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Copper Sources in Urban Runoff and Shoreline Activities

Information Update

Prepared for the Clean Estuary Partnership

November 2004

PREFACE

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ACKNOWLEDGEMENTS

The author greatly appreciates technical assistance provided by Ruby Pap, Bay Conservation and Development Commission; Joan Edwards and Karen McDowell, San Francisco Estuary Project; the Brake Pad Partnership Steering Committee and project team (Rodger Dabish, Pat Thesier, Tim Merkel, Christopher Shepley, Mark Phipps, Jim Pendergast, Michael Endicott, Mark Schlautman, and Sarah Connick); Thomas Barron; Nan Singhasemanon, California Department of Pesticide Regulation; Leigh Johnson, University of California Cooperative Extension; Brandt Grotte; Geoff Siemering, San Francisco Estuary Institute; Geoff Brosseau, Bay Area Stormwater Management Agencies Association; Arleen Feng, Alameda Countywide Clean Water Program; and Richard Looker, San Francisco Bay Regional Water Quality Control Board.

Much of the scientific literature used in this report is from the Brake Pad Partnership Technical Reference Library, a special collection in the U.S. EPA Region 9 library. Funding for development of this literature collection was provided by the U.S. Environmental Protection Agency, the San Francisco Estuary Project, and the Bay Area Stormwater Management Agencies Association.

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COPPER SOURCES IN URBAN RUNOFF AND SHORELINE ACTIVITIES

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COPPER SOURCES IN URBAN RUNOFF AND SHORELINE ACTIVITIES

EXECUTIVE SUMMARY

The purpose of this report is to summarize information on the sources of copper that is carried to San Francisco Bay in urban runoff and copper that is released directly into the Bay from shoreline activities. This report:

- Provides estimates of the amount of copper released to San Francisco Bay from each source;
- Estimates the relative degree of uncertainty in each copper release estimate and lists the sources of uncertainty for each estimate;
- Reviews available control measures for each copper source, providing control measure effectiveness information to the extent data are available;
- Identifies feasible control measures for copper sources in urban runoff and shoreline activities; and
- Identifies priorities for investigation of sources and control measures.

This report was prepared for the Clean Estuary Partnership to support Technical Task 4.11, Basin Planning Assistance for Cu/Ni North of the Dumbarton Bridge.

Tables S-1 and S-2 (on the next page) summarize urban runoff and shoreline activity copper source load estimates and the uncertainties in these estimates. Although the total of the urban runoff estimates (45,000 – 47,000 pounds per year) is somewhat less than the total estimated copper discharge in urban runoff (90,000 pounds per year), the report concludes that it is unlikely that a major copper source has not have been identified. Given the long history of investigation of copper sources in the Bay area, it is more likely that one or more of the copper load estimates understates actual copper releases.

Table S-3 (on page 3) summarizes the feasible control measures and priorities for investigation for each identified copper source.

Table S-1. Summary of Copper Sources in Urban Runoff (Pounds of Copper per Year Discharged to San Francisco Bay)

Copper Source	Load Estimate	Uncertainty[a]
Vehicle brake pads	>10,000	High
Estimate includes:		
Original equipment pads	*10,000*	
Replacement brake pads	*?*	
Brake pads on heavy-duty trucks, off-road vehicles, rail cars, and motorcycles	*?*	
Architectural copper	4,500	Moderate-High
Copper pesticides	<8,000 – <10,000	High
Estimate includes:		
Landscaping	*1,200 to 2,500*	
Wood preservatives	*1,400 to 2,800*	
Pool, spa, and fountain algaecides	*<5,000*	
Industrial copper use	3,300	Moderate
Deposition of copper air emissions	8,800[b]	Low to Moderate
Estimate includes:		
Diesel and gasoline fuel combustion	*3 – 60*	
Industrial facilities	*130*	
Residential wood burning and forest fires	*110*	
Unknown	*>8,000*	
Soil erosion	7,000	Moderate
Estimate includes:		
Construction	*2,600*	
Hydromodification	*<5,000*	
Copper in domestic water discharged to storm drains	3,000	Moderate-High
Vehicle fluid leaks and dumping	600	Moderate-High

[a]Uncertainty is defined as follows: Low indicates that the estimate has an error within 50%; Moderate indicates that the estimate has an error up to 2 fold; Moderate-high indicates that the estimate has an error up to 5 fold; High indicates an error up to 10 fold (see Section 1.4).
[b]May overlap with vehicle brake pad estimate.
Source: Section 3.

Table S-2. Summary of Shoreline Copper Sources (Pounds of Copper per Year Released to San Francisco Bay)

Copper Source	Load Estimate	Uncertainty
Marine antifouling coatings	20,000	Moderate-High
Copper algaecides applied surface waters	4,000	High

Source: Section 3.

Table S-3. Summary of Feasible Control Measures (Other than Public Outreach) and Priorities for Investigation for Copper Sources in Urban Runoff and Shoreline Activities

Copper Source	Feasible Control Measures	Priorities for Investigation
Vehicle brake pads	• Brake Pad Partnership (BPP)	• Improved load estimate (BPP)
Architectural copper	• Requirements for management of wastewater from cleaning and treatment • After completing the recommended investigation, consider limiting installation and/or requiring measures to prevent copper releases or to treat roof runoff	• Practicality and efficacy of control measures such as coatings and runoff treatment measures
Copper pesticides	• Consider developing best management practices for wood preservatives to minimize copper use where releases are most likely • Regulatory control measures for pool, spa, and fountain algaecides are feasible; use improved load estimate to determine if they are warranted	• Improved estimate of the copper load from algaecides (primarily pool, spa, and fountain algaecides); use estimate to determine whether regulatory measures are warranted • Evaluate alternative practices and pesticides for landscaping to determine if safe and effective alternatives exist
Industrial copper use	• Industrial stormwater permit program	None
Copper air emissions	• Not able to identify appropriate measures at this time • Additional controls on identified sources are not warranted	• Identify major air emissions sources • Determine overlap with brake pad wear debris (BPP studies will provide data)
Soil erosion	• Construction stormwater permit program • Hydromodification management plan requirement	None
Copper in domestic water discharged to storm drains	• None (other than public outreach)	None
Vehicle fluid leaks and dumping	• None necessary (other than public outreach)	None
Marine antifouling coatings	• Not able to identify appropriate measures at this time • Consider a non-toxic antifouling coatings pilot project	• Bay Area-specific load estimate • Participate in IACC Copper Antifouling Paint Sub-Workgroup investigation of copper problem and control measures
Copper algaecides applied to surface waters	• Aquatic pesticides permit program	None

Source: Section 3.

1.0 INTRODUCTION

1.1 Background

Copper has been a pollutant of concern in San Francisco Bay since the late 1980s. The 1989 designation of lower South San Francisco Bay as impaired by copper (listing under section 304(l) of the Clean Water Act) caused government agencies and businesses to make a significant investment in copper source identification and copper reduction measures. These activities created a wealth of information on copper releases to surface waters—and greatly expanded understanding of options to prevent or reduce copper releases to San Francisco Bay.

The most recent compilation of copper sources in urban runoff is in the lower South Bay *Copper Action Plan* (Tetra Tech *et al.*, 2000). The *Copper Action Plan*'s copper source list was based on copper source information from the mid-1990s such as the *Metals Control Measure Plan* (SCVURP, 1997), which in turn was based on a list of sources assembled in the South Bay Copper Reduction Dialogue (SBCRD, 1994).

Since the mid-1990s, activities in the San Francisco Bay Area (Bay Area) and scientific research from elsewhere have provided new information relevant to understanding copper sources and control measures. The purpose of this report is to update information on copper sources in Bay Area urban runoff. This report also explores shoreline copper sources that are not present in lower South San Francisco Bay, but that occur elsewhere in the Bay Area.

1.2 Scope of This Report

This report has been prepared for the Clean Estuary Partnership to support Technical Task 4.11, Basin Planning Assistance for Cu/Ni North of the Dumbarton Bridge. The report was originally intended to provide up to date information about copper sources in urban runoff to facilitate development of a prioritized list of potential urban runoff copper source control measures that would provide the greatest relative removals per effort expended. However, during the course of the review it became apparent that shoreline activities represent a potentially significant source of copper to San Francisco Bay that were not considered in previous evaluations of Bay copper sources. Therefore, the report was expanded to include shoreline copper sources, even though such sources are not components of urban runoff. This information will be used in any *San Francisco Bay Basin Plan* amendments that follow out of the impairment assessment. Because one of the necessary elements of a *Basin Plan* amendment package is a source analysis (which should be as quantitative as possible), this report provides quantitative load estimates to the extent possible with available information.

The focus of this report is copper sources in urban runoff to San Francisco Bay. Two types of non-runoff Bay shore copper releases not previously investigated are also included—marine antifouling paint and copper algaecides applied to shoreline lagoons. This report does not address discharges into or effluent from industrial or municipal wastewater treatment plants, nor does it address non-urban copper sources, like sediment erosion from open space, agricultural pesticide use, mine drainage, and reservoir releases.

The information in this report was assembled from available data sources. Only existing information was used; sampling and chemical analysis were not conducted.

1.3 Report Organization

Section 2 summarizes previous copper source identification studies and reviews the urban runoff copper control measures from the lower South Bay *Copper Action Plan*. Section 3 identifies the major copper sources, estimates the relative magnitude of each source and identifies the relative degree of uncertainty associated with these estimates, and reviews copper control measures, providing control measure effectiveness information to the extent it is available. Section 4 lists conclusions and recommendations and identifies priorities for follow-up activities to address critical data gaps and uncertainties relating to potentially significant copper sources.

1.4 Uncertainty

Available data do not support reliable quantitative estimates of copper releases from most copper sources. The estimates in this report are quite uncertain. While the scope of the report does not include a quantitative review of uncertainties underlying each estimate, the report identifies the sources of uncertainty and uses qualitative review of the uncertainties to categorize the level of uncertainty in each estimate according to the following definitions (Tsai *et al.*, 2001):

- *Low uncertainty* indicates that the estimate has an error within 50%;
- *Moderate uncertainty* indicates that the estimate has an error up to 2 fold;
- *Moderate-high uncertainty* indicates that the estimate has an error up to 5 fold;
- *High uncertainty* indicates an error up to 10 fold.

In each section, possible methods to reduce the uncertainty in the estimates are identified. In light of the potential magnitude of the copper sources, quality of the data underlying each estimate and the existing control measures for each source, the report recommends priorities for future investigations to improve the quality of the copper load estimates.

2.0 PREVIOUS COPPER SOURCE IDENTIFICATION STUDIES

2.1 Copper Uses

Most copper that is refined in the U.S. is used in copper wire and rod, products that have limited potential to release copper to surface waters. Other uses of copper and its compounds are highly varied, as shown in these examples compiled from the Copper Development Association and International Copper Association (CDA, 2002; CDA, 2003a: ICA, 2004):

- Plumbing pipe
- Heat exchangers, radiators
- Industrial catalysts and electrodes
- Jewelry and other decorations
- Utensils such as pots and pans
- Coins
- Fertilizer
- Firework ingredient
- Coating in cathode ray tubes
- Animal feed additive
- Dietary supplement
- Roofs, gutters, flashing, and other architectural elements
- Motor vehicle components like bearings, bushings, gears, and wiring
- Pesticide (algaecide, fungicide, wood preservative, bactericide)
- Batteries (as an electrolyte or contaminant; an ingredient in alkaline batteries)
- Blue coloring for consumer products
- Semiconductor manufacture

This report focuses on applications of copper metal, copper compounds, and copper alloys (*e.g.*, brass and bronze) that may be sources of copper releases to surface water.

2.2 Lower South San Francisco Bay Copper Source Studies

For more than a decade, San Francisco Bay Area wastewater treatment plants and urban runoff management programs have investigated the many uses of copper to identify potentially significant sources of copper releases to surface waters. The 1992 Santa Clara Valley Nonpoint Source Pollution Control Program *Source Identification and Control Report* was the region's first compilation of copper source information—and its first comprehensive plan to reduce copper levels in urban runoff (SCVNPSPCP, 1992). The South Bay Copper Reduction Dialogue assembled a comprehensive compilation of copper sources, which is summarized in Table 1 (South Bay Copper Reduction Dialogue, 1994). Additional investigation has identified that many of the listed copper "sources" actually conveyed copper from one or more uses of copper into San Francisco Bay. Table 1 (on the next page) identifies which of the listed "sources" convey copper from elsewhere and lists the primary copper sources.

In 1997, the Santa Clara Valley Urban Runoff Pollution Prevention Program was the first stormwater program in the Bay Area—and probably the first in the nation—to attempt to quantify the specific sources of copper in urban runoff. Since 1997, the report documenting this effort—the *Metals Control Measure Plan*—has provided the only available basis for prioritizing efforts to manage copper in urban runoff in the Bay Area (SCVURP, 1997). Table 2 (on page 8) presents the copper sources summary from the *Metals Control Measure Plan*.

Table 1. Copper Sources Listed by the South Bay Copper Reduction Dialogue

Copper "Source"	Primary Copper Source
Air deposition	Conveys copper from many sources
Automobile dismantlers (runoff)	Vehicle parts
Brake pads	Brake pads
Commercial and residential land uses (runoff)	Conveys copper from many sources
Construction activities—copper in sand blasting slag and copper surface finishes	Copper in waste materials used for sandblasting, copper architectural materials
Copper algaecides (swimming pools, spas, fountains, and ornamental pools)	Copper algaecides
Copper algaecides in water supply systems and reservoirs	Copper algaecides
Copper fungicides and herbicides	Copper-containing pesticides
Copper in imported water supply	Copper in source water, copper algaecides
Erosion of native soils	Soil
Gas Stations	Brake pads, other vehicle sources
Highway runoff	Conveys copper from many sources
Illicit connections	Copper in wastewater (conveys copper from many sources)
Industrial land use	Conveys copper from many sources
Landfills	Conveys copper from many sources disposed in solid waste
Open space	Soil
Parking lots and maintenance yards (runoff)	Conveys copper from many sources
Spills and illegal dumping (copper contamination in motor oil, copper-containing pesticides)	Many copper sources
Street runoff	Conveys copper from many sources
Tap water	Copper pipes, copper in source water, copper algaecides
Vehicle Fuels (Exhaust)	Vehicle fuels
Wastewater treatment plants	Copper in wastewater (conveys copper from many sources)

Source: South Bay Copper Reduction Dialogue, 1994 and analysis by TDC Environmental.

2.3 Other Copper Source Studies

A literature review identified three studies estimating contributions of various copper uses to copper levels in urban runoff. The findings of each study are briefly summarized below.

2.3.1 Stockholm

A Swedish study investigated sources of metals in runoff and sewage in a portion of Stockholm, Sweden (Sorme and Lagerkvist, 2002). The urban runoff contributions from copper roofs, brake pads, tires, and asphalt were estimated. Other sources were

Table 2. Copper Sources Summary from *Metals Control Measure Plan*

Copper Source	Estimated Load at Source (lbs/yr)	Adjusted Load to Bay (lbs/yr)[a]	% of Total Load to Bay
Point Sources (Wastewater Treatment Plants)	*2,461*	*2,461*	*28*
Nonpoint Load Estimate for Lower South San Francisco Bay	*6,400*	*6,400*	*72*
Urban Nonpoint	9,611	4,685	53
Brake Pads	7,700	3,753	42
Coolant Leaks	112	55	1
Coolant Illegal Dumping	116	57	
Oil Illegal Dumping	7	3	0
Industrial runoff	693	338	4
Tailpipe Emissions	116	57	1
Construction Erosion	93	45	1
Pesticide Application[b]	74	36	0
Water Supply/Corrosion	700	341	4
Other Nonpoint (Natural Erosion and Reservoir Spills)	3,519	1,715	19
Total		**8,861**	**100**

[a]Nonpoint Source estimates were adjusted to be consistent with the nonpoint load estimated on the basis of creek monitoring data.
[b]Agricultural and landscape maintenance applications only. Although the original table attributed this load to both fertilizers and pesticides, the calculations not appear to address copper from fertilizers.
Source: *Metals Control Measure Plan* (SCVURP, 1997).

assumed to be negligible, an assumption validated by the acceptable mass balance (sources estimated as 109-113% of measured load). Table 3 presents the load estimates. It should be noted that copper roofs are relatively common in Stockholm—study authors estimated a total copper roof area of 623,000 square meters in an area with a population of 630,100.

Table 3. Copper Sources in Stormwater Entering Henriksdal Treatment Plant, 1999

Copper Source	Estimated Copper Load (kg/yr)
Copper roofs	700-920
Brake pads	280
Tires	0.2
Asphalt	11-17
Total (Stormwater Only)	**991-1217**

Source: Sorme and Lagerkvist, 2002

2.3.2 Maryland

A University of Maryland group explored sources of copper in urban residential and commercial runoff (Davis *et al.*, 2001). While this study confused "sources" and conveyances of copper and makes some unverified assumptions, it nevertheless sheds light on the presence of copper in urban environments. The study involved washing various urban surfaces and measuring the amount of metal washed off. This technique cannot separate copper from the "source" and copper conveyed to the sources from elsewhere (*e.g.*, from air deposition). The exterior surfaces examined did not contain copper so they are unlikely to be the primary source of the measured copper (copper roofs were not examined). The study also assumes that the material collected on vehicle wheels is entirely (and exclusively) brake pad wear debris, rather than a mixture of debris from road and vehicle sources. Table 4 summarizes study results.

Table 4. Copper "Sources" in Maryland Urban Stormwater

Copper Source	Estimated Contribution to Residential Stormwater	Estimated Contribution to Commercial Stormwater
Roofs (non-copper)	9-10%	75%
Material washed from building siding	9-22%	7%
Brake pads	47-55%	15%
Tires	1%	0%
Oil	0%	0%
Wet deposition	7-8%	1%
Dry deposition	14-17%	2%

Source: Davis *et al*., 2001.

2.3.3 Copper Development Association

The industry association for copper manufacturers has compiled information about environmental copper releases into a report (CDA, 2003b). This report some of the relevant literature on copper releases and provides estimates of release rates from certain sources. These release rate estimates are summarized in Table 5.

Table 5. Estimated Copper Release Rates from Environmental Copper Sources

Copper Source	Estimated Copper Release Rate (g/m^2 material per year)
Copper roofs	0.5 – 3.0
Copper gutters	3.5 (old gutters) 7.8 (new gutters)
Composite roof shingles with copper mildewcide	0.17
Copper-based marine antifouling paint	0.7 – 10 x 10^{13} (all boats) 6 – 8 x 10^{13} (well-maintained boats)

Source: CDA, 2003b.

2.4 Lower South San Francisco Bay Copper Control Measures

The lower South Bay *Copper Action Plan* lays out measures to control copper in wastewater and stormwater (Tetra Tech *et al.*, 2000). These measures are divided into three phases: Baseline actions and Phase I and Phase II contingency plans. This section considers only the implemented (baseline) activities. Table 6 reproduces the list of *Copper Action Plan* Baseline actions. Appendix A contains lists of Baseline, Phase I and Phase II actions and the copper source addressed by each action.

