Atmospheric dry deposition of trace metals in the Los Angeles coastal region

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ABSTRACT - Emissions of trace metals to the atmosphere and subsequent deposition, either directly to the waterbody surface or indirectly to the watershed as wash-off during rain events, may contribute to the contamination observed in surface waters throughout the urban Los Angeles region. The goals of this study were (1) to provide empirical data on atmospheric concentrations of trace metals on coarse particles; and (2) to estimate the direct and indirect mass loading of these trace metals due to dry atmospheric deposition in coastal watersheds of the Los Angeles Air Basin. To achieve this goal, atmospheric concentrations of chromium, copper, lead, nickel and zinc were measured seasonally using a Noll Rotary Sampler at six urban and one non-urban site throughout the Los Angeles coastal air basin. Dry deposition fluxes were calculated by summing the product of air concentration and theoretical deposition velocities of four coarse particle fractions (6-11, 11-20, 20-29, and >29 µm). Mean fluxes at urban sites ranged from 3.2 to 9.1, 11 to 34, 3.8 to 8.8, 8.3 to 29, and 69 to 228 µg/m^2/day for chromium, copper, nickel, lead and zinc, respectively. Mean fluxes at the urban sites were significantly higher than at the non-urban site. Antecedent rainfall was a dominant factor affecting atmospheric concentrations and estimated fluxes; when sampled within 5 d of measured precipitation, trace metal concentrations at the urban sites were similar to the non-urban site. For the Los Angeles River, dry atmospheric deposition directly to the water surface produced a relatively small load of trace metals to that waterbody. In contrast, dry deposition of trace metals to the land surface within the watershed was potentially a very large contributor to watershed loadings based on comparisons to load estimates from stormwater runoff.

INTRODUCTION

Dry deposition represents a major removal pathway for many pollutants from the atmosphere (Seinfeld and Pandis 1998), and is especially important in arid and semi-arid regions where removal by wet deposition (i.e., rainfall scavenging) is greatly diminished due to limited precipitation. Atmospheric pollutants may be directly deposited onto the surface of a waterbody or may reach the waterbody indirectly through deposition onto the land surface and subsequent wash-off during rain events. Atmospheric deposition may be an acute problem in the Los Angeles Air Basin, since this region exhibits among the worst air quality in the nation (SCAQMD 2000). Emission inventories indicate significant quantities of toxic materials are regularly released into the atmosphere in this region (SCAQMD 2003), and the ultimate fate of many of these pollutants is unknown.

Recent studies have shown that atmospheric deposition represents a significant fraction of the total load to many contaminated waterbodies relative to other sources for a number of pollutants, including trace metals (Duce *et al.* 1991, Scudlark *et al.* 1994, Wu *et al.* 1994, Baker *et al.* 1997, Scudlark and Church 1997). However, studies of atmospheric deposition have been limited primarily to eastern areas of the country such as Chesapeake Bay and the Great Lakes region. While significant resources have been directed toward monitoring air quality on the west coast of the United States, this monitoring has focused on human health, assessing smog and its precursors (NO_x, SO_x, etc.) and fine aerosols. Larger particles (> 10 µm in diameter), which are less relevant to direct human health impacts, have not been studied as extensively. These large particles contribute substantially to dry deposition (Lin *et al.*

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1993, Lin *et al.* 1994, Paode *et al.* 1998, Zufall *et al.* 1998).

Moreover, despite stringent controls on point sources, many waterbodies still fail to meet water quality objectives for trace metals, increasing the need to focus on controlling non-point sources of these metals to impaired waterbodies (CSWRCB 2002). In the greater Los Angeles metropolitan area, which is home to a population of 9 million, billions of dollars are spent annually upgrading, operating, and maintaining publicly owned treatment works (POTWs) that have historically contributed the highest amounts of trace metals to impaired waterbodies in the region (Dojiri *et al.* 2003). While the Los Angeles region has seen an 80% to 99% reduction in trace metal emissions (Schiff *et al.* 2001), more than three dozen of its waterbodies are still on the State's list of impaired waterbodies. As a result, urban non-point sources are now beginning to receive attention from environmental managers, particularly as state and federal water agencies impose regulatory mechanisms such as total maximum daily loads (TMDLs).

Virtually no research has been published on dry deposition of trace metals to coastal watersheds in southern California. The most recent study by Lu *et al.* (2003) estimated the deposition of trace metals to Santa Monica Bay and its watershed based on an airshed fate and transport model. The authors concluded that atmospheric deposition was a significant source of trace metal contamination to the bay This source far exceeded annual mass contributions from traditional point sources such as industrial facilities or natural gas-powered electrical generating stations, and rivaled emissions from POTWs. Furthermore, Lu *et al.* (2003) described a differential deposition pattern whereby most of the trace metals deposit on the watershed rather than directly onto the bay's water surface This accounts for the large number of water quality impairments for trace metals in freshwater segments of coastal watersheds of Santa Monica Bay and four other coastal river systems in the Los Angeles Air Basin.

