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CONTAMINANT MONITORING AND RESEARCH

submitted to Brake Pad Partnership

# Castro Valley Atmospheric Deposition Study

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## **Brake Pad Partnership Castro Valley Atmospheric Deposition Study**

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The Brake Pad Partnership

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**ABSTRACT**

This report summarizes the results of a study of atmospheric deposition of copper and other trace elements conducted in Castro Valley, California from March 2004 through February 2005. The primary objective of the study was to characterize the wet and dry deposition of selected trace metals and trace organic pollutants from the atmosphere to the Castro Valley Creek watershed, as part of a larger effort led by the Brake Pad Partnership examining the contribution of brake pad material to the release of copper in the environment and its potential to negatively impact environmental water quality. Precipitation and dry deposition samples were collected at four sites spread to measure deposition across a range of urban development and activity in the watershed (Figure 1). For several sampling events, ambient (gaseous) samples were also collected and analyzed for benzene.

Dry deposition fluxes of copper averaged for all collection events at each site in Castro Valley ranged from 9 to 29  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ . Deposition rates varied widely among sites and among sampling events within any site over the course of the study. Volume weighted average concentrations of copper measured for each site in wet or bulk samples ranged approximately 1.0 to 3.1 ppb ( $\mu\text{g}/\text{L}$ ). Resultant average fluxes at each site (for all sampling events) in bulk and wet deposition samples ranged 2.1 to 9  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  for copper, with a large amount of variation among sampling events. The wet and dry deposition rate combined could therefore total nearly 40  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , well above previous results for sites in the San Francisco Estuary, but comparable to rates measured in other urban areas in the United States.

Large temporal variability in measured deposition rates was found as expected. Both wet and dry deposition rates are influenced by conditions during each sampling period, which typically spanned two weeks for wet and bulk deposition samples, and two days for dry deposition. Dry deposition samples were also collected during weekend periods and show small and inconsistent differences between weekday and weekend deposition rates.

Significant differences in deposition at the lowest versus highest traffic sites were found, with differences among the three monitoring sites in the densely developed areas low in the watershed being less distinct. Deposition differences among high and low traffic sites may also in part be caused by differences in elevation, with the lowest traffic areas located high in the watershed, requiring substantial vertical transport for pollutants generated in the valley to be seen.

## 1.0 INTRODUCTION

Copper, a pollutant of concern in San Francisco Bay, is present in some brake pad formulations, ranging up to nearly ~7% of brake pad mass (BPP 2004). Copper from brake pads therefore possibly contributes in part to copper loading in urban runoff to the San Francisco Bay. The Brake Pad Partnership (BPP), a consortium of manufacturers, environmental organizations, stormwater management agencies, and regulatory stakeholders joined together to implement a program to identify and prevent water quality impacts that may arise from the use of copper in automotive brake pads.

Current plans are to de-list the Lower San Francisco Bay as a copper-impaired water body, but only on the condition that copper levels remain constant or decrease. However, copper content in brake pads has increased to meet safety regulations and consumer demand, and the number of vehicles on the road continuously increases. Concerns of increased copper loadings to the Bay in urban runoff have therefore arisen, and this study, part of a larger Brake Pad Partnership effort, aims to better quantify any potential impacts that brake wear material will have on the environment to better mitigate or prevent any negative effects.

Pollutants such as copper are emitted into the atmosphere either naturally by processes such as wind driven soil resuspension, or by human activities such as industrial discharges, stationary sources such as furnaces, and mobile sources like motor vehicle operation. The distance air pollutants are carried depends on multiple factors such as weather conditions, the nature and location of the source, and the particle size distribution of pollutants (or the aggregates they may form). Deposition of atmospheric pollutants to a watershed may occur through processes including rain scavenging of gases and particles and dry deposition of particles. Because metals such as copper are largely not found in the gaseous phase, diffusive exchange and adsorption to surfaces are not significant deposition pathways of concern for these pollutants.

Previously, gross calculations of atmospheric deposition were made based on ambient air monitoring results of the California Air Resources Board (CARB) and the Bay Area Air Quality Management District (BAAQMD) (Kirschmann and Grovhoug 1996, Hauri 1998a, Hauri 1998b). In 1999-2000, the Regional Monitoring Program (RMP) Atmospheric Deposition Pilot Study (Tsai et al. 2001) directly examined deposition in precipitation and onto surrogate surfaces at three sites around the estuary. The primary objective of the previous RMP study was to estimate the deposition of several trace element pollutants directly to the San Francisco Estuary surface. Monitoring sites were therefore located as far away as possible (generally over 500m) from known sources such as roadways and as near to the water as possible.

Results of that study showed metals (including copper) in precipitation at concentrations similar to those of other locations in the United States (Table 9), with wet and dry deposition rates falling within the middle- to low-range of deposition for a number of water bodies bordered by urban areas. Although concentrations and deposition rates varied greatly among collection events in the RMP study, annual average concentrations and deposition were similar among sites, suggesting that the sampling at various locations successfully captured generalized “ambient” deposition as intended in that study.

That RMP study also provided estimated contributions of pollutants to the estuary via tributaries using simplistic assumptions of runoff and retention in surrounding watersheds, but measurements from the sampling locations studied would potentially underestimate deposition for urban land uses due to the intentional location of those monitoring sites in open space areas away from urban activities such as transportation. Concentrations of vehicle pollutants near roadways typically drop rapidly, often returning to near background concentrations in the soil within less than 50 meters of the road side (Sutherland and Tolosa, 2001, Ely et al. 2001). Unlike the case for monitoring and modeling deposition directly to the estuary surface, pollutant flux estimates for urban watershed surfaces could be highly sensitive to the spatial scale examined.

In order to address these and other limitations in our understanding of copper sources, fate, and transport in urban watersheds, the Brake Pad Partnership initiated a multi-disciplinary project examining the many facets of emissions and transport of copper to the environment from vehicle brake pads and other sources. This air deposition monitoring study is one element of that larger project. The San Francisco Estuary Institute (SFEI), coordinator of the previous RMP Atmospheric Deposition Pilot Study, collected field samples and conducted the study in collaboration with Professor Thomas Holsen's Laboratory at the Clarkson University Department of Civil and Environmental Engineering, which provided advice, sampling materials and analytical support.

Although the previous RMP study attempted crude estimates of pollutant transport in runoff and other watershed processes, in this study we do not attempt to track pollutant transport beyond its deposition to the surface, as subsequent processes are examined in other portions of the overall BPP project. Modeling of subsequent transport processes is addressed in the airshed modeling conducted by AER and watershed modeling by to be performed by EPA.

Castro Valley is moderately to densely developed, with a mix of residential, commercial, light industrial, and open space land uses. Unlike the surface of the San Francisco Bay examined in the RMP study, few areas in Castro Valley are far from a major road or highway. To obtain a range of data more suitable for examining pollutant atmospheric deposition and transport processes in a highly urbanized watershed like Castro Valley, this study monitored deposition of copper and other trace elements at sites both near and far from expected major urban sources such as highways and major roads. Methods used were largely identical to those of the RMP Atmospheric Deposition Study (Tsai et al. 2001), based on monitoring methods for trace metals in dry deposition (Holsen et al. 1993, Yi et al. 1997a, Yi et al. 1997b, Paode et al. 1998) and in precipitation (Vermette et al. 1995b) used by other researchers.

This report describes the methodology used in the Brake Pad Partnership Castro Valley Atmospheric Deposition Study (hereafter simply referred as this study) and presents the results obtained from monitoring in this study for copper and other selected trace elements. In addition to copper, iron was an element of primary interest because it was measured also in the characterization of brake wear material. Although other elements uniquely indicative of particular vehicle or non-vehicle sources have not been identified, other elements easily measured using ICP-MS were also included for reporting to aid in identification of anomalous measurements and verifying emissions estimates and transport models. This report also presents results from more limited



monitoring of gaseous benzene as a compound representative of vehicle exhaust gases. Sampling methods for ambient benzene were derived from those described in EPA Method TO-15 (EPA 1999), as specified by the contract analytical laboratory, Air Toxics, Ltd.

## 2.0 OBJECTIVES

The BPP has selected the Castro Valley Creek watershed as an area for monitoring and modeling to be representative of mixed urban and open space land uses that may be found in the San Francisco Bay area. Information from these linked studies will be examined with the intention of identifying possibilities for extrapolating or extending data and models developed for this small watershed to other watersheds in the region. The primary objectives of this study (within the larger BPP project) are to:

- measure atmospheric deposition of copper at various sites in the Castro Valley Creek Watershed.
- determine if there are significant spatial and temporal differences in deposition at the monitored sites.
- measure other trace elements and benzene to allow potential evaluation of the contributions of vehicle and other sources to copper emissions and deposition to the watershed.

Characterizing and quantifying brake emissions, modeling of atmospheric and hydrologic transport, and water monitoring in Castro Valley Creek are other major elements of the larger BPP project. This air deposition monitoring will be used in evaluating the performance of the modeling efforts to verify that the developed models reasonably reflect the actual behavior and ultimate fate of brake pad material in the environment.

Although studies in other locations have shown large differences in pollutant transport and deposition over small spatial scales (Ely et al. 2001, Sutherland & Tolosa, 2001), there are no data confirming these conceptual expectations for the San Francisco region. One important outcome of the monitoring would be the verification of similar differences over small spatial scales for the study watershed.

Deposition rates of copper and other pollutants in the Castro Valley Creek watershed are also expected to be higher than for sites near the estuary shore and away from roads and other sources. However, it is unknown whether and how much higher deposition in Castro Valley will be relative to previous monitoring by the estuary. Copper concentrations in brake pads of the new vehicle fleet have also increased since the previous atmospheric deposition study (in 2000), so the monitoring data can also be used to confirm whether these expected trends of increased copper are actually found in monitoring.

Modelers will not be using the air deposition monitoring data to directly calibrate emissions estimates or transport models of copper and other pollutants. Instead, modeled scenarios will be compared to monitoring data to evaluate overall model performance and potentially identify factors not adequately addressed in the modeling. Unless enough distinct source signatures are known or found and there is a large enough dataset to overcome sampling and analytical variability, it is generally difficult to reconstruct

multiple sources from ambient monitoring data. However, once a model is constructed from other data sources (use surveys, source material characterization, modeled environmental processes), monitoring data are useful for determining whether the model results in reasonable outcomes or is missing important sources and processes.

### 3.0 METHODOLOGY

Deposition of air pollutants to the Estuary and surrounding watersheds can occur by two general processes, wet deposition by rain scavenging of gases and particles, and dry deposition processes, including settling of particles, gaseous adsorption, and air-water exchange processes. Air-water exchange does not occur for the non-volatile trace metals addressed in this report, and deposition through condensation is not specifically targeted for quantitation in this study, although the methods employed may incidentally collect some metals deposited through this pathway. This study of atmospheric deposition consisted of wet or bulk sample collection (depending on the equipment available at the location and the weather conditions during the collection period) during rainy periods and dry deposition samples collected during non-rainy periods.

The wet deposition portion of the project measured pollutant concentrations in rainfall, captured by specific precipitation collectors like those used in the National Atmospheric Deposition Program Mercury Deposition Network (NADP/MDN) or with bulk deposition collectors for locations and times where use of the automated precipitation collectors was not possible or practical. This study employed a direct method for dry deposition monitoring, measuring pollutant concentration in particles deposited and trapped on a surrogate (greased plate) surface during dry (non-rainy) periods. Other studies such as one recently conducted by SCCWRP and UCLA in Southern California (Sabin et al. 2004) used an indirect method for measuring pollutant concentrations in ambient air and calculating deposition using relevant equations, and assumptions or measurements of particle size distributions, concentrations, and meteorological parameters. The direct method using surrogate surface plates was chosen for this study to mirror the previous atmospheric monitoring study in this estuary (Tsai et al. 2001). Ambient gaseous benzene was also measured in a limited number of samples using evacuated canisters following EPA Method TO-15.

An initial design for this study was included in the BPP Proposition 13 grant proposal to collect wet and dry atmospheric deposition samples from two sites in Castro Valley every two weeks over the course of a year. The study design was reviewed and refined subsequently by the BPP steering committee and Science Advisory Team (SAT). Components that evolved and were modified after the initial proposal over the course of the study included the suite of measured chemicals, monitoring duration and frequency, and sampling site selection. A brief description of the study scope and methods is presented below.

#### 3.1 Monitoring Parameters

This study was designed to measure a common set of elements including copper in both wet and dry deposition. Discussions among the BPP steering committee and SAT sought chemical indicators specific to brake wear material but none were identified. Antimony was identified as one metal possibly enriched in vehicle sources, and measurements of elements common in soils such as iron, aluminum, and silica (Bradford,

1996) were included as possible elements dominating non-vehicle sources. However, the latter elements are also common in automotive materials, so any estimates of “non-vehicle” contributions to copper deposition on the basis of these other elements would represent overestimates or upper bounds of such sources.

A number of these other elements mentioned previously were included in the air deposition monitoring, but none were expected to provide distinct quantitative evidence of brake wear material. A more general indicator of vehicle traffic was therefore also sought. Benzene, an aromatic hydrocarbon, constitutes approximately 1-2% of gasoline (CARB, 1997) and is emitted in vehicle exhaust from a combination of unburned fuel and as a by-product of partial combustion of other fuel components. Mobile emissions are known to be a dominant source of benzene, accounting for 78% of the total benzene emissions in Alameda County (CARB, 1999). Benzene was added late in the study in September 2004 as an additional monitored pollutant to potentially indicate general magnitudes of vehicle sources at monitored sites.

### 3.2 Monitoring Duration and Frequency

This study measured wet and dry deposition over the course of a year at various sites within the Castro Valley Creek watershed. Monitoring frequency and duration of wet deposition samples for most of the Study was set on a 14-day schedule, to include the same proportion of weekday and weekend days in most of the collected samples. Early in the study in spring 2004, some wet deposition collections were extended for one or two weeks during periods without precipitation, in an attempt to capture at least one rain event per deployment. Bulk deposition samplers were deployed in areas where automated wet deposition samplers could not be used, and they were later used in the study during late spring and early fall 2004, periods when precipitation was sporadic and the ability to collect wet samples would not be reliable. Wet or bulk deposition samples were collected beginning in March 2004 and ending February 2005.

Dry deposition samples were generally collected approximately twice a month beginning July 2004, but the samples were not distributed uniformly throughout each month. The two-day exposure periods for the dry deposition samples needed to be scheduled during periods without rain, so samplers could not be deployed on a regular set schedule. Furthermore, with exposure periods lasting only 2 days, it was hoped that significant differences between weekend and weekday samples could be captured. However, large changes in meteorological conditions that could occur over the course of a week or longer might also change deposition rates in collected samples for reasons unrelated to weekend or weekday differences in traffic and urban sources. Therefore all weekend samples were deployed immediately after weekday dry deposition samples were collected, to minimize the influence of changing weather or other longer term causes of variability. Dry deposition samples were collected until the end of the study in February 2005. However, only one dry sample was taken at each site per month for most of the wet season months in the study (Table 2). With exception of the last sampling event, all dry deposition samples were collected at least 5 days after the last previous rain event measured over 0.1 inch (2.5mm) at nearby meteorological stations.

### 3.3 Monitoring Stations

The Castro Valley Creek watershed encompasses most but not all of Castro Valley. Castro Valley is highly urbanized, with a mix of residential, commercial, light

industrial, and undeveloped (open space) land uses. There are many congested roads within Castro Valley, with the highest volume roads being the Highway 580/238 corridor, Castro Valley Boulevard, and Redwood Road.

In the San Francisco Bay region, winds originate from the west and northwest during most of the year, (BAAQMD 1998). In the winter, stormy periods with moderate and strong winds ( $>5$  m/sec) are interspersed with stagnant periods with very light winds ( $<1$  m/sec) when air masses can flow from various directions. The San Francisco Bay region has a “Mediterranean” climate with distinct wet (November to April) and dry seasons (Trujillo et al. 1991).

Where possible, especially for placing the wet deposition samplers, sampling locations were selected to comply with the siting criteria prescribed in the National Atmospheric Deposition Program (Bigelow 1984). The NADP prescribes 11 criteria for locating and maintaining sites where collectors are deployed, with the general aim of reducing deposition and changes in wind flow from surrounding buildings and other objects. Criteria most relevant to this project include the following:

1. The COLLECTOR should be installed over undisturbed land on its standard 1 m high aluminum base. Naturally vegetated, level areas are preferred, but grassed areas and slopes up to  $\pm 15\%$  will be tolerated. Sudden changes in slope within 30 m of the collector should also be avoided. Ground cover should surround the collector for a distance of approximately 30 m. In farm areas a vegetated buffer strip must surround the collector for at least 30 meters.
2. Annual vegetation within the site should be maintained at less than 2 feet in height.
3. No object or structure shall project onto the COLLECTOR or RAINGAGE with an angle greater than  $45^\circ$  from the horizontal ( $30^\circ$  is considered optimal, but  $45^\circ$  is the highest angle acceptable). Therefore the distance from the sampler to the object must be at least equal to the height of the object (preferably twice the height of the object). Residential dwellings must be kept twice their height from the collector ( $30^\circ$ ). Pay particular attention to anemometer towers and overhead wires.
4. Residential structures within 30 m of the COLLECTOR should not be within the  $30^\circ$  cone of the mean wind direction.
5. The base of the COLLECTOR should not be enclosed. Further, any object over 1 m high with sufficient mass to deflect wind should not be located within 5 meters of the COLLECTOR. Alter wind shields and open fences are excluded from this requirement.