Table 6. Lower South Bay *Copper Action Plan* Baseline Actions*

Action	Description
B-1	Vehicle washing consistency in level of implementation
B-2	Continue to track copper sulfate use by water suppliers (includes State & Federal water project)
B-3	Complete Industrial-2: investigations (based on MCMP), identify and implement reasonable controls in conjunction with industry (older printed circuit board manufacturers with copper plating) to reduce elevated levels in runoff from targeted industry including development/implementation of education and outreach plan Clarify linkage with POTW Pretreatment program
B-4	1-Provide appropriate level of local support for agreed upon quantification studies to: 2-Investigate and/or track quantification studies for a wide range of existing copper control/pollution prevention measures and sources loadings (update copper pie charts contained in MCM based on data from B-6 and B-16) 3-Collect data and prepare annual reports on the following potential indicators Copper content in new auto brake pads • Total population in basin • Auto/truck vehicle traveled in basin • Copper sulfate (*e.g.*, algaecide, pesticide, industrials; chemicals) sales in basin (aggregate basis-scaled to basin level estimate) • Copper content in macoma tissue at Sand Point (Palo Alto • Reproductivity index for macoma at Sand Point • Benthic community assemblages at Sand Point 4-Prepare issue paper on feasibility of potential field investigation to monitor long-term trends between copper from brake pads and concentration in water
B-5	Provide appropriate level of local support for agreed upon BPP activities consistent with MCM 1-Review/assess/provide input on BMC/BPP brake pad wear debris research & brake pad content data 2-Ensure that other local state and Federal players are involved appropriately on brake pads issue as it is a widespread urban concern 3-Assist in making research data that are in the public domain accessible
B-6	Review appropriateness of transportation control measures, prioritize reasonable measures and identify potential efforts for further development as part of Phase I and implementation as part of Phase II
B-7	Establish transportation/impervious surface “forum” • Consider results of VMT and imperviousness load estimates and control effectiveness evaluation; identify potential control efforts for further development as part of Phase I and implementation as part of Phase II
B-8	Continue to implement watershed classification and assessment efforts of SCBWMI and improve institutional arrangements for watershed protection (review Vol. II Chapter 5/CCMP/CONCUR findings for relevance and possible gaps as part of C-31)

*Transcribed directly from source.

Table 6. Lower South Bay *Copper Action Plan* Baseline Actions (continued)

Action	Description
B-9	Continue current efforts and track corrosion control opportunities: • Continue educational outreach, within the City of Palo Alto, to plumbers and designers to reduce corrosion of copper pipes via better design and installation • Track developments in (1) alternatives to copper piping (b) corrosion inhibitors, and (c) other methods of reducing copper corrosion
B-10	Utilize results of SEIDP indicator #5 (Sediment Characteristics and Contamination) to investigate development of an environmental indicator and investigate the linkage with SFEI sources and loading work effort
B-11	Consider need for Continuous Improvement of street sweeping controls and storm water system operation & maintenance controls (key emphasis is to develop SOP for disposal of collected materials)
B-12	Maintain existing education and outreach program for pools and spas
B-13	Track POTW Pretreatment Program efforts and POTW loadings
B-14	Track and encourage water recycling efforts
B-15	Utilize results of SEIDP to evaluate effective ness of related SCVURPPP Performance Standards and identify cost-effective modifications
B-16	Establish Information Clearinghouse (Track & disseminate new scientific research on copper toxicity, loadings, fate and transport, and impairment of aquatic ecosystems for use in CAP update; provide stakeholder resource)
B-17	Track and encourage investigation of several important topics that influence uncertainty with Lower South Bay Impairment Decision • Phytoplankton toxicity and movement (IAR Section 5.3.1) • Sediment cycling • Loading uncertainty. Encourage incorporation of appropriate bioassessment tools into ongoing monitoring programs to track presence of copper-sensitive taxa in LSB Prepare issue paper on feasibility and cost of addressing phytoplankton toxicity questions
B-18	Track and encourage investigation of important factors that influence copper and fate (potential reduction in uncertainty is moderate to high) • Investigate flushing time estimates for different wet weather conditions • Investigate location of northern boundary condition • Determine Cu-L1 and L2 complex concentrations • Investigate algal uptake/toxicity with competing metals
B-19	Continue to promote industrial water use and reuse efficiency. These programs may include workshops, outreach, incentives, or audits.
B-20	Revise copper conceptual model report findings and produce status report (revise conceptual model uncertainty table, Appendix based on available information)
B-21	1-SCVURPPP & Co-permittees evaluate feasibility of discouraging architectural use of copper & explore feasibility of related policy 2-Promote Green Building principles and identify measures to investigate as part of Phase I

Source: *Copper Action Plan* Table 4-1 (Tetra Tech *et al.*, 2000).

The *Copper Action Plan* included a wide variety of measures, such as studies relevant to one or more copper sources, tracking activities of other entities that were addressing copper sources, general measures that relate to many copper sources, and implementation of control programs for specific copper sources. For purposes of this report, those measures involving investigation or implementation of control measures for specific copper sources to urban runoff are of interest. These items are listed in Table 7. The lower South Bay experience with these actions is reflected in the control measures discussions in Section 3 of this report (SCVURPPP, 2004).

Table 7. *Copper Action Plan* Investigation and Implementation Actions and Copper Sources Addressed

Action	Description	Copper Source
B-3	Complete Industrial-2 investigations (based on MCMP), identify and implement reasonable controls in conjunction with industry (older printed circuit board manufacturers with copper plating) to reduce elevated levels in runoff from targeted industry including development/implementation of education and outreach plan	Industrial copper use
B-5	Provide appropriate level of local support for agreed upon BPP activities consistent with MCM: 1-Review/assess/provide input on BMC/BPP brake pad wear debris research & brake pad content data 2-Ensure that other local state and Federal players are involved appropriately on brake pads issue as it is a widespread urban concern 3-Assist in making research data that are in the public domain accessible	Brake pads
B-6	Review appropriateness of transportation control measures, prioritize reasonable measures and identify potential efforts for further development as part of Phase I and implementation as part of Phase II	Brake pads and other vehicle sources
B-12	Maintain existing education and outreach program for pools and spas	Copper algaecides
B-21	1-SCVURPPP & Co-permittees evaluate feasibility of discouraging architectural use of copper & explore feasibility of related policy 2-Promote Green Building principles and identify measures to investigate as part of Phase I	Architectural copper

Source: *Copper Action Plan* Table 4-1 (Tetra Tech *et al.*, 2000).

3.0 REVIEW OF COPPER SOURCES AND CONTROL MEASURES

3.1 Copper Sources Selected for Evaluation

On the basis of the *Metals Control Measure Plan*, other urban runoff copper source identification studies described in Section 2 and a review of recent literature, nine categories of copper sources were found to have the potential to make a significant contribution to copper levels in San Francisco Bay Area in urban runoff and in releases from shoreline activities. Table 8 lists these copper sources. Each copper source is considered in the subsection listed in Table 8.

Table 8. Potentially Significant San Francisco Bay Area Urban Runoff and Shoreline Activity Copper Sources

Copper Source	Section
Marine antifouling coatings	3.2
Vehicle brake pads	3.3
Architectural copper	3.4
Copper pesticides (including shoreline algaecides)	3.5
Industrial copper use	3.6
Copper air emissions	3.7
Soil erosion	3.8
Copper in domestic water discharged to storm drains	3.9
Vehicle fluid leaks and dumping	3.10

Source: TDC Environmental.

3.2 Marine Antifouling Coatings

Paints applied to boats and ships to control unwanted "fouling" growth[1] on their hulls often contain copper-based biocides. Historically, the biocide tributyltin was commonly used in marine coatings. Its use on recreational boats was phased out in the late 1980s, when U.S. EPA restricted use of tributyltin-based antifoulants to ships longer than 25 meters. Copper-based biocides—long used on recreational boats—became the primary antifouling coating option for recreational boats.

Because of the lack of marinas in the lower South San Francisco Bay,[2] marine antifouling paint was not evaluated as a copper source in the *Metals Control Measure Plan*. In the Bay north of the Dumbarton Bridge, there are major ports, industrial piers, and dozens of marinas. Thousands of boats are berthed in the Bay; recreational boaters put thousands of additional boats into the Bay for short-term use. Larger vessels include about 2,000 shipping vessels that dock in Bay ports each year (BCDC and MTC, 2003), hundreds of commercial ships involved in trade and tourism, and hundreds of government-owned vessels to manage aquatic safety and resources. Boats and ships coated with copper-containing biocides may release copper directly into the Bay during storage, operation, and in-water maintenance. On-shore maintenance activities have the potential to release copper into urban runoff.

In the process of developing a Total Maximum Daily Load (TMDL) for the Shelter Island Yacht Basin, the San Diego Regional Water Quality Control Board (San Diego RWQCB)

[1] Growth of seaweed, barnacles and other organisms. The presence of such growth on the hull reduces boat speeds and increases motor boat fuel consumption.
[2] The one small marina in Alviso indefinitely closed on October 22, 2003 due to encroachment of wetland vegetation (Santa Clara County Parks, 2004).

has explored the potential importance of copper-based antifouling paint as a source of copper in California surface waters. In a draft TMDL report, the San Diego RWQCB estimated that 98% of the approximately 2,000 pounds of copper released into the Yacht Basin each year comes from marine antifouling paints on the 2,400 boats berthed in the marina (Dobalian and Arias, 2003). Of the approximately 1.8 pounds of copper estimated released per boat per year, about 95% is believed to leach from the paint while boats are moored at the dock; the remaining 5% is believed to be released during monthly underwater hull cleaning activities.

The data that forms the basis of these estimates may not directly apply to San Francisco Bay. Water body specific factors (such as temperature, pH, salinity, and fouling rates) determine both release rates of biocides in antifouling coatings and coating maintenance and replacement requirements. The draft Shelter Island Yacht Basin TMDL report considered only dissolved copper releases and dissolved copper levels (Dobalian and Arias, 2003); it did not consider copper releases from marina sediments, which are known to contain copper released in particulate form from marine antifouling paint.

San Francisco Estuary Project's (SFEP's) Boater Education Program has worked with boaters and marinas since the early 1990s to develop and implement an education and outreach program to protect Bay water quality. The program has focused on marine waste management, encouraging boaters to use pump out and dump stations rather than discharging directly into San Francisco Bay and the Delta. SFEP is currently completing a comprehensive survey of Bay Area marinas that will provide data about boat sizes and marina occupancy levels (Patton and McDowell, 2004).

Pete's Harbor, Redwood City

The San Francisco Bay Conservation and Development Commission (BCDC) completed a pilot San Francisco Bay marina water quality study to explore the water quality impacts of marinas. To guide the monitoring study, BCDC established a multi-stakeholder task force and a technical advisory committee, each comprised of federal, state, and local agencies; environmental groups; and marina and boating organizations. The study, which includes both a literature review and sediment monitoring in four Bay Area marinas,[3] was published in August 2004 (Pap, 2004b). BCDC intends to work with the stakeholder task force to develop management strategies for any water quality problems identified by the pilot study (Pap, 2004a).

3.2.1 Background

Marine antifouling coatings rely on slow release of a biocide impregnated in the coating to prevent fouling growth on the hull. Two formulation types are common:

- Ordinary "hard" copper-containing antifouling paints must be cleaned often enough to remove early stages of fouling growth before it becomes established on the boat's

[3] Copper levels were measured in sediment samples, but not in water column samples.

hull. Cleaning frequencies and methods vary by boat owner and location. In Shelter Island Yacht Basin, boat hulls are typically cleaned by a diver about once a month.

- An alternative formulation, known as "ablative" or "soft" paint, wears away as it ages. This eliminates the need for cleaning. In San Diego, ablative paint is less common than hard paint, apparently because few ablative paint formulations meet applicable air pollutant emissions requirements (Johnson and Miller, 2002).

Marine antifouling paints are technically pesticides because they contain biocides. As such, antifouling paints are subject to the authorities of the California Department of Pesticide Regulation (DPR). DPR maintains public databases containing detailed information about pesticide formulations, sales, and use (DPR, 2004a; DPR, 2003a; DPR, 2003b). The discussion below is based on these data.

3.2.1.1 Coating Formulations

DPR product registration data show that the following copper-based biocides are used in marine antifouling coatings:[4]

- *Cuprous oxide* (copper (I) oxide)—The most popular marine antifouling paint biocide, cuprous oxide has been formulated by 11 manufacturers into 157 marine antifouling coating products that are registered for sale in California. Cuprous oxide concentrations in marine antifouling paints range from 26 to 76%; most paints are in the 40-70% range. Since cuprous oxide is 89% copper by weight, typical cuprous oxide marine antifouling paints are 36 to 62% copper by weight.
- *Cuprous thiocyanate* (copper thiocyanate)—This unusual marine biocide is formulated into 12 marine antifouling paints from one manufacturer. Cuprous thiocyanate is 52% copper by weight At concentrations of 9-23% by weight, the copper content of these paints is about 5 to 12%.
- *Copper hydroxide*—Two cuprous oxide-containing products made by one manufacturer also contain copper hydroxide. Both products are 8% copper hydroxide by weight. (Since copper hydroxide is 65% copper, this translates into about 5% copper from copper hydroxide by weight.) Since this formulation is unusual and the copper contribution in these paints is small relative to the copper in the same paints from cuprous oxide, its contribution is assumed to be negligible.

3.2.1.2 Sales

DPR compiles statewide pesticide sales data based on proceeds of DPR's funding source, the "mill tax." County-specific sales data are not available. Public data are only available for pesticides for which more than 3 companies ("registrants") had registered products during the calendar year for which sales are reported. In 2002 (the most recent year for which data are available), 1,146,625 pounds of cuprous oxide products were sold in California (DPR, 2003a). Because there is only one manufacturer of cuprous thiocyanate-containing products, it sales volume is not public.

3.2.1.3 Reported Use

Certain pesticide uses (primarily agricultural and urban applications by licensed pest control operators) must be reported to DPR. DPR compiles these reports by October of the year following application into reports organized by pesticide and by application site

[4] Two copper naphthenate-containing wood preservatives (neither of which are labeled as antifouling paints) are also allowed by the state to be used for marine antifouling applications. While it is possible that these products may occasionally be used for boat antifouling coatings, the high solubility of copper naphthenate makes this us e impractical.

(DPR, 2003b). Unfortunately, because marine antifouling coatings are paints, applying them to boats is not typically considered to be a pesticide application. For this reason, most marine antifouling paint use is not reported to the state.[5] In 2002 (the most recent year for which data are available), DPR records show that 15,184 pounds of biocides were reported applied to boats and piers—almost all of this (15,032 pounds) was copper oxide. Two other copper-containing biocides were also reported: 25 pounds of copper bronze powder (a marine antifouling paint that is no longer registered) and 52 pounds of cuprous thiocyanate.[6]

The product registration and use reporting data summarized above suggest that the cuprous thiocyanate products are not likely to comprise a significant fraction of the copper used in marine antifouling paints. For this reason—and because sales data are not available—it is not considered further in this analysis.

3.2.2 Copper Loads

Copper releases from marine antifouling coatings to surface water relate to the amount of copper applied to boats, the number of boats, the storage locations of those boats, boat use frequency, and maintenance practices.

3.2.2.1 Copper Use in Marine Antifouling Coatings

Almost all copper-containing marine antifouling coatings use cuprous oxide as the biocide—and almost all cuprous oxide products are marine antifouling paints. Copper use in marine antifouling paint can be estimating by estimating cuprous oxide use. Because regional sales data are not available, this analysis starts with a look at statewide copper-based antifouling paint use.

Of the 195 cuprous oxide biocides registered in California, 157 registered specifically as marine antifouling paints. Most of the remaining products have a broader "wood coating" registration, but are sold commercially as marine antifouling paints. Only four of the 195 products—from 2 manufacturers—have uses other than coating wood, and these other uses are almost exclusively agricultural. Since all agricultural pesticide uses must be reported, it is reasonable to assume that almost all non-reported use of cuprous oxide represents marine antifouling paint applications. In 2002, 214,000 pounds of cuprous oxide was reported used for applications other than marine antifouling paint (remaining reported use was almost exclusively agricultural, as expected). Assuming that all cuprous oxide sold was also used in 2002, non-reported use of cuprous oxide was about 917,000 pounds. Since there are few non-reportable uses of cuprous oxide other than use in marine antifouling paint, this means that as much as 932,000 pounds of cuprous oxide (as much as 830,000 pounds of copper) could have been applied to California boats in 2002.

3.2.2.2 Boat Population

California Department of Motor Vehicles (DMV) records show that 963,379 marine vessels were registered in the state as of December 31, 2003 (DMV, 2004). California registration data do not include sailboats less than 8 feet in length or commercial vessels larger than 5 net tons or 30 feet. These must be registered ("documented") by the U.S. Coast Guard, which does not have a readily available compilation of registrations by water body. California registration data are apparently compiled on the basis of the

[5] It should be noted that this treatment of marine antifouling paint is not unusual—other types of paint commonly applied by homeowners and professional painters contain biocides (*e.g.*, bathroom paint, deck paint); use of these paints is similarly not reported.

[6] About 75 pounds of tributyltin was also applied. Tributyltin may legally be applied to ships longer than 25 meters.

owner's address, rather than the boat storage location. Registrations include boats used in California lakes and rivers as well as those used in bays and coastal waters.

Vessel registration data are broken down by county—in 2003, 176,483 vessels were registered in the nine Bay Area counties (Alameda, Contra Costa, Marin, Napa, San Francisco, San Mateo, Santa Clara, Solano, Sonoma) (DMV, 2004). Most of these are pleasure craft; the remainder (a few hundred vessels) are government and commercial boats. About 20,000 are personal water craft (jet skis) (DMV, 2003).[7] Other breakdowns of boat types (sail boat, motor boat), sizes, and storage location (*e.g.*, in-water or on-shore) are not provided in the registration data summary. These data probably include some vessels used only in the ocean or other water bodies that do not drain to San Francisco Bay.

3.2.2.3 Antifouling Paint Use

Boats may be stored in the water, or on shore. On-shore storage ("dry storage") is less expensive and requires substantially less maintenance than wet storage, so most boats are stored dry, often at one of the region's many storage yards. Dry-stored boats, which only enter the water for short periods, normally are not treated with antifouling paint, which is not necessary and may be damaged during travel on a boat trailer. Only wet-stored boats typically have antifouling coatings. These boats, perhaps 10 to 15% of registered boats, typically are larger and thus more difficult to transport and to move in and out of the water than smaller boats.

The San Francisco Bay Area has about 60 yacht harbors, with about 15,000 berths (Bay and Delta Yachtsman, 2004). Not all of these berths are occupied; colloquial information from industry professionals suggests that about 10,000 to 12,000 boats are berthed in San Francisco Bay.

3.2.2.4 Annual Copper Load

Not all of the copper applied to boats has the potential to be released to California surface waters. Copper releases from marine antifouling paint may occur several ways.

