City of San Diego Aerial Deposition Study, Phase II

Final Report

March 23, 2009

City of San Diego

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Aerial Deposition Study, Phase II

Final Report

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Acronym	**Definition**
APCD	Air Pollution Control District
ARCB	Air Resources Control Board
ASBS	Area of Special Biological Significance
BMP	best management practice
BPP	Brake Pad Partnership
CAA	Clean Air Act
CASQA	California Stormwater Quality Association
CTR	California Toxics Rule
GIS	geographical information system
HAP	hazardous air pollutant
ICID	illegal connection and illicit discharge
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
MS4	municipal separate storm sewer system
NADP	National Atmospheric Deposition Program
NPDES	National Pollutant Discharge Elimination System
PCA	principal components analysis
ROW	right-of-ways
RWQCB	Regional Water Quality Control Board
SIO	Scripps Institute of Oceanography
TMDL	total maximum daily load
USEPA	United States Environmental Protection Agency
WQO	water quality objective
XRF	X-Ray Fluorescence

LIST OF UNITS

Unit	**Definition**
µg/L	microgram per liter
ppb	part per billion
$\mu g/m^2/day$	microgram per square meter per day
$mg/m^2/day$	milligram per square meter per day
mg/L	milligram per liter
µm	micrometer
mg/kg	milligram per kilogram
%	percent
km	kilometer
mph	miles per hour
mm	millimeter
cm^2	square centimeter
m^2	square meter
µm	micrometer
σ_θ	sigma theta

EXECUTIVE SUMMARY OF THE CITY OF SAN DIEGO AERIAL DEPOSITION STUDY, PHASE II

The City of San Diego contracted Weston Solutions, Inc. (WESTON) to conduct Phase II of the Aerial Deposition Study. The primary focus of this phase of the aerial deposition study is to answer specific questions relating to total maximum daily loads (TMDLs), State Water Resources Control Board 303(d) listings (primarily related to metals), and Ocean Plan requirements for the La Jolla Area of Special Biological Significance (ASBS) in the City of San Diego. Currently, Chollas Creek has a TMDL for dissolved copper, lead, and zinc with no known point sources, with the exception of the municipal separate storm sewer system (MS4). TMDLs are also being developed for San Diego Bay at the mouth of Chollas Creek, Switzer Creek, and Paleta Creek. Tecolote Creek is on the 2006 State Water Resources Control Board Section 303(d) list for cadmium, copper, lead, and zinc, and Mission Bay is on the 2006 State Water Resources Control Board Section 303(d) list for lead. The La Jolla ASBS has had copper concentrations in storm water runoff above the Ocean Plan criteria. Indirect and direct aerial deposition of metals is thought to be a contributor (to an unknown degree) to the pollutant load in this highly urbanized setting. The Phase I dry weather aerial deposition study demonstrated that several areas in the Chollas Creek Watershed had elevated deposition rates for copper (WESTON, 2007). Freeways and major roadway land uses demonstrated a link between tire wear particles and zinc concentrations. However, some areas (e.g., Tecolote Canyon and Mira Mesa) did not indicate that aerial deposition was a significant contributor to water quality problems in the areas monitored. Additionally, the Southern California Coastal Water Research Project (SCCWRP) conducted a similar aerial deposition study along with the Southern California Bight in 2006, and found the site in San Diego Bay (at the Mouth of Chollas Creek) to have the highest mean copper deposition rate of the eight sites monitored throughout Southern California (SCCWRP, 2007). As a result of the findings of Phase I study, the Chollas Creek dissolved metals TMDL was revised to require the San Diego Regional Water Quality Control Board and the local Air Resources Control Board to review regulatory gaps that may impact water quality in the Chollas Creek Watershed. Additionally, this Phase II study focused on a subset of specific areas and was designed to address the following questions, identified during the initial Dry Weather Aerial Deposition Study:

1. **What is the annual aerial deposition rate in the high loading areas identified in the initial dry weather aerial deposition study?**
2. **What is the wet weather aerial deposition rate at the SD8(1) location?**
3. **What is the solubility of copper, lead, and zinc in atmospheric deposition particles during dry and wet conditions?**
4. **What is the direct aerial deposition rate of metals in the La Jolla ASBS?**

The second phase of this study is intended to help the City of San Diego further its understanding of the contribution of metals from aerial deposition both within the Pueblo San Diego Watershed and the La Jolla ASBS. The study results will provide information related to potential sources and therefore represents a Tier II Source Investigation Watershed Activity in accordance with the City's 5-Year Strategic Plan for Watershed Activities. The study also provides baseline data for assessing future BMP effectiveness, such as the implementation of Phase I street sweeping programs (Tier II BMP), and Tier III BMP placement to assess these Phase I activities per the 5-Year Strategic Plan. The data will also provide supporting evidence for needed legislative measures, such as reduction of copper in the brake pad manufacturing process as part of the Tier I Product Substitution Watershed Activity.

This study was conducted from September 2007 to August 2008 within the City of San Diego. The monitoring program included an annual dry deposition study, a wet deposition study, and a particle solubility study.

Dry Deposition Study

The dry deposition analyses were designed to answer Study Question 1 for the sites located in the Chollas Creek area and to answer Study Question 4 for the sites located in the La Jolla ASBS area. Samples were deployed at high loading (industrial) sites, two high traffic surface streets, and two reference sites at nine sampling locations throughout the City of San Diego (Figure ES-1). Dry deposition surrogate sample plates were deployed for approximately 24 sampling events throughout the annual study.

Figure ES-1. Study Area and Aerial Deposition Sample Locations

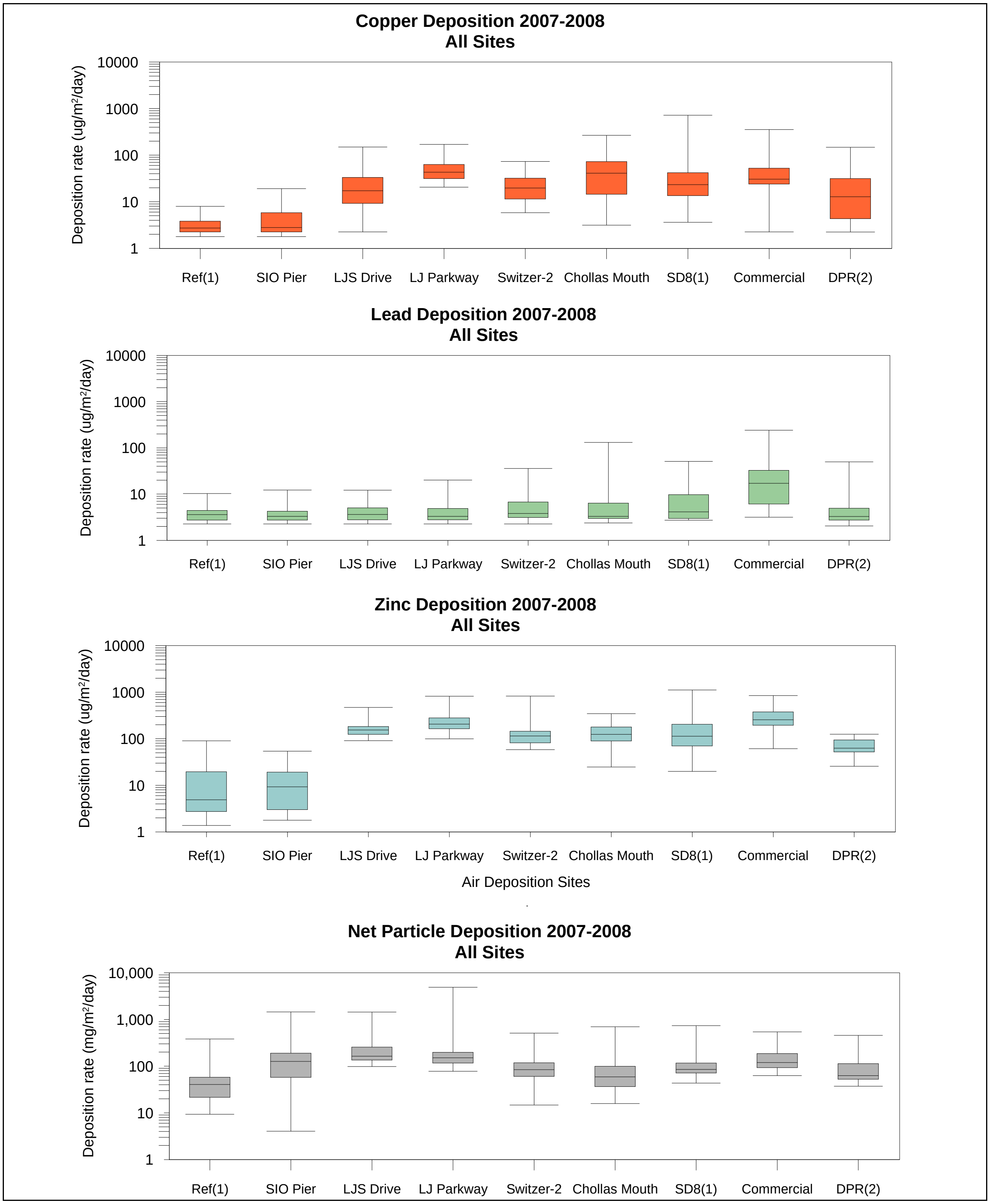
The results from the dry deposition study are presented as box and whisker plots of deposition rate results for copper, lead, zinc, and net particle deposition, shown on Figure ES-2. There was considerable variation in dry deposition rates of the main target elements across all sites, except for lead. Lead was rarely detected at most sites. However, lead was detected in 75% or more of samples at the Commercial Site in the Chollas Creek Watershed. Copper and zinc were measured at significantly higher levels at all inland sites compared with the reference sites (SIO Pier and Ref(1)) located along the coastline. Also, copper and zinc were detected in less than 75% of samples at the two reference sites.

Results indicate that the mouth of Chollas Creek (Chollas Mouth) had the highest median deposition rates of copper of all the sites in the Chollas Creek Watershed (37.6 µg/m^2/day). Statistical correlation analysis indicated that copper and zinc at the Chollas Mouth Site were highly correlated to northwest, north, northeast, and easterly wind directions which correspond to commercial, transportation, military, and industrial land uses.

The newly added site on Commercial Street in addition to the repeated Site SD8(1), located in the north fork of Chollas Creek, also had relatively high median copper deposition rates (29.5 µg/m^2/day at Commercial St.). Correlation analysis indicated that copper at Site SD8(1) was highly correlated to northeast, east, and southeast wind directions which includes commercial, and residential land uses. Commercial Street also had the highest median deposition rates for lead and zinc (15.6 µg/m^2/day and 216 µg/m^2/day, respectively). Correlation analysis indicated that zinc at the Commercial Street Site was highly correlated with north and northeast wind directions. The Commercial Street Site also provides additional supporting evidence of the higher loading areas of Chollas Creek presented in the Chollas Creek TMDL Source Loading, Best Management Practices, and Monitoring Strategy Assessment (WESTON, 2006).

Median net deposition was highest at the Commercial Site (119 mg/m^2/day). In addition, evidence of weather events, such as Santa Ana winds and local wildfires, caused maximum net deposition rates in 100% of sites located within all areas of the City of San Diego as a result ash fallout and higher resuspension rates. During the 2007 wildfires, a field screening for dioxin deposition was conducted at the Scripps Pier reference site to assess if ash fallout from wildfires is a source of dioxins to the La Jolla ASBS and watershed.

Aerial deposition rates of copper, zinc, and net deposition at the La Jolla sites were in the upper ranges of the deposition rates measured at all sites. Bromine, chlorine, and sodium deposition were highly correlated to ocean water with west, southwest, and south wind direction at LJS Drive, while copper deposition was highly correlated with east wind directions which correspond to transportation and residential land uses. At the La Jolla Parkway Site, copper deposition was highly correlated with southeast wind directions, while strontium deposition was highly correlated with north, northeast, east, and southeast wind directions corresponding to residential land use. Of particular interest is the relatively high median net deposition measured at the Scripps Institute of Oceanography (SIO) Pier Site, which is considered an additional reference site for copper, lead, and zinc measurements. The La Jolla Parkway and La Jolla Shores sites had the study's highest net deposition results with high variability. The Scripps Pier Site had the fourth highest mean net deposition of all sites (113 mg/m^2/day). Based on microscopic observation of deposition plates, it is likely that wind-blown sand from area beaches in the vicinity of the plates may be the reason for the elevated net deposition rates observed. This hypothesis is also supported by correlation analysis linking net deposition to crustal and seawater elements at SIO Pier.



Copper Deposition 2007-2008
All Sites

Lead Deposition 2007-2008
All Sites

Zinc Deposition 2007-2008
All Sites

Net Particle Deposition 2007-2008
All Sites

Figure ES-2. Box and Whisker Plots of Copper, Lead, Zinc, and Net Deposition Rates for the Period September 2007–August 2008

Wet Deposition Study

Wet weather depositional monitoring occurred at Site SD8(1) in Chollas Creek. This sampling was performed to answer Study Question 2. It is important to confirm previous studies (Sabin, 2005) that indicate the wet depositional load is generally less than 10% of the annual load in this study because of the low compliance levels in the Chollas Creek Watershed which are based on the California Toxics Rule (CTR). In this study, three storm sampling events were monitored.

Wet weather deposition rates were low but appear to be a contributing factor in wet weather exceedances of dissolved copper and zinc in the north fork of Chollas Creek (Site SD8(1)). This conclusion is based on the low compliance levels set by the CTR. Lead results were low or not detected during all three monitoring events. Based on the analyses conducted in this study, wet weather deposition of copper and zinc may be more influential for Chollas Creek than studies from other regions have previously indicated.

Particle Solubility Study

Particle solubility was analyzed at one location in the Chollas Creek Watershed. Currently, there have been no known studies of atmospheric deposition that have addressed Study Question 3. By evaluating this question, the City of San Diego will be able to determine the impact of aerial deposition in direct relation to the Chollas Creek dissolved metals TMDL and will have a better understanding of the characteristics of aerially deposited particles. Three dry weather sampling events were monitored at Site SD8(1) concurrently with the dry deposition sampling events as a basis for comparison.

Solubility tests at the north fork of Chollas Creek (SD8(1)) suggest that copper and lead have relatively low solubilities in their deposited state. The highest copper solubility was approximately 15% of the total copper concentration. The highest lead solubility was 2.49% of the total lead concentration. Zinc was relatively soluble, with the first event showing 88% of the total zinc concentration, 47% during the second event, and 58% for the third event.

When compared with the Copermittees' Regional Monitoring Program wet weather data, these results fall in the range of the solubilities measured in storm water runoff over the past seven years of monitoring. These results provide additional supporting evidence that indirect aerial deposition particulates may account for the majority of the copper and zinc and, to a lesser degree, lead that is found in Chollas Creek storm water runoff.

Although the data assessed present evidence of the processes and sources of aerial deposition, several questions were not fully answered, including:

1. **Do identified high deposition rate areas coincide with high runoff concentrations for copper, lead, and zinc?**
2. **How do metals concentrations from residential runoff areas compare to industrial/commercial runoff areas in the same relative aerial deposition area?**
3. **Are some facilities/sites contributing greater runoff concentrations of copper, lead, and zinc compared to other facilities/sites?**

The key findings from this report lead to the following recommended actions with regard to storm water management and meeting load reductions required by current and future TMDLs in City of San Diego watersheds:

It is recommended that:

- Tiered best management practice (BMP) presented in the Chollas Creek Source Loading, Best Management Practices, and Monitoring Strategy Assessment Report (WESTON, 2006) be implemented with the first tier emphasizing source controls, pollution reduction measures, and source identification studies. Source control measures are recommended to be the current focus over storm water treatment BMPs at this phase to reduce loads.
- The City of San Diego continue efforts with the Brake Pad Partnership and the CASQA Brake Pad Partnership Subcommittee.
- Inspections and monitoring of metal-related industries (both water quality and air quality monitoring) be increased based on the recommendations in the Chollas Creek Source Loading, Best Management Practices, and Monitoring Strategy Assessment Report, and this report, to identify higher loading facilities and ensure compliance with applicable storm water and air pollution control regulations.
- The Chollas Creek Dissolved Metals TMDL Implementation Plan consider high loading areas near the Mouth of Chollas Creek and near Commercial Street for BMP focus areas.

1.0 INTRODUCTION

The City of San Diego encompasses a land area of approximately 342 square miles with highly urbanized and developed land uses. Several areas within the City of San Diego experience detections of specific metals (copper, lead, and zinc) above dry weather action levels during dry weather flows or above the San Diego Basin Plan water quality objectives (WQOs) during wet weather flows. Frequently, dry weather illegal connection and illicit discharge (ICID) investigations for metals exceedances are inconclusive with no specific point sources identified. A watershed monitoring study in Chollas Creek during 1999–2001 concluded that concentrations of copper, lead, and zinc were ubiquitous in the watershed and that no specific point sources could be identified (MEC, 2002).

Aerially deposited contaminants that accumulate and subsequently wash off from dry weather or wet weather flows are suspected sources of contamination and were recognized but not studied within the City of San Diego prior to 2006. An atmospheric deposition study conducted in Santa Monica Bay Watershed concluded that the major source of contaminants to the air is re-suspended dust, primarily from roads, and that atmospheric loadings are primarily the result of dry deposition of large diameter particles (>10 µm) on the watershed (Stoltzenbach et al., 2001). A conceptual diagram of the processes affecting aerial deposition is shown on Figure 1-1.

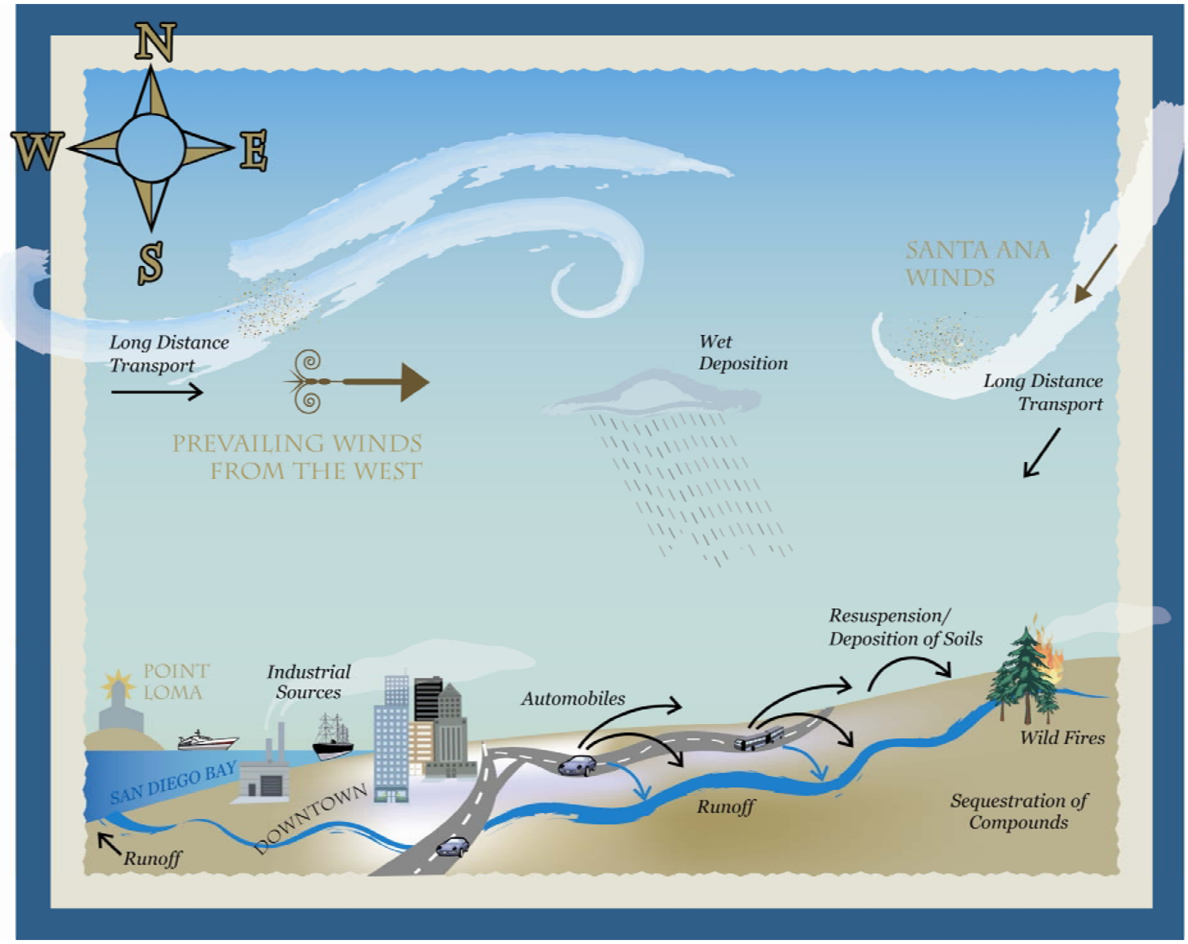


Figure 1-1. Conceptual Diagram of Processes Affecting Aerial Deposition

The City of San Diego faces TMDL and 2006 State Water Resources Control Board Section 303(d) listing regulatory compliance issues for metals pollutant loading in several waterways. The La Jolla Area of Special Biological Significance (ASBS) must also meet a daily maximum California Ocean Plan standard of 12 parts per billion (µg/L) for copper, for which there are no identified point sources in the area. Previous wet weather monitoring in the La Jolla ASBS Watershed has indicated low level exceedances of copper in storm water runoff. The contribution of aerially deposited pollutants both directly to these impaired waterbodies and indirectly through accumulation and subsequent storm water runoff in the San Diego Region was recently not fully understood. In June 2006, Weston Solutions, Inc. (WESTON®), under contract from the City of San Diego, designed and implemented the City of San Diego Dry Weather Aerial Deposition Study (WESTON, 2007c). The purpose of the study was to better understand the overall contribution of aerially deposited copper, lead, and zinc within areas of the City of San Diego. Deposition rates and particle size distribution were evaluated spatially and by distance downwind from a separate freeway transect. The key findings from the Phase I study are presented as follows:

- **Source of Particulates** – Review of the study results suggests that on a regional scale, the aerial deposition of copper particulates is likely a function of brake-wear debris and other transportation-related particulates, which is consistent with current knowledge of vehicle emissions and deposition. However, based on data review and observations, it is likely that other sources (e.g., aerial emissions from industrial, commercial, and construction activities) contribute to the presence of copper particulates near the Chollas Creek SD8(1) Site and near the mouth of Chollas Creek. Zinc is likely associated with tire and belt wear, with deposition rates being a function of proximity to roadways, although galvanized wear debris was also observed. Zinc associated with brake wear may also be a contributing factor to elevated deposition rates. Lead, while less frequently detected, is likely a function of re-suspended roadway dust, mobilization of soils during rain events, or other anthropogenic particulate sources (e.g., lead solder, paint chips, and other materials).

- **Distribution and Deposition Rates of Particulates and Proximity to Freeways** – Results of a freeway transect study conducted at Interstate 805 showed that zinc deposition rates decreased with distance from the freeway in both the deposition disks and air concentration studies. Tire and belt wear particles were frequently observed in samples collected near roadways and generally decreased with distance from freeways. Particles from anthropogenic sources (e.g., mechanically worn metals, flux condensation spheres, rust, and paper) in addition to naturally occurring particles (e.g., sand grains and plant material) were also observed. In contrast to zinc, copper was not found to have a similar deposition gradient with respect to proximity to freeways.

- **Distribution and Particle Size** – Copper from brake wear debris is primarily found in the fine particle size fraction of 1–5 microns (Haselden et al., 2006). These fine particles will travel farther from their sources as shown by air quality dispersion modeling (up to 1500 meters) and likely contribute a large percentage of the copper deposition rates observed at other sites. This may be one explanation as to why copper was generally related to areas near urban roadway environments. However, as previously mentioned, heavy industrial activities may be a more dominant source of copper with larger particle sizes and, hence, higher deposition rates in local areas near the mouth of Chollas Creek.

This *City of San Diego Aerial Deposition Phase II Report* presents the results and data analyses from dry deposition samples collected from September 10, 2007 through August 18, 2008, wet deposition samples collected between November 30, 2007 and March 16, 2008, and particle solubility samples collected between November 5, 2007 and June 16, 2008.

This report is organized by the following sections:

- Section 1—Introduction.
- Section 2—Study Design and Locations.
- Section 3—Land Use Analysis.
- Section 4—Sampling Methods.
- Section 5—Weather Monitoring.
- Section 6—Results and Discussion.
- Section 7—Assessment.
- Section 8—Conclusions and Recommendations.
- Section 9—References.

1.1 Problem Statement

Many studies relating to TMDLs and WQO exceedances are based on methods that have been developed since the inception of the Clean Water Act in 1972. These methods have been used specifically to measure the concentrations of pollutants in water. The methods have been standardized and are typically performed by laboratories certified to perform the tests, as required by federal and state regulations. Over a thousand analytical tests of water quality have been performed in San Diego County over the past decade. These data have shown that some waterbodies contain significantly higher concentrations of pollutants that pose threats to the beneficial uses listed in the San Diego Basin Plan. These data are also used to list impaired waters and develop the TMDLs. Once pollutants are identified to exceed WQOs, municipalities will often perform investigations (e.g., bacterial source tracking, ICID studies, and other general water quality tracking studies) to determine the source of the pollutants. In many of these cases, the root cause of the pollution source can be identified, since the flow of water is often continual and can be traced out using deductive reasoning. This is not the case with atmospheric deposition.

Atmospheric deposition has only recently been studied in depth to determine its contribution to water quality issues. Atmospheric deposition is highly variable depending on wind speed, direction, and the available sources that potentially contribute particulate matter to a basin. Airsheds are considerably larger than watersheds and may span multiple regions. Wind patterns and mixing may mask the true sources of the pollutants available to be dispersed. While air quality methods have also been developed over time—primarily by the USEPA and since the inception of the Clean Air Act (CAA) in 1963—they have not been developed to address water quality pollution. Many air quality standards and regulations primarily address the particles that are considered inhalable, which are discussed later in this section. Due to the complex nature of atmospheric deposition, there are no USEPA standardized methods to measure the transfer rates of pollutants to a land surface or directly to a waterbody. Though many measurement approaches have been developed to research aerial deposition for a variety of contaminants, they all have inherent variability that presents challenges in determining the sources of aerially deposited particulates.

