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## Contribution of trace metals from atmospheric deposition to stormwater runoff in a small impervious urban catchment

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#### Abstract

The contribution of atmospheric deposition to emissions of trace metals in stormwater runoff was investigated by quantifying wet and dry deposition fluxes and stormwater discharges within a small, highly impervious urban catchment in Los Angeles. At the beginning of the dry season in spring 2003, dry deposition measurements of chromium, copper, lead, nickel, and zinc were made monthly for 1 year. Stormwater runoff and wet deposition samples also were collected, and loading estimates of total annual deposition (wet + dry) were compared with annual stormwater loads. Wet deposition contributed 1–10% of the total deposition inside the catchment, indicating the dominance of dry deposition in semi-arid regions such as Los Angeles. Based on the ratio of total deposition to stormwater, atmospheric deposition potentially accounted for as much as 57–100% of the total trace metal loads in stormwater within the study area. Despite potential bias attributable to processes that were not quantified in this study (e.g., resuspension out of the catchment or sequestration within the catchment), these results demonstrate atmospheric deposition represents an important source of trace metals in stormwater to waterbodies near urban centers.

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#### 1. Introduction

Urban stormwater runoff can be highly contaminated with heavy metals and other toxic compounds, representing a significant non-point source of pollution to waterbodies within and adjacent to urban centers (Sansalone and Buchberger, 1997; Smullen et al., 1999; Buffleben et al., 2002). In Southern California, mass emissions from urban stormwater runoff can be higher than from point sources (e.g., wastewater treatment plants and industrial discharges) (Schiff et al., 2000).

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Furthermore, urban stormwater runoff can be toxic to aquatic organisms, and trace metals may be one of the constituents responsible for this toxicity (Marsalek et al., 1999; Schiff et al., 2002; Greenstein et al., 2004).

While future water quality improvements in urban areas may depend on contaminant reduction from stormwater, many of the trace metal sources to urban stormwater have not been well characterized. In semi-arid regions such as Southern California, pollutants may build-up on impervious surfaces during the extended dry season, and subsequently wash-off into nearby water-bodies once the wet season begins. Atmospheric deposition may be especially important as a source of pollutants to stormwater in these regions because significant quantities of trace metals and other pollutants are emitted

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into the atmosphere daily (SCAQMD, 2003), and the ultimate fate of the trace metals in particular is unknown.

Yet despite this potential, there are relatively few studies specifically targeting the pollutant contribution of atmospheric deposition to urban stormwater runoff in Los Angeles. The majority of atmospheric deposition research has focused on areas such as the Great Lakes and Chesapeake Bay regions (Lin et al., 1993; Baker et al., 1997; Paode et al., 1998). These areas have different atmospheric emissions and climatic parameters, and greater precipitation than Southern California, which may increase the importance of wet vs. dry deposition. Studies specific to urban atmospheric deposition have been limited even though urban areas have been shown to have higher deposition rates for a number of pollutants, including trace metals (Galloway et al., 1982; Yi et al., 2001). The present research was designed to quantify the contribution of atmospheric deposition of trace metals to stormwater loadings in a small urban catchment in Los Angeles.

#### 2. Methods

Los Angeles has a semi-arid climate, with an average annual rainfall of 33 cm. Typically, the bulk of this precipitation occurs from December to March. Starting with the beginning of the dry season in May 2003 and continuing for 1 year, dry deposition and atmospheric concentrations of chromium, copper, nickel, lead and zinc were measured for 48 h once a month, on days without rain within a defined catchment in Los Angeles. Concentrations of trace metals in rain and stormwater within the catchment were measured from December 2003 to March 2004. The data were used to estimate the contribution of atmospheric deposition to stormwater loadings within the catchment. The site was selected to minimize sources of trace metals to stormwater within the catchment other than urban background atmospheric deposition.

#### 2.1. Site description

The catchment was located in the San Fernando Valley of Los Angeles, California, within the grounds of a water reclamation plant. This site was suitable for this study as (1) the land surface was relatively flat; (2) the plant was surrounded by an earthen berm, preventing surface runoff from surrounding areas from entering the catchment; (3) sources of metals inside the plant were limited because of restricted access and lack of major industrial activities within the plant. Virtually all of the surface flow from the catchment was routed through a single catch basin, which was the site of runoff collection. The estimated drainage area to the catch basin was 5 ha based upon facility storm drain plans,

discussions with the Plant Engineer, visual inspection, and on site measurements. The drainage area consisted primarily of impervious surfaces including asphalt roads, concrete sidewalks, and concrete structures with monolithic poured foam roofs. Unpaved dirt and vegetated areas covered <20% of the drainage area. A runoff coefficient of 1.0 was assumed because pervious areas were not subject to substantial infiltration. Evaluation of this assumption led to minimal bias and any overestimation of the runoff volume would result in conservative estimates of stormwater discharges. Traffic inside the plant was limited to ~50 vehicles per day, and streets were cleaned weekly.

#### 2.2. Instrumentation

Dry deposition measurements were made using a modification of surrogate surfaces used by Paode et al. (1998) and Lin et al. (1993). Surrogate surfaces for this study were comprised of a circular PVC deposition plate, 33 cm in diameter, with a sharp edge ( $< 10^{\circ}$ angle), covered with a Mylar® sheet coated with Apezion L grease. The grease was liquefied by heating and then painted onto the Mylar® film to obtain a thin, uniform 10 µm layer. During sampling, the plate was mounted onto a tripod at a height of 2 m. Atmospheric concentrations of trace metals on total suspended particulate (TSP) were collected using a filter-based sampling system attached to a vacuum pump. The openfaced inlet was loaded with a 37 mm, 2.0 µm pore Teflon<sup>®</sup> filter, and sampling was done at a flow rate of 101/min. The open-faced inlet was expected to reduce large particle losses to the walls and inlets typical of conventional impactor samplers. Wind speed and direction, temperature, and relative humidity were measured using a portable meteorological station (PortLog, Rain Wise, Inc., Bar Harbor, Maine).

Event-based wet deposition samples were collected using an automated rainwater collector developed by the National Atmospheric Deposition Program (NADP, 1997). The cover opened during periods of precipitation and closed when precipitation ended, eliminating evaporation from the sampler and preventing contamination of the sample. A pre-cleaned container was used for each event.

Flow-weighted composite stormwater samples were collected during each storm in 500 ml plastic bottles using an ISCO 6700 automated stormwater sampler, which also logged flow to determine runoff quantity.

#### 2.3. Sample preparation and analysis

For the deposition plates, Mylar<sup>®</sup> sheets were cut into 30 cm diameter circles, wiped with methanol and soaked in 10% nitric acid followed by methanol for 5 min each, then rinsed with distilled water, and allowed to air dry.

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