Additional criteria for siting sampling locations for this study included the following:

- accessible and secure
- adequate AC power (for wet deposition samplers only)
- within the Castro Valley Creek watershed
- covering the largest possible differences in traffic sources

At the start of the study, two sampling sites were chosen using these criteria in order to accommodate the wet deposition samplers. Castro Valley Community Center (CVCC) is located on Lake Chabot Road, a four-lane road leading from downtown Castro Valley to Lake Chabot Park. The wet deposition sampler was placed on the rooftop on the western side of the building, approximately 30m east from the curb of Lake Chabot Road, and approximately 5m off the ground surface. Castro Valley Elementary (CVE) is a school on San Miguel Avenue, in a residential neighborhood and several hundred meters from Castro Valley Boulevard. The sampler at CVE was also

placed on the roof, approximately 20 meters west of San Miguel Ave, and 10m above the ground surface.

Two other sampling sites were added later in the study in order to capture a wider range of traffic conditions based on their proximity or distance from major roads. These sites had not been previously considered, as they were not suitable for deployment of the wet deposition samplers. However, it was decided that bulk and dry deposition samples should be collected at these locations. The Redwood Professional Building is located on Redwood Road, at the end of an exit ramp from eastbound Highway 580. The samplers were placed on a pole attached to the roof of the building, about 8m above the ground, and 30m east of Redwood Road. The end of the sampler pole was also about 30m south of the edge of Highway 580, and 5m below the road surface; the highway is elevated in that section of Castro Valley to pass over Redwood Road. The last sampler was placed near Madison Reservoir, a small enclosed reservoir operated by East Bay Municipal Utility District located in the upper watershed around 300m above sea level, along one of the ridges above Castro Valley. The reservoir is adjoined by two houses in the Columbia housing development about 60m to the north and south. The sampler was attached to a fence post, 3m above the ground surface, and about 30m west of Columbia Road, the main route into and out of the housing development, along a ridge about 10m higher than the road at that location.

### 3.4 Wet and Bulk Deposition

At sampling sites where continuous AC power was available, automated precipitation collectors (Figure 2) designed for the National Atmospheric Deposition Program/Mercury Deposition Network (NADP/MDN) were deployed to collect wet deposition samples. The device has been described in detail and evaluated by other investigators (Vermette et al. 1995a). Collectors (Aerochem Metrics, Inc., Bushnell, FL) were modified by the Illinois State Water Survey for the previous RMP study. Up to two sampling bottle and funnel assemblies could be deployed simultaneously in each machine. A precipitation sensor activated the lid to expose the funnels during a rain event. When the rain ceased, the sensor dried off, closing the lid.

Bulk deposition samples were collected using identical bottle and funnel assemblies, but the assemblies were loaded into a passive continuously open chimney rather than an automated sampler, and rinsed with a small volume (20ml) of water at the end of the collection period. The bulk deposition samplers would also collect some dry deposition during periods without rain, but the collecting surface, a smooth plastic funnel, allowed some resuspension and loss of dry deposited material. Procedures for the preparation of the bottles and funnels used in collecting wet and bulk samples are described below.

High-density polyethylene one-liter bottles and funnels with connecting adaptors were used to collect samples. Bottles, funnels and connectors were cleaned to reduce metal contamination. Bottles, funnels and connectors were soaked with Radiac<sup>®</sup> wash overnight, followed by a ~3% nitric acid soak for at least two hours, with multiple rinses of deionized distilled water between each solution. After these cleaning procedures, the materials were dried in a clean room under laminar-flow hood for at least 12 hours. The emptied bottles were capped, weighed, and double bagged for shipment.

Materials for wet and bulk sample collection were handled in the field using methods adapted from EPA 1669. The empty sample bottle was uncapped at the monitoring site, and a connector and funnel were attached. The assembly was checked for tightness and placed in the precipitation collector or passive sampler chimney. Site and sample conditions were noted on FOFs. At the end of the collection period, the funnel and connector were removed, and the sample bottle recapped and bagged for shipment to the laboratory.

Upon receipt at the laboratory, precipitation samples were weighed and acidified with trace-metal grade nitric acid to an acid concentration of 2 %. The samples were equilibrated for more than 48 hours before being analyzed. The samples were then analyzed using inductively coupled plasma-mass spectrometer (ICP-MS) following EPA Method 200.8. Blanks and calibration standards were measured periodically with samples in accordance with the EPA Methods and the project QAPP.

### 3.5 Dry Deposition

There are two general approaches for measuring dry deposition flux: 1) direct measurements of deposition using surrogate surfaces (direct method), and 2) calculated deposition using airborne concentration data and modeled deposition velocity (indirect method).

With direct methods, geometry of the surface, roughness, and collection substrate all influence the wind profile and local turbulence above the sampling surface, which in part controls the deposition flux. Surrogate surfaces are generally designed to minimize turbulence in the flow field so that minimum fluxes are measured.

Large particles are responsible for a large proportion of the deposition flux, but they may account for only a small fraction of the total airborne mass (Holsen & Noll 1992, Holsen et al. 1993, Shahin et al. 2000) due to large increases in deposition velocity for particles over 2  $\mu\text{m}$  diameter. Shahin et al. (2000) asserted that large particles are underrepresented in samplers used in most indirect flux estimates. Modeled fluxes are therefore often lower than those obtained by direct methods. Due to these limitations a direct method, employing surrogate surface plates, had been chosen for use in the RMP Atmospheric Deposition Pilot Study to collect dry deposition samples of trace metals.

To generate data most easily comparable to this previous monitoring effort in the San Francisco Bay region, a direct surrogate surface method was selected in this study. The sampler “Egret I” (Figure 3) used in this study and the previous RMP study was an adaptation of the prototype developed previously at Clarkson University (Holsen et al. 1991). The original sampling device, with greased Mylar films mounted on a knife-edge plate, has been described by Yi (Yi et al. 1997a, Yi et al. 1997b), and evaluated by other investigators (Holsen et al. 1993, Pirrone et al. 1995, Paode et al. 1998). A modified sampler with a larger surface area developed and manufactured for the previous RMP study was also used here. The total exposed surface area was 500  $\text{cm}^2$ . Plastic materials were used to construct the frame and various parts the sampler. In addition, transparent plastics were used whenever possible to reduce thermal microclimates induced from blackbody radiation.

A cartridge plate bearing a greased Mylar film was pointed into the wind with a leading knife-edge to provide a laminar or non-turbulent flow of air over the surface of

the film. The L-Apiezon grease applied to the Mylar film provided a sticky surface to capture particles, and prevent particle bounce and loss (Noll et al. 1990). L-Apiezon grease is largely free of the elements being monitored.

At the analytical laboratory, both surfaces of Mylar films were rinsed with deionized distilled water and cleaned and wiped with Optima<sup>®</sup> grade methanol. Other components included plastic cartridge plates, frames, binder clamps, and clips. The Mylar films and components were then soaked in Radiac<sup>®</sup> wash overnight, followed by a soak in ~3% nitric acid for at least two hours, with multiple rinses of deionized distilled water between each solution. After washing, the Mylar films and other components were dried in a clean room under a laminar-flow hood for at least 12 hours. Mylar film was mounted in the plastic cartridge plate, and approximately 100 mg of L-Apiezon grease was then applied to each film, using a piece of clean-room lint free cloth “Spec-Wiper<sup>®</sup> 4”. The Mylar film and cartridge plate was heated to aid in spreading the grease. Each cartridge plate was placed into a plastic box that was in turn enclosed in two plastic bags by the laboratory. The sampling plates were then shipped to SFEI

When installing or retrieving samples, ultra-clean field techniques adapted from EPA Method 1669 “Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels” (USEPA 1996) were practiced to minimize contamination from field operations. The Egret I sampler could hold up to two wind-vanes that pivot according to the wind direction (Figure 3). However, generally only one vane was mounted in the sampler at a time, with the exception of collection periods when field replicates were collected. For each sample to be collected a Mylar film cartridge plate assembly prepared by the laboratory was removed from its shipping container and mounted and secured to the wind-vane with plastic clips.

Each greased Mylar film was exposed 48 hours for collection. Field site and sample conditions were recorded on a field observation form (FOF). Duplicate samples as well as trip blank samples were collected for a subset of sampling events (approximately 1 for each 10 field samples). Trip blanks were transported to field sites but were not removed from their containers while in the field.

After samples were retrieved and returned to the laboratory, the greased Mylar film was rinsed with 50ml hexane to recover the collected material. The Mylar film was rinsed a second (and often a third time) with hexane to ensure that all material was recovered, with the rinses collected for separate analysis. The hexane was subsequently evaporated with a stream of ultra-pure nitrogen. After evaporation to complete dryness, 10 ml of trace-metal grade nitric acid was added to microwave digestion vessel liners. Samples were digested in the CEM microwave oven following EPA Method 3051. The samples were allowed to cool and were subsequently analyzed using inductively coupled plasma-mass spectrometer (ICP-MS) following EPA Method 200.8. Blanks were monitored to determine whether the sample preparation, the L-Apiezon grease and the hexane wash contributed to contamination. Samples concentrations were corrected by subtracting the concentrations obtained for the blank. Urban particulate matter (UPM) standard reference material (SRM) from NIST was analyzed along with samples to evaluate method recovery and quantitate accuracy.

### 3.6 Gaseous Trace Organics

Benzene in ambient air was collected and analyzed using EPA Method TO-15, which employs an initially evacuated stainless-steel canister (at sub-atmospheric pressure). Each sample canister after being initially evacuated at the analytical laboratory was individually proofed to ensure that the valve operated properly and that no contaminating gases remained in the canister. A mass flow controller (with attached vacuum gauge) was also calibrated to ensure that the proper flow rate was set for the planned deployment period. Proofed canisters and calibrated flow controllers were sent by the laboratory to SFEI for deployment.

The field team attached the flow controller to the canister and checked for tightness of the entire assembly by checking for loss of vacuum while the sample assembly was still capped and presumably closed to the atmosphere. The initial vacuum of the canister was recorded on the FOF. If all the equipment functioned properly to that point, the valve was opened for sample collection and left at the site for the collection period. The air sample is drawn through a coarse filter to exclude particles which would jam the canister valve or contaminate the canister interior. The mass flow controller regulates the rate of airflow into the pre-evacuated canister. For this study ambient air samples were collected concurrently with dry deposition samples (48 hour integrated samples). On completion of sampling, the field team closed the canister valve and noted the final vacuum of the canister. The flow controller was removed from the canister, and an identification tag and chain-of-custody (COC) form was completed. The equipment and paperwork was returned to the laboratory for analysis.

For analysis of volatile organics in ambient air samples, water vapor is reduced in the gas stream (as needed if applicable), and the VOCs are then concentrated by collection in a cryogenically-cooled trap. The cryogen is then removed and the temperature of the trap is raised. The VOCs originally collected in the trap are revolatilized, separated on a GC column, then detected by one or more detectors for identification and quantitation. In this study the analytical laboratory used gas chromatography with a mass spectrometer operated using selective ion monitoring mode (GC-MS-SIM)

### 3.7 Quality Assurance and Quality Control

Overall sample handling techniques used in the study closely followed the general clean technique principles as described in USEPA Method 1669 (USEPA 1996). Equipment and materials that had direct contact with samples were rigorously cleaned (see above). Additionally, clean sample bottles and funnels were double bagged. Surrogate surface plates with greased Mylar films were placed in polyethylene boxes before being enclosed in clean plastic bags. Powder-free polyethylene gloves were worn when handling samples.

#### 3.7.1 Wet and Bulk Deposition

For wet and bulk deposition, the majority of samples were analyzed at Clarkson University in Professor Thomas Holsen's laboratory. For samples collected during the first two wet sampling events, a commercial laboratory (Caltest) analyzed wet deposition samples for copper only. A summary of QA/QC results for the parameters reported are presented in Table 3. The copper reporting limit of the commercial laboratory was 0.2 µg/L (ppb), which was comparable to the method detection limit (MDL) for copper



reported by the Holsen laboratory of 0.23 ppb. MDLs for other analyzed elements, estimated as three times the standard deviations on replicates of laboratory blanks, are also shown in Table 3. Laboratory method blanks are used in calibrating the instrument, and trip blanks are subtracted from concentration measurements and deposition calculations.

System blanks were periodically collected to assess any contamination resulting from field operations. A system blank was generated by rinsing a small volume (20ml) of ultra-pure water through the sample funnel and collecting it in the sample bottle to determine the amount of contamination of the sampling train, similar to the process used at the end of collecting a bulk deposition sample. Table 3 also presents concentrations of analytes found in system blanks. Many of the trace elements were detected in the system blanks at concentrations above the MDL, particularly for elements typically abundant in both natural and anthropogenic sources (Mg, Al, Si, Fe, Zn). However, because the system blank volumes are small, the amounts per sample of even the most abundant contaminants (Fe and Mg) in system blanks averaged  $\sim 1 \mu\text{g}$ , well below the total amounts of these elements typically found in field samples, which typically have larger volumes.

### 3.7.2 Dry Deposition

Summary results of quality assurance and quality control (QA/QC) measurements for dry deposition samples are presented in Table 4. One blank result for copper was over 4 standard deviations from the mean of the remaining blank results and was discarded as an outlier. Method detection limits (MDL) were defined as three times the standard deviation of blanks and are shown in Table 4 (in units of  $\mu\text{g}$  per sample). Dry deposition results were also blank-corrected.

Recoveries and RSDs on replicate analyses of the UPM reference material on average met the DQOs established for the Pilot Study (Table 4). Recoveries on trace elements on average deviated from the certified value by 10% or less, with the exception of Ni and Al. The average recovery error for Ni was 18%, and the average for Al was 26%, slightly over the target DQO. Precision on replicate analyses of the reference material was generally good, ranging 1-22% RSD.

### 3.7.3 Ambient Gas Collection

Benzene sampling QA/QC consisted of blank proofs on the collection canisters, and surrogates spiked to the canister prior to analysis. All canisters were proofed by the laboratory individually prior to shipment for field sampling. Benzene was not detected in any canisters. On arrival, canisters were tested for tightness ( $< -29$  in Hg vacuum) with a vacuum gauge supplied by the laboratory. After deployment, canisters were checked for remaining vacuum. Some canisters that reached ambient pressure (due to small leaks in connectors, misadjusted flow controllers, or other reasons) at the end of sampling were not analyzed, as the time of sampling completion could not be known and some loss of gases from the canister could have occurred. At the lab prior to analysis, canisters were spiked with labeled recovery surrogates. Recoveries of all surrogates were within control limits of the lab.

## 4.0 RESULTS AND DISCUSSION

This section presents results of the monitoring and loading estimates of the selected trace metals from the atmosphere to sampling sites in the Castro Valley Creek Watershed. These estimates are further compared with estimates of trace metal loading from atmospheric deposition previously found in the San Francisco Bay area in the RMP Atmospheric Deposition Pilot Study, and with results from studies in other regions.

### 4.1 Wet Deposition

A total of 49 precipitation samples were collected and analyzed from the two to four stations monitored over the course of the study, including field replicates and bulk/wet splits (Table 1). Sample volumes ranged from approximately 20 mL to nearly 800 mL for wet and bulk samples collected. Smaller sample funnels were deployed starting in 2005 to reduce the threat of overfilling bottles during a series of severe winter storms, so collected volumes of wet samples are proportional to each other only within each of the two sampling periods (before and after December 29, 2004). Furthermore, all bulk samples contain approximately 20mL of added water used to rinse the collection funnel, so collected bulk samples include a small volume not from precipitation. A number of samples were not successfully collected over the course of the study, indicated by “MF” (malfunction) in Table 1. Malfunctions in sample collection have included failure of the automated sampler lid to open due to jamming or sensor failure, funnels becoming disconnected from bottles, and unauthorized removal of a bulk sampler (by an unknown party) in one case.

Concentrations of the measured trace elements in wet and bulk samples varied widely among sampling events at each site and among the four sites. Average concentrations measured by the laboratory in each collected sample are presented in the appendix in Table A-1. Volume-weighted average concentrations of trace elements measured in samples for each site are summarized in Table 5. For bulk samples in particular, metal concentrations would be expected to vary widely, as some bulk samples would represent 14-day periods that were entirely or nearly dry, with accumulated dry deposition in the collection funnel washed down and collected in a small volume of water at the end of the collection period. In contrast, collections from extended rainy periods would have a large volume of water effectively diluting any dry deposited material. Figure 4 shows copper concentrations in wet and bulk deposition samples as a function of the total sample volume. Larger volume samples generally showed lower concentrations of trace elements, indicating washout and dilution of atmospheric material in larger rain events.

One sample from Madison (October 20-Nov3) had an unusually high concentration of copper (~22 ppb) despite occurring during a period with only a moderate amount of rain. On reanalysis by the laboratory, the high measured concentration was reconfirmed. However, for a majority of the samples collected, a number of trace elements correlate extremely well. Data from the California Air Resources Board (CARB 2004) show generally consistent ratios of various metals to copper in air particulate (TSP) monitoring at their Fremont location (1998-2002). Ratios of zinc, iron, and lead to copper in air averaged  $4.3 \pm 0.8$ ,  $77 \pm 28$ , and  $0.48 \pm 0.23$  respectively.