The goal of this study was to provide empirical data on atmospheric concentrations of trace metals on coarse (> 6 µm) particles and to estimate the mass loading of these particles and associated trace metals due to dry atmospheric deposition in coastal watersheds of the Los Angeles Air Basin. Ultimately, the purpose of this study was to understand the importance of atmospheric deposition as a source of trace metals to contaminated waterbodies. Four subsidiary questions were asked to gain an understanding of the processes associated with dry deposition of trace metals in urban areas including: (1) Do atmospheric concentrations and associated dry deposition vary spatially both within and between coastal watersheds? (2) Do atmospheric concentrations and associated dry deposition vary temporally with season or other climatic factors? (3) How do estimates of direct dry atmospheric deposition to the surface of inland waterbodies compare to loadings of direct discharges to river systems from point sources? and (4) How does the trace metal loading from indirect dry deposition to the watershed compare to estimates of trace metal loading from wet-weather runoff?

Methods

General approach

Measurements of trace metal air concentrations on four coarse particle size fractions (>6 µm in diameter) were made at seven sampling sites in the Los Angeles coastal air basin (Table 1). Each site was sampled once in each of four seasons, corresponding approximately to the following schedule: summer (August-September); fall (November-December); winter (January-March); and spring (April-June). All samples were collected for 24 h during periods with no precipitation from August 2002 through June 2003. Estimates of deposition flux were based on the measured atmospheric concentrations and theoretical deposition velocities as a factor of local meteorological conditions recorded at the time of sampling. The measured atmospheric concentrations and estimated dry deposition fluxes were compared among sites and among seasons, and then correlated to meteorological factors. Finally, the direct trace metal loading to the waterbody surface, as well as the indirect loading to the land surface within a watershed estimated from our empirical measurements, were compared to loading estimates from point sources and stormwater runoff to assess the relative magnitude of dry deposition as a potentially important non-point source of trace metals to waterbodies in the coastal Los Angeles Air Basin.

Sampling sites

Sampling took place at six urban sites, each located near waterbodies with documented water quality impairments (Figure 1). These included three sites in the Los Angeles River watershed (LA1, LA2, LA3), one in the Dominguez Channel watershed

Table 1. Description of sites, sampling schedule and meteorological parameters.

Watershed	Site Description	Sample Date	Season	Days since rain	24-Hour Mean Temperature (C)	24-Hour Mean Wind Speed (m/s)	24-Hour Mean Relative Humidity
Los Angeles River	North Long Beach SCAQMD station (LA1)	1-Aug-02	Summer	60	20	1.6	77%
		21-Nov-02	Fall	13	21	0.66	40%
		26-Feb-03	Winter	1	14	3.1	68%
		21-May-03	Spring	18	18	1.4	80%
	North Main SCAQMD station (LA2)	28-Aug-02	Summer	60	21	1.7	67%
		10-Dec-02	Fall	13	14	1.9	68%
		5-Mar-03	Winter	6	14	2.1	67%
		11-Jun-03	Spring	39	17	2.0	77%
	Tillman Water Reclamation Plant (LA3)	11-Sep-02	Summer	60	24	1.0	53%
		26-Nov-02	Fall	17	19	2.8	13%
		17-Feb-03	Winter	5	14	0.61	66%
		7-May-03	Spring	4	15	1.9	70%
Ballona Creek	Wilshire Police Station (BC)	18-Sep-02	Summer	60	20	1.0	73%
		11-Dec-02	Fall	12	14	0.89	59%
		5-Feb-03	Winter	38	14	1.3	32%
		30-Apr-03	Spring	16	15	1.6	68%
Dominguez Channel	Cal State University Dominguez Hills (DC)	24-Sep-02	Summer	60	20	1.8	61%
		18-Dec-02	Fall	1	11	1.0	63%
		12-Mar-03	Winter	8	17	0.56	81%
		28-May-03	Spring	25	21	0.50	73%
Santa Ana River	Orange County Public Facilities and Resources Department (SA)	3-Oct-02	Summer	60	18	0.88	51%
		5-Dec-03	Fall	7	14	0.74	77%
		29-Jan-03	Winter	30	15	1.0	77%
		14-May-03	Spring	11	16	1.6	73%
Malibu Creek	Malibu Lagoon State Beach (MA)	24-Mar-03	Winter	8	15	2.0	84%
		23-Jun-03	Spring	50	16	2.0	77%

(DC), one in the Ballona Creek watershed (BC), and one in the lower Santa Ana River watershed (SA). Two sites, LA1 and LA2, were located at existing air monitoring stations operated by the South Coast Air Quality Management District (SCAQMD). Both BC and SA were located on rooftops, while LA3 was located within the grounds of a water reclamation facility, and DC was located on the grounds of a university. We also sampled at one non-urban coastal site at Malibu Lagoon State Beach within the Malibu Creek watershed (MA).

