

**2004 Sampling and Analysis Plan: Brake Pad Partnership Castro Valley  
Atmospheric Deposition Study**

Prepared for the Brake Pad Partnership



submitted by:  
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## **Introduction**

Toxic pollutants such as copper are routinely emitted into the atmosphere by either nature or human activities such as industrial sources (stationary sources) and motor vehicles (mobile sources). A number of factors such as weather conditions, the form pollutants are in (solid, liquid, condensed vapor, or gas), and the particle size affect pollutant distribution in the atmosphere and the ways and rates they are removed from the atmosphere. The deposition of air pollutants to surface water can occur by several processes, including rain or snow scavenging of gases and particles, dry deposition of dust and particles, deposition through cloud and fogwater, air-water exchange, and air-terrestrial exchange processes.

Copper is one contaminant of concern in the San Francisco Bay region, due to concentrations in the Bay surface waters approaching (and occasionally exceeding) water quality criteria. Recent work has indicated that a local site specific objective with a higher copper criterion is appropriate, but increases in copper loading would result in renewed concern. Because copper is a major component brake pad material, there is some concern of an increase in copper loading to the Bay from increased copper content of brake pads and increases in vehicle traffic for the region. The purpose of the Castro Valley Atmospheric Deposition Study (as a portion of a larger Brake Pad Partnership (BPP) project investigating copper fate and transport in Castro Valley) is to provide temporally and spatially resolved measurements of the deposition of selected pollutants (particularly copper) from the air directly to the Castro Valley Creek watershed. Data from the study will be used to calibrate a model of air transport and deposition of copper in the watershed for the BPP project. The workplan for this project is adapted from the 1999-2000 RMP Atmospheric Deposition Pilot Study.

## **Site Selection**

Two sampling sites will be located in the Castro Valley Creek watershed to represent general urban and open space land uses. Site requirements include the following.

- a. There are no major point source emissions situated near the site.
- b. The site has all-weather access, adequate power supply (120VAC), and a security fence if not otherwise secured.
- c. The site is large enough to allow adequate spacing between (two) samplers.
- d. Major obstruction objects (e.g. building, trees, etc.) near the site do not project onto the site with an angle of greater than 45°.

Preliminary discussions with air modelers on the project have indicated that building rooftops in urban and open space areas (e.g. administrative buildings) or similar structures might be suitable (i.e., elevation above ground for the collectors will not greatly impact results), providing they have the other needed site characteristics. Identification and selection of specific sites will be made in consultation with Alameda County staff.

## **Sampling Schedule**

Sampling is scheduled on an approximately biweekly basis during two seasons (wet and dry) over an 8 month period. Due to the need to complete sampling within 8 months, samples will be collected every 12 days to cover a range of days within a week over each sampling season.. Sampling will begin as soon as appropriate sites are selected and equipment and analytical laboratories are prepared, likely beginning in mid to late January continuing through the end of August. Wet deposition samples will be collected

continuously over each 12 day sampling period. Dry deposition samples will be collected for 24 hour periods over the first day of each 12 day sampling period.