To better understand aerial deposition, two key factors must be understood:

1. Aerially deposited pollutants originate from land use sources. Metals sources can be attributable to brake pads and tires from automobiles, galvanized fencing and gutters, roof tiles, fertilizers and fungicides, welding operations, painting, sanding and sandblasting, auto-dismantling, and various other industrial practices.

2. Wind is the driving factor that mobilizes these pollutants. Natural wind and wind from automobiles on freeways and roadways are the two primary forces in aerial deposition particle transport. While natural wind is typically the mechanism that carries pollutants and dictates the direction in which the pollutants travel, automobiles can also be a key factor in re-suspension of particles into the air from turbulence. Particle size and density also play a role in the distance the particles will travel.

The primary focus of this study is directed to answer specific questions relating to TMDLs and State Water Resources Control Board Section 303(d) listings (primarily related to metals) and questions related to the La Jolla ASBS in the City of San Diego. Currently, Chollas Creek has a TMDL for dissolved copper, lead, and zinc with no known point sources, with the exception of the MS4. TMDLs are also being developed for San Diego Bay at the mouth of Chollas Creek, Switzer Creek, and Paleta Creek. Tecolote Creek is on the 2006 State Water Resources Control Board Section 303(d) list for cadmium, copper, lead, and zinc. Mission Bay is on the 2006 State Water Resources Control Board Section 303(d) list for lead. Indirect and direct aerial deposition of pollutants is known to be a contributor to the pollutant load in this highly urbanized setting. The Phase I Dry Weather Aerial Deposition Study demonstrated that several areas in the Chollas Creek Watershed had elevated deposition rates of copper. Freeways and major roadway land uses demonstrated a link between tire wear particles and zinc concentrations. However, some areas (e.g., Tecolote Canyon and Mira Mesa) did not indicate that aerial deposition was a significant contributor to water quality problems at these areas mentioned. Additionally, the Southern California Coastal Water Research Project (SCCWRP) conducted a similar aerial deposition study along the Southern California Bight in 2006, and found the site in San Diego Bay (at the Mouth of Chollas Creek) to have the highest mean copper deposition rate of the eight Southern California sites monitored (SCCWRP, 2007). As a result of the findings of Phase I study, the Chollas Creek dissolved metals TMDL was revised to require the San Diego Regional Water Quality Control Board and the local Air Resources Control Board to review regulatory gaps that may impact water quality in the Chollas Creek Watershed. Additionally, this Phase II study focused on a subset of specific areas and was designed to address the following questions, identified during the initial Dry Weather Aerial Deposition Study:

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1.2 Air Quality and Water Quality Concepts and Overview

The terminology used throughout this document bridges two fundamental sciences, the study of air quality and the study of water quality.

- **Emission** – The release of gases or particulates into the atmosphere. Emission rates are a measure of the pollutant mass released from a point source over time (e.g., grams of copper per day).
- **Dispersion** – The spreading of gasses or particulates from a small volume of air near the emission source into the surrounding atmosphere.
- **Deposition** – The process of particulates being transferred from the atmosphere to the underlying surface.
- **Flux** – For the purposes of this report, flux, or mass flux, is the rate of a specific metal depositing from the atmosphere to a surface. The units are typically presented as micrograms of metal per square meter per day ($\mu g/m^2/day$).
- **Net Flux** – Similar to the example above, the net flux is the rate of the total mass that deposits on a surface and includes both inorganic and organic particulates ($\mu g/m^2/day$ or $mg/m^2/day$).
- **Buildup** – A term used in water quality studies to explain the process of particulate accumulation. Similar to a surface (e.g., as a roadway, sidewalk, or automobile) that accumulates dust and dirt that may be available to contribute pollutants to storm water runoff during wash off.
- **Wash Off** – The process of removing the particulates from the surface. This is primarily associated with rainfall, but may occur with irrigation, car washing, power washing, and other processes.
- **TMDL** – A regulatory water quality term used to define the total amount of a pollutant that can be discharged to a waterbody. The load can be assigned as pounds per year of a given pollutant or also on a concentration basis in terms of milligrams per liter (mg/L) or micrograms per liter (µg/L).

The Air Resources Control Board (ARB) is the lead air agency in the state responsible for enforcing the Federal CAA. Industrial and commercial emissions are controlled by 35 local districts, including the San Diego Air Pollution Control District (APCD). Air quality regulations are primarily based on threats to human health and do not consider impacts to aquatic ecological health. Many of the toxic air compounds monitored by the San Diego APCD (e.g., ozone, nitrogen dioxide, carbon monoxide, and sulfur dioxide) are not considered to impact the water quality of the San Diego Region. However, particulate matter is monitored by the San Diego APCD. Elevated concentrations of particulate matter can cause both health and water quality impairments. Particulates are classified as fine, coarse, and large particles. Particles that are less than 10 µm in aerodynamic diameter are called PM_{10} (inhalable particles). Particles less than 2.5 µm in aerodynamic diameter are called $PM_{2.5}$ (respirable particles). Particles will settle out based on several factors related to particle size, density, and wind speed and are summarized below.

Fine particles (< 2.5 µm):

- Greatest health relevance (increased disease and premature death greatest health relevance).
- Low deposition rates and mass contribution.
- Long transport distances.

Coarse particles (2.5–10 µm):

- Moderate health relevant (increased disease and premature death).
- Moderate deposition rates and mass contribution.
- Shorter transport distances.

Large particles (> 10 µm):

- Not health relevant (not inhalable; relatively sparse recent data).
- High deposition rates and mass contribution.
- Short transport distances, decreasing with increased particle size.

Particulates are comprised of nitrates, sulfates, organic chemicals, metals, soil, dust, and other material. Some particulates are directly emitted to the air from a variety of sources as follows:

- Cars, trucks, buses, and heavy equipment.

Smog – Source: JimmyAkin.org

- Industrial sources, construction sites, stone crushing and finishing, sandblasting, welding, and painting.

Concrete Cutting Photo Source: Health and Safety Executive (CIS No. 54)

Sandblasting Photo. Source: WESTON, 2006.

- Resuspended dust from paved and unpaved areas.

Leaf Blower – Source: Goldenspirit.com

- Wood burning and forest fires.

Image acquired October 22, 2007 at 17:52 UTC – European Space Agency (http://www.esa.int/esaEO/SEM8U23Z28F_index_0.html)

Particles may also be formed in the air via condensation, nucleation, and coagulation from the vapor phase. However, the majority of these particles are typically smaller than 1 µm. Particles larger than 1 µm are generally derived from mechanically generated processes. As previously stated, particles smaller than 2.5 µm tend to have low deposition rates and lower mass contributions and are dispersed over much larger areas. The San Diego APCD reports that San Diego meets the Federal $PM_{2.5}$ standard, but has not attained the state $PM_{2.5}$ or the federal and state PM_{10} air quality standard (County of San Diego APCD, 2006). Particulate matter larger than 10 µm is not regulated by the ARB since it is not considered to be an inhalable fraction.

The State Water Resources Control Board is the lead water quality agency in the state responsible for enforcing the Clean Water Act and California's Porter Cologne Water Quality Act. Water quality discharges are regulated by the nine regional boards, including the San Diego Regional Water Quality Control Board, which regulates both human health and aquatic life impacts. Aquatic life criteria for copper and zinc are roughly 100 times lower than the human health standard for consumption. However, both copper and zinc are not listed as regulated hazardous air pollutants (HAPs) under the CAA. The CAA establishes a National Ambient Air Quality Standard (NAAQS) for lead and lists lead compounds as a category of HAPs.

On February 9, 2006, a joint Air Resources Board–State Water Resources Control Board meeting occurred in Sacramento. Several topics were discussed between the two agencies to gain a more comprehensive understanding between air quality and water quality regulations and concepts.

The following is a summary of the principles of storm water regulations and why air regulations do not address water quality concerns.

Storm Water Permits

- Urban runoff is regulated under general storm water permits.
- Permits use a BMP approach to regulate pollutants.
- The owner or operator of a storm drain system is generally responsible for pollutants discharging from the storm drain (e.g., pesticides in runoff from lawn watering that ends up in the storm drain becomes the system owner's responsibility). The same is true for pollutants in storm water due to aerial deposition.
- Storm water inspectors will often visit industrial/commercial sites to ensure what is running off as point source pollution will not impair water. Though BMPs may be in place to control pollutant runoff (e.g., controlling parking lot runoff), the daily emissions from activities from these sites may spread over several kilometers and may not appear as a visual concern. However, as buildup occurs over time, the non-visual pollutant that was emitted may be significant. As previously mentioned, there is no regulatory framework to control aerial emissions of copper and zinc.

TMDL Program

- Aerial deposition can be a significant source of pollutants to an impaired waterbody and can be a critical element in some TMDL calculations.
- If aerial deposition occurs directly onto a waterbody, the deposition can be assigned a load allocation as a non-point source. If aerial deposition indirectly affects water quality through storm water runoff, the owner or operator of the storm drain can be assigned a waste load allocation. However, this waste load allocation comes in the form of the discharge of water in the storm drain system. This is the case for the Chollas Creek Watershed.

Permits

- There are no cases in which aerial sources (e.g., industrial facilities are considered point sources) are subject to an National Pollutant Discharge Elimination System (NPDES) permit solely on the basis of their air emissions (i.e., some facilities with air emissions may also have NPDES permits due to other discharge issues).
- USEPA considers aerial deposition to be a non-point source.

One observation from the joint Air Resources Board–State Water Resources Control Board meeting was that the meeting was a one-sided issue. It was apparent that air pollutants can cause water quality degradation, while poor water quality rarely causes poor air quality. Human health criteria are different from aquatic health criteria, and as a result, the air quality regulations do not address water quality issues related to aerial deposition. Air quality studies are often performed on an airshed basis, while water quality studies are performed on a watershed basis. Airsheds are considerably larger and often cover multiple watersheds and regions. If aerial deposition from transportation sources is the primary contributor to water quality issues in the Chollas Creek area, then it is logical to assume it occurs at similar rates in other similar watersheds. If the aerial deposition is higher in the Chollas Creek area compared with similar transportation-dense areas, it stands to reason that other emission sources may be influencing the water quality concentrations. Based on this concept, localized emission sources may play a significant role on a watershed scale.

1.3 Pollutants of Concern

The primary pollutants of concern for this study were copper, lead, and zinc. Other elemental data were also collected and are discussed in Section 4, Sampling Methods. This section describes the background information and sources of each pollutant of concern.

1.3.1 Copper

Copper (Cu) has an estimated crustal abundance of approximately 55 mg/kg (Kennedy, 2003). Copper commonly substitutes in minerals such as plagioclase and apatite and ranges from 10 mg/kg in granite to 100 mg/kg in basalt (Kennedy, 2003). Copper has a specific gravity of 8.96. Copper is an essential element for all higher living organisms. However, dissolved copper is considered to be toxic to aquatic organisms, such as algae, salmon, and other marine species, even in minute concentrations. The Chollas Creek metals TMDL WQO for dissolved copper is based on the CTR and varies depending on the hardness concentration from the sample collected. At a hardness concentration of 100 mg $CaCO_3$/L, the dissolved copper CTR acute WQO is 13.4 µg/L. The saltwater numeric criterion for dissolved copper for the Shelter Island Yacht Basin Dissolved Copper TMDL is set at 4.8 µg/L for the acute criteria. In comparison, the Federal Safe Drinking Water Act maximum contaminant level goal for total or dissolved copper is set at 1,300 µg/L.

Copper is a common consumer product used in building construction (e.g., plumbing, architectural copper roofs, mailboxes, and railings), electrical and electronic products (e.g., wiring and cables), metal plating and alloys, antifouling paints, and sandblasting material. Copper is also used as an algaecide and fungicide for swimming pool treatments and as a wood preservative. As of December 2008, the USEPA announced it is taking legal action to ban the use of acid copper chromate (ACC) in wood preservatives for residential use. Copper has also been shown to erode from overhead trolley wires from electric trains (Kennedy, 2003).

Copper is also used in brake pads as an additive to prevent brake disk screeching. Copper in brake pads has been extensively studied in recent years by the Brake Pad Partnership. The Brake Pad Partnership is an organization of government regulators, brake pad manufacturers, storm water management agencies, and environmentalists. The brake pad manufacturers have agreed to change their product formulations "if brake pad wear debris is found to impair water quality" (Sustainable Conservation, 2006). The Brake Pad Partnership has a technical library of over 197 studies related to the fate and transport of copper associated with brake wear debris. Currently, the California Stormwater Quality Association (CASQA) has formed a Brake Pad Partnership Subcommittee to implement a legislative bill to remove copper from brake pads.

Copper slag is used for sandblasting as an economical choice of abrasive grain for shipyards and contractors. Shipyard related industries are concentrated in the areas around the San Diego harbor. Many of the facilities in the vicinity of Chollas Creek have also reported their annual emissions of copper to be in the range of several hundred to several thousand pounds per year. This information is readily available for San Diego Region on the California ARB Community Health Air Pollution Information System (CHAPIS) website (http://www.arb.ca.gov/ch/chapis1/chapis1.htm). These facilities may include the use of copper slag and copper based paints in their processes.

1.3.2 Zinc

Zinc (Zn) is the 23rd most abundant element in the earth's crust (USGS, 2006). It is the fourth most common metal used, behind iron, aluminum, and copper. In the United States, approximately two-thirds of zinc is produced from ores (primary zinc) and the remaining one-third from scrap and residues (secondary zinc). Zinc uses range from metal products to rubber and medicines. Approximately three-fourths of zinc used is consumed as metal, mainly as a coating to protect iron and steel from corrosion (galvanized metal), as alloying metal to make bronze and brass, as zinc-based die casting alloy, and as rolled zinc. The remaining one-fourth is consumed as zinc compounds, mainly by the rubber, chemical, paint, and agricultural industries. Zinc is also a necessary element for proper growth and development of humans, animals, and plants; it is the second most common trace metal, after iron, naturally found in the human body. Though, in its dissolved form, it has been shown to cause toxic responses to aquatic organisms in elevated concentrations (Councell et al., 2004). The USEPA has set the maximum water quality goal for zinc at 120 µg/L. The Chollas Creek metals TMDL WQO for zinc is based on the CTR and varies depending on the hardness concentration from the sample collected. At a hardness of 100 mg $CaCO_3$/L, the dissolved zinc CTR acute WQO is 117 µg/L. In comparison, the Federal Safe Drinking Water Act does not regulate the concentration of zinc in drinking water. California sets the secondary (aesthetic) maximum contaminant level, which is non-promulgated, at 5,000 µg/L.

Sources of zinc to air and water include fertilizer, cement production, and transportation activities (e.g., combustion exhaust, galvanized parts, fuel and oil, brake wear, and tire wear). Zinc chromate primer is commonly used in the marine and aircraft industries. Zinc oxide is used in the vulcanization process for tires and rubber (estimated at 1% by weight). In urban environments, several studies reviewed by Councell et al. (2004) reported positive correlations of zinc to traffic volume, primarily as tire-wear. Researchers concluded that 60% of the total zinc load in south San Francisco Bay was attributable to tire-wear debris. There is less information related to zinc contamination from fan belt wear from automobiles. It stands to reason that the density of cars, trucks, and other industrial motors, including ventilation fans, air compressors, and other machinery using rubber belts, may also be a significant source of zinc containing particulates. However, further investigation is needed to determine the contribution of fan belt wear to atmospheric deposition.

Galvanized metal is also used in numerous products that have the potential to release zinc containing particulates to the atmosphere. These include fences, sign posts, guardrails, and galvanized metal roofs, which are frequently observed in San Diego County industrial areas. Galvanized roofs have been shown to release elevated concentrations of zinc in storm water runoff captured directly from these sources. Other sources of galvanized products include scrap metal recycling and auto-dismantling operations. Several automotive dismantling facilities have been observed in the area of Commercial Street and directly west of the north fork of Chollas Creek.

1.3.3 Lead

Lead (Pb) has the highest atomic number (82) of all stable elements. The main lead mineral is called galena (lead sulfide), which contains approximately 86% lead. It is estimated that 50% of the lead used today comes from recycling. Lead is not an essential element to living organisms and is known historically to be toxic to both humans and aquatic organisms. Lead has been shown to damage the nervous system and cause brain and blood disorders. It is detrimental to the development of young children. While lead awareness has significantly increased and exposure to public health has significantly decreased, lead is still commonly found in the environment. The USEPA suggests the primary sources of lead exposure in the urban environment are:

- Deteriorating lead-based paint.
- Lead-contaminated dust.
- Lead-contaminated residential soil.

The USEPA's Lead Awareness Program continues to work to protect human health and the environment against the dangers of lead. Information regarding lead can be found on the USEPA website (http://www.epa.gov/lead/). The Federal Safe Drinking Water Act sets the drinking water action level for lead at 15 µg/L, and the maximum contaminant level goal is 0 µg/L. The Chollas Creek metals TMDL WQO for dissolved lead is based on the CTR and varies depending on the hardness concentration from the sample collected. At a hardness of 100 mg $CaCO_3$/L, the dissolved lead CTR acute WQO is 64 µg/L, and the chronic WQO is considerably lower at 2.5 µg/L.

Lead has been widely used in the transportation industry, primarily for lead acid batteries, solder, bearings, and wheel balancing weights. Lead is a soft malleable metal also used for lead shot, fishing weights, sailboat keels for ballast, leaded glass, and television glass. Lead has been used historically in paint and is commonly found in homes built prior to 1978. Many older homes will often have larger concentrations of lead in soil in the areas directly adjacent to the home where paint chips will degrade and eventually slough off. Homeowners and remodelers have often used mechanical sanders to remove this older paint, in some cases, unaware of the hazards involved in releasing this material to the atmosphere as inhalable articulates. Lead was also used in gasoline to prevent engine knock. The use of leaded gasoline peaked during the 1970s but was eventually phased out during the 1980s. Many researchers have shown that lead in soil is primarily a residual effect of the historic use of leaded gasoline and that storm water containing lead is likely a result of the erosion of soils near roadways. The concentration of lead in soil is steadily decreasing over time. Total lead in Chollas Creek has also shown a significant decreasing trend (WESTON, 2006).

2.0 STUDY DESIGN

Three integral studies were performed for this project (dry deposition, wet deposition, and particle solubility) to answer questions related to how much, where, and which metals are being deposited as a result of aerial deposition within the City of San Diego. All three studies were performed within the City of San Diego. The following section describes the reasoning and methodology of the three studies.

2.1 Dry Deposition Analysis

The dry deposition analyses were designed to answer Study Question 1—*What is the annual aerial deposition rate in the high loading areas identified in the initial dry weather aerial deposition study?* Dry deposition surrogate samples were deployed approximately two times per month for approximately 24 measurements over the course of a monitoring year. Samples were deployed at high loading (industrial) sites, two high traffic surface streets, and two reference sites, including two new locations in the La Jolla ASBS Watershed, which has shown water quality exceedances of total and dissolved copper during storm events. A total of nine sample locations identified for this study included (Figure 2-1):

- Ref (1) – Reference site located near the southern end of Point Loma.
- SIO Pier – Scripps Institute of Oceanography Pier (reference site for La Jolla).
- LJS Drive – La Jolla Shores Drive (high traffic surface street with high braking).
- LJ Parkway – La Jolla Parkway (high traffic surface street, high braking).
- Switzer-2 – Switzer Creek adjacent to Interstate 5.
- Chollas Mouth – Area near the mouth of Chollas Creek.
- SD8(1) – Chollas Creek (north fork).
- Commercial – Commercial Street (industrial corridor in Chollas Creek).
- DPR(2) – Chollas Creek (south fork).

Samples were targeted for four-day deployments (e.g., deployed on Monday and retrieved on Friday). Samples were analyzed using USEPA Compendium Method IO3.3 (Protocol 9) similar to the Phase I Dry Weather Aerial Deposition Study (WESTON, 2007c). Approximately 14 rain events were recorded during the sampling period, with more events occurring in some months than in others, resulting in the rescheduling of deployments for dry weather samples.

File: \\Fsca02\Warehouse\GIS\California\San_Diego_County\CityofSanDiego\CitySD_NewProjects2007\Annual Air Dep\Air_Dep_2007\MXDs\2007_Study_Area1.mxd, 03-May-08 15:51, rodriguc

Figure 2-1. Sample Location Map for the 2007–2008 Phase II Aerial Deposition Study

2.2 Wet Deposition Analysis

Wet weather depositional monitoring occurred at the SD8(1) Site located in the north fork of Chollas Creek. This sampling was performed to answer Study Question 2—*What is the wet weather aerial deposition rate at the SD8(1) location?* It is important to confirm previous studies (Sabin, 2005) that indicate the wet depositional load is generally less than 10% of the annual load in this study because of the low compliance levels in the Chollas Creek Watershed, which are based on the CTR. Rainwater samples were collected in large volume sample vessels to capture sufficient volume for analysis. Three storm events were sampled by exposing the sample vessels just prior to the rainfall event and then closing them immediately following the determination of sufficient sample volume. Samples were analyzed for both total and dissolved metals by USEPA Method 200.8. Wet deposition sampling events occurred on November 30, 2007, February 2, 2008, and March 16, 2008.

2.3 Particle Solubility Analysis

Particle solubility was analyzed at one location in the Chollas Creek Watershed. Currently, there have been no known studies of atmospheric deposition that have addressed Study Question 3—*What is the solubility of copper, lead, and zinc in atmospheric deposition particles?* By evaluating Study Question 3, the City of San Diego will be able to determine the impact of aerial deposition in direct relation to the Chollas Creek dissolved metals TMDL and will have a better understanding of the characteristics of aerially deposited particles. WESTON addressed this question by conducting monitoring at the SD8(1) location by deploying two, 1-meter square, pre-cleaned Mylar film surrogate surfaces that were exposed to the atmosphere for a total of four days. The surfaces were allowed to accumulate dust particles in an exposed state (i.e., no Apiezon grease or mineral oil coating). Samples were analyzed for both total and dissolved metals by USEPA Method 200.8. Particle solubility sampling events occurred on November 5, 2007, March 17, 2008, and June, 16, 2008. These events occurred in parallel with the dry deposition events for comparison.

3.0 LAND USE ANALYSIS

The City of San Diego is highly urbanized and consists of many land uses. Aerial deposition is often a function of the sources and activities that occur in specific regions. The Phase I Dry Weather Aerial Deposition Study demonstrated that the majority of particles greater than 2.5 μm will generally settle out (or deposit) within 1,000 meters of the emission source (WESTON, 2007). To better understand the observed results from the sample stations selected, land use analysis was employed to characterize the sample sites within 1,000 meters. Land use information combined with directional wind data provides relevant information pertaining to potential emission sources.

3.1 Site Descriptions and Spatial Assessment

A total of nine study sites were located throughout the City of San Diego and were shown previously on Figure 2-1.

A geographical information system (GIS) was used to create buffer zones of influence and wind direction sectors to characterize the landscape of each site. To accomplish this, a series of five different buffer zones or concentric circles were generated, each originating at the sample location and extending out at radii of 25, 100, 250, 500, and 1,000 meters to characterize land use patterns within the immediate area defined by the concentric circles near each site. Each circle was subdivided into eight wind direction sectors, centered on the eight compass points (north, northeast, east, etc.). At each sampling site, the total amount of land area that lies within each land use class was calculated within each buffer and prominent wind direction sector. The results of this spatial analysis provide information to help examine relationships between observed aerial deposition, land use, and proximity to nearby roadways. The results are illustrated for each site, respectively (Appendix C).

A GIS database of current regional land use developed by the San Diego Association of Governments (SANDAG, 2007) was used to develop the land use summaries. The land use classifications in the SANDAG database include approximately 100 specific land use codes. For this spatial analysis, the land use codes found within the 1,000-meter site buffer regions were grouped into ten general categories:

- Low density residential.
- High density residential.
- Public facility.
- Industrial.
- Freeways.
- Other roads and utilities (including surface street right-of-ways (ROWs)).
- Commercial.
- Open space / parks and recreation.
- Military.
- Water.

3.1.1 Dry Deposition Study Sites

Sites are described regionally from north to south in this section, with the exception of the study reference sites, Ref(1) and Scripps Institute of Oceanography (SIO) Pier, which are described first. Predominant land use descriptions are based on land usage within the 1,000 meter buffer. Impervious surface calculations are based on land use categories including water.

3.1.1.1 Point Loma Reference Site

Site Ref(1) (32.67078ºN, 117.24095ºW, elevation: 409 feet) was located within Cabrillo National Monument near the southern end of Point Loma. The site was bounded by the Pacific Ocean to the west and south and by San Diego Bay to the east. This site was chosen as a reference location due to its location within a federally protected park with limited traffic and little development. The deposition surrogate sample plate was mounted on the northwest corner of the fence that surrounds Navy Bunker T-17, south of the old lighthouse, at 2.3 meters above the ground. The Point Loma Wastewater Treatment Plant was located approximately 1 km northwest of the sample site. There are also several unidentified US Navy facilities located approximately one mile to the north of the site on the western edge of Point Loma. Low flying aircraft bound for North Island Naval Air Station on Coronado Island may also fly over the site.

The predominant land use within the 1,000 meter ring is the Pacific Ocean (61.7%), and Cabrillo National Monument which is designated as open space / parks and recreation (26.8%). The total percentage of impervious surfaces within the 1,000 meter circle was approximately 11%.

3.1.1.2 Scripps Institute of Oceanography Pier

SIO Site Pier (32.86683ºN, 117.25652ºW, elevation: Sea Level) was located approximately 200 meters along the Scripps Pier, at the SIO. The deposition surrogate sample plate was mounted 2 meters above the pier and adjacent to the SIO weather monitoring station located approximately halfway down the pier. During the 2007 wildfires, a field screening for dioxin deposition was conducted at the Scripps Pier to assess if ash fallout from wildfires is a source of dioxins to the La Jolla ASBS and watershed.

The predominant land use within the 1,000 meter ring is water, which totals (61.0%). The University of California, San Diego occupies the next largest portion of area within the 1,000 meter ring with (15.8%) designated as Public Facility. Low density residential housing also occupies a large portion of the 1,000 meter ring with (11.9%) of the total area. The total percentage of impervious surfaces within the 1,000 meter circle was approximately 16%.