In wet and bulk samples collected in Castro Valley, copper concentrations also correlate well with zinc and other elements not shown, but one sample from Madison in this period did not, with a ratio of Cu/Zn well outside the usual range (Figure 5). This value was therefore flagged as an outlier and was not included in calculations of flux rates or in statistical analyses.

Fluxes for wet and bulk deposition rates ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ) at the various sampling sites were calculated by using equation (1) shown below:

$$F = C \cdot V / A / EP \quad (1)$$

Where

- F = Deposition flux rate
- C = Concentration of trace elements in the collected sample
- V = Volume of sample collected, including water for funnel rinse
- A = Cross sectional surface area of the collection funnel
- EP = The exposure period

The surface area of collection funnels was calculated from their diameters at their tops, and the other parameters were measured or recorded for each sample collected. Deposition fluxes for all the wet and bulk deposition samples are calculated using this equation and tabulated in the Appendix in Table A-2. No meteorological stations were colocated with the wet or bulk samplers, but the approximate precipitation at any given station over a collection interval can be estimated (from  $V/A = \text{mL} / \text{m}^2 \cdot 0.001 = \text{mm}$  precipitation). Table A-3 shows the precipitation calculated by this method for the various monitoring sites compared to precipitation over the same collection period at Oakland South and Dublin Firehouse, stations with data compiled on the California Data Exchange Center, <http://cdec.water.ca.gov>. Although precipitation is expected to vary spatially, especially for small rain events, calculated precipitation totals among the Castro Valley sites (from volume and collection area data) and the CDEC sites nearby are generally similar.

For a number of measured elements, a large number of concentration results measured in wet and bulk samples were below the MDL (defined as  $3 \cdot \text{stdev}$  of replicate blank analyses determined at the laboratory), but it was decided to use the concentrations reported at less than MDL to calculate fluxes, as measures commonly used to assign values to non-detect records (e.g. assigning 0, half the MDL, or the MDL) can potentially introduce biases to a data set.

Similar to concentrations, flux rates in bulk and wet samples also varied widely among sites and between collection events within any particular site. Despite the variability, when the data are aggregated for each site and type of collection, some patterns emerge. Table 6 shows averages and standard deviations of calculated flux rates for all wet and bulk collection events at each site during the study.

As shown in Table 6, for many of the trace elements, flux rates at Redwood averaged higher than at other sites. Mean copper deposition rates for Redwood were significantly higher ( $p < 0.05$ ) than at the other sites using both parametric (Student's T-test, Tukey HSD) and nonparametric (Kruskal Wallis) statistical tests. Other elements for which deposition was significantly higher for Redwood than at other sites include Fe, Zn, Sr, Sb, and Ba. Parametric and nonparametric analyses generally agreed on significance

of differences, although the Tukey HSD test indicated a significant difference for Pb, whereas the Kruskal-Wallis did not.

On three occasions, bulk samplers were deployed at one or both of the wet deposition locations in order to collect both sample types side by side. On two of those events, either one or both of the samplers malfunctioned, and a sample could not be collected. However, two bulk samples (one at CVE and one at CVCC) were collected on events where the precipitation sampler appeared to be functioning properly. For the CVE sample (collected 29-Dec-2004 to 12-Jan-2005), the mass of water collected differed only by approximately the amount of water used for the collection rinse (651-633g = ~20mL). However, for the CVCC sample (collected during 9-Feb to 23-Feb-2005), the sample volumes collected differed by over 150mL, even though the automated precipitation sampler was functioning properly at the time the sample was collected. One possibility is that power to the roof outlet had been turned off for part of the collection period.

As was expected, wet deposition collected in these samples was lower than bulk deposition in the samples from the same period at the same sites. Despite the collected volumes being virtually identical, deposition rates for nearly all elements in the bulk collection bottle at CVE 29-Dec to 12-Jan were higher than for the corresponding wet deposition sample collected (Figure 6). Similarly, the pair of samples from CVCC 9-Feb to 23-Feb had greater deposition rates for nearly all trace elements in the bulk sample (Figure 7) as well, although the larger difference in collected volumes also contributed to the differences in measured deposition.

All other bulk and wet deposition samples were collected on different events at the various sites, and biases may occur because the bulk of bulk samples were collected from wet deposition sites during periods where rain was expected to be sporadic. However, the patterns seen are consistent with the expectation that for any given site and event; bulk samples would contain at the least all the elements in precipitation collected in wet deposition samples, plus a fraction of additional dry deposition occurring during periods when it was not raining.

#### 4.2 Dry Deposition

A total of 47 dry deposition samples were collected at up to the four monitoring stations over the course of the study. For some of the sampling events, duplicate samples were collected from one of the stations. The exposure duration was 48 hours for all collection events.

Similar to the wet and bulk deposition monitoring, the dry deposition rate ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ) at any given sampling site can be calculated using the same general formula:

$$F = C*V/A/EP \quad (1)$$

Where here

- F = Deposition flux rate
- C = Concentration of trace element in the analyzed extract
- V = Volume of final extract (10 ml)
- A= Exposed area of the surrogate surface collector
- EP = The exposure period

Dry deposition fluxes for individual samples, including field replicates, are tabulated in appendix Table A-4. Dry deposition fluxes varied among sampling events at all the sampling locations and dry deposition rates are averaged for all sampling events at each site in Table 7.

Similar to trends seen in the wet and bulk deposition data, for nearly all elements, deposition at Redwood was significantly higher (for Ti, V, Mn, Fe, Co, Cu, Zn, Sr, Ba, Pb, using both Tukey HSD and Kruskal Wallis tests) than at least one other site. Generally Redwood was significantly different from at least Madison, but for some elements Redwood was significantly higher than all other sites. Similarly, dry deposition at Madison was nearly always the lowest, with significant differences from one or more other sites. CVCC and CVE generally fell in between, significantly different from Redwood or Madison for some elements but not others.

Unlike results found previously in the San Francisco Bay area (Tsai et al. 2001), dry deposition fluxes were not significantly lower during the wet season, although a contributing factor may have been the small sample number for any given site (a maximum of five wet season sampling events, and eight dry season events). Similarly, comparisons of weekend versus weekday samples taken on three occasions showed no significant differences. Although other studies have measured lower measured airborne pollutants for samples taken less than five days after a rain event, nearly all dry deposition samples collected in this study were preceded by at least five days of dry weather with only trace amounts of rainfall (Table 2). As a result, the lack of any significant difference in dry deposition between the dry and wet season may not be surprising.

Average dry deposition flux rates (converted to an annual basis) were higher than reported in the previous RMP atmospheric deposition study (Table 8). Dry deposition fluxes in Castro Valley fell within the middle and upper range of those observed in urban areas and around other lakes and bays in the USA (Holsen et al. 1993, Wu et al. 1994, Golomb et al. 1997, Paode et al. 1998, Sweet et al. 1998, Zufall et al. 1998, Shahin et al. 2000). Results are most comparable to other studies using similar methods, as direct methods such as surrogate surface plates often yield measurements much higher than indirect methods with ambient air samplers. This differences between sampling methods is apparent in Table 8, as indirect methods generally reported lower deposition rates.

Concentrations of copper detected in precipitation samples collected from Castro Valley were similar to those in a previous study of the San Francisco Estuary and those found in the Great Lakes area (Sweet et al. 1998) (Table 9). In Table 9, all wet and bulk results for this study are aggregated to derive volume weighted average concentrations. Deposition fluxes of trace metals to Castro Valley estimated in this study were also similar but higher than those in the RMP pilot study and within the range of the fluxes reported for the Great Lakes (Sweet et al. 1998), Massachusetts Bay (Golomb et al. 1997), and Chesapeake Bay (Scudlark et al. 1994).

Dry deposition fluxes around Lake Michigan from December 1993 to October 1995, using an automated dry deposition sampler with knife-edge surrogate surfaces, were approximately 10, 7, 0.2, and 1.0  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$  (corresponding to 3,650, 2,555, 73, and 365  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ ) for Cu, Ni, Cd, and Cr, respectively (Shahin et al. 2000). Indirect

estimates made using a dichotomous sampler during 1993 and 1994 and an estimated overall deposition velocity for Lake Michigan IADN monitoring stations yielded lower dry deposition fluxes of 1,300, 320, 380, 130  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$  for Cu, Ni, Cd, and Cr, respectively (Sweet et al. 1998). Golomb et al. (1997) used both direct and indirect methods to measure the dry deposition of trace metals to the Massachusetts Bay, and found deposition flux of chromium for a direct method higher than an indirect method by a factor of two.

Although both this study and the previous RMP study in San Francisco Bay both used the same sampler design for direct measurements of dry deposition, the much higher Cu deposition fluxes measured in Castro Valley (e.g.  $\sim 18 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  or  $\sim 6500 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ ) compared to bay sites are not surprising. That study located monitoring sites as near to the bay as possible while avoiding sources such as roads as much as practicable, whereas this study aimed to capture the maximum range in impact of traffic and urban activities. A second factor possibly contributing to increased copper deposition rates in the current study may be a general increase in copper content of brake materials; brake pad copper content in a survey of 40% of the new vehicle market increased from an average 2.8% of brake material by mass in 1998 to 6.6% in 2003 (BPP 2004). Similar to sites used in the previous study, the Madison site was intentionally located as far as practicable from major roads. Despite that, copper deposition rates at Madison still averaged over a factor of two higher than in the previous study, perhaps reflecting the general trend of increasing copper in brake materials.

#### 4.3 Benzene Monitoring

Results of Benzene monitoring are presented in Table 10. Ambient benzene concentrations ranged 0.10 to 0.48 ppbv. For all sampling events, benzene concentrations at Redwood were higher than those at Madison. One pair of samples taken concurrently at Redwood (Nov 19-21) averaged  $0.34 \pm 0.05$  ppbv, whereas a sample from Madison taken at the same time (a weekend period) measured 0.14 ppbv. A sample taken at Madison on the prior weekdays (Nov 17-19) measured 0.25 ppbv, suggesting a weekend versus weekday difference in ambient benzene. However, considering the variability of field replicate samples taken, and assuming that variability at Madison would be similar ( $\pm 0.05$  ppbv), the weekend/weekday difference would not be statistically significant ( $p > 0.05$ ) in large part due to the small sample number. When all the sampling events are considered together, the difference between Redwood and Madison is significant. Ambient benzene concentrations are moderately correlated to copper deposition rates ( $R^2 = 0.49$ , Figure 8).

Although both brake pad copper and benzene are expected from vehicle sources, the correlation between their measurements may be weakened by a number of factors: (1) brake pad wear is generated while braking, whereas benzene is generated continuously during vehicle operation, and (2) the atmospheric behavior of particle-bound copper is different from gas-phase benzene measured. Contributions of copper from non-vehicle sources may also decrease the correlation between copper and benzene. Despite these confounding factors, the general pattern of higher copper deposition and benzene concentrations in the high traffic site (Redwood) relative to the low traffic site (Madison) matches our expectations given vehicles sources for both pollutants.

#### 4.4 Ratios of Copper to Other Elements

Examining the ratio of Cu to other elements measured in samples is one method of potentially verifying or placing reasonable bounds on source estimates used in modeling of brake pad copper emissions and transport, particularly if the sources have unique or distinct elemental distributions. In the previous RMP Atmospheric Deposition Pilot Study, the Cu/Ni ratio was explored as a possible indicator of different pollutant sources or transport mechanisms. However, because the detection limit for nickel in this study is higher than in the RMP study, determining ratios with more abundant elements (such as Fe) is preferable, as Cu/Ni ratios would be highly variable and uncertain when many measurements of Ni are below or near its detection limit.

Iron is measured in nearly all air deposition samples collected in this study, and it is also one of the primary elements measured in the studies characterizing representative and airborne brake wear debris (Schlautman & Haselden 2005, Haselden et al. 2005) for the Brake Pad Partnership. The Fe/Cu ratio was approximately 100 in dry deposition samples measured here. This is in contrast to a ratio of 10-20 in the precipitation samples, and 30 in bulk deposition samples. All these are in a range similar to a Fe/Cu ratio of around 60 for the NIST 1648 UPM (used in this study as an SRM for analyzing samples). Although “not represented to be typical of the area in which it was collected” (NIST, 1998), the relative abundance of copper and iron in the NIST UPM falls in the middle of the range for deposition samples collected in Castro Valley, and suggests that deposition in Castro Valley may be similar to that of particulate materials deposited in other urban areas.

The relative abundance of iron to copper in brake wear material averaged 2.4:1 for an estimated composite of the most common (by vehicle market share) copper containing formulations (Haselden et al. 2005). However, the Fe/Cu ratios for the individual formulations vary widely, from ~0 (Fe below detection, for a formulation with Cu ~6% of total mass) to over 5 (27% Fe/5% Cu). The Brake Pad Partnership Copper Use Monitoring Program survey comprising about 40% of the light-duty vehicle market (1998-2003) found copper as a percentage of total friction material mass ranging ~3% in 1998 to nearly 7% in 2003, similar to the average in the wear material characterization studies. However, neither the surveys nor the wear material studies include friction materials from older vehicles, which will generally contain less copper.

Another possible source of Fe, Cu, and other elements in collected samples is soil. The average ratio of Fe/Cu in California soils is approximately 1300 (Bradford, 1996), so differing ratios of copper enhancement in samples may reflect differing contributions of iron from soil sources diluting copper from brake pads and other urban pollution sources. Because of the much smaller fraction of copper in soil compared to brake wear material, soil would effectively dilute the copper from brake material by adding primarily iron with little additional copper, resulting in the higher Fe/Cu ratios seen in collected urban deposition samples versus those in brake wear material.

Figure 9 illustrates the results of a simple mixing model assuming only brake wear material and soil contribute to a deposition sample. When the contribution of soil to total mass is less than 60%, Fe/Cu ratio decreases approximately linearly with the decrease in %soil in the mixture. If the average Fe/Cu ratio is similar to the average from the airborne brake material characterization (2.4), a composition with 92-99% soil by

mass in the deposited material would result in the range of Fe/Cu ratios (approximately 10-100) seen in the wet, bulk, and dry deposition samples collected in Castro Valley. However, even with a Fe/Cu ratio of 100 (~99.5% soil), less than 10% of the total copper would come from soil. Other sources exclusively or primarily contributing iron would also result in a similar mixing profile.

Given the analytical uncertainty in deposition sample measurements and the range in relative abundances for elements found in various potential sources such as brake wear materials and soils, reconstructing sources from elemental ratios is beyond the scope of this study. However, once sources have been characterized and modeled via other methods and data, elemental ratios can be used as a tool to verify whether the behavior of a model is sufficiently realistic and includes most of the important factors.

#### 4.5 Considerations for Loading Estimates

In the previous RMP atmospheric deposition study, one objective was to quantify the contribution of atmospheric deposition relative to other sources and pathways of pollutants (Table A-5). Loading estimates via atmospheric deposition were based on measurements of deposition flux at the sites in that previous study. Although many of the assumptions used in that exercise were quite crude, it served as a screening level evaluation, highlighting first-order estimates for various sources and pathways, and revealing the large uncertainties associated with many of these estimates.

One goal of this BPP project is to combine monitoring and modeling to develop our best integrated understanding of pollutants (particularly copper) from their emissions, to their transport and ultimate fate in the environment. Other members of the project team will be engaged in measuring and modeling those components of the study of the environmental fate of brake pad wear material. Therefore, for this portion of the study, refining the previous calculated watershed loadings of pollutants and their transport to the Bay was not included an objective, as those questions will be better addressed by the detailed modeling components of the study.

However, it should be noted that bulk deposition rates measured in Castro Valley for this study for copper are at least 50% higher than the combined wet and dry copper flux estimates found previously for San Francisco Estuary sites in the RMP pilot study. Although those measurements were more appropriate for determining direct deposition to the water surface given the closer proximity of those monitoring sites to the bay, for estimates of pollutant deposition and loading rates in the watersheds, this study likely provides more appropriate data for the range of land uses and development density in the surrounding watersheds.

One open question is whether surfaces in the watershed behave more like the surrogate surface plates, which prevent resuspension once particles are deposited, or more like the bulk collectors, on which materials can be continually deposited and sometimes resuspended. Watersheds are likely to have both types of surfaces, but the surfaces that are most likely to prevent wind resuspension such as vegetated soils are also most likely to retard surface runoff of deposited particles, whereas smooth impervious surfaces that will allow rapid surface runoff of particles are also likely to yield particles to wind resuspension. When using the dry deposition flux rates from this study, models of air transport may need to include resuspension or other loss terms to model net



deposition flux for surfaces that collect particulates less irreversibly than the greased surrogate surface.

## 5.0 CONCLUSIONS

Copper and other trace elements of interest in samples collected at various locations in the Castro Valley Creek watershed were similar to results from a previous study in San Francisco Bay. Although concentrations found in samples varied widely among sites and among collection events for any site, average wet, bulk, and dry deposition rates fell within the range seen for other urban areas in the United States, with average deposition rates generally exceeding those measured previously for sites in the region located nearer the bay.

Wet or bulk deposition rates were significantly different among the sites for some trace elements, with the site at Redwood Road near Highway 580 receiving the most deposition. However, for many of the trace elements, the Redwood site was higher but not significantly above the other sites in the lower watershed, Castro Valley Community Center and CVE. The site at Madison Reservoir, high in the watershed, generally received the least deposition, as vehicle traffic and other activities around the site primarily include only those of residents of the housing development located there.