- *Passive leaching and in-water hull cleaning*. Because San Francisco Bay marinas probably have cooler temperatures than San Diego Bay marinas, available copper leaching data is likely to overestimate both passive and cleaning-related copper releases. Colloquial information from boaters and boat maintenance facilities suggests that underwater hull cleaning is not common in San Francisco Bay, and frequent only among special groups (*i.e.*, competitive sailors). In the absence of data relevant to San Francisco Bay, the release rate estimates from San Diego Bay can be used as a starting point to understand the potential magnitude of releases. Assuming that the copper release rates estimated for San Diego Bay (about 1.8 pounds per 12.2 meter boat per year) apply to boats in San Francisco Bay, and that boat sizes are similar (averaging 12.2 meters), the 10 to 12,000 boats wet stored in San Francisco Bay could release as much as 20,000 pounds of copper per year. It is not known what fraction of this copper remains in marinas and what fraction moves into the main part of the Bay.
- *Boat use*. Available studies of copper antifouling paint do not estimate copper releases while boats are in motion; however, data suggest that release rates are likely to be higher than releases from stationary boats because motion removes biofilms that reduce copper releases. In the absence of data, it is assumed that

[7] In 2002, 21,416 of the registered vessels in the 9 Bay Area counties were personal watercraft; 2003 data are not available.

releases from watercraft in motion are the same as in-dock passive leaching rates and thus included in the above estimate. Because dry-stored boats normally are not treated with antifouling paint, their use is assumed not to release copper.

- *On-shore maintenance*. Boat maintenance—such as on-shore hull cleaning and painting—has the potential to release copper to the environment, if the maintenance discharges are not controlled. Discharges from boat maintenance facilities in the Bay Area are regulated by stormwater management agencies and wastewater treatment plants. While some unregulated maintenance activities may occur at marinas, for purposes of this report, discharges are assumed to be negligible because they should be managed with best management practices and/or directed to wastewater treatment plants.

3.2.3 Control Measures

Currently there are no specific control measures in place to limit copper releases from marine antifouling paint in the San Francisco Bay Area. In response to concerns raised in San Diego, DPR and the State Water Resources Control Board are working together to explore the relationship between marine antifouling paints and copper levels in surface waters. To facilitate exploration of this issue, the Interagency Coordinating Committee (IACC), an existing working group composed of 28 State agencies involved in implementing California's Nonpoint Source Pollution Control Program, has created the Copper Antifouling Paint Sub-Workgroup of its Marina and Recreational Boating Workgroup. The purpose of the subgroup is to assess the degree and geographical distribution of copper pollution caused by copper antifouling paints in California's aquatic environments. The subgroup, which held its first meeting in March, has not yet established a workplan or schedule. One of the goals of the committee's work is to facilitate the evaluation of control measures by DPR and Regional Water Quality Control Boards.

Alternative marine antifouling coatings. Other marine antifouling coatings exist. In recent years, coatings designed to prevent adhesion of fouling growth to boat hulls have entered the market. The University of California has evaluated these epoxy and silicone coatings (Carson *et al.*, 2002) and has published an education piece for boaters about non-toxic antifouling strategies for boats (Johnson and Miller, 2002). To date, non-toxic alternatives have not been widely accepted in the boating industry, due to concerns about practicality and cost. If adopted, these alternatives would eliminate copper loads from marine antifouling paint.

Hull cleaning best management practices. Although modifying underwater hull cleaning practices to minimize copper release is possible, data from San Diego suggest that even with relatively frequently underwater cleanings, modified procedures are likely have little impact on copper loads (Schiff *et al.*, 2003; Carson *et al.*, 2002).

Prohibiting use of copper antifouling coatings. To date, no California agency has prohibited use of copper marine antifouling coatings. A San Diego RWQCB proposal that would effectively phase out their use in Shelter Island Yacht Harbor has met with stiff resistance (San Diego RWQCB, 2003). DPR has the authority to restrict their use, but has determined that further investigation of the need for restrictions through the IACC Copper Antifouling Paint Sub-Workgroup should be completed prior to consideration of possible restrictions (which would need to be based on data identifying the contribution of copper marine antifouling paints to surface water quality impairment).

3.2.4 Uncertainty

Due to the lack of San Francisco Bay-specific information (such as the specific number and types of marine craft moored in the Bay, which marine antifouling paints are most common, copper release rates in Bay water, hull cleaning frequencies, and recoating frequencies) this estimate has moderate-high uncertainty. Sources of uncertainty in the current estimate include (but are not limited to):

- *Marine craft information*. Information about the number and sizes of boats, commercial ships, and government vessels wet-stored in San Francisco Bay is needed. Data needs include boat and ship numbers, typical sizes, cleaning frequency, common antifouling paint types, length of time in Bay waters, and recoating frequency.
- *Marina information*. Most copper releases from antifouling paints probably occur into water and sediments in marinas. Both the Regional Water Quality Control Board and BCDC have marina sediment copper data. While the BCDC data shows copper enrichment, the Water Board data do not (it is not clear whether this data represents the active layer) (Pap, 2004b; RWQCB, 2004b). The extent to which this copper is transferred to the water column and sediments in the Bay is unknown.
- *No total copper measurements*. Studies prepared for the Shelter Island Yacht Harbor TMDL evaluated release of dissolved copper. Total copper releases were not measured. These studies note that paint particles are released upon hull cleaning. These paint particles, which probably contain copper (since such a high fraction of copper-based antifouling paint is copper), are assumed to deposit into marina sediments and become stabilized in a manner that prevents future contribution to dissolved copper levels. San Francisco Bay research has demonstrated that fluxes from copper bound in Bay sediments contribute to dissolved copper levels in the water column (URS and Tetra Tech, 1998).
- *Local environmental different than San Diego Bay*. The release rates of biocides in antifouling coatings are influenced by temperature, pH, salinity, and fouling rates; these factors may be water body specific.
- *Boat usage increases copper release rates*. The above copper release measurements were necessarily made in static conditions. Increased copper release rates have been measured from coatings after periods of motion (Valkirs *et al.*, 2003). The increased copper release was attributed to the motion-induced loss of the biofilm that forms on antifouling paints (Valkirs *et al.*, 2003).
- *Paint types unknown*. Ablative paints may have somewhat higher copper release rates than hard paints, but received little attention in the San Diego studies because colloquial information suggested that they are little used due to region-specific air pollutant compliance requirements.
- *Other biocides*. Contribution of biocides other than cuprous oxide are omitted (*e.g.*, cuprous thiocyanate).
- *Applications to materials other than boats*. No available data suggests that copper-based antifouling paint is commonly applied to marine structures other than boats and ships; however, most marine antifouling paints are registered for use on other structures.

3.2.5 Next Steps

- *Load Estimate*. Given the potential magnitude of copper releases from marine antifouling paint, a region-specific investigation of the copper load and related issues is a priority. An estimate would most efficiently be prepared in coordination with the two entities currently working with Bay Area marinas (SFEP and BCDC) and with the IACC Copper Antifouling Paint Sub-Workgroup.
- *Control Measures*. The IACC Copper Antifouling Paint Sub-Workgroup plans to facilitate evaluation of control measures, assuming its investigations identify the need to reduce copper releases from marine antifouling paint. Among the possible control measures that could arise from the subgroup are potentially costly measures like education programs and cost-effective measures like state agency restrictions on copper antifouling paint use.[8] Given the lack of acceptance of non-toxic alternatives to copper antifouling paint, a non-toxic antifouling coatings pilot project would be an appropriate precursor to future control programs.

3.3 Vehicle Brake Pads

San Francisco Bay Area drivers use their brakes millions of times a day, each time releasing small amounts of brake wear debris to the environment. In 1993, the Santa Clara Valley Nonpoint Source Pollution Control Program retained Woodward-Clyde to investigate the potential that vehicle brake wear debris contained water pollutants. The resulting report (Woodward-Clyde, 1994a) identified vehicle brake pads as a potentially significant source of copper in urban runoff, sparking Santa Clara Valley water quality agencies' interest in vehicle brake pads, and eventually leading to the formation of a partnership with the brake pad industry and other interested stakeholders to explore the issue.

Behind the wheel: vehicle disc brake pads and rotor

The *Metals Control Measure Plan* relied on the 1994 Woodward-Clyde report to estimate the copper load from vehicle brake pads. Substantial errors in these estimates, which were identified through the Brake Pad Partnership, are probably part of the reason that the copper load estimate in the *Metals Control Measure Plan* was about double the measured copper release from urban runoff into lower South San Francisco Bay.[9]

The Brake Pad Partnership is currently conducting investigations that will lead to a reliable estimate of the contribution of vehicle brake pads to copper levels in San Francisco Bay. The approach of the Brake Pad Partnership is to characterize brake wear debris and to conduct environmental transport and fate modeling to predict how copper released from brake pads enters the Bay and affects both the short-term and long-term concentrations of copper in the Bay. Results of these studies, which involve air, watershed, and Bay modeling, are anticipated in 2006.

[8] In considering such restrictions, DPR usually relies on other agencies to develop region-specific data identifying the contribution of the pesticide to surface water quality impairment.
[9] Estimated copper loads from urban runoff and other non-point sources were divided by a factor of 2 to match creek copper load estimates.

3.3.1 Background

Currently, the Bay Area Air Quality Management District (BAAQMD) estimates that vehicles drive an average of 167.2 million miles per day in the San Francisco Bay Area (BAAQMD, 2004). More than 5 million vehicles are registered to Bay Area residents and businesses (MTC, 2004a). All of these vehicles rely on the friction between their brake pads ("brake linings") and a rotor or drum to stop.

While drum brakes are still common, most new vehicles have disc brakes that are open to the environment. With a disc brake, each vehicle stop wears off a tiny amount of the brake pad material ("friction material"), which may be deposited on the road, on the vehicle, or elsewhere in the urban area.

Vehicle brake pads are manufactured by automobile parts companies that supply vehicle manufacturers—not by vehicle manufacturers themselves. Brake pad manufacturers use a wide variety of ingredients—including copper—in formulating brake pads. Manufacturers consider formulations, customer identity, and pad sales data to be trade secrets. Since brake pad composition is not regulated by any government agency, there is no independent central data source for information about vehicle brake pads.

3.3.2 Copper Loads

Estimating copper releases from vehicle brake pads into urban runoff involves two steps: estimating copper releases in the watershed, and then estimating the fraction of copper released that is washed off in runoff. The Brake Pad Partnership is currently exploring both of these questions. The estimate in this section is intended to serve as a placeholder until such time as the Brake Pad Partnership's cooperative investigations are complete.

Disc brake pads

The discussion in this section is based primarily on preliminary information obtained from the Brake Pad Partnership.[10] The estimate of copper releases to Bay Area watersheds involves use of the best available data and assumptions that the Brake Pad Partnership believes are as accurate as currently possible given the available data. Because the Brake Pad Partnership has not yet addressed the potential for wash-off of copper in vehicle brake wear debris, the estimate of the fraction of copper that is washed off in urban runoff does not involve input from the Brake Pad Partnership; it is based on preliminary results of U.S. EPA modeling of copper runoff in Castro Valley.

3.3.2.1 Copper Release to Bay Area Watersheds

The annual copper release from vehicle brake pads can be represented by the following equation:

$$\text{Cu Release} = N_{vehicles} \times \%_{wear} \times Cu_{vehicle}$$

Where:

Cu Release—Annual quantity of copper released (Lb Cu/yr)
$\mathbf{N_{vehicles}}$—Number of vehicles
$\mathbf{\%_{wear}}$—Percent of brake pad (friction material) worn off each year
$\mathbf{Cu_{vehicle}}$—Average brake pad copper content per vehicle (Lb Cu/vehicle)

[10] Please note that this discussion represents the analysis of the report preparer; it does not represent the views of the Brake Pad Partnership.

Ideally, this equation would be used to calculate the total annual copper contribution from vehicles driven in the San Francisco Bay Area. Unfortunately, since the copper content of vehicle brake pads is considered proprietary by manufacturers, the data to perform vehicle-specific calculations are not available. Limited aggregate data are available; these can be used with the above equation to generate a preliminary aggregate estimate of copper releases, as described below.

Copper content per vehicle. The best available data on brake pad copper content is from the Brake Pad Partnership. As part of the Brake Pad Partnership, U.S. brake pad manufacturers have developed a procedure for reporting on the amount of copper used in brake pads on new vehicles each year. Reporting began in 1998; data are currently available through vehicle model year 2002 (see Table 9) (Brake Pad Partnership, 2004). The annual report provides the average quantity of copper per vehicle for vehicles in the reported model year. Although these data are not intended for use in copper load calculations, they are the most comprehensive and reliable data available regarding the copper content of automotive brake pads.

Table 9. Copper Use in Brake Pads on the 20 Best Selling Domestic Light Duty Vehicles, Model Years 1998-2002

Model Year	1998	1999	2000	2001	2002
Copper per vehicle (kg)	0.0402	0.0517	0.0564	0.0561	0.0766
Copper per vehicle (lb)	0.0886	0.114	0.124	0.124	0.169

Source: Brake Pad Partnership, 2004

These data are for "original equipment" brake pads used in cars and light trucks. According to brake pad industry representatives these vehicles are most likely to have copper-containing brake pads. The data do not include "aftermarket" (replacement) brake pads or brake pads used on heavy-duty trucks, rail cars, off-road vehicles, or motorcycles.[11] Brake manufacturers indicate that the copper content of aftermarket brake pads is small, but no public data are available to confirm that statement. Colloquial information from brake manufacturers also suggests that copper use in trucks and off-road vehicle brake pads is limited and that motorcycle brake pads, while often containing copper, are so physically small that they comprise only a small fraction of on-road brake pad material.

The available data provide the basis for an estimate of the amount of copper released from "original equipment" brake pads used in cars and light trucks. At this time, it is not possible to estimate the contributions from other types of brake pads.

Annual brake pad wear. Generally, automobile owners replace disc brake pads before the pad material has worn off (this is done as preventative maintenance and avoids damage to the rotor). Normally, all pads are replaced at once, leaving some pad material permanently unused. In early Brake Pad Partnership discussions of wear debris calculation methods, manufacturers provided colloquial information that on average, about 60% of brake pad material is worn off prior to replacement. This assumption has not been verified.

Since brake pads are not replaced annually, the brake pad material wears off over the course of several years. According to brake pad manufacturers, original equipment brake pads are replaced, on average, after about 3 years of service. This estimate has not been verified, but it is consistent with typical automobile maintenance schedules.

[11] Manufacturers of these other friction material types are not currently participating in the Brake Pad Partnership.

The actual lifetime of individual pads is highly variable, and pad lifetime on individual vehicles may differ significantly from the estimated three-year average.

Due to the variability of pad lifetimes, it would be relatively complicated to develop the data needed to estimate the portion of brake pad wear that occurs from each vehicle with original equipment pads each year. However, since about the same fraction of material is worn off of all pads prior to replacement—and a similar mix of new vehicles enters the San Francisco Bay region every year, the overall wear rate for original equipment brake pads in the San Francisco Bay Area is relatively constant. Assuming that vehicle sales and the Bay Area fleet mix are relatively constant, the calculation can be simplified with the assumption that the amount of original equipment brake pad wear each year is equal to 60% of the amount of brake pad material sold on new vehicles each year.

Number of vehicles in use. To account for variation in vehicle sales, three years worth of data were averaged (this is consistent with the assumed typical 3-year lifetime of original equipment brake pads). In the San Francisco Bay Area, there are 5,432,514 registered cars and trucks (MTC, 2004a). While annual vehicle sales data for the San Francisco Bay Area are not readily available,[12] California DMV data show that 33.63% of non-commercial registered vehicles are less than 3 years old (DMV, 2002), reflecting a recent average of about 609,000 vehicles sold each year.

Copper release estimate. To account for variation in brake pad copper content, original equipment brake pad copper content data for the most recent three model years were averaged (0.139 lb/vehicle) (this is consistent with the assumed typical 3-year lifetime of original equipment brake pads). Putting this value and the above estimates into the equation yields an estimate of about 51,000 pounds of copper released to San Francisco Bay Area watersheds annually from wear of original equipment brake pads on passenger cars and light duty trucks. This estimate does not include contributions from replacement brake pads nor brake pads used on heavy-duty trucks, rail cars, off-road vehicles, or motorcycles.

3.3.2.2 Copper Washoff into Urban Runoff

Available information suggests that brake pad wear debris is deposited not only on roads, but also is widely dispersed in urban areas. Brake pad wear debris is comprised of very small particles (less than 10 microns in diameter), making air emissions a significant release method and a likely important transport pathway for brake pad wear debris (BMC/PEC, 2001; Garg, 2000; Sanders, 2002). Information from the literature shows that elevated copper concentrations appear at soil surfaces within about 20 meters of roads (Heath *et al.*, 1999; Sutherland and Tolosa, 2001), suggesting that a significant amount of brake pad wear debris is deposited near roads. Since most vehicle use occurs on roads in urbanized portions of Bay Area watersheds, this analysis assumes that most deposition occurs in the urbanized portion of Bay Area watersheds.

Potential for wash-off. The City of Palo Alto and the Bay Area Stormwater Management Agencies Association (BASMAA) funded Clemson University to characterize brake wear debris from one brake pad provided by the Brake Manufacturers Council Product Environmental Committee (BMC/PEC). Clemson conducted copper leaching tests, using standard extraction test methods and some modified methods with environmentally relevant reagents to measure the ability of copper in brake pad wear debris to leach out in the environment. Test results show that a substantial fraction of copper in the tested brake wear debris can be mobilized in the environment

[12] These data may be purchased for a fee from automotive industry sources.

(Schlautman, 2002; Schlautman, 2003a; Schlautman, 2003b; Hur *et al.*, 2003; Hur *et al.*, in press). The copper solubility in the tested brake wear debris is probably due to the high surface area of brake wear debris[13] and the chemical form of the copper in the wear debris.

If these data from one brake pad are typical of all copper containing brake pads,[14] the results would mean that in the long term, most of the copper can probably be mobilized from brake wear debris that remains exposed to water flows. This analysis assumes that the behavior of copper in vehicle brake wear debris has wash-off behavior similar to other anthropogenic urban copper sources.

Preliminary wash-off estimate. No specific estimates of brake pad wear debris copper wash-off are currently available. A rough estimate of wash-off can be made from preliminary watershed modeling information in combination with simplifying assumptions. On behalf of the Brake Pad Partnership, U.S. EPA staff has set up a model of copper runoff from the Castro Valley watershed. This preliminary model has not yet been incorporated into the Brake Pad Partnership's investigations. In preliminary runs of this model based on currently available data (no data specific to vehicle brake pads), between 31 and 48% of anthropogenic copper annually deposited on impervious surfaces was estimated to be transported to San Francisco Bay in urban runoff (Carleton, 2004).[15]

In the modeled watershed (Castro Valley), the impervious surface area is about 50% of the total surface area. Assuming that all vehicle brake wear debris is deposited in urbanized portions of Bay Area watersheds and that Castro Valley's impervious surface fraction is typical for the urbanized portion of Bay Area watersheds, this suggest that 15 to 24% of copper in brake pad wear debris may be transported to San Francisco Bay in urban runoff.

3.3.2.3 Annual Copper Load

Combining the two above estimates (about 50,000 pounds per year of copper released from original equipment brake pads, of which 15 to 24% may be transported to the Bay in urban runoff) yields a copper load estimate of about 7,600 to 12,000 pounds per year (or with one significant figure, about 10,000 pounds per year). This estimate is highly uncertain (see below).