The prevailing winds, flowing in a westerly direction, are guided from the Pacific Ocean onto shore. The winds flowing from the Pacific Ocean allow this site to be used as a reference as there is little to no aerial deposition from anthropogenic sources to the west.

3.1.1.3 La Jolla Shores Drive

Site LJS Drive (32.86356ºN, 117.25305ºW, elevation: 57 feet) was located adjacent to 8582 La Jolla Shores Dr. The deposition surrogate sample plate was mounted approximately 2.5 meters above the ground. A new University of California facility was under construction approximately 300 meters west of the site. This site shares land use characteristics with the Scripps Pier Site which predominant land uses within the 1,000 meter ring are water (37.0%), low density residential (24.7%), and public facility (16.8%). The total percentage of impervious surfaces within the 1,000 meter circle was approximately 27%.

3.1.1.4 La Jolla Parkway

Site LJ Parkway (32.85039°N, 117.251906°W, elevation: 68 feet) is located in the Northwest corner of the La Jolla Parkway and Torrey Pines Road intersection. The deposition surrogate sample plate is mounted approximately 2.5 meters above an island where Torrey Pines Road merges into La Jolla Parkway. The intersection receives high traffic volumes coming from Interstate 5 from the east, and traffic on La Jolla Parkway from the West.

The predominant land use within the 1,000 meter concentric circle of the site was primarily low density residential (57.0%), followed by other roads and utilities (19.9%) and open space / parks and recreation (12.2%). The total percentage of impervious surface within the 1,000 meter circle was approximately 48%.

3.1.1.5 Switzer Creek

Site Switzer-2 (32.715937°N, 117.146745°W, elevation: 80 feet) was moved from its previous location of 1970 B Street near the southern edge of Balboa Park during the phase I study, to the northwest corner of 19th Street and Broadway Street, east of the overpass crossing the Highway 94–Interstate 5 interchange. The site was bounded by high density residential areas to the east and south and freeways, transportation, and commercial sites to the west and south. The site was chosen to be representative of the downtown San Diego area, with high urban surface street traffic volume. The freeway interchange is situated approximately 15 feet below the sample location while the width of the Interstate 5 is generally upwind of the sample location based on the prevailing westerly winds. The deposition surrogate sample plate was mounted on top of a street sign approximately 3.0 meters above the overpass.

The predominant land uses within the 1,000 meter concentric circle of the site were transportation (33.4%), public facility (14.3%), and freeways (13.3%). The total percentage of impervious surface within the 1,000 meter circle was approximately 68%.

3.1.1.6 Commercial Street

The Commercial Site (32.705399°N, 117.125122°W, elevation: 76 feet) was located on the southeast corner of Commercial Street and 32nd Street, adjacent to the Commercial Street Trolley Station. The site was bounded by the industrial corridor to the west, Interstate 15 to the east, and residential neighborhoods to the north and south. The trolley runs east and west along the industrial corridor. The deposition surrogate sample plate was mounted on a street sign approximately 3.0 meters above the sidewalk.

The predominant land uses within the 1,000 meter concentric circle of the site were low density residential (35.3%) and transportation (29.7%). The total percentage of impervious surface within the 1,000 meter circle was approximately 59%.

3.1.1.7 SD8(1)

Site SD8(1) (32.78222ºN, 117.19417ºW, elevation: 38 feet) was located in a primarily residential neighborhood near the north fork of Chollas Creek. The site was bounded by residential neighborhoods to the north and south and was located near a low traffic volume urban surface street. The nearest publicly accessible roadway was a cul-de-sac with a posted speed limit of 25 mph. Interstate 15 was located approximately 45 meters to the east, or downwind, based on the prevailing west wind. The adjacent freeway was considered to have a particulate mixing zone that included the site. The site was approximately 400 meters east of Commercial Street, which has numerous potential emission sources (e.g., auto wrecking yards, sandblasting, and painting facilities). The deposition surrogate sample plate was mounted atop the rain gauge mounting pole of the San Diego County Municipal Storm Water Program mass loading station approximately 3.5 meters above the ground.

The predominant land uses within the 1,000 meter concentric circle of the site were low density residential (34.3%), transportation (27.4%), and public facility (14.6%). The total percentage of impervious surface within the 1,000 meter circle was approximately 60%.

3.1.1.8 DPR(2)

Site DPR(2) (32.413210ºN, 117.064441°W, elevation: 16 feet) was located in a primarily residential neighborhood adjacent to 38th Street near the intersection of 38th Street and Alpha Street, and located adjacent to the south fork of Chollas Creek. The site was chosen to represent a low traffic volume urban surface street. The site was bounded by residential neighborhoods to the north and south and was approximately 700 meters east of Interstate 5. The deposition surrogate sample plate was mounted atop the rain gauge mounting pole of a City of San Diego Storm Water Program mass loading station at an elevation of 3.5 meters above the ground.

The predominant land uses within the 1,000 meter concentric circle of the site were low density residential (35.3%), transportation (23.6%), and open space / parks and recreation (10.2%). The total percentage of impervious surface within the 1,000 meter circle was approximately 56%.

3.1.1.9 Chollas Mouth

The Chollas Mouth Site (32.68770°N, 117.13077°W, elevation: 9 feet) was located within Naval Station San Diego near the intersection of 32nd Street and East Harbor Drive. The sample site was located directly adjacent and on the south side of the mouth of Chollas Creek. The Chollas Mouth Site was also approximately 400 meters to the east from the General Dynamics NASSCO Shipyard. During the deployment event series, several large ships were docked nearby undergoing repairs or were under construction. The deposition surrogate sample plate was mounted on a portable concrete pier base on top of the Port Operations Building No. 150 at an elevation of 2 meters above the building roof and 6.2 meters above the ground.

The predominant land uses within the 1,000 meter concentric circle of the site were water (36.2%) and industrial (29.4%). The total percentage of impervious surface within the 1,000 meter circle was approximately 45%.

4.0 SAMPLING METHODS

The following section describes the methodology used for data collection in this project. Three methods were used, including a surrogate sample disk method for dry deposition analysis, rainwater collection method for wet deposition analysis, and a particle solubility method.

4.1 Surrogate Sample Disk Method for Dry Deposition

4.1.1 Dry Deposition Flux Measurements

Dry deposition flux measurements were obtained using a pre-tared 47 mm oil-coated Teflon® disk mounted in a Teflon® passive sampler. The exposed surface area of the disk mounted in its holder was 39.5 mm in diameter. The oil coating is a metal-free mineral oil that provides adequate adhesion to prevent particle bounce and subsequent analyte loss. The Teflon® oil-coated disks were mounted in a cassette sample holder (Figure 4-1) and were then deployed on a surrogate surface plate with leading knife edge (<10°) to prevent turbulent flow (Figure 4-2 and Figure 4-3). One to three sample disks were mounted on the plate using the three marked recessed positions so that duplicate or triplicate samples could be collected.

Figure 4-1. Surrogate Sample Disk Cartridge

Figure 4-2. Cross Sectional View of the Aerodynamic Deposition Plate – Leading Edge is at a 10° Angle

Figure 4-3. View from above the Aerodynamic Deposition Plate Showing Three Positions Available for the Sample Cartridges

4.1.2 Sample Duration

Sample disks for dry deposition analysis were deployed for approximately 72–96 hours to ensure adequate loading of particulate matter to the disk surface area. Access to sample locations also resulted in slight variations of the sample duration, depending on the site.

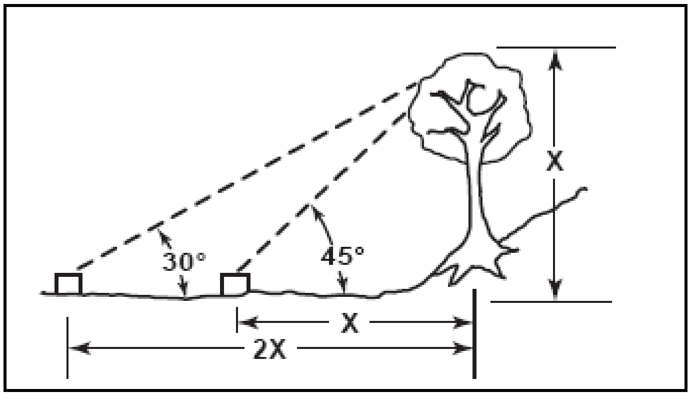
4.1.3 Sample Deployment and Deposition Plate Location

The National Atmospheric Deposition Program (NADP) Instruction Manual on Site Selection and Installation (NADP Manual 2001-01) provides guidelines on selecting stations for measuring concentrations in the air. These guidelines recommend placing collectors no less than 100 meters from transportation related sources, maintenance yards, or parking lots for local studies. The guidelines also recommend placing collectors no less than 10 km (upwind) or 20 km (downwind) from industrial or manufacturing sources in regional studies. These guidelines are designed to ensure representative measurements of background atmospheric conditions, rather than studying source-related impacts.

It should be made clear that the purpose of this investigation was to determine if differences in particulate and metals deposition rates exist within the City of San Diego and to relate the locations with areas where water quality problems related to metals exist. Also, it would be nearly impossible to meet the NADP locating criteria in the highly developed and urban setting of San Diego. While the NADP guidelines are useful, they are intended to be used for regional assessments on an airshed scale rather than a watershed scale.

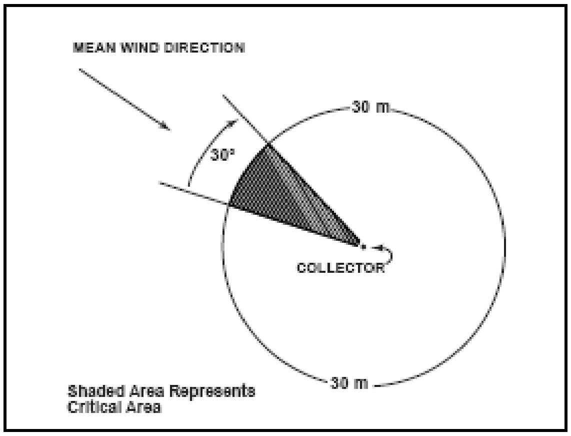
Fully assembled surrogate sample disks were deployed on an aerodynamic plate mounted on a pole at a minimum height of 2 meters and a maximum of 10 meters (or a single story roof top). Aerodynamic plates were also placed on existing rain gauge mounting poles where available (Figure 4-4). Sample locations were ideally located approximately two times the distance away from the tallest objects in the nearby vicinity, as depicted on Figure 4-5. Samplers are also located so there are few or no obstacles within 30 meters of the collector in a 30-degree wide corridor centered on the prevailing wind direction (Figure 4-6).

Figure 4-4. Aerodynamic Deposition Plate Mounted on the Rain Gauge Pole at Site DPR(2)



Source: NADP Manual 2001-01

Figure 4-5. Ideal Distance from Objects of Taller Height (if samplers can not be placed farther from the object, sampler height should be increased to minimize the effects of the surrounding object)



Source: NADP Manual 2001-01

Figure 4-6. Samplers Should be Placed in an Area with Respect to the Critical Area of Effects in Relation to the Mean Wind Direction

Each sampling event was recorded on a sample field log (Appendix E). Site conditions, weather, confounding factors, and other general observations were recorded for each sample deployment and sample retrieval. The dates and times of sample deployment and retrieval were recorded for each sampling event immediately after each action.

Weekly area observations, weather conditions, and news events were also documented, including local fires, wind, and weather conditions (e.g., fog, rain, Santa Ana winds, fireworks events, and other news) that may indicate unusual site conditions and would otherwise go unnoticed during field deployments.

4.1.4 Disk Handling Procedures

The 47-mm deposition disks were received pre-tared from the laboratory in a disk shipping cartridge (Figure 4-7). Sample disks were removed from the shipping cartridge and were then assembled in the passive sampler cassette (Figure 4-8). Disks were transferred using pre-cleaned stainless steel forceps to avoid contact and damage during transfer into sample cassettes.

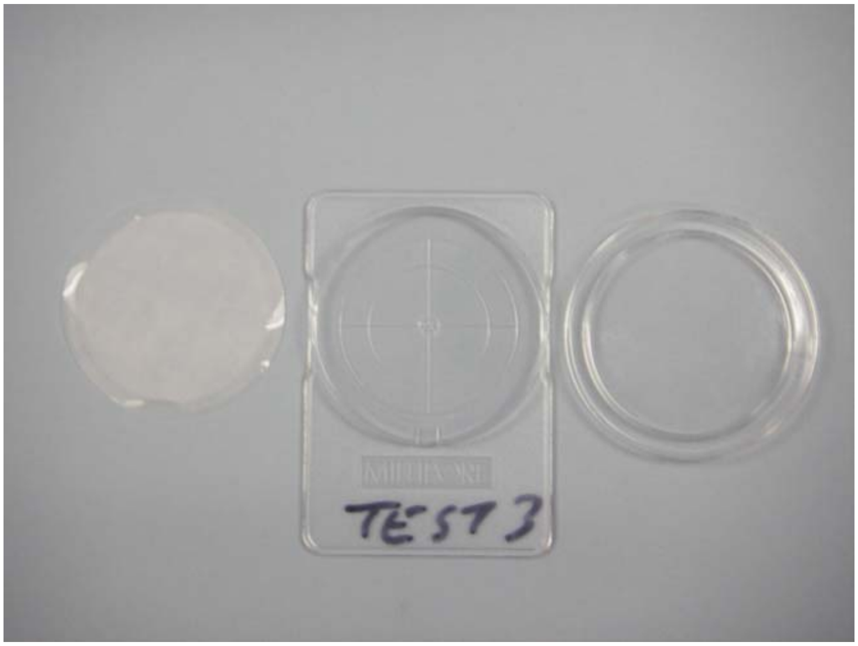


Figure 4-7. Teflon Sample Disk (left), Shipping Cartridge (middle), and Cover (right)

Figure 4-8. Teflon Sample Disk (left) and Passive Sampler Cassette Parts, Backing Screen (second from left), Base (second from right), and Top (right)

Samplers were handled and assembled no more than one day prior to deployment. Assembled samplers were promptly enclosed in a new 5.5-ounce plastic soufflé cup until deployment. Samples were not exposed until just prior to placement in the aerodynamic plate holder at the site and were removed and transferred to the laboratory under chain of custody in the same manner. Samples were removed in the order which they were deployed. Care was taken to ensure that samples were kept level after deployment. A field sample log was completed during each plate deployment and plate recovery (Appendix E).

4.1.5 Sample Inspection Process

All samples were inspected for acceptable quality prior to submittal to the analytical laboratory. Samples with obvious tears, abrasion, damage, bird droppings, or other factors causing suspect sample integrity were rejected from lab submittal (Figure 4-9). Sample inspection information was documented on the field sample forms.

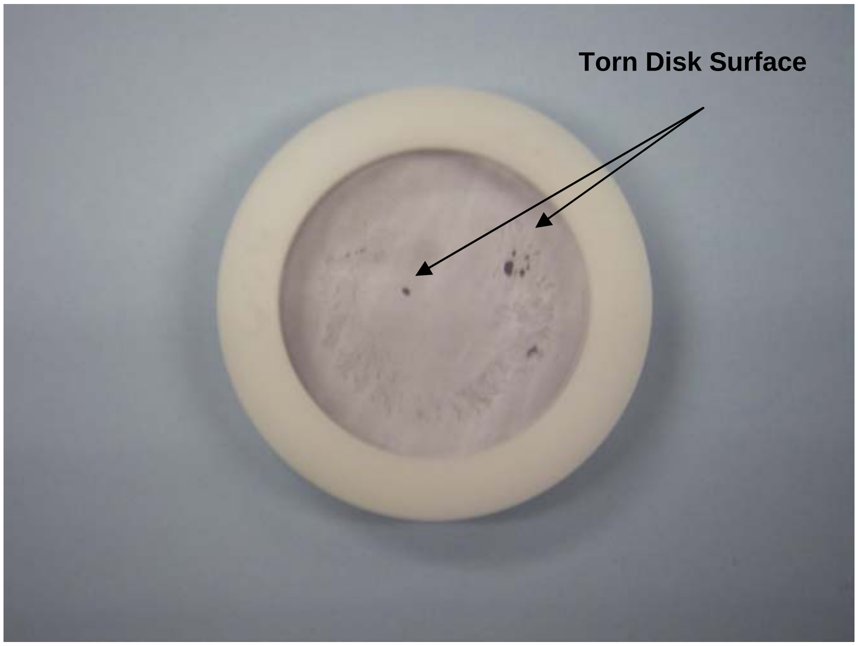


Figure 4-9. Example of Surrogate Sample Disk Rejected from Sample Submittal to Laboratory

4.1.6 Laboratory Analyses

Samples were analyzed by Chester LabNet in Tigard, Oregon for individual metals by X-Ray Fluorescence (XRF) following USEPA Compendium Method IO-3.3 (EPA/625/R-96/010a). The samples were also analyzed for total accumulated mass by gravimetry. These analyses are non-destructive and enable further analyses to be conducted.

4.2 Rainwater Collection Method for Wet Deposition

Wet deposition sampling was conducted using multiple 16-ounce, certified clean glass sample jars. Sample containers are deployed by opening the jars immediately prior to rainfall occurring and leaving the jars open for the duration of the rainfall event to ensure sufficient rainwater is collected to perform the sample analysis. Each 16-ounce glass jar has an approximate surface area of 38.5 cm^2. The glass sample jars were placed in a pre-cleaned plastic container for the exposure period (Figure 4-10). Following sampling, the samples were then stored on ice and transferred under chain of custody to CRG Marine Laboratories, Inc. for analyses. Analysis was then performed using USEPA Method 200.8 by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). One unopened sample filled with deionized water was used as a container blank check sample. Samples were analyzed for total and dissolved metals, as outlined in Table 4-1.

Figure 4-10. Wet Deposition Sampling at Site SD8(1)

4.3 Particle Solubility Analysis Method

Particle solubility was analyzed at the SD8(1) location by deploying two, 0.05 m^2 pre-cleaned mylar film surrogate surfaces that were exposed to the atmosphere for a total of four days (Figure 4-11). The surfaces were allowed to accumulate dust particles in an exposed state (e.g., no Apeizon grease or mineral oil coating). Samples were deployed at the same time as the deposition disks to determine if differences in methodology resulted in different total deposition rates. Following exposure, the surfaces were carefully rinsed with deionized water into a clean sample vessel with a known volume. One sample was preserved and analyzed for total metals. The second surface was rinsed with deionized water into an extraction vessel with a known volume and tumbled for 18 hours. The sample was then filtered through a 0.45-µm filter and analyzed for dissolved metals. The resulting concentrations were used to determine the concentration of total and dissolved metals in $\mu g/m^2/day$. Samples were analyzed for total and dissolved metals, as presented in Table 4-1.

Table 4-1. List of Analytes by Method and Laboratory

Task	**Dry Weather Deposition**	**Wet Deposition**	**Particle Solubility**
Method	**XRF (EPA IO3.3)**	**ICP-MS (EPA 200.8)**	**ICP-MS (EPA 200.8)**
Laboratory	**Chester LabNet**	**CRG Marine Labs**	**CRG Marine Labs**
Analytes	Aluminum	Aluminum (Total+Dissolved)	Aluminum (Total+Dissolved)
	Antimony	Antimony (Total+Dissolved)	Antimony (Total+Dissolved)
	Arsenic	Arsenic (Total+Dissolved)	Arsenic (Total+Dissolved)
	Barium	Barium (Total+Dissolved)	Barium (Total+Dissolved)
	Bromium	Beryllium (Total+Dissolved)	Beryllium (Total+Dissolved)
	Cadmium	Cadmium (Total+Dissolved)	Cadmium (Total+Dissolved)
	Calcium	Chromium (Total+Dissolved)	Chromium (Total+Dissolved)
	Chlorine	Cobalt (Total+Dissolved)	Cobalt (Total+Dissolved)
	Chromium	Copper (Total+Dissolved)	Copper (Total+Dissolved)
	Cobalt	Iron (Total+Dissolved)	Iron (Total+Dissolved)
	Copper	Lead (Total+Dissolved)	Lead (Total+Dissolved)
	Gallium	Manganese (Total+Dissolved)	Manganese (Total+Dissolved)
	Germanium	Molybdenum (Total+Dissolved)	Molybdenum (Total+Dissolved)
	Indium	Nickel (Total+Dissolved)	Nickel (Total+Dissolved)
	Iron	Selenium (Total+Dissolved)	Selenium (Total+Dissolved)
	Lanthanum	Silver (Total+Dissolved)	Silver (Total+Dissolved)
	Lead	Strontium (Total+Dissolved)	Strontium (Total+Dissolved)
	Magnesium	Thallium (Total+Dissolved)	Thallium (Total+Dissolved)
	Manganese	Tin (Total+Dissolved)	Tin (Total+Dissolved)
	Mercury	Titanium (Total+Dissolved)	Titanium (Total+Dissolved)
	Molybdenum	Vanadium (Total+Dissolved)	Vanadium (Total+Dissolved)
	Nickel	Zinc (Total+Dissolved)	Zinc (Total+Dissolved)
	Palladium		
	Phosphorus		
	Potassium		
	Rubidium		
	Selenium		
	Silicon		
	Silver		
	Sodium		
	Strontium		
	Sulfur		
	Tin		
	Titanium		
	Vanadium		
	Yttrium		
	Zinc		
	Zirconium		

Figure 4-11. Particle Solubility Apparatus Mounted with a Surrogate Sample Disk Apparatus at Site SD8(1)

4.4 Analytical Methods

Several laboratory analytical techniques were used to analyze sample media collected during this study. Energy dispersive XRF was used to analyze the surrogate dry deposition disks. The wet deposition and particle solubility samples were analyzed by ICP-MS. The following subsections further describe each method.

4.4.1 Energy Dispersive X-Ray Fluorescence

Surrogate deposition disks collected from the area-wide and transect studies were analyzed by USEPA Compendium Method IO-3.3 (EPA/625/R-96/010a) using energy dispersive XRF by Chester LabNet in Tigard, Oregon. Total mass deposited on the pre-tared deposition disks was measured by gravimetry prior to XRF analysis. Chester LabNet used a Kevex EDX-770 energy dispersive x-ray spectrometer, which uses secondary excitation from selectable targets or fluorescers and is calibrated with thin metal foils and salts for 44 chemical elements. Elements analyzed for this project are presented in Table 4-1. Protocol 6 was used for the elements sodium through cobalt and palladium through lanthanum. All other elements listed (including copper, lead, and zinc) were analyzed using Protocol 9, which provides roughly an order of magnitude lower detection capability.

Comprehensive quality control measures were taken to provide data on a broad range of parameters, excitation conditions, and elements. Each analytical batch of samples includes the analysis of precision and accuracy data. Precision is measured using a Micromatter Multi-Elemental Quality Control Standard. Accuracy is measured using a National Institute of Standards and Technology Standard Reference Material (NIST SRM 1832 and 1833).

4.4.2 Inductively Coupled Plasma Mass Spectrometer

Samples collected from SD8(1) for the wet deposition and particle solubility analyses were submitted to CRG Marine Laboratories, Inc. in Torrance, California for analyses. Mylar film samples were solvent extracted, digested in a strong acid, and analyzed by ICP-MS detection using USEPA Method 200.8. Elements analyzed are presented in Table 4-1. Each analytical batch of samples included the analysis of method blanks, laboratory control samples, and duplicate samples.

5.0 WIND DATA PROCESSING

Atmospheric conditions are an important component in evaluating ambient air measurements, including deposition. Specifically, wind direction is a major determinant of ambient air impacts, especially at measurement sites near sources of emissions (e.g., freeways, roadways, and industrial and commercial areas). Combining geographical data on sources and records of wind direction during sampling can provide insights into measured air concentrations or deposition.

Wind data recorded at two stations operated by the San Diego County APCD in the study area were used to aid in the analyses of the deposition data collected during the study. The wind data were used to generate three types of information to support the data analyses:

1. Wind roses to visualize the frequencies of hourly wind speeds and directions.
2. Direction distribution variables for each sampling period for statistical analyses.
3. Mean downwind and crosswind component variables for statistical analyses at two locations near emissions sources of interest.

The following subsections describe the data available from the APCD and the processing of the data for use in the study.

5.1 Air Pollution Control District Wind Data

APCD operates a network of continuous ambient air monitors for criteria pollutants including sulfur dioxide (SO_2), mono-nitrogen oxides (NO_x), ozone (O_3), and carbon monoxide (CO), which includes meteorological stations at several locations. The locations of these meteorological stations relative to the air deposition sampling sites are depicted in Figure 5-1.

Based on their proximity to the deposition sites, two of these stations were used to develop the wind data sets for analysis: the San Diego Beardsley (downtown) and Del Mar Winston School (Del Mar) stations. The downtown station was used to represent all deposition sites located in the Chollas Creek Watershed as well as Ref(1), and the Del Mar station was used to represent the La Jolla ASBS sites, including SIO Pier.

The wind data collected at these stations included three parameters that were used for analysis: hourly vector mean wind direction, hourly scalar mean wind speed, and standard deviation of horizontal wind direction (also referred to as sigma theta, sigma, or σ_θ). The hourly vector mean wind direction was the only available wind direction parameter. Although scalar mean wind directions are more appropriate for use in conjunction with σ_θ, vector mean wind directions are generally within a few degrees of the scalar average wind direction. The data used were taken from the raw daily report files posted to the Internet by the APCD (http://www.jtimmer.cts.com/).

