lead, but refined other metals. Smelter operations produced massive piles of ore slag, which were disposed in tidal and sub-tidal waters of San Pablo Bay. Beginning in 1989, remedial actions were undertaken by responsible parties to contain and cap solid waste piles, remove contaminated sediments by dredging, and contain surface waters. The site is currently undergoing additional remedial investigations and feasibility studies, with a report scheduled for completion 12/31/2005. According to the Department of Toxic Substances Control (DTSC), one of the primary areas to be addressed by further investigation activities is the metals mass loading from the site into San Pablo Bay (DTSC CALSITES Database, Site ID #07330031 – ASARCO).

Figure 3.3. Salinity Distributions



The downward concavity in the salinity distributions of dissolved copper, nickel, arsenic, and cadmium in the northern reach of San Francisco Bay indicates internal inputs. The distributions shown have been consistently observed in every summer cruise of the RMP since the program began in 1993.

The question of metals mass loading from the Selby Site posed by DTSC is extremely important, given that observed distributions of dissolved trace elements in the northern reach indicate substantial inputs. Preliminary assessments indicate that dissolved copper and nickel loadings in the order of 100 – 400 kg per day are required to explain the distributions shown in **Figure 3.3** [Abu-Saba, 1998]. The fact that arsenic and cadmium have similar patterns could indicate pollutant mobilization from ore slag. The mechanism for this could be tidal pumping through exposed slag along the shoreline, or erosion of exposed slag coupled to dissolution within Bay waters.

There are alternative processes that could explain the observed internal inputs in the northern reach, including benthic remobilization and desorption from suspended sediments as fresh water mixes with salt, so the available evidence does not provide a definitive link to the Selby site. Resolving whether or not the observed internal inputs of copper and nickel could be reduced or eliminated through additional remedial measures at this site (e.g., hydraulic containment) is an important management question.

3.3.6 Describe types and magnitude of other sources of each metal

3.3.6.1 Future Loading from Sediment

A USGS study collected sediment cores from four locations in northern San Francisco Bay. In addition, cores were also collected at one ‘control’ location (Tomales Bay) to assess historical trends of copper in Bay sediments. Metals were analyzed in sediments fraction less than 64 um in size.

Data show that baseline concentrations of copper ranged from 23.7 ± 1.2 ug/g to 41.4 ± 2.4 ug/g. Maximum concentrations of copper in the cores were less than 3 times the baseline [Hornberger *et al*., 1999]. It was concluded that copper is only moderately enriched in Bay sediments. The enrichment factor (concentration in horizon / baseline value) is similar to southern California coastal waters and less than sediments near the head of Narragansett Bay (where there is extreme contamination). The results of tests for copper in San Francisco Bay cores can be found in **Figure 3.4**.

It was determined that concentrations of nickel in Bay sediments are greater than the mean crustal content, and greater than concentrations found in many other coastal sediments. Erosion of ultramafic rock formations in the watershed appears to be the predominant source [Hornberger *et al*., 1999]. The results of tests for nickel in San Francisco Bay cores can be found in **Figure 3.5**.

Figure 3.4. San Francisco Bay Sediment Core Copper Data

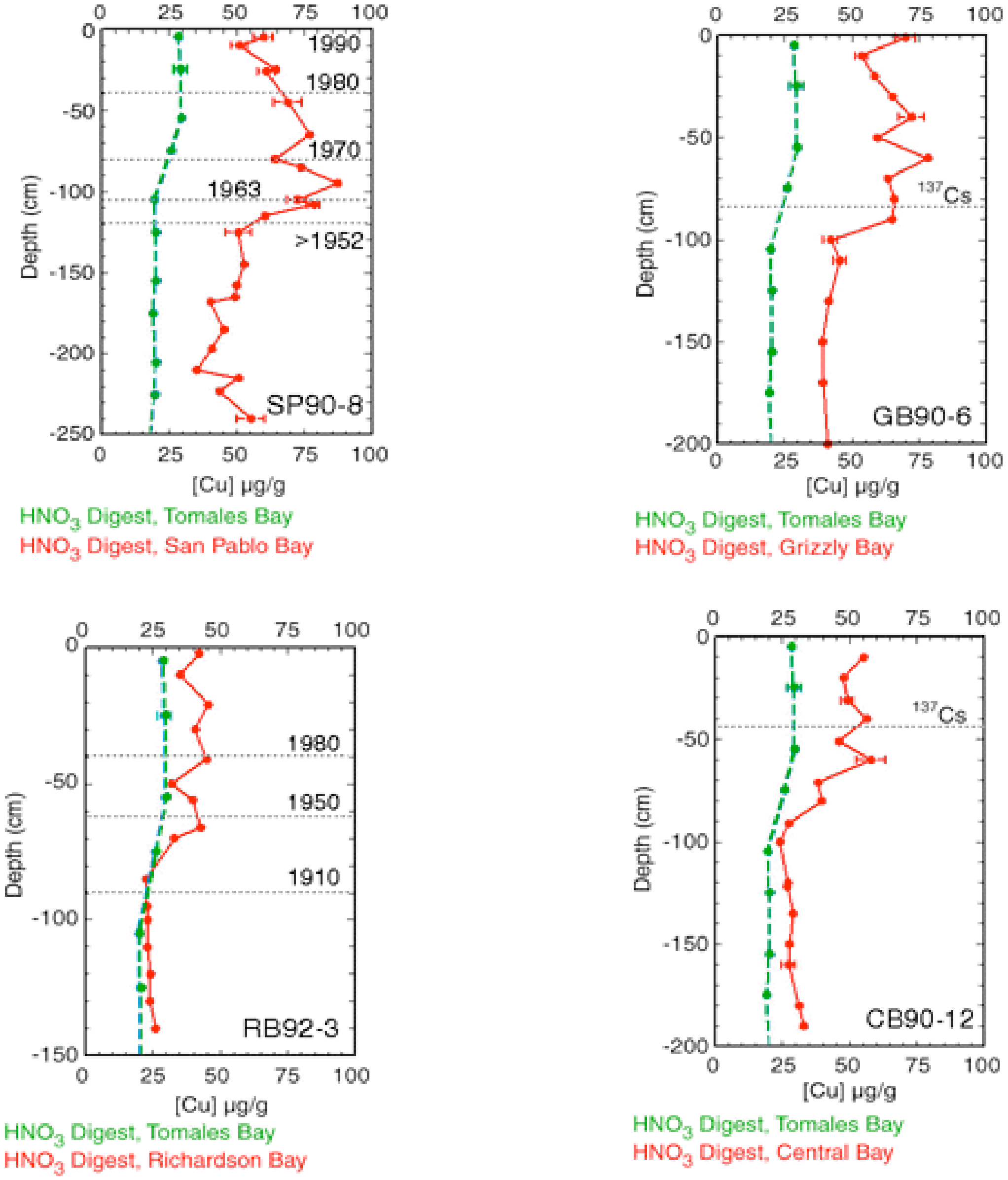
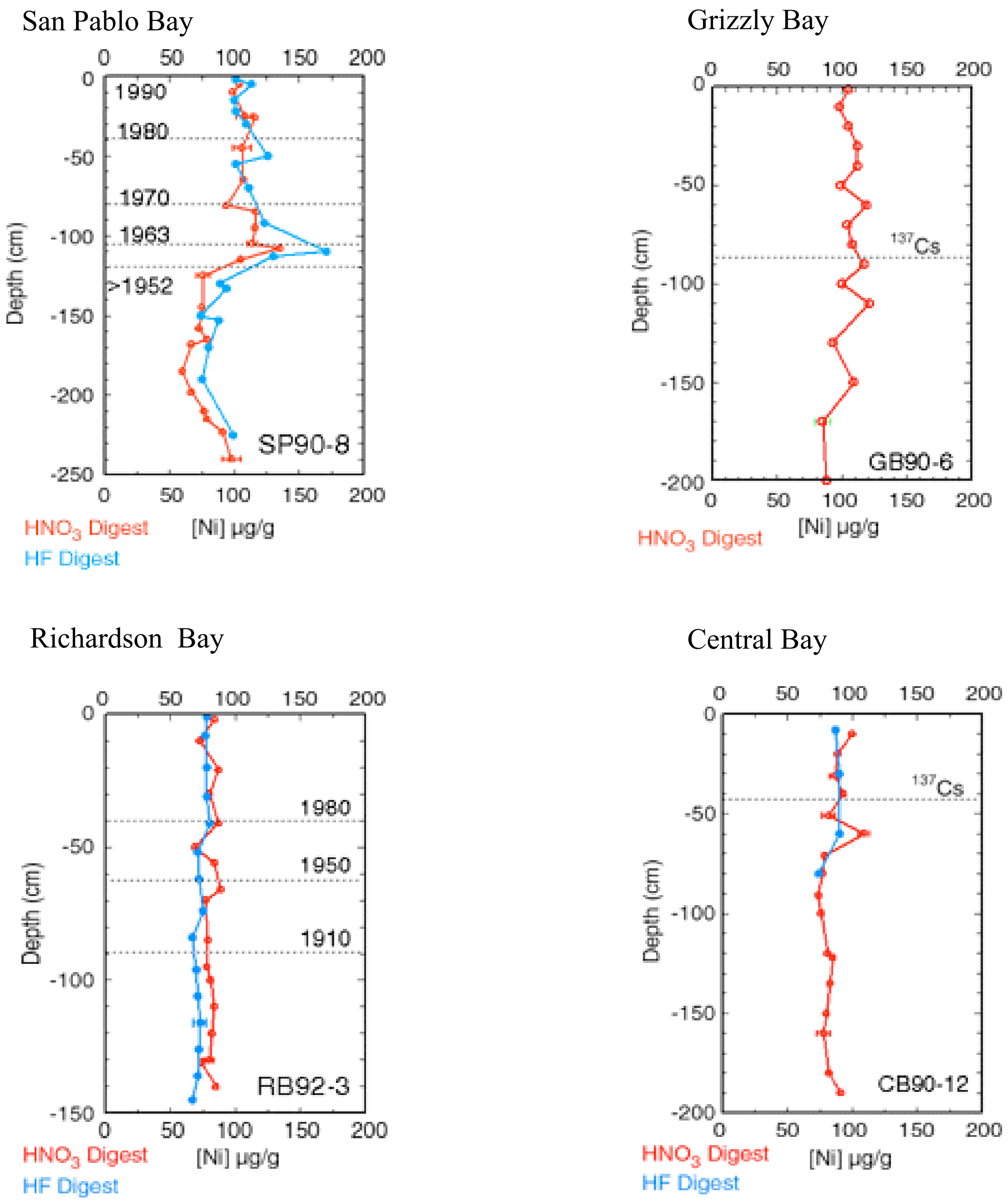


Figure 3.5. San Francisco Bay Sediment Core Nickel Data



San Pablo Bay

Grizzly Bay

Richardson Bay

Central Bay

Sediment copper and nickel concentrations vary throughout the San Francisco Bay with an overall average of approximately 40 mg Cu/kg sediment and 85 mg Ni/kg sediment. **Table 3.5** reports the mean and standard deviations for sediment copper and Ni concentrations from 1993-1999 at eight of the sites sampled in this study. Also included in **Table 3.5** is the percent of fine grains found in the sediment at each site. Metals tend to attach to finer grains, so this parameter is very important when studying metal concentrations in sediments.

Table 3.5. Sediment Copper and Nickel Concentrations in San Francisco Bay Based on Data collected 1993-2001 (mg/kg sediment) [sorted by % fines]

Location		Mean Cu	σ	Mean Ni	σ	% Fines (<63um)
BC60	Red Rock	16.1	10.5	72.0	16.1	13.1
BG20	Sacramento River	23.2	7.8	85.5	14.2	19.3
BD41	Davis Point	20.1	5.8	72.7	10.0	19.4
BF10	Pacheco Creek	20.0	3.9	73.8	9.8	20.4
BC21	Horseshoe Bay	25.1	6.6	64.5	9.0	43.9
BG30	San Joaquin River	33.5	10.3	70.3	12.7	47.6
BB30	Oyster Point	33.2	5.3	74.9	13.5	63.5
BC11	Yerba Buena Island	36.0	6.6	69.4	14.2	69.1
BB15	San Bruno Shoal	37.5	7.8	79.2	19.9	74.6
BD31	Pinole Point	51.2	10.6	96.6	16.1	75.3
BB70	Alameda	42.1	4.6	86.0	15.2	76.0
BC32	Richardson Bay	34.8	8.2	76.2	15.9	79.5
BA41	Redwood Creek	40.9	7.9	82.3	21.3	80.8
BD22	San Pablo Bay	49.1	4.1	84.6	9.7	84.2
BC41	Point Isabel	40.9	4.2	84.7	14.3	86.3
BA30	Dumbarton Bridge	41.7	5.0	87.2	18.5	90.5
BD50	Napa River	62.0	6.5	101.7	15.5	91.3
BF40	Honker Bay	62.7	8.5	110.1	19.0	94.9
BD15	Petaluma River	55.3	5.3	107.1	20.5	95.9
BF21	Grizzly Bay	59.1	7.4	105.1	18.5	98.3

Table 3.6. Average Grain Sizes in North and Central San Francisco Bay Sediments

Station Code		% Fines (<63µm)	% Clay (<4µm)	% Silt (4µm-63µm)	% Sand (63µm-2mm)	% Gravel+Shell (>2mm)
BA30	Dumbarton Bridge	90.5	59.9	30.4	8.1	1.4
BA41	Redwood Creek	80.8	56.4	24.6	12.6	6.5
BB15	San Bruno Shoal	74.6	50.6	24.1	22.4	2.9
BB30	Oyster Point	63.5	42.6	21.0	32.6	3.6
BB70	Alameda	76.0	50.1	26.0	24.1	0.0
BC11	Yerba Buena Island	69.1	46.8	22.1	26.8	4.3
BC21	Horseshoe Bay	43.9	25.4	18.4	54.0	2.1
BC32	Richardson Bay	79.5	40.8	38.9	20.3	0.1
BC41	Point Isabel	86.3	51.4	34.9	13.8	0.1
BC60	Red Rock	13.1	8.7	4.1	82.9	4.1
BD15	Petaluma River	95.9	63.3	32.5	3.7	0.4
BD22	San Pablo Bay	84.2	52.0	32.2	15.2	0.5
BD31	Pinole Point	75.3	49.8	25.4	24.3	0.3
BD41	Davis Point	19.4	12.6	6.9	79.4	1.2
BD50	Napa River	91.3	66.2	25.1	5.6	3.1
BF10	Pacheco Creek	20.4	13.1	7.2	78.4	1.3
BF21	Grizzly Bay	98.3	62.5	35.8	1.8	0.1
BF40	Honker Bay	94.9	57.9	37.0	4.9	0.0
BG20	Sacramento River	19.3	11.5	7.8	80.6	0.1
BG30	San Joaquin River	47.6	24.8	22.8	52.3	0.0

Box plots of copper and nickel in San Francisco Bay sediments, north of the Dumbarton Bridge can be found in **Figures 3.10 & 3.12.**

A conceptual model study of the Lower South San Francisco Bay (Lower Bay) was conducted by Tetra Tech in 1999. Many of the conclusions of that report can be applied generally to the rest of San Francisco Bay. This study found that the two largest sources of copper and nickel to the Lower Bay are sediment exchange during resuspension and nonpoint source loads from tributaries [Tetra Tech, 1999]. These sources account for approximately 80-90% of the total copper and nickel loads to the Lower South Bay.

3.4 Chemistry, fate, transformations and transport of each metal

3.4.1 Describe state of knowledge regarding fate and transport for each metal

3.4.1.1 Sediment Transport Processes

Sediment transport is important to the cycling of copper and nickel in San Francisco Bay, since sediment re-mobilization is acknowledged to be one of the largest sources of these metals. The particle size distribution of suspended sediments is smaller than the particle size distribution of sediments in the bed. This affects the fate and transport of the adsorbed metals, since they associate more strongly and therefore have higher concentrations on the smaller clay or silt particles. A fraction of the sediments that erode from the watershed appear to be deposited in streambeds in the flatlands, and may enter the Bay during subsequent storm events.

3.4.1.2 Copper and Nickel Cycling

Copper and nickel cycling is important in San Francisco Bay because it plays a major role in both the fate and toxicity of the metal loads entering the estuary. The conceptual model of cycling involves chemical speciation of the metals and the chemical, physical, and biological processes that influence their fate, concentrations, and interactions between chemical forms. The species considered are the free metal ions; inorganic complexes with chlorides, hydroxides, carbonates, and sulfates; organic complexes with strong and weak ligands; and adsorbed forms and other particulate forms. Speciation is very important since only free metal ions and labile inorganic complexes are bioavailable for uptake. Therefore, these are also the forms that determine toxicity.

Only a small fraction of the total copper and nickel in the water column occurs in these forms. Much of the dissolved copper and nickel is complexed with organic ligands, and particulate forms also represent a significant fraction of the total metal concentrations. The free ions and inorganic complexes have been estimated to range from 8 - 20 % of the total dissolved copper and 50 - 66 % of the total dissolved nickel in South San Francisco Bay [Donat *et al.*, 1994]. However, this distribution could change as metal loads or ligand loads to the estuary change, or if other changes occur in the Bay that effect the internal cycling of the metals. Therefore, it is important to understand the processes that control the transformations between different chemical forms of the metals, since these will determine the speciation and concentrations of the metals as loads or internal cycling processes change in the future.

3.4.1.3 Speciation Processes

Complexation and adsorption are the main processes that control copper and nickel speciation. Inorganic complexation reactions are fast, and can be considered as equilibrium processes. Seasonal salinity variations have the largest effect on these reactions, since salinity determines the concentrations of the inorganic ligands that complex with the metals. Organic complexation and sorption reactions are slower, and are considered to be kinetically limited. These kinetic relationships make the organic complexes and sorbed species unavailable for uptake, as well as influencing their fate and transport in the estuary.

Adsorption processes are believed to depend on free metal ion concentrations. Organic complexation reactions depend on the relative concentrations of organic ligands and dissolved metals.

3.4.1.4 Biological Cycling

Organisms influence biogeochemical cycling through uptake and excretion processes, incorporation into biological tissues, production of organic detrital material containing the metals, and subsequent metals release during decomposition and mineralization. Uptake removes dissolved metals from the water column and incorporates them in the biota, while excretion returns metals back to the water in soluble forms. However, this biological processing can change the form and bioavailability of the metals. Free metal ions and weak inorganic complexes are the forms that are most readily assimilated from the water, while excreted forms may be complexed with organic ligands that are much less available for uptake. In addition, phytoplankton excrete cellular exudates that chelate copper ions, effectively reducing copper bioavailability and toxicity.

Particulate organic detrital copper and nickel are produced through food web processing. Following accumulation of the metals in the biota, processes such as phytoplankton settling, plankton mortality, and egestion generate organic detrital metals that settle and deposit the metals in the sediments. These metals are released as soluble forms to the water column and sediment porewaters as the organic material decomposes. Solubilization of the metals by benthic animals feeding on phytoplankton and detritus could also be an important process, as could benthic bioturbation/irrigation effects on sediment release.

3.4.1.5 Food Web Accumulation

Accumulation of copper and nickel in the aquatic food web depends on uptake from two routes of exposure, water and food. Accumulation can be calculated from the metal uptake rates from water; metal assimilation efficiencies from food; metal elimination rates from the organisms; organism growth rates, consumption rates, and dietary preferences; and metal concentrations in food items. The uptake and elimination rates must consider the effects of metal regulation by the organisms, at least for copper. A steady-state approach can be used to estimate total metal concentrations in different organisms and relative contributions from water and food. Alternatively, a dynamic food web model can be constructed to predict metal concentrations throughout the food web in response to changing exposure conditions, for example, from seasonal variations in the loading and cycling of the metals, or to future projected conditions in the South Bay. Currently, copper and nickel measurements in aquatic organisms in San Francisco Bay are limited to benthic bivalves.

Copper and nickel partition between the dissolved and particulate phase in San Francisco Bay. Processes of sorption and desorption impact this partitioning. The ratio of adsorption to desorption is referred to as the partition coefficient (K_d). This coefficient depends on metal chemistry and site-specific factors, including salinity, suspended solids, and dissolved organic carbon.

Dissolved copper and nickel exist as inorganic complexes, organic complexes, colloids and free cationic species. The ionic forms of copper and nickel are most toxic to aquatic organisms, as they are the forms, which most readily diffuse or are taken up across cell membranes. The complexation of dissolved copper has a direct effect on copper toxicity in San Francisco Bay. Complexation of nickel is neither observed nor expected to effect nickel toxicity in the Bay. Neither copper nor nickel bioaccumulate in organisms to a significant degree.

In the northern reach of the estuary, dissolved copper and nickel both have non-conservative excesses. Copper excesses in the northern reach are relatively consistent during both wet and dry seasons, whereas dissolved nickel excesses are as much as ten-fold greater during the wet season. This difference is due to several coupled processes. These include weathering of nickel-enriched serpentines, formation of soluble nickel-sulfide complexes, and episodic flushing of adjacent wetlands.