Specific site selection criteria for all sites incorporated the recommendations of the National Atmospheric Deposition Program (NADP 2000). These criteria included: (1) areas generally representative of the region, with minimal impact of local

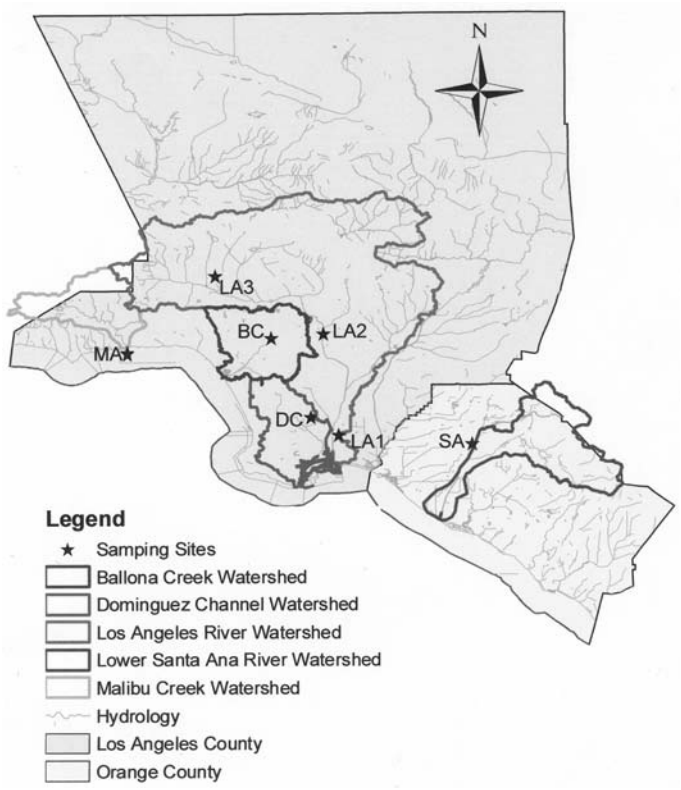

Figure 1. Sampling sites in the coastal Los Angeles air basin.

point or area sources; (2) areas a minimum distance of 100 meters from major line sources; and (3) all objects or structures located a distance of at least twice their height from the sampling equipment. These recommendations were followed to the extent possible in heavily populated urban areas. Site selection constraints included safety of field personnel and equipment and logistical requirements (access to the site, sufficient space for personnel and equipment, and availability of a power source).

Instrumentation

Atmospheric concentrations and coarse particle size distributions of trace metals were measured using a Noll Rotary Impactor (NRI), which consisted of a multi-stage rotary impactor that operated by simultaneously rotating four rectangular collector stages of different widths through the air. This instrument has been used successfully to measure air concentrations on coarse particle size fractions in other studies and is described elsewhere (Noll and Fang 1986). The instrument was operated at 320 rpm, producing cut diameters of 6, 11, 20, and 29 µm for the four collector stages. Mylar® strips, sized according to the desired cut point, were coated with a thin layer of Apezion L grease and mounted onto each of the four collector stages.

Meteorological data were also measured during each sampling period, including wind speed and direction, temperature, relative humidity, and barometric pressure, using a portable meteorological station (PortLog, Rain Wise, Inc., Bar Harbor, ME). The 24-h means were used to characterize meteorological conditions during each sampling event.

Sample preparation

Prior to sampling, Mylar® strips were cut to the desired size and cleaned by immersing in methanol, hexane, and 10% nitric acid for 5 min each. After cleaning, the Mylar® was rinsed with distilled water and allowed to air dry. Mylar® strips were coated with a thin layer of grease and mounted on the NRI stages 1 d prior to sampling. The NRI stages were stored in airtight containers for transport to the field. After sampling, the Mylar® strips were removed from the NRI stages in the field using clean, Teflon-coated forceps, and each strip stored in a clean petri dish prior to analysis.

Chemical analysis

Mylar® strips were placed into clean 15 mL plastic centrifuge tubes. Ten mL of 5% Optima Grade nitric acid was added to the tubes and capped tightly. The samples were then heated to 65ºC under sonication for a minimum of 24 h. The digested samples were transferred to a second centrifuge tube and analyzed for metals per EPA Method 200.8 using inductively coupled plasma-mass spectroscopy (ICP-MS).

Target metals included chromium, copper, lead, nickel, and zinc (Table 2). Method detection limits and the minimum detectable air concentrations for these target metals based on the typical air volumes sampled during this study are given in Table 2. Laboratory blanks were analyzed with each batch of 15 or less samples. All laboratory blanks were not detectable. In addition to samples, field blanks (greased Mylar® strips) were prepared and taken to the sampling sites and analyzed along with the samples, including duplicate blank Mylar® strips for each stage of the NRI. All field blanks contained levels of metals above the detection limits, so all samples were corrected for levels measured in their respective field blank.