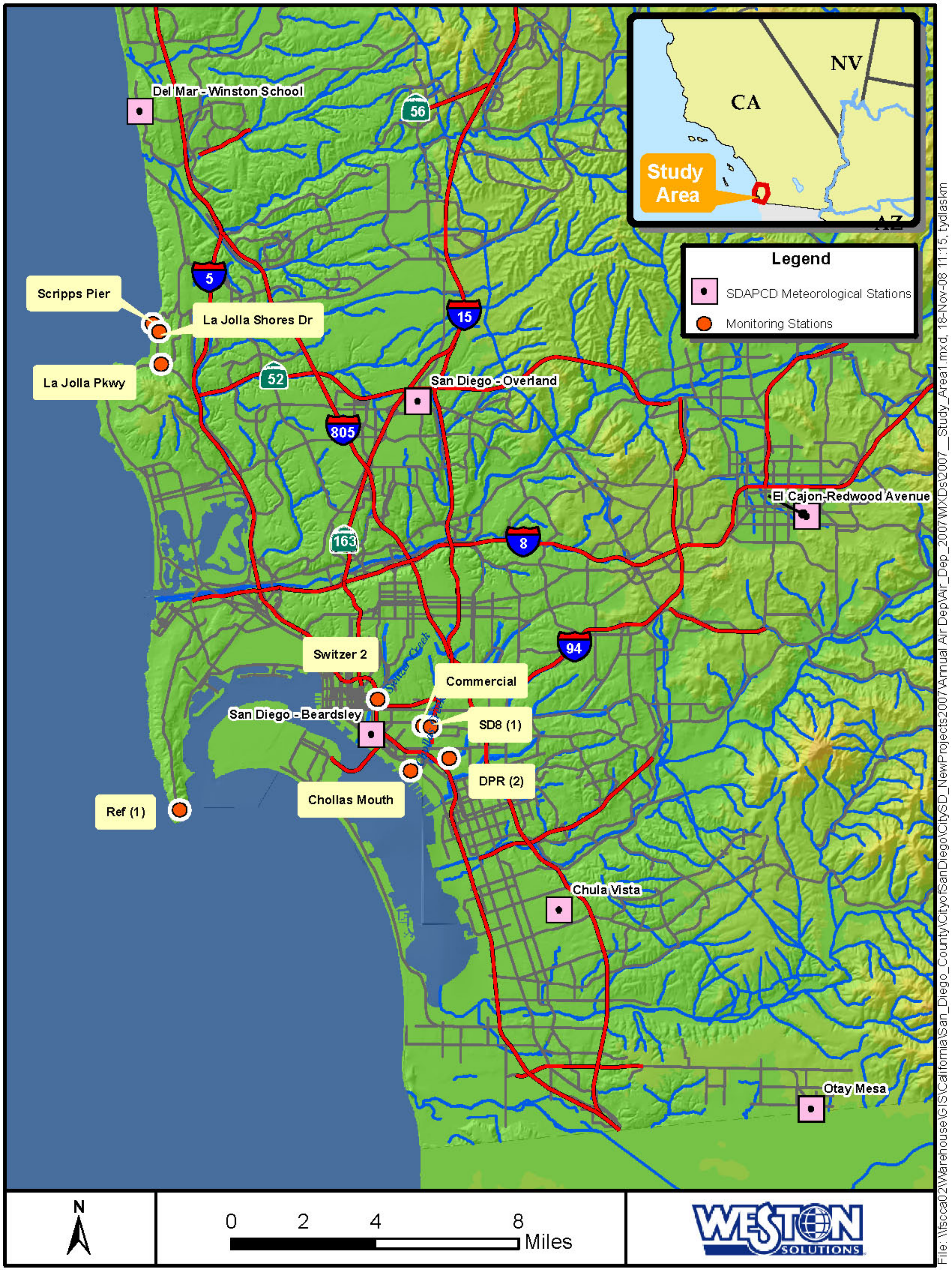


Figure 5-1. San Diego Area Meteorological Stations

5.2 Wind Roses

Wind roses are graphical tools used to visualize the joint variations in wind speed and wind direction over time at meteorological stations. They are most often used with long-term climatological data, but are equally useful for ambient air sampling applications. Wind roses are based on two-way frequency counts, using categories of wind direction and wind speed.

Wind direction is typically divided into 16 sectors centered on points of the compass (north, east–northeast, northeast, north–northeast, etc.), each 22.5° wide. However, other numbers of sectors (e.g., eight or 36) can be used for specific applications. The sector range endpoints fall halfway between adjacent directions. Wind speed is typically divided into six categories, with lower limits chosen to suit the application. Calm winds are tabulated separately. Each observation of wind is counted in an appropriate speed and direction bin (96 bins for a typical rose). The resulting total counts in the speed and direction bins are then converted to percentages of the total observations for plotting.

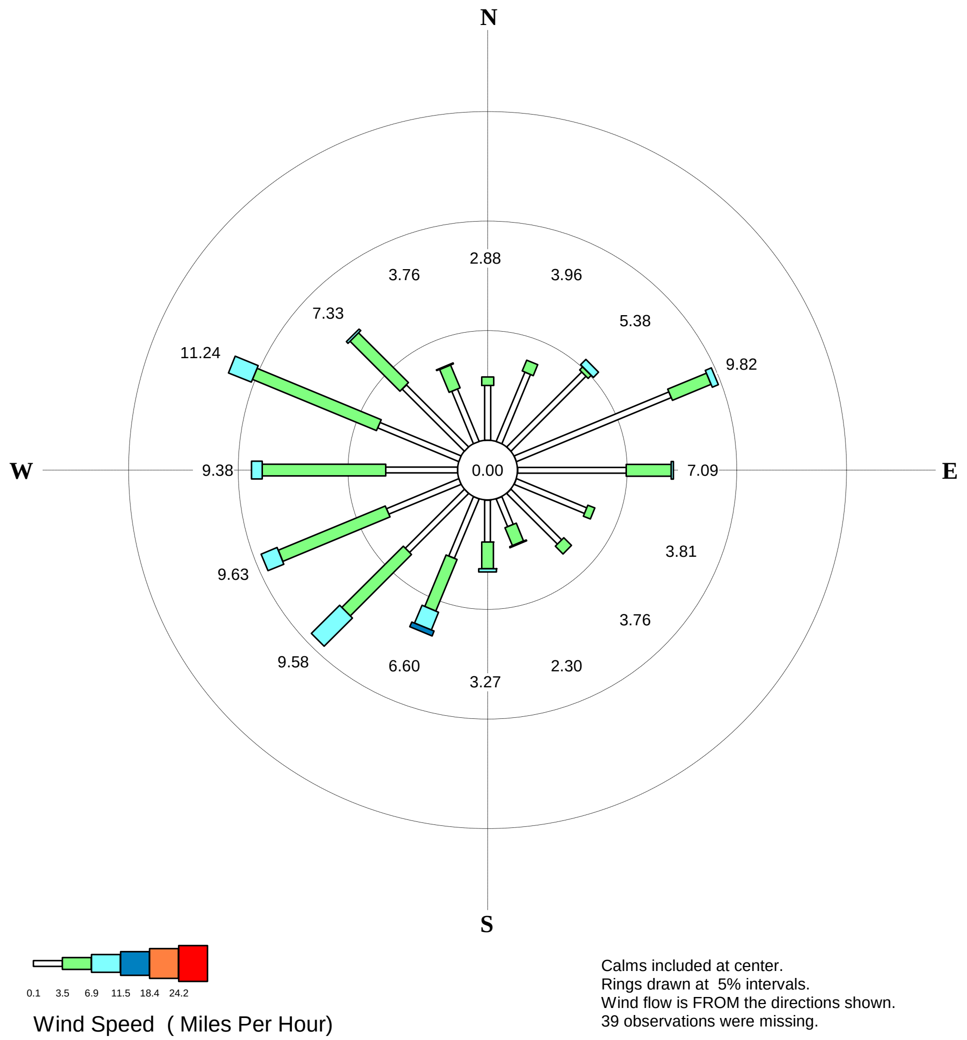
For this study, eight sectors were used to generate wind roses. This provides a convenient number of sectors for statistical analysis and or visualization of wind data in conjunction with land use data. The eight directions match the main cardinal and ordinal directions: north, northeast, east, southeast, south, southwest, west, and northwest.

Annual wind roses applicable to all dry deposition disk deployment periods are shown on Figure 5-2 and Figure 5-3. The Del Mar station (Figure 5-2) was used as the basis for wind distributions for the reference site (Scripps Pier) and the La Jolla ASBS area dry deposition sites (LJS Drive and LJ Parkway). The downtown station (Figure 5-3) was used as the data source for the reference site Ref(1) and the Chollas Creek dry deposition sites (Switzer-2, Chollas Mouth, SD8(1), Commercial, and DPR(2)). The wind roses include a table depicting the percentages (as decimal fractions) within each of the 48 bins (eight direction categories multiplied by six speed categories). These percentages are proportional to the lengths of the segments in each "petal" of the rose.

The annual wind roses indicate slight differences between the Del Mar and downtown meteorological stations. Del Mar has a prevailing west–northwest direction, with 46% of winds from the south–southwest/west–northwest range of directions. Downtown has a slightly more prevailing west direction, with 55% of winds from the south–southwest/west–northwest range of directions. Del Mar also has a secondary peak in frequency from the east–northeast, while Downtown has secondary frequency peaks from the north–northeast and northeast. These are likely due to localized land/sea breeze circulations.

Wind roses were also generated for each deposition disk deployment period (Appendix D). These individual wind roses were based on the times of deployment of the first disk and retrieval of the last disk. Time variances in deployment and recovery were due to travel times between sites. Therefore, differences between the actual roses for individual sites are minor. For consistency with the statistical wind analysis, the roses were generated with eight direction sectors, 45° wide (north, northeast, east, southeast, south, southwest, west, northwest). Each rose was based on the hourly data available for each period from the appropriate APCD stations.

APCD Del Mar Station
Dry Deposition Sampling Periods Only
September 2007 - August 2008



Calms included at center.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
39 observations were missing.

PERCENT OCCURRENCE: Wind Speed (Miles Per Hour)
LOWER BOUND OF CATEGORY

DIR	0.1	3.5	6.9	11.5	18.4	24.2
N	2.49	0.39	0.00	0.00	0.00	0.00
NNE	3.42	0.54	0.00	0.00	0.00	0.00
NE	4.84	0.20	0.34	0.00	0.00	0.00
ENE	7.62	1.91	0.29	0.00	0.00	0.00
E	4.94	2.05	0.10	0.00	0.00	0.00
ESE	3.47	0.34	0.00	0.00	0.00	0.00
SE	3.27	0.49	0.00	0.00	0.00	0.00
SSE	1.37	0.88	0.05	0.00	0.00	0.00

TOTAL OBS = 2046 MISSING OBS = 39

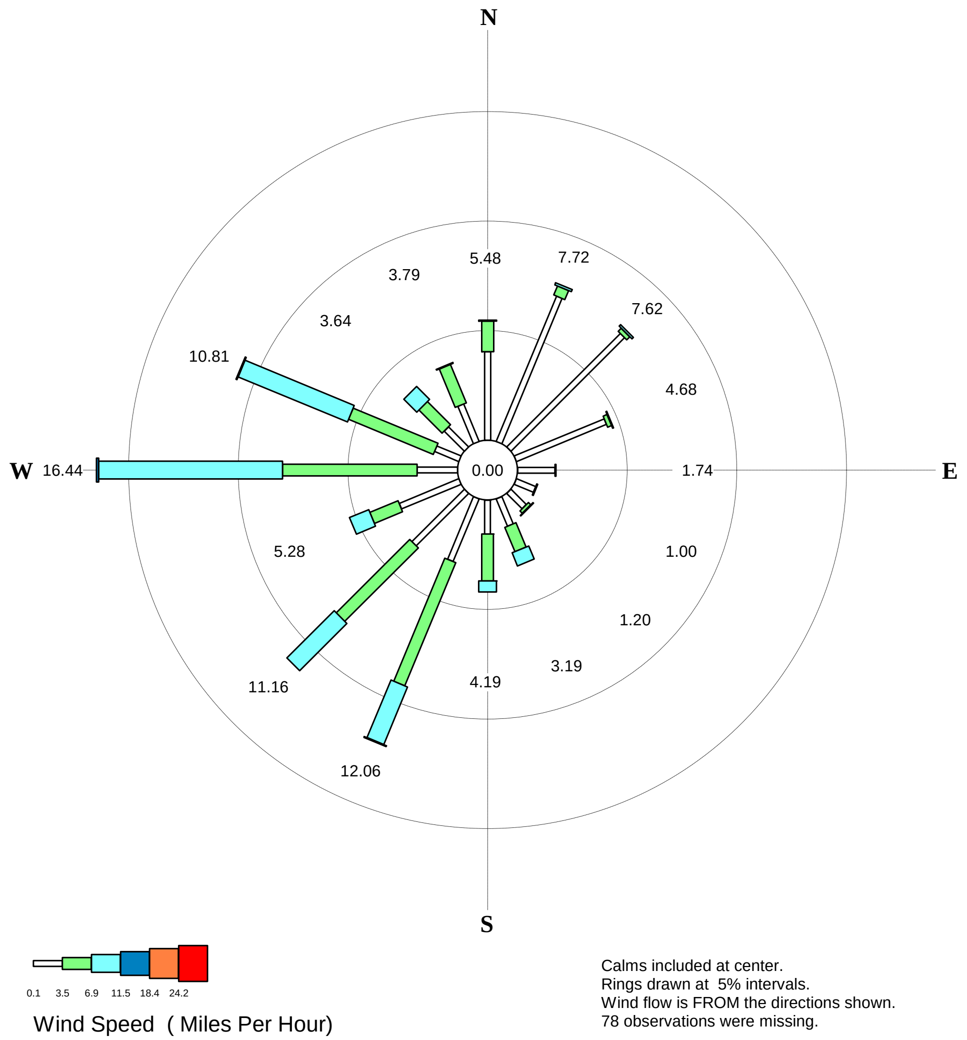
PERCENT OCCURRENCE: Wind Speed (Miles Per Hour)
LOWER BOUND OF CATEGORY

DIR	0.1	3.5	6.9	11.5	18.4	24.2
S	1.91	1.22	0.15	0.00	0.00	0.00
SSW	2.93	2.54	0.88	0.24	0.00	0.00
SW	3.81	3.96	1.81	0.00	0.00	0.00
WSW	3.57	5.28	0.78	0.00	0.00	0.00
W	3.27	5.62	0.49	0.00	0.00	0.00
WNW	4.01	6.11	1.12	0.00	0.00	0.00
NW	4.01	3.23	0.10	0.00	0.00	0.00
NNW	2.59	1.12	0.05	0.00	0.00	0.00

CALM OBS = 4 PERCENT CALM = 0.00

Figure 5-2. Annual Wind Rose for Scripps Pier and the La Jolla Area Dry Deposition Sites

APCD Downtown Station
Dry Deposition Sampling Periods Only
September 2007 - August 2008



Calms included at center.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
78 observations were missing.

PERCENT OCCURRENCE: Wind Speed (Miles Per Hour)
LOWER BOUND OF CATEGORY

DIR	0.1	3.5	6.9	11.5	18.4	24.2
N	4.04	1.40	0.05	0.00	0.00	0.00
NNE	7.17	0.45	0.10	0.00	0.00	0.00
NE	7.32	0.20	0.10	0.00	0.00	0.00
ENE	4.43	0.20	0.05	0.00	0.00	0.00
E	1.69	0.05	0.00	0.00	0.00	0.00
ESE	0.95	0.05	0.00	0.00	0.00	0.00
SE	1.00	0.15	0.05	0.00	0.00	0.00
SSE	1.35	1.20	0.65	0.00	0.00	0.00

TOTAL OBS = 2007 MISSING OBS = 78

PERCENT OCCURRENCE: Wind Speed (Miles Per Hour)
LOWER BOUND OF CATEGORY

DIR	0.1	3.5	6.9	11.5	18.4	24.2
S	1.54	2.14	0.50	0.00	0.00	0.00
SSW	3.09	6.08	2.84	0.05	0.00	0.00
SW	3.39	4.73	3.04	0.00	0.00	0.00
WSW	2.94	1.40	0.95	0.00	0.00	0.00
W	1.84	6.13	8.37	0.10	0.00	0.00
WNW	1.20	4.19	5.38	0.05	0.00	0.00
NW	1.30	1.49	0.85	0.00	0.00	0.00
NNW	1.84	1.89	0.05	0.00	0.00	0.00

CALM OBS = 0 PERCENT CALM = 0.00

Figure 5-3. Annual Wind Rose for Ref(1) and the Chollas Creek Dry Deposition Sites

Wind direction is a constantly fluctuating parameter due to turbulence in the atmosphere. Average wind direction captures information on the main transport direction during a period, but loses information on variability of the wind direction. The standard deviation of wind direction (σ_θ) parameter can be used to compensate for some of this lost information. For statistical analyses, the hourly σ_θ data were used to calculate frequency distributions compensated for fluctuations in wind direction during each hour of a deployment period. These compensated distributions provide more representative variables for correlation with observed deposition rates, compared to strictly using a wind rose frequency bin tabulation.

More representative frequencies can be calculated using σ_θ data to reduce bias introduced by discrete binning of mean wind directions. The bias applies when the mean is near a sector boundary. Compensated distributions are calculated by considering the σ_θ values to be analogous to the standard deviation of a normal distribution and by spreading the frequency during the hour according to the resulting bell curve. This is illustrated on Figure 5-4.

Figure 5-4 shows an example compensated frequency distribution for a mean wind direction of 189° ($\sigma_\theta = 20°$). The shape of the normal curve is shown along with the sector endpoints of a typical 16-sector rose. The sectors are labeled with their direction and the total integrated frequency in the sector for the hour. The frequency for the hour is spread over six sectors. The central south and south–southwest sectors share the majority of the frequency (approximately 39% and 35%, respectively). The next two sectors from the center (south–southeast and southwest) split 24% of the frequency. The remaining 2% falls into the southeast and west–southwest sectors.

The compensation process effectively smoothes out the more discrete frequency distribution generated by a simple wind rose histogram. The continuous distributions are more suitable for statistical correlations because they preserve the major patterns while limiting the potential bias that can exist in discretely calculated distributions.

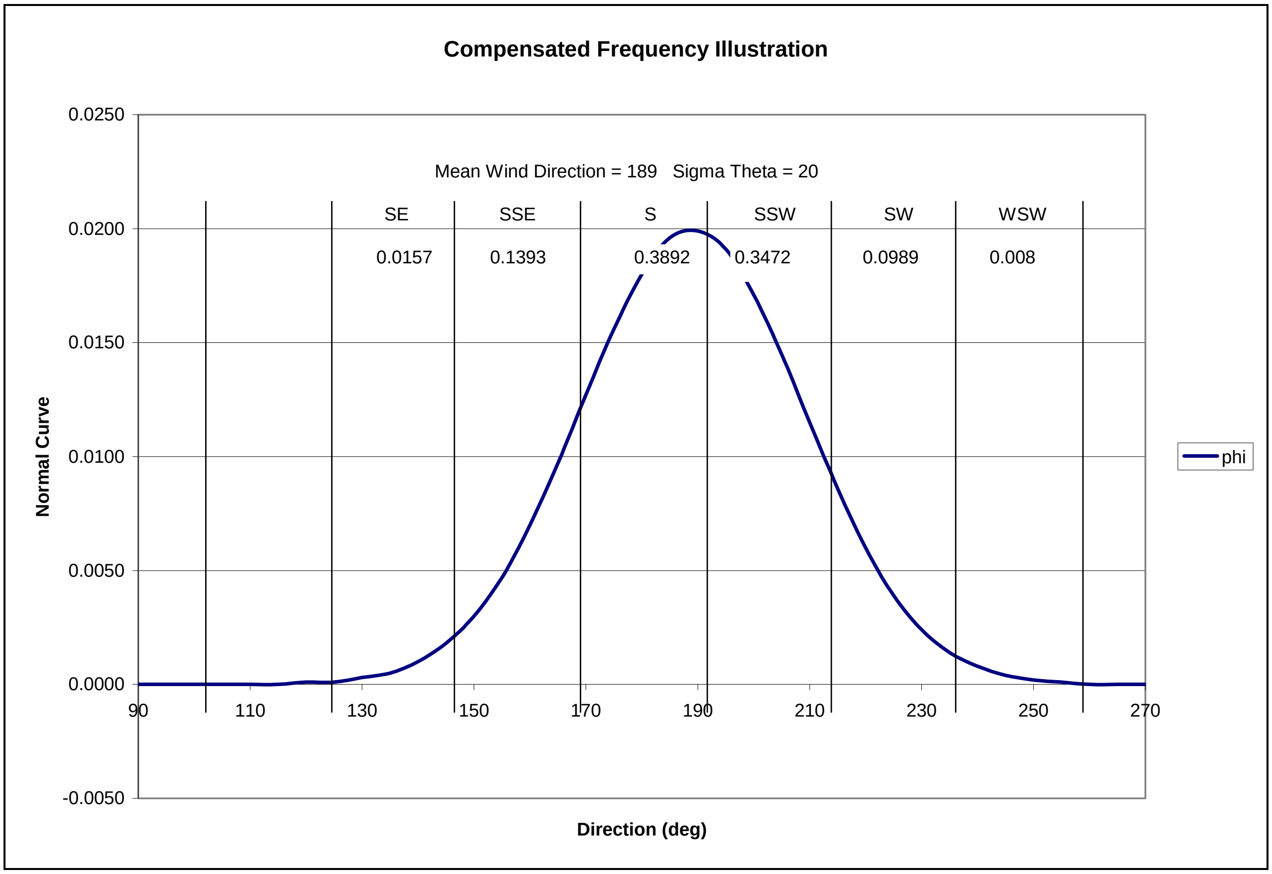


Figure 5-4. Example of a Compensated Frequency Distribution

For this study, eight sector-compensated distributions were calculated for each disk deployment period. The hourly wind direction and σ_θ data were used to calculate fractional frequencies in all eight sectors for each hour. These were summed in each sector over all hours, and divided by the total number of hours. The compensated frequencies were used as variables in the statistical analysis presented in Section 6.

6.0 RESULTS AND DISCUSSION

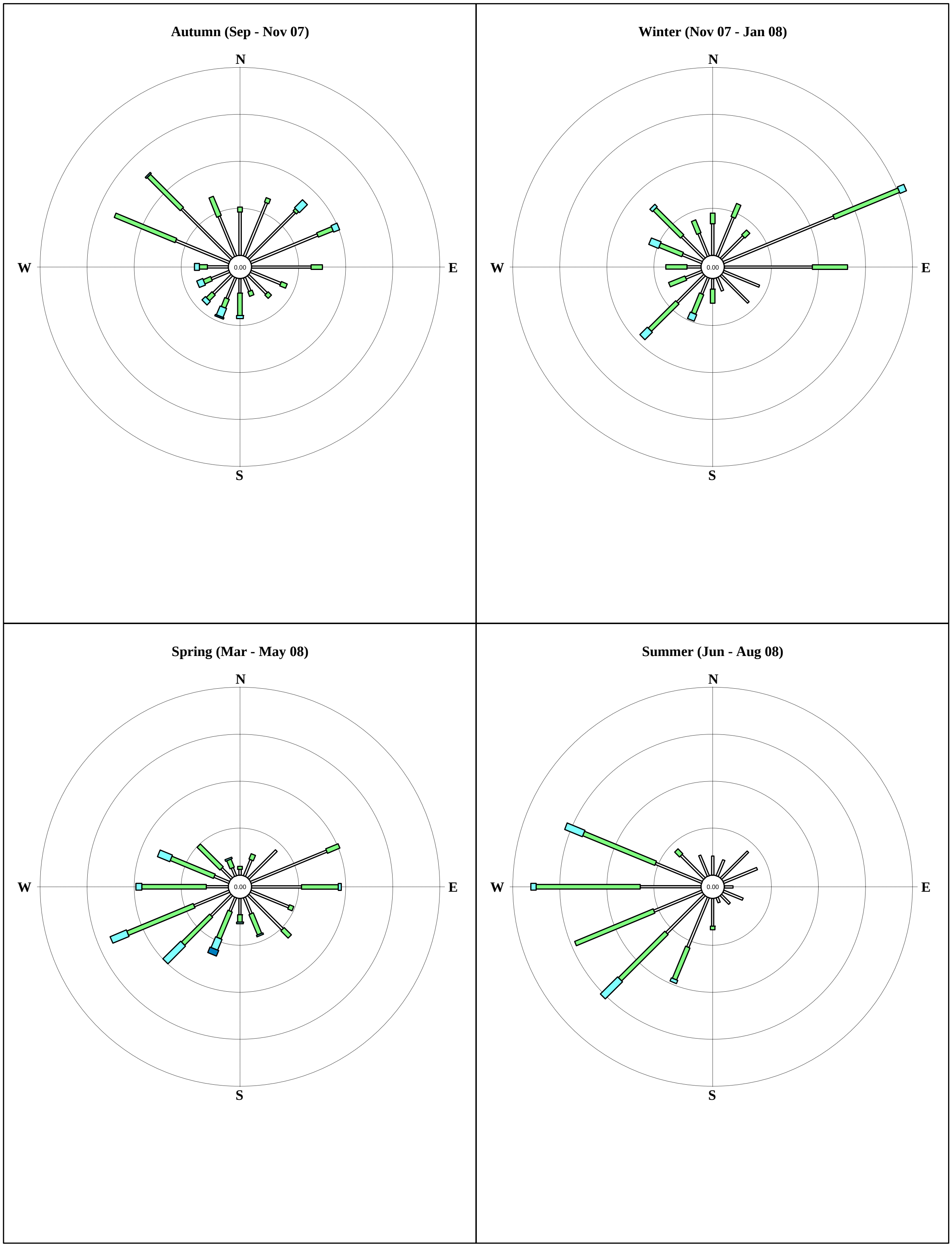
The following sections present the results of the dry deposition, wet deposition, and solubility analyses performed during the course of this study. Several elemental results were analyzed and reviewed during this study period in addition to copper, lead, zinc, and net deposition. All laboratory analytical results are presented in Appendix B.

6.1 Meteorological Conditions

This assessment was conducted to determine if aerial deposition rates differ throughout the course of the monitoring period. Significant weather events and conditions likely affect the rate of aerial deposition due to wind speed, humidity, rainfall, wildfires, and Santa Ana conditions. Applicable events are described in this section.

6.1.1 Seasonal Wind Patterns

The seasonal wind roses on Figure 6-1 (Del Mar weather station) and Figure 6-2 (San Diego weather station) show distinctive seasonal differences at both locations. However, both locations tend to follow a similar relative seasonal pattern. Autumn (September–November) at both stations is characterized by more northerly and westerly winds. In the winter months (December–January), stronger southwest winds are present along with most of the northeast and east–northeast winds observed during the study. Spring (March–May) is characterized by mainly southwest winds. Summer (June–August) has mainly south–southwest through west–northwest winds and a distinct lack of winds from the eastern quadrants.