- Copper and nickel are enriched near Petaluma River mouth
- Copper distributions are similar year-round.
- Nickel, in contrast, shows a ten-fold increase during winter (high-flow season).
- Internal inputs amount to 100-400 kg per day, orders of magnitude greater than combined municipal / industrial discharges (10-20 kg per day).
- Sedimentary diagenesis in marshes, wetlands, mudflats is a likely source - metals are released from dissolution of oxide surfaces in suboxic sediments (e.g., Rivera Duarte and Flegal, 1997).
- Nickel also has a substantial watershed source, probably originating from nickel-rich ultramafic minerals common to California (e.g., serpentines).
- Copper has a substantial internal input that is tenfold greater than municipal and industrial discharges to the region

3.4.1.6 Schematic – Copper Model

Figure 3.6. Conceptual Model of Copper for San Francisco Bay

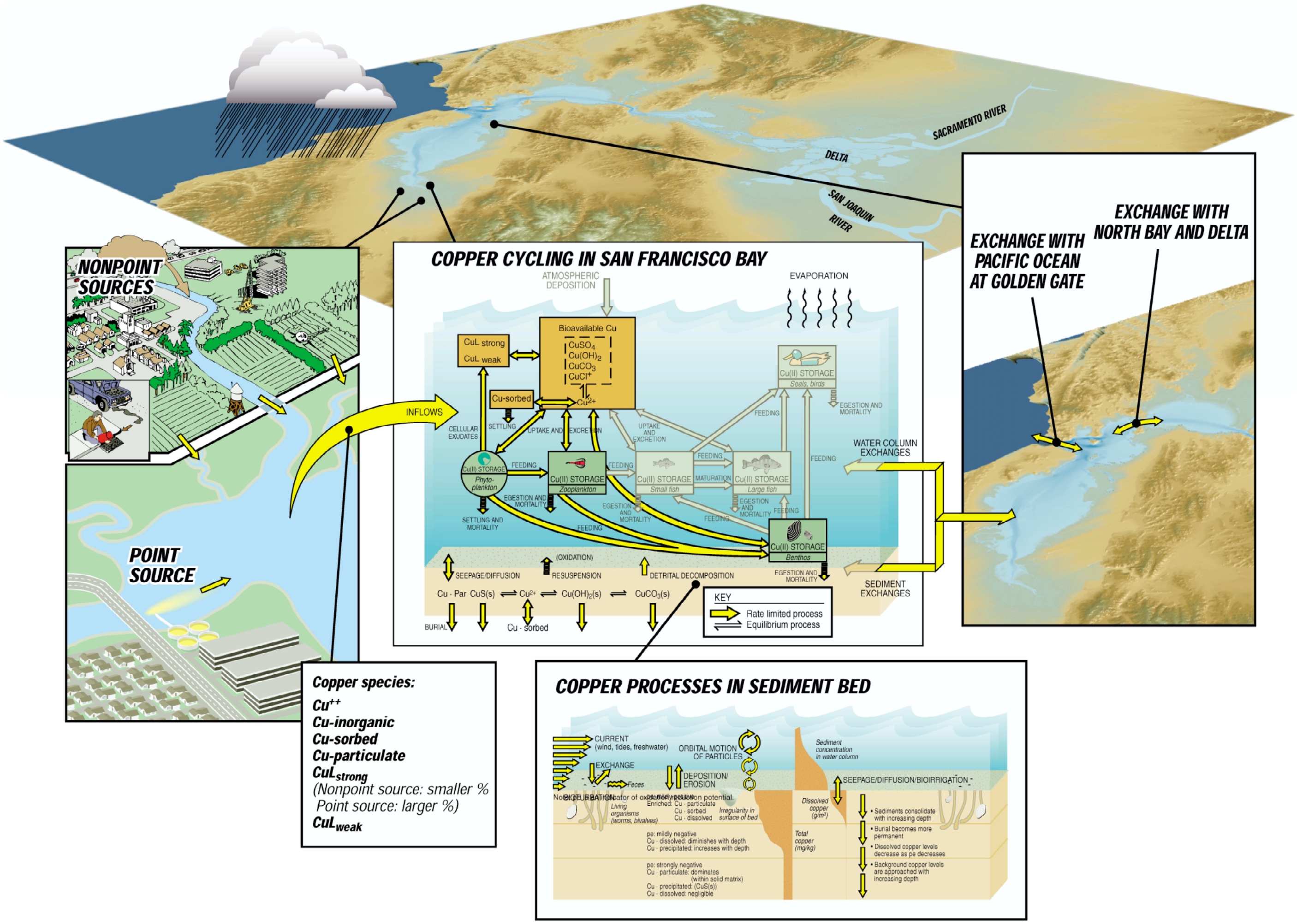


Figure derived from *Conceptual Model Report for Copper and Nickel in Lower South San Francisco Bay* (Tetra Tech, 1999)

3.4.1.7 Schematic – Nickel Model

Figure 3.7. Conceptual Model of Nickel for San Francisco Bay

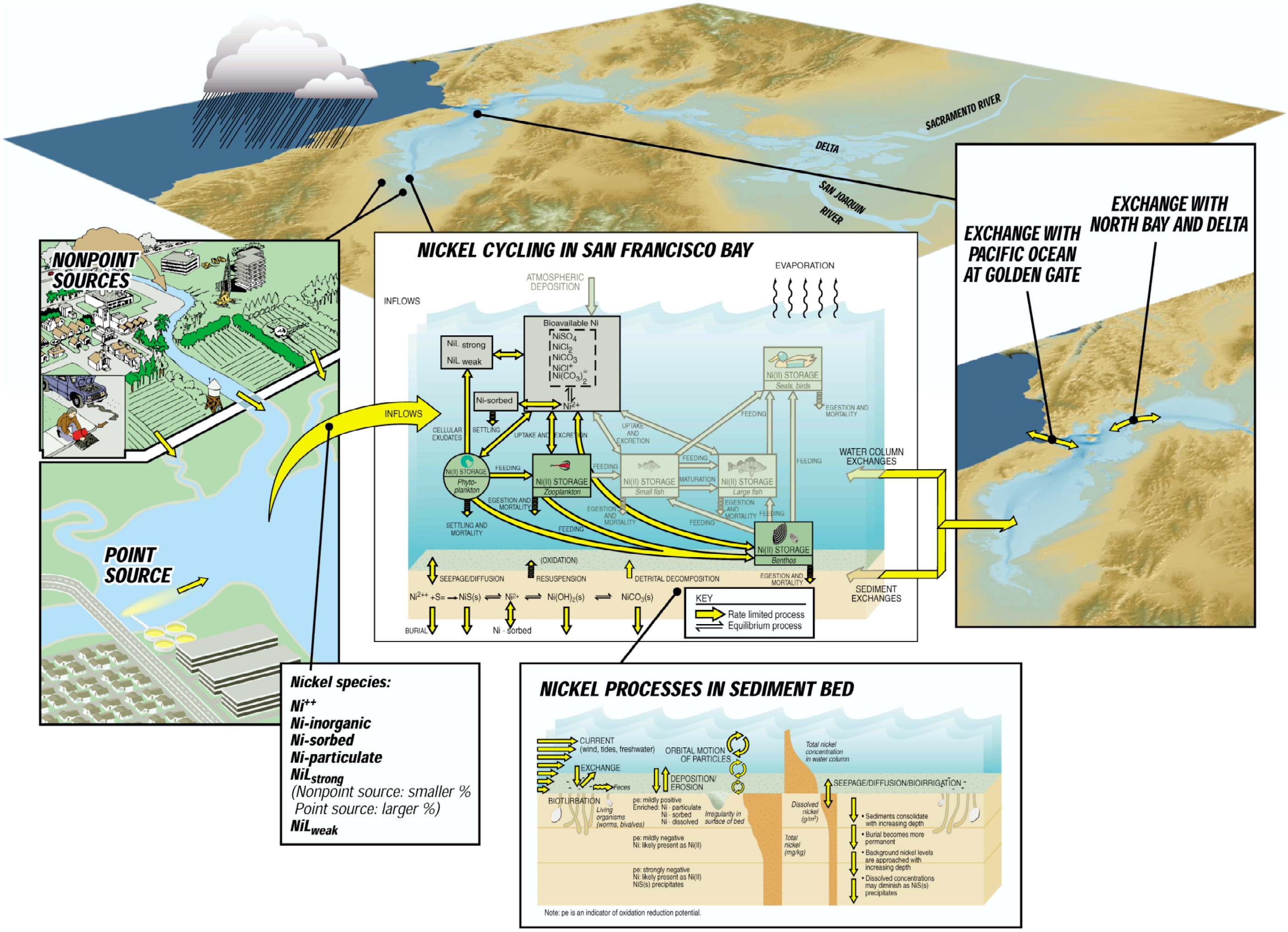


Figure derived from *Conceptual Model Report for Copper and Nickel in Lower South San Francisco Bay* (Tetra Tech, 1999)

3.4.2 Mechanism of toxicity of copper and nickel

Copper toxicity is related to uptake of free ionic copper concentrations [Sunda *et al*, 1988]. Complexation of copper by organic ligands or competitive uptake of dissolved manganese at binding sites in aquatic organisms substantially reduces copper toxicity [Bruland *et al.*, 1992]. This reduction in copper toxicity through complexation is a phenomenon driving the observed Water Effect Ratio results (greater than 1.0) in San Francisco Bay.

Mechanisms of nickel toxicity are varied and complex (USEPA, 1986). Significant effects occur at cell membranes and in membranous tissues (e.g. gills). Nickel does not exhibit the same reduction in toxicity as copper due to complexation. As a result, Water Effect Ratios for nickel in San Francisco Bay have approximated 1.0.

3.4.3 Effects of current inputs of copper and nickel on surface sediment concentrations

The influence of current source inputs of copper and nickel on surface sediment concentrations in San Francisco Bay is an area of ongoing uncertainty. Review of Bay-wide copper and nickel concentrations in surface sediments over time does not indicate identifiable trends, despite reductions in each of these metals in POTW discharges.

The concern has been raised that increasing the water quality objectives for copper and nickel, and a subsequent increase in NPDES effluent limits for copper and nickel concentrations, will produce an increase in the loading of these metals to the sediments in the Bay. Further, the concern exists that such loadings will increase concentrations of copper and nickel in surface sediments, may enhance sediment toxicity and will create a long-term effect on water column concentrations of copper and nickel.

To begin, it has not been established that increasing copper and nickel effluent limits will increase the concentrations of copper and nickel discharged into the Bay, since NPDES treatment facilities typically cannot manipulate treatment operations or effluent concentrations to precisely match effluent concentrations for individual trace constituents. Typical practice in the Bay area is to optimize treatment plant operation at a best achievable level and to maintain a “cushion” below effluent limits to provide reliability in the achievement of those permit requirements.

Second, changes in effluent limits will only impact those sources that are currently restricted by NPDES permits. Changes in loadings to sediment would need to be evaluated in comparison to the total current loading, considering all sources.

If, for the sake of argument, copper and nickel loads from NPDES sources are assumed to increase in response to changes in effluent limits, analytical tools now exist to examine the effects of this change on ambient sediment and water column concentrations. A mathematical model of hydrodynamics, sediment transport and water quality in San Francisco Bay (MIKE 21) has been developed for use in the evaluation of the San Francisco Airport expansion. This model addresses the impact of various sources on water and sediment quality in the Bay. The model includes mechanistic relationships between sediment and water column that are necessary to address the impact of varied loadings on surface sediment quality. The model has been externally peer reviewed and accepted for use by federal agencies, including NOAA and the Federal

Aviation Board. This tool can be used, under varying source load scenarios, to directly assess the incremental changes in sediment and water quality of concern.

As described above, the current approach to ensuring that copper and nickel loads to the Bay do not become a problem would be to periodically monitor selected areas of the Bay. If copper or nickel levels in water column (or in sediments) increase significantly, if the increase is correlated to increases in NPDES loadings, and if there is potential for toxicity problems in water or sediment due to increased sediment copper and nickel concentrations, NPDES sources will need to implement source control alternatives. The action levels to trigger such activity NDB have been described above.

3.4.4 Effect of Sediment Concentrations on Ambient Water Column Levels

The transport of sediment into, within, and out of the Bay is an important component of the copper and nickel cycling process because both copper and nickel are adsorbed to the surfaces of, or embedded within the matrix of, solid particles. Large net loading of copper and nickel into the water column are thought to originate as particulates from the bed and then a net desorption occurs that acts as an internal source of dissolved copper. The overall process of sediment cycling is referred to as the sediment budget.

Solids that enter the Bay from freshwater inflows are subject to flocculation, since the salinity of the Bay is typically high enough to destabilize the solid particles (salinities typically range from 5 to 35 psu). Once in the Bay, the solids are subjected to gravitational forces and depositional shear stresses that tend to cause them to settle to the bed, as well as hydrodynamic forces such as erosional shear stresses that tend to keep the solids suspended [McDonald and Cheng, 1996].

Redox conditions are lower in the sediments, producing different chemical reactions than occur in the water column. Soluble fluxes between the water column and sediments are low compared to other sources of the metals. However, sediment resuspension and desorption may release large quantities of dissolved copper and nickel to the water column, making this a major source of dissolved metals.

Again, as described above, available mathematical modeling tools can provide answers regarding the relative impact of sediment concentrations on dissolved levels of copper and nickel in the Bay.

3.5 Mass loading budget for Municipal and Industrial sources for each metal

Load estimates for each municipal and industrial discharger to San Francisco Bay are presented in **Tables 3.7 & 3.8**, below. Loads were estimated using the average maximum daily metals concentrations, along with the average daily effluent flow.

3.5.1 POTW Data

Municipal discharger copper and nickel mean effluent concentrations and loads are presented in **Table 3.7**.

Table 3.7. POTW Effluent Copper and Nickel Concentrations and Loads (2001-2003)

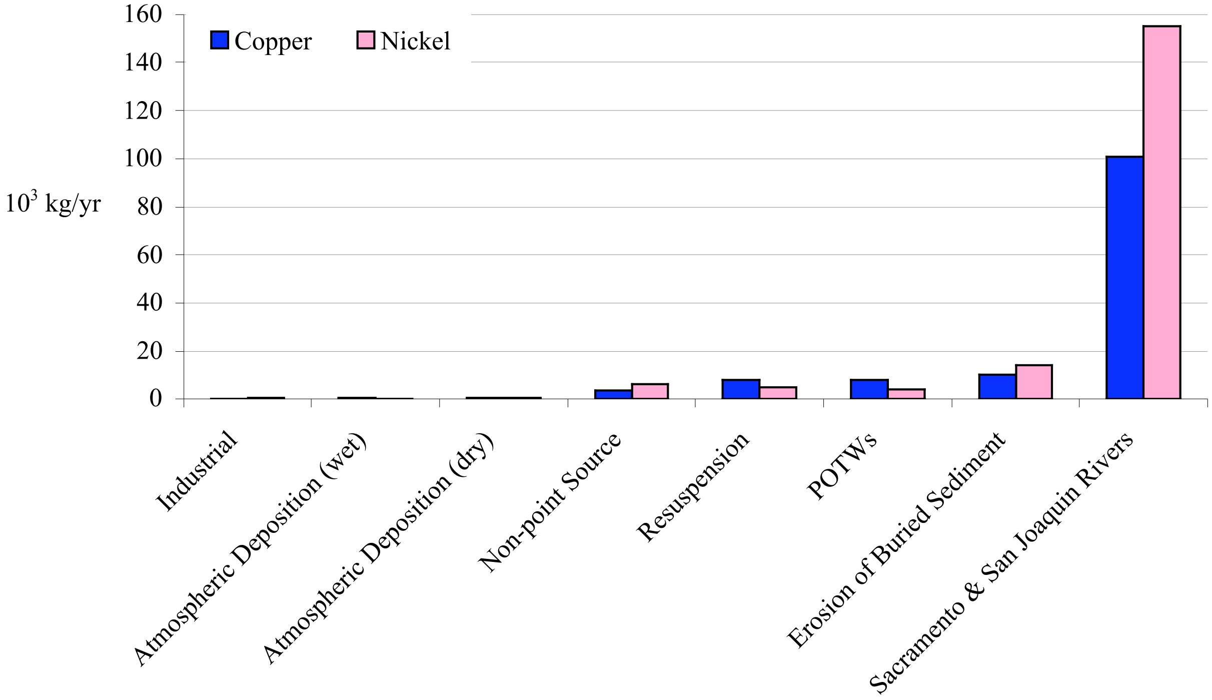
Discharger	Ave. Flow	Mean Cu	Cu Load	Mean Ni	Ni Load
	MGD	µg/L	g/day	µg/L	g/day
City of Benicia	3.02	6.8	78.0	4.7	53.4
Burlingame	4.02	9.8	149.7	3.5	53.1
Central Contra Costa	43.89	6.6	1091.5	1.6	262.7
Central Marin	10.43	2.8	110.5	4.2	165.8
Delta Diablo Sanitation District	9.94	7.6	285.3	8.3	310.8
Dublin San Ramon Services District Permit	10.52	44.2	1758.3	2.9	115.7
EBDA:	27.56	13.9	1452.9	7.5	780.1
E-001	74.96	12.3	3498.8	6.6	1863.1
Castro Valley	15.37	9.7	565.5	5.0	290.9
Hayward	13.07	24.1	1192.0	12.5	620.3
San Leandro	5.45	9.1	188.2	5.6	115.2
Union SD	29.1	14.3	1572.3	7.7	844.6
EBMUD	73.49	9.9	2743.0	6.6	1821.9
Fairfield-Suisun Sewer District	16.57	4.4	274.6	3.9	242.6
Las Gallinas Valley SD Permit	3.34	12.6	159.7	5.5	69.8
Millbrae	1.86	8.8	62.2	3.6	25.5
Mt. View Sanitary District	1.96	5.0	37.2	3.7	27.5
North San Mateo	6.83	22.5	581.7	50.0	1292.6
Novato Sanitary District Permit:	3.25	8.1	99.6	2.3	27.7
Ignacio Plant	4.49	5.2	88.4	2.2	37.4
Novato Plant	2.01	11.0	83.7	2.3	17.1
Pacifica Calera Creek	3.59	5.6	75.8	3.2	43.5
Palo Alto	25.1	6.4	609.2	4.2	394.3
Petaluma Permit	7.3	3.6	99.1	4.3	119.7
Pinole-Hercules	3.2	4.6	55.8	4.4	52.9
Rodeo Sanitary District Permit	0.76	3.2	9.1	3.6	10.3
S.F. Airport, Water Quality Control Plant	0.75	7.0	19.7	2.5	7.1
San Francisco City & County Southeast	71.17	13.7	3695.5	4.1	1099.9
San Francisco City & County Bayside (wet)	22.75	48.2	4146.1	4.7	405.1
San Francisco Oceanside	16.38	16.0	994.9	2.4	150.0
San Jose & Santa Clara	110.16	3.3	1362.2	6.3	2629.3
San Mateo City	12.81	6.0	291.6	5.1	248.1
Sausalito-Marin Sanitary District Permit	1.67	11.2	70.5	4.3	27.1
Sewerage Agency of Southern Marin Permit	3.11	15.5	183.0	4.3	50.9
Sonoma Valley Permit	3.32	7.7	96.7	3.0	38.0
South Bay System Authority	16.91	10.1	643.5	5.7	363.3
South San Francisco & San Bruno	9.91	10.6	398.5	6.7	251.5
Sunnyvale	12.73	1.9	92.0	2.1	102.1
Tiburon Treatment Plant Permit	0.706	18.2	48.5	6.9	18.5
US Navy Treasure Island Permit	0.417	12.5	19.7	2.5	3.9
Vallejo San & Flood Control District	14.02	6.4	341.1	2.9	153.3
West County/Richmond Permit	8.87	7.4	248.5	7.3	245.7

3.5.2 Industrial effluent data

Table 3.8. Industrial Effluent Copper and Nickel Concentrations and Loads (2001-2003)

Discharger	Ave. Flow	Mean Cu	Cu Load	Mean Ni	Ni Load
	MGD	µg/L	g/day	µg/L	g/day
Chevron Richmond Refinery	6.32	3.5	83.1	18.9	451.8
ConocoPhillips (at Rodeo)	1.49	6.7	37.7	3.3	18.7
Dow Chemical Company Permit	0.26	8.8	8.7	10.9	10.7
General Chemical Permit	0.32	3.7	4.5	4.8	5.8
General Electric Company	0.052	8.3	1.6	4.8	0.9
GWF E 3rd St (Site I) Permit	0.043	21.9	3.6	16.8	2.7
GWF Nichols Rd (Site V) Permit	0.047	20.0	3.6	12.7	2.3
Martinez Refining Company	5.98	5.4	122.6	20.4	462.6
Morton Permit	0.027	10.6	1.1	8.5	0.9
Rhodia Basic Chemicals Permit	0.109	10.7	4.4	20.4	8.4
S.F.Airport, Industrial	0.69	5.5	14.5	6.5	17.1
SAM Permit	1.71	15.3	99.0	3.1	20.1
Tesoro Golden Eagle Refinery	4.22	4.6	74.1	16.5	262.9
USS – Posco	7.6	2.7	78.9	2.7	78.9
Valero Benicia Refinery	2.07	7.6	59.3	12.3	96.5

Figure 3.8. Total Mass Budget



	(kg/yr)	
	Copper	Nickel
Industrial	218	526
Atmospheric Deposition (wet)	510	165
Atmospheric Deposition (dry)	760	440
Non-point Source	3800	6100
Resuspension	8000	5000
POTWs	8170	4257
Erosion of Buried Sediment	~10000	14235
Sacramento & San Joaquin Rivers	100990	155129

3.6 Ambient Copper and Nickel Conditions

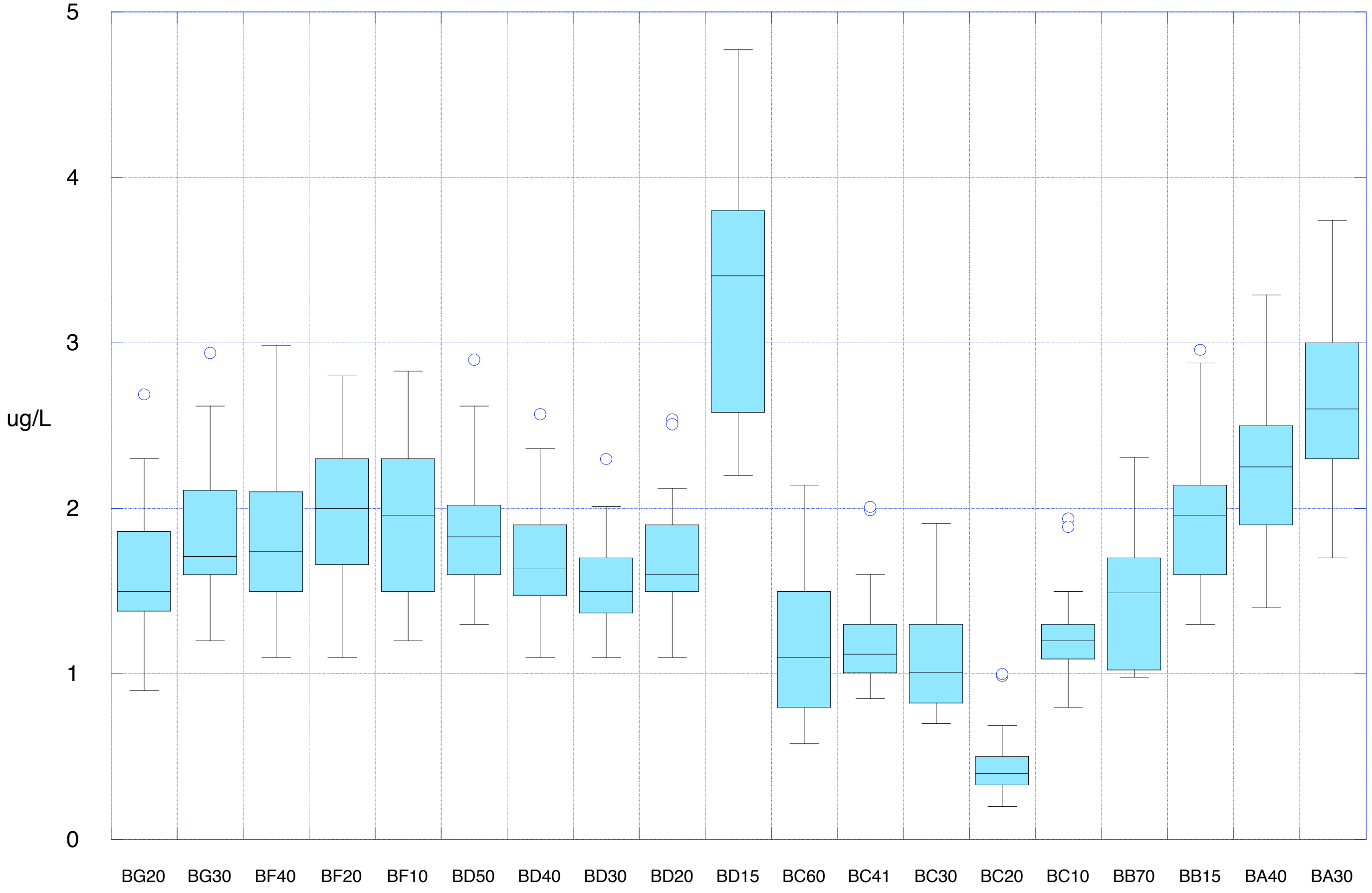
Ambient data were collected from 1993 – 2001 by the San Francisco Estuary Institute's Regional Monitoring Program and as part of the Copper and Nickel North of Dumbarton Bridge study. Water column and sediment data are presented in the box plots below.

The plots present the median, the 25th percentile, the 75th percentile, extreme values and outliers. The lower and upper boundaries of the box represent the 25th and 75th percentiles, respectively. The horizontal line inside the box represents the median. The length of the box corresponds to the inter-quartile range (IQR), which is the difference between the 75th and 25th percentiles. The whiskers indicate the general spread of the data, up to 1.5 times the IQR. Outliers (>1.5 times the IQR) are identified as circles outside the whiskers.