Dry deposition fluxes were also found to be significantly different among the various sites, again with the Redwood Road site generally showing the highest flux, Madison showing the lowest as expected, and the other two sites falling in between. Dry deposition rates measured for the surrogate plates were much higher than previously found for sites in San Francisco Bay. Sampling site conditions spanned the range of those that may be found in many Bay area communities, from heavily traveled highway corridors and commercial districts, to quiet residential neighborhoods. Deposition rates (whether bulk, wet, or dry) measured here likely spans the typical range of conditions seen in regional watersheds that would be needed for modeling and estimating atmospheric pollutant loads.

As expected, bulk deposition samplers colocated with automated precipitation samplers on two sampling events measured additional deposition not captured by the wet sampler. On one occasion, the differences in collected precipitation were negligible, so it is likely that the added deposition was from dry material deposited in the collector in dry periods during the sampling. In the other case, the bulk collector also captured more deposition, but the cause was less clear as it also collected a greater volume of fluid than the wet deposition sampler.

However, even the highest deposition rates measured for bulk samplers remain below those seen for the greased surrogate surface plates (dry deposition collectors). Unlike the grease on the surrogate surface plate, which prevents resuspension and loss of deposited material, bulk collector surfaces do not bind the deposited particles and thus allow resuspension losses, resulting in lower measured net flux. Despite the complications of modeling and interpreting measured results for bulk samplers versus more idealized collectors such as dry surrogate plates and wet-only precipitation collectors, their simplicity, small size, and low expense allowed monitoring at sites that would be otherwise difficult to utilize.

For a limited number of dry deposition collection events near the end of the study, the canister collectors deployed to capture ambient benzene showed patterns similar to those for the dry deposition samples. As expected, the ambient concentrations at the Redwood Road site were higher than for Madison Reservoir. However, one sample taken at CVE indicates concentrations similar to those at Redwood, within the analytical variability for a pair of replicates collected simultaneously at Redwood. The benzene data further confirms our expectations from observations that traffic volume and thus benzene and other automotive pollutants are likely to be higher at Redwood than at the upper watershed site at Madison Reservoir. However, similar to the trace element deposition data, the benzene concentration measurements do not clearly indicate differences among sites in the lower watershed

The data collected in this study show that deposition rates of trace element pollutants such as copper, zinc, and other metals associated with vehicle traffic and other urban activities would be found higher than at sites in a previous San Francisco Bay region study that intentionally located monitoring sites away from such sources. The data suggest average copper deposition rates four to five times those previously measured, although results are likely skewed by location of one of the sites virtually below one of the region's busiest highways. However, data from less impacted but still highly urbanized sites within Castro Valley indicate deposition rates still well above those in the previous regional study. The range of sites monitored in Castro Valley greatly improves our knowledge of local atmospheric deposition for the modeling of pollutant transport within this watershed, as well as providing more appropriate data for extending modeling efforts and atmospheric pollutant load estimates to other urban watersheds surrounding San Francisco Bay.

## 6.0 REFERENCES

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

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

**Bradford, G.R, A.C. Chang, A.L. Page, D. Bakhtar, J.A. Frampton, H. Wright. 1996.** Background Concentrations of trace and Major Elements in California Soils. Kearney Foundation of Soil Science, Division of Agriculture and Natural Resources, University of California, Riverside, CA.

**Brake Pad Partnership. 2004.** Copper Use Monitoring Program Results for Model Years 1998 - 2003. Sustainable Conservation, San Francisco, CA. December 3, 2004.

**CARB. 1997.** Toxic Air Contaminant Identification List Summaries – Benzene. ARB/SSD/SES September 1997. <http://www.arb.ca.gov/toxics/tac/factshts/benzene.pdf>

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

**CARB. 2000.** 1996 California Toxics Inventory (revised 8/ 28/ 00), Air Resources Board, California Environmental Protection Agency, Sacramento, CA.  
<http://www.arb.ca.gov/toxics/cti/cti1996082800.pdf>

**CARB. 2004.** California Ambient Toxics Data Summary, Air Resources Board, California Environmental Protection Agency, Sacramento, CA.  
<http://www.arb.ca.gov/adam/toxics/toxics.html>

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

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

**Ely, J. C., C. R. Neal, C. F. Kulpa, M. A. Schneegurt, , J. A. Seidler, and J.C. Jain. 2001.** Implications of Platinum-Group Element Accumulation along U. S. Roads from Catalytic-Converter Attrition. Environmental Science & Technology, 2001, Vol. 35, p. 3816.

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

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

**Haselden, A., C. Christoforou, and M. Schlautman. 2005.** Characterization of Airborne Brake Wear Debris. Final Report Submitted to Association of Bay Area Governments. January 2005. Clemson University School of the Environment, Anderson, SC.

**Hauri, J. 1998a.** Effect of aerial deposition of pollutants on water quality of the San Francisco Bay.

**Hauri, J. 1998b.** Scoping study of air deposition monitoring information relevant to water quality of San Francisco Bay.

**Holsen, T.M. and K.E. Noll. 1992.** Dry deposition of atmospheric particles: application to current models of ambient data. *Environ. Sci. Technol.* 26: 1807-1815.

**Holsen, T.M., K.E. Noll, G.C. Fang, W.J. Lee, J.M. Lin and G. Keeler. 1993.** Dry deposition and particle size distributions measured during the Lake Michigan Urban Air Toxics Study. *Environ. Sci. Technol.* 27: 1327-1333.

**Holsen, T.M., K.E. Noll, S.P. Liu and W.J. Lee. 1991.** Dry deposition of polychlorinated biphenyls in urban areas. *Environ. Sci. Technol.* 25: 1075-1081.

**Kirschmann, H. and T. Grovhoug. 1996.** Gross estimates of atmospheric deposition to South San Francisco Bay. City of San Jose, San Jose, CA.

**NIST. 1998.** Certificate of Analysis, Standard Reference Material 1648 - Urban Particulate Matter. National Institute of Standards and Technology, Gaithersburg, MD.

**Noll, K.E., P.F. Yuen and K.Y.P. Fang. 1990.** Atmospheric coarse particulate concentrations and dry deposition fluxes for ten metals in two urban environments. *Atmospheric Environment* 24A: 903-908.

**Paode, R.D., S.C. Sofuoglu, J. Sivadechathep, K.E. Noll, T.M. Holsen and G.J. Keeler. 1998.** Dry deposition fluxes and mass size distributions of Pb, Cu, and Zn measured in Southern Lake Michigan during AEOLUS. *Environ. Sci. Technol.* 32: 1629-1635.

**Pirrone, N., G.J. Keeler and T.M. Holsen. 1995.** Dry deposition of trace elements to Lake Michigan: A hybrid-receptor deposition modeling approach. *Environ. Sci. Technol.* 29: 2112-2122.

**Sabin, L.D., K.C. Schiff, J.H. Lim, and K.D. Stolzenbach. 2004.** Atmospheric dry deposition of trace metals in the Los Angeles coastal region. Department of Civil and Environmental Engineering, University of California, Los Angeles, CA.

**Schlautman, M.A. and A. Haselden. 2005** Chemical Characterization of the Nonairborne Fraction of the Representative Brake Pad Wear Debris Sample. Submitted to: Association of Bay Area Governments. Clemson University School of the Environment, April 2005. Anderson, SC.

**Scudlark, J.R., K.M. Conko and T.M. Church. 1994.** Atmospheric wet deposition of trace elements to Chesapeake Bay: CBAD Study year 1 results. *Atmospheric Environment* 28: 1487-1498.

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

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

**Stolzenbach, K.D., R. Lu, C. Xiong, S. Friedlander, R. Turco, K. Schiff, L. Tiefenthaler. 2001.** Measuring and Modeling of Atmospheric Deposition on Santa Monica Bay and the Santa Monica Bay Watershed. Final Report to Santa Monica Bay Restoration Project. September 2001.

**Sutherland, R. A., and C. A. Tolosa. 2001.** Variation in Total and Extractable Elements with Distance from Roads in an Urban Watershed, Honolulu, Hawaii, *Water, Air, and Soil Pollution*, 2001, Vol. 127, pp. 315-338.

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

**Tsai, P., R. Hoenicke, E. Hansen and K. Lee. 2001.** San Francisco Bay Atmospheric Deposition Pilot Study - Part 2: Trace elements Final Report). San Francisco Estuary Institute. Final Report. Richmond, CA.

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

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

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

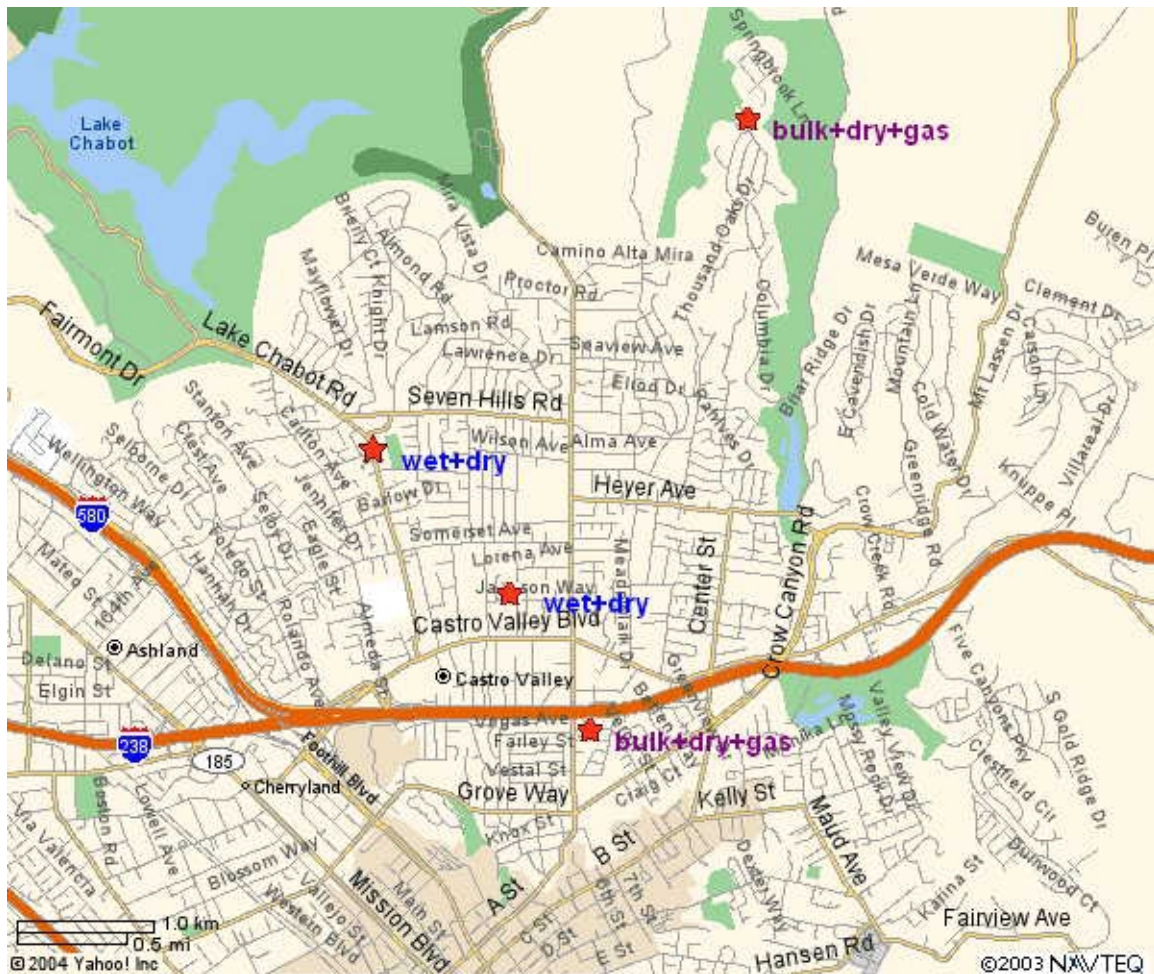
**Vermette, S.J., M.E. Peden, T.C. Willoughby, S.E. Lindberg and A.D. Weiss. 1995b.** Methodology for the sampling of metals in precipitation: results of the National Atmospheric Deposition Program (NADP) pilot network. *Atmospheric Environment* 29: 1221-1229.

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

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

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

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



**Figure 1. Sampling Sites in Castro Valley**

(left to right) Castro Valley Community Center, CV Elementary, Redwood Professional Building, Madison Reservoir

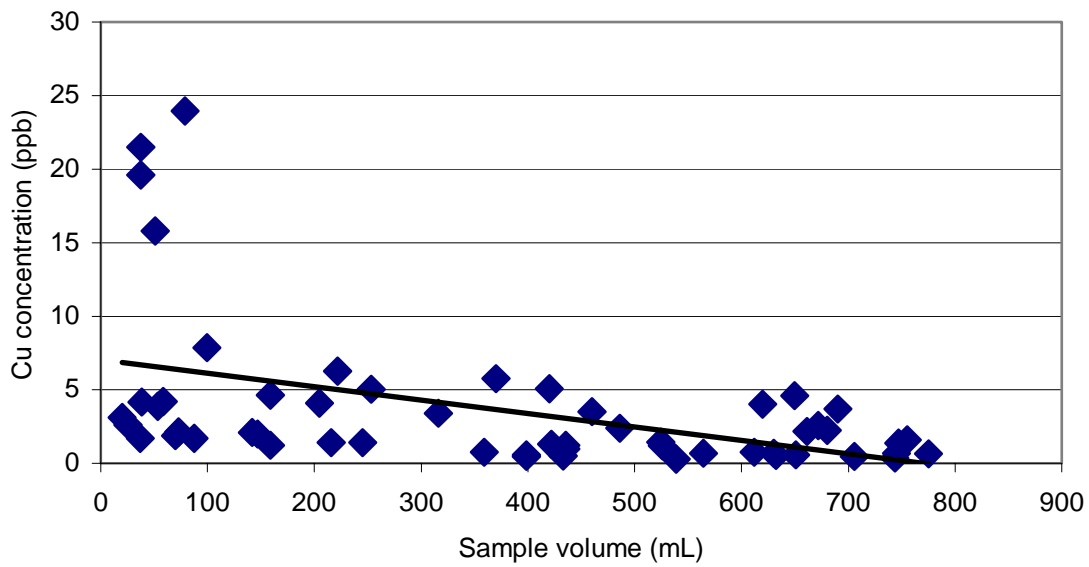


**Figure 2. Wet Deposition Sampling Device**

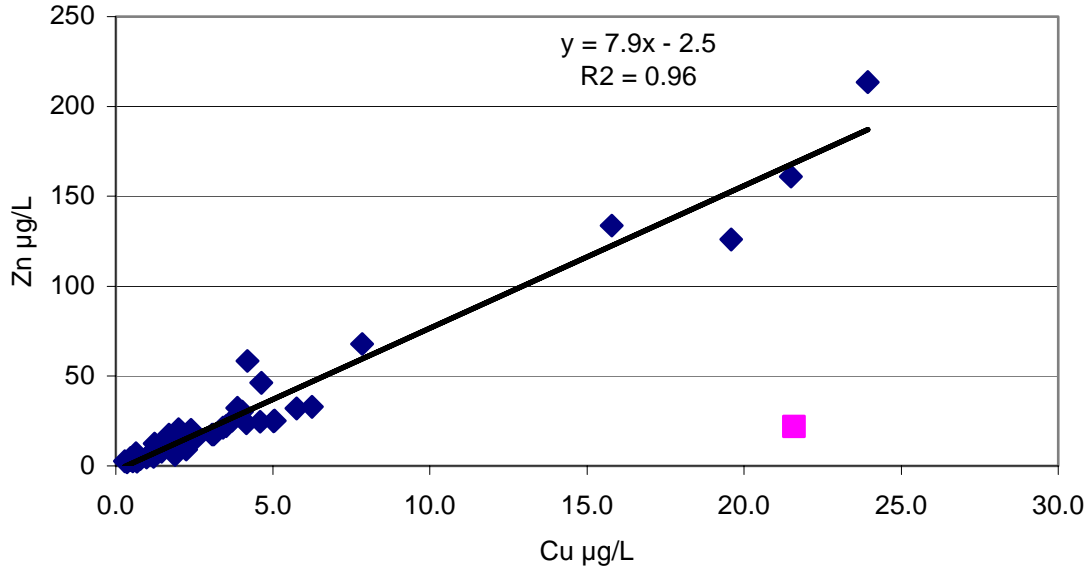




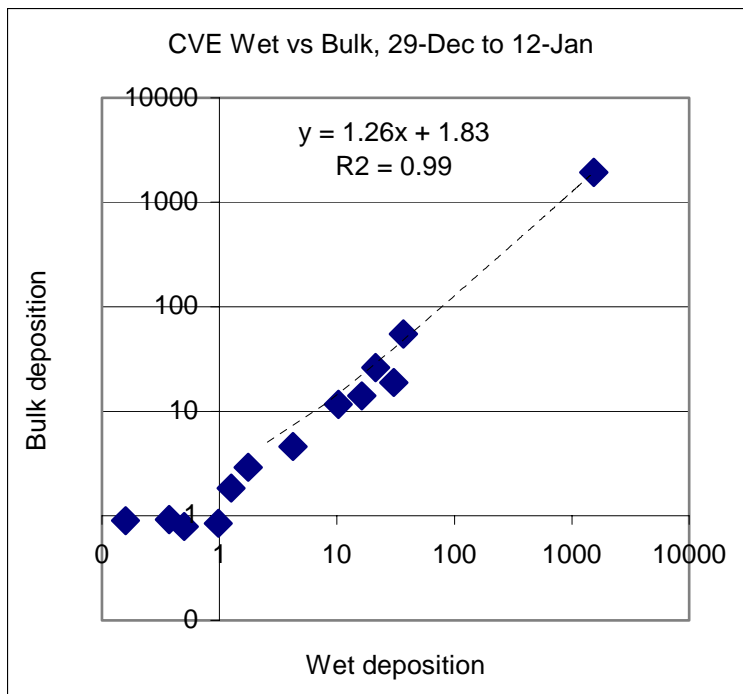
**Figure 3. Dry Deposition Sampling Device (Egret I)**