Autumn (Sep - Nov 07)

Winter (Nov 07 - Jan 08)

Spring (Mar - May 08)

Summer (Jun - Aug 08)

Figure 6-1. Seasonal Wind Roses for La Jolla Area of Special Biological Significance Dry Deposition Sites

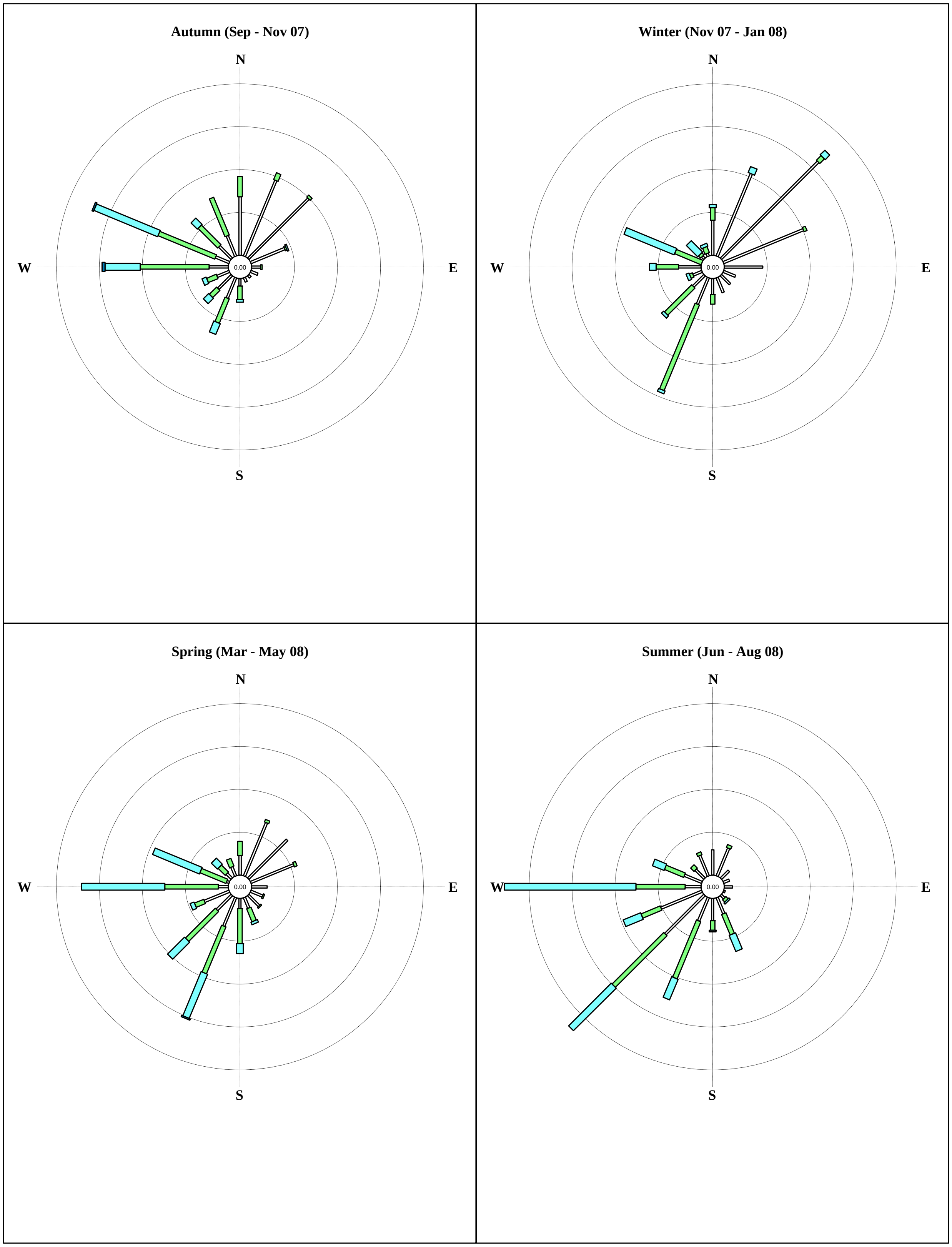


Figure 6-2. Seasonal Wind Roses for Chollas Creek Area Dry Deposition Sites

6.1.2 Wet Weather Events

The 2007–2008 wet weather monitoring period total rainfall was slightly below average. While frequent and significant rainfall occurred from late November through February, March 2008 and April 2008 were uncharacteristically dry. Precipitation data recorded at the City of San Diego's Lindbergh Field from July 2007 through May 2008 showed that rainfall accumulation was 32% below normal, with 7.23 inches, compared with a standard accumulation of 10.68 inches per year. During the course of the monitoring period, 14 of the dry weather deposition sampling events required rescheduling or postponement due to predicted rainfall or rainfall occurring during the week of scheduled sampling. As a result, no dry deposition samples were collected during the month of December. Sampling events for dry weather deposition were increased during the month of March to make up for the lack of dry sampling events in December.

6.1.3 2007 San Diego County Fires

The 2007 San Diego County Wildfires began on Sunday, October 21, 2007, and were not contained until November 10, 2007. Satellite imagery of the area one day after the fires began clearly shows smoke trailing from the fires to the west over the City of San Diego and the Pacific Ocean (Figure 6-3). This imagery depicts (aside from the smoke from the wildfires) blowing sands from desert regions on the coasts of mainland and Baja Mexico. Sediment transport via the Santa Ana winds is visually evident at distances up to approximately 120 miles. Conditions were indicative of a classic strong Santa Ana event with winds blowing from the east to the west coupled with very low humidity. Four separate, significant fires occurred in San Diego County (Witch Fire, Harris Fire, Rice Fire, and Poomacha Fire) and burned approximately 347,000 acres and 2,580 structures (California Department of Forestry and Fire Protection, 2008). One sampling event occurred from October 22, 2008 through October 24, 2008, to capture the unique event for a short duration due to excessive particulate loading of the samples with ash and personnel safety concerns for the monitoring teams.

Image acquired October 22, 2007 at 17:52 UTC – European Space Agency (http://www.esa.int/esaEO/SEM8U23Z28F_index_0.html)

Figure 6-3. Satellite Imagery of the 2007 San Diego County Wildfires

6.2 Dry Aerial Deposition Results

Dry aerial deposition rates are presented as box and whisker plots on Figure 6-4 through Figure 6-7. The figures show the maximum and minimum results as the whiskers. The boxes represent the upper and lower 25th percentiles of the data, while the median is shown as the horizontal line within the box. Summary statistics are presented in Table 6-1. In the event where results were not detectable, half the laboratory method detection limit was used for calculation purposes.

All dry deposition rates were log transformed prior to data analyses (i.e., the analyses were performed using the base-10 logarithms of the original data). Results collected during the 2007 San Diego County Wildfires (October 22, 2008) were not outliers relative to the entire dry deposition data set and were not segregated prior to data analyses. One hundred percent of maximum net, 10% of maximum copper, 40% of maximum lead, and 20% of maximum zinc deposition results (Figure 6-4 through Figure 6-7) were measured during the fires on October 22, 2008.

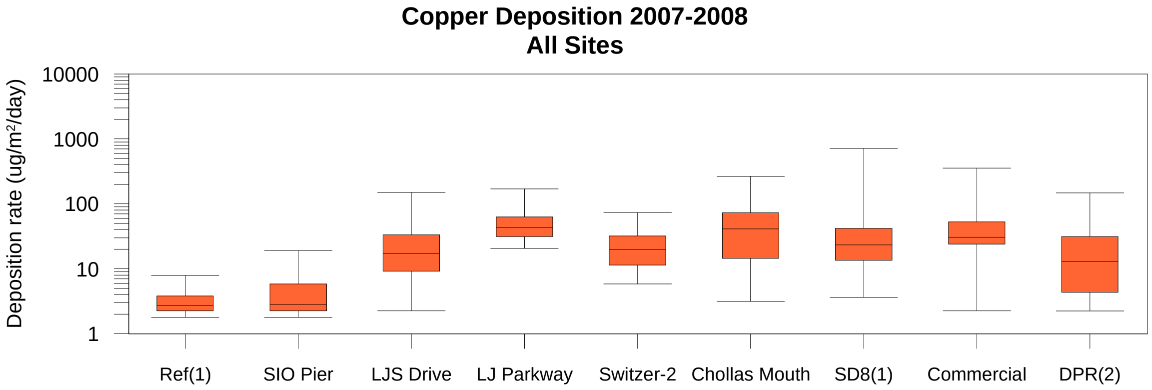


Figure 6-4. Box and Whisker Plots of Copper Deposition Rates from September 2007–August 2008

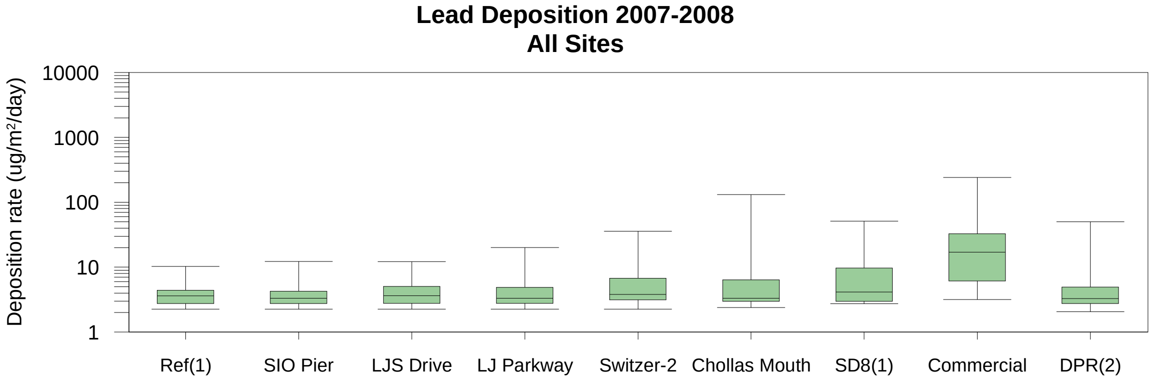


Figure 6-5. Box and Whisker Plots of Lead Deposition Rates from September 2007–August 2008

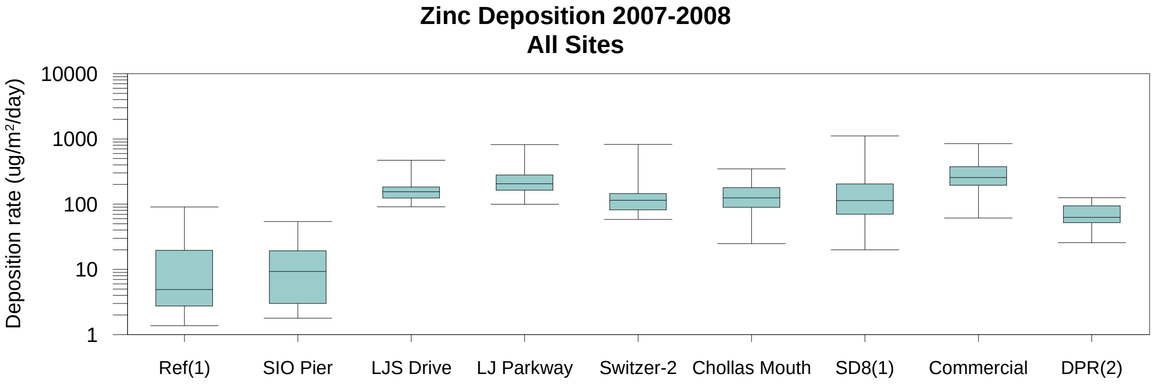


Figure 6-6. Box and Whisker Plots of Zinc Deposition Rates from September 2007–August 2008

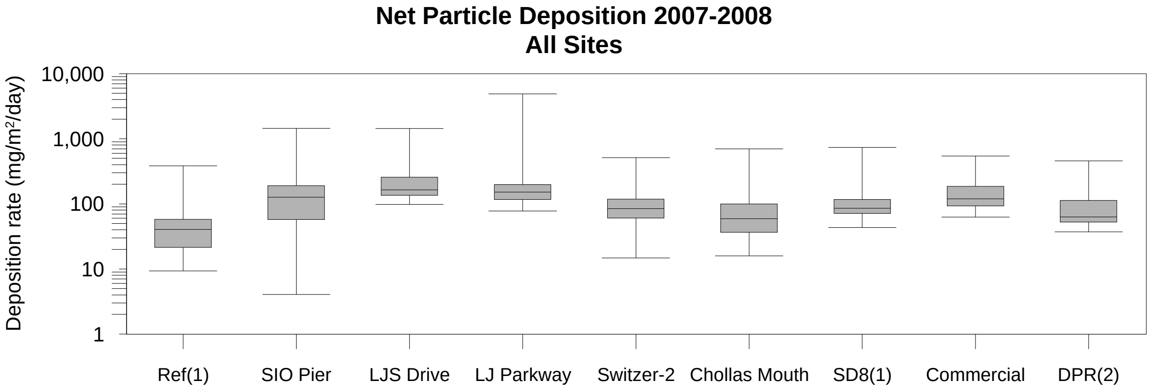


Figure 6-7. Box and Whisker Plots of Net Deposition Rates from September 2007–August 2008

Table 6-1. Summary Statistics of Copper, Lead, Zinc, and Net Deposition

	Reference Sites		La Jolla ASBS Sites		Downtown San Diego Sites				
	Ref(1)	**SIO Pier***	**LJS Drive**	**LJ Parkway**	**Switzer-2**	**Chollas Mouth**	**SD8(1)**	**Commercial**	**DPR(2)**
	Copper µg/m^2/day								
Number of samples	24	24	24	24	23	24	24	24	24
Number of ND	23	20	2	0	0	1	3	2	7
Minimum result	1.8	1.8	2.3	17.3	5.8	3.2	3.6	2.2	2.2
25th percentile	2.3	2.3	9.3	29.2	11.4	12.6	13.7	23.6	5.4
Median result	2.6	2.6	15.4	36.8	19.6	37.6	22.5	29.5	12.7
75th percentile	3.0	3.4	21.4	53.2	28.6	60.1	40.9	38.9	29.4
Maximum result	6.0	19.1	90.0	170	49.7	266	604	206	148
Mean result	2.8	4.5	19.3	46.5	20.3	51.1	49.8	38.0	23.3
CV (%)	38	113	93	68	57	112	240	101	138
	Lead µg/m^2/day								
Number of samples	24	24	24	24	23	24	24	24	24
Number of ND	24	24	23	23	19	20	17	6	22
Minimum result	2.3	2.2	2.3	2.3	2.3	2.4	2.7	3.2	2.1
25th percentile	2.7	2.7	2.7	2.8	3.0	2.9	3.1	7.7	2.8
Median result	3.3	3.2	3.5	3.3	3.6	3.2	4.1	15.6	3.2
75th percentile	4.2	3.7	3.8	4.0	4.9	4.9	9.3	24.3	4.6
Maximum result	6.1	7.0	12.2	6.1	35.8	131	38.4	57.0	50.0
Mean result	3.5	3.4	3.9	3.6	5.5	9.8	8.2	18.6	5.6
CV (%)	28	31	53	29	124	265	115	74	170
	Zinc µg/m^2/day								
Number of samples	24	24	24	24	23	24	24	24	24
Number of ND	13	9	0	0	0	0	0	1	0
Minimum result	1.4	1.8	90.7	99.5	58.5	24.8	20.0	61.3	25.7
25th percentile	2.5	2.7	128	163	81.9	81.4	75.2	193	52.4
Median result	4.1	4.9	148	197	106	107	114	216	62.7
75th percentile	14.6	11.4	168	240	135	135	177	289	92.2
Maximum result	90.7	53.9	233	315	478	294	573	758	125
Mean result	12.8	9.6	149	201	126	121	143	255	72.4
CV (%)	165	120	23	29	68	60	81	56	39
	Net Deposition mg/m^2/day								
Number of samples	24	24	24	24	23	24	24	24	24
Number of ND	0	1	0	0	0	0	0	0	0
Minimum result	9.3	4.0	97.8	77.6	14.7	15.9	43.2	62.7	37.2
25th percentile	20.0	57.7	135	117	60.3	38.2	71.6	93.9	53.8
Median result	34.9	113	150	132	75.6	59.1	85.6	119	63.0
75th percentile	49.7	157	202	172	97.4	83.1	113	160	106
Maximum result	384	1,448	1,445	1,768	510	696	738	543	457
Mean result	52.8	165	249	212	98.1	90.4	115	139	91.8
CV (%)	142	172	121	157	95	149	118	69	91

CV = Coefficient of variation represents the statistical variation of individual results. Coefficient of variations above 100 suggests results are more variable and less predictable in comparison to the mean results.

ND = Non-detect results

*SIO Pier is within La Jolla ASBS and also provides direct deposition rates to the ocean surface in the ASBS.

6.2.1 Reference Sites

Site Ref(1) in Point Loma and the Scripps Pier Site (SIO Pier) had the lowest deposition rates of copper, lead, and zinc overall. Median copper deposition at both reference sites were equal, at 2.6 µg/m^2/day, which reflects the limits of detection of the sampling and analytical method because copper was rarely detected at these sites (17% of samples at SIO Pier and 4% at Ref(1)). The median copper deposition rates at both Ref(1) and SIO Pier were approximately five to 14 times lower than median deposition rate for sites located in La Jolla ASBS and downtown San Diego where copper was frequently detected. Lead deposition was not detected in 24 samples analyzed from each reference site and was infrequently detected or detected at low concentrations at the other seven sites. Median zinc deposition at Ref(1) and SIO Pier (4.1 µg/m^2/day and 4.9 µg/m^2/day, respectively) were approximately 13 to 53 times lower than the other seven La Jolla ASBS and downtown San Diego sites. Zinc was also not frequently detected at either reference site (46% of samples at SIO Pier and 63% at Ref(1)). However, the median net deposition rate at SIO Pier was approximately three times greater than Ref(1) (113 mg/m^2/day and 34.9 mg/m^2/day, respectively). SIO Pier median net deposition was similar to or greater than all five downtown San Diego sites and was slightly less than both La Jolla ASBS sites.

6.2.2 La Jolla Area of Special Biological Significance

Two sites were monitored within the La Jolla ASBS Watershed, including La Jolla Shores Drive (LJS Drive) and La Jolla Parkway (LJ Parkway). Based on the data collected in the La Jolla ASBS, the median deposition results for copper were highest at the La Jolla Parkway Site (36.8 µg/m^2/day) relative to the La Jolla Shores Drive Site (15.4 µg/m^2/day). Lead was detected in only one of the 24 samples taken at each of the LJS Drive and LJ Parkway sites (median 3.5 µg/m^2/day and 3.3 µg/m^2/day, respectively). In contrast, zinc deposition rates were high compared to the deposition rates of copper and lead and were detected in 100% of the samples collected at each La Jolla ASBS site. The median deposition rates for zinc were 197 µg/m^2/day at LJ Parkway and 148 µg/m^2/day at LJS Drive. The highest median net particle deposition rates were found at both LJS Drive and LJ Parkway (150 mg/m^2/day and 132 mg/m^2/day, respectively) compared with the sites within the Chollas Creek Watershed.

In addition to the dry deposition sampling, a field screening for dioxins was conducted on October 25, 2007. The field screening was conducted to assess the contribution of dioxins to the La Jolla ASBS and watershed from ash fallout from wildfires. One sample was collected by using a methanol saturated wipe filter and wiping a 0.181 m2 area for analysis. The sample was then submitted to Pacific Analytical, Inc. for dioxin analysis by EPA Method 1613. The screening results are provided in Table 6-2. Results indicate that ash fallout from the 2007 San Diego Wildfires contributed an estimated 5.702 pg/m^2 of total toxicity equivalent 2,3,7,8-TCDD dioxins which was based on only 2 of 16 isomers being detected.

Table 6-2. Dioxin Field Screening Results from Ash Fallout at Scripps Pier

PCDD/PCDF Toxicity Equivalence Summary				
Date Sampled: 10/25/2007				
Sample Type: Surface Wipe (0.181 m^2)				
PCDD/PCDF Congeners	**Concentration (pg)**	**TEF**	**TEF Adjusted Concentration (pg)**	**TEF Adjusted Concentration (pg/m^2)**
2,3,7,8-TCDD	0.000	1.0000	0.000	0.000
1,2,3,7,8-PeCDD	0.000	1.0000	0.000	0.000
1,2,3,4,7,8-HxCDD	0.000	0.1000	0.000	0.000
1,2,3,6,7,8-HxCDD	0.000	0.1000	0.000	0.000
1,2,3,7,8,9-HxCDD	0.000	0.1000	0.000	0.000
1,2,3,4,6,7,8-HpCDD	97.096	0.0100	0.971	5.375
OCDD	593.388	0.0001	0.059	0.327
2,3,7,8-TCDF	0.000	0.1000	0.000	0.000
1,2,3,7,8-PeCDF	0.000	0.0500	0.000	0.000
2,3,4,7,8-PeCDF	0.000	0.5000	0.000	0.000
1,2,3,4,7,8-HxCDF	0.000	0.1000	0.000	0.000
1,2,3,6,7,8-HxCDF	0.000	0.1000	0.000	0.000
1,2,3,7,8,9-HxCDF	0.000	0.1000	0.000	0.000
2,3,4,6,7,8-HxCDF	0.000	0.1000	0.000	0.000
1,2,3,4,6,7,8-HpCDF	0.000	0.0100	0.000	0.000
1,2,3,4,7,8,9-HpCDF	0.000	0.0100	0.000	0.000
OCDF	0.000	0.0001	0.000	0.000
TOTAL			1.030	5.702

TEF = Toxicity Equivalency Factor

6.2.3 Downtown San Diego

Five sites were monitored within the downtown San Diego area, including Switzer-2, Chollas Mouth, SD8(1), Commercial, and DPR(2). Based on the data collected during this study, mean deposition results for copper were highest at two sites, including Chollas Mouth and Commercial (37.6 μg/m^2/day and 29.5 μg/m^2/day, respectively). Similar to the La Jolla ASBS sites, lead deposition rates were infrequently detected or were low compared to other metals. However, the median lead deposition rate was particularly high at the Commercial Site (15.6 μg/m^2/day), approximately four to five times greater than the other sampling locations within the La Jolla ASBS and downtown San Diego. The frequency of lead detected at the Commercial Site was higher (75%) compared to detection frequencies (8–17%) at other sites within this study. Median deposition rates for zinc and net particles in the Chollas Creek area were also highest at the Commercial Site (216 μg/m^2/day and 120 mg/m^2/day, respectively).

6.3 Wet Deposition Results

Wet weather deposition monitoring occurred at SD8(1), located in the north fork of Chollas Creek. It is important to confirm previous studies (Sabin et al., 2005) that indicate the wet deposition load is generally less than 10% of the annual load in this study due to the low compliance levels in the Chollas Creek Watershed. This process is important to compare the additive concentrations from wet deposition to the TMDL compliance levels.

Wet deposition results and the respective solubility estimates are presented in Table 6-3 through Table 6-5 for the three rainfall events measured. For the first two monitoring events, copper, lead, and zinc wet deposition results were similarly low, but not considered negligible in light of the low CTR compliance levels set for the Chollas Creek Watershed. However, the third wet deposition monitoring event on March 15, 2008 was considerably elevated for total and dissolved copper and zinc relative to the two previous wet events.

Table 6-3. Wet Weather Deposition Concentrations and Solubility for Event 1

Event Exposure Date · Time	**November 30, 2007 · 10:35–16:00**		
Total Event Rainfall	**1.48 inches**		
	Copper	**Lead**	**Zinc**
Total (µg/L)	1.1	0.21	4.4
Dissolved (µg/L)	0.8	<0.05	3.6
Estimated Solubility	73%	12%	82%

Table 6-4. Wet Weather Deposition Concentrations and Solubility for Event 2

Event Exposure Date · Time	**February 3, 2008 · 07:00–14:00**		
Total Event Rainfall	**0.39 inch**		
	Copper	**Lead**	**Zinc**
Total (µg/L)	0.8	<0.05	4.3
Dissolved (µg/L)	0.8	<0.05	4.1
Estimated Solubility	100%	–	95%

Table 6-5. Wet Weather Deposition Concentrations and Solubility for Event 3

Event Exposure Date · Time	**March 15, 2008 · 17:00–March 16, 2008 · 07:30**		
Total Event Rainfall	**0.32 inch**		
	Copper	**Lead**	**Zinc**
Total (µg/L)	4.2	1.27	85.6
Dissolved (µg/L)	1.7	<0.05	65.6
Estimated Solubility	40%	2%	77%

6.4 Particle Solubility Results

Particle solubility was analyzed at one location (SD8(1)) located in the north fork of Chollas Creek. The solubility analyses allow for direct comparison to the Chollas Creek dissolved metals TMDL. Results for the solubility analyses events are presented in Table 6-6 through Table 6-8. Solubility tests were conducted using deionized water, which has a neutral pH (pH= 7.0), which is consistent with the rainwater observed at the Chollas Creek monitoring site. In comparison to studies conducted for the Brake Pad Partnership in the San Francisco Bay area, the solubility results presented in the tables below are similar in nature to the pH of the extraction fluid used in the Brake Pad Partnership studies. Solubility tests conducted by Clemson University researchers found a wide range of solubility depending on the extraction fluid used for each metal (Schlautman and Haselden, 2006). The dry weather particles collected in the north fork of Chollas Creek were relatively soluble for zinc, slightly soluble for copper, and relatively insoluble for lead. However, these particle solubility results would likely increase with a more acidic extraction fluid.

Table 6-6. Dry Deposition Solubility Results for Event 1 – November 5, 2007

Parameter	Copper	Lead	Zinc
Total deposition rate (µg/m^2/day)	13.4	7.5	95.2
Soluble deposition rate (µg/m^2/day)	1.2	0.005	83.4
Estimated Solubility	**9%**	**0.06%**	**88%**

Table 6-7. Dry Deposition Solubility Results for Event 2 – March 17, 2008

Parameter	Copper	Lead	Zinc
Total deposition rate (µg/m^2/day)	55.1	17.8	194
Soluble deposition rate (µg/m^2/day)	6.3	0.4	90.6
Estimated Solubility	**11%**	**2.49%**	**47%**

Table 6-8. Dry Deposition Solubility Results for Event 3 – June 16, 2008

Parameter	Copper	Lead	Zinc
Total deposition rate (µg/m^2/day)	82.2	14.9	210
Soluble deposition rate (µg/m^2/day)	12.1	0.2	121
Estimated Solubility	**15%**	**1.32%**	**58%**

The historical wet weather water quality metals data collected from 2000–2007 at Site SD8(1) were evaluated to determine the percentage of solubility of dissolved metals from total metals. This analysis provides information relative to the form of metals found in storm water for comparison to the results collected for the particle solubility analyses. Summary statistics are presented in Table 6-9 showing the minimum, maximum, and mean solubility of copper, lead, and zinc. In the event that results were not detectable, half the laboratory method detection limit was used for calculation purposes. The variability of these results is likely a function of rainfall totals, intensity, and number of dry days prior to each rainfall event. This data provides a direct relationship between particle solubility and the dissolved metals TMDL.