3.6.1 Water Column and Sediment Data

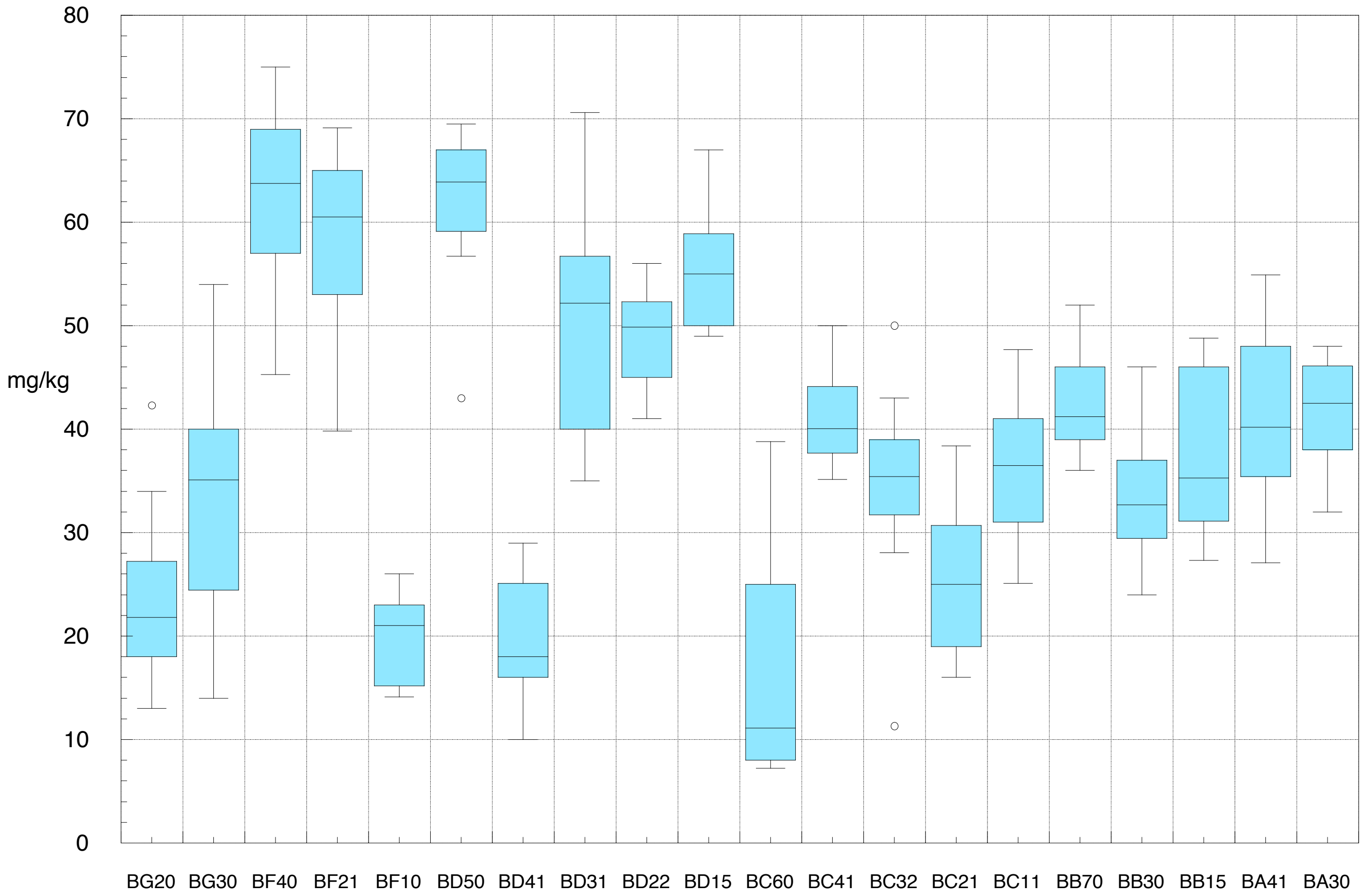
Variations in the copper concentrations in Bay waters are exhibited in **Figure 3.9**. The BC20 station represents the Golden Gate Bridge samples, and the lowest concentrations of dissolved copper in the Bay (ocean water). The Petaluma River station (BD15) represents the highest concentrations, and is discussed in further detail later in this section. To the left of BC20 in **Figure 3.9**, concentrations increase somewhat steadily to Grizzly Bay (BF20), excluding BD15 and begin to decrease at the Sacramento and San Joaquin River mouths. To the right of BC20, concentrations of dissolved copper increase steadily as stations move toward the Dumbarton Bridge.

Figure 3.9. Dissolved Copper in San Francisco Bay Water North of the Dumbarton Bridge (1993 – 2001) [SFEI, 2001a]



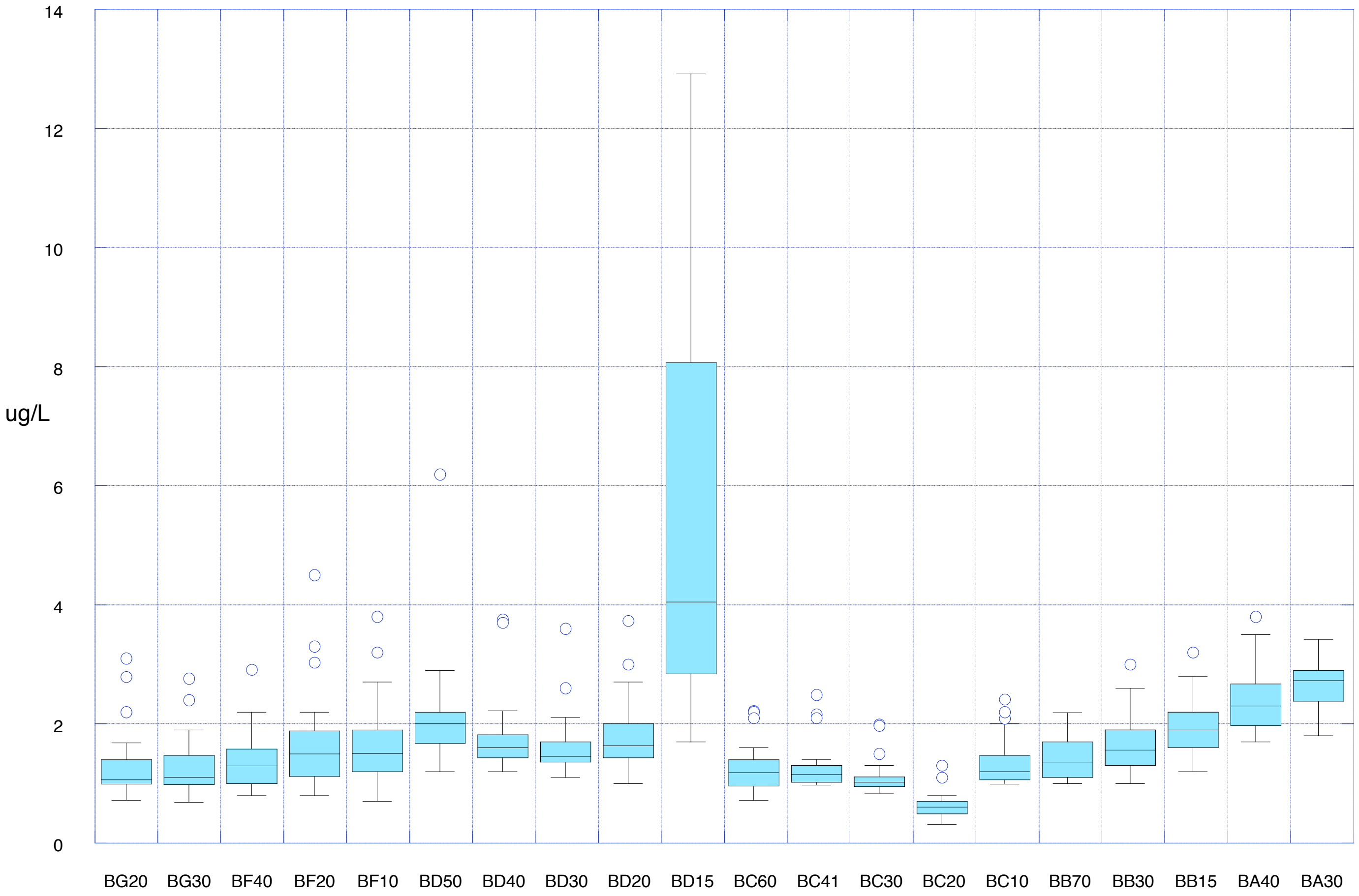
Variations in copper concentrations in Bay sediments are exhibited in **Figure 3.10**. These concentrations are likely a function of the types of sediments found in each area. For instance coarse sands at BG20 and BG30 correlate with lower binding of metals, while the fine grain sediments at BF40 and BF21 correlate with high metals concentrations.

Figure 3.10. Dissolved Copper in San Francisco Bay Sediment North of the Dumbarton Bridge (1993 – 2001) [SFEI, 2001a]



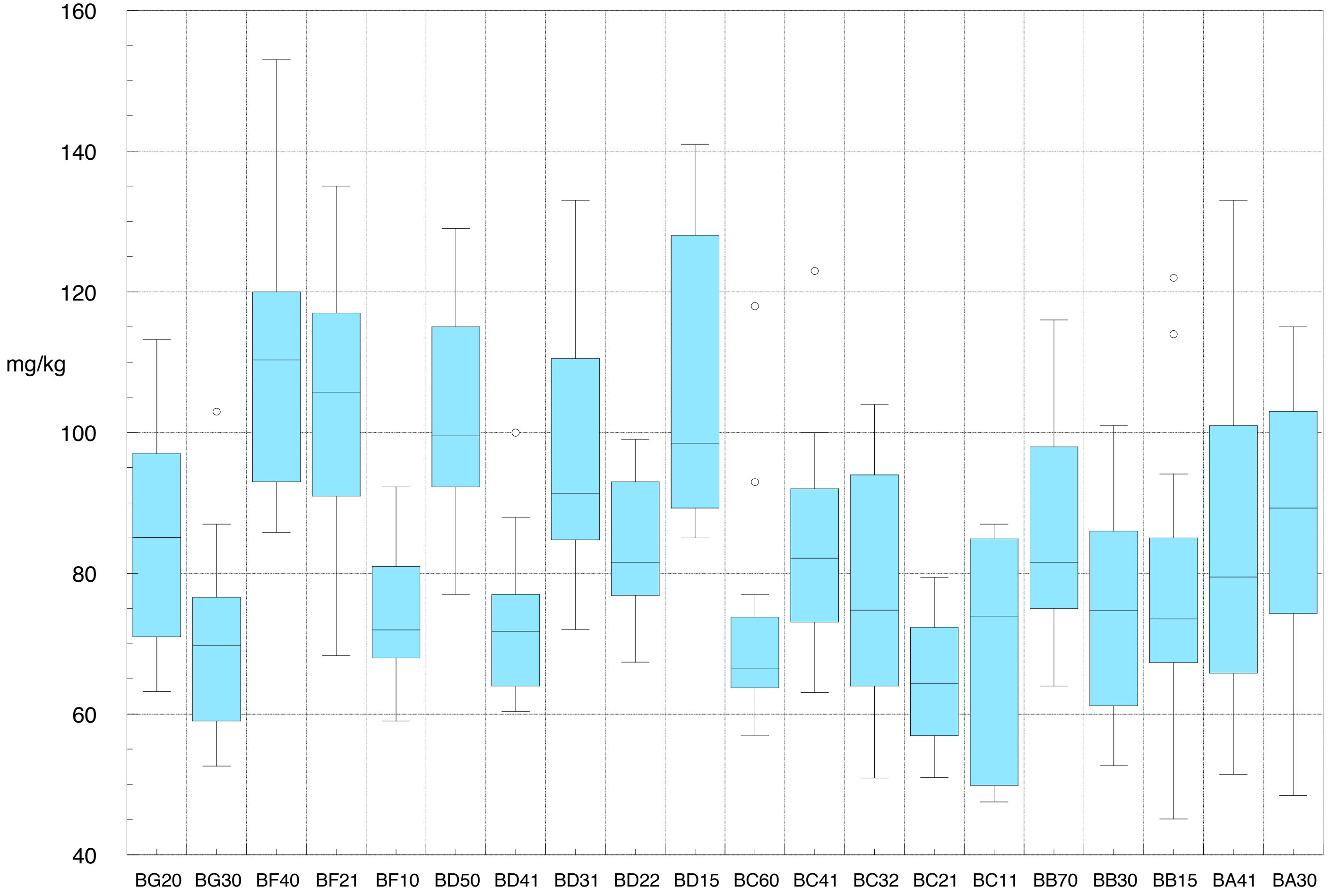
Variations in dissolved nickel concentrations in Bay waters are exhibited in **Figure 3.11**. The BC20 station represents the Golden Gate Bridge samples, and the lowest concentrations of dissolved nickel in the Bay (ocean water). The Petaluma River station (BD15) represents the highest concentrations, and is discussed in further detail later in this section. To the left of BC20 in **Figure 3.11**, concentrations increase somewhat steadily to the Napa River stations (BD50) {excluding BD15} and then decrease toward the Sacramento and San Joaquin River mouths. To the right of BC20, concentrations of dissolved nickel increase steadily as stations move toward the Dumbarton Bridge.

Figure 3.11. Dissolved Nickel in San Francisco Bay Water North of the Dumbarton Bridge (1993 – 2001) [SFEI, 2001a]



Variations in nickel concentrations in Bay sediments are exhibited in **Figure 3.12**. These concentrations are likely a function of the types of sediments found in each area. For instance, coarse sands at BG20 and BG30 correlate with lower binding of metals, while the fine grain sediments at BF40 and BF21 correlate with high metals concentrations.

Figure 3.12. Dissolved Nickel in San Francisco Bay Sediment North of the Dumbarton Bridge (1993 – 2001) [SFEI, 2001a]



3.6.2 Sediment Dynamics

Many contaminants of greatest concern in San Francisco Bay, are primarily associated with sediment particles rather than dissolved in water. Therefore, the movement and fate of sediment determines the movement and fate of many contaminants in the Bay.

Through study of suspended sediment dynamics, the RMP is developing a better understanding of trends and patterns of contaminants and how the Bay will respond to management actions during the next several decades. Recent RMP efforts to develop predictive models of contaminant fate in the Bay have highlighted the fundamental importance of understanding sediment dynamics. Sediment movement in the Bay is determined by tides, wind, and freshwater inflow. Tides flood and ebb twice a day, wind typically is strongest in the afternoon, and freshwater inflow is greatest during the winter rainy season.

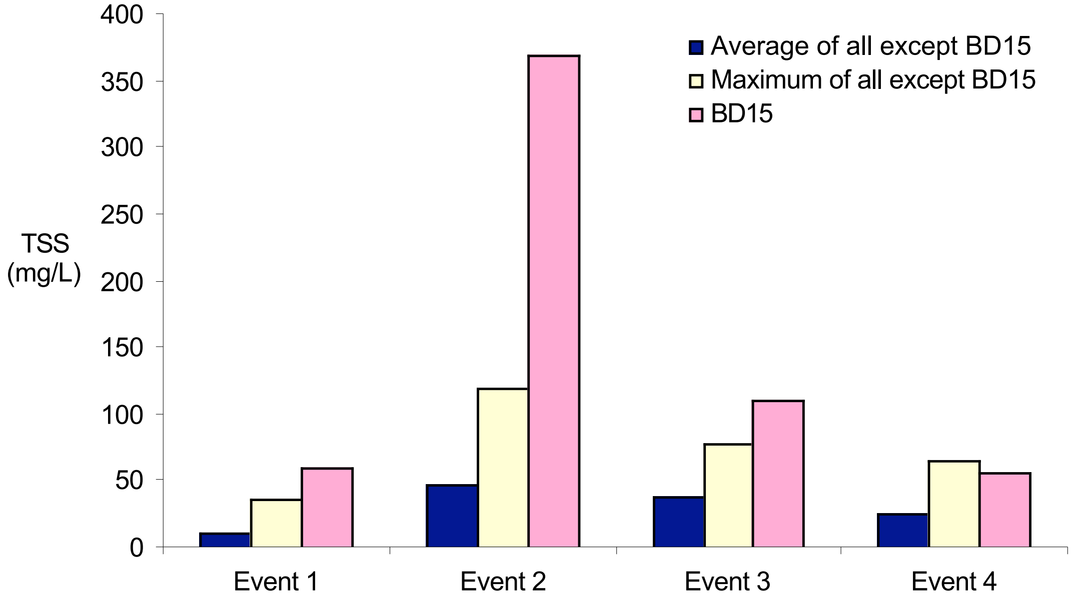
3.6.3 Sediment Transport Explains Contaminant Distribution: Petaluma River

The RMP consistently has measured high concentrations of contaminants in the mouth of the Petaluma River, which drains into northern San Pablo Bay [RMP, 2002]. Sediment transport between the Petaluma River and San Pablo Bay creates high suspended sediment concentrations, which largely explains the area's high concentrations of contaminants. The USGS and the University of California at Davis collected continuous hydrodynamic and suspended sediment concentration data in the Petaluma River from January 1999–August 1999, and from September 2000–March 2001 [Barad et al., 2001]. The geometry and tidal currents in the area create a process of sediment erosion and deposition that repeats with each tidal cycle (about every 12.4 hours). As water flows seaward on ebb tides, the tidal currents apply force to the riverbed. An upstream deposit of sediment on the bed of the Petaluma River is eroded and mixed into the water column. As this suspended sediment mass moves downstream, very high suspended sediment concentration are present (>500 mg/L). Once the suspended sediment mass reaches San Pablo Bay, the slack tide and broad area allow sediment to drop out of the water, forming a downstream sediment deposit. As water begins flowing landward immediately after the tide turns from slack to flood, the downstream sediment deposit is re-suspended and transported upstream. This to and fro process then repeats, with the same sediment mass oscillating back and forth between the Petaluma River and San Pablo Bay. Sediment effectively is trapped within this area, except during large flows in the Petaluma River. This process accounts for the high concentrations of suspended sediment concentration and contaminants in RMP samples collected at the mouth of the Petaluma River.

As was be seen in the plots above (**Figures 3.9 & 3.11**), site BD15 stands out from the other sites as having higher metal concentrations. The highest observed dissolved nickel concentration of 17.2 µg/L occurred during Event 2 at site BD15. The associated total nickel concentration was 47.6 µg/L. Fine grain size as a result of upstream erosion sources and marsh resuspension may contribute to high natural nickel concentrations in this part of San Francisco Bay.

The 2003 Pulse of the Estuary provides a detailed discussion of sediment transport of contaminants at the Petaluma River mouth [SFEI, 2003]. **Figure 3.13** illustrates the elevated TSS at site BD15 compared to the other twelve sites monitored. The BD15 suspended solids were greater than the average and maximum TSS concentrations at all of the other sites, except for site SPB03 during Event 4. Elevated total copper and nickel concentrations appear at least partially linked to the elevated suspended solids (at BD15). Higher concentrations of complexing ligands may be responsible at least in part to the higher dissolved metals concentrations also observed.

Figure 3.13. Suspended Solids (mg/L) at BD15



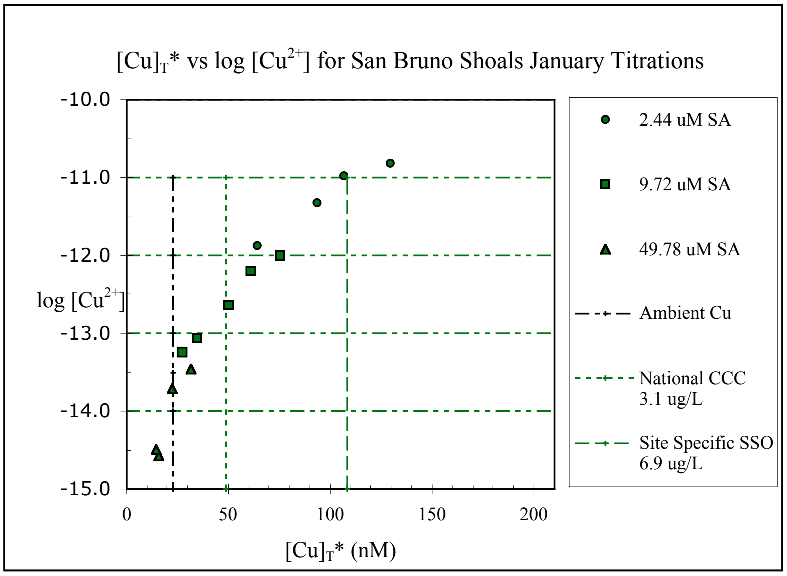
3.6.4 RWQCB Speciation Study Results

Buck and Bruland [2003] performed a study on copper speciation in San Francisco Bay. Total dissolved copper concentrations and the chemical speciation of the dissolved copper were determined at six sites throughout San Francisco Bay (Dumbarton Bridge, Redwood Creek, San Bruno Shoals, Yerba Buena Island, San Pablo Bay, and Grizzly Bay) during January and March 2003 to compliment data sets from previous summertime samplings. Overall, the data from the winter months correlates well with the summer month data. The highest [Cu^{2+}] values were found at Yerba Buena Island, where there was the least excess of strong L_1 ligands. The lowest [Cu^{2+}] values were observed at the Grizzly Bay site, and the second lowest at Dumbarton Bridge.

Throughout San Francisco Bay the total dissolved copper is strongly complexed by natural ligands in solution. Results indicate that the strong copper-binding ligand concentrations (organic ligands) exceed the dissolved copper concentrations at each site, and that in every case the dissolved copper is greater than 99.9% complexed by the natural L_1 strong ligand class. This strong organic complexation of the copper results in very low free hydrated Cu^{2+} ion concentrations. Regardless of site or season, the [Cu^{2+}] values throughout San Francisco Bay did not exceed 10^{-13} M, suitably below the toxicity limit for aquatic organisms [Brand et al., 1986]. Thus, the strong copper-binding ligands appear to effectively buffer the free Cu^{2+} at low concentrations and supports the finding that San Francisco Bay is not likely impaired by the existing levels of dissolved copper in the water column.

The method for determining speciation incorporates salicylaldoxime (SA) as the added ligand, which forms an electroactive $Cu(SA)_2^0$ complex. Using this method, one can predict the $[Cu^{2+}]$ resulting from an increase in the $[Cu^*_T]$ to, for example, national guidelines (see **Figure 3.14** below). At the site-specific SSO guideline of 6.9 µg/L, or approximately 108 nM, results from the South Bay sites predict that the $[Cu^{2+}]$ will reach 10^{-11} M, which approaches the threshold value for copper toxicity to phytoplankton.

Figure 3.14. Copper Speciation Study Results



A $[Cu^*_T]$ versus $[Cu^{2+}]$ plot for San Bruno Shoals January titrations at three unique analytical windows (2.44uM, 9.72uM, 49.78uM) was used to determine the carrying capacity of the ligand pool. The carrying capacity of the ligand pool describes to what level of total dissolved copper the water will tolerate before the free Cu^{2+} concentrations exceed the toxicity threshold of the phytoplankton community. In the above plot it can be seen that at the ambient dissolved copper concentration, $[Cu_{amb}]$, the $[Cu^{2+}]$ is $10^{-13.5}$ M. It can also be seen that the $[Cu^{2+}]$ would exceed 10^{-11} M at a $[Cu_T]$ of 108 nM (or 6.9 µg/L). This observation supports the results of the site-specific toxicity studies done in South San Francisco Bay, which proposed the level of 6.9 µg/L as the toxicity threshold for this region. It is important to note, however, that exceeding this dissolved copper level may lead to toxic conditions for phytoplankton, as the free Cu^{2+} concentrations exceeds 10^{-11} M.

3.6.5 Describe dissolved to total relationships (translators)

The relationship between dissolved and total concentrations of copper and nickel in San Francisco Bay NDB has been reviewed extensively in a separate CEP report (*North of Dumbarton Bridge, Copper and Nickel Development and Selection of Final Translators*, EOA/LWA, 2004).

The key finding in that report is that choices exist regarding the adoption of acute (90th percentile) and chronic (median) translator values for use in NPDES permitting. These values may be adopted for Central Bay, for North Bay, or as single values for the entire Bay. As was done in the Lower South Bay, the report recommends that the final selection of translator values be considered jointly with the determinations regarding site-specific objectives values for copper and nickel NDB.

3.7 Summarize other key elements and findings in the conceptual model report for copper and nickel for South Bay

The "*Conceptual Model Report for Copper and Nickel in Lower South San Francisco Bay*" [Tetra Tech, 1999] (CMR) stated the following:

> ***The highest priority should be to quantify the speciation of copper and nickel*** *and the cycling processes that influence speciation, since this determines bioavailability, uptake, and toxicity to aquatic organisms.* ***If*** *it is determined that the potential exists for the impairment of beneficial uses due to copper or nickel concentrations in Lower South San Francisco Bay, then steps should be taken to better quantify the sources of these metals. Four key areas have been identified for future studies: 1) biogeochemical processes influencing chemical speciation, 2) effects of speciation and competing metals on phytoplankton uptake and toxicity, 3) resuspension fluxes and other sediment-water interactions, and 4) wet season tributary loads* (emphasis added).

As stated previously, speciation studies have been performed NDB which have provided greater understanding regarding the concentrations of important chemical forms (free ionic, strongly and weakly complexed) and the probable impact of these conditions on aquatic toxicity. Other areas of emphasis identified in the LSB effort are discussed below.

3.8 Uncertainties

Several processes have been identified that would be important to the development of the SSOs for copper and nickel, but for which there is either a lack of sufficient information or a high degree of uncertainty. These processes may be the focus of future studies, if deemed necessary. The major sources of uncertainties are summarized below, followed by recommendations for future studies to reduce these uncertainties.