3.3.3 Control Measures

The Brake Pad Partnership has served as the primary control measure for copper in vehicle brake wear debris. Initiated by Santa Clara Valley Urban Runoff Pollution Prevention Program members in the mid-1990s, the Brake Pad Partnership is a cooperative effort of government regulators, brake pad manufacturers, stormwater management agencies, and environmentalists aimed at identifying and preventing impacts on surface water quality that may arise from the use of automotive brake pads. Together, the partners are investigating the issue of copper from vehicle brake pads in urban runoff. The Brake Pad Partnership anticipates completing its investigations in 2006. As part of their participation in the Partnership, brake pad manufacturers have committed to voluntarily introducing reduced copper products within five years if the

[13] Clemson's data show that brake wear debris has a much higher specific surface area (31 m^2/g) than the standard copper-containing minerals tested (< 1.5 m^2/g).
[14] In 2004, the Brake Pad Partnership plans to repeat the extractions on a representative sample of brake wear debris to answer this question.
[15] Because this modeling effort involved matching washoff estimates and creek monitoring data, it accounts for copper removal via control measures like street sweeping and runoff treatment systems.

Brake Pad Partnership determines that copper from brake pads is a significant cause of water quality impairment. While the Partnership's investigations proceed, brake pad manufacturers are conducting research to develop low copper or copper-free pad formulations that meet safety standards.

Other control measures involve collecting copper after it is released to the environment or reducing vehicle use. The major options are:

- *Street sweeping*—collects particles from streets and highways. Municipalities already sweep most Bay Area streets. Because street sweepers are relatively inefficient in collecting fine particles (Woodward-Clyde Consultants, 1994b; Brown and Caldwell, 1997), and wear debris probably deposits on many urban impervious surfaces not subject to street sweeping, street sweeping is not a very effective control measure for copper in vehicle brake wear debris. Available data are insufficient to determine if increasing street sweeping frequencies or adding more rural streets to the sweeping program would increase copper removal significantly (Claytor, undated).

- *Treating urban runoff*—Runoff treatment devices vary in their ability to remove copper from urban runoff, with typical efficiencies in the 40-60% removal range (Winer, 2000). Removal efficiencies for dissolved copper are typically lower than those for total copper (Winer, 2000). Many devices are designed to remove trash and sediments from stormwater in watersheds; these devices are not designed to remove very fine particles like brake wear debris. Such devices are not very effective at copper removal (Woodward Clyde, 1996).[16] Vegetation-based treatment methods—like grassy swales—and infiltration methods generally have the highest removal efficiency for copper (Winer, 2000).

  Urban runoff agency permits will soon require treatment of runoff from much of new urban development in the Bay Area. This requirement will require substantial financial investment for installation and maintenance of the treatment facilities. Treating runoff from existing development, while theoretically possible, would involve an enormous infrastructure investment (much greater than for new development, where installation can be paid for by developers)—plus significant annual maintenance costs. Treatment facility costs vary greatly—a BASMAA survey listed costs from $160 to $122,000 per acre (not including land costs) (Minton, 2003). While vegetation based systems are generally at the lower end of the cost range (hundreds to thousands of dollars per acre), Bay Area land costs—assuming land is even available—would likely make retrofitting such measures on a widespread basis cost-prohibitive.

- *Reducing vehicle miles traveled*. Reducing vehicle use would reduce release of vehicle brake wear debris. In response to Federal and California Clean Air Act requirements, the California Air Resources Board, the Bay Area Air Quality Management District, and Bay Area municipal congestion management and transportation agencies have worked for the last several decades to reduce vehicle use. Due to population increases and land use patterns, these efforts have been unsuccessful—the number of vehicle miles traveled in the Bay Area increases each year and is anticipated to increase for the foreseeable future (MTC, 2004b).

[16] As it flows through watersheds, copper transfers to larger particles, generally after hours of contact time (Sansalone and Buchberger, 1997). In typical Bay Area urban watersheds, this transfer occurs in creeks, which have flows that are much too high for typical urban runoff treatment devices.

3.3.4 Uncertainty

Given the many assumptions and omissions in the estimation of the vehicle brake pad copper load, this estimate should be treated as highly uncertain. Most of the data gaps will be filled by the much more complete and reliable estimate anticipated from the Brake Pad Partnership.

Sources of uncertainty in the current estimate include (but are not limited to):

- *Most brake pads are not included in the estimate*. Because limited copper use data is available for replacement brake pads or brake pads used on heavy-duty trucks, off-road vehicles, rail cars, or motorcycles, the copper contribution from these pads was not estimated.
- *Estimates assume that the behavior of copper in vehicle brake wear debris has wash-off behavior similar to other anthropogenic urban copper sources*. This assumption is based on data from only one copper-containing brake pad. There are several different chemical forms of copper used in brake pad formulations.
- *Copper use data are not designed for mass load calculations*. The Brake Pad Partnership's copper use reporting program does not document total copper use; instead, it assumes that copper usage in disc brake pads for the top 20 models of domestically-manufactured light vehicles (accounting for approximately 40% of vehicle sales) serves as a valid indicator of the industry's overall copper use.
- *Vehicle fleet mixes vary*. Within a region or watershed, variations in fleet mix and vehicle use patterns also contribute to differences in copper content and amounts of wear debris released to the environment.

3.3.5 Next Steps

- *Load Estimate*. The Brake Pad Partnership is currently conducting investigations that will lead to a reliable estimate of the contribution of vehicle brake pads to copper levels in San Francisco Bay.
- *Control Measures*. Continue participation in the Brake Pad Partnership, which serves as the primary control measure for copper in vehicle brake wear debris.

3.4 Architectural Copper

Architects and building occupants enjoy the beauty and longevity of copper architectural features like roofs, gutters, and flashing. Nationally, architectural use of copper has increased in recent years (CDA, 2003b). Copper roofs and gutters cost far more than ordinary materials, limiting their use to a relatively small number of structures in the San Francisco Bay area.

Copper roof, Redwood Shores California

Perhaps due to the relative rarity of copper roofs, the *Metals Control Measure Plan* did not estimate copper releases from architectural copper features. Since the late 1990s, a series of papers in the literature have revealed relatively high concentrations of copper in copper roof and gutter runoff (Barron, 2001;

Wallinder and Leygraf, 1997; Zobrist *et al.*, 2000; Wallinder and Leygraf, 2001; Leuenberger-Minger *et al.*, 2002). In some studies, copper concentrations in roof runoff exceeded 1,000 µg/l (Barron, 2001). Concerned about these findings and an upward trend in the use of copper roofs and gutters in new construction, Palo Alto commissioned a study to estimate copper releases from copper architectural features (Barron, 2001). The Palo Alto study estimated that architectural copper runoff comprises about 20% of the copper load in Palo Alto creeks.

3.4.1 Background

While all copper pieces start with a shiny metal appearance, if left untreated, the copper will develop a patina, oxidizing to shades of green and brown as it ages. Oxidation forms compounds that are soluble in water. Factory or field treatments immediately give the copper a desired patina, by oxidizing the surface to create a complete coating of oxides. Occasionally, architectural materials may be clear coated to maintain a desired hue (typically a penny-colored brown).

Some composite roofing shingles are treated with copper granules to retard moss and mildew growth. Like the copper in pure copper roofs, the copper granules will age, become covered with an oxide patina, and be subject to runoff when it rains.

3.4.2 Copper Loads

3.4.2.1 Copper Release to Bay Area Watersheds

The amount of copper washed off architectural copper features is proportional to the area of those features and the copper release rate. Both of these can be estimated using information compiled by Palo Alto (Barron, 2001). The major types of architectural copper features (roofs, gutters, and copper-treated composite shingles) are included in this estimate; the contribution from other materials (flashing, ornamentation) is assumed to be relatively small.

Copper roof section, prior to installation

Presence of copper architectural features. No quantitative data is available about the presence of architectural copper or the installation rate of new copper roofs and gutters (Barron, 2001). The Palo Alto estimate relied on colloquial information obtained from a survey of contractors, building departments and similar entities and a visual inspection of buildings in Palo Alto to create a very rough estimate that copper roofs are installed on 0.05% of residences, 0.3% of industrial commercial buildings, and 1.5% of other structures. The "other structures" category was region-specific,[17] to reflect the relatively high frequency of copper use in the institutional structures in that region (Barron, 2004). The Palo Alto study estimated that 0.03% of residential roofs use composite roofing shingles with copper biocides, and that these shingles had negligible use on structures in other land uses. Roof coverage was assumed to be 30% for residential land and 50% for other developed land.

[17] The region includes East Palo Alto, Los Altos, Los Altos Hills, Mountain View, Palo Alto, and Stanford.

Using these estimates, the copper roof area can be estimated as follows:

$$\text{Copper roof area}_{LU} = \text{Acres}_{LU} \times \text{Roof Coverage}_{LU} \times \text{Copper Roof Fraction}_{LU}$$

Using land use data from the Association of Bay Area Governments (ABAG, 2003) the copper roof area in the San Francisco Bay Area is estimated to be about 466 acres and the composite shingle with copper biocide roof area is estimated to be about 39 acres (see Table 10).

For copper gutters, the method was very similar (Barron, 2004)—except 0.06% of residential buildings were assumed to have copper gutters (to reflect the presence of copper gutters on some buildings without copper roofs). The surface area of building gutters was assumed to be about 3.25% of the roof surface area. Using these figures, the estimated copper gutter area in the San Francisco Bay area is 15.5 acres (2.5 acres residential; 13 acres commercial/industrial/institutional).

Table 10. Copper Roof Area Estimate

Land Use	**Land use area (Acres)**	**Total Roof Coverage**	**Copper Roof Fraction**	**Copper Roof Area (Acres)**	**Copper Biocide Roof Fraction**	**Copper Biocide Roof Area (Acres)**
Residential	428,660	30%	0.05%	64	0.03%	39
Commercial/Industrial/ Institutional	267,630	50%	0.3%	402	--	--

*Local streets and some highways are included within land use estimates (ABAG, 2003).
Source: TDC Environmental calculations based on data from ABAG, 2003 and Barron, 2001.

Copper release rates. Published literature and limited measurements conducted by Palo Alto provide the estimates of copper releases from copper architectural features listed in Table 11 (on the next page) (Barron, 2004). Note that the copper release rates are within the range of the release rate estimates provided by the Copper Development Association (see Table 5 on page 9).

3.4.2.2 Copper Washoff into Urban Runoff

Since the copper release rates for architectural copper are based on copper concentrations in runoff, no additional adjustment for wash-off fraction is necessary. Since discharge configurations vary—and often involve direct discharge to storm drains—this analysis assumes that the net copper load is essentially the same as the quantity of copper in runoff from architectural copper features. This approach does not account for losses of copper between the release point (*i.e.*, downspout) and surface waters. While there is a potential for significant reduction in copper levels in roof runoff if the runoff flows through vegetation or passes through a treatment device, the variation in discharge locations for copper roofs provides no rational basis for assuming a certain fraction removal of the copper.

3.4.2.3 Annual Copper Load

Multiplying the architectural copper roof area estimate by the estimated copper release rates gives the copper load estimates in Table 11 (on the next page), a total of about 4,500 pounds per year of copper releases.

Table 11. Architectural Copper Release Estimate

Architectural Material	Estimated Area (Acres)	Estimated Release Rate (g/m^2 material per year)	Estimated Copper Release (lb Cu/year)
Copper Roofs	466	1	4,200
Composite Roofs with Copper Biocide	39	0.17	59
Copper Gutters	15.5	2	280
Total			**4,500**

Source: TDC Environmental calculations based on data above.

3.4.3 Control Measures

Many control measures to reduce architectural copper releases are possible—measures could include public education to reduce copper use, coating copper to reduce releases, treating runoff to collect released copper, and restricting copper use. In the San Francisco Bay Area, a few municipalities have used education to limit use of copper architectural features; one municipality (Palo Alto) has prohibited most architectural copper use.

Public education. Education of architects, planners, and the public has the potential to reduce copper use in buildings. SCVURPPP has encouraged South Bay municipalities to incorporate avoiding copper architectural features into municipal green building programs. Ordinarily, green building programs do not address copper architectural features. The general effectiveness of such educational programs is unknown, although colloquial information suggests that education can limit copper use.

Treating copper or runoff. In theory, architectural copper features could be coated in a manner that would maintain the copper's appearance, but would prevent release of copper to the environment. In practice, the efficacy and maintenance requirements for such coatings have not been demonstrated. As described in Section 3.3.3, treatment of runoff for copper removal is also possible. Treatment systems have significant technical downsides—they require management and maintenance and have incomplete copper removal. Costs for treatment would include building owner costs for installation and maintenance, and municipal costs to ensure that treatment systems meet performance standards.

Collecting copper wastewater. Cleaning and treating copper architectural features (particularly patina treatments) involves corrosive solutions that may contain relatively high concentrations of copper. These solutions could be collected, tested to determine their waste classification, and managed according to accepted best management practices for wastewater from building surface cleaning activities (BASMAA, 2000).

Prohibiting architectural copper use. Local governments have the authority to regulate the use of building materials. Many attractive alternative roofing materials do not contain copper (Barron, 2001). In August 2002, the City of Palo Alto adopted an ordinance prohibiting the use of copper for new roofs. Prohibitions include copper metal roofing, asphalt shingles containing copper granules, and copper gutters. Copper flashing and ornaments are exempted. The ordinance, which became effective on January 1, 2003, includes provisions to protect historic buildings.

3.4.4 Uncertainty

The major source of uncertainty in this estimate is the uncertainty in the surface area of copper architectural features in the Bay Area. This, combined with the uncertainty in copper release rates, suggests a moderate-high uncertainty for this estimate. Sources of uncertainty in the current estimate include (but are not limited to):

- *Surface area*. Estimates of the area of copper architectural features are based on colloquial information and are highly uncertain. No method to improve the estimates has been identified, though field surveys or photographic analysis may be practical for small watersheds.
- *Release rates*. Copper release rate estimates relate to weather conditions, air quality, distance from salt water and other region-specific factors. This analysis assumes that the copper release rate selected on the basis of the literature is representative of San Francisco Bay Area release rates.
- *Patina treatments and cleaning solutions*. Load from runoff of field treatments to create a patina and cleaning solutions is not estimated. Since field treatments involve corrosive solutions, spent treatment solution and rinsate could have elevated copper levels. While construction stormwater regulations should prevent discharge of such solutions, improper discharges of such solutions could comprise a meaningful copper load.
- *Copper removal from runoff*. Some fraction of the copper released from architectural features may be removed from runoff if the discharge flows over landscaping or across other materials to which copper may bind. Depending on the drainage configuration, copper removal from runoff from some architectural copper features may be significant.

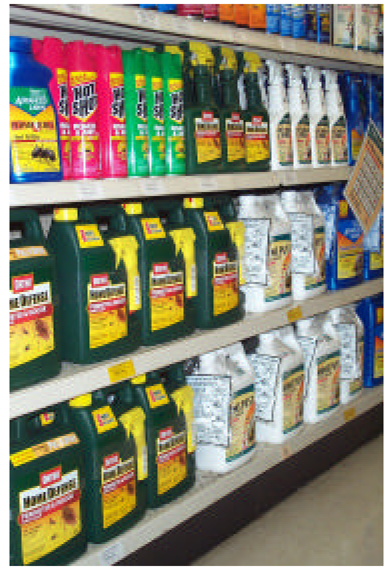
3.4.5 Next Steps

- *Load Estimate*. Although the load estimate is uncertain, the cost involved in preparing a more accurate load estimate—particularly the cost to inventory copper roofs in the entire region—is probably not justified. Community-specific load estimates may be necessary to support local decisions regarding restrictions on use of architectural copper features.
- *Control Measures*. Measures to control runoff from cleaning and treatments (*e.g.*, patina treatments) of copper architectural features should be considered. Questions remain regarding the practicality and efficacy of measures to prevent copper releases (*e.g.*, coatings) or to treat roof runoff. If such measures are practical and sufficiently reduce copper discharges, they offer a technically more complicated—but perhaps politically less difficult alternative to prohibiting architectural copper use (which is technically feasible). Architectural copper use limitations are feasible; these could be structured to allow installation with appropriate treatment measures, if such measures are found to be practical and effective.

3.5 Copper Pesticides

Since the inception of copper control programs in the San Francisco Bay area, municipalities have sought to reduce use of copper-based pesticides. Pesticide use may release copper to urban runoff, to Bay area shorelines, to Bay area surface waters, or to wastewater treatment plants.

In response to a request from the Regional Water Quality Control Board in the early 1990s, some water suppliers have limited their use of copper-based algaecides. Wastewater treatment plants worked with the state legislature and the Department of Pesticide Regulation (DPR) to secure a 1995 prohibition on the sale and use of copper-based root control products in the San Francisco Bay Area (Palo Alto, 1999). Many municipalities have conducted public outreach efforts to reduce copper algaecide use in swimming pools, spas, and fountains.



Retail pesticide display

Copper-based pesticides are among the most commonly used pesticides in surface water bodies. In response to a 2001 Federal court decision, the State Water Resources Control Board (SWRCB) initiated a program to regulate applications of pesticides to surface waters (SWRCB, 2004a). Concurrently, the SWRCB commissioned a study of the environmental effects of aquatic pesticide applications. The study, conducted by the San Francisco Estuary Institute (SFEI) found that dissolved copper from aquatic pesticide applications caused lethal and sublethal toxicity in juvenile trout for at least 24 hours after application, toxicity in *ceriodaphnia dubia* (water flea) for at least a week after application, and may relate to increased sediment copper concentrations (though results on sediment toxicity were inconclusive) (Siemering, 2004).

The presence of the permit requirements has increased incentives for applicators (who are primarily public agencies) to reduce use of aquatic pesticides. The SWRCB permit has planning, monitoring, and reporting requirements on the use of copper-based aquatic pesticides (SWRCB, 2004a), increasing the incentives for applicators to transition to alternative pesticides or to non-pesticide control methods for aquatic weeds and algae.

While the *Metals Control Measure Plan* included an estimate of copper releases from pesticides, the estimate was based only on use of copper sulfate-containing pesticides by professional pest control operators. Recognizing that use of any of the more than a dozen copper-containing pesticide active ingredients, for the last several years Palo Alto's annual *Copper Action Plan Report* has compiled information about all copper containing pesticides and their use in Santa Clara Valley (Palo Alto, 2003).

3.5.1 Background

Copper-containing pesticides are widely used to control fungi, mildew, algae, and roots. Common applications include controlling fungi on plants; controlling roots and other plant growth in sewers; controlling algae in swimming pools, ponds and lakes; controlling aquatic plant growth on boat hulls; serving as biocides in commercial products; and preventing rot and mildew on wood, roofing, and other outdoor surfaces.

As of February, 2004, there were 19 copper-containing pesticide active ingredients in products registered for sale in California. Primary uses are as algaecides, marine antifouling paint biocides, root killers, and wood preservatives, agricultural and garden fungicides. Table 12 (on the next page) summarizes the registered copper-containing pesticide active ingredients and their urban uses.