**Figure 4. Copper Concentrations vs. Collected Volumes for Wet and Bulk Samples**  
Samples with lower volumes of collected precipitation generally contained lower concentrations of copper and other trace elements

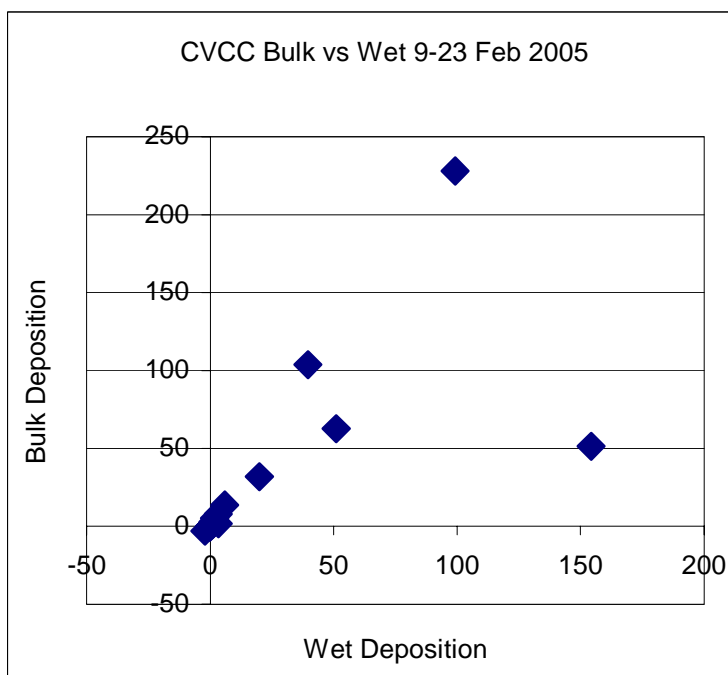


**Figure 5. Copper and Zinc Correlation in Wet & Bulk Samples**  
One likely outlier from Madison (Oct20-Nov3) in contrasting color



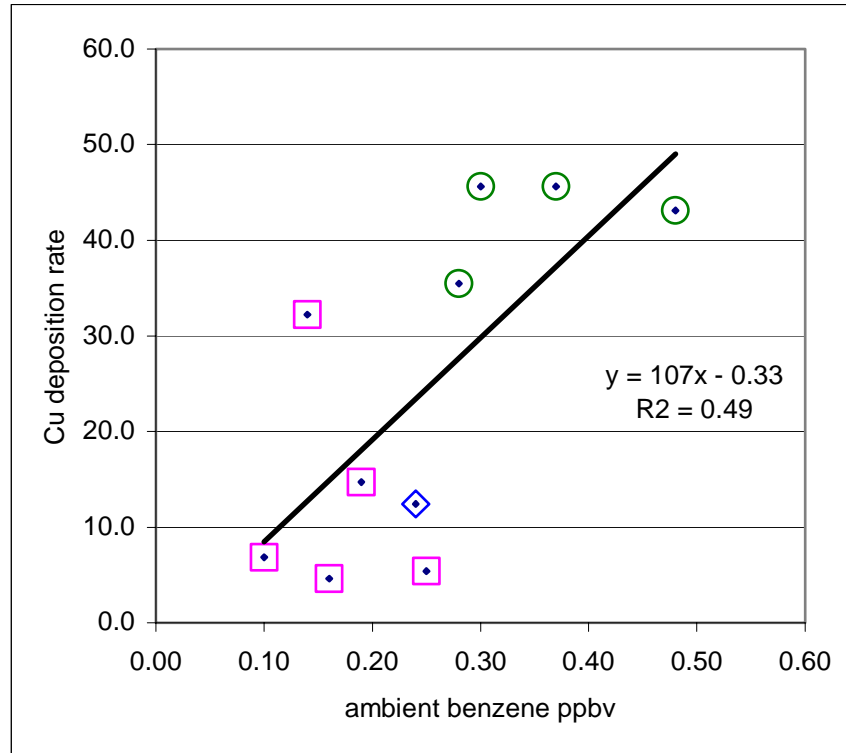
**Figure 6. Colocated Wet versus Bulk Samples CV Elementary**

Wet sample deposition rates were lower for most trace elements despite similar volumes

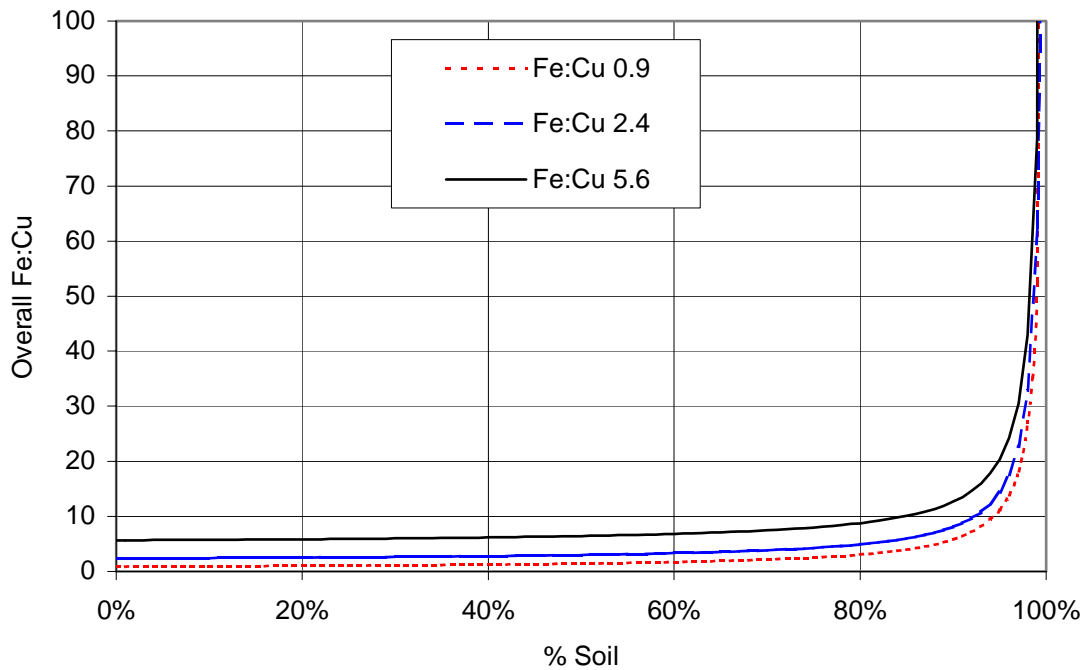


**Figure 7. Colocated Wet vs Bulk Samples CV Community Center**

Like in previous figure (CVE), most elements in bulk sample > wet



**Figure 8. Relationship of Cu Dry Deposition Rate to Ambient Benzene Measurements** (□Madison ○ Redwood ◇ CVE )



**Figure 9. Fe/Cu Ratios for Simple Two-Source Mixing Model**  
(Brake Wear Material with Fe/Cu of 1, 2.4, or 5 Mixed with Soil of 1300:1)

**Table 1. Wet and Bulk Samples Collected**

Start	end	wet	CVCC	CVE	Madison	Redwood	bulk	CVCC	CVE	Madison	Redwood
3/17/2004	3/31/2004		1	1							
3/31/2004	4/21/2004		1	1							
4/21/2004	5/26/2004		NR	NR							
5/26/2004	6/9/2004		MF	1							
6/9/2004	7/7/2004							1	1	1	
10/6/2004	10/20/2004							1	1	1	1
10/20/2004	11/3/2004							1	1	1	1
11/3/2004	11/17/2004							1	1	1	1
11/17/2004	12/3/2004		1	1						MF	1
12/3/2004	12/17/2004		MF	MF				1	1	2	1
12/17/2004	12/29/2004		1	1						1	1
12/29/2004	1/12/2005		MF	1				1	1	2	1
1/12/2005	1/26/2005										
1/26/2005	2/9/2005		1	1						1	1
2/9/2005	2/23/2005		1	2				1		2	1
	<b>total</b>		<b>6</b>	<b>9</b>				<b>7</b>	<b>6</b>	<b>12</b>	<b>9</b>

MF = malfunction of sampler or sampling train

NR = no rain on wet collection

**Table 2. Dry and Gaseous (Benzene) Samples Collected**

Start	end	previous rain (days)	dry	CVCC	CVE	Madison	Redwood	gas	CVCC	CVE	Madison	Redwood
7/7/2004	7/9/2004	40		1		1	1					
7/28/2004	7/30/2004	61		1		1	1					
8/18/2004	8/20/2004	82		1		1	1					
8/20/2004	8/22/2004	84		1		1	1					
8/31/2004	9/2/2004	95		2		1	1					
9/15/2004	9/17/2004	110		2		1	1					
9/29/2004	10/1/2004	11		2		1	1					
10/1/2004	10/3/2004	12		2		1	1					
11/17/2004	11/19/2004	6		1	1	1	1				1	
11/19/2004	11/21/2004	8		1	1	MF	1				1	2
12/15/2004	12/17/2004	7		1	1	1	1				1	1
1/19/2005	1/21/2005	9		1	1	1	1				1	MF
2/9/2005	2/11/2005	2		1	1	1	1			1	1	1
	<b>total</b>			<b>17</b>	<b>5</b>	<b>12</b>	<b>13</b>			<b>1</b>	<b>5</b>	<b>4</b>

MF = malfunction of sampler or sampling train

previous rain = number of days since the last rain event over 0.1" (2.5mm)

**Table 3. QA/QC for Wet and Bulk Deposition Samples (in ppb)**

	Method blank stdev	MDL	System blank avg	System blank stdev	Average RSD
<b>24Mg</b>	0.083	0.25	57	1.5	17%
<b>27Al</b>	0.1	0.3	19	0.95	19%
<b>28Si</b>	1.454	4.36	7.7	0.5	22%
<b>47Ti</b>	0.209	0.63	0.22	0.07	32%
<b>51V</b>	0.26	0.78	0.077	0.03	9%
<b>52Cr</b>	0.067	0.20	0.35	0.018	16%
<b>55Mn</b>	0.016	0.048	0.85	0.021	9%
<b>56Fe</b>	0.15	0.45	54.7	0.99	17%
<b>59Co</b>	0.006	0.018	-0.014	0.003	26%
<b>60Ni</b>	0.287	0.86	-0.21	0.04	13%
<b>65Cu</b>	0.076	0.23	0.77	0.021	14%
<b>66Zn</b>	0.095	0.29	8.19	0.12	13%
<b>88Sr</b>	0.006	0.018	0.07	0.004	8%
<b>111Cd</b>	0.006	0.018	0.021	0.004	12%
<b>121Sb</b>	0.002	0.006	-0.054	0.006	20%
<b>137Ba</b>	0.022	0.066	0.21	0.019	9%
<b>208Pb</b>	0.005	0.015	0.33	0.006	29%

MDL - Method detection limit

RSD – Relative Standard Deviation of lab replicate analyses, for FS averaging at least 3xMDL

**Table 4. Quality Assurance and Quality Control Parameters for Dry Deposition Samples (in µg/sample)**

	Method&trip blank avg	Method&trip blank stdev	MDL	RSD on SRM	SRM %ERR avg
<b>24Mg</b>	0.67	0.48	1.43		
<b>27Al</b>	1.53	1.34	4.03	4%	26
<b>28Si</b>	4.38	3.15	9.46		
<b>47Ti</b>	0.08	0.08	0.24		
<b>51V</b>	0.01	0.03	0.09		
<b>52Cr</b>	0.41	0.28	0.85		
<b>55Mn</b>	0.13	0.32	0.95		
<b>56Fe</b>	1.65	1.37	4.11	4%	10
<b>59Co</b>	0.01	0.03	0.09		
<b>60Ni</b>	-0.02	0.13	0.38	22%	19
<b>65Cu</b>	0.18	0.61	1.84	6%	6
<b>66Zn</b>	0.88	0.81	2.43	1%	8
<b>88Sr</b>	0.02	0.04	0.13		
<b>111Cd</b>	0.02	0.04	0.11	2%	8
<b>121Sb</b>	0.004	0.03	0.08	2%	9
<b>137Ba</b>	0.07	0.12	0.36		
<b>208Pb</b>	0.09	0.14	0.41	2%	7

MDL – Method detection limit

RSD – Relative standard deviation

SRM – Standard reference material NIST UPM (1648)

%ERR – % difference from certified value

**Table 5. Volume Weighted Average Wet and Bulk Sample Concentrations (ppb) in Castro Valley**

	<b>CVCC bulk</b>		<b>CVCC wet</b>		<b>CVE bulk</b>		<b>CVE wet</b>		<b>Madison bulk</b>		<b>Redwood bulk</b>	
	<b>av</b>	<b>sd</b>	<b>av</b>	<b>sd</b>	<b>av</b>	<b>sd</b>	<b>av</b>	<b>sd</b>	<b>av</b>	<b>sd</b>	<b>av</b>	<b>sd</b>
<b>24Mg</b>	176	± 218	39	± 74	193	± 153	93	± 114	119	± 102	128	± 95
<b>27Al</b>	74	± 160	20	± 11	85	± 98	21	± 46	19	± 30	62	± 57
<b>28Si</b>	71	± 172	10	± 11	106	± 115	0	± 0	20	± 40	73	± 66
<b>47Ti</b>	1.2	± 1.3	0.3	± 0.2	1.6	± 1.3	0.3	± 1.3	0.6	± 0.7	1.5	± 1.1
<b>51V</b>	0.3	± 0.6	0.1	± 0.1	0.4	± 0.3	0.1	± 0.1	0.2	± 0.2	0.3	± 0.2
<b>52Cr</b>	0.02	± 0.31	-0.06	± 0.14	0.04	± 0.19	-0.10	± 0.24	-0.11	± 0.10	0.06	± 0.19
<b>55Mn</b>	5.5	± 9.4	0.8	± 0.6	5.2	± 6.4	0.8	± 0.9	1.9	± 4.4	4.4	± 3.9
<b>56Fe</b>	89	± 151	14	± 13	103	± 102	10	± 10	25	± 30	114	± 101
<b>59Co</b>	0.1	± 0.2	0.0	± 0.0	0.1	± 0.1	0.0	± 0.1	0.0	± 0.1	0.1	± 0.1
<b>60Ni</b>	0.4	± 0.8	-0.1	± 0.3	0.6	± 0.5	-0.1	± 0.5	0.1	± 0.5	0.4	± 0.6
<b>65Cu</b>	2.9	± 3.9	1.3	± 1.4	2.9	± 3.0	1.1	± 0.7	1.0	± 1.9	3.1	± 2.4
<b>66Zn</b>	19	± 34	6	± 6	17	± 18	7	± 6	8	± 15	21	± 19
<b>88Sr</b>	2.5	± 3.6	0.5	± 0.5	2.7	± 2.4	1.1	± 0.9	1.1	± 1.4	3.7	± 3.1
<b>111Cd</b>	0.03	± 0.04	0.01	± 0.02	0.03	± 0.03	0.01	± 0.05	0.02	± 0.04	0.02	± 0.03
<b>121Sb</b>	0.2	± 0.1	0.0	± 0.0	0.2	± 0.2	0.1	± 0.1	0.1	± 0.1	0.2	± 0.2
<b>137Ba</b>	4.6	± 7.3	1.1	± 0.8	4.7	± 4.4	1.8	± 1.2	1.7	± 2.0	7.0	± 5.0
<b>208Pb</b>	1.6	± 2.9	0.4	± 0.3	1.3	± 1.7	0.5	± 0.5	0.4	± 0.8	1.2	± 1.0

**Table 6. Average Wet and Bulk Deposition Rates ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ) of Castro Valley Sites**