3.8.1 Key Questions regarding Copper and Nickel in San Francisco Bay

3.8.1.1 Copper and nickel management questions

As identified in the impairment assessment portion of this report, several major management questions exist which are fundamental to Regional Board actions in the adoption and implementation of site-specific objectives for copper and nickel. Two of these questions have particular connection with the conceptual models for copper and nickel.

1. Will the adoption of site-specific objectives lead to increased loadings from point sources that will have a measurable impact on dissolved water column copper and nickel concentrations in SF Bay?

> This question has been described previously and relates to several factors, including the change in effluent limitations resulting from adoption of site-specific objectives, the sensitivity of effluent quality changes at NPDES treatment facilities to relaxed effluent limitations, the magnitude of NPDES source loadings from a Bay-wide or sub-

embayment standpoint, and the effect of changes in copper and nickel loadings from the existing baseline condition resulting from such changes in effluent quality.

At least a portion of these uncertainties can be resolved through use of water quality modeling, as described later.

2. What implementation measures are needed to ensure that existing copper and nickel concentrations in the water column and surface sediments of the Bay will not increase significantly?

This question is a follow-up to the previous question. If increased NPDES inputs of copper and nickel resulting from relaxed effluent limits are determined to have a significant effect on ambient conditions in the Bay, additional controls will be needed to minimize such increased inputs. The effectiveness of various control measures in reducing NPDES inputs must be understood to enable prioritization and implementation of appropriate control measures. Again, water quality modeling will be useful in the resolution this question, as described later. In addition to these primary management questions, a number of technical uncertainties remain. The need to address these areas of uncertainty will be a determination to be made by the CEP after review of this document.

3.8.1.2 Sedimentation/Resuspension Dynamics

Interactions between the sediments and water column are important, both because metals released through resuspension and porewater diffusion are significant sources of metals to the water column and because external metal loads accumulate in the sediments and produce exposure through the benthic food web. Unfortunately, limited information is available on the sedimentation dynamics of the Bay.

A detailed sediment budget has not been developed. The magnitude, seasonal variations, and year-to-year variations of external sediment loads from the watersheds are highly uncertain due to limited data. Information on the temporal variations in sedimentation and resuspension fluxes is also sparse. No information is available on the exchange of sediments between the shoals and the channel. Understanding the differences in the sedimentation and resuspension dynamics between the shallow shoal areas and the deeper channel areas is important for quantifying resuspension fluxes and metals release to the water. Sediment rheology parameters such as erodability have also not been measured. Sediment transport processes and sediment exchange with other areas of the Bay have not been well quantified.

3.8.1.3 Adsorption/Desorption Kinetics

Desorption of copper and nickel during sediment resuspension is an important source of dissolved metals to the water column, yet very limited information is available on the rate constants for the adsorption and desorption reactions. These rates will vary depending on the size and nature of the suspended particles, so the particle size distributions of both suspended particles and sediments also need to be quantified.

3.8.1.4 Limited Sediment Core Data

Information on copper and nickel concentrations in sediments and sediment porewaters is limited to only a few cores and sampling dates. More data are necessary to better determine metal release fluxes due to resuspension and porewater diffusion, and to estimate the long-term sediment recovery from the previously higher historical loadings.

3.8.1.5 Nonpoint Source Tributary Loads

Wet season tributary loads of copper and nickel are currently the largest external sources, but their magnitudes and temporal variations have high uncertainties. The streams have not been regularly monitored for metals and suspended particle concentrations, so the loadings are based on simulation model predictions [URS Greiner Woodward Clyde, 1998]. The resulting estimates are uncertain because the data used in the model have a high degree of variability, land-use data from the late 1980's were used, limited data were available for metal concentrations in runoff from open space and industrial land uses, large correction factors were required during model calibration, and several simplifying assumptions were used in the model (e.g., metal concentrations in runoff are independent of flow rates and antecedent conditions) [URS Greiner Woodward Clyde, 1998]. The Sources, Pathways and Loadings work group of the Regional Monitoring Program, in cooperation with the Clean Estuary Partnership, is undertaking studies to improve the methodologies for estimation of wet season loadings from small and large tributaries (McKee and Leatherbarrow, 2003). This effort includes high flow monitoring studies at Mallard Island and on the Guadalupe River that may provide useful tools for estimation of wet season copper and nickel tributary loads.

3.8.1.6 Food Web Transfer

With the exception of bivalves, copper and nickel have not been measured in higher trophic level organisms such as zooplankton and fish in San Francisco Bay. This makes it difficult to estimate food web transfer of the metals and the relative contributions of water versus food uptake. Limited information is available in the literature on copper and nickel uptake rates from water, assimilation efficiencies from food, and depuration rates. Much less information is available for nickel than for copper. Most of the available data are for different species than those in San Francisco Bay. Although information from other species can be used to estimate uptake and accumulation of copper and nickel in South San Francisco Bay organisms, these estimates would be speculative without some measurements of copper and nickel concentrations in the target organisms and their key food sources. Although tissue concentration data are available for benthic bivalves, no data are available for their major food sources (phytoplankton, organic detritus).

3.8.1.7 Limited Information on Nickel

Much less is known about the cycling, bioavailability, uptake, accumulation, and toxicity of nickel than of copper. This is true of the literature in general, as well as for studies conducted specifically in San Francisco Bay.

3.8.1.8 Limited Wet Season Data

Less information is available for wet season cycling and transport processes than for the dry season. Most of the existing transport studies have focused on dry season conditions. The effects of seasonal variations in Delta outflows and flushing effects on the fate of copper and nickel in the Bay are uncertain.

3.8.2 Approaches to Resolve Uncertainty

3.8.2.1 Areas of Uncertainty that can be Addressed through Water Quality Modeling

The following areas of ongoing uncertainty have been identified, which can be significantly reduced through the use of mathematical hydrodynamic and water quality models (e.g. MIKE 21).

a. Incremental water quality impacts that may result at various locations in San Francisco Bay due to changes in (1) concentrations and/or (2) mass loadings from existing POTW and Industrial discharges of treated wastewater. This is important to the Regional Board's assessment of the effect of adopting site-specific water objectives for copper and nickel for San Francisco Bay. Water quality objectives are used in the determination of numeric effluent limitations. Concern exists that an increase in the water quality objectives for copper and nickel to higher allowable water column concentrations in the Bay will result in higher effluent limits and, thereafter, higher concentrations in NPDES effluents. Concern also exists that such increases in effluent concentrations will produce higher concentrations of dissolved copper and nickel in the Bay. The Regional Board must address a potential change in ambient water quality as a result of adoption of SSOs for copper and nickel to determine consistency with state and federal anti-degradation policies. In the South Bay, this issue was addressed through implementation of the ambient monitoring/ambient trigger approach. This empirical approach linked enhanced source control at NPDES discharges to results of Bay monitoring. The working hypothesis for this program was that control of mass loadings from NPDES discharges (POTWS and urban runoff) was key to control of ambient water quality.

   The mathematical model can address this issue by replicating existing ambient water quality conditions with existing NPDES loadings, Delta outflow, etc. and then increasing or reducing the loadings from some or all sources to assess incremental changes in water quality at various locations in the Bay.

b. Incremental changes in surface sediment concentrations of copper and nickel that may result from increased loadings of copper and nickel from NPDES discharges, as described above. The concern is that incremental increases in mass loads from NPDES dischargers will increase the mass of copper and nickel in surface sediments, resulting in increases in concentration.

   The mathematical model can predict the change in surface sediment concentrations under the existing NPDES loading condition and various other loading scenarios. The *model can also address the resulting interactions between surface sediments and water column concentrations.*

c. The impact of the erosion of bedded sediments on Bay water quality. Available sediment cores indicate that elevated levels of copper and nickel exist at specific locations in the Bay. The Selby Slag disposal area is an example of one such area. If erosion of Bay sediments occurs in these areas, concern exists that exposure of sediments with elevated concentrations will cause and increase in ambient dissolved copper and nickel water column concentrations.

   The mathematical model can be employed to assess the effect of significantly elevated areas of surface sediment concentration on dissolved copper and nickel concentrations around the Bay.

d. The relative magnitude and importance of copper and nickel sources to Bay water quality. While the mass loadings of copper and nickel in POTWs and industrial treated effluents are accurately quantified, the mass loadings from urban runoff, atmospheric deposition, riverine sources and in-Bay sediments are not.

   The mathematical model simulates source loadings based on available data for all significant sources. The sensitivity of Bay water quality at any location to changes in other significant sources (apart from NPDES discharges) is a direct result that can be obtained from the model. The results from the ongoing Brake Pad Partnership modeling effort will assist greatly in the quantification of urban runoff loadings to the Bay.

3.8.2.2 Resuspension Fluxes and Other Sediment-Water Interactions

One of the largest sources of both dissolved and particulate copper and nickel is estimated to be resuspension from the sediments. Although external loads are highest during the wet season, water column concentrations of both dissolved and particulate copper and nickel are highest during the dry season. The dry season is also the windy season, when resuspension rates are highest. During sediment resuspension, desorption can release significant quantities of dissolved metals to the water column. Mass balance analyses of dry season loadings, inventories, and residence times in the water column of the Lower South Bay indicate that desorption during resuspension could be a major source of dissolved copper and nickel during the dry season. The other loadings cannot account for the currently observed dissolved metal concentrations in the water column. This internal source is also the most difficult to quantify, and therefore has the highest uncertainty and the least amount of information available. Decomposition and mineralization of settled phytoplankton could also be an important sediment source, as could remineralization of suspended particles during benthic grazing and benthic bioturbation/ irrigation effects on sediment release. Therefore, studies to better quantify copper and nickel release during resuspension and biological effects on sediment cycling may be warranted.

Of related importance are studies to quantify the accumulation of metals into the sediments. Since the sediments are a main repository of both historical and continuing loads, and since they continue to reintroduce copper and nickel into the water column through resuspension, sediment diffusion, and biological cycling, it would be useful to get a better understanding of the movement of copper and nickel into the sediments from existing external loading sources.

It may be appropriate to convene an expert panel to develop ideas for further studies to quantify these processes. Laboratory experiments could be conducted to estimate desorption fluxes using surficial sediments and water collected from the Bay. Since the metal concentrations adsorbed to particles appear to vary with particle size, additional information to establish these relationships, along with particle size distributions in the Bay, could be established through field and/or laboratory studies. This information should be used in conjunction with model analyses to estimate the resuspension and other sediment exchange fluxes, since it is not practical to obtain direct estimates from field studies. Studies by Moss Landing Marine Laboratories (MLML) of soluble metal fluxes from Bay sediments could be used to refine the current estimates of these fluxes. Analysis of historical bathymetry changes along with geochemical studies of sediment cores could provide additional information on metal accumulation in sediments.

3.8.2.3 Wet Season Tributary Loads

Wet season tributary runoff loads are the most important of the external load sources, both in terms of magnitude and in terms of potential for load reductions by watershed management or stormwater treatment. The existing load estimates also have a fair amount of uncertainty associated with them, and they could be refined using more current or projected land use information, more recent and complete runoff loading data, and more advanced models than were available when the original estimates were made. Therefore, wet season loads should continue to be the primary focus of additional work on refining external load estimates. POTW loads have already been substantially reduced and the load estimates are well characterized through frequent monitoring. Atmospheric loads are uncertain, but are very small compared to other sources and therefore do not merit additional work. Sediment diffusion loads appear to be small relative to resuspension loads. However, these estimates were based on limited data, and they should be refined in conjunction with the other sediment studies recommended above. Even though the wet season tributary loads occur during the period when water column concentrations of copper and nickel are at their lowest, they are still the largest external source, and therefore probably contribute significantly to the sediment inventories, which in turn contribute to the water column through resuspension during the dry season.

3.8.2.4 Track and Encourage

The Copper Action Plan (CAP) developed as part of the Lower South San Francisco Bay copper and nickel studies includes efforts to "track and encourage" activities and research intended to reduce the scientific uncertainties associated with the impairment assessment and conceptual model reports' conclusions [Tetra Tech, 2000b]. Many of these uncertainty reduction activities are applicable to assessing potential copper impacts throughout the Bay NDB.

The Santa Clara Valley Urban Runoff Program has contracted with both SFEI and the Clean Water Fund (CWF) to develop web-based clearinghouses for "uncertainty" studies and pollution prevention studies, respectively, for copper and nickel. The SFEI effort is scheduled to be completed at the end of 2004. The CWF effort on pollution prevention studies is scheduled to be completed in mid 2005. The Brake Pad Partnership is also establishing a website to address copper issues, pending receipt of Proposition 13 grant funding.

3.8.2.5 Coordination

SCVURPPP, as one of its South Bay CAP activities, has developed a prototype Copper P2 Clearinghouse website. The site contains pages describing about 15 copper sources with links to documents and other sites with information on potential control measures for both POTWs and stormwater programs. It incorporates the latest information from, and is intended to be a complementary resource to the Pollution Prevention Menus project report and the Copper Sources in Urban Runoff and Shoreline Activities report. It was released in December 2004. The website has been designed as a bay-wide resource and is recommended to be continued as such.

3.8.2.6 Compile Regional Research Documents

A significant amount of basic and applied research has been undertaken in the region investigating copper and nickel processes and effects in various segments of the Bay. Much of this work is scattered about in various reports both off-line, and on-line located at websites for particular research institutions, scientific journals, stakeholder groups, and agencies. Although many of these efforts already cite and cross-reference each other, compiling these various data sources together at one location would benefit any parties interested in research on Cu/Ni processes in the region.

SCVURPPP contracted with SFEI to develop a prototype website that groups technical uncertainties into six categories (see below) and provides links to documents and other sites with applicable information.

- Environmental Distribution
- Sources and Loads
- Transport Processes
- Chemical Processes
- Bioavailability and Effects
- Comprehensive Studies

Most of these uncertainties apply to issues and phenomena bay-wide such as copper speciation and sediment toxicity. The intent is to use the site as a vehicle for keeping track of new information bearing on the identified scientific uncertainties and on potentially newly identified uncertainties. It was released in December 2004. The website has been designed as a bay-wide resource and is recommended to be continued as such.

4. REFERENCES

ABAG. **2001**. Projections 2002: Forecasts for the San Francisco Bay Area to the Year 2025.

Abu-Saba, K.E. **1998**. Spatial and temporal variability in the aquatic cycling of chromium. Ph.D. dissertation in Chemistry, University of California, Santa Cruz.

Anderson *et al.* **2001**. Influence of sample manipulation on contaminant flux and toxicity at the sediment-water interface. *Mar. Environ. Res.,* 15:191-211.

Barad *et al.* **2001**. CISNet San Pablo Bay network of environmental stress indicators: the CISNet hydrodynamic database. State of the Estuary Conference.

Brand *et al*. 1986. Reduction of marine phytoplankton reproduction rates by copper and cadmium. *Exp. Mar. Bio. Ecol.*, 96, 225-250.

Bruland, K.W. **1991**. Interactive influences of bioactive trace metals on biological production in oceanic waters. *J. of Limn. & Oceanog.*, 36, 1555-1577.

Buck, K.N and Bruland, K.W. **2003**. Copper Speciation in San Francisco Bay. Draft Report for the State Water Resources Control Board.

Carlson *et al.* **1984**. Guidelines for deriving Numerical Aquatic Site-Specific Water Quality Criteria by Modifying National Criteria. USEPA (EPA-600/3-84-099).

Census. **2000**. Selected Census 2000 data for the San Francisco Bay Area. http://census.abag.ca.gov/

Cheng, R.T. and Gartner, J.W., **1985.** Harmonic analysis of tides and tidal current in South San Francisco Bay, California: Estuarine, Coastal and Shelf Science, v. 21, p. 57-74.

City of San Jose. **1998**. Development of a Site-Specific Water Quality Criterion for Copper in South San Francisco Bay. San Jose/Santa Clara Water Pollution Control Plant. Environmental Services Department. San Jose, CA. May 1998.

Davis *et al.* **2000.** Contaminant loads from stormwater to coastal waters in the San Francisco Bay Region, San Francisco Estuary Institute, Richmond, CA, 82 pp. http://www.sfei.org/rmp/reports/AB1429/ab14.html

Davis *et al.* **2001**. Technical Report of the Sources, Pathways, and Loadings Workshop. March.

Donat *et al.* **1994**. Speciation of dissolved copper and nickel in South San Francisco Bay: a multi-method approach. *Analytica Chimica Acta.*, 284, 547-571.

EOA, Inc. and LWA, Inc, **2000**. Work Plan for Copper and Nickel Impairment Assessment to Assist in Preparation of 2002 303(d) List: San Francisco Bay, North of Dumbarton Bridge.

Prepared for North Bay Dischargers Group, Bay Area Dischargers Association and Western States Petroleum Association, August 17, 2000.

EOA, Inc. and LWA, Inc., **2002**. Copper & Nickel North of the Dumbarton Bridge. Step 1: Impairment Assessment Report, Ambient Concentrations and WERs, September 2000 – June 2001.

EOA, Inc. and LWA, Inc., **2004**. Clean Estuary Partnership: North of Dumbarton Bridge Copper and Nickel Site-Specific Objective (SSO) Derivation. March.

EOA, Inc. and LWA, Inc., **2004**. Copper & Nickel North of the Dumbarton Bridge, Development of Action Plans. Final. March.

Gunther *et al*. **1987**. An Assessment of the Loading of Toxic Contaminants to the San Francisco Bay-Delta. Aquatic Habitat Institute, Richmond, CA.

Hornberger *et al.* **1999**. Historical Trends of Metals in Sediments of San Francisco Bay, California. *Marine Chemistry*, 64, 39-55.

Katen, K. **2001**. Staff Report – Statistical Analysis of Pooled Data From Regionwide Ultraclean Mercury Sampling For Municipal Dischargers. California Regional Water Quality Control Board.

Kimmer, W. **2003**. Draft. Open Water Processes of the San Francisco Estuary. White Paper Prepared for the CALFED Ecosystem Restoration Program. May.

Long *et al.* **1995**, Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Env. Management*, v. 19, no. 1, p. 81-97.

Long, E.R. and Morgan, L.G. **1990**. The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. Seattle, Wash., National Oceanic and Atmospheric Administration, NOAA Technical Memorandum NOS OMA 62, 175 p.

Luoma *et al.* **1998**. Metal Uptake by Phytoplankton during a Bloom in South San Francisco Bay: Implications for Metals Cycling in Estuaries. *Limnology and Oceanography*, 43, 1007-1016.

McDonald, E.T. and Cheng, R.T. **1996**. A numerical model of sediment transport applied to San Francisco Bay, California. *J. of Marine Env. Eng.*, 4, 1-41.

McKee *et al.* **2002**. Estimates of Suspended-sediment Flux Entering San Francisco Bay from the Sacramento and San Joaquin Delta. SFEI Contribution 65. December.

Nichols and Pamatmat, 1988

Ning *et al.* **2000**. Spatial and temporal variability of picocyanobacteria *Synechococcus sp.* in San Francisco Bay. *Limn. & Oceanog.*, 45, 695-702.

Phillips *et al.* **2000**. Causes of Sediment Toxicity to *Mytilus galloprovincialis* in San Francisco Bay, California

RWQCB. **2002**. Staff Report on Proposed Site-Specific Water Quality Objectives and Water Quality Attainment Strategy for Copper and Nickel for San Francisco Bay South of the Dumbarton Bridge. May.

Rivera-Duarte, I. and Flegal, A.R. **1997**. Porewater gradients and diffusive benthic fluxes of Co, Ni, Cu, Zn, and Cd in San Francisco Bay. *Croatia Chimica Acta*, 70, 389-417.

SCVURPPP, **2001**. Santa Clara Valley Urban Runoff Pollution Prevention Program (SCVURPPP) NPDES Permit Number CAS029718, Order Number 01-024. February 21.

SCVURPPP, **2002**. Summary of SCVURPPP Copper and Nickel Action Plans FY01-02 Activities and Response to RWQCB staff Revised Comments on CAP/NAP Sections of the FY 2000-2001 Annual Report – July 3, 2002.

Sedlak *et al.* **1997**. Strongly complexed Cu and Ni in wastewater effluents and surface runoff. *Env. Sci. & Tech.*, 31, 3010-3016.

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

SFEI, **2001b**. Regional Monitoring News. Volume 6, Issue 2. www.sfei.org, Winter.

Save the Bay (STB), **2000**. *An Introduction to the San Francisco Estuary*, prepared by A. Cohen, December, pp. 2 to 9. San Francisco Estuary Project, and San Francisco Estuary Institute.

Sunda, W.G. and Huntsman, S.A. **1998**. Processes regulating cellular metal accumulation and physiological effects: Phytoplankton as model systems. *Sci. Tot. Env.*, 219, 165-181.

SWRCB. **2002**. Watershed Management Initiative Integrated Plan Chapter. January. www.swrcb.ca.gov

TDC Environmental, **2004**. Copper Sources in Urban Runoff.

Tetra Tech, **1999a**. Task 1. Conceptual Model Report for Copper and Nickel in Lower South San Francisco Bay. December.

Tetra Tech, **1999b**. Task 2. DRAFT: Impairment Assessment Report for Copper and Nickel in Lower South San Francisco Bay. August.

Tetra Tech, **2000a**. Task 2. Impairment Assessment Report for Copper and Nickel in Lower South San Francisco Bay. June.

Tetra Tech, **2000b**. Task 10. Copper Action Plan for Lower South San Francisco Bay. Revised February 2001. June.

Tetra Tech, **2000c**. Task 10. Nickel Action Plan for Lower South San Francisco Bay. Revised February 2001. August.

Thompson *et al.* **1999**. Relationships between sediment toxicity and contamination in San Francisco Bay. Mar Environ Res 48:285-309.

Topping *et al.* **2001**. What Regulates Dissolved-nickel Concentrations in the South Bay? USGS poster

Topping *et al.* **2001**. Benthic Flux of Dissolved Nickel into the Water Column of South San Francisco Bay: USGS Open-File Report 01-89, 50 p. http://pubs.water.usgs.gov/ofr01089

Topping, B.R. and Kuwabara, J.S., **1999**. Flow-Injection-ICP-MS Method Applied to Benthic Flux Studies of San Francisco, In USGS Water Resources Investigation Report 99-4018B, p. 131-134.

Tsai *et al.* **2001**. San Francisco Bay Atmospheric Deposition Pilot Study, Part 2: Trace Metals. SFEI Contribution 73.

URS Greiner Woodward Clyde. **1998**. Copper and Nickel Source Characterization for the Lower South San Francisco Bay TMDL Project. *Report prepared for the City of San Jose.*

US Army Corps of Engineers, **2001**. The Model of San Francisco Bay and the Delta. www.spn/usace.army.mil/bmvc/model.htm

USEPA. **1994**. Interim Guidance on Determination and Use of Water-Effects Ratios for Metals. Office of Water, Office of Science and Technology. EPA-823/B-94-001. February.

USEPA. **1986**. Ambient Water Quality Criteria for Nickel. EPA-440/5-86-004. Washington, DC.

USEPA. **2000**. 40 CFR Part 131: Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California; Rule

Watson *et al.* **1996**. Recalculation of the National Marine Water Quality Criterion for Nickel and Development of a Site-Specific Criterion. City of San Jose ESD, San Jose, CA and Tetra Tech, Inc. Owings Mills, MD.

Watson *et al.* **1999**. Nickel Acute-to-Chronic Ration Study. City of San Jose water Pollution Control Plant. Environmental Service Department.

Appendix A

City of San Jose Comment Letter,
May 18, 2004

Note:
Requested changes in the attached letter were made to the body of the report.

Dear Mr. Hardin:

The City of San José (City) appreciates the opportunity to submit comments on the April 2004, Clean Estuary Partnership's *North of Dumbarton Bridge Copper and Nickel Conceptual Model and Impairment Assessment Report (Draft Report)*.

Based on the City's previous experience with the copper and nickel impairment assessment and conceptual model development for the South Bay, the CMIA's should include the following three elements:

1. estimated loadings, mass balances, and inventories of the pollutants;
2. description of processes thought to be most important in controlling the pollutant, and;
3. a discussion of pollutant cycling effects on uptake and toxicity to aquatic organisms.