Table 12. Copper-Containing Pesticides Active Ingredients and their Urban Uses

Pesticide Active Ingredient Name	Number of products	Algaecide	Marine Paints	Root Killer	Wood Preservative	Garden Fungicide
Copper	49	X			X	X
Copper 8-quinolinoleate	8				X	
Copper Ammonia Complex	5					X
Copper Ammonium Carbonate	4				X	
Copper Carbonate	8	X			X	
Copper Ethanolamine Complexes, Mixed	11	X			X	
Copper Ethylenediamine Complex	1	X				
Copper Hydroxide	45		X			X
Copper Naphthenate	27				X	
Copper Oxide (Cuprous)	212		X			
Cupric Oxide	12				X	
Copper Oxychloride	13					X
Copper Oxychloride Sulfate	6					
Copper Resinate	3					
Copper Soap (Copper Octanoate)	4					X
Copper Sulfate (Basic)	25					X
Copper Sulfate (Pentahydrate)	61	X		X	X	X
Copper Thiocyanate	16		X			
Copper Triethanolamine Complex	8	X				

Source: DPR Product database (DPR, 2004a)

3.5.2 Copper Loads

Using DPR data, it is possible to develop a gross estimate of copper containing pesticide use in the San Francisco Bay Area. The estimate uses pesticide sales data, reported pesticide use data, and a calculation of unreported use as described below. To ensure consistent use of pesticide data, DPR provides its reports in units of pounds of pesticide “active ingredient” (A.I.). With a simple calculation based on the copper mass fraction of each copper-based pesticide, this can be converted to pounds of copper.

Pesticide Sales Data. DPR compiles statewide pesticide sales data based on proceeds of DPR’s funding source, the “mill tax.” County-specific sales data are not available. Public data are only available for pesticides for which more than three companies (“registrants”) had registered products during the calendar year for which sales are reported.

Reported Pesticide Use. Certain pesticide applications are required to be reported to the County Agricultural Commissioner, who, in turn, reports the data to DPR.[18] In general, the pesticide uses that require reporting are agricultural uses or urban applications done by licensed pest control operator. DPR compiles pesticide use reports annually into a document that identifies pesticide application locations by broad categories that are sufficiently defined to allow differentiation of urban uses from other uses, but not to evaluate the details of urban uses.

Unreported Pesticide Use. Assuming all pesticides sold are used within a particular year, unreported pesticide use is (approximately) equal to the difference between pesticide sales and reported pesticide use. The primary exceptions to the use reporting requirements are urban uses: home and garden use and most industrial and institutional uses. (Pesticides used in consumer products are also often unreported.) Additional analysis of the uses of particular active ingredients can improve this assumption somewhat, but it is a highly uncertain estimate.

Table 13 (on the next page) presents an estimate of the copper content in copper-containing pesticides used in the San Francisco Bay Area (see Appendix B for additional details). The estimate is based on an estimate of statewide urban use of copper-based pesticides, which is a sum of reported urban pesticide use and unreported pesticide use. Assuming that urban copper pesticide use per capita is the same in the San Francisco Bay Area as it is statewide, the statewide urban copper estimate was adjusted on the basis of population to create a Bay Area estimate.

The next step in the analysis is to evaluate how the copper-containing pesticides are used and the potential for each to be released to surface waters. To simplify the analysis, the seven pesticides with estimated Bay area use less than10 pounds are not considered further. The remaining pesticides are divided into the following groups (recognize that some pesticides have multiple uses and therefore fall into multiple groups):

- *Landscaping fungicides*—copper, copper ammonia complex, copper hydroxide, copper oxychloride, copper sulfate (basic);
- *Wood preservatives*—copper, copper carbonate, copper ethanolamine complexes (mixed), copper naphthenate, cupric oxide, copper sulfate (pentahydrate);
- *Algaecides*—copper, copper carbonate, copper ethanolamine complexes (mixed), copper ethylenediamine complex, copper sulfate (pentahydrate), copper triethanolamine complex (the copper content of potable water discharged to storm drains is discussed in Section 3.9);[19]

Marine antifouling paint (copper oxide [cuprous], copper thiocyanate, and negligible quantities of copper hydroxide)—primarily a shoreline copper source, not an urban runoff source—is discussed in Section 3.2. Root control products (copper sulfate) are assumed not to be used, in compliance with the state prohibition on their sale and use (Palo Alto, 1999).

[18] Pesticide uses for the production of any agricultural commodity, except livestock; for the treatment of post-harvest agricultural commodities; for landscape maintenance in parks, golf courses, and cemeteries; for roadside and railroad rights-of-way; for poultry and fish production; any application of a restricted material; any application of a pesticide designated by DPR has having the potential to pollute ground water when used outdoors in industrial and institutional settings; and any application by a licensed pest control operator must be reported the County Agricultural Commissioner, who, in turn, reports the data to DPR.
[19] The copper content of reservoir releases is not an urban stormwater copper discharge and thus is not included in this report.

Table 13. Bay Area Copper-Containing Pesticide Use Estimate, 2002

Pesticide	**2002 Statewide Sales (lb A.I.)**	**2002 Statewide Reported Use (lb A.I.)**	**Estimated Statewide Urban Use (lb A.I.)**	**Copper in Statewide Estimated Use (lb Cu/yr)**	**Estimated Bay Area Copper Use[a] (lb Cu/yr)**
Copper	326,000	45,857	286,805	286,805	56,501
Copper 8-quinolinoleate	--[b]	10	10	2	0
Copper Ammonia Complex	14,277	5,543	9,697	9,697	1,910
Copper Ammonium Carbonate	--	42	12	4	1
Copper Bronze Powder	--	25	0	0	0
Copper Carbonate	14,274	7,878	6,228	3,550	699
Copper Ethanolamine Complexes, Mixed	171,230	17,721	166,318	166,318	32,765
Copper Ethylenediamine Complex	--	2,557	1,456	1,456	287
Copper Hydroxide	3,940,156	2,592,460	1,355,936	881,358	173,628
Copper Naphthenate	380,620	84,476	380,605	38,061	7,498
Copper Oxide (Cupric)	--	127,523	126,210	100,968	19,891
Copper Oxide (Cuprous)	1,146,625	229,214	918,075	817,087	160,966
Copper Oxychloride	84,997	58,934	26,489	15,364	3,027
Copper Oxychloride Sulfate	--	174,700	0	0	0
Copper Resinate	--	18,612	35	3	1
Copper Soap (Copper Octanoate)	250	0.007	250	45	9
Copper Sulfate (Basic)	1,455,054	876,722	579,200	306,976	60,474
Copper Sulfate (Pentahydrate)	5,646,324	2,916,477	2,649,632	675,656	133,104
Copper Thiocyanate	--	61	9	5	1
Copper Triethanolamine Complex	256	2	256	256	50
TOTAL				**3,303,610**	**650,811**

[a]19.7% of statewide estimate, based on a California' population of 35,591,000 and a San Francisco Bay Area population of 6,994,500 as of January 1, 2003 (DOF, 2003).
[b]Data not made public by DPR because there are 3 or fewer registrants.
Source: TDC Environmental calculations with data from DPR (DPR, 2004a; DPR 2003a; DPR, 2003b).

3.5.2.1 <u>Landscaping</u>

<u>Copper Release to Bay Area Watersheds</u>. Most urban uses of copper ammonia complex, copper hydroxide, copper oxychloride, and copper sulfate (basic) are as lawn and garden fungicides. Although there are other miscellaneous uses (*e.g.*, copper hydroxide is incorporated into soil to prevent root growth into structures), this analysis assumes that all estimated Bay Area urban use of these products is on urban landscaping. Almost all products with copper metal as the active ingredient are

algaecides; however, there are 2 professional turf products that use copper metal. Since professional pesticide applications should be reported, the outdoor garden use of copper metal is assumed to equal to the extrapolated Bay Area fraction of its statewide reported landscaping use, 672 pounds. Similarly, use of the one copper sulfate product registered for landscape use (which is assumed to be a professional product as it was not observed in a recent retail shelf survey) is assumed to equal to the extrapolated Bay Area fraction of its statewide reported landscaping use, 6,800 pounds. Using these assumptions, Table 14 presents the total San Francisco Bay area use of copper in copper-containing landscaping pesticides.

Table 14. Bay Area Copper-Containing Landscaping Pesticide Use Estimate, 2002

Pesticide	**Estimated Bay Area Copper Use (lb Cu/yr)**
Copper	672
Copper Ammonia Complex	1,910
Copper Hydroxide	173,628
Copper Oxychloride	3,027
Copper Sulfate (Basic)	60,474
Copper Sulfate (Pentahydrate)	6,800
TOTAL	**250,000**

Source: Table 13; see text.

Copper Washoff into Urban Runoff. Only a small fraction the copper applied to landscaping is washed off in storm water runoff, as copper tends to bind to soil and vegetation. A study of copper runoff from tomatoes treated with copper fungicides found that about 1% of applied copper was washed off of a tomato cultivation study area (Dietrich and Gallagher, 2002). This study involved the use of plastic mulch for the tomatoes, which is known to increase pesticide wash-off rates (Rice *et al.*, 2001). The runoff fraction is consistent with known washoff rates of many other pesticides, which are typically less than 0.5% of the amount applied (Wauchope, 1978).

Annual Copper Load. Assuming the runoff fraction is 0.5 - 1%, the copper release to San Francisco Bay Area urban runoff from landscaping pesticide use would be about 1,200 to 2,500 pounds.

3.5.2.2 Wood Preservatives

Copper Release to Bay Area Watersheds. The primary uses of copper carbonate, copper naphthenate, and cupric oxide are for wood treatment. These may be used individually or combined with other ingredients to produce well-known wood preservatives like chromated copper arsenate (CCA). Most or all of the estimated Bay Area use of these three pesticides (about 28,000 pounds of copper) is assumed to be for wood protection. While three other pesticides (copper, copper ethanolamine complexes [mixed], copper sulfate [pentahydrate]) may be formulated into wood preservative products, these are believed to be minor uses of these pesticides based on the relatively small number of products.

Copper Washoff into Urban Runoff. Copper is known to leach out of wood treated with copper-based wood preservatives. The amount of copper leaching, particularly after the first few months, is not well understood (CDA, 2003b). A recent U.S. Geological Survey (USGS) study of a 580-acre watershed with a 27 acre lake suggests that even in a watershed with relatively extensive use of copper-treated wood, the wood preservatives are a relatively minor source of copper releases to surface water (Rice *et al.*, 2002). In the USGS study watershed, CCA-treated wood is used for bank stabilization along about 75% of the lake shoreline. In addition, the watershed contained copper-treated decks and docks. Nevertheless, copper leaching from preserved wood was estimated to represent only about 4% of the annual copper load in the small watershed; the main source (comprising about 90% of the copper) was road runoff. Since copper-treated wood use in the San Francisco Bay area is far less dense than in study watershed studied by the USGS, it is reasonable to conclude that copper-based wood preservatives release only a relatively small amount of copper to San Francisco Bay.

In the USGS study, the authors note that most of the copper in treated wood is removed when the wood is removed from service, typically after 10 to 20 years of use. Since they estimated that it would take about 180 years to leach all the copper from treated wood posts and pilings submerged in water, a conservative assumption would be that about 8% of copper used to treat wood (15 years divided by 180 years) is released while it is used. In the San Francisco Bay area, the main uses of copper wood preservatives are not along shorelines, but in fences, decks, and other outdoor landscaping. It is therefore reasonable to assume that wood preservative copper releases would be attenuated by runoff across soil surfaces in a manner similar to runoff losses of other urban copper releases, and therefore that the runoff fraction would be similar to the runoff fraction for other copper pesticides used in landscaping (see above).

<u>Annual Copper Load</u>. To simplify the estimate, it is assumed that all copper that will be released from a year's worth of wood preservative use occurs in the first year—in other words, it is assumed that all the copper released from annual sales of 28,000 pounds of copper wood preservatives occurs in the year the wood is sold. If the runoff fraction is 0.5 - 1%, the copper release to San Francisco Bay Area urban runoff from wood preservative use would be about 1,400 to 2,800 pounds.

3.5.2.3 <u>Algaecides</u>

<u>Copper Release to Bay Area Watersheds</u>. Most urban uses of copper ethanolamine complexes (mixed), copper ethylenediamine complex, and copper triethanolamine complex are as algaecides, so this analysis assumes that other uses of these three pesticides are negligible. Since most copper carbonate products are wood preservatives, algaecide use is assumed to be minor. Separating out algaecide uses of copper metal and copper sulfate (pentahydrate) is quite difficult. Of 61 copper sulfate (pentahydrate) products, 16 are root control products; 3 are wood treatments; one product is for landscaping, 9 are agricultural products; 27 are swimming pool algaecides, and the remainder are specialize algaecides (*e.g.*, for aquaria, industrial water). The mix of products containing copper metal is similarly confusing. With this mix of products and the limitations of available data, it is not possible to estimate quantitatively all algaecide uses, though it is likely that use exceeds 50,000 pounds per year. Table 15 (on the next page) summarizes available information about San Francisco Bay Area copper algaecide use.

Table 15. Bay Area Copper-Containing Algaecide Use Estimate, 2002

Pesticide	**Estimated Bay Area Copper Use (lb Cu/yr)**	**Number of Swimming Pool Products**	**Notes**
Copper[a]	Unknown (<55,829)	24 of 49	Unclear what fraction is used as an algaecide.
Copper Ethanolamine Complexes, Mixed	32,765	4 of 11	
Copper Ethylenediamine Complex	287	0	
Copper Sulfate (Pentahydrate) [b]	Unknown (<126,304)	27 of 61	Unclear what fraction is used as an algaecide
Copper Triethanolamine Complex	50	7 of 8	

[a]Total reduced by 672 pounds to reflect reported use of professional landscaping products.
[b]Total reduced by 6,800 pounds to reflect reported use of professional landscaping product.
Source: Table 13 and DPR product information (DPR, 2004a); see text.

Copper Washoff into Urban Runoff. Copper-based algaecides are applied to many different types of water, with very different potential to release copper to urban runoff or San Francisco Bay. The primary uses are considered below:

- *Surface water applications to non-drinking water bodies*—While some non-drinking water surface waters may be treated with copper algaecides, the majority of such treatments in the San Francisco Bay Area are treatments by municipalities made to lagoons and sloughs bordering San Francisco Bay (RWQCB, 2004a). Since lagoons and sloughs generally release water directly to San Francisco Bay, this analysis assumes that all copper applied to non-drinking water bodies is released to the Bay and is therefore a shoreline copper source, rather than an urban runoff copper source (actual releases are somewhat lower due to copper deposition in the treated water body).

- *Reservoirs and water supply conveyance channels*—These common applications to prevent unpleasant taste and odor from algae growth and to ensure smooth operation of potable water systems are part of the copper considered in Section 3.9.

- *Industrial applications*—Copper has many industrial algae control applications, often in systems that do not regularly discharge to either the sewer or storm drain systems (*e.g.*, irrigation ponds, recirculated cooling water). Stormwater discharges from industrial facilities are considered in Section 3.6.

- *Swimming pools, spas, and fountains*—much of the applied copper is collected by a pool's filtering system, or bound to pool, spa, or fountain walls and fixtures, but an unknown fraction remains in the water. When emptied (not a common event), pools, spas, and fountains may be discharged to sewers or to storm drains (under municipal stormwater permits, dechlorinated swimming pool water is an exempted discharge). No estimate of the fraction discharged to storm drains is available; however, based on copper's efficient binding to solids like pool, spa, and fountain surfaces and materials in pool filtration systems, it is reasonable to assume that less than 5% of pool, spa, and fountain algaecide copper is discharged to storm drains.

Annual Copper Load. Of the above algaecide uses, all must be reported to DPR except homeowner applications to swimming pools, spas and fountains. DPR has a database tool that allows reported pesticide uses to be obtained for specific California counties. This tool was used to obtain reported non-industrial copper-containing pesticide applications to surface water bodies in the nine San Francisco Bay Area counties (a region larger than the area discharging urban runoff to the Bay) Reported applications were 3,700 pounds in 2002 (DPR, 2004b).

This report may not very accurately reflect actual copper algaecide use in Bay Area surface waters. Aquatic pesticide application permit records for 2002 (RWQCB, 2004a) provided numerous examples of copper algaecide applications to surface waters that do not appear in the DPR database results, suggesting that the database does not include accurately classification of use reports (or possibly that some uses reported to the Water Board were not reported to DPR). It should be noted that this report includes applications to reservoirs and water supply conveyance channels, which are not shoreline copper sources.

Of the remaining application types listed above, copper algaecide use in pools, spas, and fountains is most likely to have a potential to release meaningful quantities of copper into runoff. A rough estimate of this algaecide use can be made by assuming that the swimming pool, spa, and fountain use of copper pesticides with multiple uses is proportional to the fraction of products labeled for pool, spa, and fountain applications. This assumption gives a rough estimate of <95,000 pounds. Assuming that less than 5% of this copper is discharged to storm drains, a rough load estimate would be <5,000 pounds.

3.5.3 Control Measures

Control measures are available for all types of copper pesticide uses. In the San Francisco Bay Area, control measures have focused on copper algaecide uses.

Algaecides for pools, spas, and fountains. Currently, the primary control measure to prevent copper releases from pools, spas, and fountains to San Francisco Bay is public outreach. Outreach discourages uses of copper (copper-free alternatives, such as hypochlorite-containing shock treatments, are available), and encourages discharge of copper-containing pool, spa, and fountain water to the sewer, not the storm drain. SCVURPPP developed model source control measures for pools, spas and fountains. These model measures provide (1) that there be no direct discharge of pools to storm drains or sanitary sewer manholes; (2) pools should be drained to the sanitary sewer via a clean-out (with POTW permission); and (3) for new pools, local codes should require installing a clean-out in accessible area near the pool. In the lower South San Francisco Bay, outreach about copper-containing algaecide use and pool water discharge started in the mid-1990s. Outreach programs target both residential pool owners and pool maintenance professionals. SCVURPPP has concluded that effectiveness of these programs cannot be measured at this time (instead, performance evaluation is based on the quantity of outreach materials distributed) (SCVURPPP, 2004).

Other algaecides applied to surface waters. The primary control measure for copper-based pesticide applications to surface waters is the Aquatic Pesticide General Permit program, managed by the State and Regional Water Quality Control Boards. (Certain municipal stormwater permits also include provisions requiring development of performance standards for aquatic pesticide applications.) The aquatic pesticide general permit requires an Aquatic Pesticides Application Plan describing best management practices to mitigate effects to water quality resulting from pesticide application, monitoring, and reporting of pesticide applications and monitoring results to the Regional

Water Quality Control Board (SWRCB, 2004a). In response to permit requirements, copper algaecide use in lagoons and sloughs discharging to San Francisco Bay has declined significantly (RWQCB, 2004a).

Alternative algae control methods. In addition to applying registered pesticides, aquatic pests can be controlled with biological, physical, and mechanical control methods, non-conventional chemical control methods, and/or preventive measures. Some alternative control measures have the potential to impact water quality and aquatic habitats adversely, though a study by SFEI showed that many alternatives had lesser impacts than aquatic pesticides (Greenfield, 2004). Appropriate alternatives methods need to be identified on a site-specific basis, which means that testing is a necessary step in transitioning to a non-copper control measure. The relative cost-effectiveness of conventional pesticides versus alternative methods varies among different management scenarios (Mann and Wittmann, 2003).

Copper landscaping pesticides. Currently there are few control measures in place specifically addressing copper-based pesticides used in landscaping. Some municipal integrated pest management policies include measures to limit use of copper-based pesticides. Little or no public outreach regarding use of copper pesticides has occurred. The transition to integrated pest management (IPM) by municipalities and efforts to promote IPM to communities are likely to reduce use of copper-based pesticides, but the reduction is unknown. Because copper-based landscaping pesticides are often less toxic to humans than alternative pesticides, any transition away from copper landscaping pesticides needs to be managed with caution.