Table 6-9. Summary of Historical Wet Weather Water Quality Solubility Results from the SD8(1) Site from 2000–2007

	Copper	Lead	Zinc
Minimum	7.14%	1.04%	2.02%
Maximum	100%	51.9%	100%
Mean	34.5%	8.24%	27.9%

6.5 Multivariate Analysis and Discussion

Multivariate analyses of site, land use, and wind direction data were completed to address the main questions of the project. The deposition rate data for the subsets of elements detected greater than 75% of the time at each site were used to examine relationships that may provide insights into possible links to pollutant sources or land uses.

6.5.1 Multivariate Methods

The multivariate analysis of deposition rate results for this project consisted of a preparation step and two different multivariate approaches to the prepared data set. The two statistical approaches used were principal components analysis (PCA) and Spearman Rank correlations.

The preparation step defined and standardized the data sets used for all further analysis. All data were examined for frequency of detection, because non-detectable results were prevalent with several elements. Only those elements with a frequency of detection greater than 75% at each individual site were included in further analysis for that site. There were a total of 17 metals detected in at least 75% of samples for at least one site:

- Aluminum
- Bromine
- Calcium
- Chlorine
- Copper
- Iron
- Potassium
- Magnesium
- Manganese
- Sodium
- Lead
- Sulfur
- Silicon
- Strontium
- Titanium
- Zinc
- Zirconium

The other components of the data set used in the multivariate analyses included net mass deposition (net), percent wind direction (eight sectors) for each sample, and wind-direction-weighted land use influence estimates for each sample. Also, due to the skew of the data (i.e., lower deposition rates are much more common than high deposition rates), all deposition rate data were logarithmically transformed prior to analysis (i.e., the analyses were performed using the base-10 logarithms of the original data). Non-detected values were included in the analyses as half of the laboratory method detection limit.

PCA was used as a data reduction and interpretation technique. PCA was applied because the number of variables (from ten to 16 at any given site) was prohibitive of as-is interpretation. PCA replaces a large set of original variables with an equivalent smaller set of new variables, (i.e., the components) derived from the originals. The advantage of using this technique is that patterns in the data can be recognized by examining the derivation of the components, and the components can also be used as a proxy for the original variables in further analyses. The derivation of the components can reveal potential fingerprints (i.e., combination of elements) that may potentially be related to land use. Because each site has a unique geographic character, a PCA was run for each site. The results were used to examine relationships between sample sites and also for inclusion in the correlation analysis.

A Spearman Rank correlation analysis was run and included the PCA components from each site with the wind direction and related land use data for each sample date. The purpose of the analysis was to relate the reduced data set to predominant wind directions and surrounding land use. Caution is warranted through for extrapolating land use data as one local emission source (e.g., a freeway or industrial facility) may potentially skew the results and be mistakenly interpreted as the land use influencing the emissions.

6.5.2 Principal Components Analysis

As previously discussed, a PCA was completed for each sample site. The PCA replaces the original frequently detected (at least 75% frequency) deposition rate variables with a statistically equivalent set of new variables that are combinations of the originals. The new variables are the components, and they represent linear combinations of the original variables that share similar patterns of variation (Afifi, 1990). In PCA, the components are ordered by the amount of variation in the original variables they represent. The first component represents the greatest amount, followed by the second, third, etc. In general, PCA on a set of variables this size typically produces several components that will represent the majority of the variation in the original variables. In addition, the components have useful statistical properties (i.e., they are on a standard normal scale with a mean of zero and a standard deviation of one) and are not correlated to one another.

Original variables (metals and total mass) strongly correlated to a component are said to be loaded on the component. Usually, for ambient air data, a component will only have positive loadings associated with it. Positively loaded metals are strongly positively correlated in the original data, and high deposition rates will create higher values of the factor score.

Table 6-10 summarizes the overall results of the PCA at each site. The table presents the loading pattern of the elements, along with the percentages of variation explained by each component. The numbers for each element indicate whether the element had its highest loading on the first, second, third, etc. component (e.g., an entry of three for copper indicates that copper was loaded on the third component). Each site has a different number of components, depending on how many were needed to capture the maximum loadings of all the original variables. Table 6-10 also shows the total amount of variability captured at each site, over 90%.

Table 6-10. Principal Components Analysis Summary

	Ref(1)	SIO Pier	LJS Drive	LJ Parkway	Switzer-2	Chollas Mouth	SD8(1)	Commer-cial	DPR(2)
Variables	10	12	16	15	12	14	13	14	12
Components	2	3	5	5	4	4	4	4	3
Element	**Component Assignment**								
Aluminum	1	–	1	1	1	1	1	1	1
Bromine	2	1	2	2	–	4	–	–	–
Calcium	1	2	1	1	1	1	1	1	1
Chlorine	2	1	2	2	3	3	4	4	3
Copper	–	–	5	4	4	2	3	2	–
Iron	1	2	1	1	1	1	1	1	1
Potassium	1	1*	1	1	1	1	1	1	1
Magnesium	–	1	4	–	–	–	–	–	–
Manganese	–	–	1	1	–	1	1	1	1
Sodium	–	3	2	–	–	–	–	–	–
Lead	–	–	–	–	–	–	–	2	–
Sulfur	2	1	2*	2*	1*	3*	2	1*	2*
Silicon	1	2	1	1	1	1	1	1	1
Strontium	–	2	1*	3	1	1	1	1	1
Titanium	1	2	1	1	1	1	1	1	1
Zinc	–	–	3	3	2	2	2*	3	2
Zirconium	–	–	–	5	–	–	–	–	–
Net flux	1	1*	1	1	1	1	1	1	1
Component	**Percent Total Variation**								
PC1	65.1%	43.3%	49.1%	49.4%	60.6%	55.1%	57.0%	58.5%	63.3%
PC2	28.1%	42.1%	20.1%	15.7%	12.3%	16.2%	13.8%	12.8%	17.5%
PC3	–	8.3%	7.9%	11.1%	10.8%	11.0%	12.4%	11.0%	10.4%
PC4	–	–	7.7%	9.3%	9.8%	10.4%	11.4%	10.6%	–
PC5	–	–	–	7.0%	–	–	–	–	–
Total	93.2%	93.8%	92.5%	92.5%	93.5%	92.6%	94.5%	93.0%	91.2%

*Element loading (maximum correlation with component score) < 0.7

Table 6-10 shows two distinct and relatively consistent signature groups of elements that emerged from the analyses. The first group is a set of elements that are among the most abundant elements in the Earth's outer crust and/or are common rock-forming elements, including (in order of relative abundance) silicon, aluminum, iron, cadmium, sodium, potassium, magnesium, titanium, phosphorus, and manganese (Allaby and Allaby, 1999). Components loading these elements were primarily crustal in nature and represent general dust loading. Other elements were occasionally loaded with these crustal elements (e.g., sulfur and strontium). Many of these crustal and other elements could also represent industrial sources of emissions. However, when loaded along with background dust, such influences are impossible to discern. The relative abundance of the crustal elements for each site is presented on Figure 6-8. Note that the sites located close to the open ocean tend to have slightly different relative distribution of crustal elements. This is most likely due to the saltwater influence at those three sites (Ref(1), SIO Pier, and La Jolla Shores Drive).

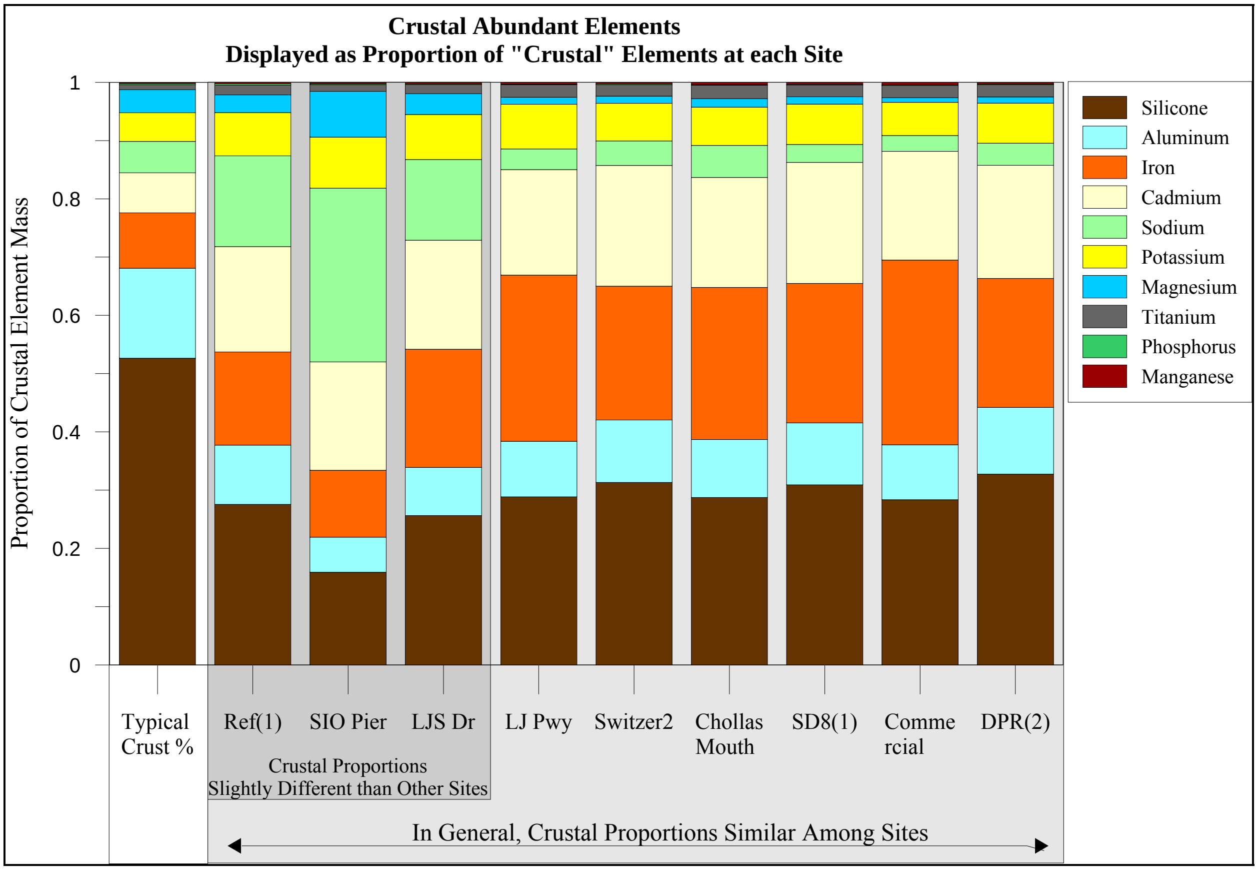


Figure 6-8. Relative Abundance of Crustal Elements at Study Sites

The second set of elements observed is connected to sea spray and includes bromine, calcium, chlorine, potassium, magnesium, sodium, and sulfur. These are among the main chemical constituents of sea water and were only observed together on components at sites near the Pacific Ocean. Specifically, SIO Pier was the only site where the sea spray component represented more variation than the crustal component.

Two of the main elements of interest in this study (copper and zinc) were often loaded on their own components at each site. The two metals are primarily related to anthropogenic sources. These metals were on individual components at all sites where they were detected, except for Chollas Mouth. At Chollas Mouth, they shared a single component. These patterns suggest that the sources of copper and zinc are somehow different in nature at most sites, but appear similar at Chollas Mouth.

The other metal of primary interest (lead) generally had less than detectable deposition rates and was included in the PCA at one site. The only site where lead was detected in at least 75% of the samples was the Commercial Site. At the Commercial Site, lead was loaded along with copper on the second component. These results are consistent with the Phase I study, which only found detectable lead deposition rates in primarily industrial areas and also found extremely low lead levels in high-volume air samples.

6.5.3 Correlation Analysis

Correlation analysis was done to calculate the Spearman Rank correlation coefficients between the principal component scores and variables representing wind direction and wind-direction-weighted land use influence for each sampling event. The Spearman Rank correlation is a non-parametric technique that measures the strength of association between two variables based on the ranks of each result for each variable rather than the values themselves. This approach is robust with respect to the underlying distribution of the variables and to outliers (i.e., extremely high or low values) (Zar, 1999).

The correlation coefficients range from -1.0 to 1.0. Based on the number of samples compared, the statistical significance of the correlation can be evaluated. Coefficients that were significant at the 90% and 95% levels were interpreted to represent potentially significant links between the wind/land use variables and the components. For a sample size of 24, an absolute value of the correlation result of 0.406 was significant at 95% and 0.344 at 90%. For a sample size of 23, an absolute value of the correlation result of 0.415 and 0.353 were significant at the 95% and 90% levels, respectively.

A total of 34 principal components (Table 6-10) and 20 wind/land use variables were considered. The 20 wind/land use variables included:

- Sigma compensated wind direction frequency for eight sectors (north, northeast, east, southeast, south, southwest, west, northwest), as described in Section 5.2.
- Mean downwind and crosswind vector components for east–west and north–south axes.
- Mean downwind and crosswind vector components for northeast–southwest and southeast–northwest axes.
- Land use influence expressed as frequency of time a site was downwind of eight land use categories by sector within a 1-km radius weighted by the eight wind sector frequencies.

The land use influence variables were introduced in an attempt to link the unique land use character of each site to the deposition rate. The link was made by weighting the wind sector frequency variables by the land uses in each sector and totaling them for each sampling period. For instance, on the coast, a sample period with all easterly winds would have 0% ocean influence, and the converse would be true for all west winds (100% ocean influence). Table 6-11 illustrates an example calculation of land use influence variables based on a wind distribution of 80% from the north and 20% from the northeast.

Table 6-11. Example Land Use Influence Calculation

Land Use	Sector		Wind Weighted		Land Use Influence
	North	Northeast	North = 0.8	Northeast = 0.2	
Other	10.00%	40.00%	8.00%	8.00%	16.00%
Residential	40.00%	20.00%	32.00%	4.00%	36.00%
Commercial	20.00%	0.00%	16.00%	0.00%	16.00%
Transportation	20.00%	30.00%	16.00%	6.00%	22.00%
Freeway	10.00%	10.00%	8.00%	2.00%	10.00%
Totals	**100.00%**	**100.00%**	**80.00%**	**20.00%**	**100.00%**

Table 6-11 shows that for this period, residential influence was prevailing with a value of 0.36 (36%). Each sector's land use percentage is multiplied by the corresponding wind sector percentage for a sampling period, and then summed. For example, the north sector residential proportion of 40% is multiplied by the north wind frequency of 80% (0.4 x 0.8 x 100% = 32%), and the same calculation is done for the northeast sector (0.2 x 0.2 x 100% = 4%). These two values are then added to get the total residential influence of 36%. This procedure was applied to all eight wind sectors and for all eight land use categories.

The eight land use influence categories were a slight simplification of the 11 land use categories used for the land use analysis presented in Section 3. Some land use categories were combined to make the number of categories more manageable and maintain focus on specific source-related land uses. The high-density and low-density residential land uses were combined into the single residential influence category. Ocean and water land uses were combined into the single water influence category. Finally, the open space / parks and recreation and public facility land uses were combined into the single other influence category.

Results of the correlation analysis are summarized in Table 6-12. In general, components representing copper and/or zinc were often correlated to wind directions from the north, northeast, and east and were related to transportation, residential, and freeway land uses. Copper was also found to be highly correlated to residential land use at some sites (La Jolla Parkway and Switzer-2). However, it should be noted that La Jolla Parkway has an east–west corridor of high surface street traffic. Much of the west bound traffic coming down hill will have significant braking. As previously mentioned, brake pads are a known source of copper. Chlorine was the other element often represented individually by the PCA and was correlated to winds from the south and southeast, but without a highly correlated land use. Appendix B includes the individual PCA and correlation results for each site.

Table 6-12. Spearman Correlation Summary Results

Site	Component	Analyte	Wind Direction	Land Use Influence
Ref(1)	PC2	Cl, Br, S	Southeast*	None
SIO Pier	PC1	Br, Cl, Mg, S	East*, southeast, west (DW 270), and southeast (CW 45)	Other, residential, and transportation
La Jolla Shores Dr (LJS Dr)	PC2	Br, Cl, Na	West*, southwest, westerly (DW 270), southerly (CW 270), and southwesterly (DW 45)	Water
	PC5	Cu	East* and easterly (DW 270)	Transportation*
La Jolla Parkway (LJ PWY)	PC3	Sr	North, northeast, east, southeast, easterly (DW 270), and northeasterly (DW 45)*	Residential*
	PC4	Cu	Southeasterly (CW 45)	Residential*
	PC5	Zr	Northerly (CW 270) and northeasterly (DW 45)*	None
Switzer-2	PC2	Zn	Northeast, east, easterly (DW 270)*, northerly (CW 270)*, and northeasterly (DW 45)	None
	PC4	Cu	Southeast and south	Residential
Chollas Mouth[1]	PC2	Cu, Zn	North, northeast, east, southeast*, northwest, and easterly (DW 270)	Other, residential, rransportation*, freeway*, commercial, and military
	PC3	Cl	South and southeasterly (CW 45)	None
	PC4	Br	Southeasterly (CW 45)*	None
SD8(1)	PC2	S	East*, northwest*, northerly (CW 270)*, and northeasterly (DW 45)	None
	PC3	Cu	Northeast, east, southeast, and easterly (DW 270)	Other, commercial, and freeway
	PC4	Cl	Southeasterly (CW 45)	None
Commercial[2]	PC3	Zn	Northeast* and east*	Freeway*
	PC4	Cl	Southeasterly (CW 45)	None
DPR(2)	PC2	Zn	North*, northeast, east, easterly (DW 270)*, northerly (CW 270), and northeasterly (DW 45)	Residential, commercial, and transportation
	PC3	Cl	Southeasterly (CW 45)*	None

* $p<0.10$, versus $p<0.05$
CW=crosswind; DW=downwind
1. Chollas Mouth is directly downwind (south) of a major industrial source.
2. Commercial Site is directly adjacent to a significant industrial and commercial corridor.

To enable further understanding of the correlation results, the summary results are presented on GIS maps that include wind direction and land use (Figure 6-10 through Figure 6-18). Elements highly correlated to a wind direction are presented in the 1,000-meter radius indicated on the maps, and any associated land use is also highlighted (Figure 6-9). Emphasis was placed on correlations to analytes that appeared alone or were not indicative of crustal elements or seawater.

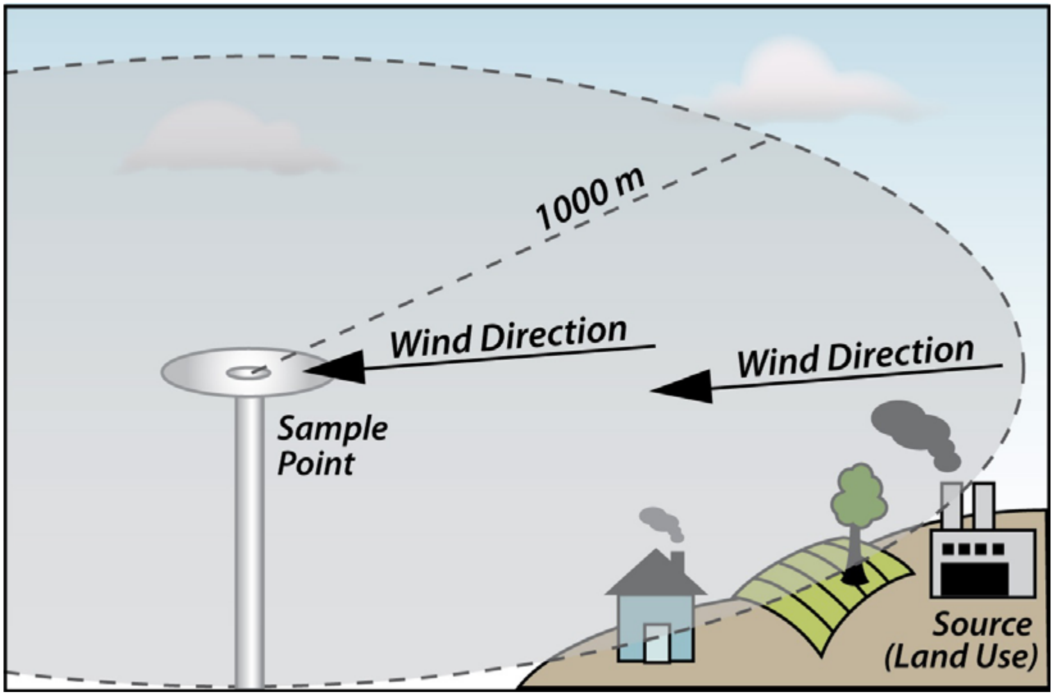


Figure 6-9. Wind Direction and Land Use Correlation Concept Diagram

Ref(1)

Chlorine, bromine, and sulfur were highly correlated with the southeasterly wind direction and is indicative of seawater from the Pacific Ocean (Figure 6-10).

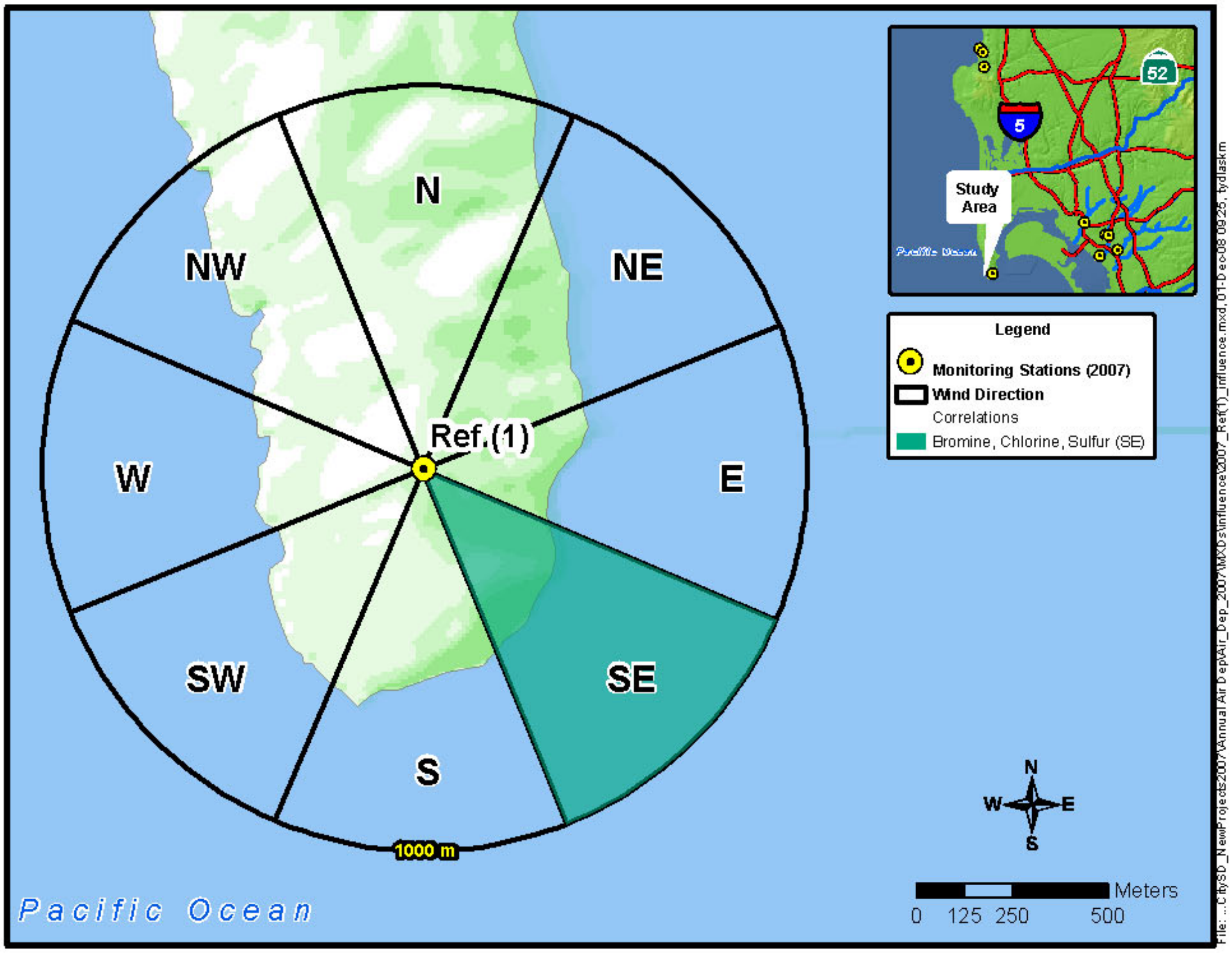


Figure 6-10. Wind Direction and Land Use Correlation Map – Ref(1) Site

Scripps Pier

No correlations were found between wind direction and land use at the Scripps Pier. Links were found to either crustal elements or seawater components only (Figure 6-11).