	<b>CVCC bulk avg sd</b>		<b>CVCC wet avg sd</b>		<b>CVE bulk avg sd</b>		<b>CVE wet avg sd</b>		<b>Madison bulk avg sd</b>		<b>Redwood bulk avg sd</b>	
<b>24Mg</b>	604	± 545	104	± 100	671	± 658	284	± 484	489	± 642	425	± 406
<b>27Al</b>	186	± 143	50	± 52	224	± 185	53	± 32	60	± 66	175	± 107
<b>28Si</b>	175	± 108	24	± 16	275	± 267	33	± 19	58	± 87	204	± 140
<b>47Ti</b>	3.4	± 3.1	0.7	± 0.2	4.4	± 3.5	0.8	± 0.5	1.8	± 1.7	4.0	± 2.4
<b>51V</b>	0.9	± 0.6	0.2	± 0.1	1.1	± 0.6	0.2	± 0.1	0.5	± 0.3	0.7	± 0.4
<b>52Cr</b>	-0.1	± 0.7	-0.1	± 0.3	0.0	± 0.7	-0.3	± 0.6	-0.5	± 0.6	0.1	± 0.6
<b>55Mn</b>	14.4	± 14.1	1.6	± 0.4	13.8	± 17.3	1.9	± 0.9	5.4	± 8.8	12.4	± 8.6
<b>56Fe</b>	236	± 165	31	± 9	271	± 224	31	± 25	77	± 81	321	± 158
<b>59Co</b>	0.2	± 0.3	0.0	± 0.1	0.2	± 0.2	0.0	± 0.1	0.0	± 0.2	0.2	± 0.2
<b>60Ni</b>	1.1	± 2.1	-0.4	± 1.1	1.8	± 1.1	-0.7	± 2.1	-0.1	± 2.4	1.0	± 2.5
<b>65Cu</b>	8.5	± 4.2	2.1	± 1.4	7.9	± 4.8	2.5	± 2.3	3.6	± 1.9	9.0	± 3.0
<b>66Zn</b>	50	± 22	13	± 4	46	± 31	19	± 15	25	± 11	64	± 22
<b>88Sr</b>	7.4	± 5.1	1.1	± 0.5	7.9	± 6.1	3.1	± 3.1	3.9	± 3.9	12.2	± 9.5
<b>111Cd</b>	0.1	± 0.1	0.0	± 0.0	0.1	± 0.1	0.0	± 0.1	0.1	± 0.1	0.1	± 0.1
<b>121Sb</b>	0.5	± 0.3	0.1	± 0.1	0.6	± 0.3	0.3	± 0.4	0.2	± 0.3	0.7	± 0.2
<b>137Ba</b>	13.7	± 6.5	2.6	± 1.7	13.4	± 9.0	5.6	± 5.6	6.4	± 5.7	21.1	± 6.1
<b>208Pb</b>	4.1	± 3.5	1.0	± 1.1	3.3	± 2.6	1.5	± 2.2	1.5	± 0.8	3.5	± 1.4

(deposition rates for all sample events of a given type (bulk or wet) at each site were combined to derive the averages)



**Table 7. Average Dry Deposition Rates ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ) to Castro Valley Sites**

	<b>CVCC</b> dry avg sd		<b>CVE</b> dry avg sd		<b>Madison</b> dry avg sd		<b>Redwood</b> dry avg Sd	
<b>24Mg</b>	586	± 315	391	± 433	211	± 172	1292	± 1460
<b>27Al</b>	862	± 463	773	± 741	302	± 249	2707	± 4112
<b>28Si</b>	76	± 47	69	± 14	50	± 33	91	± 43
<b>47Ti</b>	39	± 17	38	± 31	18	± 9	95	± 73
<b>51V</b>	2.8	± 1.3	2.6	± 2.3	1.2	± 0.6	6.2	± 5.0
<b>52Cr</b>	5.1	± 2.6	7.7	± 3.3	3.1	± 2.3	8.6	± 5.7
<b>55Mn</b>	30	± 13	32	± 26	14	± 6	63	± 44
<b>56Fe</b>	1553	± 844	1165	± 1054	583	± 468	4594	± 4321
<b>59Co</b>	0.7	± 0.3	1.0	± 0.7	0.2	± 0.2	1.3	± 1.0
<b>60Ni</b>	4.2	± 1.6	8.4	± 8.6	1.5	± 1.6	6.3	± 3.6
<b>65Cu</b>	17.0	± 5.0	14.5	± 7.6	8.8	± 7.8	28.9	± 10.5
<b>66Zn</b>	72	± 23	70	± 22	24	± 12	164	± 62
<b>88Sr</b>	7.5	± 3.0	6.9	± 3.8	3.1	± 1.7	24.8	± 13.5
<b>111Cd</b>	0.1	± 0.3	0.5	± 0.2	0.1	± 0.5	0.2	± 0.3
<b>121Sb</b>	0.5	± 0.2	0.6	± 0.2	0.2	± 0.2	0.8	± 0.3
<b>137Ba</b>	20.1	± 7.2	18.2	± 9.9	8.6	± 3.4	51.8	± 22.4
<b>208Pb</b>	9.6	± 4.3	7.6	± 5.3	3.9	± 2.4	13.9	± 6.0

(deposition rates for all sample events at each site were combined to derive the averages)

**Table 8. Estimated Dry Deposition Flux of Trace Metals Reported in the Literature**

Sampling Site	Sampling Method	Cr	Ni	Cu	Cd	Citation
Urban Chicago <sup>2</sup>	D	NA	NA	21900	NA	Paode et al. 1998
Lake Michigan <sup>2</sup>	D	NA	NA	3650	NA	Paode et al. 1998
South Haven, MI <sup>2</sup>	D	NA	NA	2555	NA	Paode et al. 1998
Lake Superior <sup>3</sup>	I	130	570	2400	380	Sweet et al. 1998
Lake Michigan <sup>3</sup>	I	130	320	1300	380	Sweet et al. 1998
Lake Erie <sup>3</sup>	I	1000	460	3300	400	Sweet et al. 1998
So. Lake Michigan <sup>4</sup>	D	NA	NA	2000	NA	Zufall et al. 1998
Massachusetts Bay <sup>5</sup>	D	1200	930	2000	130	Golomb et al. 1997
Massachusetts Bay <sup>6</sup>	I	470	NA	NA	NA	Golomb et al. 1997
Chesapeake Bay <sup>7</sup>	I	110-300	330-910	290-810	11-32	Wu et al. 1994
Lake Michigan	D	360	2550	3650	75	Shahin et al. 2000
SF Estuary <sup>8</sup>	D	1300±900	600±350	1100±730	22±15	Tsai et al. 2001
<b>Castro Valley*</b>	<b>D</b>	<b>2140±1570</b>	<b>1640±1520</b>	<b>6500±4050</b>	<b>67±130</b>	<b>This study</b>

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

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

<sup>3</sup> Average of monthly composite samples taken between summer 1993 and summer 1994.

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

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

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

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

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

\* Average flux for all events and sites combined

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

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

NA – Not analyzed.

**Table 9. Comparison of Trace Metal Concentrations and Deposition Fluxes Reported in the Literature to Results from this Study.**

	<b>Cu</b>	<b>Ni</b>	<b>Cd</b>	<b>Cr</b>	<b>Citation</b>
<b>Concentration in Precipitation (µg/L)</b>					
Lake Superior	0.9±0.5	0.3±0.3	0.1±0.1	0.1±0.1	Sweet et al. 1998
Lake Michigan	0.8±0.1	0.4±0.4	0.1±0.3	0.1±0.2	Sweet et al. 1998
Lake Erie	0.9±0.1	0.3±0.2	0.1±0.1	<0.1	Sweet et al. 1998
San Francisco Estuary*	1.2	0.4	0.1	0.2	Tsai et al. 2001
<b>Castro Valley*</b>	<b>2.07</b>	<b>0.26 (&lt;MDL)</b>	<b>0.023</b>	<b>0.0 (&lt;MDL)</b>	<b>This study</b>
<b>Wet Deposition Flux (µg·m<sup>-2</sup>·d<sup>-1</sup>)</b>					
Lake Superior	1.92	0.63	0.21	0.21	Sweet et al. 1998
Lake Michigan	1.56	0.79	0.20	0.20	Sweet et al. 1998
Lake Erie	2.33	0.77	0.26	0.17	Sweet et al. 1998
Massachusetts Bay	1.37	1.70	0.38	4.11	Golomb et al. 1997
Chesapeake Bay	0.71	0.70	0.13	0.24	Scudlark et al. 1994
San Francisco Estuary	1.73	0.63	0.16	0.33	Tsai et al. 2001
<b>Castro Valley^</b>	<b>2.30</b>	<b>ND</b>	<b>0.02</b>	<b>ND</b>	<b>This study</b>
<b>Total (Dry+Wet) Deposition Flux (µg·m<sup>-2</sup>·d<sup>-1</sup>)</b>					
Southern Quebec, Canada	3.26	1.62	0.74	0.63	Gelinas et al. 2000
Lake Superior	8.49	2.19	1.25	0.57	Sweet et al. 1998
Lake Michigan	5.12	1.67	1.24	0.55	Sweet et al. 1998
Lake Erie	11.37	2.03	1.35	2.91	Sweet et al. 1998
Massachusetts Bay	6.85	4.11	0.74	7.40	Golomb et al. 1997
Commencement Bay, WA	20-149	8.4-49	NA	4.0-17	Crecelius 1991
San Francisco Estuary	4.66	2.25	0.22	3.84	Tsai et al. 2001
<b>Castro Valley (bulk deposition)^</b>	<b>7.2</b>	<b>0.96</b>	<b>0.071</b>	<b>ND</b>	<b>This study</b>

\* Volume-weighted average concentration

^ Average flux for all events and sites combined

NA – Not analyzed

**Table 10. Ambient Benzene Concentrations in Castro Valley**

site	start date	end date	conc ppbv	conc ug/m3
Madison	11/17/2004	11/19/2004	0.25	0.81
Madison	11/19/2004	11/21/2004	0.14	0.46
Madison	12/15/2004	12/17/2004	0.19	0.6
Madison	1/19/2005	1/21/2005	0.16	0.53
Madison	2/9/2005	2/11/2005	0.10	0.32
Redwood A	11/19/2004	11/21/2004	0.30	0.97
Redwood B	11/19/2004	11/21/2004	0.37	1.2
Redwood	12/15/2004	12/17/2004	0.48	1.5
Redwood	1/19/2005	1/21/2005	MF	
Redwood	2/9/2005	2/11/2005	0.28	0.88
CVE	2/9/2005	2/11/2005	0.24	0.75

**APPENDIX Data Tables**

**Table A-1 Wet and Bulk Sample Concentrations (ppb)**

Site	start date	end date	Field Rep	g water	area m <sup>2</sup>	b/w/d	24Mg	27Al	28Si	47Ti	51V	52Cr	55Mn	56Fe	59Co	60Ni	65Cu	66Zn	88Sr	111Cd	121Sb	137Ba	208Pb
CVCC	17-Mar-04	31-Mar-04		205	0.01227	wet											4.1						
CVCC	31-Mar-04	21-Apr-04		37	0.01227	wet											1.7						
CVCC	09-Jun-04	07-Jul-04		79	0.01227	bulk	1384	964	1044	3.50	3.10	1.65	54.3	882.3	1.093	3.94	23.9	213	21.9	0.251	0.63	45.3	16.79
CVCC	06-Oct-04	20-Oct-04		650	0.01227	bulk	193	114	78	1.98	<del>0.41</del>	<del>0.10</del>	11.9	133.3	0.214	<del>0.64</del>	4.6	25	4.6	0.022	0.24	7.3	2.96
CVCC	20-Oct-04	03-Nov-04		460	0.01227	bulk	166	105	101	2.54	<del>0.65</del>	<del>0.13</del>	4.4	140.5	0.115	0.99	3.5	22	2.5	0.031	0.28	4.7	1.99
CVCC	03-Nov-04	17-Nov-04		316	0.01227	bulk	180	114	126	3.05	<del>0.76</del>	0.22	4.7	164.6	0.135	<del>0.69</del>	3.4	21	2.6	0.039	0.29	4.9	2.13
CVCC	17-Nov-04	03-Dec-04		147	0.01227	wet	45	39	39	0.78	<del>0.24</del>	<del>0.11</del>	2.5	44.7	0.094		2.0	21	1.3	0.019	0.15	3.0	0.81
CVCC	03-Dec-04	17-Dec-04		MF 378	0.01227	wet	61	23	26	<del>0.53</del>	<del>0.14</del>	<del>-0.13</del>	1.1	28.5	<del>0.013</del>	<del>0.33</del>	1.9	6	0.8	<del>0.007</del>	0.08	1.4	0.43
CVCC	03-Dec-04	17-Dec-04		755	0.01227	bulk	88	12	16	<del>0.21</del>	<del>0.03</del>	<del>-0.13</del>	3.1	18.2	0.019	<del>0.18</del>	1.6	12	1.0	0.041	0.07	2.0	0.30
CVCC	17-Dec-04	29-Dec-04		399	0.01227	wet	26	15	5	<del>0.28</del>	<del>0.02</del>	<del>-0.04</del>	0.7	12.0	<del>0.011</del>		0.6	5	0.4	<del>0.013</del>	0.05	0.8	0.17
CVCC	17-Dec-04	29-Dec-04		399	0.01227	wet	26	15	6	<del>0.22</del>	<del>0.04</del>	<del>-0.26</del>	0.7	11.2	<del>-0.004</del>	<del>0.00</del>	0.5	5	0.3	<del>-0.001</del>	0.03	0.7	0.17
CVCC	29-Dec-04	12-Jan-05		MF 209	0.00581	wet	104	61	11	<del>0.04</del>	<del>0.08</del>	<del>-0.15</del>	0.5	6.9	<del>-0.007</del>	<del>0.14</del>	0.8	4	0.8	0.026	0.22	3.0	0.18
CVCC	29-Dec-04	12-Jan-05		612	0.00581	bulk	238	8	7	<del>0.18</del>	<del>0.05</del>	<del>-0.16</del>	0.5	10.9	<del>0.003</del>	<del>0.40</del>	0.8	4	1.4	<del>0.012</del>	0.11	1.8	0.19
CVCC	12-Jan-05	26-Jan-05		39	0.00581	wet	94	36	10	<del>0.53</del>	<del>0.16</del>	<del>0.17</del>	1.7	28.3	0.024	1.29	4.2	24	1.0	0.087	0.19	2.3	1.25
CVCC	26-Jan-05	09-Feb-05		70	0.00581	wet	353	26	31	0.94	<del>0.33</del>	<del>0.09</del>	1.7	41.0	<del>0.015</del>	<del>-0.19</del>	1.9	11	2.4	<del>0.006</del>	0.08	2.5	0.91
CVCC	09-Feb-05	23-Feb-05		359	0.00581	wet	22	35	12	<del>0.21</del>	<del>0.06</del>	<del>-0.01</del>	0.4	9.0	<del>-0.023</del>	<del>-0.46</del>	0.8	5	0.3	<del>0.001</del>	<del>0.00</del>	1.4	0.75
CVCC	09-Feb-05	23-Feb-05		526	0.00581	bulk	35	8	10	<del>0.14</del>	<del>0.08</del>	<del>-0.12</del>	0.8	16.1	<del>-0.006</del>	<del>-0.49</del>	1.2	5	0.4	<del>-0.008</del>	0.04	2.1	0.29
CVE	17-Mar-04	31-Mar-04		216	0.01227	wet											1.4						
CVE	31-Mar-04	21-Apr-04		26	0.01227	wet											2.6						
CVE	26-May-04	09-Jun-04		88	0.01227	wet	181	42	44	<del>0.53</del>	<del>0.34</del>	<del>-0.08</del>	4.0	32.6	0.076	<del>0.18</del>	1.7	17	2.6	0.046	0.29	2.4	0.90
CVE	09-Jun-04	07-Jul-04		38	0.01227	bulk	1255	660	707	3.13	2.17	0.95	34.9	615.4	0.764	2.48	19.6	126	16.5	0.240	1.29	31.6	11.99
CVE	06-Oct-04	20-Oct-04		690	0.01227	bulk	207	137	191	2.28	<del>0.46</del>	<del>0.13</del>	12.1	160.7	0.155	<del>0.75</del>	3.7	25	4.6	0.024	0.22	7.4	1.97
CVE	20-Oct-04	03-Nov-04		420	0.01227	bulk	182	127	142	2.99	<del>0.68</del>	<del>0.15</del>	5.0	162.1	0.105	1.24	5.1	25	2.7	0.036	0.32	5.9	1.81
CVE	03-Nov-04	17-Nov-04		253	0.01227	bulk	185	129	153	3.03	<del>0.70</del>	<del>0.16</del>	5.0	168.9	0.106	1.02	5.0	25	2.7	0.033	0.26	5.9	1.80
CVE	17-Nov-04	03-Dec-04		159	0.01227	wet	75	17	14	<del>0.34</del>	<del>0.18</del>	<del>-0.01</del>	1.5	17.4	0.262		1.2	12	1.3	0.019	0.31	1.8	0.33
CVE	03-Dec-04	17-Dec-04		MF	0.01227	wet	333	344		11.97	0.86	1.98	6.2		0.224	1.88	3.1	17	4.2	0.023	0.97	2.7	0.93
CVE	03-Dec-04	17-Dec-04		20	0.01227	wet	399	477	379	13.23	0.87	2.21	6.3		0.239		3.1	17	4.2	0.034	0.92	2.7	0.93
CVE	03-Dec-04	17-Dec-04		747	0.01227	bulk	95	38	50	1.02	<del>0.19</del>	<del>0.01</del>	1.9	52.3	0.057	<del>0.24</del>	1.4	9	1.2	0.052	0.10	2.3	0.63
CVE	17-Dec-04	29-Dec-04		433	0.01227	wet	48	30	9	<del>0.21</del>	<del>0.05</del>	<del>-0.16</del>	0.9	12.8	<del>0.008</del>	<del>0.24</del>	0.5	4	1.8	<del>0.012</del>	0.04	0.9	0.19
CVE	29-Dec-04	12-Jan-05		633	0.00581	wet	197	5	4	<del>0.13</del>	<del>0.06</del>	<del>-0.19</del>	0.2	<del>-0.4</del>	<del>-0.014</del>	<del>0.16</del>	0.5	3	1.3	<del>-0.002</del>	0.02	2.1	0.05
CVE	29-Dec-04	12-Jan-05		651	0.00581	bulk	241	7	2	<del>0.11</del>	<del>0.10</del>	<del>-0.18</del>	0.4	5.3	<del>-0.002</del>	<del>0.23</del>	0.6	3	1.5	<del>0.002</del>	0.11	1.8	0.11
CVE	12-Jan-05	26-Jan-05		53	0.00581	wet	82	39	11	<del>0.48</del>	<del>0.22</del>	<del>0.07</del>	1.5	26.0	0.031	1.17	3.9	32	2.3	0.288	0.28	2.6	0.89
CVE	26-Jan-05	09-Feb-05		73	0.00581	wet	508	61	36	1.52	<del>0.44</del>	<del>0.15</del>	1.5	38.4	<del>-0.001</del>	<del>-0.06</del>	2.1	12	4.1	0.062	0.26	7.5	0.93
CVE	09-Feb-05	23-Feb-05	A	422	0.00581	wet	17	17	12	<del>0.16</del>	<del>0.06</del>	<del>-0.14</del>	0.5	11.1	<del>-0.016</del>	<del>-0.71</del>	1.3	7	0.6	<del>-0.007</del>	0.12	2.4	1.31
CVE	09-Feb-05	23-Feb-05	B	436	0.00581	wet	17	18	11	<del>0.17</del>	<del>0.03</del>	<del>-0.12</del>	0.6	13.4	<del>-0.020</del>	<del>-0.69</del>	1.2	9	0.3	<del>-0.009</del>	0.22	1.4	0.63
Madison	09-Jun-04	07-Jul-04		38	0.01227	bulk	621	285	374	6.78	1.93	0.64	43.9	218.6	0.543	2.38	21.5	161	15.9	0.181	0.40	21.7	9.20
Madison	06-Oct-04	20-Oct-04		680	0.01227	bulk	250	65	86	1.50	<del>0.28</del>	<del>-0.07</del>	8.7	77.0	0.133	<del>0.63</del>	2.2	9	2.6	0.040	0.07	3.8	0.70
Madison	20-Oct-04	03-Nov-04		380	0.01227	bulk	83	25	15	0.78	<del>0.48</del>	<del>-0.07</del>	1.6	29.6	0.033	<del>0.26</del>	OL 22	22	0.9	<del>0.018</del>	0.30	1.5	0.89
Madison	03-Nov-04	17-Nov-04		245	0.01227	bulk	154	41	32	1.38	<del>0.73</del>	<del>-0.01</del>	1.7	46.8	0.025	<del>0.20</del>	1.4	9	1.3	0.026	0.10	1.9	0.97
Madison	03-Dec-04	17-Dec-04	A	745	0.01227	bulk	72	24	19	1.05	<del>0.06</del>	<del>0.02</del>	1.0	43.2	<del>0.013</del>	<del>0.40</del>	0.7	5	0.7	<del>0.014</del>	0.07	0.9	0.31
Madison	03-Dec-04	17-Dec-04	B	775	0.01227	bulk	60	11	7	<del>0.41</del>	<del>0.10</del>	<del>-0.14</del>	0.8	17.6	<del>0.004</del>	<del>0.14</del>	0.6	7	0.7	0.046	0.06	0.8	0.26
Madison	17-Dec-04	29-Dec-04		435	0.01227	bulk	21	8	6	<del>0.28</del>	<del>0.04</del>	<del>-0.18</del>	0.9	12.4	<del>0.001</del>	<del>0.12</del>	1.0	5	0.3	0.118	0.04	0.9	0.22
Madison	29-Dec-04	12-Jan-05	A	706	0.00581	bulk	187	3	4	<del>0.07</del>	<del>0.04</del>	<del>-0.20</del>	0.3	3.8	<del>-0.005</del>	<del>0.10</del>	0.5	3	1.1	<del>0.000</del>	0.05	1.1	0.09
Madison	29-Dec-04	12-Jan-05	B	744	0.00581	bulk	218	5	4	<del>0.17</del>	<del>0.04</del>	<del>-0.17</del>	0.4	6.5	<del>-0.004</del>	<del>0.16</del>	0.3	2	1.3	<del>0.011</del>	0.08	2.2	0.10
Madison	12-Jan-05	26-Jan-05		58	0.00581	bulk	73	31	23	1.34	<del>0.30</del>	<del>0.07</del>	2.2	47.1	0.035	1.15	4.2	58	1.4	0.069	0.22	3.0	1.45
Madison	26-Jan-05	09-Feb-05		142	0.00581	bulk	253	24	24	<del>0.62</del>	<del>0.36</del>	<del>-0.03</del>	1.7	22.8	0.024	<del>0.21</del>	2.1	11	2.2	<del>0.008</del>	0.07	2.7	1.31
Madison	09-Feb-05	23-Feb-05	A	539	0.00581	bulk	10		3	<del>0.08</del>	<del>0.07</del>	<del>-0.15</del>	0.2	4.3	<del>-0.029</del>	<del>-0.81</del>	0.3	3	0.1	<del>-0.015</del>	<del>-0.03</del>	0.5	0.11
Madison	09-Feb-05	23-Feb-05	B	564	0.00581	bulk	12	1	4	<del>0.08</del>	<del>0.05</del>	<del>-0.13</del>	0.3	5.7	<del>-0.027</del>	<del>-0.76</del>	0.7	2	0.2	<del>-0.008</del>	<del>-0.01</del>	1.5	0.45
Redwood	06-Oct-04	20-Oct-04		620	0.01227	bulk	178	121	165	2.79	<del>0.45</del>	0.22	10.2	196.8	0.155	1.47	4.0	30	5.3	0.018	0.28	9.4	1.78
Redwood	20-Oct-04	03-Nov-04		370	0.01227	bulk	166	96	99	2.74	<del>0.63</del>	<del>0.18</del>	5.6	185.9	0.101	<del>0.83</del>	5.8	32	4.5	0.030	0.35	11.1	2.05
Redwood	03-Nov-04	17-Nov-04		222	0.01227	bulk	175	100	115	3.20	<del>0.70</del>	<del>0.20</del>	5.7	202.1	0.109	<del>0.36</del>	6.3	33	4.4	0.033	0.59	11.5	2.06
Redwood	17-Nov-04	03-Dec-04		159	0.01227	bulk	99	98	153	2.56	<del>0.34</del>	0.31	8.4	235.1	0.140		4.6	46	4.2	0.131	0.37	12.0	2.71
Redwood	03-Dec-04	17-Dec-04		661	0.01227	bulk	90	43	44	1.00	<del>0.13</del>	<del>-0.06</del>	2.9	79.3	0.032	<del>0.21</del>	2.2	14	2.3	<del>0.014</del>	0.18	5.1	0.80
Redwood	03-Dec-04	17-Dec-04		672	0.01227	bulk	95	46	57	1.35	<del>0.20</del>	<del>0.20</del>	3.3	90.4	0.056		2.6	16	2.6	0.038	0.20	5.6	0.88
Redwood	17-Dec-04	29-Dec-04		486	0.01227	bulk	53	46	55	1.21	<del>0.16</del>	<del>-0.03</del>	3.0	84.4	0.047	<del>0.52</del>	2.4	20	1.9	<del>0.014</del>	0.28	5.7	0.82
Redwood	29-Dec-04	12-Jan-05		630	0.00581	bulk	193	9	10	<del>0.26</del>	<del>0.09</del>	<del>-0.16</del>											