## **Sampling Methods**

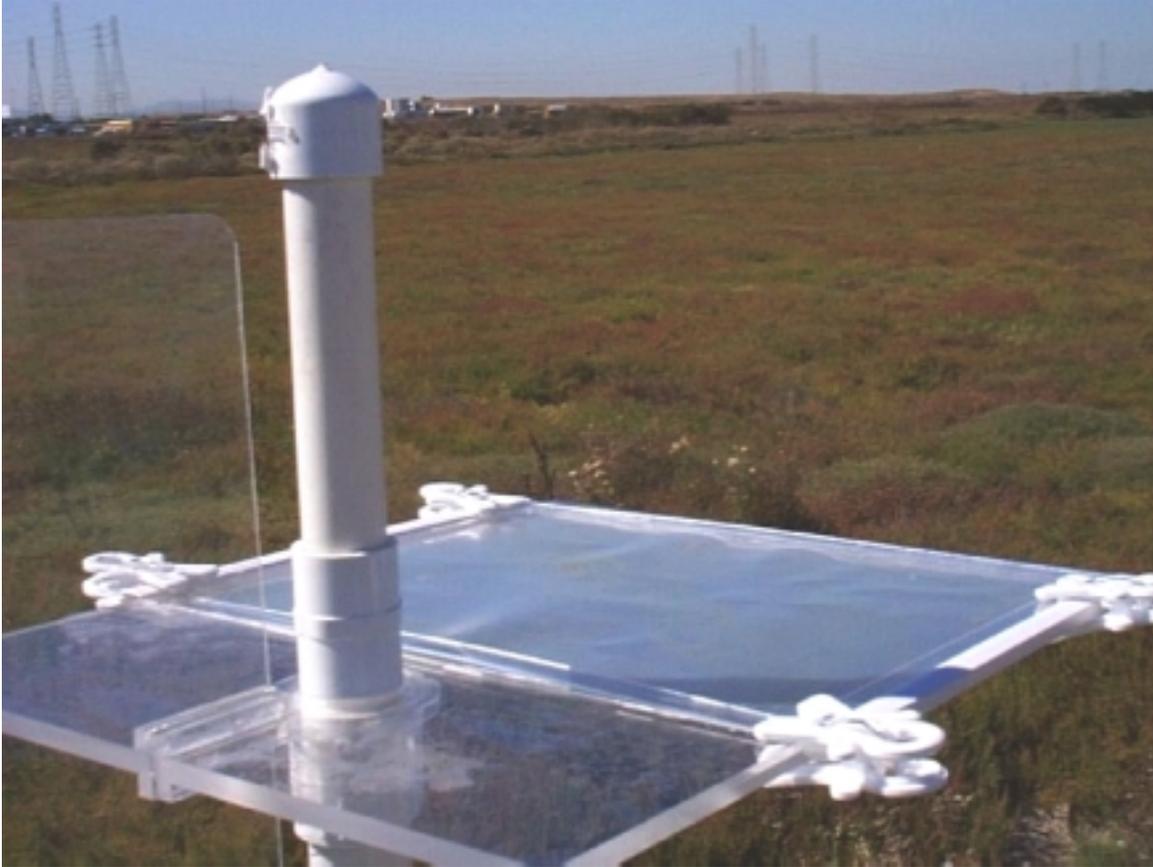
Standard operating procedures (SOPs) for field sampling methods have been prepared collaboratively by San Jose Environmental Services Department (direct dry deposition) and SFEI (feedback to all) for the previous RMP Atmospheric Deposition Pilot Study. Those methods with minor modification will be used for this study. The methods follow principles established for collection of trace metal clean samples. SOPs for wet deposition have been adapted from those used by NADP/MDN. SOPs for the applicable cleanup procedures, sample preparation, and sample handling are those approved or recommended by the U.S. EPA and used by the corresponding analytical laboratories. Sample collection procedures are described in brief below.

### ***Dry Deposition Sampling***

This study will use surrogate plates to collect dry deposition samples of trace metals in particles from the air. The “Egret I” sampler (Figure 1) to be used in this Pilot Study is an adaptation of the prototype developed by other investigators (Holsen et al. 1991). The original sampling device, with greased Mylar films mounted on a knife-edge plate, has been described by Yi and associates (Yi et al. 1997a; Yi et al. 1997b), and evaluated by other investigators (Holsen et al. 1993; Paode et al. 1998; Pirrone et al. 1995). The prototype is further modified for this study. The total exposed surface area is enlarged from 123 cm<sup>2</sup> to 500 cm<sup>2</sup>, and all components of the device were made with metal-free materials.