Copper wood preservatives. The U.S. EPA phase-out of chromated copper arsenate (CCA) has stimulated a transition to other copper-based wood preservatives. Colloquial information suggests that the most commonly available alternatives are also copper-based (but do not contain chromium or arsenic), such as copper naphthenate and ammoniacal copper quat. Borates are also commonly available, but are intended primarily for indoor (dry) applications. Based on an evaluation of wood preservative alternatives, San Francisco is considering adoption of a policy to minimize use of copper wood preservatives for structures built in or over water or where significant runoff would contact the treated wood (Dickey, 2003). Non-wood alternative materials, rather than wood treated with a different wood preservative, are likely to be environmentally preferable—but some alternative materials have potential adverse environmental effects (Dickey, 2003).

Regional copper-based pesticide sales or use restrictions. Another possible option is to ask DPR to consider regulating copper-containing pesticides. Given the relative magnitude of the potential copper load and the cost of alternative control measures, regulation would be most cost-effective for controlling copper-based pool, spa, and fountain algaecides. This option has not been explored to date. DPR generally requires quantitative information about the water quality and/or permit compliance problems associated with a pesticide (including quantification of the pesticide's relative contribution to the problem) before it will consider restricting a pesticide's sales and use.

3.5.4 Uncertainty

Given the major data gaps, the estimated release from copper pesticides is highly uncertain. Sources of uncertainty in the current estimate include (but are not limited to):

- *Sales data*. Extrapolation of statewide pesticide sales data to the San Francisco Bay Area creates highly uncertain pesticide sales estimates. The lack of sales data for 8 of the 19 copper-containing pesticides on the market only increases the uncertainty of the estimates made in this analysis.

- *Region-specific factors*. Estimates do not account for climate, lot size, regional pest problems or other reasons that pesticide use per person might vary across the state.
- *Simplifying assumptions*. The analysis relies on many simplifying assumptions (primarily regarding the relative importance of various uses of each copper-containing pesticide active ingredient), each of which is noted in the text above.
- *Washoff rates*. Pesticide wash-off rates are based on very limited data.
- *Inaccuracies in DPR databases*. In general, DPR quality assurance programs ensure that DPR databases provide data with low uncertainty; however, review of records of surface water applications of copper-containing pesticides identified discrepancies between DPR records and reports filed with the Regional Water Quality Control Board, suggesting that the database does not include accurately classification of use reports (or possibly that some uses reported to the Water Board were not reported to DPR).
- *Assumptions about pool, spa, and fountain algaecides*. The load estimate relies on two assumptions that cannot be verified—(1) the assumption that the swimming pool, spa, and fountain use of copper pesticides with multiple uses is proportional to the fraction of products labeled for pool, spa, and fountain applications and (2) the assumption that less than 5% of this copper is discharged to storm drains.

3.4.5 Next Steps

- *Load Estimate*. Given the potential magnitude of copper releases from algaecides, an improved estimate of the copper load from algaecides (primarily pool, spa, and fountain algaecides) is a priority. Such a load estimate could determine whether voluntary programs are sufficient or regulatory programs (*e.g.*, sale and use restrictions and/or more stringent controls on pool, spa, and fountain water management) are warranted.
- *Control Measures*. Evaluate alternative practices and pesticides for landscaping to determine if safe and effective alternatives exist. Consider developing best management practices for wood preservatives to minimize use of copper wood preservatives where releases are most likely to occur. Since the Aquatic Pesticides General Permit regulates surface water algaecide applications, additional controls should not be needed (unless the permit does not continue to create a disincentive for copper use). Appropriate control measures for pool, spa, and fountain algaecides should be determined on the basis of a better load estimate.

3.6 Industrial Copper Use

Industry has long been a focus of environmental regulatory programs, including both wastewater pretreatment and stormwater permit programs. Any industrial facility in one of 10 broad categories of industrial activities must participate in the State Water Resources Control Board's industrial stormwater permit program. About 1,400 industrial facilities in the San Francisco Bay Area are currently active participants in the program.

The *Metals Control Measure Plan* used a specialized estimate based on industrial stormwater runoff monitoring data compiled from the industrial stormwater permit program (Grotte, 1996; SCVURP, 1997). That analysis involved special categorization of industry to separate out metal-using industry categories and to focus particularly on three types of companies with relatively high copper levels in their reported monitoring data (electroplaters, metals finishers, and semiconductor manufacturers) (Grotte, 1996).

Subsequently, three Santa Clara Valley studies looked at elements of the *Metals Control Measure Plan* industrial copper load estimate. A detailed analysis of facilities in Palo Alto and Mountain View found that the previous estimates were imperfect, but the variations in subsequent monitoring data suggested that the imperfections reflect, in part, real variation in industrial monitoring data (Cooke and Bodine, 1997). Similarly, two subsequent studies of Santa Clara Valley electroplaters, metals finishers, and semiconductor manufacturers concluded that results were similar to previous estimates, given the inherent variability of the data (SCVURPPP, 1998; SCVURPPP, 2003b).

3.6.1 Background

Although quite a few industrial activities involve use of copper-containing materials, many of these activities occur indoors, where most copper releases would not have the potential to be released to runoff. Certain processes—like heated plating tanks—could potentially release droplets of copper-containing solutions into building air exhaust system and out onto building roofs and the surrounding area (SCVURPPP, 1998).[20]

3.6.2 Copper Loads

The specific analysis conducted for the *Metals Control Measure Plan* cannot be repeated with available information. While a similar analysis of region wide industrial stormwater monitoring data would be useful, such a significant effort was not possible within this project's scope and budget.

Since no recent or region-wide analysis of industrial stormwater monitoring data has been identified, the estimate used in the *Metals Control Measure Plan* was assumed to be sufficiently representative of current industrial stormwater discharges to be extrapolated to a Bay-wide estimate. The extrapolation on the basis of the number of acres of industrial facilities in the San Francisco Bay Area (89,266), as determined from the State Water Resources Control Board Industrial Stormwater Database for the San Francisco Bay Area (SWRCB, 2004b). Since previous total industrial acreage was not available, the number of acres of industrial facilities in Santa Clara County (18,835) was assumed to have remained constant since 1997. The extrapolated copper load is 3,300 pounds per year.

3.6.3 Control Measures

The primary control measure for industrial runoff is the Industrial Storm Water General Permit program, managed by the State and Regional Water Quality Control Boards. The industrial stormwater permit requires the implementation of management measures that will achieve the performance standards of "best available technology economically achievable" and "best conventional pollutant control technology." Facilities covered by the permit must prepare and implement Storm Water Pollution Prevention Plans and monitoring plans. The state regulatory program is supplemented by the required commercial/industrial element of municipal stormwater programs.

Individual municipalities have explored a variety of methods to enhance the effectiveness of their industrial stormwater programs. For example:

[20] Copper that is emitted to the air is considered in Section 3.7.

- Many municipalities combine industrial stormwater inspections with other routine inspections of the same facilities (*e.g.*, by wastewater pretreatment programs or certified unified program agencies).
- On the basis of its investigations of copper in industrial runoff, the Santa Clara Valley Urban Runoff Pollution Prevention Program initiated a unique pilot outreach campaign designed to increase compliance with industrial stormwater permit requirements. The effort includes a partnership with industry to increase familiarity with practical best management practices to reduce pollutant levels in runoff. The effectiveness of this pilot project has not yet been evaluated (SCVURPPP, 2003b).

No data are currently available to estimate the effectiveness of these regulatory and education programs in reducing copper discharges.

3.6.4 Uncertainty

Although the estimate involves significant extrapolations, since it was based on actual industrial runoff monitoring data, the industrial copper load estimate is moderately uncertain. Sources of uncertainty in the current estimate include (but are not limited to):

- *Monitoring data*. The estimate assumes that previous monitoring data is representative of current industrial stormwater discharges (regulatory efforts have probably reduced the industrial copper load.)
- *Extrapolation*. The estimate assumes that the previous estimate is representative of the industrial contribution to runoff from all industrial facilities.
- *Industrial facility area*. The estimate assumes that the number of acres of industrial facilities in Santa Clara County have remained constant since 1997 (substantial growth followed by a substantial economic downturn have occurred since that time.)

3.6.5 Next Steps

- *Load Estimate*. Although the load estimate is uncertain, given that the control measures are unlikely to change, a more accurate load estimate is not necessary at this time. Using industrial stormwater permit data to compare previous and current pollutant loads could, however, be generally helpful in understanding the efficacy of stormwater permits as a control measure.
- *Control Measures*. Since the Industrial Storm Water General Permit already regulates industrial runoff, additional controls are not needed.

3.7 Copper Air Emissions

Air deposition conveys copper from copper air emissions sources into San Francisco Bay and onto surfaces subject to urban runoff. The actual emissions sources of the copper deposited onto the Bay and Bay watersheds are not fully known at this time. Sources include vehicle fuel combustion, fires, industrial air emissions, vehicle components, soils, and industrial air emissions.

The *Metals Control Measure Plan* estimated copper emissions from motor vehicle fuel combustion, but not from other copper air emissions sources. The basis of the *Metals Control Measure Plan* estimates was the California Air Resources Board model BURDEN7F. The metals data in this model are not recent—in fact they represented emissions from leaded gasoline, which was phased out in 1992. Although the copper emissions estimates were not noteworthy, the emissions estimates for several metals were high enough to merit follow-up investigation to obtain a more accurate—and region-specific—load estimate. BASMAA coordinated with the California Air Resources Board and the University of California Santa Cruz to measure metals concentrations in San Francisco Bay Area gasoline and diesel fuel (Brosseau, 2004).

In 2001, the San Francisco Estuary Institute (SFEI) published results of a pilot study to measure wet and dry deposition of copper and other metals in the San Francisco Bay area (Tsai *et al.*, 2001). The report included an estimate of the quantity of copper deposited from the air into Bay Area watersheds and—based on a general estimate of the wash-off fraction—the estimated copper load to San Francisco Bay from air-deposited copper. Samples were collected at locations somewhat away from human activity with the intent of obtaining a regional background load estimate not influenced by specific sources (like roads or industrial facilities). While this report did not identify the copper emissions sources, it provided a relatively reliable estimate of the contribution of copper deposited from the air to the quantity of copper in urban runoff.

3.7.1 Background

Air emissions may result from ordinary industrial or residential activities, like combustion of industrial fuels and firewood containing trace amounts of copper. Although copper emissions have not been a focus of air quality agencies, air pollutant emissions from industrial facilities and from vehicles are closely regulated by California air quality agencies.

In the San Francisco Bay Area, vehicle fuel combustion has proven of interest to water quality agencies due to the relatively large volume of fuel used in the Bay Area. Each day, almost 9 million gallons of gasoline and more than one million gallons of diesel fuel provide the power for San Francisco Bay Area vehicles to travel 167.2 million miles (BAAQMD, 2004). Given these fuel volumes, there exists the potential that even trace impurities in fuels could result in environmentally meaningful releases of water pollutants. Unlike lead, copper is not intentionally added to motor vehicle fuels. Copper is an impurity that comes from the crude oil or from equipment in the refining process. Because fuel transportation is expensive, motor vehicle fuels are typically distributed regionally. Most of the San Francisco Bay Area's supplies come from the region's own oil refineries. The characteristics of fuel in a region are defined by the oil source, and to a lesser extent the specific refinery processes used to create the fuel from crude oil.

3.7.2 Copper Loads

3.7.2.1 <u>Copper Release to Bay Area Watersheds</u>

Although some fraction of copper emissions travel outside the Bay Area, because deposition patterns are source specific and unknown, all release estimates below assume that all emitted copper is deposited in Bay Area watersheds.

<u>*Vehicle Fuels*</u>. Pre-publication data provided by BASMAA (Brosseau, 2004) was used to estimate the copper releases from motor vehicle fuel combustion. Eighteen diesel fuel samples and 19 gasoline samples (five premium, one mid-range, 13 regular) were tested for copper concentrations. Copper was not detected in most samples; it was detected in one diesel and one premium gasoline sample. Assuming that these detects represent normal variation in copper concentrations, an average copper concentration range of 0.6 – 8 parts per billion (ppb) was calculated for the diesel samples (low value assumes non-detected values were 0; high value assumes that non-detected concentrations equaled the detection limit). The concentrations were similarly averaged to estimate a copper concentration range of 0.7 – 8 ppb for gasoline, assuming that the sample mix was adequately representative of the sales fraction of the three gasoline grades. Fuel

densities were assumed to be equal to the density of octane (gasoline) and cetane (diesel) (Lide, 1998).

Fuel use estimates were obtained as follows:

- *Gasoline*. BAAQMD estimates 2003 San Francisco Bay Area gasoline use was 8.8 million gallons per day (BAAQMD, 2004).
- *Diesel*. Since BAAQMD did not provide a diesel fuel use estimate, diesel use was estimated on the basis of statewide fuel use data from the California Department of Finance (DOF, 2002b). Assuming the fraction of the state's diesel used in the San Francisco Bay Area is the same as the fraction of the state's gasoline used in the Bay Area (21%), about 1.6 million gallons of diesel are used daily in the San Francisco Bay Area.

On the basis of this data, the copper released to Bay Area watersheds is estimated to be in the range of 10-200 pounds.

Industrial Air Emissions. The Bay Area Air Quality Management District (BAAQMD) prepares an annual inventory of air toxics emissions in the San Francisco Bay Area, based on reports from facilities with air pollutant emissions permits (BAAQMD, 2003). Although copper emissions are not required to be reported by any facility emitting less than 463 pounds per year, 53 industrial facilities reported a total of 410 pounds of copper air emissions in 2001 (BAAQMD, 2003).

Fires. The Copper Development Association (CDA) estimated statewide copper releases from residential wood burning and forest fires (CDA, 2003b). Bay Area emissions can be roughly estimated on the basis of these statewide estimates.

- *Residential wood burning*. CDA estimated annual copper emissions of 1371 pounds statewide (CDA, 2003b). Assuming wood burning is proportional to population, Bay Area emissions would be 19.7% of statewide emissions (based on a California population of 35,591,000 and a San Francisco Bay Area population of 6,994,500 as of January 1, 2003 [DOF, 2003]), or 270 pounds.
- *Forest fires*. CDA estimated annual copper emissions of 1720 pounds statewide (CDA, 2003b). Assuming forest fire emissions are proportional to land area, Bay Area emissions would be 4.0% of statewide emissions (based on the Bay Area Air Basin area of 6,619 square miles [BAAQMD, 2004] and California land area of 163,696 square miles [DOF, 2002b]), or 69 pounds.

Together, these emissions total 340 pounds. These estimates do not include emissions from structural fires, which could release copper from wood and other copper-containing building components.

3.7.2.2 Copper Washoff into Urban Runoff

Copper deposited on Bay Area watersheds from both wet and dry deposition may run off to San Francisco Bay. SFEI estimated that 32% of copper in both wet and dry deposition is washed into San Francisco Bay (Tsai *et al.*, 2001). In the absence of source-specific washoff information, this analysis assumes that the SFEI estimate is applicable to all air deposition sources.

3.7.2.3 Annual Copper Load

Using the above copper release and wash-off fraction estimates, the loads from identified copper air emissions sources can be estimated as follows:

- *Vehicle Fuels*. If 32% of the 10 to 200 pounds of copper emitted from fuel combustion is washed into the Bay, the copper load would be 3 to 64 pounds per year.
- *Industrial air emissions*. If 32% of the 410 pounds of reported industrial copper emissions are washed into the Bay, the copper load would be 130 pounds per year.
- *Fires*. If 32% of the estimated release of 340 pounds is washed off, the copper load would be 110 pounds per year.

The total of the above copper loads (240 to 300 pounds per year) is substantially less than SFEI's total estimate of copper load to San Francisco Bay from copper air deposition in Bay Area urban watersheds, 8,800 pounds per year (Tsai *et al.*, 2001).

3.7.3 Control Measures

No control measures specific to copper air emissions have been identified. The BAAQMD regulates industrial air emissions to reduce releases of various air pollutants, including toxic air pollutants. It also conducts education programs that address all pollutant sources, including residential fireplaces. Many measures that reduce air pollution would also reduce copper emissions. Because the BAAQMD has not identified copper-containing compounds as a source of air quality problems, it has not specifically addressed copper emissions other than through the reporting requirements of its air toxics program.

The California Air Resources Board regulates air emissions from vehicles. While regulations technically address all air emissions, they focus on tailpipe emissions, which are significant contributors to major air quality problems in California. Vehicle emissions control devices probably remove some of the copper prior to emission from a vehicle's tailpipe. This amount is unknown.

Measures to reduce vehicle miles traveled would reduce copper air emissions from diesel and gasoline fuel combustion. (See Section 3.3.3 for a discussion of these measures).

3.7.4 Uncertainty

The total air deposition quantity is based on actual measurements of copper deposition in the Bay area. After reviewing the data behind the estimate, its uncertainty was determined by SFEI to be low to moderate (Tsai *et al.*, 2001). Sources of uncertainty in the estimates in this report include (but are not limited to):

- The *industrial air emissions* estimate may significantly understate copper air emissions, because BAAQMD does not require reporting of copper emissions less than 463 pounds per year. All reporting facilities emitted less than the reporting threshold. The high threshold may mean that many emitters are not reporting emissions.
- The *vehicle fuel* estimate does not reflect any potential vehicular emissions from metals worn from engine parts that come in contact with the fuel, nor any metals losses within a vehicle engine or exhaust system.
- The *fire* estimate does not include emissions from structural fires.
- *Vehicle brake pads* are known to release copper to the air but are not included in this estimate because they are considered in Section 3.3. The extent to which air deposition measurements reflect copper from vehicle brake pads is currently not known. Investigations underway by the Brake Pad Partnership will estimate the

transport distance of vehicle brake wear debris. Using this information and information about the SFEI air deposition monitoring sampling locations, it will be possible to estimate the contribution of vehicle brake pads to the air deposition load estimated by SFEI.

- The contribution of *other copper air emissions sources*, such as wind and vehicle suspension of soils, is unknown.

3.7.5 Next Steps

- *Load Estimate*. Identification of the copper emissions that are the sources of measured air deposition is a priority. Since copper from vehicle brake pad wear may contribute to the measured deposition, the most cost-effective approach would be to wait to initiate the source investigation until after the Brake Pad Partnership completes its air deposition modeling (anticipated in spring, 2005).
- *Control Measures*. Additional controls on identified sources are not warranted. Feasibility of control measures for other copper air emissions sources should be explored once those sources are identified.

3.8 Soil Erosion

Each year, hundreds of construction sites cover thousands of acres of San Francisco Bay Area land, digging up the soil to build new homes, businesses, industries, and infrastructure. In order to prevent releases of soil and other pollutants into stormwater runoff, the State Water Resources Control Board requires all construction sites larger than 1 acre to participate in the construction stormwater permit program. There were about 700 active construction sites in the San Francisco Bay Area in 2003 (SWRCB, 2004b).

Construction of new impervious surfaces in Bay Area watersheds also changes the quantity and timing of runoff flows in urban creeks. These changes can accelerate erosion of stream banks—potentially contributing significantly to sediment loads in runoff. Recent new development related amendments to urban runoff agency permits require development of hydromodification management plans to protect beneficial uses in Bay Area creeks.