Table 2. Target trace metals and method detection limits (MDL).

Trace Metal	MDL (ng)	Minimum Detectable Air Concentration (ng/m^3)
Chromium	1	0.009
Copper	1	0.009
Lead	0.5	0.005
Nickel	1	0.009
Zinc	1	0.009

Data analysis

Data analysis for atmospheric concentrations and dry deposition fluxes proceeded through three steps: (1) spatial comparisons among sites; (2) temporal comparisons among seasons and meteorological variables; and (3) watershed loading estimates. While atmospheric concentrations of trace metals were measured directly, deposition fluxes of trace metals were estimated from the air concentrations. Dry deposition fluxes were calculated for each coarse particle size fraction by multiplying the air concentration for a given particle size fraction by the deposition velocity for that particle size fraction estimated from theoretical calculations (Seinfeld and Pandis 1998) and neutral atmospheric stability. The fluxes for each of the four size fractions were then summed to determine the total flux during a sampling event. Meteorological data (wind speed, relative humidity, and temperature) measured during each sampling event were used as inputs in the deposition velocity calculations. Mean deposition velocities estimated for the four particle sizes measured during this study are presented in Table 3. More details on the methods used to calculate the deposition velocities can be found elsewhere (Lu *et al.* 2003).

The spatial characterization focused initially on comparing the mean atmospheric concentrations and estimated dry deposition fluxes among sites. Differences between sites were determined using analysis of variance (ANOVA) (Rao 1998). In addition, sites were stratified into urban (LA1, LA2, LA3, BC, DC, and SA) and non-urban (MA) sites. Significant differences between urban and non-urban sites were examined using a T-test (Rao 1998).

The temporal characterization initially focused on the mean atmospheric concentrations and estimated dry deposition fluxes between seasons. Differences between seasons were determined using ANOVA (Rao 1998). In an attempt to explain differences between sampling events, atmospheric concentrations were correlated with several meteorological variables including mean daily wind speed, maximum sustained wind speed, mean daily temperature, mean daily relative humidity and antecedent rainfall. For antecedent rainfall, sampling events were classified as less than or greater than 5 d since measurable precipitation. Significant differences in atmospheric concentrations and estimated dry deposition fluxes between rainfall strata were tested using a T-test.

Watershed loadings were examined in three different ways. First, total annual dry deposition, including both direct loading to the waterbody surface and indirect loading to the watershed, was estimated for each of the five watersheds by taking the product of the mean deposition flux from all sample events within a watershed, the number of days without rainfall (approximately 332 d per year), and the area of the watershed. To understand the relative magnitude of these watershed loadings the annual estimated indirect dry deposition loading in the Los Angeles River, Ballona Creek and Dominguez Channel watersheds were compared to loading estimates from wet-weather runoff in the same watershed. Wet-weather runoff to these waterbodies was obtained from a calibrated and validated watershed runoff model (Ackerman and Schiff 2003) for the same year as our study. In addition, direct dry deposition to the Los Angeles River was compared to the direct discharges to the river from POTWs. The POTW input data were generated from a special study of these inputs in 2000 (Ackerman *et al.* 2003).

Table 3. Calculated mean deposition velocities for four coarse particle size fractions.

Particle Size Fraction	N	Deposition Velocity (cm/sec)
6-11 µm	26	0.44 ± 0.01
11-20 µm	26	1.4 ± 0.01
20-29 µm	26	3.4 ± 0.03
29-60 µm	26	12 ± 0.1

Results

Meteorological data

The range of measured meteorological parameters at each sampling event varied by parameter type (Table 1). Mean wind speeds ranged from 0.5 m/s to 3 m/s, mean temperatures ranged from 11 C to 24 C, and mean relative humidity ranged from 13% to 81%. These relatively small ranges for mean wind speed and mean temperature, both of which typically have large diurnal variations, were in part due to the use of 24-h averages (corresponding to the 24-h integrated air concentration measurements). The number of days since the previous rainfall ranged from 1 d to 38 d in the winter, to more than 60 d in the summer, depending on the site. Four sample events occurred within 5 d of recorded rainfall at three different sites; two site-events were in winter, one site-event was in fall, and the last was in spring.

Air concentrations and deposition fluxes among sites

Annual mean air concentrations were within a factor of two to three among all of the urban sites, depending upon the trace metal of interest (Table 4). There were no significant differences between urban sites for air concentrations of chromium and lead, while significant differences were observed for copper ($p=0.02$), nickel ($p=0.04$), and zinc ($p=0.03$). Post hoc testing indicated that LA3 was different from the other urban sites for these three metals. This difference was attributable to a single springtime sampling event at this site that biased the annual mean. If this single event were removed from the data for this site, then LA3 would have been similar to all other sites except for copper ($p=0.05$).