The Draft Report reasonably discusses the first two elements above with one important exception. The processes controlling existing in-Bay inventories of copper and nickel and the role of new inputs to the system are not completely understood. However, this should not be a critical information gap since dissolved copper and nickel concentrations in the Bay have remained uniform over the past decade, despite significant efforts to reduce point and non-point source contributions. Finally, the report does a good job in describing copper speciation and the dominant role of the ionic species in copper toxicity to Bay organisms. The report presents technical data and information so that an individual unacquainted with the subject matter can understand the issues and includes all of the elements described above. In addition, the report thoroughly discusses the data uncertainties, and requisite next steps.

The Draft Report recommends significant additional modeling to reduce uncertainties. The City does not support further numerical modeling as part of this project since ambient concentrations of copper and nickel have remained uniform in the Bay. CEP funding is very limited, and other pollutants where impairment is likely should be the priority. A Water Quality Attainment Strategy (WQAS) along with ambient monitoring such as required for the Lower South Bay, provides adequate assurances that beneficial uses are protected. Additional numerical modeling may be appropriate at a later date if increasing ambient concentrations are documented

The Draft Report often alludes to the Lower South Bay (LSB) Site-Specific Objective (SSO) development process without summarizing its findings. This may be an inconvenience to readers who may not have that document available to them. Such references to the LSB work should include summaries of approaches, processes, results, and conclusions. One example of this is the useful graphic of the conceptual model for copper and nickel developed for the LSB effort. However, the copy of this model used in the Draft Report is small and difficult to read. It is suggested that it be enlarged so that readers can review its contents.

Response: *Reference was made to Section1 of the July 2002* Copper & Nickel North of the Dumbarton Bridge Step 1: Impairment Assessment Repor*t, which summarizes the LSB work. Additionally, the conceptual model figures were made larger in this report.*

Copper & Nickel: Impairment Unlikely

City staff concludes that the Draft Report demonstrates that impairment of the Bay due to copper and nickel is unlikely. With the exception of dissolved nickel concentrations at the BD15 site (mouth of Petaluma River), water column measurements for copper and nickel North of the Dumbarton Bridge (NDB) are well below potential Site-Specific Objectives for these metals. In addition, sediment copper concentrations are well below ERM criteria (Long *et al*. 1995) which are indicative of sediments expected to exhibit toxicity.

City staff has the following additional comments on the Draft Report.

Impairment Assessment Specific Comments:

- Page iii

  "For copper in Lower South Bay, observed WER values ranged from 2.7 to 3.5 based on measured dissolved copper."

  Page 12

  "For copper, the City of San Jose used the Indicator Species Procedure in its Impairment Assessment. Observed WER values ranged from 2.5 to 5.2 based on measured dissolved copper."

  Comment:

  The numbers quoted on p. iii are a range of station means rather than a range of WER values. The "adjusted" (-14%) geometric **mean** Final WERs (FWERs) were 2.670, 2.876, and 3.535, respectively, for the Dumbarton North, Dumbarton South and Coyote Creek stations in Lower South Bay (LSB).

  Response: *Text replaced with "For copper, the geometric mean Final WERs (FWERs) were 2.670, 2.876, and 3.535, respectively, for the Dumbarton North, Dumbarton South and Coyote Creek stations in Lower South Bay (LSB)."*

  The range of 2.5 – 5.2 cited on p. 12 is for the unadjusted (observed) WER values for the two Dumbarton Bridge stations. These values were not used directly in the LSB calculations. The range of adjusted WERs for the two Dumbarton stations used to derive a LSB Final WER and SSO was 2.2 to 4.5.

  Response: *Text replaced with "The range of adjusted WERs for the two Dumbarton stations used to derive a LSB Final dissolved copper WER and SSO was 2.2 to 4.5.*

- Page 11, footnote 1

> *"a WER is the ratio of toxicity of a given pollutant in laboratory water to toxicity in site water."*
>
> **Comment:** This statement transposed the words "laboratory" and "site". In the "ratio", site water results are the numerator and lab water results are the denominator (the lab water is the standard denominator).
>
> ***Response:*** *Footnote has been edited appropriately.*

- Page 12

  "A recommended range of chronic copper SSOs of 6.8 to 8.4 NDB has been developed from the observed WER values [EOA/LWA 2004]."

  Comment:

  The numbers 6.8 and 8.4 do not represent a range at all. Rather, they are both derived using the arithmetic mean for all 13 NDB sites multiplied by either 3.1 (the "CTR SSO") or 2.5 (the "Recalc SSO"). In a comment letter dated 4/1/2004 concerning the NDB SSO report, the City recommended the development and evaluation of Final WERs by Bay Region. Using a modified national criterion of 2.5 (referred to as "Recalc SSO" in the report) and the Bay regional WERs recommended in the City's letter, City staff calculated a range of NDB SSOs of 6.0 (Region 2) to 7.3 (Region 4). This represents an appropriate range of FWERs for the Bay NDB.

  Response: *Range has been edited to 6.0 to 8.6, for Regions 1-2-3, and Region 4. This range incorporates both the current 3.1 µg/L and the recalculated 2.5 µg/L criterion.*

P. 17

"Causes of sediment toxicity have been further investigated using toxicity identification evaluations (TIEs)…However, the TIE findings were not conclusive regarding the contribution of copper to observed sediment toxicity effects."

"It is therefore recommended that the results from TIE testing should only be used to develop a more definitive test procedure to confirm the suggested toxicant. Chemical specific data must also be used to verify the source of toxicity conclusively"

> **Comment:**
>
> City staff agrees with these statements. The SFEI sponsored Phillips *et al.* (2000) TIE paper implicating copper is a working example of flawed science and why confirmatory Phase III TIEs are needed.[3] Papers such as Phillips et al. (2000) need greater peer review, evaluation,

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[3] The City's comments on the Phillips *et al.* (2000) paper are included as Attachment 1.

and oversight prior to publication. The overstatement of the data in the conclusions is subjective and does not serve the needs of this report.

Response: *Included Phillips et al. paper and San Jose's comments in Appendix A of this report, and referenced this addition in the body of the report.*

- P. 24

  "*Regardless of site or season, the [Cu2+] values throughout San Francisco Bay did not exceed* 10^{-13} *M, suitably below the toxicity limit for aquatic organisms*."

  Comment:

  Since this is a direct quote from Buck and Bruland (2003), please cite the work and put the statement in quotation marks. It is important that the reader understands that this is the conclusion of Drs. Buck and Bruland.

  Response: *Clarified reference and changed sentence so that it was not a direct quote.*

- P. 24, Section 2.5.10 CVRWQCB Algae Toxicity Study

  This section discusses problems with algal toxicity tests and TIE methods in a study funded by CALFED. During the Lower South Bay SSO development process, City staff evaluated the potential problems (confounding factors, extrapolation to the field, and salient endpoint to regulate) associated with algal toxicity testing. Those comments are included as Attachment 2.

  Response: *Added the following text "During the Lower South Bay SSO development process, San Jose staff evaluated the potential problems (confounding factors, extrapolation to the field, and salient endpoint to regulate) associated with algal toxicity testing (see comments in Attachment 2 to City of San Jose letter dated May 18, 2004 in Appendix A).*

- Page 46, Table 2.3

Table 2.3 Trigger Levels Relating to the Ideal Sampling Scheme (μg/L)

		Region 1	*Region 2*	*Region 3*	*Region 4*
Copper μg/L	*increment*	*0.82*	*1.29*	*0.79*	*0.79*
	concentration	*2.87*	*3.47*	*2.23*	*3.16*
Nickel μg/L	*increment*	*0.80*	*1.18*	*0.76*	*1.22*
	concentration	*2.16*	*3.26*	*2.18*	*3.55*

"*It is assumed that RMP sampling will provide 12 samples in Region 2 and 8 samples in Region 4, to provide a 99% level of power in the monitoring effort.*"

Comment:

The report should note that some power (ability to detect a statistical difference) is lost in using an n of 8 for Region 4 compared to using an n of 12, as is recommended for Region 2. The report should note what the added cost would be to sample Region 4 twelve times so that the power analysis for each Bay Region would be based on the same n.

Power analysis indicates the increase in copper (or nickel) that can be statistically detected. This is not likely an increase that is ecologically or biologically significant. A biologically significant endpoint is the SSO itself.

Response: *Added the following text "Some power (ability to detect a statistical difference) is lost in using an n of 8 for Region 4 compared to using an n of 12, as is recommended in Region 4 (Draft Development of Action Plans, EOA/LWA, June 2003, Appendix 3). Power analysis results simply indicate the incremental increase in ambient copper (or nickel) concentrations that can be statistically detected at a given level of significance (in this case 99%). This level of increase is not likely one that is ecologically or biologically significant. A biologically significant endpoint is the SSO itself."*

Conceptual Model Specific Comments:

- P. 75

"Elevated copper and nickel concentrations appear at least partially linked to the elevated suspended solids" (at BD15).

Comment:

High TSS values at BD15 explain the higher total metals concentrations often observed at that station. Please explain in the report the reason (i.e. source of complexing ligands) for the higher dissolved metals concentrations also observed at that station.

Response: *Added the following text "Higher concentrations of complexing ligands may be responsible at least in part to the higher dissolved metals concentrations also observed."*

- P. 77

Concerning acute and chronic translators, the report asserts that *"These values may be adopted for Central Bay, for North Bay, or as single values for the entire Bay. As was done in the Lower South Bay, the report recommends that the final selection of translator values be considered jointly with the determinations regarding site-specific objectives values for copper and nickel NDB."*

Comment:

The City supports the derivation of regional translators for Bay Regions 1-4. It may be appropriate to combine chronic (median) translators for Bay Regions 3 & 4 (Central Bay) since they are similar (0.72 & 0.76). It may not be appropriate to combine median translators for Bay Regions 1 (San Pablo Bay) & 2 (Suisun Bay) into one North Bay translator since translators for these two regions are not entirely similar (0.35 & 0.44) and since these Bay regions are separate embayments.

The City supports the application of a single SSO of 6.9 to Bay Regions 4 & 5. The City also supports combining SSOs for Bay Regions 1-3 into a single SSO. Since the derived translators for Bay Regions 4 (NDB) & 5 (Lower South Bay) are 0.76 and 0.53, respectively, there is little likelihood that only one or two translators and one or two SSOs will be appropriate for the entire Bay (Regions 1-5). The focus should be on the best available science not just on the most simplistic regulatory approach. As recommended in the report, there is no reason why these two decisions (translators and SSOs) cannot be considered jointly.

Response: *These issues will be dealt with in the translator report and the Basin Plan Amendment process.*

Appendix A, Attachment 1

San José comments on the Phillips *et al.* (2000) paper

Title: Causes of Sediment Toxicity to *Mytilus galloprovincialis* in San Francisco Bay, California

This paper presents some critical information and results characterizing the persistent toxicity associated with Grizzly Bay sediments. Sediment toxicity at this station and its underlying causes appears to be variable, complex, and enigmatic. The paper helps to clarify the role of copper in the persistent toxicity observed at this station. There is concern, however, that the role of copper in the sediment toxicity at this station may have been overstated in the paper's conclusions. The following remarks describe some of these concerns.

The paper describes results of TIE manipulations done on three Grizzly Bay sediment samples. Three of the paper's conclusions (restated below) are critically reviewed with regard to the TIE results obtained for the three samples.

Conclusion 1, stated in the Abstract: "TIE results and chemical analyses of elutriate samples suggested that divalent metals were responsible for the observed toxicity."

Conclusion 2, stated in the Discussion section: "Chemical analyses of three elutriate samples demonstrated copper concentrations were within the range toxic to bivalves."

Conclusion 3, stated in the Discussion section: "Although metal concentrations in Grizzly Bay samples were measured above *M. galloprovincialis* tolerance limits only in the third TIE, it is possible that low concentrations of metals might be working additively or synergistically to cause toxicity."

Comment 1: Regarding Conclusion 1, divalent metals may have been responsible for **some** of the observed toxicity. It could be argued that the toxicity that was not ameliorated by EDTA or cation column was as (or more) significant than the toxicity actually removed by those treatments. For example, 54%, 67%, and 32% of the toxicity in samples 1-3, respectively, was not removed by EDTA or Cation column. None of the observed toxicity in the 100% elutriate samples was removed by any of the treatments.

Comment 2: Conclusions 2 and 3 are overstated. All three samples showed significant toxicity in an elutriate concentration in which the copper concentration was clearly not "within the range" or "above…tolerance limits…" for *M. galloprovincialis.* Copper was measured at 2.5, 0.23, and 8.7 μg/L, respectively, in the three (100%) elutriate samples. Therefore, copper levels in the 50% elutriate concentrations were 1.25, 0.12, and 4.4 μg/L, respectively. All three concentrations are well below the current EPA Final Acute Value (EC50) of 9.625 μg/L for *M. galloprovincialis*, below the author's EC50 of 7.8 μg/L cited in Table 2, and below the author's (MPSL unpublished data cited in RMP contribution # 43) LOEC of 5.6 μg/L for this species. Notwithstanding the reduction in sample 2 toxicity by EDTA, it would be unreasonable and misleading to describe the effect of 0.12 μg/L copper as potentially "synergistic" since the mean oceanic concentration of copper in the North Pacific Ocean is 150 ng/kg (approx. 0.15 μg/L, Bruland 1980). Further, in sample 3, there appears to be a significant effect in the 6.25% elutriate sample (the author does not say). The concentration of copper in that sample would have been 0.5 μg/L.

Comment 3: The source of toxicity in Grizzly Bay sediment samples is clearly enigmatic. There are several issues that require more investigation before the role of copper can be clearly understood. The increase in toxicity following an upward pH adjustment to sample 2 is one example. As the author mentions, this anomaly requires additional investigation. The results with C18 column treatment is also quite puzzling since one would expect some organic pollutant contamination at the Grizzly Bay station and since C18 is known to remove some divalent cation toxicity (e.g. zinc). It is helpful to keep in mind that the TIE manipulations may not address all of the potential toxicity sources. In fact, it may not address any of them. For example, the author states in RMP contribution # 43 that "Toxicity was not significantly mitigated in any of the TIE manipulations performed on the San Joaquin River sample." Does this mean that there was no "organic" contaminant and no "divalent cation" toxicity in the sample?

This paper increases our understanding of Grizzly Bay sediment toxicity. However, there is much more that we need to know and characterize before we can adequately assess the role of copper in toxicity of elutriate samples from that station.

Appendix A, Attachment 2

San José comments on the potential problems associated with algal toxicity tests

Confounding Factors:
The confounding factors (EDTA, filtration, nutrient additions, cultured vs. wild stock, species selection) in conducting copper toxicity tests with algae are summarized below.

- In summary, the chief confounding factor is the 0.22 μm-pore-size filtration (rather drastic) required for sterilizing the test medium prior to use. This removes an unknown amount of binding capacity, may alter the site water chemistry in unknown ways (adsorb toxicity-ameliorating ions?) and may add some toxicity (membrane filters may contain toxic substances even following a rinsing procedure).
- EDTA can be omitted from saltwater tests. EDTA is a confounding factor for freshwater algal tests.
- Nutrient additions chemically alter the site water. These should be kept to a minimum. Can exponential growth be obtained without the addition of nitrogen and phosphorus?
- Species maintained in the laboratory for many years may respond very differently from wild populations of the same species.
- Surrogates don't express natural population responses and tests with single species can produce results very different from that of mixed cultures or natural assemblages.

Extrapolation to the Field:
A major criticism of the use of toxicity testing in NPDES permitting is that it may not be a good predictor of in situ effects. This concern is greater for plants than for animals due to their greater sensitivity and variability in their response to physical and chemical factors. The laboratory variables which make extrapolation of the results of algal tests to the field difficult include: nutrient additions, duration, species selection, and the actual physical characteristics of the testing situation.

- The rapid log-phase growth required in typical algal toxicity tests might simulate natural bloom conditions but it would certainly not simulate natural background phytoplankton densities. Natural background densities are usually several degrees of magnitude below densities of laboratory (test) cultures. One would expect the response of phytoplankton in the field at lower nutrient levels and densities to be very different from that of lab test cultures.
- Lab results vary with the amount and type of added nutrients. For example, Walsh et al. (1987) found that EC50s of three algal species for several organic compounds varied with the growth media used. He concluded that responses to toxicants in different media are the results of interactions between algae, growth medium, toxicant and solvent carrier. Which nutrient enrichment best simulates field conditions? None?
- Algal tests are usually conducted for 96 hours. When this result is applied (extrapolated) to the field, there is no time limitation. Walsh (1983) found that EC50 values for five species of algae exposed to various pesticides were lowest (i.e. greatest toxicity was exhibited) after 48 h of exposure and that after 96 h of exposure the maximum growth rates of treated cultures had recovered compared to control cultures. If phytoplankton are impaired at 48 hrs but not

at 96 hrs, does this fit the regulatory definition of impairment? Which test duration is the best one to extrapolate the results to the field?

- If algal/copper toxicity test results are affected by temperature, which temperature should be chosen? 15°C? 20°C? 25°C? The possible choices are the average site temperature or the temperature at which the test species show the greatest sensitivity.
- Algal/copper toxicity test results are certainly dependent upon the quantity and quality of light. Which field condition (overcast, high turbidity, full sunlight) should be simulated in the lab?
- In contrast, none of these physical parameters (temperature, light, turbidity) in the ranges encountered in the lab or field would be expected to affect the results of Mytilus (animal) embryo/larval development tests. Thus, some extrapolation problems are peculiar to plant responses.

Salient Endpoint to Regulate:

Using the latest techniques, several endpoints including oxygen production, carbon dioxide consumption, cell ion transport, flagellar motility, and culture growth can be chosen to evaluate toxicity. Toxicity testing usually measures culture growth, specific growth rate or biomass as measured by final cell densities or chlorophyll *a* content. The endpoint usually reported for short-term algal toxicity tests is an EC50 based on growth.

Which endpoint best evaluates whether South Bay phytoplankton are impaired due to copper? Our definition of impairment might be different from that used for animals for the following reasons:

- With few exceptions, toxicological responses in animals are irreversible. A *Mytilus* larva that has developed abnormally due to copper will die. Algal responses, except at very high copper concentrations (ppm) are not algicidal (causing death of the organism). In algae, growth may be arrested, cells may encyst or lose their flagella, but they likely will live to grow another day.
- Growth in unicellular algae is very rapid and populations can recover much more rapidly than animal species.
- A chronic endpoint can be measured in animals. The only true chronic test for marine algae is *Champia,* a multicellular macrophyte for which an EPA testing protocol exists (tests with unicellular algae are not considered true chronic tests).
- Autotrophs are affected by a myriad of physical (and chemical) variables that have little effect on hererotrophs. This makes algal toxicological responses more variable than animal responses.
- When a population of animals dies or its growth is inhibited, it is unlikely that another less sensitive species will immediately fill the same niche. When the population of a given species of phytoplankton declines, a less sensitive species will likely fill the same niche.

In the final analysis, a sound scientific approach to regulating copper in the South Bay based on phytoplankton responses must answer the following questions.

- What is an acceptable endpoint to regulate in phytoplankton? EC50? EC25? EC10?

- Which species should be regulated? The most sensitive? The least sensitive? The most abundant? The least abundant? The most ecologically important?
- If the beneficial uses of "estuarine habitat" and "fisheries" are protected, is there still "impairment" because a single phytoplankton species is sensitive to copper below the SSO?

Literature Cited

Walsh, Gerald E. 1983. Cell death and inhibition of population growth of marine unicellular algae by pesticides. EPA-600/J-82-014. Aquat. Toxicol. 3(3):209-214.

Walsh, Gerald E., Mark J. Yoder, Leslie L. McLaughlin and Emile M. Lores. 1987. Responses of marine unicellular algae to brominated organic compounds in six growth media. EPA-600/J-87/331. Ecotoxicol. Environ. Saf. 14 (3):215-222.

Appendix B

Multibox Contaminant Transport Model Development

Note:
The model discussed below may assist in efforts to resolve uncertainty relating to loading and sediment. This model is also referenced in the Response to Comments in Appendix D.

CONCEPTUAL SCOPE OF WORK
[CEP TC Meeting 10/13/04 Attachment 3]

MULTIBOX CONTAMINANT TRANSPORT MODEL DEVELOPMENT

October 5, 2004

The Clean Estuary Partnership's Technical Memorandum on the *Use of Conceptual and Numerical Models to Guide TMDL Development and Implementation in San Francisco Bay* (CEP, 2004) described the role of computer modeling to achieve a better understanding of the basic ecosystem processes that control pollutant fate and transport and to support water quality management activities. This Conceptual Scope of Work describes a multiyear, systematic plan, building on model-development efforts already underway, to construct a basic mechanistic model that will advance our understanding of contaminant behavior in the estuary and will make an essential contribution to the existing water quality management toolbox.

The goals of this project include (1) developing a better tool for predicting future contaminant concentrations and testing potential management actions, (2) clarify uncertainty of existing model predictions; (3) identifying key areas where field work can be done to reduce the uncertainties; (4) develop unambiguous documentation regarding the model for future professionals working on these issues as part of adaptive implementation. The CEP Technical Memorandum on Modeling (CEP, 2004) described four levels of computer models that are developed to support water quality management activities. This document describes the development of a Level 2 model: a multibox model that provides the first step in the development of a predictive methodology. The multibox model represents physical and chemical processes the affect the fate, transport and residence times of pollutants in the estuary.
The representation of these processes is based on empirical relationships derived from the existing knowledge. The construction of this multibox model will provide the opportunity to perturb the system, evaluate the response, and gauge uncertainty associated with predicted outcomes.

1. Introduction and Background

The San Francisco Bay Regional Water Quality Control Board (Water Board) is in the process of developing a Total Maximum Daily Load (TMDL) for several contaminants in San Francisco Bay whose predominant source, because of accumulation from past discharges/releases to the Bay, is the sediment and whose environmental transport is dominated by sediment processes. For example, efforts are underway by the Water Board to determine what concentrations of PCBs in the sediments of the Bay are required to achieve acceptable human-health and ecological risk levels and to establish a sediment-based approach to regulating PCBs in San Francisco Bay. Similar efforts are underway to understand and to predict the behavior of mercury, legacy pesticides, dioxins, PAHs and PBDEs.

Understanding the ecological significance of changes in sediment and water-column concentrations of contaminants in response to alternative management actions and the ability to achieve these changes is a critical information need. Some of the key management questions associated with the evaluation and development of alternative TMDL implementation strategies are:

- *How much will concentrations of a pollutant in the sediment and water column change in response to a given percentage reduction in inflowing load?*
- *How will beneficial uses (related to concentrations in biota) be affected by changes in the sediment and water column concentration?*
- *Are there differences in the effectiveness of alternative loading reduction strategies?*
- *How long will it take for the responses to become apparent?*

These questions are central to any TMDL analysis, and data collection alone cannot provide the information necessary to make the required predictions. Modeling, based on proper calibration and evaluation of uncertainty, is therefore a vital part of a TMDL (NRC, 2001). Models can be used to integrate our knowledge on environmental system components to estimate chemical transport and fate processes in the Bay, allowing us to predict concentrations and effects on beneficial use in response to different management actions.

Numerous coordinated efforts are underway to build better predictive capabilities to support a wide range of water quality management activities. The Regional Monitoring Program (RMP) has initiated work on the development of a multi-box mass budget model to improve the understanding of the long term fate of PCBs in San Francisco Bay. This model builds on the results of a single box model of PCB transport and cycling in the Bay (Davis, 2004). The multibox model development by RMP is coupled to the U.S. Geological Survey's development of a sediment-transport model (Lionberger and Schoellhamer, 2003) and a tidally averaged salinity box model of San Francisco Bay previously developed by Uncles and Peterson (1995). The Bay is represented by 51 segments composed of 2 layers representing the channel and shallows. Calculations are made using a daily time step. Sediment dynamics have been parameterized, calibrated, and validated using extensive suspended sediment concentration data collected for the RMP over the past 10 years and changes in bathymetry observed from 1950 to 1990. PCB fluxes into and out of each box are calculated primarily using equations developed previously for a one-box model of the Bay. Improvements being incorporated in this version of the model include a more realistic treatment of sediment mixing and sediment erosion and deposition.

Also underway is the development of a San Francisco Bay PCB Food-Web Model (Gobas and Wilcockson, 2003) to estimate the concentrations of PCBs in a set of indicator species as a result of PCB contamination in sediments and water in the Bay. The food-web model can be used to determine what concentrations of PCBs in the sediment and water need to be reached to achieve an acceptable level of risk to wildlife and humans living in the Bay area.