**Table A-2 Wet and Bulk Sample Deposition Rates ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ )**

Site	start date	end date	Field Rep	g water	area m <sup>2</sup>	b/w/d	24Mg	27Al	28Si	47Ti	51V	52Cr	55Mn	56Fe	59Co	60Ni	65Cu	66Zn	88Sr	111Cd	121Sb	137Ba	208Pb
CVCC	17-Mar-04	31-Mar-04		205	0.012272	wet											4.89						
CVCC	31-Mar-04	21-Apr-04		37	0.012272	wet											0.24						
CVCC	09-Jun-04	07-Jul-04		79	0.012272	bulk	318	222	240.1	0.80	0.71	0.38	12.49	203	0.25	0.91	5.50	49.1	5.04	0.06	0.15	10.42	3.86
CVCC	06-Oct-04	20-Oct-04		650	0.012272	bulk	730	430	295.1	7.47	1.56	0.37	45.19	504	0.81	2.44	17.40	93.2	17.54	0.08	0.92	27.70	11.18
CVCC	20-Oct-04	03-Nov-04		460	0.012272	bulk	445	281	269.9	6.81	1.75	0.34	11.88	376	0.31	2.64	9.42	59.6	6.58	0.08	0.75	12.57	5.32
CVCC	03-Nov-04	17-Nov-04		316	0.012272	bulk	331	210	231.7	5.60	1.40	0.40	8.68	303	0.25	1.08	6.27	39.5	4.76	0.07	0.54	9.09	3.91
CVCC	17-Nov-04	03-Dec-04		147	0.012272	wet	34	29	29.1	0.59	0.18	0.08	1.84	33	0.07		1.50	15.4	0.96	0.01	0.11	2.21	0.61
CVCC	03-Dec-04	17-Dec-04		MF 378	0.012272	wet																	
CVCC	03-Dec-04	17-Dec-04		755	0.012272	bulk	387	53	72.0	0.91	0.15	-0.56	13.70	80	0.08	0.78	7.03	51.0	4.48	0.18	0.33	8.78	1.33
CVCC	17-Dec-04	29-Dec-04		399	0.012272	wet	70	40	13.5	0.76	0.06	-0.09	2.00	33	0.03		1.58	12.7	1.00	0.03	0.14	2.08	0.45
CVCC	17-Dec-04	29-Dec-04		399	0.012272	wet	71	40	17.1	0.58	0.10	-0.71	1.84	30	-0.01	0.01	1.30	12.4	0.87	0.00	0.09	1.97	0.46
CVCC	29-Dec-04	12-Jan-05		MF 209	0.005809	wet																	
CVCC	29-Dec-04	12-Jan-05		612	0.005809	bulk	1787	57	50.4	1.38	0.40	-1.14	3.83	82	0.02	3.00	5.82	28.7	10.39	0.09	0.82	13.69	1.45
CVCC	12-Jan-05	26-Jan-05		39	0.005809	wet	45	17	4.8	0.25	0.08	0.08	0.79	13	0.01	0.61	1.98	11.2	0.46	0.04	0.09	1.09	0.59
CVCC	26-Jan-05	09-Feb-05		70	0.005809	wet	303	23	26.5	0.81	0.28	0.08	1.49	35	0.01	-0.16	1.62	9.2	2.07	0.01	0.07	2.16	0.78
CVCC	09-Feb-05	23-Feb-05		359	0.005809	wet	99	154	50.9	0.91	0.27	-0.05	1.88	40	-0.10	-2.04	3.38	20.0	1.20	0.00	-0.01	5.99	3.30
CVCC	09-Feb-05	23-Feb-05		526	0.005809	bulk	228	51	62.6	0.90	0.52	-0.76	5.22	104	-0.04	-3.18	7.81	31.9	2.74	-0.05	0.28	13.69	1.85
CVE	17-Mar-04	31-Mar-04		216	0.012272	wet											1.76						
CVE	31-Mar-04	21-Apr-04		26	0.012272	wet											0.26						
CVE	26-May-04	09-Jun-04		88	0.012272	wet	92	21	22.6	0.27	0.17	-0.04	2.03	17	0.04	0.09	0.87	8.9	1.33	0.02	0.15	1.23	0.46
CVE	09-Jun-04	07-Jul-04		38	0.012272	bulk	137	72	77.2	0.34	0.24	0.10	3.81	67	0.08	0.27	2.14	13.8	1.80	0.03	0.14	3.44	1.31
CVE	06-Oct-04	20-Oct-04		690	0.012272	bulk	830	551	765.6	9.16	1.83	0.53	48.47	645	0.62	3.00	14.87	101.5	18.41	0.10	0.90	29.81	7.90
CVE	20-Oct-04	03-Nov-04		420	0.012272	bulk	446	311	346.1	7.31	1.67	0.36	12.19	396	0.26	3.04	12.38	61.3	6.58	0.09	0.77	14.51	4.43
CVE	03-Nov-04	17-Nov-04		253	0.012272	bulk	273	190	226.0	4.47	1.03	0.23	7.42	249	0.16	1.50	7.40	36.7	3.95	0.05	0.39	8.74	2.64
CVE	17-Nov-04	03-Dec-04		159	0.012272	wet	61	14	11.2	0.27	0.15	-0.01	1.18	14	0.21		1.01	10.1	1.05	0.01	0.25	1.43	0.27
CVE	03-Dec-04	17-Dec-04		MF	0.012272	wet																	
CVE	03-Dec-04	17-Dec-04		20	0.012272	wet	47	56	44.2	1.54	0.10	0.26	0.73		0.03		0.36	2.0	0.49	0.00	0.11	0.31	0.11
CVE	03-Dec-04	17-Dec-04		747	0.012272	bulk	414	164	219.1	4.42	0.84	0.03	8.09	227	0.25	1.06	5.99	38.0	5.28	0.22	0.45	9.99	2.72
CVE	17-Dec-04	29-Dec-04		433	0.012272	wet	140	88	26.7	0.62	0.14	-0.46	2.72	38	0.02	0.63	1.49	11.7	5.17	0.03	0.12	2.66	0.56
CVE	29-Dec-04	12-Jan-05		633	0.005809	wet	1531	37	30.5	0.98	0.50	-1.49	1.76	-3	-0.11	1.26	4.22	21.4	10.30	-0.01	0.16	16.35	0.37
CVE	29-Dec-04	12-Jan-05		651	0.005809	bulk	1928	55	18.9	0.85	0.79	-1.45	2.93	43	-0.02	1.85	4.63	26.1	11.64	0.02	0.89	14.08	0.92
CVE	12-Jan-05	26-Jan-05		53	0.005809	wet	54	25	7.2	0.32	0.14	0.05	0.97	17	0.02	0.77	2.53	21.1	1.50	0.19	0.18	1.73	0.58
CVE	26-Jan-05	09-Feb-05		73	0.005809	wet	455	55	31.9	1.36	0.39	0.13	1.36	34	0.00	-0.05	1.91	10.9	3.69	0.06	0.23	6.68	0.83
CVE	09-Feb-05	23-Feb-05	A	422	0.005809	wet	86	89	60.6	0.84	0.33	-0.74	2.77	58	-0.08	-3.66	6.82	36.5	2.85	-0.03	0.62	12.41	6.78
CVE	09-Feb-05	23-Feb-05	B	436	0.005809	wet	90	96	58.6	0.92	0.17	-0.62	3.35	72	-0.11	-3.68	6.64	47.1	1.74	-0.05	1.18	7.46	3.36
Madison	09-Jun-04	07-Jul-04		38	0.012272	bulk	68	31	40.8	0.74	0.21	0.07	4.79	24	0.06	0.26	2.35	17.6	1.74	0.02	0.04	2.37	1.00
Madison	06-Oct-04	20-Oct-04		680	0.012272	bulk	989	256	340.8	5.95	1.12	-0.27	34.38	305	0.53	2.48	8.89	36.5	10.26	0.16	0.27	15.11	2.78
Madison	20-Oct-04	03-Nov-04		380	0.012272	bulk	184	55	33.8	1.72	1.07	-0.16	3.48	66	0.07	0.57		48.3	1.90	0.04	0.67	3.21	1.97
Madison	03-Nov-04	17-Nov-04		245	0.012272	bulk	220	58	45.3	1.97	1.04	-0.01	2.37	67	0.04	0.28	2.04	12.4	1.89	0.04	0.15	2.73	1.39
Madison	03-Dec-04	17-Dec-04	A	745	0.012272	bulk	312	105	83.0	4.55	0.27	0.08	4.46	187	0.06	1.73	3.06	21.3	3.15	0.06	0.28	3.77	1.34
Madison	03-Dec-04	17-Dec-04	B	775	0.012272	bulk	270	51	33.3	1.83	0.43	-0.64	3.55	79	0.02	0.62	2.89	32.6	3.11	0.21	0.25	3.49	1.17
Madison	17-Dec-04	29-Dec-04		435	0.012272	bulk	61	25	17.8	0.82	0.12	-0.54	2.51	37	0.00	0.34	2.89	13.9	1.00	0.35	0.11	2.75	0.64
Madison	29-Dec-04	12-Jan-05	A	706	0.005809	bulk	1622	25	12.0	0.64	0.36	-1.75	2.36	33	-0.05	0.87	4.05	29.5	9.60	0.00	0.47	9.17	0.77
Madison	29-Dec-04	12-Jan-05	B	744	0.005809	bulk	1994	46	35.1	1.52	0.38	-1.57	3.89	60	-0.03	1.44	3.20	17.9	11.68	0.10	0.74	20.26	0.94
Madison	12-Jan-05	26-Jan-05		58	0.005809	bulk	52	22	16.3	0.96	0.22	0.05	1.58	34	0.02	0.83	3.01	41.9	0.99	0.05	0.16	2.19	1.04
Madison	26-Jan-05	09-Feb-05		142	0.005809	bulk	441	42	42.3	1.09	0.62	-0.05	2.91	40	0.04	0.37	3.69	19.3	3.76	0.01	0.12	4.71	2.29
Madison	09-Feb-05	23-Feb-05	A	539	0.005809	bulk	66		19.5	0.53	0.44	-0.98	1.62	29	-0.19	-5.35	1.94	18.7	0.99	-0.10	-0.21	3.59	0.72
Madison	09-Feb-05	23-Feb-05	B	564	0.005809	bulk	80	9	29.4	0.52	0.38	-0.87	1.96	40	-0.18	-5.25	4.72	16.8	1.20	-0.06	-0.10	10.12	3.10
Redwood	06-Oct-04	20-Oct-04		620	0.012272	bulk	644	438	593.7	10.08	1.61	0.80	36.98	710	0.56	5.29	14.50	109.5	19.18	0.06	1.01	33.98	6.43
Redwood	20-Oct-04	03-Nov-04		370	0.012272	bulk	358	207	212.3	5.90	1.37	0.39	12.03	400	0.22	1.79	12.38	69.2	9.67	0.06	0.75	23.85	4.40
Redwood	03-Nov-04	17-Nov-04		222	0.012272	bulk	226	129	148.1	4.13	0.91	0.26	7.40	261	0.14	0.46	8.08	42.6	5.75	0.04	0.76	14.83	2.67
Redwood	17-Nov-04	03-Dec-04		159	0.012272	bulk	80	79	123.5	2.07	0.28	0.25	6.82	190	0.11		3.76	37.4	3.39	0.11	0.30	9.75	2.19
Redwood	03-Dec-04	17-Dec-04		661	0.012272	bulk	345	167	168.7	3.83	0.51	-0.22	11.20	305	0.12	0.80	8.34	53.4	8.97	0.05	0.69	19.46	3.09
Redwood	03-Dec-04	17-Dec-04		672	0.012272	bulk	372	178	222.0	5.29	0.77	0.78	13.01	354	0.22		10.00	61.8	10.31	0.15	0.80	21.77	3.45
Redwood	17-Dec-04	29-Dec-04		486	0.012272	bulk	174	153	181.3	4.00	0.53	-0.11	9.90	278	0.16	1.71	7.91	66.2	6.14	0.05	0.93	18.72	2.70
Redwood	29-Dec-04	12-Jan-05		630	0.005809	bulk	1497	73	77.3	2.01	0.71	-1.26	5.60	145	0.01	1.83	5.34	44.1	36.99	0.01	0.86	24.25	4.98
Redwood	12-Jan-05	26-Jan-05		51	0.005809	bulk	192	219	214.7	2.56	0.53	0.50	13.28	431	0.21	1.36	9.87	83.6	15.94	0.10	0.57	22.06	4.12
Redwood	26-Jan-05	09-Feb-05		100	0.005809	bulk	675	236	221.3	2.59	0.75	0.43	12.76	297	0.19	0.32	9.61	83.0	12.66	0.07	0.68	24.69	3.35
Redwood	09-Feb-05	23-Feb-05		524	0.005809	bulk	110	45	75.8	2.04	0.29	-0.81	7.20	162	-0.07	-4.52	9						