The copper load estimate in the *Metals Control Measure Plan* used construction stormwater permit data and a rough estimate of erosion to estimate construction copper loads. Since that time, expansion of the permit system to include sites as small as 1 acre has probably reduced construction site soil erosion and thus copper loads. The *Metals Control Measure Plan* assumed that remaining sediments in urban creeks were from natural erosion. Any contribution from changes in creek flows or other urban activities (*e.g.*, landscaping) was not identified or estimated.

In runoff, eroded soils become “suspended solids” because they are entrained in water flows before they deposit in creeks or the Bay. The San Francisco Estuary Institute (SFEI) estimated the total quantity of suspended solids in urban runoff in the report *Contaminant Loads From Stormwater to Coastal Waters in the San Francisco Bay Region* (Davis *et al.*, 2000). The study estimated that about half (51%) of the solids in Bay Area stormwater come from agricultural land uses. Open space (22%) and urban areas (residential, commercial, and industrial land uses, 27%) each comprised about a quarter of the solids load.

3.8.1 Background

San Francisco Bay area soils—like soils from elsewhere in the nation—contain trace levels of copper naturally. When soil washes off urban areas, it carries copper with it to San Francisco Bay. While a certain amount of soil erosion is normal, human activities in Bay Area watersheds have accelerated soil erosion. Watershed modifications like dams and flood control projects also change the flow of sediments to San Francisco Bay.

3.8.2 Copper Loads

3.8.2.1 Construction Sites

The estimation method from the *Metals Control Measure Plan* was used to estimate the regional copper releases to urban runoff from copper in construction site soils, starting with data from the State Water Resources Control Board Construction Stormwater Database for the San Francisco Bay Area (SWRCB, 2004b). The methodology involves the following estimates:

- *Area under construction*. Using the information in the database, the average number of acres under construction during the rainy season (November-April) in 2003 was estimated to be 9,067 acres.
- *Erosion rate and soil copper concentrations*. The *Metals Control Measure Plan* values (7,500 pounds per acre and 38.57 mg/kg, respectively) were used.

Using the above values, the copper load from construction sites is estimated to be about 2,600 pounds per year.

3.8.2.2 Development-Related Hydromodification

No basis exists to prepare a specific quantitative estimate of the copper load from hydromodification of Bay Area urban creeks. The way creeks are affected by changes in flows are highly variable, depending on the characteristics of the watershed and the new development. Preparing an estimate would require an assessment of each Bay Area watershed affected by hydromodification. The load can, however, be bracketed by the copper load estimated from total urban suspended solids loads (below).

3.8.2.3 Annual Copper Load—All Soil Erosion Sources

Using SFEI's best estimate of suspended solids discharges in stormwater runoff and the *Metals Control Measure Plan* soil copper concentration estimate, the annual copper load in urban runoff from soil erosion can be estimated. SFEI estimates that 27% of the best estimate of 680,000,000 pounds of suspended solids in all Bay Area runoff is from urban areas—a total of 180,000,000 pounds of solids. These solids contain about 7,000 pounds of copper attributed to urban soil erosion.

3.8.3 Control Measures

Control measures are already in place for both construction and hydromodification-related soil erosion.

Construction. The primary control measure for construction site stormwater is the Construction Storm Water General Permit program, managed by the State and Regional Water Quality Control Boards. Facilities covered by the permit must prepare and implement Storm Water Pollution Prevention Plans and monitoring plans. The state regulatory program is supplemented by the required new development and construction controls element of municipal stormwater programs.

Individual municipalities have explored a variety of methods to enhance the effectiveness of their construction stormwater programs. For example, many municipalities combine construction stormwater inspections with other routine inspections of the same sites (*e.g.*, by building code enforcement). Construction stormwater best management practices information is routinely distributed by municipal building departments. As municipalities incorporate new requirements for post-construction stormwater treatment measures, they are changing their relationships with construction sites, which may modify the level of oversight occurring during the construction phase.

No data are currently available to estimate the effectiveness of the regulatory and education programs in reducing copper discharges.

Hydromodification. The primary control measure for soil erosion from creek hydromodification due to urban development is the hydromodification management requirement within the new development requirements incorporated in Bay Area stormwater agency permits. This requirement addresses new development; it does not require retrofitting to manage erosion increases from past development, which may continue to occur for many years after the development is in place. Municipalities are just beginning to implement the required planning actions, so no data are available regarding their effectiveness in reducing soil erosion.

3.8.4 Uncertainty

On the basis of the uncertainty in SFEI's total sediments load estimate Davis *et al.*, 2000), the soil erosion copper load estimate is moderately uncertain. Sources of uncertainty in the current estimate include (but are not limited to):

- *Hydromodification-related sediment loads*. Although site-specific studies have included sediment load estimates, no regional assessment of hydromodification-related sediment loads has been prepared. Site-specific studies (*e.g.*, SCVURPPP, 2003a) suggest that hydromodification related sediment loads—and thus copper loads—have the potential to be significantly higher than the <5,000 pounds suggested by the regional total sediment load estimate minus the construction load estimate.
- *Construction site sediment releases*. The primary source of uncertainty in the construction estimate is that the sediment release estimate, which is based on colloquial information and does not account for the soil erosion reductions achieved by the use of construction site best management practices required by construction stormwater permits. Metals concentrations used in the estimate (data from the Calabazas Creek watershed in Santa Clara Valley) may not be representative of copper concentrations in soils elsewhere in the Bay Area.
- *Omission of small construction sites*. Since the Construction Stormwater Database does not includes sites smaller than 1 acre, small sites are not included. While small sites may contribute additional copper loads, this error is expected to be less important than other sources of uncertainty.
- *Omission of soil erosion from non-construction urban activities*. Accelerated soil erosion due to ordinary residential and business activities other than construction (such as landscaping) are not included in the load estimate.

3.8.5 Next Steps

- *Load Estimate*. Given that the control measures are unlikely to change, a more accurate load estimate is not necessary at this time. Using the construction stormwater permit data to compare previous and current sediment loads could, however, be generally helpful in understanding the efficacy of stormwater permits as a control measure.
- *Control Measures*. Since the Construction Storm Water General Permit already regulates construction stormwater runoff, and the new development hydromodification planning requirement will control hydromodification-related soil erosion, additional controls are not needed.

3.9 Copper in Domestic Water Discharged to Storm Drains

Most of the San Francisco Bay Area's drinking water supply flows into homes and businesses, where it is used indoors and discharged to the sewer—or piped outdoors to irrigate landscaping. A small fraction of drinking water flows into gutters and storm drains from activities like hydrant flushing, water main cleaning, outdoor water-based cleaning activities, and irrigation overflows. This water carries the traces of copper it contains into creeks and San Francisco Bay.

The *Metals Control Measure Plan* used detailed South Bay-specific information to estimate copper levels in the drinking water supply. This information was combined with a somewhat generic estimate of the fraction of drinking water that flows to storm drains (10% of the volume of drinking water not discharged to sewers). The estimate assumed that all drinking water flows through copper pipes. Most of the estimated copper load was from corrosion of copper pipe.

3.9.1 Background

Copper in the drinking water supply comes from the following sources:

- *Trace copper in the raw water supply*. This copper comes from natural minerals, or (in river water supplies) from upstream stormwater and wastewater discharges to the water source.
- *Algaecides*. To control nuisance algae—and prevent the unpleasant taste and odor associate with it—some water supply agencies apply copper-containing algaecides to reservoirs.
- *Corrosion of copper pipes in buildings*. Although copper pipe is long-lasting, it slowly wears down during use, through a combination of chemical corrosion and physical erosion of the pipe surface. Corrosion rates—and therefore drinking water copper content—vary by water supply, depending on factors like pH and trace ionic composition.

Most—but not all—drinking water receives some type of purification treatment prior to distribution to homes and businesses. Water purification treatments typically remove a portion of the copper in the source water. Subsequent to purification, disinfectants (*e.g.*, chlorine or chloramines) and additives to modify the water supply's corrosivity and fluoride levels are added. Because additives are high purity chemicals, they are not believed to add significant amounts of copper to the water supply.

3.9.2 Copper Loads

No additional information was identified to improve the load estimation method used in the *Metals Control Measure Plan*. Since water use is generally proportional to population, the previous copper load estimate (700 pounds/year) was adjusted on the basis of the ratio of the San Francisco Bay Area population–6,994,500 (DOF, 2003) to the 1995 Santa Clara County population—1,568,200 (DOF, 2002a),[21] to estimate that copper releases from urban storm drains discharge of drinking water is 3,000 pounds per year.

3.9.3 Control Measures

Both reducing discharge of drinking water to storm drains and reducing the copper level in drinking water can reduce copper loads from domestic water discharged to storm drains.

Reducing storm drain discharges. Most San Francisco Bay Area water suppliers have water conservation programs; some municipalities also have their own programs. These programs work in tandem with public outreach from municipal stormwater programs. However, most such programs emphasize messages other than reducing drinking water discharges to storm drains. Two water conservation pilot programs by the Irvine Ranch Water District (IRWD) have recognized and evaluated storm drain discharge reductions as a benefit of improved irrigation water management (IRWD, 2004).

- Installation of evapotranspiration irrigation controllers and generally improving irrigation water management in a test neighborhood reduced dry weather storm drain discharges by about 20% (IRWD, 2003).
- Wick irrigation of lawns is being tested in lawns; this method has the potential to almost eliminate lawn irrigation-related storm drain discharges.

Although IRWD materials do not specify the costs of these measures, costs are not insignificant, as these systems required physical installation of new irrigation controllers and/or new irrigation water distribution systems, in addition to outreach and education.

Reducing copper levels in drinking water. Water suppliers and wastewater treatment plants have explored options to reduce copper levels in drinking water. These options have been explored on a voluntary basis, because only the California Department of Health Services regulates drinking water supply quality. Many water suppliers have reduced copper-based algaecide use (see Section 3.5). Water supply modifications to reduce corrosivity have proven more challenging. The potential for copper reduction is very water supply specific, thus specific measures need to be developed and tested just to determine if reductions are feasible. Water suppliers vary in their willingness to consider modifying water supply corrosivity; they must grapple with customer acceptance, regulatory, cost, and management issues.

3.9.4 Uncertainty

Because of the many region-specific data used in the estimate extrapolated to the Bay Area, this estimate has moderate-high uncertainty. Sources of uncertainty in the current estimate include (but are not limited to):

- *Contact with copper pipe*. Most of the estimated copper load comes from the assumption that all discharged water flows through copper pipes. Since exterior copper pipes are relatively rare, this is approximately the same as assuming that discharged water flows through buildings. Much of the water discharged to storm drains never enters buildings. For example, water for hydrant flushing, water main cleaning, water supply system leaks, and some irrigation water—particularly for

[21] The *Metals Control Measure Plan* water supply use estimate was based on 1995 data.

common irrigation overflow locations like median strips and large landscaped areas—never enters copper pipe.

- *Fraction of drinking water discharged to storm drains*. The estimate of the amount of drinking water discharged to storm drains is based on limited data from Santa Clara Valley water purveyors and wastewater treatment plants, and the assumption that storm drain discharges comprise 10% of the volume of drinking water not discharged to sewers. This estimate may not reflect conditions elsewhere in the Bay Area, and may not accurately reflect discharge volumes.

- *Representativeness of Santa Clara Valley water supply copper data*. The copper concentrations in water supplies in other portions of the Bay Area differ from those in Santa Clara Valley. It is uncertain whether this might bias the estimate high or low.

3.9.5 Next Steps

- *Load Estimate*. Developing a more accurate estimate would be costly, and would be unlikely to modify the ability to control the discharge.

- *Control Measures*. Since the available control measures are already being pursued by other agencies and have shown only limited efficacy, additional controls are not warranted.

3.10 Vehicle Fluid Leaks and Dumping

Photos of motor oil in water bodies—and the negative public reaction to this visible water pollution—was one of the motivations for initiation of Federal programs to regulate urban stormwater runoff. Oil spots in streets, parking lots, and driveways remain a visual reminder of this ubiquitous source of water pollution.

Since their inception, municipal urban runoff programs have targeted illegal dumping and other improper discharges of pollutant-containing materials. Although little quantitative data are available to characterize improper discharges, increasing public awareness that storm drains carry water directly to creeks, San Francisco Bay, and the Pacific Ocean without treatment suggests that urban runoff programs have reduced improper discharges. Regulation of industrial and certain commercial discharges has terminated thousands of improper discharges in the San Francisco Bay area, eliminating many potential copper sources. Since municipalities focused on eliminating—rather than measuring—improper discharges, little or no quantitative data exists on such copper releases.

The *Metals Control Measure Plan* used colloquial and limited quantitative information to estimate copper releases from leaks and illegal dumping of vehicle fluids (motor oil and coolant). A recent study also estimated the potential contribution from vehicle fluids to copper in urban runoff, finding a negligible contribution (Davis *et al.*, 2001). Measurements of copper concentrations in motor oil for that study found a typical concentration similar to that used in the *Metals Control Measure Plan* estimate. While other copper-containing improper discharges certainly occur, it is likely that urban runoff education and regulatory programs have directed the most copper-laden of these discharges (*e.g.*, cooling water, vehicle service facility discharges, commercial vehicle wash water) away from storm drains.

3.10.1 Background

Neither motor oil nor coolants typically contain meaningful concentrations of copper. While inside vehicles, both fluids pick up copper from copper and brass vehicle parts. Spent solutions may be enriched in copper and other metals.

3.10.2 Copper Loads

Previous estimates from the Metals Control Measure Plan were adjusted as follows:

- Activity factor adjustment. Adjustments were made on the basis of the activity factor used in the *Metals Control Measure Plan* (MCM Plan)—see Table 16. The number of registered cars and trucks (5,432,514 in 2002) was obtained from the Metropolitan Transportation Commission (MTC, 2004a). The annual vehicle miles value (167.2 million miles per day or 6.1 x 10^{10} miles per year in 2003) was obtained from the Bay Area Air Quality Management District (BAAQMD) (BAAQMD, 2004).
- Do-it-yourself vehicle maintenance survey data adjustment. Two assumptions were adjusted on the basis of a statewide do-it-yourself vehicle maintenance survey by the California Integrated Waste Management Board (CIWMB, 2002). The estimated fraction of do-it-yourself fluid changes was reduced from 50% to 19% and the estimated improper disposal fraction was reduced from 50% to 19%.

Table 16. Motor Vehicle Fluid Improper Discharge Estimates

Improper Discharge	Previous Estimate (lb Cu/yr)	Previous Activity Factor	Current Regional Activity Factor	Regional Estimate (lb Cu/yr)
Coolant leaks	112	1,130,000 vehicles	5,432,514 vehicles	500
Coolant dumping	116	1.2 x 10^{10} miles driven per year	6.1 x 10^{10} miles driven per year	90
Oil leaks	<1	1,130,000 vehicles	5,432,514 vehicles	<1
Oil dumping	7	1,130,000 vehicles	5,432,514 vehicles	4
Total				**600**

Source: TDC Environmental calculations based on data sources and assumptions above.

3.10.3 Control Measures

All municipal urban runoff programs include commercial/industrial, illicit discharge, and public information programs as core program elements. Together these program elements address all types of improper discharges. Other than the survey information used in developing the load estimate (which implies a reduction in illegal dumping), no quantitative data are currently available to estimate the effectiveness of these regulatory and education programs in reducing improper discharges of vehicle fluids.

3.10.4 Uncertainty

Given the paucity of data characterizing improper discharges, the estimate is moderately-highly uncertain. Sources of uncertainty in the current estimate include (but are not limited to):

- *Copper concentrations in waste oil and coolant are from rather elderly sources*. Current copper levels in waste fluids may differ, particularly because manufacturer-recommended fluid replacement frequencies are lower, so fluids spend more time in contact with copper-containing vehicle parts.
- *Manufacturer-recommended fluid change frequencies have decreased*.
- *Leakage and dumping estimates were based on colloquial information*. Data gaps include quantity, frequency, and copper content of improper discharges. In the

absence of authoritative data on leakage and dumping rates, the *Metals Control Measure Plan* relied on colloquial information and professional judgment. Given the effectiveness of education programs and improved vehicle designs in the last decade, both leak and dumping rates are likely to have declined.

- *Estimates assume that all released copper flows to San Francisco Bay*. Some or all of the copper in leaked fluids is likely to build up and wash off in a manner similar to other anthropogenic copper deposited on impervious surfaces, suggesting less than complete wash-off to San Francisco Bay (Carleton, 2004).

3.10.5 Next Steps

- *Load estimate*. Although the load estimate is uncertain, it is small enough that additional study of this source is not warranted.
- *Control measures*. Control measures already in place have addressed this source. Given the relatively small load estimate, additional controls are not warranted.

3.11 Sources Not Evaluated

In theory, there are thousands of potential sources for copper in urban runoff and shoreline activities. Since the purpose of this report was to identify major sources, it does not include a comprehensive review of other possible copper sources. This subsection provides a brief description of the reasons for omission of some of the copper sources mentioned in previous studies or in the literature.

The following “sources” convey copper from primary copper sources into urban runoff:

- Runoff from residential, commercial, industrial, and institutional land uses
- Car washing
- Streets
- Parking Lots

The following are copper sources, but are not significant sources to urban runoff or from shoreline activities:

- Wastewater treatment plants and all discharge sources to the sewer system
- Mines
- Local reservoir releases, including algaecides directly discharged
- Non-urban soil erosion
- Agricultural pesticide and fertilizer use
- Landfills

The following sources are anticipated to be relatively small sources of copper release in urban runoff:

- *Tires*. Other stormwater source identification studies have not found tires to be a significant copper source (Sorme and Lagerkvist, 2002; Davis *et al*., 2001; CDA, 2003b). Although tires wear off on roads during use, the copper content of tires (about 2 parts per million) is relatively low (less than 10% of the copper concentration in Bay Area soils).
- *Illicit connections and improper discharges*. Illicit connections and improper discharges have been among the major focuses of urban runoff programs, which have sought to eliminate all identified improper discharges. Around the San Francisco Bay area, it is likely that thousands of discharge sources have been eliminated or redirected to the sewer system. Although copper-containing discharges (like cooling water from industry or debris from waste materials used in

sandblasting) may have occurred in the past, municipal, industrial, and construction stormwater permit requirements have ensured that regulators from Bay Area agencies and staff from local businesses and institutions have worked diligently to eliminate such discharges. It is unlikely that significant numbers of illicit connections remain after about 10 years of urban runoff regulation.

- *Building paint*. According to the Copper Development Association (CDA), copper pigments and biocides are commonly present in exterior paint. The CDA cites only one investigation of paint copper content, which found a medial concentration of 21 parts per million (CDA, 2003b). Since this concentration is relatively low (lower than the copper concentration in Bay Area soils) if the data are representative, paint is probably a negligible source.
- *Exposed electrical wires*. Most electrical wires are made of copper. The only identified exposed electrical wires in the Bay Area are those associated with San Francisco MUNI's electric bus and streetcar operations. The copper in these wires may wear off as streetcar electrical connections pass by them. These lines occur primarily (if not exclusively) in areas where the stormwater runoff flows to wastewater treatment plants, and thus are unlikely to contribute significantly to copper levels in San Francisco Bay area urban runoff.
- *Asphalt*. In an area with accelerated asphalt pavement wear due to use of studded snow tires, asphalt's contribution to urban runoff copper levels was estimated to be relatively small (Sorme and Lagerkvist, 2002).