Egret I has two wind-vanes that pivot according to the wind direction. Particles from the ambient air deposit directly onto a 20x25 cm Mylar film coated with a thin-layer of L-Apiezon grease. The Mylar film is placed on a surrogate surface plate, which in turn was mounted and secured to the wind-vane with plastic clips. The cartridge plate is pointed into the wind with a leading knife-edge to provide a laminar or non-turbulent flow of air over the surface of the Mylar film. The L-Apiezon grease applied to the Mylar film provided a sticky surface to capture particles, and prevent particle bounce (Noll et al. 1990). The non-volatile grease is relatively free of the chemicals being monitored in the Study. Blank samples of unexposed plates will be analyzed in the laboratory to ensure minimal blank contamination from sampling materials.

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**Figure 1. Dry Deposition Sampling Device (Egret I)**

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

Mylar film will be cleaned sequentially with methanol, 2% nitric acid, and deionized distilled water. After the Mylar film is air-dried, approximately 150 mg of L-Apiezon grease is evenly applied. The Mylar film is weighed before and after the grease was applied to ensure that same amount of grease is applied. Greased Mylar film will be exposed to the ambient air for 24 hours. Actual exposure duration, along with other pertinent field operating information and sample conditions, will be recorded on a field observation form (FOF). Duplicate samples are to be collected at each site once every 14 days. Periodically during sample installation and retrieval, field blanks will be collected. Field blanks are sample plates removed from their transport containers for instantaneous exposure and returned to the containers immediately.



**Figure 2. Wet Deposition Sampler (Aerochem Metrics)**

### ***Wet Deposition Sampling***

An automatic collector specifically designed for the National Atmospheric Deposition Program/Mercury Deposition Network (NADP/MDN) will be used to collect precipitation samples. The device has been described in detail and evaluated by other investigators (Vermette et al. 1995). A sampler (Aerochem Metrics, Inc., Bushnell, FL) modified by the Illinois State Water Survey is used for collecting precipitation samples for trace metals (Figure 2). A precipitation sensor activates a lid to expose collection funnels during a precipitation event. At the end of the precipitation event, the sensor dries off, closing the lid.

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

Sampling bottles and funnels will be loaded into the sampler using adaptations of EPA Method 1669 techniques to minimize sample contamination. Field blanks will be periodically collected by loading the sampler, and immediately collecting the bottle. Wet deposition bottles deployed during periods with no precipitation may also be analyzed to assess longer term contamination from deployment in the sampler.

## **Analytical methods**

### ***Dry deposition sample analysis***

After sample retrieval, particles collected on the greased Mylar film are recovered by rinsing with 50 mL hexane. The samples are then dried under vacuum before they were digested in 20 mL of 10% ultra-pure HNO<sub>3</sub> for 30 minutes in a microwave oven. Samples are subsequently analyzed by inductively coupled plasma-mass spectrometry (ICP-MS, EPA Method 200.8) or other another method suitable for trace metal analysis. For quality assurance and quality control purposes, a externally generated standard reference material (e.g., from NIST) is to be analyzed to verify accuracy of analytical quantitation.

### ***Wet Deposition Sample Analysis***

Precipitation samples are weighed and acidified with trace-metal grade nitric acid to an acid concentration of 0.2%. The samples are equilibrated for more than 48 hours before being analyzed. For samples containing less than 10 mL of precipitation, 20.0 mL of reagent water is added, and the sample is acidified to 0.2%. Before analysis, concentrated HNO<sub>3</sub> is added to 10 mL of the sample until it contains 2% nitric acid. The sample is then digested at 85°C for 2 hours. The digested samples are then analyzed by ICPMS (USEPA method 1638 or 6020) or other method appropriate for trace metal analysis in water.

### **Analysis schedule**

Analyses will start when samples begin arriving at the analytical laboratory. Samples from multiple collections may be batched for analysis. Although holding times for trace metal samples of up to 6 months are permitted, target turnaround times for laboratory analysis will be 30 days or less after receipt of samples. Final samples collected may be subjected to a rush analysis to allow sufficient time for other project elements.

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