Annual mean dry deposition fluxes of trace metals were within a factor of two for all urban sites exception for lead and zinc, which were within a factor of four among all urban sites (Table 4). Significant differences in mean annual fluxes between sites were found for chromium ($p=0.04$), copper ($p<0.01$), lead ($p<0.01$), and zinc ($p=0.01$). Post hoc testing indicated that, similar to air concentrations, fluxes at LA3 were significantly lower than all other sites for copper, lead, and zinc. This resulted from the same single springtime sampling event at this site. In addition, post hoc testing indicated that DC and SA had significantly higher fluxes of chromium and zinc, respectively, than all other sites. Similar to LA3, these differences were attributable to a single sampling event for each metal in winter (SA) and spring (DC).

Strikingly different air concentrations and fluxes were found between non-urban and urban sites (Table 4). Mean annual air concentrations were between 3-fold and 9-fold greater at urban sites than at the non-urban site, depending upon the trace metal. Mean annual flux estimates were between 5-fold and 12-fold greater at urban sites compared to the non-urban site, depending upon the trace metal. Significant differences between air concentrations at urban and non-urban sites were found for all metals ($p<0.05$) except nickel. Differences in fluxes between urban and non-urban sites were also signifi-

Table 4. Mean trace metal air concentrations and dry deposition fluxes (± standard deviation) measured at seven sites in the Los Angeles coastal region[1].

Air Concentration (ng/m^3)	Urban Sites						All Urban Sites	Non-Urban Site (MA)
	LA1	LA2	LA3	BC	DC	SA		
Chromium	1.6 ± 0.6	1.5 ± 0.7	1.1 ± 0.6	1.6 ± 0.1	2.4 ± 1.5	1.8 ± 0.4	1.7 ± 0.8	0.41 ± 0.03
Copper	7.8 ± 3.7	11 ± 4	5.2 ± 2.7	13 ± 3	7.5 ± 0.3	12 ± 2	9.3 ± 3.8	2.9 ± 1.0
Lead	4.0 ± 1.1	7.4 ± 3.3	2.2 ± 2.3	5.7 ± 2.1	4.7 ± 3.1	3.5 ± 1.3	4.8 ± 2.5	0.62 ± 0.13
Nickel	1.9 ± 0.8	1.9 ± 0.5	1.1 ± 0.5	1.9 ± 0.6	2.6 ± 0.8	2.8 ± 0.9	2.0 ± 0.8	0.84 ± 0.01
Zinc	38 ± 10	40 ± 18	19 ± 14	35 ± 7	29 ± 9	68 ± 35	38 ± 22	4.5 ± 0.5
Flux ($\mu g/m^2/day$)								
Chromium	4.3 ± 1.3	5.2 ± 2.5	3.2 ± 2.0	5.0 ± 1.1	9.1 ± 4.3	4.8 ± 1.2	5.3 ± 2.8	1.1 ± 0.1
Copper	22 ± 7	34 ± 13	11 ± 5	31 ± 8	21 ± 3	23 ± 3	24 ± 10	3.7 ± 0.4
Lead	13 ± 4	29 ± 14	8.3 ± 9.1	17 ± 5	16 ± 11	9.9 ± 2.5	16 ± 10	1.4 ± 0.01
Nickel	5.0 ± 1.8	6.8 ± 4.0	3.8 ± 2.7	5.2 ± 1.1	8.8 ± 3.5	5.6 ± 1.2	5.9 ± 2.8	1.3 ± 0.4
Zinc	116 ± 31	151 ± 61	69 ± 52	119 ± 9	91 ± 34	228 ± 102	129 ± 72	15 ± 1

[1]Detection Limit was used for non detects when calculating statistics

cant for chromium (p=0.05), copper (p=0.01), nickel (p=0.04), and zinc (p=0.04), but not for lead.

Effect of seasonal trends and meteorological variables

Mean air concentrations and estimated dry deposition fluxes were similar among seasons (ANOVA p >0.05). The range in air concentrations differed by less than a factor of two, on average, among seasons for all of the trace metals examined (Table 5). The range in dry deposition fluxes also differed by less than a factor of two, on average, among seasons for all of the trace metals examined (Table 5). There were no significant correlations between air concentrations and mean wind speed, temperature, or relative humidity, with the exception of nickel, which was significantly correlated with mean wind speed (r = -0.5, p=0.01). Other metrics, such as maximum sustained wind speeds or temperatures, were also not significantly correlated with either air concentrations or fluxes for any of the metals.