While no previous copper source identification study has found the following sources to be significant, available information does not provide sufficient evidence to evaluate their significance:

- *Airplane brakes*. While airplane brakes are known to contain copper, the exact copper content is not known. The primary point of potential copper release is on airport runways. At larger airports runways are cleaned (frequency unknown). At most airports the runoff is subject to some type of treatment. At Bay Area airports without runoff management systems, the runoff flows through vegetated areas prior to entering a drainage system or a surface water body. Airport stormwater monitoring data would likely be able to shed light on whether airport runoff is elevated in copper as compared to other urban runoff.
- *Electrical motors*. Most electrical equipment is used indoors or in relatively weatherproof outdoor locations, as water and moisture-related corrosion may damage it. Electrical motors and generators contain parts that may wear off, potentially releasing copper-containing particles. Some older design motors ("brush DC") incorporate brushes that usually contain copper. If electrical motors are commonly placed in manners that do not contain wear debris—and if wear rates for copper-containing parts are significant—they could meaningfully contribute to copper levels in urban runoff.
- *Fertilizers*. CDA reports that about 54 million tons of commercial fertilizers were used in the U.S. in 1996 (CDA, 2003b). Many fertilizers contain copper, according to the CDA at concentrations from 0 to 39,900 parts per million (CDA, 2003b) The average copper concentration of fertilizers is not available. Since plants use the copper as a micronutrient, it is unclear how much copper enrichment of soil surfaces occurs as a result of fertilizer application. The fraction of this copper that may wash off is not known, though it would be reasonable to assume that wash-off fractions are

similar to those for copper-containing pesticides applied to soils and therefore are probably small.

4.0 CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

Conclusion 1. The significant sources of copper in urban runoff flowing to San Francisco Bay Area are vehicle brake pads, copper air emissions, architectural copper, industrial copper use, domestic water discharged to storm drains, soil erosion, and copper pesticides. Table 17 summarizes the copper load estimates and their uncertainties.

Table 17. Summary of Copper Sources in Urban Runoff (Pounds of Copper per Year Discharged to San Francisco Bay)

Copper Source	Load Estimate	Uncertainty[a]
Vehicle brake pads	>10,000	High
Estimate includes:		
Original equipment pads	*10,000*	
Replacement brake pads	*?*	
Brake pads on heavy-duty trucks, off-road vehicles, rail cars, and motorcycles	*?*	
Architectural copper	4,500	Moderate-High
Copper pesticides	<8,000 – <10,000	High
Estimate includes:		
Landscaping	*1,200 to 2,500*	
Wood preservatives	*1,400 to 2,800*	
Pool, spa, and fountain algaecides	*<5,000*	
Industrial copper use	3,300	Moderate
Deposition of copper air emissions	8,800[b]	Low to Moderate
Estimate includes:		
Diesel and gasoline fuel combustion	*3 – 60*	
Industrial facilities	*130*	
Residential wood burning and forest fires	*110*	
Unknown	*>8,000*	
Soil erosion	7,000	Moderate
Estimate includes:		
Construction	*2,600*	
Hydromodification	*<5,000*	
Copper in domestic water discharged to storm drains	3,000	Moderate-High
Vehicle fluid leaks and dumping	600	Moderate-High

[a]Uncertainty is defined as follows: Low indicates that the estimate has an error within 50%; Moderate indicates that the estimate has an error up to 2 fold; Moderate-high indicates that the estimate has an error up to 5 fold; High indicates an error up to 10 fold (see Section 1.4).
[b]May overlap with vehicle brake pad estimate.
Source: Section 3.

Conclusion 2. Shoreline copper sources have the potential to contribute significantly to copper levels in San Francisco Bay. Table 18 summarizes shoreline copper load estimates and their uncertainties.

Table 18. Summary of Shoreline Copper Sources (Pounds of Copper per Year Released to San Francisco Bay)

Copper Source	Load Estimate	Uncertainty
Marine antifouling coatings	20,000	Moderate-High
Copper algaecides applied surface waters	4,000	High

Source: Section 3.

<u>*Conclusion 3*</u>. The total of all estimated urban runoff copper loads (45,000 – 47,000 pounds per year, assuming air deposition does not overlap with other identified sources) is less than the total estimated stormwater copper load to San Francisco Bay (90,000 pounds per year, see Table 19). (Marine antifouling coatings and copper algaecides applied to non-industrial surface waters are assumed not contribute to urban runoff copper loads). Since many source estimates are highly uncertain, it is entirely possible that one or more estimates understates actual copper releases. While it is also possible that a significant copper source has not been identified, given the extensive investigations of copper sources for nearly 15 years in the San Francisco Bay Area, it is unlikely that a major source would not have been identified.

Table 19. Copper Load Estimates for San Francisco Bay

Sources	**Copper Load (lb/yr)***
All sources (excluding contribution from Delta)	160,000
Stormwater runoff from all land uses	150,000
Urban portion of total stormwater copper load (Residential, commercial, and industrial land uses)	90,000

*"Best estimate"
Source: *Contaminant Loads From Stormwater to Coastal Waters in the San Francisco Bay Region* (Davis *et al*., 2000)

4.2 Recommendations

<u>*Recommendation 1*</u>*. C*ontrol measures are warranted for vehicle brake pads, copper air emissions, architectural copper, industrial copper use, domestic water discharged to storm drains, soil erosion, and copper pesticides. Control measures are already in place for most of these sources. Table 20 (on the next page) summarizes identified feasible control measures (many of which are already being implemented by one or more San Francisco Bay Area agencies) and recommended priorities for investigation. In addition to the listed control measures, public outreach is feasible for all copper sources.

<u>*Recommendation 2*</u>. Control measures are warranted for marine antifouling coating copper shoreline releases. No control measures are currently in place for this source. Prior to implementing control measures, additional investigation is recommended and a pilot project should be considered (see Table 20).

<u>*Recommendation 3*</u>. Improved load estimates for copper pool, spa, and fountain algaecides are needed to determine the appropriate types of control measures.

<u>*Recommendation 4*</u>. Investigation is needed to determine appropriate control strategies for copper marine antifouling coatings and copper air emissions sources.

<u>*Recommendation 5*</u>. Because measures to reduce landscaping copper pesticide use could adversely impact human health or the environment, potential measures and their impacts should be evaluated for safety and effectiveness prior to implementation.

Table 20. Summary of Feasible Control Measures (Other than Public Outreach) and Priorities for Investigation for Copper Sources in Urban Runoff and Shoreline Activities

Copper Source	Feasible Control Measures	Priorities for Investigation
Vehicle brake pads	• Brake Pad Partnership (BPP)	• Improved load estimate (BPP)
Architectural copper	• Requirements for management of wastewater from cleaning and treatment • After completing the recommended investigation, consider limiting installation and/or requiring measures to prevent copper releases or to treat roof runoff	• Practicality and efficacy of control measures such as coatings and runoff treatment measures
Copper pesticides	• Consider developing best management practices for wood preservatives to minimize copper use where releases are most likely • Regulatory control measures for pool, spa, and fountain algaecides are feasible; use improved load estimate to determine if they are warranted	• Improved estimate of the copper load from algaecides (primarily pool, spa, and fountain algaecides); use estimate to determine whether regulatory measures are warranted • Evaluate alternative practices and pesticides for landscaping to determine if safe and effective alternatives exist
Industrial copper use	• Industrial stormwater permit program	None
Copper air emissions	• Not able to identify appropriate measures at this time • Additional controls on identified sources are not warranted	• Identify major air emissions sources • Determine overlap with brake pad wear debris (BPP studies will provide data)
Soil erosion	• Construction stormwater permit program • Hydromodification management plan requirement	None
Copper in domestic water discharged to storm drains	• None (other than public outreach)	None
Vehicle fluid leaks and dumping	• None necessary (other than public outreach)	None
Marine antifouling coatings	• Not able to identify appropriate measures at this time • Consider a non-toxic antifouling coatings pilot project	• Bay Area-specific load estimate • Participate in IACC Copper Antifouling Paint Sub-Workgroup investigation of copper problem and control measures
Copper algaecides applied to surface waters	• Aquatic pesticides permit program	None

Source: Section 3.

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APPENDIX A. Lower South San Francisco Bay *Copper Action Plan* Actions

Information in this appendix:

Table A-1. *Copper Action Plan* Baseline (Table 4-1) Actions

Table A-2. *Copper Action Plan* Phase I (Table 4-2) Actions

Table A-3. *Copper Action Plan* Phase II (Table 4-3) Actions

Table A-1. *Copper Action Plan* Baseline (Table 4-1) Actions

Action	Description	Copper Source
B-1	Vehicle washing consistency in level of implementation	Vehicle washing, including mobile cleaners (conveys copper from brake pads, other vehicle sources, and soil)
B-2	Continue to track copper sulfate use by water suppliers (includes State & Federal water project)	Copper algaecides
B-3	Complete Industrial-2: investigations (based on MCMP), identify and implement reasonable controls in conjunction with industry (older printed circuit board manufacturers with copper plating) to reduce elevated levels in runoff from targeted industry including development/implementation of education and outreach plan Clarify linkage with POTW Pretreatment program	Industrial copper uses
B-4	1-Provide appropriate level of local support for agreed upon quantification studies to: 2-Investigate and/or track quantification studies for a wide range of existing copper control/pollution prevention measures and sources loadings (update copper pie charts contained in MCM based on data from B-6 and B-16) 3-Collect data and prepare annual reports on the following potential indicators Copper content in new auto brake pads • Total population in basin • Auto/truck vehicle traveled in basin • Copper sulfate (*e.g.*, algaecide, pesticide, industrials; chemicals) sales in basin (aggregate basis-scaled to basin level estimate) • Copper content in macoma tissue at Sand Point (Palo Alto • Reproductivity index for macoma at Sand Point • Benthic community assemblages at Sand Point 4-Prepare issue paper on feasibility of potential field investigation to monitor long-term trends between copper from brake pads and concentration in water	All sources

Table A-1. *Copper Action Plan* Baseline (Table 4-1) Actions (Continued)

Action	Description	Copper Source
B-5	Provide appropriate level of local support for agreed upon BPP activities consistent with MCM 1-Review/assess/provide input on BMC/BPP brake pad wear debris research & brake pad content data 2-Ensure that other local state and Federal players are involved appropriately on brake pads issue as it is a widespread urban concern 3-Assist in making research data that are in the public domain accessible	Brake pads
B-6	Review appropriateness of transportation control measures, prioritize reasonable measures and identify potential efforts for further development as part of Phase I and implementation as part of Phase II	Brake pads and other vehicle sources
B-7	Establish transportation/impervious surface "forum" • Consider results of VMT and imperviousness load estimates and control effectiveness evaluation; identify potential control efforts for further development as part of Phase I and implementation as part of Phase II	Brake pads and other vehicle sources
B-8	Continue to implement watershed classification and assessment efforts of SCBWMI and improve institutional arrangements for watershed protection (review Vol. II Chapter 5/CCMP/CONCUR findings for relevance and possible gaps as part of C-31)	n/a
B-9	Continue current efforts and track corrosion control opportunities: • Continue educational outreach, within the City of Palo Alto, to plumbers and designers to reduce corrosion of copper pipes via better design and installation • Track developments in (1) alternatives to copper piping (b) corrosion inhibitors, and (c) other methods of reducing copper corrosion	Copper pipes
B-10	Utilize results of SEIDP indicator #5 (Sediment Characteristics and Contamination) to investigate development of an environmental indicator and investigate the linkage with SFEI sources and loading work effort	n/a
B-11	Consider need for Continuous Improvement of street sweeping controls and storm water system operation & maintenance controls (key emphasis is to develop SOP for disposal of collected materials)	Brake pads, other vehicle sources, and soil
B-12	Maintain existing education and outreach program for pools and spas	Copper algaecides

Table A-1. *Copper Action Plan* Baseline (Table 4-1) Actions (Continued)

Action	Description	Copper Source
B-13	Track POTW Pretreatment Program efforts and POTW loadings	Wastewater (conveys copper from many sources)
B-14	Track and encourage water recycling efforts	Wastewater (conveys copper from many sources)
B-15	Utilize results of SEIDP to evaluate effective ness of related SCVURPPP Performance Standards and identify cost-effective modifications	n/a
B-16	Establish Information Clearinghouse (Track & disseminate new scientific research on copper toxicity, loadings, fate and transport, and impairment of aquatic ecosystems for use in CAP update; provide stakeholder resource)	n/a
B-17	Track and encourage investigation of several important topics that influence uncertainty with Lower South Bay Impairment Decision • Phytoplankton toxicity and movement (IAR Section 5.3.1) • Sediment cycling • Loading uncertainty. Encourage incorporation of appropriate bioassessment tools into ongoing monitoring programs to track presence of copper-sensitive taxa in LSB Prepare issue paper on feasibility and cost of addressing phytoplankton toxicity questions	n/a
B-18	Track and encourage investigation of important factors that influence copper and fate (potential reduction in uncertainty is moderate to high) • Investigate flushing time estimates for different wet weather conditions • Investigate location of northern boundary condition • Determine Cu-L1 and L2 complex concentrations • Investigate algal uptake/toxicity with competing metals	n/a
B-19	Continue to promote industrial water use and reuse efficiency. These programs may include workshops, outreach, incentives, or audits (see Appendix 4-1 #35)	Industrial copper use (and other water supply sources)
B-20	Revise copper conceptual model report findings and produce status report (revise conceptual model uncertainty table, appendix __ based on available information)	n/a
B-21	1-SCVURPPP & Co-permittees evaluate feasibility of discouraging architectural use of copper & explore feasibility of related policy 2-Promote Green Building principles and identify measures to investigate as part of Phase I	Architectural copper

Table A-2. *Copper Action Plan* Phase I (Table 4-2) Actions

Action	Description	Cu Source
I-1	Update findings and recommendations of BPP efforts and implement agreed upon Phase I measures and develop Phase II Work Plan	Brake pads
I-2	Update findings and recommendations of transportation/impervious surface "forum" and implement agreed upon Phase I measures and develop Phase II Work Plan	Brake pads, other vehicle sources
I-3	Update and re-evaluate source identification (MCMP for copper) and prioritize sources based on effectiveness evaluation of future potential control actions. Prepare and implementation plan reflecting the priorities and implement agreed upon Phase I control actions.	All sources
I-4	Prepare and implement a Phase I plan for improved corrosion control based on evaluation of results of Baseline measures	Copper pipes
I-5	Evaluate street sweeping and other design, operation and maintenance practices to identify potential improvements. Prepare and implementation plan reflecting the priorities and implement agreed upon Phase I control actions.	Brake pads, other vehicle sources, soil
I-6	Follow-up on relevance of copper in diesel exhaust	Diesel fuel
I-7	Develop Phase II Implementation Plan for POTW expansion for water recycling	Wastewater (conveys copper from many sources)
I-8	Evaluate and investigate important topics that influence uncertainty with LSB Impairment Decision • Phytoplankton toxicity and movement (IAR Section 5.3.1) • Sediment cycling • Loading uncertainty	n/a
I-9	Evaluate and investigate important factors that influence copper fate (potential reduction in uncertainty is moderate to high) • Investigate flushing time estimates for different wet weather conditions • Investigate location of northern boundary condition • Determine Cu-L1 and L2 complex concentrations Investigate algal uptake/toxicity with competing metals	n/a
I-10	Evaluate results of tracking industrial virtual closed-loop wastewater efficiency measures and develop potential actions. Prepare an implementation plan reflecting the priorities and implement agreed upon Phase I control actions.	Industrial copper uses
I-11	Develop Phase II implementation plan for POTW process optimization	Wastewater (conveys copper from many sources)
I-12	Develop a Phase II plan include a re-evaluation for Phase I actions	All sources

Table A-3. *Copper Action Plan* Phase II (Table 4-3) Actions

Action	Description	Cu Source
II-1	Reconsider usefulness of management stormwater through POTWs	Urban runoff (conveys copper from many sources)
II-2	Implement agreed upon Phase II surface control measurement (transportation/imperviousness/brakepad)	Brake pads, other vehicle sources
II-3	Implement plan for additional corrosion control measures	Copper pipes
II-4	Discourage use of copper based pesticides	Copper-based pesticide
II-5	Implement control actions identified for copper in diesel exhaust	Diesel fuel
II-6	Implement Phase II POTW process optimization measures	Wastewater (conveys copper from many sources)
II-7	Implement agreed upon Phase II expansion of water recycling programs	Wastewater (conveys copper from many sources)
II-8	Re-evaluation Phase II Plan (developed as part of I-1) and finalize for implementation	All sources

APPENDIX B. Pesticide Calculations

Information in this appendix:

Table B-1. Bay Area Copper-Containing Pesticide Use Estimate, 2002

Pesticide	% Cu	2002 Sales (lb A.I.)	2002 Statewide Reported Use (lb A.I.)	Reported Ag. Use (lb A.I.)	Reported Boat Use (lb A.I.)	Reported Water Use (lb A.I.)	Estimated Statewide Urban Use (lb A.I.)	Copper in Statewide Estimated Use (lb Cu/yr)	Estimated Bay Area Copper Use* (lb Cu/yr)
Copper	100	326,000	45,857	38,661	0	534	286,805	286,805	56,501
Copper 8-quinolinoleate	18		10	0	0	0	10	2	0
Copper Ammonia Complex	100	14,277	5,543	4,580	0	0	9,697	9,697	1,910
Copper Ammonium Carbonate	33		42	30	0	0	12	4	1
Copper Bronze Powder	100		25	0	25	0	0	0	0
Copper Carbonate	57	14,274	7,878	0	0	1,650	6,228	3,550	699
Copper Ethanolamine Complexes, Mixed	100	171,230	17,721	19	0	4,893	166,318	166,318	32,765
Copper Ethylenediamine Complex	100		2,557	0	0	1,101	1,456	1,456	287
Copper Hydroxide	65	3,940,156	2,592,460	2,584,220	0	0	1,355,936	881,358	173,628
Copper Naphthenate	10	380,620	84,476	15	0	0	380,605	38,061	7,498
Copper Oxide (Cupric)	80		127,523	1,313	0	0	126,210	100,968	19,891
Copper Oxide (Cuprous)	89	1,146,625	229,214	213,518	15,032	0	918,075	817,087	160,966
Copper Oxychloride	58	84,997	58,934	58,508	0	0	26,489	15,364	3,027
Copper Oxychloride Sulfate	100		174,700	174,700	0	0	0	0	0
Copper Resinate	9		18,612	18,577	0	0	35	3	1
Copper Soap (Copper Octanoate)	18	250	0.007	0	0	0	250	45	9
Copper Sulfate (Basic)	53	1,455,054	876,722	875,681	0	173	579,200	306,976	60,474
Copper Sulfate (Pentahydrate)	25.5	5,646,324	2,916,477	2,867,412	0	129,280	2,649,632	675,656	133,104
Copper Thiocyanate	52		61	0	52	0	9	5	1
Copper Triethanolamine Complex	100	256	2	0	0	0	256	256	50
TOTAL								**3,303,610**	**650,811**

Source: TDC Environmental calculations with data from DPR (DPR, 2004; DPR 2003a; DPR, 2003b).