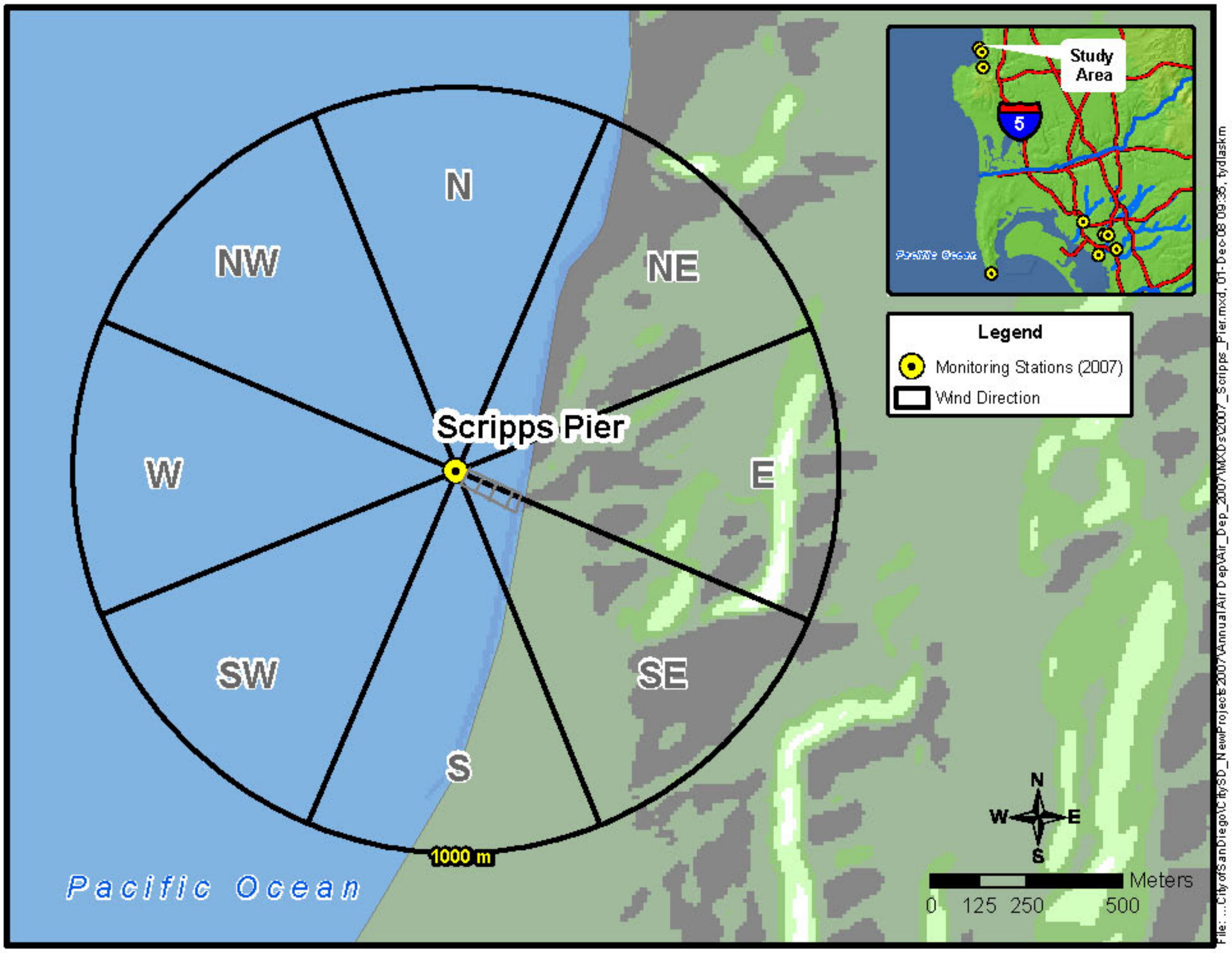


Figure 6-11. Wind Direction and Land Use Correlation Map – Scripps Pier Site

La Jolla Shores Drive

Bromine, chlorine, and sodium are highly correlated with wind coming from the west, southwest, and south, indicative of seawater from the Pacific Ocean. Copper was correlated with the east wind direction and was also strongly correlated with transportation land use influence (Figure 6-12).

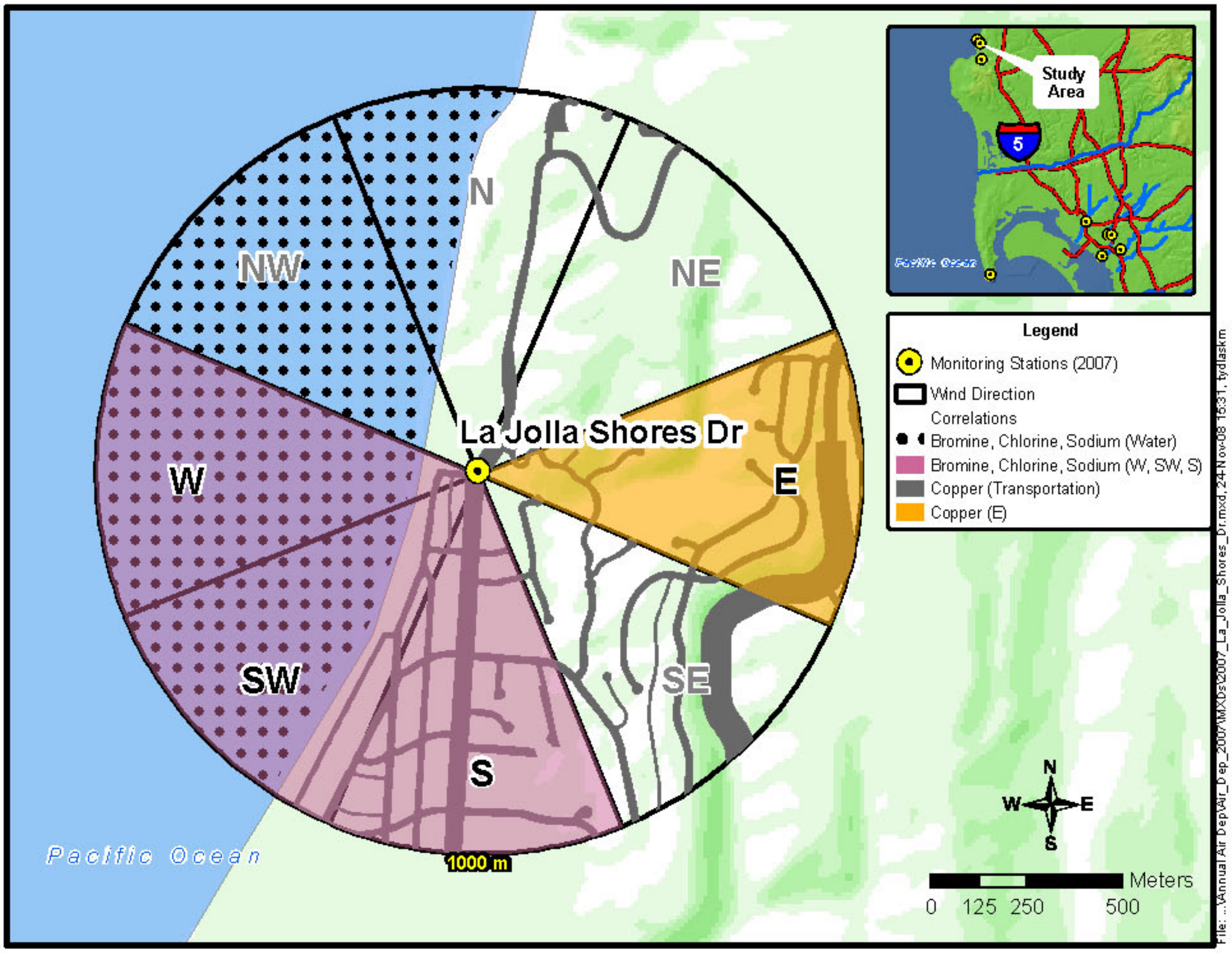


Figure 6-12. Wind Direction and Land Use Correlation Map – La Jolla Shores Drive Site

La Jolla Parkway

Strontium was correlated with the north, northeast, east, and southeast wind direction sectors and was highly correlated with residential land use influence. Copper from the southeast wind direction component was also highly correlated with residential land use which includes transportation land use. La Jolla Parkway provides high surface street traffic volumes entering La Jolla from the southeast quadrant. This traffic enters La Jolla via a steep downhill section that requires high braking and also approaches a major intersection at La Jolla Shores Drive. Zirconium was correlated with the north and northeast wind direction sectors, but no correlation found with any particular land use influence (Figure 6-13).

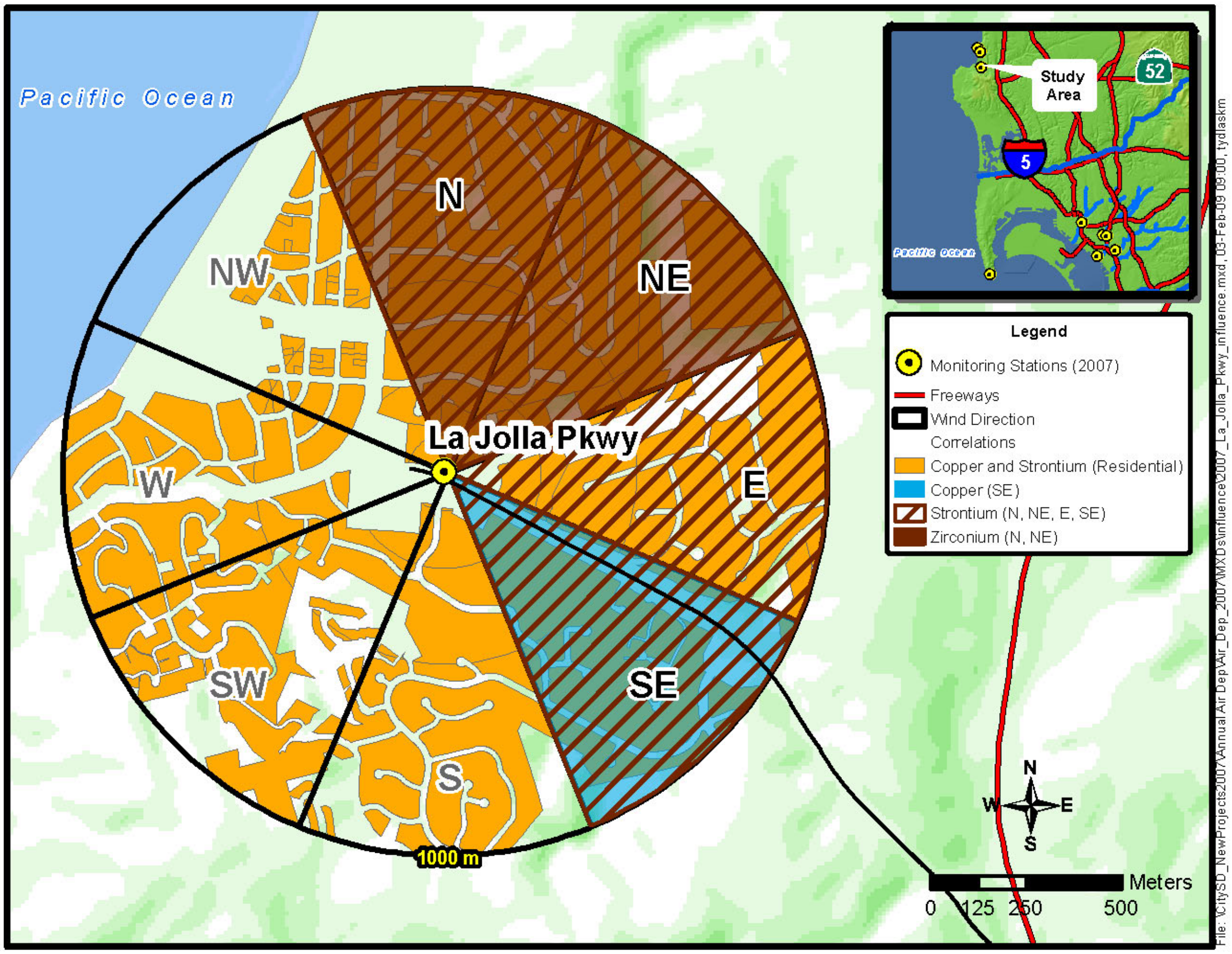


Figure 6-13. Wind Direction and Land Use Correlation Map – La Jolla Parkway Site

Switzer-2

Zinc was correlated with the north, northeast, and east wind direction sectors and had no apparent association with a particular land use influence, while copper was independently correlated with both southeast wind direction and residential land use influence (Figure 6-14). It should be noted that Highway 94 cuts directly through the southeast and residential sector. Traffic coming west must brake at the interchange with Interstate 5 and downtown San Diego.

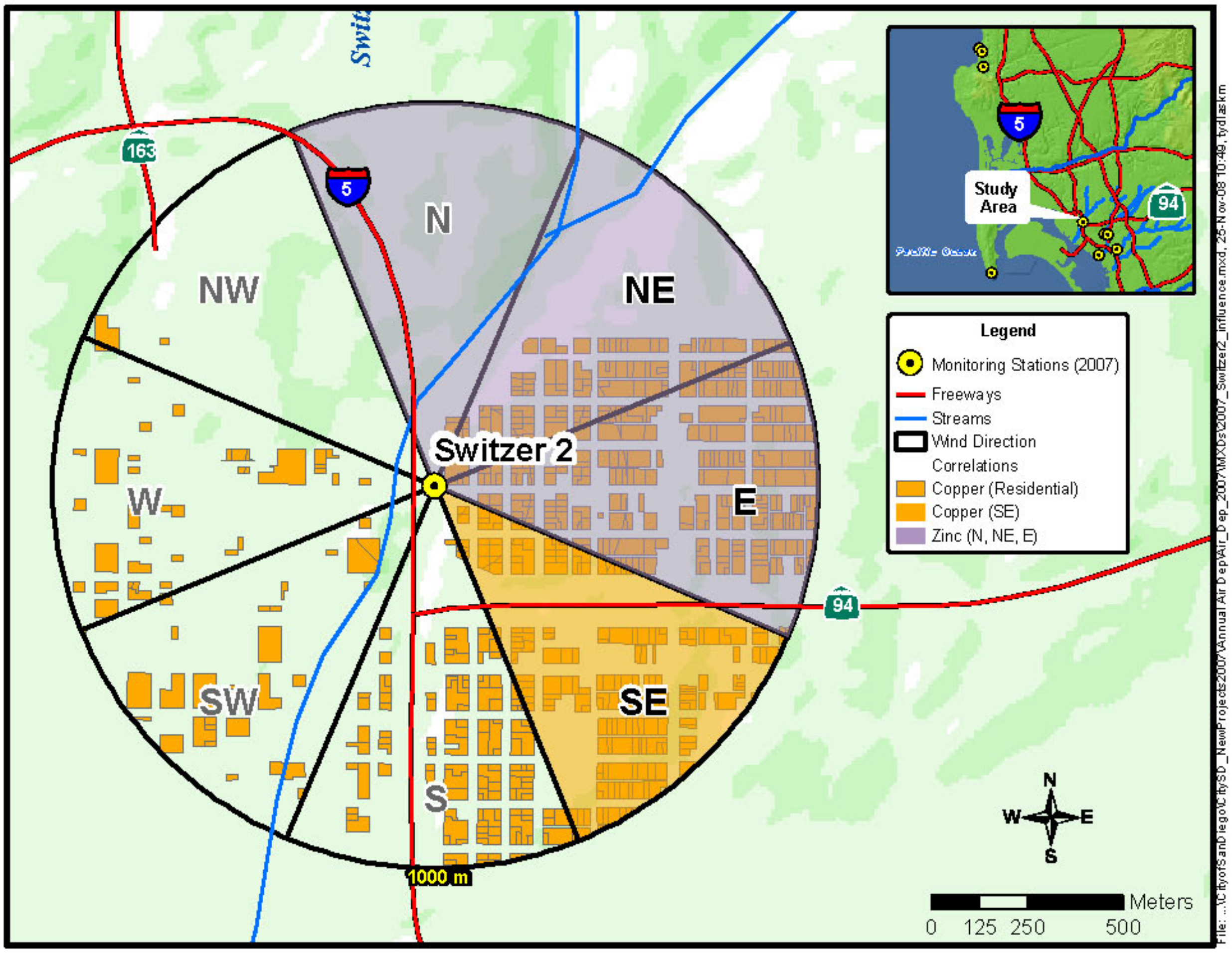


Figure 6-14. Wind Direction and Land Use Correlation Map – Switzer-2 Site

Chollas Mouth

Chollas Mouth Site copper and zinc are highly correlated to primarily northwest, north, northeast, and easterly wind directions. This corresponds to various land uses, including transportation, freeway, commercial, and military. It should be noted that significant industrial shipyards lie in the northwest sector of the site. Bromine was correlated with the southeast wind direction, and chlorine was correlated with the southeast wind direction. Neither element had any apparent land use influence correlation (Figure 6-15).

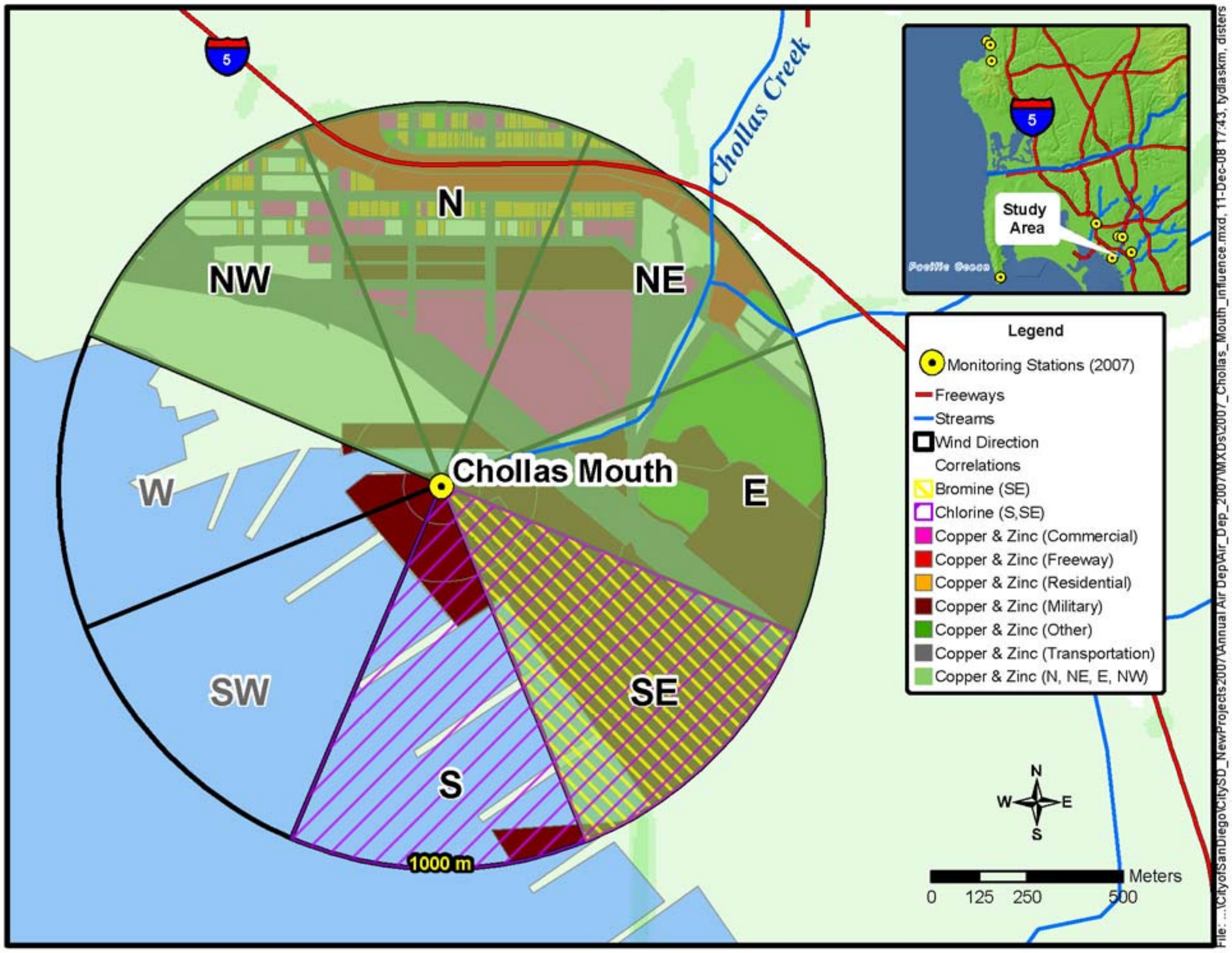


Figure 6-15. Wind Direction and Land Use Correlation Map – Chollas Mouth Site

SD8(1)

Correlation analysis indicated that copper was highly correlated to northeast, east, and southeast wind directions, which correspond to the freeway, commercial, and other land use influences. Sulfur was correlated with the northwest, north, northeast, and east wind direction, and chlorine was correlated with the southeast wind direction. Neither element had significant land use influence correlation (Figure 6-16).

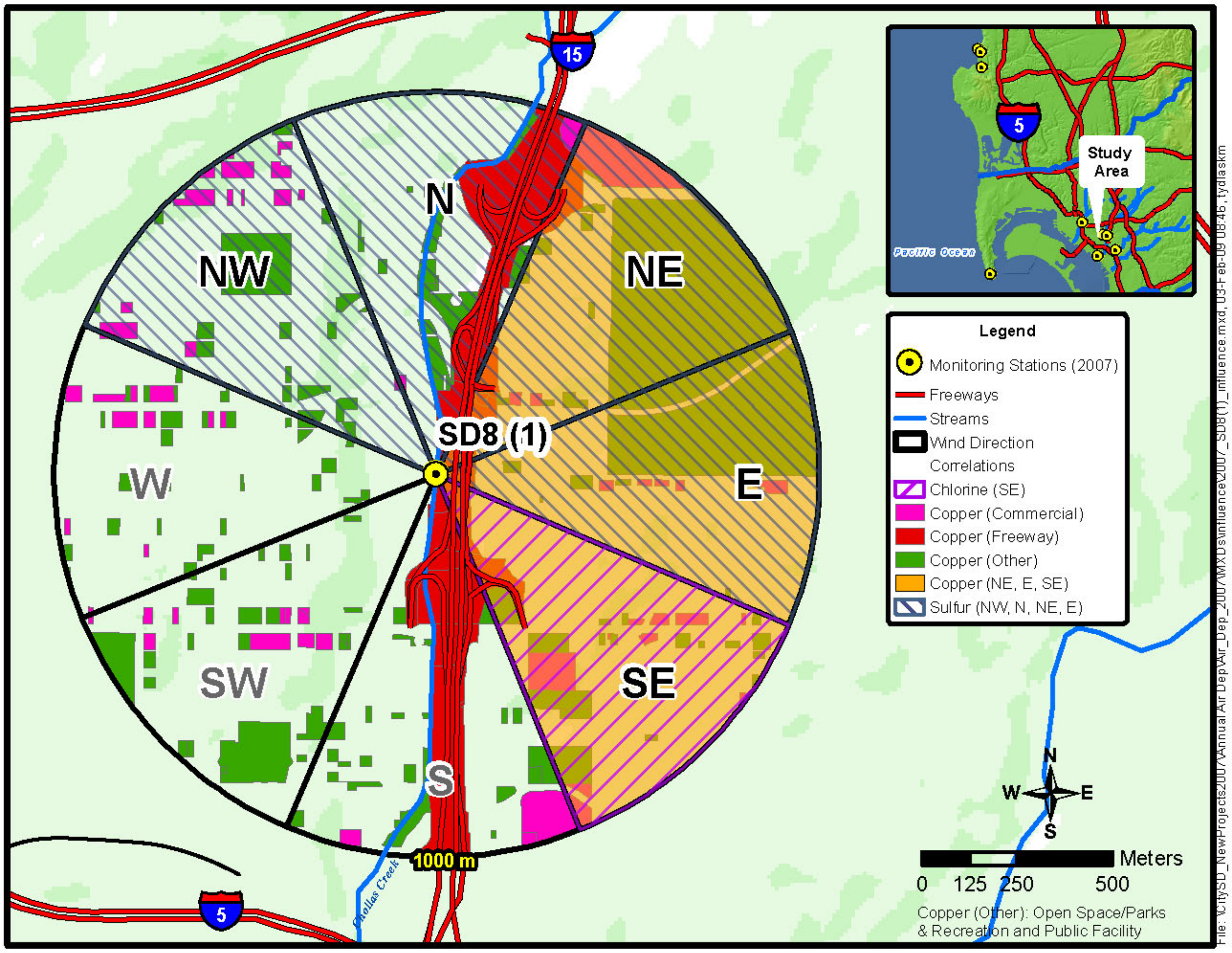


Figure 6-16. Wind Direction and Land Use Correlation Map – SD8(1) Site

Commercial

Zinc was correlated with the northeast and east wind directions and freeway land use influence. Chlorine was correlated with the southeast wind direction and had no land use influence correlation (Figure 6-17).

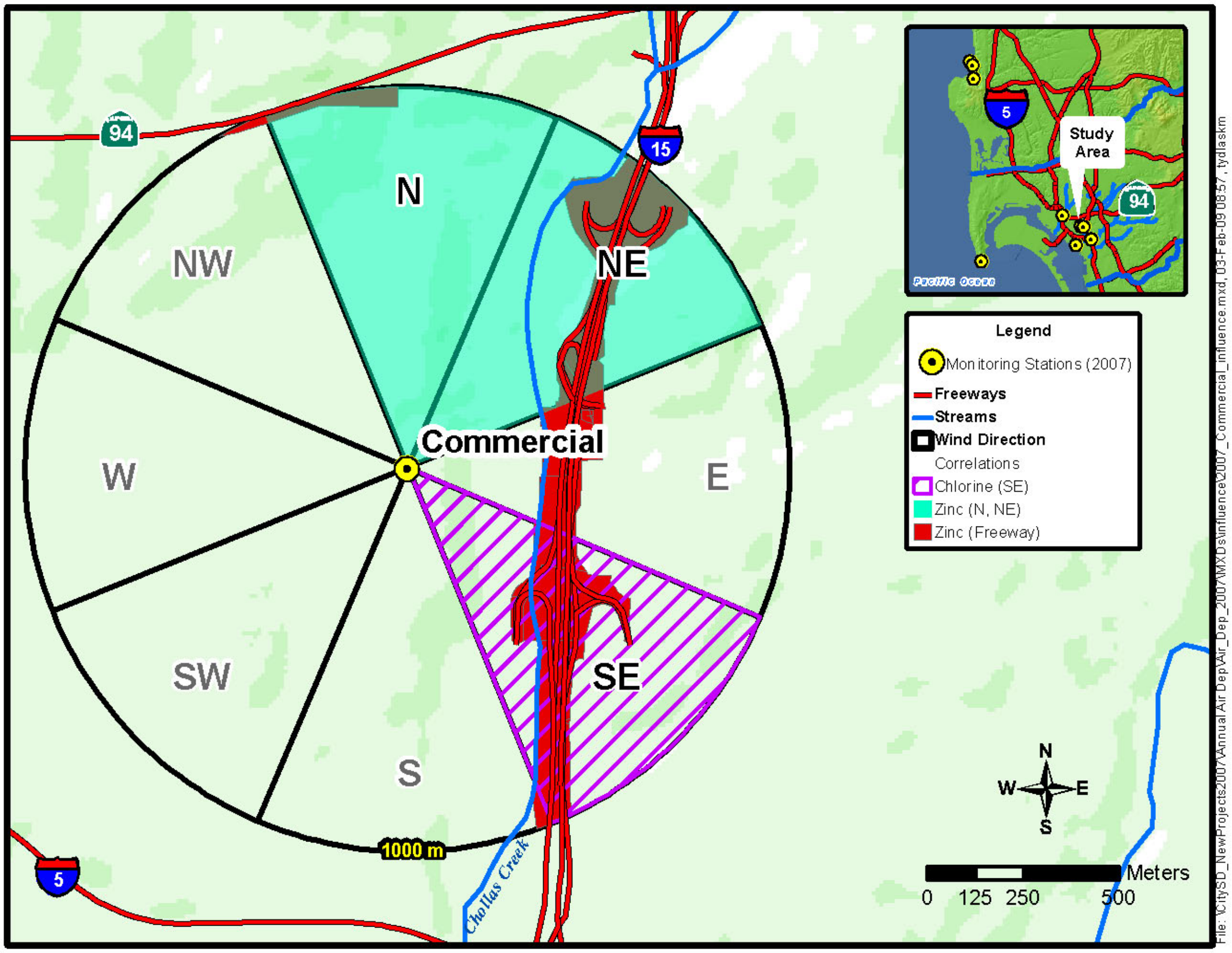


Figure 6-17. Wind Direction and Land Use Correlation Map – Commercial Site

DPR(2)

Zinc at the DPR(2) Site was correlated with the north, northeast, and east wind directions along with residential, commercial, and transportation land use influences. Chlorine was correlated with the southeast wind direction and had no correlation with any particular land use influence (Figure 6-18).