2. Statement of Work

This Conceptual Scope of Work lays out a multiyear process for the development of predictive modeling tools that can be used to guide data collection efforts, enhance our understanding of pollutant fate and transort in the Bay, and provide a quantitative basis for the regulatory decision making process. Phase 1 of the multiyear process begins with documentation and rigorous evaluation of the existing modeling tools. Most of the modeling efforts to date have been focused on efforts to aid the PCB TMDL development. Phase 2 of the project will begin with the application of the SFEI Version 1 of the multibox model to the assessment of fate and transport processes of other contaminants in the Bay (e.g., Hg, Cu, legacy pesticides, dioxins, PAHs, PBDEs). These contaminants are the subject of TMDL development, the TMDL implementation phase, or are chemicals with a significant amount of relevant information. Phase 2 of the project also includes the collection of new sediment data, especially sediment cores, that are needed to obtain a better understanding of sediment dynamics in the Bay. These sediment data will also be critical to the validation of the multibox model. Finally, Phase 2 includes a reassessment of the multibox model and the development of specific plans of action for enhancing the model further and extending its applicability.

This work will provide a foundation for modeling the fate of persistent, particle-associated contaminants in the Bay in support of both RMP monitoring and TMDL development and implementation for years to come.

Phase 1 – Model Documentation and Testing

Task 1. Prepare Documentation for USGS Sediment and Water Transport Model and Augment Model Output

USGS has developed, calibrated and validated a tidally averaged sediment transport model of San Francisco Bay (Lionberger and Schoellhamer, 2003). This model provides a basis for the PCB multibox model. However, the efforts of USGS have been focused on model development and testing. The model documentation is not adequate to permit wide use of the model. The first task will be the preparation of the model documentation. The product of this task is a USGS report with the tentative outline provided in Table 1.

Table 1. Proposed Outline for USGS Model Documentation

A tidally-averaged sediment transport model for San Francisco Bay, California
1) Abstract
2) Introduction
    a) Tidally averaged
    b) Uses box model approach (well-mixed)
    c) Daily time step, simulates over decadal time scale
3) Purpose and Scope
    a) Why use the UP model?
    b) PCB and sediment budgets
4) Acknowledgments
5) Description of the study area
6) UP Salinity model
    a) Model domain an discretization
        i) 51-with averaged segments
        ii) Each segment composed of two layers
    b) Required Input data
        i) Tide data at the GG
        ii) Coastal salinity
        iii) Delta outflow
        iv) Tributary flows
        v) Evaporation, Precipitation
    c) Salinity boundary Conditions
        i) Lower layer at the GG
        ii) Zero at the Delta and for tributary inputs
        iii) Left free in SB
    d) Applications: literature review
7) Sediment transport
    a) Required Input data
        i) Mallard Island SSC
        ii) Daily average wind speed
        iii) Tributary loads
    b) SSC boundary Conditions
        i) Mallard Island
        ii) Pacific Ocean
        iii) Tributaries
    c) Algorithm
        i) Advection/dispersion
        ii) Tributaries
        iii) Erosion/deposition
        iv) Bed Model
    d) Calibration to SSC
        i) Results at PSP and DMB
        ii) Comparison to bathymetry
    e) Calibration to bathymetry
    f) Sensitivity analysis
        i) Adjust coefficients 10%
            (1) Percent change SSC
            (2) Percent change sedimentation
8) Display of model results: tables, graphics, and animation
9) Conclusions

Task 2. Create Graphic Output

It is important that the results of computer models can be communicated to a wide audience. The purpose of this task is to provide graphical output for SFEI's version 1.0 of the Multibox PCB Model. The following are some of the graphics and animation that are being considered:

- Graphical presentations of simulation results that provide geographical reference points, e.g., aerial views of different parts of the bay, including the whole bay; cross-sections of different locations in the bay, etc.

- Presentation of time variable loadings that are considered in the model from all sources, e.g., total mass emission rates/total loading variations over time, with options of showing the results of major parts of the bay.
- Representations of mass in the bay and sediments (active layer and below), spatially segregated and composites as desired. These masses are time variable as the bay responds to clean up efforts.
- Animation of model results showing concentrations through selected time intervals of key variables, e.g., PCBs and salinity, throughout the bay in each box and by sediment layers.

Task 3. Conduct Initial Testing of SFEI PCB Model (Version 1.0) and Conduct Sensitivity Analyses

The product of SFEI's Version 1.0 of the PCB Multibox Model will be documentation of the model and initial testing and a draft report that will go out for peer review. Task 3 will be conducted in two parts. In part one, the model verification and calibration efforts by SFEI will be independently reviewed. In part two, sensitivity analyses will be conducted to identify the parameters and processes that that are most important in determining the model outcome. The sensitivity analysis results will be used to address the uncertainties in our understanding of the system as well as the performance of the model.

The review process will be documented in sufficient detail that it can be independently replicated. Some of the elements of this subtask are:

- Review model test case I/O, the model code, the compiled version, and draft documentation prepared (user manual, technical support manual, test results, etc.).
- Review the theoretical equations and verify that the theoretical equations are formulated and solved correctly.
- Test key parts of the model: salinity distribution, sediment transport, and PCB transport.
- Using realistic data sets, check the model's general behavior, and anticipated responses to changes in forcing, parameter values, etc.

The product of Part 1 of this task will include the results of all tests, procedures, and outcomes. If problems, or anomalous behaviors are noted, the reviewers will meet with the developers to see if these issues can be resolved before the testing is completed.

The variability of computer model results provides a measure of the uncertainty that exists in our understanding of the environmental processes simulated. Excluding measurement errors or the mis-specification of the model structure, the observed variability in model output is primarily the result of the variation in a subset of the most important parameters. Parameter sensitivity is used to refer to the variation in output of a mathematical model with respect to changes in the values of the model's input parameters. Sensitivity analysis therefore involves the determination of the change in the response of a model to changes in individual model parameters and specifications.

The results of a sensitivity analysis are used to identify the magnitude of the contribution of individual parameters to the observed variation in the predicted endpoint.

Sensitivity analyses, using Monte Carlo simulation methods, will be conducted as Part 2 of this task. The results will provide an improved understanding of the simulated system and serves as a guide for designing field surveys and laboratory experiments that will increase our knowledge of important natural processes. A better understanding of model uncertainty will also lead to improved credibility of projections and enhance the ability to produce realistic values of state variables for use in regulatory decision making and planning. The initial focus of the sensitivity analyses will focus on sediment erodability and mixing processes, areas already identified by the model developers to be of special concern. The examination of the model sensitivity to variations in contaminant profiles is also a primary objective. The results of these analyses will contribute to the efforts planned in Phase 2 of the project. A technical memorandum will be prepared to summarize the results of Task 3.

Phase 2 - Field Data Collection, Further Model Test, and Program Planning

Task 4. Conduct Sediment Sampling and Testing

The RMP's Contaminant Fate Work Group (CFWG) recommended improvements in the collection of field data (particularly cores) to determine the distribution of contaminants with depth, the erodability profile of sediments, and the rate of mixing of surface sediments with deeper sediments. This task will be conducted in two parts. The first part of the task will be to prioritize remaining information gaps using existing data and to design the most effective sediment sampling program to obtain data necessary to support modeling efforts and regulatory management decisions. Existing data on spatial variability (both horizontally and vertically) will be used to select the location and variables measured in a sediment-core sampling program.

Preliminary estimates using erosion rates (0.5 cm/yr) and average concentrations of PCBs (~10 ppb) at depth within the middle range seen in some areas of the Bay would lead to PCB inputs of ~70 kg/yr (for the whole Bay), roughly equal to the overall loss rate estimated from the one box model. As a result, even without external loads, continued erosion of sediments at that concentration would lead to no change in surface sediment concentrations so long as that concentration is found in the eroding sediment bed. Maximum concentrations in deeply buried sediments (~50 cm depth) have measured up to 35 ppb and might provide comparable PCB loads even at much lower erosion rates. Thus more extensive data on contaminant concentrations with depth are needed, as loads from legacy deposits in the Bay exposed through erosion could easily swamp all other new inputs.

It is proposed that the initial sample collection and analysis of sediment cores be conducted in the South Bay because:

1) It is one area with sediment contaminant concentrations typically higher than the Bay average
2) Shallow water depths in many areas expose sediments to erosion/deposition and mixing

forces

3) There is less previous information on sediment mixing and contaminant profiles than in north and central SF Bay, for which there are at least one core each with high quality contaminant profiles (metals and organics from USGS) and measurements of mixing/deposition processes at a large number of sites (USACE dredge disposal tracer studies)
4) there may be opportunity for cost-sharing (or at least joint data interpretation) with data collection for the South Bay Salt Pond project.

Because in the short term it is impossible to representatively sample with just a few sites in a segment, the highest priority is to constrain the range of possible contribution from contaminated sediments within the system. We propose initially collecting a small number of cores at locations within the segment exhibiting the highest erosion rates. These sites are preferred because depositional sites with high pollutants at depth would be expected to progressively pose less risk as sediments are buried beyond the mixed and biologically active zone. Sites selected would preferably be in areas found with above average surface concentrations in previous sampling, as high surface concentrations would indicate either continued loading from a nearby source (an thus possibly long term historical loading from the same source), or vertical or lateral mixing from more contaminated sediments in proximity. A smaller number of sites with lower or average surface concentrations should be sampled as well, as mixing may not yet have reintroduced more contaminated deeper sediments to the surface mixed layer, but may pose a risk in the future as the mixed layer encroaches on the buried deposits.

Based on the results from the analysis of the initial set of sediment cores, additional sampling will be conducted to further reduce our gaps in knowledge concerning contaminant profiles in other portions of the Bay. A multi-year sampling and analysis effort is planned. Interim reports will be prepared each year.

Task 5. Apply SFEI Multibox Model to Other Pollutants

In addition to PCBs there are other contaminants of concern for which a sufficient database exists to calibrate and test the multibox model. A single box model has been previously used to model copper concentrations in the sediments and water column of the South Bay. The comparison of the single and multiple box model approaches would provide a quick indication of the benefits of extending the spatial coverage of the model. Likewise, a single box model was used to estimate the response time of the Bay to significant reductions in mercury loading. Examination of the differences in the predictions of the single- and multibox models would be instructive. A technical memorandum will be prepared to summarize the results of Task 5.

Task 6. Plan Next Generation of Sediment and Pollutant Transport Models

The results of the multibox-model testing linked with the analysis of the sediment core samples will provide a sound and well-structured examination of model performance. The final report will assess the efficacy of the multibox model as a primary tool for establishing loading limits in the TMDL process and in the evaluation of the projected rates of recovery associated with specific load reductions. The final report will also provide recommended enhancements in existing models and a guide for the expected benefits of more complex models to the overall goal of effective management of the water quality and beneficial uses of the estuary.

Schedule and Deliverables

The following milestones reflect planned activities. The first milestone, the Detailed Scope of Work, will provide explicit links between milestones and the six tasks described above. The contractor will work closely with the CEP Program Coordinator to identify required technical support for management of modeling efforts.

Milestone	Start Date	End Date
Detailed Scope of Work	10-14-04	11-19-04
Task 1. Prepare Documentation for USGS Sediment Transport Model and Augment Model Output		
• Draft Report	10-14-04	03-31-05
• Final Published Report	03-31-05	09-30-05
Task 2. Create Graphic Output	10-25-04	02-28-05
Task 3. Conduct Initial Testing of SFEI PCB Model and Conduct Uncertainty Analyses	11-19-04	05-06-05
Task 4. Conduct Sediment Sampling and Testing	10-01-05	09-28-07
Task 5. Apply SFEI Multibox Model to Other Pollutants	05-05-05	04-09-06
Task 6. Plan Next Generation of Sediment and Pollutant Transport Models	10-01-07	02-30-08

Budget

The task budgets are estimated values. The actual values will depend on the direction provided by the CEP Program Coordinator and the Technical Committee. A more detailed budget will be prepared for the Detailed Scope of Work. The estimated budget is presented by task and by year.

Task	Estimated Budget
Detailed Scope of Work	$ 10,000.
1. Prepare Documentation for USGS Sediment Transport Model	$ 40,000.
2. Create Graphic Output	$ 20,000.
3. Conduct Testing and Uncertainty Analysis	$ 55,000.
4. Conduct Sediment Sampling and Testing	$220,000.
5. Apply SFEI Multibox Model to Other Pollutants.	$120,000
6. Plan Next Generation of Models	$ 35,000.
Total Estimated Cost	$500,000.

Fiscal Year		Estimated Budget
2005	Detailed Scope of Work, Tasks 1 – 3.	$125,000
2006	Task 4 Planning and Initial Sediment Core Sampling and Analysis, Task 5 Part 1	$170,000.
2007	Task 4 Additional Sampling and Analysis. Task 5 Part 2	$170,000.
2008	Task 6	$ 35,000.

Recommended Contractor: SFEI and Tetra Tech, Inc.

Alternative Contractor:

References

CEP, 2004. Use of Conceptual and Numerical Models to Guide TMDL Development and Implementation in San Francisco Bay. Tetra Tech, Inc. March 15, 2004.

Davis, J., 2004. The longterm fate of PCBs in San Francisco Bay. Environmental Toxicology and Chemistry. *In Press*

Gobas, F. and J. Wilcockson. 2003. San Francisco Bay PCB Food-Web Model. San Francisco Bay Regional Monitoring Program Technical Report. SFEI Contribution 90, December 2003.

Lionberger, M.A. and D. H. Schoellhamer, 2003. A tidally averaged sediment transport model of San Francisco Bay, California: Proceedings of the 6th biennial State-of-the Estuary Conference, Oakland, California, October 21-23, 2003, p. 118.

National Research Council (NRC). 2001. Assessing the TMDL approach to water quality management. Report to the Committee to Assess the Scientific Basis of the Total Maximum Daily Load Approach to Water Pollution Reduction. National Research Council. National Academy Press. Washington, D.C.

Uncles, R.J. and Peterson, D.H. 1995. A computer model of long-term salinity in San Francisco Bay: Sensitivity to Mixing and inflows. Environmental International 21: 647-656.

Appendix C

Action Plan Information

Information regarding POTW size, source categories addressed and control strategies utilized is highlighted below for the 39 POTW respondents:

# of POTWs in each size range	
< 5 mgd	8
5-20 mgd	17
> 20 mgd	6
no P2	8

Source Categories Being Addressed
Industrial
Commercial
Residential
Corrosion
Stormwater (onsite only)

Control Strategies Utilized
Source identification/quantification
Permitting
Zero discharge facilities
BMPs
Outreach/education
Participation in the BAPPG
Recognition programs
Legislative controls
Other methods than listed above

Source control activities conducted throughout the Bay Area correspond well with the actions included in the South Bay CAP/NAP. POTW source control activities that could be or have been implemented in other parts of the Bay Area include:

- CB-1 (1): Outreach regarding residential vehicle washing
- CB-1 (2): BMPs for vehicle/equipment washing for new development and redevelopment
- CB-1 (3): Mobile surface cleaner training and certification
- CB-2: Tracking copper sulfate usage in water supply reservoirs
- CB-9: Track corrosion control opportunities
- CB-12: Outreach regarding copper discharges from pools and spas
- CB-13/NB-3: Track Pretreatment Program efforts and POTW loadings
- CB-14/NB-4: Track and encourage water recycling efforts
- CB-19/NB-6: Track industrial virtual closed-loop wastewater efficiency measures

It should be noted that some of these measures like BMPs for vehicle washing or pool and spa discharges are often implemented by stormwater programs. However, because discharges from these activities are often redirected to the sanitary sewer, POTW pollution prevention programs have also developed programs targeting these sources.

Of the 39 POTWs discharging to the San Francisco Bay area, 8 were small (i.e., <5 MGD). These agencies had not identified copper or nickel as problem constituents and, therefore, had not conducted copper or nickel P2 programs. The other 31 POTWs had conducted some level of copper source control activities. Much less activity occurred to specifically target nickel sources, although some of the copper source control activities would indirectly address nickel as well (e.g., some commercial and industrial sources such as vehicle service facilities, metal plating, carwashes). Nickel-specific source control activities were most likely to target industrial sources. Five POTWs reported such activities targeting industrial and commercial nickel sources. Three of these POTWs (all >20 MGD) reported influent reductions in nickel associated with source control activities. There was no obvious correlation between POTW size and the types of source control actions taken. Size and available resources would be more likely to influence the total number of source control actions taken or the time frame over which actions were implemented.

A POTW with more resources may implement several control measures simultaneously while a smaller POTW with less resources would be more likely to implement control measures one at a time. Another factor that will influence the source control actions taken is which sources are identified as the largest. For copper, there are several possible source categories (e.g., corrosion, metal finishers, vehicle service facilities) and the water supply and makeup of the service area will determine which source is the largest in each service area.

With respect to copper source control, the source categories most likely to be addressed included:

- Corrosion of copper plumbing
- Commercial sources (i.e., vehicle service facilities, printers)
- Industrial sources (i.e., metal finishers, electroplaters)
- Residential sources (i.e, copper sulfate root control products, pools and spas)

Greater than 90% of the 31 POTWs had conducted source control activities targeting vehicle service facilities, root control products, and pools and spas. All three of these sources were targets of Bay Area Pollution Prevention Group (BAPPG) projects, which may explain the high percentage of agencies working with these sources. More than half the POTWs had targeted corrosion, industry, and printers.

Of the 31 POTWs with pollution prevention programs, 12 reported observed influent or effluent reductions attributable to source control efforts. These reductions were attributed to a variety of factors with most of the larger reductions attributed to pH control of the water supply to reduce corrosion.

In general, corrosion of copper plumbing was identified as the largest source of copper to wastewater treatment plant influent. For example, the three South Bay POTWs (Palo Alto, San Jose, and Sunnyvale) have estimated that corrosion accounts for 30-58% of the copper loading in their respective influents. Five POTWs attributed reductions in influent or effluent copper levels to reduced corrosivity of the water supply through pH adjustment. Other efforts that were reported to contribute to measurable impacts on influent or effluent copper levels include industrial source control and P2 programs targeting vehicle service facilities and printers. Two POTWS attributed reductions to industrial source control and two POTWs attributed reductions to commercial source control actions. The remaining 3 of 12 POTWs reporting influent or effluent reductions did not attribute reductions to a specific source control actions. While several POTWs reporting conducting source control activities targeting residential sources, measurable reductions were not attributed to these actions. Outreach regarding residential source control served more to raise awareness regarding water pollution issues than to effect measurable reductions.

Baseline actions that maintain existing source control efforts and implement additional program as needed are discussed below. In addition, Phase 1 actions that would be conducted should the identified triggers be met are also discussed. It should be noted that the specific Baseline and Phase 1 programs developed will vary from POTW to POTW depending on which sources are determined to be the most significant and the resources available to the POTW. Some general guidelines in developing the program are discussed below. In addition, the actions described in

Appendix 4 will also provide guidance on the types of actions that can be taken. More detailed guidance for developing effective source control programs is being developed by BACWA through the P2 Menus Project. Under this project, comprehensive lists of source control actions are being developed for several constituents. In addition, guidance will be developed on choosing the actions that will be most effective.

Baseline actions

Most agencies are conducting copper source control programs targeting their largest sources. Actions implemented under the Baseline condition should be those actions most likely to achieve measurable reductions or maintain reductions achieved previously. Therefore, the initial Baseline actions (**Table 2.1**) should be to determine if corrosion is a significant source and to determine the other significant sources of copper contributing to the POTW's influent. Based on this evaluation a POTW should develop a plan to implement source control measures that are consistent with its resources and that targets the largest source categories. In addition, a periodic update or evaluation of ongoing control measures should be conducted to determine if the measure is being implemented properly or if it is still necessary. For example, a program where vehicle service BMPs were distributed to businesses should be evaluated periodically to determine if the businesses are continuing to implement the BMPs. Additionally, a review of influent and effluent data trends should be completed every 5 years to evaluate the effectiveness of source control activities.

Agencies should assess the feasibility of achieving reductions through corrosion control by determining average influent copper levels and water supply pH. For agencies with elevated effluent copper concentrations, discussions should be initiated with the service area's water purveyor to investigate the feasibility of implementing pH adjustment or other form of corrosion control of the water supply.

Permitted industries, particularly metal finishers, should have copper effluent limits and P2 requirements in their permits. In addition, vehicle service facilities have been identified as a source of copper, nickel, other trace metals and other priority pollutants (e.g., PAHs). Outreach materials and BMPs are readily available for vehicle service facilities. Therefore, implementing an outreach and education program directed at this category is a straightforward project requiring minimal resources for most POTWs. Materials are also available for other source categories including printers, pools and spas, and plumbing activities. These materials would facilitate implementation or updating of programs for other sources determined to be significant.

Phase I Actions

If the ambient water quality monitoring trigger is exceeded, additional actions targeting corrosion and vehicle service facilities may need to be undertaken. In addition, other sources could be investigated for reduction potential. Additional sources to investigate could include printers, copper-containing pesticides, pools and spas, cooling towers and heating and cooling facilities. Programs that were voluntary under the Baseline condition should be upgraded to regulatory (**Table 2.2**).

Water supply corrosion control should be pursued more aggressively. It should be noted that this option may not be under the direct control of the POTW. The cooperation of the water purveyor is critical should this source be found to be significant.

Additional actions should also be considered. Incentives for vehicle service facilities to become zero-dischargers could be included in a regulatory program. In addition, agencies may consider evaluating laundry graywater as a copper source and developing approaches to reducing copper loadings from this source.

Industrial

Direct discharges to surface waters from the industrial sector are closely regulated through the NPDES program, making source control and pollution prevention important aspects of their operations. In general, nickel and copper levels in the effluent from direct industrial dischargers to San Francisco Bay are below permit limits. Therefore, source control targeting these constituents has not been a major element of the dischargers source control program. Even so, industry conducted source investigations for metals in the early 1990s, identified copper and nickel sources and conducted source control actions needed.

The primary source of copper to Bay Area industrial dischargers has been identified as the water supply. Other sources include corrosion in heat exchangers, trace copper contaminants in the ferric chloride used in the selenium precipitation process, and domestic waste within the refinery. Efforts to reduce copper include optimizing solids separation processes, adding Granular Activated Carbon Units in the treatment process, switching to a ferric chloride product with less heavy metal contamination, optimization of process conditions to minimize corrosion, and increasing cooling tower water cycles.

Nickel sources were identified as water supply, corrosion in heat exchangers, nickel catalysts, byproduct of Flexicoking Process, and trace contaminant in ferric chloride. Efforts to reduce nickel discharges included some of the same actions listed above for copper including optimizing solids separation processes, adding Granular Activated Carbon Units in the treatment process, process optimization to minimize corrosion, and increasing cooling tower water cycles. In addition, specific nickel reduction efforts included optimization of the Flexicoking process and segregation of wash waters contacting nickel catalysts. Despite these efforts, nickel effluent levels have not changed significantly.

Table B1. Baseline Actions

Baseline Number	Description	Lead Party	Implementation Mechanism
B-1	Assess corrosion control potential	POTWs	Investigate previous studies on corrosion control. Evaluate influent data to determine if copper levels are indicative of corrosion (i.e., >100 µg/L). Evaluate water supply pH to determine if pH is indicative of corrosivity (i.e., <8).
B-2	Evaluate other copper sources	POTWs	Conduct source identification studies by either scaling source loading estimates from other communities to fit POTW service area or conduct trunkline monitoring to determine largest influent copper sources.
B-3	Pursue source control actions for 1-3 largest copper sources depending on POTW resources. Actions to choose from include B-3a-g.	POTWs	
B-3a	Require copper source control at permitted industries	POTWs	Include requirements in permit for pretreatment and/or BMPs
B-3b	Conduct outreach to commercial establishments	POTWs	Distribute BMPs and conduct site visits to determine if BMPs are implemented properly.
B-3c	Conduct vehicle washing outreach to businesses	POTWs	Distribute BMPs and conduct site visits to determine if BMPs are implemented properly.
B-3d	Conduct vehicle washing outreach to residents	POTWs	Newspaper ads, radio, newsletters, direct mail
B-3e	Implement mobile cleaner BMPs	POTWs	Conduct training sessions and workshops. Provide incentives for mobile cleaners to become certified.
B-3f	Track copper sulfate use by water suppliers	POTWs	Report copper in source water concentrations monthly/annually using low level detection limits.
B-3g	Control copper in stormwater from industrial sources	POTWs	Meet with industrial facilities to discuss performance improvements
B-4	Track pretreatment program and recycling P2 efforts.	POTWs	Monitoring and inspections reports can be used to track reductions achieved through these programs.