Antecedent rainfall appeared to have a larger effect on air concentrations than seasonality (Figure 2A). The lowest air concentrations were consistently observed within 5 d of a rain event compared to air concentrations measured more than five d after rainfall, regardless of season. For example, concentrations of lead averaged 1.5 ng/m^3 within 5 d of rainfall, but increased to 5.2 ng/m^3 when there was more than five d between sampling and rainfall. Significant differences in mean air concentrations stratified by antecedent rainfall also were found for copper (p<0.01), lead (p=0.04), nickel (p<0.01), and zinc (p=0.01), but not for chromium.

Estimated dry deposition fluxes were also reduced within 5 d of rainfall (Figure 2B). For example, the estimated dry deposition of lead averaged 5.4 µg/m^2/day immediately following rainfall, but increased to an average 17 µg/m^2/day when samples were collected more than 5 d after measured rainfall. Similar to air concentrations, the differences based on stratified antecedent rainfall were significant for all trace metals (p<0.05) except chromium.

Watershed loading estimates

The Los Angeles River watershed had the highest annual loadings for all metals (Table 6). Estimated annual watershed loading in the Los Angeles River watershed was between a factor of two (for zinc) and eight (for lead) greater than the other urban watersheds. This is mostly a result of the Los Angeles River's large watershed area, which was an order of magnitude greater than Ballona Creek, Dominguez Channel, or lower Santa Ana River watersheds. In contrast, the Malibu Creek watershed had the lowest annual loadings (Table 6). Despite its comparable watershed area relative to Ballona Creek, Dominguez Channel, or lower Santa Ana River watersheds, the non-urbanized Malibu Creek watershed experienced roughly an order of magnitude lower trace metal loadings than its urbanized counterparts.

Table 5. Mean trace metal air concentrations and dry deposition fluxes (± standard deviation) at urban sites in the Los Angeles coastal region by season1.

	Season			
	Summer	Fall	Winter	Spring
Mean Temperature	20.8 ± 1.9	15.7 ± 3.7	14.5 ± 1.2	17.1 ± 2.5
Air Concentration (ng/m^3)				
Chromium	1.5 ± 0.2	1.8 ± 0.3	1.4 ± 0.5	2.0 ± 1.5
Copper	8.4 ± 2.7	11 ± 4	9.1 ± 4.9	8.1 ± 3.6
Lead	5.1 ± 2.9	5.5 ± 2.9	4.2 ± 1.3	4.2 ± 3.1
Nickel	2.0 ± 0.3	2.0 ± 0.6	2.0 ± 1.3	2.1 ± 1.0
Zinc	40 ± 5	44 ± 22	40 ± 38	29 ± 12
Flux (µg/m^2/day)				
Chromium	4.7 ± 1.8	6.2 ± 2.0	4.1 ± 1.1	6.0 ± 4.9
Copper	23 ± 11	30 ± 12	21 ± 8	21 ± 9
Lead	18 ± 13	19 ± 12	11 ± 5	15 ± 10
Nickel	7.4 ± 3.4	6.2 ± 3.2	4.8 ± 2.3	5.2 ± 2.4
Zinc	141 ± 28	144 ± 72	128 ± 121	103 ± 46

[1]Detection Limit was used for non detects when calculating statistics.

Deposition estimates vs. stormwater loadings

Trace metal loading estimated from dry atmospheric deposition to the land surface of the Los Angeles River watershed (indirect deposition) was greater than the estimated trace metal loading from urban stormwater runoff (Table 6, Figure 3). Loading from runoff comprised approximately 20% of the dry deposition loading for chromium, copper, nickel and zinc, and 10% of the deposition loading for lead. Trace metal loading from dry deposi-

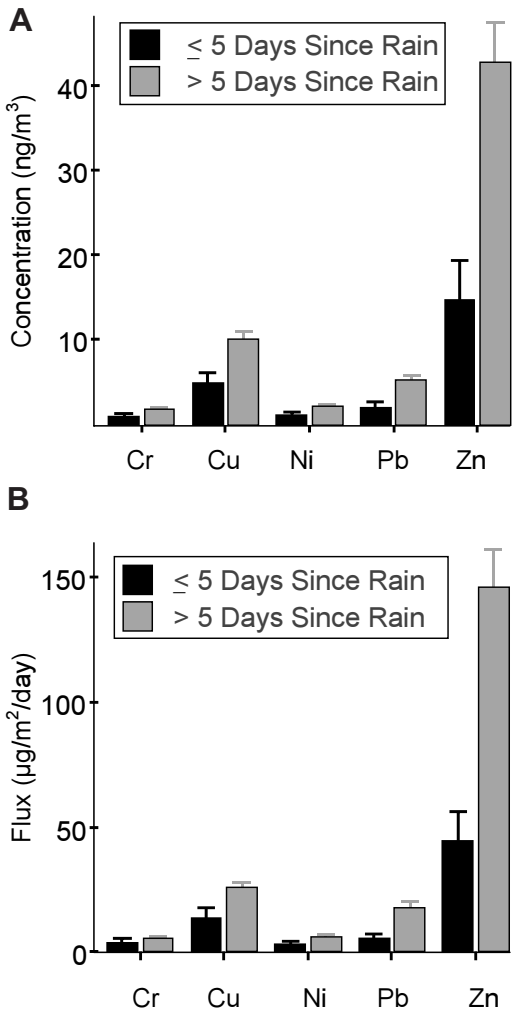

Figure 2. Mean atmospheric concentrations (A) and fluxes (B) of trace metals on coarse particles (>6 µm) at urban sites with and without rainfall in the previous five days. Error bars represent the standard error of the mean.