**Table A-3 Cumulative Precipitation During Wet and Bulk Collection Periods (in mm)**

		<b>CVCC</b>	<b>CVE</b>	<b>Madison</b>	<b>Redwood</b>	<b>Oakland South</b>	<b>Dublin Firehouse</b>
<b>17-Mar-04</b>	<b>31-Mar-04</b>	17	18			25	
<b>31-Mar-04</b>	<b>21-Apr-04</b>	3	2			7	
<b>26-May-04</b>	<b>09-Jun-04</b>		7			2	3
<b>09-Jun-04</b>	<b>07-Jul-04</b>	6	3	3		0	0
<b>06-Oct-04</b>	<b>20-Oct-04</b>	53	56	55	51	70	87
<b>20-Oct-04</b>	<b>03-Nov-04</b>	37	34	31	30	46	42
<b>03-Nov-04</b>	<b>17-Nov-04</b>	26	21	20	18	39	16
<b>17-Nov-04</b>	<b>03-Dec-04</b>	12	13		13	18	11
<b>03-Dec-04</b>	<b>17-Dec-04</b>	62	61	63	55	79	47
<b>17-Dec-04</b>	<b>29-Dec-04</b>	32	35	35	40	69	
<b>29-Dec-04</b>	<b>12-Jan-05</b>	105	112	128	109	91	203
<b>12-Jan-05</b>	<b>26-Jan-05</b>	7	9	10	9		7
<b>26-Jan-05</b>	<b>09-Feb-05</b>	12	13	24	17		25
<b>09-Feb-05</b>	<b>23-Feb-05</b>	91	75	97	90		79

precipitation data for Oakland South and Dublin Firehouse from CDEC <http://cdec.water.ca.gov>



**Table A-4 Dry Deposition Rates ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ )**

site	start date	end date	field rep	g water	area m <sup>2</sup>	b/w/d	24Mg	27Al	28Si	47Ti	51V	52Cr	55Mn	56Fe	59Co	60Ni	65Cu	66Zn	88Sr	111Cd	121Sb	137Ba	208Pb
CVCC	07-Jul-04	09-Jul-04		10	0.05	DRY	992	1413	86.1	42.2	2.66	3.03	25.3	2622	0.41	5.77	14.0	76.7	8.22	-0.06	0.70	21.0	7.69
CVCC	28-Jul-04	30-Jul-04		10	0.05	DRY	634	976	71.5	48.0	3.59	3.87	31.6	1960	0.57	2.90	19.7	81.0	9.25	-0.06	0.34	25.8	12.36
CVCC	18-Aug-04	20-Aug-04		10	0.05	DRY	663	1072	64.4	39.6	3.39	3.44	31.3	2222	0.66	4.24	19.6	88.8	9.17	-0.06	0.52	21.1	15.39
CVCC	20-Aug-04	22-Aug-04		10	0.05	DRY	502	858	65.2	32.1	3.03	3.69	25.0	1676	0.49	2.25	16.8	77.4	6.48	-0.07	0.32	19.3	14.01
CVCC	31-Aug-04	02-Sep-04	A	10	0.05	DRY	481	760	74.3	42.4	2.89	3.74	27.4	1344	0.53	2.09	14.3	66.1	8.58	-0.14	0.23	19.2	9.92
CVCC	31-Aug-04	02-Sep-04	B	10	0.05	DRY	565	818	75.1	39.5	2.84	3.71	30.8	1642	0.61	2.92	17.9	72.5	8.80	-0.10	0.31	20.4	13.29
CVCC	15-Sep-04	17-Sep-04	A	10	0.05	DRY	1320	1969	147.3	83.0	6.22	9.07	58.6	3373	1.32	6.96	22.8	121.3	14.47	-0.04	0.59	37.7	14.49
CVCC	15-Sep-04	17-Sep-04	B	10	0.05	DRY	1230	1736	77.6	77.0	5.96	8.12	60.9	3134	1.32	7.35	29.8	123.5	15.83	0.10	0.38	37.2	17.97
CVCC	29-Sep-04	01-Oct-04	A	10	0.05	DRY	530	732	57.9	37.7	2.26	3.04	22.3	1313	0.72	1.65	18.0	59.4	7.11	-0.14	0.96	18.0	5.58
CVCC	29-Sep-04	01-Oct-04	B	10	0.05	DRY	600	827	25.1	38.3	2.50	0.46	23.0	1433	0.88	3.51	13.5	66.8	7.15	-0.08	0.24	18.3	5.95
CVCC	01-Oct-04	03-Oct-04	A	10	0.05	DRY	233	433	33.6	21.1	1.42	2.02	12.6	785	0.27	1.63	8.3	35.1	5.38	-0.15	0.16	12.6	5.06
CVCC	01-Oct-04	03-Oct-04	B	10	0.05	DRY	275	485	44.7	22.3	1.54	1.67	13.5	773	0.32	8.58	9.4	34.8	5.65	-0.13	0.51	13.8	5.11
CVCC	17-Nov-04	19-Nov-04		10	0.05	DRY	307	719	216.6	43.5	2.69	4.87	21.7	951	0.95	3.77	15.8	71.4	6.26	0.46	0.91	18.8	8.08
CVCC	19-Nov-04	21-Nov-04		10	0.05	DRY	740	1292	52.9	58.6	4.27	8.73	54.9	2024	1.21	6.51	14.2	95.1	8.65	0.54	0.65	28.2	13.13
CVCC	15-Dec-04	17-Dec-04		10	0.05	DRY	238	411	65.3	21.3	1.39	8.35	23.0	667	0.53	3.50	26.3	60.7	3.48	0.42	0.47	13.5	3.92
CVCC	19-Jan-05	21-Jan-05		10	0.05	DRY	171	309	59.2	20.0	1.76	7.61	25.1	613	0.57	4.15	14.9	50.1	4.07	0.43	0.53	12.5	5.72
CVCC	09-Feb-05	11-Feb-05		10	0.05	DRY	749	274	42.0	22.0	1.38	7.35	26.4	555	0.57	3.68	13.1	48.9	5.47	0.47	0.41	12.0	5.94
CVE	17-Nov-04	19-Nov-04		10	0.05	DRY	225	501	76.6	30.3	2.55	4.41	16.3	812	1.00	2.78	11.7	63.1	5.69	0.72	0.95	16.3	6.59
CVE	19-Nov-04	21-Nov-04		10	0.05	DRY	1165	2095	82.1	92.9	6.59	12.95	78.3	3042	2.19	8.77	27.9	106.6	13.08	0.70	0.62	35.7	16.44
CVE	15-Dec-04	17-Dec-04		10	0.05	DRY	205	487	72.3	23.8	1.41	8.12	24.6	724	0.70	23.10	10.7	72.8	8.01	0.40	0.59	15.2	4.85
CVE	19-Jan-05	21-Jan-05		10	0.05	DRY	188	414	46.5	20.3	1.39	7.70	22.2	697	0.50	4.11	9.5	58.0	4.39	0.32	0.56	13.0	7.41
CVE	09-Feb-05	11-Feb-05		10	0.05	DRY	170	366	67.5	21.7	1.25	5.35	18.6	547	0.40	3.13	12.5	49.3	3.50	0.17	0.34	11.1	2.55
Madison	07-Jul-04	09-Jul-04		10	0.05	DRY	600	886	35.9	23.6	1.29	1.29	14.7	1677	0.14	0.76	4.4	23.7	5.11	-0.15	0.17	10.4	3.62
Madison	28-Jul-04	30-Jul-04		10	0.05	DRY	261	470	122.8	31.4	2.09	2.65	19.8	870	0.22	1.94	11.3	45.7	5.69	-0.10	0.36	13.3	8.51
Madison	18-Aug-04	20-Aug-04		10	0.05	DRY	256	414	117.6	23.9	1.94	2.42	20.2	863	0.22	0.69	8.8	33.8	5.35	-0.12	0.21	12.6	7.25
Madison	20-Aug-04	22-Aug-04		10	0.05	DRY	237	336	30.4	20.5	1.83	1.80	22.6	777	0.16	1.20	7.7	30.1	3.67	-0.16	0.36	12.7	5.73
Madison	31-Aug-04	02-Sep-04		10	0.05	DRY	212	209	33.4	11.9	0.89	0.12	10.1	449	0.04	-0.09	3.3	17.8	2.45	-0.14	0.11	6.5	2.84
Madison	15-Sep-04	17-Sep-04		10	0.05	DRY	477	633	49.3	31.8	2.03	2.56	22.8	1120	0.36	1.22	6.9	28.9	4.74	-0.10	0.16	12.3	6.24
Madison	29-Sep-04	01-Oct-04		10	0.05	DRY	255	298	23.2	19.8	1.03	2.00	10.6	556	0.08	-0.75	4.4	20.6	2.92	-0.15	-0.09	8.4	1.81
Madison	01-Oct-04	03-Oct-04		10	0.05	DRY	152	171	22.6	12.5	1.09	0.67	6.1	373	0.02	0.59	3.1	4.9	2.81	-0.19	-0.07	6.5	2.41
Madison	17-Nov-04	19-Nov-04		10	0.05	DRY	64	92	49.0	12.0	1.16	3.30	4.2	159	0.78	1.30	5.4	10.8	1.66	0.74	0.74	4.5	2.41
Madison	19-Nov-04	21-Nov-04		10	0.05	DRY	126	236	31.1	18.0	0.94	6.03	21.1	401	0.35	4.63	32.3	42.0	2.63	1.37	0.29	9.5	4.95
Madison	15-Dec-04	17-Dec-04		10	0.05	DRY	29	41	51.9	9.9	0.47	6.85	16.1	144	0.34	4.38	14.7	19.5	1.21	0.43	0.35	6.4	2.21
Madison	19-Jan-05	21-Jan-05		10	0.05	DRY	31	60	49.7	6.2	0.41	7.18	12.3	112	0.24	3.04	4.6	24.2	1.11	0.29	0.21	5.3	1.91
Madison	09-Feb-05	11-Feb-05		10	0.05	DRY	44	81	32.6	6.7	0.31	3.43	7.8	79	0.10	1.12	6.9	12.4	0.84	0.12	0.01	3.4	1.07
Redwood	07-Jul-04	09-Jul-04		10	0.05	DRY	5760	15679	117.3	207.4	17.07	9.82	136.3	16120	3.42	9.15	33.8	148.1	32.43	-0.01	0.26	60.4	16.75
Redwood	28-Jul-04	30-Jul-04		10	0.05	DRY	697	1288	127.9	72.5	4.01	5.22	38.5	2709	0.77	4.10	20.1	137.8	14.57	-0.04	0.78	39.9	10.80
Redwood	18-Aug-04	20-Aug-04		10	0.05	DRY	955	1508	134.5	69.0	4.76	5.88	49.0	3632	1.05	5.97	30.0	184.1	36.21	-0.01	0.89	47.9	17.13
Redwood	20-Aug-04	22-Aug-04		10	0.05	DRY	483	832	149.4	46.4	3.25	5.24	25.9	1937	0.46	4.71	24.1	124.2	20.74	-0.05	0.87	30.5	13.55
Redwood	31-Aug-04	02-Sep-04		10	0.05	DRY	450	679	52.2	37.6	2.37	3.36	24.7	1476	0.51	2.14	16.1	92.7	10.50	-0.12	0.41	23.7	7.62
Redwood	15-Sep-04	17-Sep-04		10	0.05	DRY	987	1400	45.4	64.5	4.55	5.92	56.1	3072	1.07	4.76	19.7	146.0	19.38	-0.07	0.61	48.7	10.81
Redwood	29-Sep-04	01-Oct-04		10	0.05	DRY	556	814	64.1	44.7	2.48	3.37	23.1	1600	0.38	1.11	13.5	81.2	8.88	-0.14	0.68	25.7	4.92
Redwood	01-Oct-04	03-Oct-04		10	0.05	DRY	310	502	37.6	27.7	1.77	2.16	16.9	1103	0.26	2.61	22.7	77.7	7.76	-0.09	0.61	25.3	9.39
Redwood	17-Nov-04	19-Nov-04		10	0.05	DRY	1016	1962	134.9	124.8	7.14	12.87	82.7	5076	1.87	7.87	40.5	246.8	24.43	0.69	1.34	74.7	17.48
Redwood	19-Nov-04	21-Nov-04		10	0.05	DRY	2615	5720	123.4	282.2	16.69	20.65	159.9	11182	3.22	14.28	45.6	256.8	41.87	0.53	0.76	86.2	20.59
Redwood	15-Dec-04	17-Dec-04		10	0.05	DRY	1014	1830	107.1	84.5	5.74	15.13	71.5	4592	1.54	9.43	43.1	214.9	35.12	0.76	1.07	77.6	13.76
Redwood	19-Jan-05	21-Jan-05		10	0.05	DRY	1156	1608	51.5	94.8	6.15	15.26	77.4	4279	1.62	9.10	30.9	231.7	50.99	0.51	1.06	79.6	27.64
Redwood	09-Feb-05	11-Feb-05		10	0.05	DRY	800	1363	39.3	73.1	4.78	7.21	56.8	2938	1.21	6.09	35.4	186.1	19.84	0.28	0.59	52.6	10.73

**Table A-5. Trace Metal Loadings to the San Francisco Estuary from Atmospheric Deposition and Other Sources/Pathways (kg/year)**

Sources/Pathways	Copper	Nickel	Cadmium	Chromium	Citation
Total Atmospheric Deposition	5,900	2,800	280	4,800	Tsai et al. 2001
Direct Atmospheric Deposition (dry + wet)	1,900	930	90	1,600	Tsai et al. 2001
Indirect Atmospheric Deposition <sup>1</sup>	4,000 (6%) <sup>2</sup>	1,900 (4%) <sup>2</sup>	190 (8%) <sup>2</sup>	3,200 (8%) <sup>2</sup>	Tsai et al. 2001
Effluent Discharges <sup>3</sup>	6900-7300	5600-6100	98-330	1500-2000	Davis et al. 2000
Stormwater Runoff from San Francisco Bay Region <sup>4</sup>	66,000 (36,000 - 150,000)	49,000 (27,000 - 78,000)	2,300 (1,300 - 3,700)	40,000 (22,000 - 64,000)	Davis et al. 2000
Stormwater Runoff from Central Valley Region <sup>4,5</sup>	270,000	410,000	1,600	550,000	Davis et al. 2000

<sup>1</sup> Indirect atmospheric deposition is derived from runoff and tributaries that are atmospheric in origin.

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

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

<sup>4</sup> Include loading that is atmospheric in origin

<sup>5</sup> Crude estimates, according to Davis et al. (2000)