B-5	Follow up Quantification studies	POTWs	Estimate effectiveness of copper source control/pollution prevention measures and resulting source loadings
B-6	Data reports *NOTE: B-6 is not really targeting a wastewater related source*	POTWs	Collect and report influent, effluent and source data as applicable for use in periodic updates of source identification and program effectiveness evaluation
B-7	Conduct follow-up activities to assess and update ongoing source control actions	POTWs	Periodic review of ongoing programs should be conducted. For example, Return site visits to commercial establishments or follow-up monitoring should be conducted every 2-3 years to determine if BMPs are being properly implemented.

Table 2.2. Phase I Actions

Phase I Number	Description	Lead Party	Implementation Mechanism
I-1	Identify additional sources beyond those for which programs were developed in Baseline	POTWs	Perform literature research and conduct monitoring as necessary
I-2	Develop voluntary BMP based programs for additional sources	POTWs	Conduct outreach and education for residential sources and conduct site visits for commercial sources.
I-3	Upgrade all voluntary programs to regulatory	POTWs	Include regulations in permit
I-4	Aggressively pursue corrosion control	POTWs/Water Purveyor	Work with purveyors to implement pH control
I-5	Offer incentives to zero-dischargers	POTWs	Provide monetary or other rewards for zero-discharge
I-6	Evaluate laundry graywater as copper source	POTWs	Perform literature research and conduct monitoring as necessary
I-7	Pursue modifications to regulations for lead and copper in drinking water to more actively trigger corrosion control programs for drinking water systems based on impacts to POTWs.	POTWs/DHS	This would require a cooperative regional effort to work with DHS to accomplish these modifications.

Municipal Stormwater Program Copper Control Activities

Overview

Municipal stormwater programs in the Bay area conduct a variety of activities that are directly and/or indirectly targeted at reducing copper in municipal stormwater runoff. A survey of the major programs was conducted in spring 2003 (updated early 2004) to characterize the range of activities being conducted. An overall survey goal was to provide information to assist in identifying reasonable and appropriate baseline copper control measures to be included in Copper Action Plans being considered for stormwater agencies north of the Dumbarton Bridge.

Detailed survey results are contained in an Appendix to the BACWA sponsored report titled *Copper & Nickel North of the Dumbarton Bridge, Development of Action Plans* (EOA/LWA, 2004b].

From the survey, programs were grouped into four categories. First are the so-called "second generation" programs. These programs implement general programmatic measures aimed at reducing pollutants in general, rather than copper in particular.

Next are the "third generation" programs. These programs have specific Provisions in their NPDES permits requiring them to develop and implement pollutant reduction plans for several pollutants of concern, including copper. The subsequent category includes the wide range of copper control baseline activities being conducted by the Santa Clara Valley Urban Runoff Pollution Prevention Program (SCVURPPP) and Co-permittees pursuant to the June 2000 Copper Action Plan (CAP).

The last category includes a discussion of the activities being taken to develop a next-generation "focused" or "streamlined" CAP, pursuant to the adaptive management process built into the CAP. As part of this effort, a CEP funded project is underway to develop updated information on the most important copper sources in stormwater and on the most effective potential control activities. One possible outcome may be a single Bay-wide CAP with a menu of prioritized control measures.

Stormwater Permit History

Unlike NPDES permits issued to publicly owned treatment works (POTWs), municipal stormwater NPDES permits within the San Francisco Bay Region do not contain numerical effluent limits. Instead, municipalities are required to implement Storm Water Management Plans (SWMPs). These SWMPs include stormwater control measures necessary to demonstrate control of pollutants in stormwater to the maximum extent practicable (MEP) and measures to effectively prohibit non-stormwater discharges into municipal storm drain systems and watercourses.

The SWMP serves as the framework for identification, assignment and implementation of control measures and best management practices during the term of the permit. Best management practices (BMPs) are practical ways to significantly reduce potential discharges of pollutants to nearby storm drains and watercourses. In addition, SWMPs include performance standards that represent the baseline level of effort required to implement activities that constitute MEP based on current technical knowledge, available resources and local conditions. Through a continuous improvement process, the Permittees are expected to modify and improve their performance standards to achieve reduction of pollutants in stormwater to MEP.

Each San Francisco Bay region stormwater agency (excluding Vallejo Sanitation and Flood Control District) is an association of cities, towns and/or other governmental agencies which share a common NPDES permit to discharge stormwater to San Francisco Bay. In addition, each Program (excluding Vallejo Sanitation and Flood Control District and Fairfield Suisun Urban Runoff Management Program) is organized, coordinated and implemented based upon a mutual Memorandum of Agreement (MOA) signed by the participating public agencies. The MOA defines roles and responsibilities of all Permittees. Each Program (excluding Vallejo Sanitation and Flood Control District and Fairfield Suisun Urban Runoff Management Program) has a Management Committee that is responsible for making Program decisions. The Management Committee consists of one designated voting member from each Permittee. Fairfield Suisun Urban Runoff Management Program has a Program Oversight and New Development Committee responsible for making Program decisions.

In June 1990, the Regional Water Quality Control Board (Regional Board) issued the SCVURPPP its first NPDES permit. Permit provisions recognized that the Program had already accomplished significant work considered equivalent to specific municipal stormwater permitting requirements promulgated by EPA in October 1990.

The first five-year NPDES stormwater permits ("first generation") were subsequently issued in the early to mid 1990's for the other four Phase I agencies requiring similar stormwater management activities and SWMPs (e.g., Alameda Countywide Clean Water Program (ACCWP), Contra Costa Clean Water Program (CCCWP), San Mateo Countywide Stormwater Pollution Prevention Program (STOPPP), Fairfield Suisun Urban Runoff Management Program (FSURMP)).

In 1995, the SCVURPPP developed and submitted a second SWMP (SCVURPPP refers to their SWMP as an Urban Runoff Management Plan) as part of the five-year NPDES permit cycle. The SWMP included a *Revised Metals Control Measures Plan* to reduce copper, nickel and seven other metals in stormwater. The second five-year NPDES permit ("second generation") adopted in 1995 required SCVURPPP to develop model performance standards for various stormwater control measures and to incorporate them into their SWMP.

The second five-year NPDES permits ("second generation") were adopted for the three of the other four Phase I stormwater agencies (excluding FSURMP) in 1997 – 1999. These required monitoring for pollutants of concern (e.g., metals) in stormwater discharges and identification of potential sources, but not reduction measures. In October 1999, FSURMP submitted a complete permit reapplication package. This package, which included a Storm Water Management Plan for FY 1999-2000 to FY 2004-2005, provided a description of FSURMP's efforts to target urban runoff pollutants of concern. Copper, nickel and other metals were identified as pollutants of concern. Standard task controls/programs for each pollutant were also identified. FSURMP did not have a "second generation" permit.

The third five-year NPDES permits ("third generation") issued so far [SCVURPPP, 2001] require Permittees to implement control programs for pollutants that have the reasonable potential to cause or contribute to exceedances of water quality standards. Specific control programs include copper, nickel, mercury, pesticides, PCBs, dioxins and sediments. SCVURPPP is also required to continue to implement the 2000 Copper and Nickel Action Plans.

Second Generation Stormwater NPDES Programs (CCCWP, STOPPP) and Non-NPDES (MCSTOPPP) with General Pollutant Reduction Activities

Stormwater NPDES Programs with General Pollutant Reduction Activities

Programs now operating under their second-five year NPDES permits ("second generation") are not required to conduct specific copper control activities. Instead, Programs were required to develop monitoring programs to assess existing or potential impacts on beneficial uses caused by pollutants of concern (e.g., metals) in stormwater discharges, to identify potential sources of pollutants of concern found in stormwater discharges, etc. The two current "second generation" NPDES permits include:

- Contra Costa Clean Water Program
- San Mateo Countywide Stormwater Pollution Prevention Program

Both Programs have similar approaches to controlling pollutants in stormwater that are organized around several core programmatic activities as outlined in their individual Storm Water Management Plans. These activities are aimed at reducing pollutants in general (versus copper specifically) from reaching and contaminating stormwater runoff. The six core activities include the following:

- Illicit Discharge Controls
- Industrial/Commercial Business Controls
- Municipal Government Maintenance Activities
- New Development and Redevelopment Activities
- Watershed Awareness and Collaborative Activities
- Public Information and Participation

These six activities, while not necessarily directly targeting copper may result in indirect reductions in copper in stormwater runoff. For example, street sweeping and storm drain and inlet cleaning can reduce copper to the extent it captures and removes copper-containing brake pad debris. In addition, controlling pollutants from new and redevelopment activities, pre and post-construction, can reduce copper in stormwater to the extent that erosion and copper-containing sediments are prevented from reaching waterways. Since stormwater programs are based on the implementation of best management practices to reduce pollutants to MEP, these practices are practical and cost-effective methods to significantly reduce potential discharges of pollutants to nearby storm drains and waterways.

Stormwater Non-NPDES Programs with General Pollutant Reduction Activities

The Marin County Stormwater Pollution Prevention Program (MCSTOPPP) is in the process of receiving its first Phase II permit. Phase II permits do not require the implementation of pollutant reduction plans for copper or other specific pollutants of concern. While it has not been operating under an NPDES permit, MCSTOPPP has been performing essentially the same programmatic activities as the "second generation" NPDES permittees (with the same likely impacts on reducing copper in stormwater runoff).

Third Generation NPDES Permits with Pollutant Reduction Plans

The third-five year NPDES permits ("third generation") require the stormwater agencies to implement control programs for pollutants that have the reasonable potential to cause or contribute to exceedances of water quality standards. The first stormwater agency within the San Francisco Bay Region required to implement pollutant reduction plans was the Santa Clara Valley Urban Runoff Pollution Prevention Program. This requirement was part of their NPDES Permit reissued on February 21, 2001. A full description of their copper reduction plans is provided in the next section.

The second stormwater agency in the Bay area required to implement pollutant reduction plans was the Alameda Countywide Clean Water Program (ACCWP). This requirement was part of their reissued Municipal Stormwater Discharge NPDES Permit (Order R2-2003-0021) adopted on February 19, 2003. Provision C.10 required the Permittees to develop and implement programs to control discharges of copper and other pollutants of concern. In addition, Provision C.10 required the Permittees to refine the Pollutant Reduction Plans to incorporate specific activities and to provide detailed descriptions of the planned activities by fiscal year. Provision C.10.a does not require specific additional activities related to controlling the discharge of copper. It does require a refinement of the Copper Pollutant Reduction Plan and a description of activities by fiscal year.

Information prepared for the SCVURPPP in 1994 had estimated the largest single source of copper in stormwater to be wear debris from automobile brake pads. Other potentially significant sources included copper algaecides, building materials, swimming pool discharges and erosion of native soils. Based in part on this information, the major tasks included within the ACCWP Copper Pollutant Reduction Plan were:

- Participating in the Brake Pad Partnership (BPP);
- Monitoring copper in stormwater discharges;
- Evaluating the significance of potential sources copper other than brake pad wear debris;
- Municipal maintenance activities; and
- Public education and outreach to businesses.

The copper reduction measures selected by the ACCWP target the largest source of copper discharged to the Bay (brake pad debris) and include on an extensive business outreach and inspection program. The incorporation of public education and outreach programs by stormwater agencies within the San Francisco Bay region has been shown to change behaviors that adversely affect water quality and to increase the public's understanding of and appreciation for the Bay.

Fairfield Suisun Urban Runoff Management Program (FSURMP) NPDES permit was reissued in April 2003. This NPDES permit included specific permit requirements to develop pollutant reduction plans (PRP) for several pollutants, including copper, by November 2003. The PRP was to include control actions which include/relate to new/redevelopment and monitoring. This requirement is similar to the requirements found in a "third generation" permit. However, FSURMP's current permit is their second NPDES permit. In addition, FSURMP was to refine a list of tasks targeted to control copper by providing more detailed descriptions of activities. The CCCWP and SMSTOPPP NPDES permits are scheduled for reissuance in July 2004 and will likely include similar PRP and copper control measure requirements.

SCVURPPP and CAP/NAP

Copper Action Plan

In June 2000, the final Copper Action Plan (CAP) was developed for SCVURPPP. The final CAP contained specific baseline actions to be implemented by various entities. The complete list of CAP actions applicable to the Co-permittees was incorporated by the RWQCB into the Program's NPDES Permit Number CAS029718, Order Number 01-024, dated February 21, 2001, (see Appendix B of permit).

The overall purpose of the CAP was to serve as a non-degradation plan to ensure that: existing water quality is maintained; beneficial uses are protected; and that exceedances of the site-specific water quality objectives for copper did not occur in the Lower South San Francisco Bay. The CAP included current control measures/actions being used to minimize copper releases to the Bay; ambient monitoring "triggers" that would initiate additional measures/actions; actions necessary to address uncertainty; and a proactive framework for addressing increases to future copper concentrations in LSSFB, if they occur.

Each action was assigned a priority level that determined what condition and the order in which the action was to be conducted. More specifically, these "baseline" actions included programmatic actions by public agencies; special studies that track and address specific technical areas of uncertainty identified in the *Impairment Assessment Report* and the *Copper Conceptual Model Report*; and planning-type studies to track, evaluate, and/or develop additional indicators to use and future potential indicators and triggers (i.e., indicators for growth, development, or increased use or discharge of copper in the watershed).

These baseline activities were selected through an extensive stakeholder process from the array of potential copper reducing activities that had been considered in the South Bay since the late 1980's. Some selected baseline activities are unique due to the South Bay location and environment. Other watershed and planning type activities were unique for the South Bay due to the existence of the Santa Clara Valley Watershed Management Initiative (WMI) and its various programs. Some activities were selected to develop the additional information needed to evaluate the extent to which they may, or may not be effective in reducing sources of copper or better evaluating the potential impacts of copper loading on the Bay. A listing of each baseline activity is provided below.

The CAP also required the monitoring of municipal wastewater copper loading and dissolved copper in Lower South San Francisco Bay during the dry season. If the mean dissolved copper concentrations measured at certain specified stations increases from ambient (typically ~3.2 µg/L) to 4.0 µg/L or higher (Phase I Trigger Level), Phase I actions would be triggered to further control copper discharges. If the mean dissolved copper concentration increases to 4.4 µg/L (Phase II Trigger Level), Phase II actions would be triggered. If dischargers into the Lower

South San Francisco Bay demonstrate that the increases in copper concentrations are due to factors beyond their control, the CAP states that the Regional Board will consider eliminating or postponing actions required under Phase I or Phase II of the CAP.

Implementation of Copper/Nickel Baseline Activities

The majority of copper baseline (CB) actions have been implemented by SCVURPPP at the Program level (except for several assigned to San Jose, Sunnyvale and Palo Alto). Baseline actions conducted or proposed to be conducted are included in the SCVURPPP Annual Reports and Work Plans, respectively. They include the following 21 copper and 7 nickel baseline actions:

- CB-2: Water supplier copper sulfate use;
- CB-4 (1): Quantification studies of copper in vehicle brake pads;
- CB-4 (2): Quantification studies of brake pad copper debris fate and transport;
- CB-4 (3): Potential copper sources, loadings and impact indicators;
- CB-4 (4): Issue paper on feasibility of monitoring brake pad copper fate and transport;
- CB-5: Local support for Brake Pad Partnership (BPP);
- CB-9: Continue current efforts and track corrosion control opportunities;
- CB-10/NB-2: Measures associated with utilizing the Sediment Characteristics and Contamination Environmental Indicator;
- CB-13-NB-3: Track POTW pretreatment program efforts and POTW loadings;
- CB-14/NB-4: Track and encourage water recycling efforts;
- CB-15/NB-5: Measures to evaluate effectiveness of Performance Standards and identify cost- effective modifications to reduce discharges of copper (see NB-1, CB-3 and CB-11);
- CB-16: Measures to establish an Environmental Clearinghouse;
- CB-17 (1): Phytoplankton species toxicity and prevalence;
- CB-17 (2): Measures to assess cycling and fluxes between water column, phytoplankton, sediment and benthos;
- CB-17 (3): Measures to assess wet season tributary loading and loading uncertainty;
- CB-17 (4): Bio-assessment tools to track presence of copper sensitive taxa in Lower South Bay;
- CB-17 (5): Assess feasibility of phytoplankton bioassays to measure toxicity;
- CB-18 (1): Investigate flushing time estimates for different wet weather conditions;
- CB-18 (2): Investigate location of northern boundary conditions;
- CB-18 (3): Determine Cu-L_1 and L_2 complex concentrations (copper speciation);
- CB-18 (4): Investigate algal uptake/toxicity with competing metals;
- CB-19/NB-6: Track industrial virtual closed-loop wastewater efficiency measures as part of POTW source control programs;
- CB-20: Measures to revise the Copper Conceptual Model Report findings; and
- NB-7: Measures to establish a watershed model linked to process oriented Bay model.

The Regional Board also expects Co-permittees to implement appropriate actions at the local level. SCVURPPP has identified copper control activities that are feasible to implement to varying degrees at the Co-permittee level, based on the size, urbanization, etc. of a given Co-permittee's service area. These activities include the following:

- CB-1: Measures to reduce copper discharges from vehicle washing operations;
- CB-3: Measures to control copper in discharges of stormwater in targeted industrial sources;
- CB-6, 7: Measures to reduce traffic congestion/promote alternative transportation;
- CB-8: Measures to classify and assess watersheds and improve institutional arrangements for watershed protection;
- CB-11: Measures to improve street sweeping controls and stormwater system operation and Maintenance;
- CB-12: Measures to control copper discharges from pools and spas;
- CB-21: Measures to discourage architectural use of copper; and
- NB-1: Measures to control nickel discharges from construction sites (sediment).

Individual Co-permittees include measures to address each of these activities, as applicable in their Work Plans. In addition, the SCVURPPP and certain Co-permittees as appropriate will continue to prepare a Copper/Nickel Work Plan as part of the SCVURPPP draft Work Plan submitted March 1 of each year.

Next Generation CAP

The Copper Action Plan developed for the Lower South San Francisco Bay was designed to incorporate lessons learned from implemented action items and from scientific and technical information from other sources. The update will be completed every five years, as part of the NPDES permitting process, and regular review of conditions in LSSFB. The review, which is conducted by a temporary work group, using a collaborative, stakeholder based adaptive management process. The updated CAP would be evaluated within the context of the technical products used in its development, including the TMDL loading analysis, conceptual model and impairment assessment. If revisions were found to be needed prior to the five-year update, the CAP provided that the Regional Board could amend the CAP through Co-permittees annual Work Plans or other regulatory actions. The first major review/update of the CAP since it was adopted in June 2000 began in mid-2003 with revisions to the baseline activity reporting table format.

The Santa Clara Basin Watershed Management Initiative Bay Modeling and Monitoring (BM&M) workgroup has agreed that further efforts at fine-tuning the CAP baseline activities may not be a productive use of stakeholder's time due to certain inherent problems with the current CAP/NAP language. Instead, together with Regional Board staff they are working towards an approach that will streamline the current CAP to focus on activities that will remove the largest amount of copper.

To assist in the identification of key baseline copper control activities that are most effective in removing copper, the Clean Estuary Partnership (CEP) is currently funding a project to update information on copper sources in Bay Area urban runoff. This project is part of the North of

Dumbarton Cu/Ni site-specific objective (SSO) project. Updated copper source information will be compiled, based on scientific literature, reliable technical reports and other information from the South Bay. The project will produce a short technical report with updated copper source, control, and quantification information. The report will develop a prioritized list of potential stormwater copper source control measures that will remove the largest amount of copper per effort expended. A menu of these prioritized activities could form the nucleus for a "next generation", potentially Bay-wide CAP. The activities and approach included in the ACCWP Copper Pollutant Reduction Plan represent one potential vision of what parts of a next generation CAP might look like.

Regional Board staff has indicated a desire to work towards a single Bay-wide CAP. One potential approach would be to develop the baseline activity language for the North Bay Cu/Ni Action Plans and then to incorporate the language directly (or perhaps by reference) into the appropriate North Bay stormwater permits. Next, following the prior South Bay approach, the Basin Plan would be amended to include both the North Bay SSOs and references to the "next generation" CAP/NAP in the implementation section. Concurrently, the existing Basin Plan language regarding the South Bay CAP/NAP activities would also be amended to be consistent with the North Bay language and CAP/NAP approach.

An overarching goal of a revised CAP would be to facilitate a more intensive effort on a smaller number of the most effective copper control actions, implemented with on-going input from Regional Board staff. The development and implementation of a Bay-wide CAP would be one means to help to ensure a reasonable and equitable level of participation among all stormwater programs within the Bay.

Ambient water quality triggers and monitoring

The Action Plans for North of the Dumbarton Bridge are concerned primarily with (1) development of water quality monitoring triggers and (2) development of an effective source control program. The presumption is that the majority of source control effort will be focused on copper, with knowledge that such efforts will have a collateral benefit in reducing nickel at similar sources. The intent of the North Bay Action Plans was to utilize the South Bay Action Plans [Tetra Tech, 2000b,c], thereby creating templates for use by the North Bay entities. It was found that municipal and industrial dischargers have existing copper control program information that could be readily adapted into the South Bay templates.

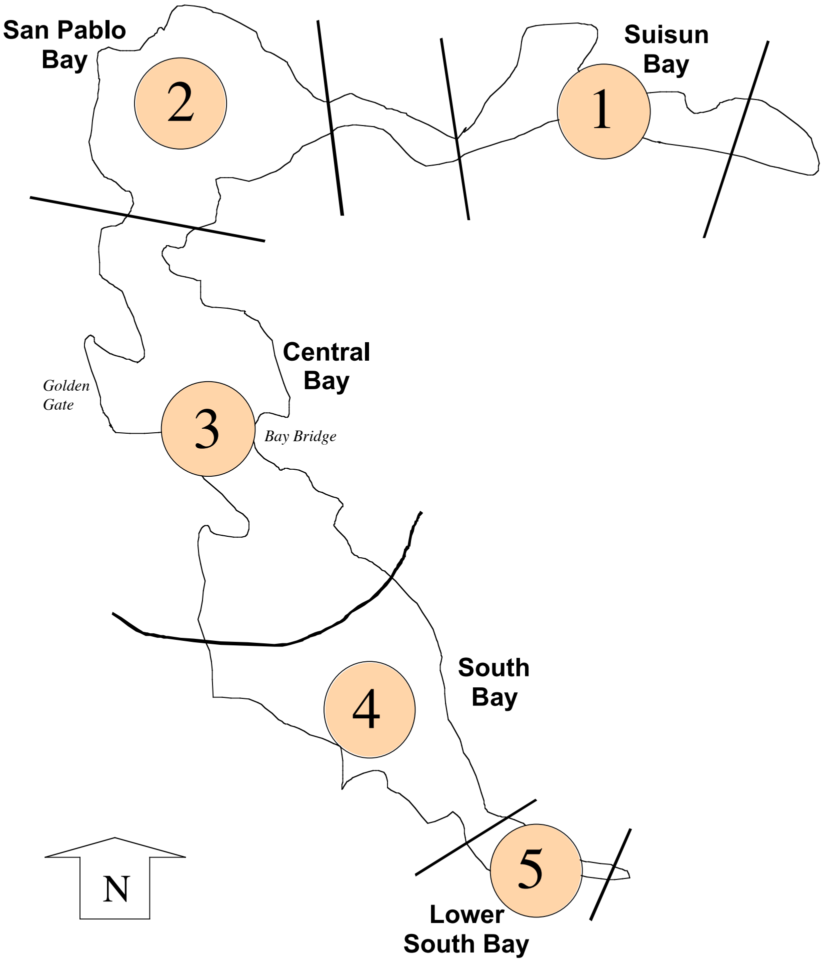
Municipal, industrial and stormwater copper and nickel sources were investigated to determine feasible baseline and subsequent actions for controlling discharges to the North Bay if loadings from these sources are found to be significant. Previous pollution prevention and source control work in these areas was incorporated for this effort.