tion to the land surface of the Ballona Creek and Dominguez Channel watersheds, which are both highly urbanized, was also greater than estimated stormwater loadings in these watersheds (Table 6). In the Ballona Creek watershed, loading from runoff comprised only 10-20% of the dry deposition loading form copper and lead, and 30-40% for chromium, nickel and zinc. In the Dominguez Channel watershed, runoff comprised 10-20% of the chromium, nickel and lead, and 30-40% of the copper and zinc loadings from dry deposition to the watershed surface.

In stark contrast, dry deposition of copper, lead, nickel, and zinc to the water surface of the Los Angeles River (direct deposition) was negligible compared with the contribution of trace metals from POTW discharges (Figure 3). The POTW discharges contributed one (lead, nickel), two (zinc), and three (copper) orders of magnitude more trace metals than direct dry deposition to the water surface. No data were available on POTW discharges of chromium.

Discussion

Urban watersheds had greater air concentrations of trace metals and, subsequently, greater estimated dry deposition than the non-urban watershed in the coastal Los Angeles Air Basin during this study. This is not surprising, since these urban areas have a greater proportion of air emissions from mobile, point, and area sources (Lu *et al.* 2003). In the case of our study sites, the non-urban Malibu Creek watershed is upwind of the Los Angeles metropolitan area, which further removes it from an urban influence. An unexpected element of our study, however, was the similarity of mean air concentrations among the remaining six urban sites despite being in uniquely different watersheds separated by tens of kilometers. The urban areas of coastal Los Angeles accounted for in this study are extensive, covering an area of no less than 3000 km^2. Air concentrations were not steady state, however, since air concentrations varied within a site during different sampling periods. Increased sample size may have documented greater differences among urban sites, and may illustrate one limitation of this study. Regardless, we expect differences between urban sites would not have been as extreme as between any of the urban sites and the non-urban site.

It was apparent from our data that rain has a large effect on urban air concentrations. Rainfall scavenging of particles has been documented in other studies (Hicks et al. 1984, Scudlark *et al.* 1994, Scudlark and Church 1997), but differences in air concentrations of trace metals on coarse particles before and after rainfall in urban air have not been previously reported. The effect was so significant that atmospheric concentrations at urban sites following rainfall resembled atmospheric concentrations at the non-urban site during other times of the year. The effect of rainfall was more significant than any seasonal or meteorological components examined. The lack of seasonality may be a result of the temperate climate experienced in southern California; daily mean temperature, wind speed, and

Table 6. Mean annual loadings of trace metals to watersheds in the Los Angeles coastal region.[1]

	Chromium	Copper	Nickel	Lead	Zinc
Atmospheric Deposition (MT/Year)					
Los Angeles River	3.0 (2.1-3.9)	16 (10-22)	3.7 (2.4-5.1)	12 (6-18)	80 (54-110)
Ballona Creek	0.56 (0.37-0.75)	3.5 (2.0-5.0)	0.59 (0.39-0.79)	2.0 (1.1-2.8)	13 (12-15)
Dominguez Channel	0.9 (0.24-1.6)	2.1 (1.6-2.6)	0.9 (0.33-1.5)	1.6 (-0.1-3.3)	9.4 (3.8-15)
Lower Santa Ana River	0.78 (0.47-1.1)	3.8 (3.0-4.6)	0.9 (0.6-1.2)	1.6 (1.0-2.3)	37 (11-64)
Malibu Creek	0.10 (0.09-0.1)	0.35 (0.32-0.38)	0.13 (0.10-0.15)	0.14 (<DL-0.14)	1.4 (1.3-1.5)
Stormwater Runoff[2]					
Los Angeles River	0.68	3.11	0.86	1.04	17.30
Ballona Creek	0.17	0.72	0.21	0.23	3.72
Dominguez Channel	0.13	0.65	0.17	0.23	4.00
Watershed Transmission Efficiency[3]					
Los Angeles River	23%	19%	23%	9%	22%
Ballona Creek	30%	21%	35%	11%	29%
Dominguez Channel	13%	31%	18%	14%	43%

[1]95% confidence intervals shown in parentheses, expect for Malibu Creek, which has the range.
[2]From watershed runoff model (Ackerman and Schiff 2003).
[3]Calculated as the ratio of stormwater runoff to indirect atmospheric deposition.