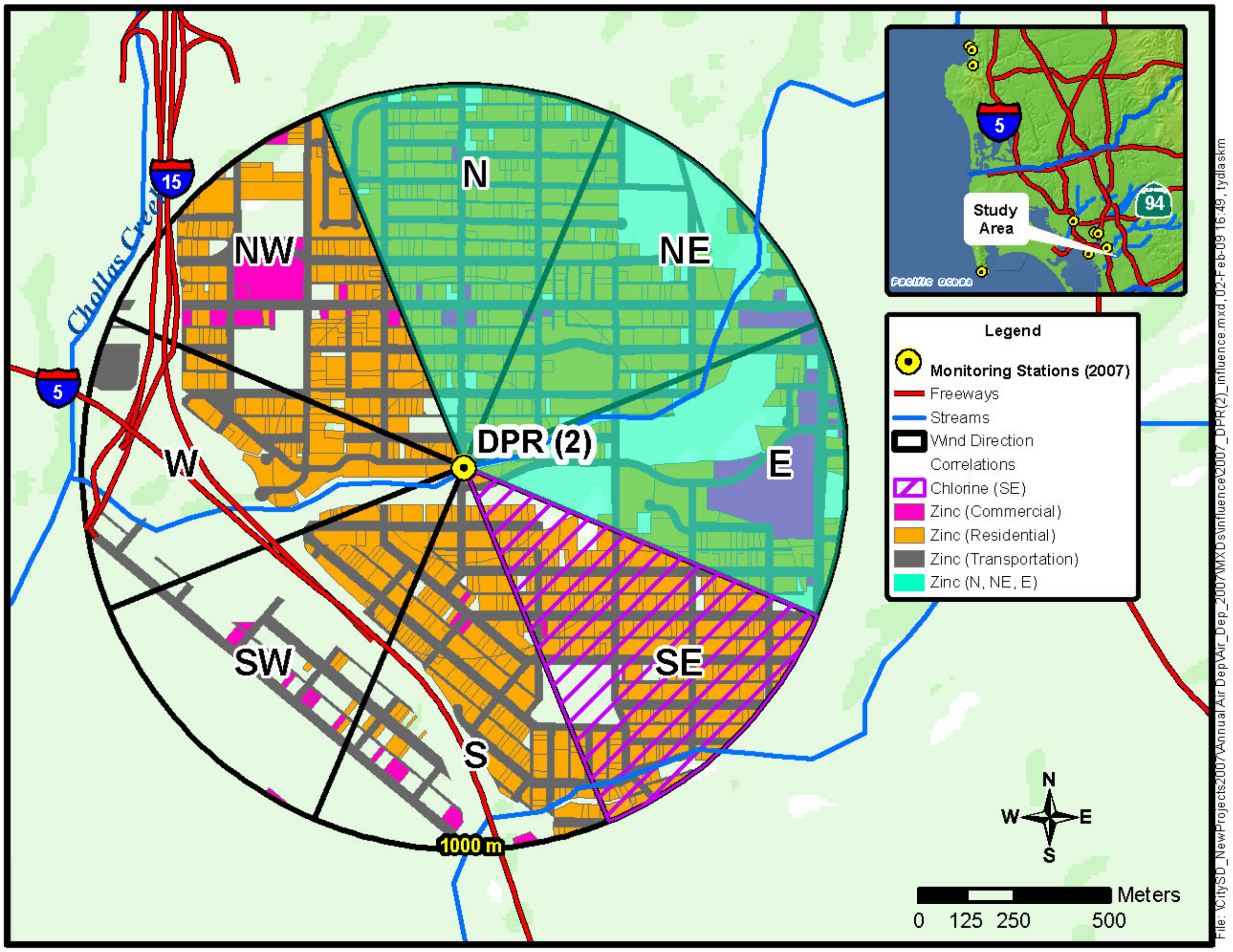


Figure 6-18. Wind Direction and Land Use Correlation Map – DPR(2) Site

7.0 FINDINGS, CONCLUSIONS, AND RECOMMENDATIONS

This Phase II study was intended to assess the contributions of metals from aerial deposition and its impact to concentrations of metals in storm water within the City of San Diego. Three related studies were conducted from September 2007 through August 2008 to answer the study questions presented below, which were unanswered during the initial Dry Weather Aerial Deposition Study.

1. **What is the annual aerial deposition rate in the high loading areas identified in the initial dry weather aerial deposition study?**
2. **What is the wet weather aerial deposition rate at the SD8(1) location?**
3. **What is the solubility of copper, lead, and zinc in atmospheric deposition particles during dry and wet conditions?**
4. **What is the direct aerial deposition rate of metals in the La Jolla ASBS?**

The three studies included a dry deposition study, a wet deposition study, and a solubility study. Collectively, results will help the City of San Diego further its understanding of the contribution of metals from aerial deposition both within the Pueblo San Diego Watershed and the La Jolla ASBS. The study results will provide information related to potential sources and therefore represents a Tier II Source Investigation Watershed Activity in accordance with the City's 5-Year Strategic Plan for Watershed Activities. The study also provides baseline data for assessing future BMP effectiveness, such as the implementation of Phase I street sweeping programs (Tier II BMP), and Tier III BMP placement to assess these Phase I activities per the 5-Year Strategic Plan. The data will also provide supporting evidence for needed legislative measures, such as reduction of copper in the brake pad manufacturing process as part of the Tier I Product Substitution Watershed Activities.

The following assessment of the data is provided to answer the Phase II study questions:

1. **What is the annual aerial deposition rate in the high loading areas identified in the initial dry weather aerial deposition study?**

There was considerable variation in dry deposition rates of the main target elements across all sites, except for lead. Lead was rarely detected at most sites, but was detected in 75% or more of samples at the Commercial Street Site in the Chollas Creek Watershed. Copper and zinc were measured at significantly higher levels at all inland sites compared to the reference sites (SIO Pier and REF-1) located along the coastline. Also, copper and zinc were detected in less than 75% of samples at the two reference sites.

Table 7-1 summarizes the median dry deposition rates measured during the study at all sites. The highest loading sites based on medians in the Chollas Creek basin were found at the Commercial Site (Pb, Zn, and net) and Chollas Mouth Site (Cu).

Table 7-1. Chollas Creek Watershed Annual Median Deposition Rates

Deposition Rate	Reference Sites		Chollas Creek				
	REF-1	SIO Pier	Switzer-2	Chollas Mouth	SD8(1)	Commercial	DPR(2)
Copper ($\mu g/m^2/day$)	2.6**	2.6*	19.6	**37.6**	22.5	29.5	12.7*
Lead ($\mu g/m^2/day$)	3.3**	3.2**	3.6*	3.2*	4.1*	**15.6**	3.2*
Zinc ($\mu g/m^2/day$)	4.1*	4.9*	106	107	114	**216**	62.7
Net Deposition ($mg/m^2/day$)	34.9	113	75.6	59.1	85.6	**120**	63

Maximum medians in watershed areas are in **bold** and shaded

*Detected in less than 75% of samples at this site

**Detected in less than 50% of samples at this site

Results indicate that the mouth of Chollas Creek (Chollas Mouth) and La Jolla Parkway had the highest median deposition rates of copper (37.6 $\mu g/m^2/day$ and 36.8 $\mu g/m^2/day$, respectively). Statistical correlation analysis indicated that copper and zinc at the Chollas Mouth Site was highly correlated to primarily northwest, north, northeast, and east wind directions. Copper and zinc were also correlated with varying land use influences, including transportation, freeway, commercial, military residential, and other land uses at the Chollas Mouth, which also has significant industrial land uses within 500 m of the site. At the La Jolla Parkway Site, copper deposition was highly correlated to southeast wind direction and residential land use, while strontium deposition was highly correlated with north, northeast, east, southeast wind direction and residential land use.

The newly added site on Commercial Street, in addition to the repeated Site SD8(1) located in the north fork of Chollas Creek, also had relatively high median copper deposition rates (29.5 $\mu g/m^2/day$ and 22.5 $\mu g/m^2/day$, respectively). Analysis indicated that copper at the SD8(1) Site was highly correlated to northeast, east, and southeast wind direction and commercial, freeway, and other land uses. Commercial Street also had the highest median deposition rates for lead and zinc (15.6 $\mu g/m^2/day$ and 216 $\mu g/m^2/day$, respectively). Analysis indicated that zinc at the Commercial Street Site was highly correlated to north and northeast wind direction and freeway land uses. The Commercial Street Site also provides additional supporting evidence of the higher loading areas of Chollas Creek presented in the Chollas Creek TMDL Source Loading, Best Management Practices, and Monitoring Strategy Assessment (WESTON, 2006).

Median net deposition was highest at the La Jolla ASBS sites (LJS Drive and LJ Parkway) with 150 $mg/m^2/day$ and 132 $mg/m^2/day$, respectively, as well as at the Commercial Street Site with 120 $mg/m^2/day$. In addition, evidence of weather events (e.g., Santa Ana winds and local wildfires) caused maximum net deposition rates in 100% of sites located within all areas of the City of San Diego as a result of ash fallout and higher re-suspension rates.

2. What is the wet weather aerial deposition rate at the SD8(1) location?

Table 7-2 summarizes the wet weather deposition rates and estimated solubility of copper, lead, and zinc measured during the study at the SD8(1) Site. Wet weather deposition rates were low but appear to be a contributing factor in wet weather exceedances of dissolved copper and zinc in the north fork of Chollas Creek (SD8(1) Site). This conclusion is based on the low compliance levels set by the CTR. Because the compliance levels are so low (due to low hardness in the water) even a low concentration from wet deposition is adds to the potential for exceeding the CTR limit. Lead results were low or not detected during all three monitoring events. Based on the analyses conducted in this study, wet weather deposition of copper and zinc may be more influential in Chollas Creek than studies from other regions have previously indicated.

Table 7-2. Wet Weather Deposition Concentrations and Estimated Solubility in the North Fork of Chollas Creek

Event 1 Date	**November 30, 2007**		
Total Event Rainfall	**1.48 inches**		
Parameter	**Copper**	**Lead**	**Zinc**
Total (µg/L)	1.1	0.21	4.4
Dissolved (µg/L)	0.8	<0.05	3.6
Estimated Solubility %	**73%**	**12%**	**82%**
Event 2 Date	**February 3, 2008**		
Total Event Rainfall	**0.39 inch**		
Parameter	**Copper**	**Lead**	**Zinc**
Total (µg/L)	0.8	<0.05	4.3
Dissolved (µg/L)	0.8	<0.05	4.1
Estimated Solubility %	**100%**	**NA**	**95%**
Event 3 Date	**March 15, 2008–March 16, 2008**		
Total Event Rainfall	**0.32 inch**		
Parameter	**Copper**	**Lead**	**Zinc**
Total (µg/L)	4.2	1.27	85.6
Dissolved (µg/L)	1.7	<0.05	65.6
Estimated Solubility %	**40%**	**2%**	**77%**

3. What is the solubility of copper, lead, and zinc in atmospheric deposition particles?

Table 7-3 summarizes the particle solubility of copper, lead, and zinc measured during the study at Site SD8(1). Solubility tests at the north fork of Chollas Creek (Site SD8(1)) suggest that copper and lead have relatively low solubilities in their deposited state. The highest copper solubility was approximately 15% of the total copper concentration. The highest lead solubility was 1.32% of the total lead concentration. Zinc was relatively soluble, with the first event showing 88% of the total zinc concentration and showing 47% and 58% for the other two events.

Table 7-3. Particle Solubility Tests in the North Fork of Chollas Creek

Event 1 Date	**November 5, 2007**		
Parameter	**Copper**	**Lead**	**Zinc**
Total deposition rate (mg/m^2/day)	13.4	7.5	95.2
Soluble deposition rate (mg/m^2/day)	1.2	0.005	83.4
Estimated Solubility	**9%**	**0.06%**	**88%**
Event 2 Date	**March 17, 2008**		
Parameter	**Copper**	**Lead**	**Zinc**
Total deposition rate (mg/m^2/day)	55.1	17.8	194
Soluble deposition rate (mg/m^2/day)	6.3	0.4	90.6
Estimated Solubility	**11%**	**2.49%**	**47%**
Event 3 Date	**June 16, 2008**		
Parameter	**Copper**	**Lead**	**Zinc**
Total deposition rate (µg/m^2/day)	82.2	14.9	210
Soluble deposition rate (µg/m^2/day)	12.1	0.2	121
Estimated Solubility	**15%**	**1.32%**	**58%**

When compared with the Copermittee Regional Monitoring Program wet weather data, these results fall in the range of the solubilities measured in storm water runoff over the past seven years of monitoring. The results provide additional supporting evidence that indirect aerial deposition particulates may account for the majority of the copper, zinc, and, to a lesser degree, lead that is found in Chollas Creek storm water runoff.

4. What is the direct aerial deposition rate of metals in the La Jolla ASBS?

There was considerable variation in dry deposition rates of the main target elements across all sites, except for lead. Lead was rarely detected at the La Jolla ASBS sites. Copper and zinc were measured at significantly higher levels at both La Jolla inland sites compared with the reference site along the coastline (SIO Pier). Also, copper and zinc were detected in less than 75% of samples at the SIO Pier Site.

Table 7-4 summarizes the median dry deposition rates measured during the study at the La Jolla ASBS sites and the associated reference site (SIO Pier). La Jolla Shores Drive had the highest median net deposition rate, while La Jolla Parkway had the highest median copper and zinc deposition rate. La Jolla Parkway provides high surface street traffic volumes entering La Jolla from the southeast quadrant. This traffic enters La Jolla via a steep downhill section that requires high braking and also approaches a major intersection at La Jolla Shores Drive. Each site in the La Jolla ASBS region had only one detectable deposition rate of lead in the 24 samples collected through the year at each location.

Table 7-4. Annual Median Deposition Rates in La Jolla Area of Special Biological Significance

Deposition Rate	Reference Sites		La Jolla ASBS	
	REF-1	SIO Pier	LJS Drive	LJ Parkway
Copper (µg/m^2/day)	2.6**	2.6*	15.4	**36.8**
Lead (µg/m^2/day)	3.3**	3.2**	3.5**	3.3**
Zinc (µg/m^2/day)	4.1*	4.9*	148	**197**
Net Deposition (mg/m^2/day)	34.9	113	**150**	132

Maximum medians in watershed areas are in **bold** and shaded

*Detected in less than 75% of samples at this site

**Detected in less than 50% of samples at this site

Aerial deposition rates of copper, zinc, and net deposition at the La Jolla sites were in the upper ranges of the deposition rates measured amongst all sites. Bromine, chlorine, and sodium deposition was highly correlated to ocean water with west, southwest, and south wind direction at La Jolla Shores Drive, while copper deposition was highly correlated to east wind direction and transportation land uses. At the La Jolla Parkway Site, copper deposition was highly correlated to southeast wind direction and residential land use, while strontium deposition was highly correlated to north, northeast, east, southeast wind direction and residential land use. A relatively high median net deposition was measured at the Scripps Pier Site, which is considered a reference site for copper, lead, and zinc measurements. Net deposition at the La Jolla Parkway and La Jolla Shores sites (150 mg/m^2/day and 132 mg/m^2/day, respectively) were the study's highest results with high variability. The Scripps Pier Site (113 mg/m^2/day) had the fourth highest net deposition of all sites. Based on microscopic observation of deposition plates, it is likely that wind blown sand from area beaches in the vicinity of the plates may be the reason for the elevated net deposition rates observed. This is also supported by correlation analysis linking net deposition to crustal and seawater elements at SIO Pier.

7.1 Conclusions

The Chollas Creek dissolved metals TMDL (Section 10.3, page 67) states that "MS4 discharges are point source discharges because they are released from channelized, discrete conveyance pipe systems and outfalls. Background loads and loads from air deposition are negligible compared to the loads delivered from the MS4s..."

This study demonstrates that aerially deposited particulates are not negligible and can account for the majority of the concentration of copper and zinc and, to a lesser degree, lead in storm water runoff found in Chollas Creek. Multivariate analyses of site, land use, and wind direction data suggest that copper and zinc particulates originate from primarily anthropogenic sources, including, but not limited to, transportation, freeway, localized industrial activities, commercial, military, and residential land uses. These sources were often correlated to specific wind directions that varied by metal and by site. Industrial land uses fell within several wind quadrants coinciding with wind direction correlations. Lead generally had less than detectable deposition rates but was detected in at least 75% of the samples in only one site (Commercial Street). At the Commercial Site, lead was correlated with copper and was consistent with the Phase I study, which only found detectable lead deposition rates near industrial areas and also found low lead levels in high-volume air samples.

There was considerable variation in dry deposition rates of the main target elements across all sites, except for lead. Lead was rarely detected at most sites and was only detected in 75% or more of samples at the Commercial Site in the Chollas Creek Watershed. Copper and zinc were measured at significantly higher levels at all inland sites compared to the reference sites (SIO Pier and Ref(1)) located along the coastline. In addition, evidence of weather events, such as Santa Ana winds and local wildfires, caused maximum net deposition rates in 100% of sites located within all areas of the City of San Diego as a result ash fallout and higher resuspension rates.

Wet weather deposition rates of dissolved copper and zinc were low but appear to be a contributing factor in wet weather exceedances of dissolved copper and dissolved zinc in the north fork runoff results in Chollas Creek (SD8(1)). The waste load allocation in the Chollas Creek TMDL is based on the acute and chronic hardness based concentrations listed in the California Toxics Rule. The low levels detected from wet deposition are additive to the runoff concentrations which are frequently just above the CTR exceedance levels. Particle solubility tests at SD8(1) also suggest that copper and lead have relatively low solubilities in their deposited state. Dissolved lead results were low or not detected during both wet weather deposition and particle solubility tests.

Results suggest that aerial loading of metals to watersheds is likely driven by localized deposition of larger particles near transportation and industrial sources. Concentrations of copper, lead, and zinc vary within different areas of the City of San Diego, within different watersheds, and within different subwatershed areas, as previously discussed.

As described in the Phase I study, freeways and surface streets are not the only contributors of copper and zinc particulates. Small unpermitted facilities may also contribute particulates that result in elevated deposition rates, yet there are no regulatory programs that restrict facilities from emitting coarse particulates greater than 10 microns in aerodynamic diameter. Particulates finer than 10 microns aerodynamic diameter (PM_{10}) are regulated on both the state and federal levels. Air quality programs in California address some sources of toxic air pollution. However, there are two major components paramount to the deposition of metals, which subsequently result in watershed impacts that are not captured in the air toxics program. The first issue is the disconnect between contaminants of concern across the different media and environmental regulations. Copper and zinc are not considered toxic air compounds of concern but are of concern in water quality. The second issue is the nature of these emissions, often from a large number of small unregulated businesses originating from activities (e.g., soldering, welding, painting, brazing, and scrap metal operations). It is important to understand where industrial sources may be contributing to degradation of water quality. Water quality regulators may need to consider the daily practices of industrial activities and how their emissions may impact subwatershed and watershed areas. Performing inventories of facility activities and establishing their proximity to receiving waters is also important.

Air quality and water quality are of significant importance to the public. However, the regulatory differences and pollutants of concern create a regulatory gap that allows some pollutant sources to remain without regulatory control. The San Diego Regional Water Quality Control Board regulates point source runoff and relies on the municipalities to also perform industrial inspections. Storm water regulations focus on reducing pollution runoff from sites and not particulate emissions. The Chollas Creek dissolved metals TMDL has been revised to require the San Diego Regional Water Quality Control Board and the local Air Resources Control Board to review regulatory gaps that may impact water quality in the Chollas Creek Watershed.

As previously mentioned, the emissions may not be of concern to the San Diego Air Pollution Control District if the emissions are related to copper, zinc, or particulate matter greater than 10 microns. Copper and zinc emissions are not considered toxic air compounds (to human health via inhalation) by the ARB and are not regulated. However, copper is toxic to aquatic organisms and is one of the primary water quality concerns in the Chollas Creek Watershed. Water quality regulatory agencies promote controlling sources as the first step in reducing the impacts to water quality. Some of these facilities have NPDES permits regulating the runoff from their sites but not their air emissions. The importance of this gap in regulatory control is significant because it does not prevent these facilities from emitting copper containing particulates that may settle out on areas directly adjacent to the facility, and these particulates are not required to be monitored or controlled off site by the responsible parties. The particulates will then accumulate and become the responsibility of the owner of the MS4 system (in this case the City of San Diego and other jurisdictions in the Chollas Creek Watershed). Based on this finding, the implementation of treatment BMPs to control copper and zinc may not be successful at reducing the impact of copper loading near the Mouth of Chollas Creek which the Chollas Creek metals TMDL is intended to protect.

The City of San Diego has been actively involved with the Brake Pad Partnership over the past year by contributing data and support of legislative changes related to removing copper from brake pads. The City San Diego is also working with the CASQA Brake Pad Partnership Subcommittee to implement a legislative bill requiring manufacturers to remove copper from the brake pad manufacturing process.

The City of San Diego has also conducted several studies in the La Jolla ASBS and has conducted a Street Sweeping Assessment Program. By combining the data from these studies, the City of San Diego will be able to assess both sources and BMPs for these areas. Additionally, the Chollas Creek Metals TMDL Implementation Plan will benefit from the data provided by this aerial deposition study by providing focus areas for high loading subwatershed areas.

7.2 Study Data Gaps

Although the data assessed present evidence of the processes and sources of aerial deposition, several questions were not fully answered, including:

1. **Do identified high deposition rate areas coincide with high runoff concentrations for copper, lead, and zinc?**
2. **How do metals concentrations from residential runoff areas compare to industrial/commercial runoff areas in the same relative aerial deposition area?**
3. **Are some facilities/sites contributing greater runoff concentrations of copper, lead, and zinc compared to other facilities/sites?**

The City is moving forward with a Phase III study to address these questions during FY08-09. The key findings from this report lead to the following recommendations with regard to storm water management and meeting load reductions required by current and future TMDLs in City of San Diego watersheds:

7.3 Recommendations

The City of San Diego is implementing watershed activities in Chollas Creek, Tecolote Creek, and the La Jolla ASBS watersheds where aerial deposition studies have been completed to address pollutant loading to receiving waters. Activities underway that reduce the amount of particulate matter that carries pollutants to receiving waters via urban and storm water runoff include:

- Baseline (Jurisdictional) street sweeping and aggressive targeted (watershed specific) street sweeping.
- Baseline and targeted storm drain and catchment inspections and maintenance.
- Baseline and higher frequency targeted inspection programs of commercial facilities that have been identified to have a likely potential for pollutants, such as, targeted inspections of auto related and priority industrial facilities.
- Source identification studies that target a set of sources that are likely or unknown pollutant loading sources, for example, investigating the sources of copper and zinc in the watershed.
- Product substitution efforts, such as, participation in the Brake Pad Partnership.

BMPs focused on removing particle sizes greater than 10 microns in size may have the greatest success in reducing the concentrations of zinc found in roadway dust and, subsequently, urban runoff. Additional benefits may be gained by removing smaller particles, but with diminishing returns on a cost per benefit relationship as the particle size decreases below 5 microns. Large particles containing lead and copper may also be reduced by implementing these BMPs. However, copper associated with brake-pad wear is less likely to be removed effectively without using treatment train BMPs, as mentioned in the *Chollas Creek Source Loading, Best Management Practices, and Monitoring Strategy Assessment Report* (WESTON, 2006).

Based on the findings of the Phase I and Phase II aerial deposition studies, the following recommendations are presented for consideration:

It is recommended that:

- Tiered BMP presented in the *Chollas Creek Source Loading, Best Management Practices, and Monitoring Strategy Assessment Report* (WESTON, 2006) and 5-Year Strategic Plan be implemented with the first tier emphasizing source controls, pollution reduction measures, and source identification studies. Source control measures are recommended to be the current focus over storm water treatment BMPs at this phase to reduce loads.
- The City of San Diego continue efforts with the Brake Pad Partnership and the CASQA Brake Pad Partnership Subcommittee.
- Inspections and monitoring of metal-related industries (both water quality and air quality monitoring) be increased based on the recommendations in the *Chollas Creek Source Loading, Best Management Practices, and Monitoring Strategy Assessment Report,* the 5-Year Strategic Plan, and this report to identify higher loading facilities and to ensure compliance with applicable storm water and air pollution control regulations.
- The Chollas Creek Dissolved Metals TMDL Implementation Plan consider high loading areas near the mouth of Chollas Creek and near Commercial Street for BMP focus areas. This has been represented in the sector maps in the 5-Year Strategic Plan and the Preliminary Draft of the Chollas TMDL Implementation Plan.

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