Trigger Development

The next step in developing the Action Plans was preparing a plan to monitor dissolved copper and dissolved nickel concentrations in the Bay north of the Dumbarton Bridge. The 2002 revised Regional Monitoring Program (RMP) monitoring approach [SFEI, 2001b], with fixed stations plus randomized stations by Bay segment (see map below), was reviewed with RMP staff to confirm that the sites provide adequate shallow and deepwater spatial coverage for tracking ambient copper concentrations (this was partly how sites were selected during the RMP redesign). Additionally, LSSFB trigger development was reviewed prior to the development of triggers north of the Dumbarton Bridge.

Multiple trigger concentrations were determined using a power analysis (one-sided t-test of means with an alpha value of 0.05) on previous dissolved copper and dissolved nickel water quality data collected north of the Dumbarton Bridge.

Figure 2.2. Regions of San Francisco Bay Defined by Revised Regional Monitoring Program



Trigger Program

Ambient water quality trigger levels were established for dissolved copper and dissolved nickel in each of the four Bay regions north of the Dumbarton Bridge using the statistical methods described above (see **Table 2.3**).

Table 2.3. Trigger Levels Relating to the Ideal Sampling Scheme (µg/L)

		Region 1	Region 2	Region 3	Region 4
Copper	increment	0.82	1.29	0.79	0.79
(µg/L)	concentration	2.87	3.47	2.23	3.16
Nickel	increment	0.80	1.18	0.76	1.22
(µg/L)	concentration	2.16	3.26	2.18	3.55

To properly test the established indicators, concentrations of copper in the Bay north of the Dumbarton Bridge will be monitored during the dry season. The monitoring plan for LSSFB included monthly monitoring at each of the identified trigger stations. The proposed monitoring in the Bay north of the Dumbarton Bridge will utilize results obtained by the RMP monitoring. The proposed option is to sample for triggers in regions 2 and 4 only, as these are the two regions with the highest (most sensitive) copper and nickel concentrations and it is judged that changes in these areas will be indicative of changes in the Bay NDB. It is assumed that RMP sampling will provide 12 samples in Region 2 and 8 samples in Region 4, to provide a 99% level of power in the monitoring effort. Some power (ability to detect a statistical difference) is lost in using an n of 8 for Region 4 compared to using an n of 12, as is recommended for Region 2. It would cost an additional ($910) to sample an n of 12 in Region 4 (*Draft Development of Action Plans, EOA/LWA, June 2003, Appendix 3*).

Power analysis results simply indicate the incremental increase in ambient copper (or nickel) concentrations that can be statistically detected at a given level of significance (in this case 99%). This level of increase is not likely one that is ecologically or biologically significant. A biologically significant endpoint is the SSO itself.

Response actions have been described above to address situations where the trigger levels are activated. In addition, point source monitoring and cumulative load tracking is necessary on an annual basis to report and assess the relationship, if any, between increases in ambient concentrations and point source loads. It is proposed that the Regional Board's Electronic Reporting System be used to obtain the effluent data from NPDES dischargers for use in this tracking activity.

Appendix D

Response to Comments

Copper-Nickel CMIA Review – Richard Looker – April 19, 2004

1) Generally, did the report follow the prescribed outline in terms of coverage, tone, level of detail, graphics? *Is this report supposed to adhere to the outline since it was in process prior to those guidelines being established? Generally yes, the report has the content. For impairment assessment, I think it is all there. For CM, it is there, but the order is a bit odd. I think. I will give specific comments later.*

2) Regarding the Impairment Assessment Section:

a. Was there a clear statement of the relevant water quality standards and whether or not they are met in the Bay? *Yes*

b. Was there a clear statement of the beneficial uses threatened? *Yes*

c. Was there a clear statement of the basis of impairment? *Yes*

d. Was there a clear discussion of indicators of impairment and values of those indicators in the Bay? *Yes*

3) **Impairment unlikely:** The evidence clearly supports the judgment that the contaminant is not causing a negative impact to beneficial uses. This finding includes some uncertainty.

e. Based on your reading of the Impairment Assessment section, which level of certainty is most applicable for the contaminant (refer to discussion above)? Please give a brief explanation of why you chose this level of certainty. *I choose Impairment Unlikely. The reasons are the same as why that level was chosen for the south of Dumbarton project. The weight of evidence points to "no impairment", but there are uncertainties and some possible avenues to explore for impairment (sediment and phytoplankton) that are still unresolved.*

f. Are there specific problems with tone or miscellaneous editorial problems that you would prefer be corrected in the final draft? *Yes, quite a few:*

4) Pg. iii : "CTR established each of these objectives as numeric value times a WER" (error, WER only applies to copper).

San José Response: *San Jose staff believe the author of the CMIA was only stating that the EPA WER procedure was officially promulgated first with the National Toxics Rule (1992, Amended 1995) and recently with the California Toxics Rule. In this latter rule (see footnote "i" to the water quality criteria table in the CTR), the WER applies to some ten metals (arsenic, cadmium, chromium III, chromium VI, copper, lead nickel, selenium, silver and zinc). While the WER procedure applies to all these metals, the NDB study participants (and the state) are developing a state-approved WER for copper only. While a WER is not being developed in the present case for nickel, the "CTR established each of these objectives (copper & nickel) as numeric value*

(EPA criteria) times a WER." Staff does not perceive an "error" was made in this statement by the CMIA authors.

5) Pg. v:" Complexation of nickel is neither observed nor expected to effect nickel toxicity." I think this is incorrect. Please refer to Sedlak et al. 1997 *Strongly Complexed Cu and Ni in wastewater effluents and surface runoff*. ES&T 31(10): 3010-3016

Response: *Text changed to " Complexation of nickel does not demonstrate a similar effect on nickel toxicity."*

6) Page v: what is non-conservative excess?

Response: *Non-conservative excess refers to the idea that there are in Bay sources (such as benthic remobilization from the Selby Slag site (see Section 3.3.5).*

7) Page 1 of REL comments: Pg. 18: "…the water column-based site-specific objectives for copper and nickel directly account for toxicity to sensitive benthic invertebrates." REL Comment: Not necessarily. You are establishing water column dissolved values that are likely lower than pore water concentrations. Those (presumably) higher pore water concentrations could be a problem through sediment toxicity.

San José Response: *Critical life stages of many benthic invertebrates are protected by the dissolved copper criteria. Larvae of mussels, oysters, sea urchins, clams, and scallops develop in the water column. Forty-four genera are represented in the draft EPA copper criteria document (2003). Most of these animals have critical (larval) life stages that develop in the water column. Three of these (mussels, oysters, sea urchins) are among the four-most-sensitive genera from which the Final Acute Value (FAV) for copper is derived. The FAV is lowered from 10.39 to 9.625 ppb to protect Mytilus sp. The tests with Mytilus sp. were conducted with sensitive life stages (embryos), which develop in the water column. Of the 44 genera listed in the EPA database, those most likely to be affected by pore water are animals with developing young in close contact with the sediment. These are:*

Above Benthos: Crabs – GMAV = 41.06 – 502.8 ppb
Polychaete worms – GMAV = 100.6 – 136.9 ppb
Sand Shrimp - GMAV = 816.3 ppb
Within Benthos: Amphipods – GMAV = 209.5 – 502.8 ppb
Polychaete worms – GMAV = 318.3 ppb
Nematode – GMAV = 217.9 ppb

Crab tests are performed on larval stages and a site-specific objective of 6.9 ppb (for example) is likely protective of the Dungeness crab, which has an acute value of 41.06 ppb, especially since its larvae are planktonic. The greatest unknown is amphipods, since there are no test procedures *for developing young. However, adult amphipods are not very sensitive to copper (GMAV = 209.5 – 502.8 ppb).*

g. Are there big problems in terms of presentation or interpretation of data that must be resolved before we go any further with this report?

8) Pg. iii: Be careful about using term like "recommended range of SSOs". This implies there is some scientific reason why these were recommended. This is not the case and the discussion should not be limited to that range.

Response: *Deleted the word recommended.*

9) Pg. iv: I cannot accept this implication of benthic remobilization as having nothing to do with anthropogenic inputs. There is almost no mention in the report that the sediments are a bigger source than they otherwise would be because they are enriched by human inputs. Please discuss more fully the concept that anthropogenic inputs can contribute to dissolved concentrations either directly or indirectly as those inputs are stored in the sediments from future release. In this way, the sediment source is correctly viewed as being composed as a background component and a component that would not be there were it not for historical and ongoing loading. There is almost no mention of this possibility at all. The sediments are characterized as dwarfing ongoing inputs and this is a disingenuous characterization of the story in my opinion.

Response: *The importance of ongoing loadings cannot be understated, however there is a lot of uncertainty on the concept of "anthropogenic inputs contributing to dissolved concentrations either directly or indirectly. The sediment source is correctly viewed as being composed as a background component and a component that would not be there were it not for historical and ongoing loading." This uncertainty will be addressed in the multibox modeling exercise and can be addressed using the MIKE (URS) model. SFEI has been funded by the CEP to improve the model regarding sediments impact in San Francisco Bay. (See Appendix B).*

10) Pg iv: you say that "results of studies regarding phytoplankton and sediment quality indicate that copper and/or nickel are not likely to be causing impairment of phytoplankton or benthic communities in the Bay". I think that this statement is probably a fair statement for phytoplankton, but the evidence presented for sediment toxicity on p. 17 makes the statement for sediment misleading. I do not think you can make the claim for sediment. The jury is still out.

San José Response: *The City agrees with the statement that phytoplankton impairment is no longer an issue due to the speciation results published by Buck and Bruland (2003) and because we now know that sensitive phytoplankton (picocyanobacteria) are commonly found in the Bay. The paper (in preparation) by Buck and Bruland (4/12/04 version) states that: "Regardless of site or season, the [Cu^{2+}] values throughout San Francisco Bay did not exceed 10^{-13} M, suitably below the toxicity limit for aquatic organisms….the data from Lessin et al. (unpubl.) in summer 2001, from Beck et al. (2002) in April 2000, and from this study in January and March 2003, all support the conclusion that copper speciation in San Francisco Bay is dominated by a strong L1* *ligand class that maintains free [Cu^{2+}] to levels easily tolerated by the ambient phytoplankton communities." (bold added). Clearly, there is no longer uncertainty with regard to the effect of Bay copper concentrations on phytoplankton in the Bay.*

The City agrees with the CMIA authors that much (if not all) of the work done to link observed sediment toxicity to copper has been poorly done (e.g. Phillips et al. 2000). Technically speaking, the Phillips et al. study (2000) did not establish a meaningful link to copper or to any other single toxicant. Unless or until Phase III, confirmatory TIEs are done (these and intermediate evaluations are expensive) any "demonstrated linkage" will be poor at best. One evaluation reported by Phillips et al. (2000), linked copper to sediment elutriate toxicity even though none of the toxicity in the 100% elutriate samples was ameliorated by manipulations designed to remove copper (i.e. EDTA addition and cation exchange treatment). In the same study, the authors described the effect of 0.12 µg/L copper as potentially "synergistic."

This is unreasonable and misleading since the mean oceanic concentration of copper in the North Pacific Ocean in 150 ng/kg (approximately 0.15 µg/L; Bruland 1980). The discussion of copper-related sediment toxicity on p. 17 does not contradict the statement on p. iv (quoted above by REL) but concludes that "the source of toxicity in Grizzly Bay sediment samples is clearly unknown." The City agrees with this conclusion.

11) Pg. 30 - : Way too much info on the Action Plans. This was a distraction to me. The only part that seems to fit was information about the origin of copper and nickel found in WW effluent and UR. I do not need this information in the CMIA report.

Response: *Information on Action Plans has been moved to Appendix C.*

h. Is there a clear statement of the relevant data gaps? Do you agree with those findings? *Pretty good treatment here on the relevant uncertainties.*

*Regarding the Conceptual Model Section:

Analogous to the discussion above about level of certainty in the impairment finding, there are three categories for level of support for findings about the conceptual model:

The conceptual model findings are well supported with existing data and these data are cited and presented clearly.

The findings are based on limited data with the data gaps clearly identified

The findings are based on seriously insufficient data or on nothing

12) a. Is the system adequately described? What is the state of certainty regarding the findings (which category from above) made regarding the system description? *Findings are based on a level of certainty somewhere between adequate data and limited data. There are reasonably*

ample data for some things like ambient conditions and the toxicity studies. However, the loading information is poor. The information about the significance of sources is poor (e.g. how do CV watershed inputs impact ambient conditions compared to local trib loading).

Response: *Information on loadings continues to be developed. New reports and models can assist in determining more accurate and complete loading estimates. The goal of this report was to outline some of the major areas believed to contribute copper and nickel to the water column of San Francisco Bay.*

13) b. Are all relevant sources included, and what is the level of certainty regarding the findings? *Yes, high level of uncertainty regarding sources it seems.*

Response: *See response to 12).*

14) c. Is the significance of each source or load described and what is the level of certainty regarding these findings? *The significance of each source is only described in terms of gross magnitude, but not significance. For example, CV inputs are big, but they may just shoot through. This sort of hydrodynamic consideration is only touched upon briefly. So, level of uncertainty for these findings is high.*

Response: *There are two things that have to be considered when evaluating the significance of a source:*

> *1) to what degree does the source maintain or increase the concentration of copper and nickel in Bay sediments;*
> *2) to what degree does the source maintain or increase dissolved, free ionic copper and nickel concentrations in Bay waters?*

We care about sediment concentrations because the sediments serve as a long-term reservoir for metals – simple equilibrium considerations tell you that when copper concentrations in sediments increase, desorption rates of copper from those sediments will increase, elevating dissolved copper concentrations. Also, metals in sediments have the potential for direct effects on benthic organisms, which is going to be addressed through the State's Sediment Quality Objectives guidance. This is why one of the goals of the copper action plan is to ensure that metal concentrations in Bay sediments do not increase over time, and why we have to evaluate effects on the long term metal concentration in sediments when we talk about the significance of a source. From that standpoint, it is appropriate to simply look at the gross magnitude of the source in a simple box-model active layer approach to talk about its significance.

POTWs remove particles, so in effluent dominated waterbodies (like the receiving water sloughs of lower South Bay), you see a shift towards dissolved metals. However, the recent work of Sedlak et al, and Bruland before that, showed that copper and nickel discharge from POTWs is strongly complexed by organic ligands, so POTWs don't turn out to be significant sources of free ionic copper.

From reviewing RMP data, plus recent translator studies carried out on the margins (Sonoma Creek, Napa River), it becomes apparent that the most significant factor affecting dissolved copper and nickel in the Bay is mobilization from particles at interfacial areas – lower south Bay, Carquinez straits, the Napa River, anywhere fresh water mixes with salt water in a turbidity maximum zone seems to be associated with a localized peak in dissolved copper concentrations.

To summarize: the gross magnitude of a source is a good predicter of it's significance, as long as you normalize it to the sediment load of the source. Metal loads that result from large volumes of sediment with moderate to low metal concentrations (e.g., erosion from open spaces) aren't as much of a concern as metal loads that result from erosion of solid material with high metal concentrations (like the submerged slag pile off of Davis Point). Beyond that, the significant factor that drives dissolved metal concentrations isn't really the nature of the metal source. The question is where in the estuary are metals mobilized from sediments into the dissolved phase, and how do sources affect the baseline concentration of metals in sediments that are transported into these mobilizing zones.

15) d. Are the relevant fate/transport/transformations/effects described clearly, and what is the level of certainty regarding any findings made? *No, these processes are not described adequately. I think that the beginning of conceptual model should take care of this. There are some confusing passages about processes that I will discuss later. The chemistry and biological effects are ok, but the transport and physical cycling is not clearly presented.*

Response: *See response to 14).*

16) e. Are there specific problems with tone or miscellaneous editorial problems that you would prefer be corrected in the final draft? *Yes.*

Response: *Comment noted. Edits have been made.*

17) Pg 55: in section titled "erosion of bed sediment" you talk about benthic flux load. I think this is a confusing section because you have not identified and defined the major processes. I think it could be a terminology problem here. In the past, I have seen three processes involving sediments: 1) resuspension of sediments and dissolution, 2) erosion of buried (previously unavailable) sediments containing metals, and 3) benthic flux of dissolved copper. Please define the processes up front and perhaps include a picture early on to help the reader.

Response: *Conceptual model figures have been moved to Section 1.3, as well as an introduction to resuspension of sediments and dissolution, erosion of buried sediments containing metals, and benthic flux of dissolved copper.*

18) Pg. 64: Do the first and last bullets contradict each other?

Response: *Bullets have been edited to state the findings more clearly.*

19) Pg. 64: perhaps should have started the CM with figures like this and then explained the processes contained in them.

Response: *Figures have been moved up to Section 1.3.*

20) Pg. 66: Why no mention of UR loadings in the discussion of effects of current inputs of copper and nickel on surface sediment concentrations?

Response: *A lot of loadings from urban runoff are already particulate bound. A load might look big but if it is not dissolved, there may be no adverse impact on aquatic life. The question can then be posed as to whether the particulate bound metals might be remobilized in the benthic layer. It is known that copper and nickel are in urban runoff, which adds to the pounds of these metals in surface sediments (if they are in particulate form). The degree to which these affect surface sediment concentrations is not well understood. The Multibox Model (Appendix B) and the Brakepad Partnership work will both address this concern.*

21) Pg. 70: Uncertainties in loading numbers?

Response: *There are very high uncertainties in the loading numbers, some of which are discussed in Section 3.3. Estimates of copper and nickel loading vary from day-to-day and year-to-year. For example, a high rainfall year increases the flow (and potentially loading) in the Rivers that empty into the Bay. Additionally, wet deposition will vary during increased or decreased rainfall years. Dry deposition estimates have error bars of 50-80%. POTW and industrial loads were calculated using average daily maximum copper and nickel values, so will be variation from these means in addition to the plants being spread out around the Bay.*

f. Are there big problems in terms of presentation or interpretation of data that must be resolved before we go any further with this report?

22) There was no mention of the anthropogenic impact on sediment concentrations. It is as if that copper and nickel magically got there or is just background. This is not the case. Copper and nickel inputs likely stay in the estuary a long time (~ years) so they are a major part of what later is viewed as merely a legacy sediment problem.

Response: *See response to 12) and 14).*

23) Pg. 77: You failed to mention or show the titrations/results from Central Bay stations. The conclusion from the Central Bay titrations is that you reach the phytoplankton toxicity threshold well below 6.9 µg/L. Please present a more thorough picture of these data. There are some areas where 6.9 µg/L will not be unambiguously protective of phytoplankton according to the Bruland results.

San José Response: *Predicting the impact of copper on Bay phytoplankton has been the subject of much recent experimentation and debate. The work of Dr. Bruland and his co-workers has dramatically increased our understanding of the potential toxicity of copper to phytoplankton. It is important to review phytoplankton protection as part of the SSO process. However, it may not be prudent to regulate on phytoplankton as discussed in the City comments on the NDB Cu/Ni CMIA report (confounding factors, extrapolation to the field, salient endpoint to regulate, and whether you should regulate on primary production in general or on a single algal species). In addition, the recent history of the scientific debate over this issue points out the shortcomings of attempting to "predict" Bay phytoplankton responses to ambient copper concentrations. That history and some further considerations are summarized below.*

At the South Bay Copper Impairment Assessment Workshop, Dr. Bruland suggested that South Bay $[Cu^{2+}]$ *was sufficiently high to impact diatoms. He hypothesized that the co-occurrence of other ions (e.g.* Mn^{2+} *and* Zn^{2+}*) was the reason why South Bay diatom blooms did not appear to be affected by copper. He suggested that cyanobacteria were not in the South Bay because they are much more sensitive than diatoms.*

Subsequent communications with USGS and further studies revealed that cyanobacteria are routinely found in South Bay.

The 4/12/04 Kristin Buck & Ken Bruland draft paper entitled "Copper Speciation in San Francisco Bay" concluded that "Regardless of site or season, the [Cu2+] values throughout San Francisco Bay did not exceed 10^{-13} *M, suitably below the toxicity limit for aquatic organisms." Table 1 of that paper shows the range of concentrations for the January and March 2003 samplings to be from* $10^{-13.3}$ *M at Yerba Buena Island and San Bruno Shoals to* $10^{-15.5}$ *M at Grizzly Bay. This appeared to contradict the original* $[Cu^{2+}]$ *prediction that suggested cyanobacteria would be affected.*

It is helpful to review the titration results of Buck & Bruland (2004). For example, they seem to indicate that the 6.9 ppb SSO established for South Bay is protective. However, there are other factors that should be considered in addition to the titration graphs and the $[Cu^{2+}]$ *in the Bay. These include competition by other ions and source and fate of ligands in the Bay.*

In addition to $[Cu^{2+}]$ *in the Bay, one must also evaluate the role of* $[Mn^{2+}]$ *and* $[Zn^{2+}]$*. The role of ion interactions in ameliorating the toxicity of copper to phytoplankton is not well understood. However, these ions appear to be a significant factor.*

The role of organic ligands (L1 and L2) in copper speciation is well known (Buck & Bruland 2004). However, the source and fate of the ligand populations in the Bay is not well understood. The copper speciation work of Buck & Bruland (2004) indicated that the Bay could assimilate more copper and still be protective of Bay phytoplankton.

Many algae produce exudates in order to regulate the amount of available metal in their environment. This affects both plant and animal populations. The Copper Project Report (Buck, Bruland, and Hurst) dated 3/18/04, reported that the South Bay ligand sources "may be due to either industrial inputs or biological activity." The report also noted that there was an observed *decrease in ligand concentrations during the March 2003 sampling despite the presence of a very large diatom bloom. The report concluded that there "is no real motivation for the biology (phytoplankton) to produce additional ligands" since "the free copper concentrations observed in the bay are not at toxic levels to any ambient microorganisms" (diatoms). These statements suggest a further assimilative capacity in the Bay due to excess ligands and the ability of algae to produce additional ligands to regulate [Cu^{2+}] in the Bay.*

The Regional Board Study determined acute algal WERs for Thalassiosira Pseudonana using 13 samples from six locations throughout S.F. Bay. Mean WERs for total and dissolved copper, respectively, were 6.1 and 2.3. Filtering site water may drastically alter its assimilative capacity for copper, rendering it more sensitive. However, EPA laboratory waters for algal testing are filtered through 0.45 micron pore-size filters as a matter of procedure. Thus, the 2.3 dissolved copper WER for T. Pseudonana may be underestimated as indicated by the mean WER for total copper of 6.1.

The Guidelines For Deriving Numerical National Water Quality Criteria For The Protection Of Aquatic Organisms And Their Uses (EPA 1985) indicates that "the Final Plant Value should be obtained by selecting the lowest result from a test with an important aquatic plant species in which the concentrations of test material were measured and the endpoint was biologically important." The only true chronic test with algae is Champia, an east coast red macrophyte species (Dave Hansen, personal communication). It is primary production in general that ought to be protected rather than individual phytoplankton species, which ecologically may be responding to a variety of natural pressures (competition, nutrients, light, grazing).

24) Pg. 83 top of page "…it would be **useful** to get a better understanding of the movement of copper and nickel into the sediments from existing external loading sources". I would say essential. I think this is the only place in the report where you raise this issue, and it is barely a mention and it is on the second to last page. To me, this is an important issue that needs to be clearly presented for consideration. The previous box modeling from the LSSFB work was flawed in that it did not consider this issue and it used hydraulic residence times instead of particle residence times. Thus, you cannot rely on those modeling results or that framework for this report.

Response: *SFEI has been funded by the CEP to prepare a multibox model for understanding sediment impact in San Francisco Bay (see Appendix B).*

25) g. Is there a clear statement of the relevant data gaps? Do you agree with those findings? *Not really a separate statement of data gaps for the CM section. I think the presentation was pretty clear in the IA portion. It is possible that the CM could have pointed out a few more, but not sure at this point.*

Response: *Comment noted.*

e. Next Steps

Did the report make suggestions for appropriate next project steps and provide reasonable support for those suggestions? Do you agree with the suggestions based on your evaluation of the material presented in the Impairment Assessment and Conceptual Model sections? If not, what next steps do you feel are appropriate and why? *This section did not appear. It could be because the suggested outline predated development of this report.*

Response: *Section predated development of report. We're already doing the recommendations.*