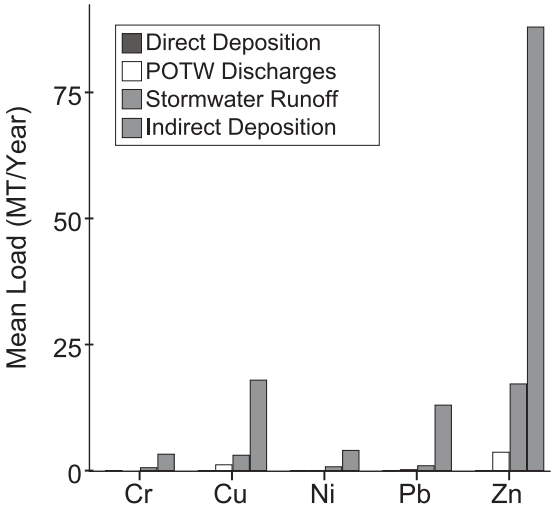

Figure 3. Comparison between mean loadings of trace metals to the Los Angeles River from direct deposition to the water surface, POTW discharges, stormwater runoff, and dry atmospheric deposition to the land surface of the watershed (indirect deposition).

humidity typically do not vary tremendously between seasons.

With few exceptions, atmospheric concentrations of trace metals on coarse particles measured in coastal Los Angeles during this study were similar to those measured in previous studies in Los Angeles and Chicago using the same sampling methodology (Table 7). These results indicate urban air is consistently of poor quality and should be of concern to environmental as well as public health managers. The similarities in atmospheric concentrations of trace metals from the Los Angeles Air Basin measured in 1987 (Claremont, California) and those observed 15 years later during this study demonstrate that the issue of trace metal contamination in urban air, and subsequent dry deposition to urban watersheds, is not improving over time. The only exception was for lead, which had considerably lower air concentrations in recent studies, likely because of the elimination of lead from gasoline in the late 1980s.

Indirect dry deposition to the land surface within a watershed has the potential to be a large influence on the quality of stormwater runoff in urban areas. Particles that deposit on urban surfaces during dry weather can be easily mobilized by surface flows during storms because rainfall in impervious urban areas is more likely to run off than in non-urban areas. This may be especially significant in the Los Angeles area, since the impervious area is so extensive. In the present study, the estimated annual trace metal loads from indirect dry deposition to the land surface of the Los Angeles River, Ballona Creek and Dominguez Channel watersheds were far larger than the estimated annual trace metal loads found in stormwater emanating from the same watershed, similar to findings of other studies (Hamilton *et al.* 1987, Riedel *et al.* 2000). The necessary watershed transmission efficiencies of 10% to 20% we estimat-

Table 7. Comparison of measured air concentrations of trace metals on large particles.

Air Concentration (ng/m^3)	Year	Chromium	Copper	Lead	Nickel	Zinc
Los Angeles, CA (this study)	2003	1.7	9.3	4.8	2.0	38
[1]Claremont, CA (Los Angeles Basin)	1987		9.4	26	3.7	16
[1]Chicago	1988		8.5	11		27

[1]Noll *et al.* 1990

ed were similar to those estimated by Riedel *et al.* (2000) in their discussion of sources of trace metals in the Patuxent River, which drains the highly urbanized area between Washington D.C. and Baltimore, Maryland.

Other recent studies have investigated specific sources of trace metal contamination to urban stormwater runoff, including the contribution from vehicles, building materials, and atmospheric deposition. Van Metre and Mahler (2003) estimated atmospheric deposition contributes 6%, 10%, 15%, 28% and 35% of chromium, nickel, copper, lead, and zinc concentrations, respectively, to runoff from rooftops during the first flush. Davis *et al.* (2001) concluded dry deposition accounts for 3%, 10%, and 14% of the total load to urban residential stormwater runoff for zinc, lead, and copper, respectively. However, as the estimates of dry deposition rates used by Davis *et al.* (2001) were an order of magnitude lower than those measured in the present study, these percentages likely underestimate the contribution from dry deposition in semi-arid regions such as Los Angeles. Few other studies have investigated the contribution from dry atmospheric deposition on the watershed and subsequent run-off to waterbody loadings of trace metals. Clearly, the connection between dry deposition of trace metals in urban areas and urban stormwater runoff requires further study.

In contrast to indirect dry deposition, it appears that direct dry deposition to the surface of the water has little potential influence on overall water quality in the coastal river systems of Los Angeles. For the Los Angeles River, this is a reflection of two factors. First, this river system averages only a few meters in width and the resulting small water surface area functionally limits the quantity of material that can deposit directly. Second, approximately 75% of the flow in this system during dry weather is a result of POTW discharges (Ackerman *et al.* 2003), and this contribution overwhelms most other direct sources to the river during dry weather.

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