

ATMOSPHERIC DRY DEPOSITION OF TRACE METALS IN THE COASTAL REGION OF LOS ANGELES, CALIFORNIA, USA

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Abstract—Emissions of trace metals to the atmosphere and subsequent deposition, either directly to a waterbody surface or indirectly to the watershed as washoff during rainfall, represents a potential source of contamination to surface waters near urban centers. The present study provides measurements of atmospheric concentrations of particle-bound trace metals, and it estimates the dry deposition mass loading of trace metals in coastal watersheds in the Los Angeles, California, USA, air basin. Coarse-particle atmospheric concentrations of metals were measured seasonally using a Noll Rotary Impactor at six urban sites and one nonurban site. Dry deposition fluxes were calculated by summing the product of air concentration and the theoretical deposition velocity for each particle size fraction. 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 $\mu\text{g}/\text{m}^2/\text{d}$ for chromium, copper, nickel, lead, and zinc, respectively. Mean concentrations and fluxes were significantly higher at urban sites compared with the nonurban site, although differences between urban and nonurban sites were reduced when sampling took place within 5 d after rainfall. Dry deposition to watershed land surfaces was substantial, representing a potentially large source of trace metals based on comparisons with load estimates from stormwater runoff.

Keywords—Coarse particles Urban Trace metals

INTRODUCTION

Dry deposition represents a major removal pathway for many pollutants from the atmosphere [1], and it is especially important in arid and semiarid regions where removal by wet deposition (i.e., rainfall scavenging) is greatly diminished because of limited precipitation. Atmospheric pollutants may be deposited directly onto the surface of a waterbody or may reach the waterbody indirectly through deposition onto the land surface and subsequent washoff during rain events. Atmospheric deposition may be an acute problem in the Los Angeles (CA, USA) air basin, because the air quality in this region ranks among the worst in the nation. Emission inventories indicate that significant quantities of toxic materials are regularly released into the atmosphere in this region (<http://www.aqmd.gov/aqmp/AQMD03AQMP.htm>) [2], and the ultimate fate of the heavy metals in particular 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 [3–7]. These studies have been limited primarily to eastern areas of the country, such as Chesapeake Bay and the Great Lakes region. Whereas 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 (volatile organic compounds, NO_x , SO_x , etc.) and fine particles. Large particles (diameter, $>10 \mu\text{m}$), which are less relevant to direct human health impacts, have not been studied as extensively, even though large particles contribute substantially to dry deposition [8–11].

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 nonpoint sources of these metals to impaired waterbodies (http://www.swrcb.ca.gov/tmdl/303d_lists.html) [12]. In the greater Los Angeles metropolitan area, which is home to a population of more than 10 million people, millions of dollars are spent annually upgrading, operating, and maintaining publicly owned treatment works (POTWs) that historically have contributed the highest amounts of trace metals to impaired waterbodies in the region [13]. The Los Angeles region has seen an 80 to 99% reduction in trace-metal emissions [14], but more than three dozen of its waterbodies are still on the state's list of impaired waterbodies. As a result, urban nonpoint sources are beginning to receive attention from environmental managers, particularly as state and federal water agencies impose regulatory mechanisms, such as total maximum daily loads.

Virtually no research has been published regarding dry deposition of trace metals to coastal watersheds in southern California. The most recent study by Lu et al. [15] estimated the deposition of trace metals to Santa Monica Bay and its watershed based on an airshed fate-and-transport model. Those 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 it rivaled emissions from POTWs. Furthermore, Lu et al. 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 may account for a 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.

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

Site	Sample date	Season	Days since rain	24-Hour mean		
				Temperature (°C)	Wind speed (m/s)	Relative humidity
LA1	1 Aug 2002	Summer	60	20	1.6	77
	21 Nov 2002	Fall	13	21	0.66	40
	26 Feb 2003	Winter	1	14	3.1	68
LA2	21 May 2003	Spring	18	18	1.4	80
	28 Aug 2002	Summer	60	21	1.7	67
	10 Dec 2002	Fall	13	14	1.9	68
LA3	5 Mar 2003	Winter	6	14	2.1	67
	11 Jun 2003	Spring	39	17	2.0	77
	11 Sep 2002	Summer	60	24	1.0	53
BC	26 Nov 2002	Fall	17	19	2.8	13
	17 Feb 2003	Winter	5	14	0.61	66
	7 May 2003	Spring	4	15	1.9	70
DC	18 Sep 2002	Summer	60	20	1.0	73
	11 Dec 2002	Fall	12	14	0.89	59
	5 Feb 2003	Winter	38	14	1.3	32
SA	30 Apr 2003	Spring	16	15	1.6	68
	24 Sep 2002	Summer	60	20	1.8	61
	18 Dec 2002	Fall	1	11	1.0	63
MA	12 Mar 2003	Winter	8	17	0.56	81
	28 May 2003	Spring	25	21	0.50	73
	3 Oct 2002	Summer	60	18	0.88	51
DC	5 Dec 2003	Fall	7	14	0.74	77
	29 Jan 2003	Winter	30	15	1.0	77
	14 May 2003	Spring	11	16	1.6	73
MA	24 Mar 2003	Winter	8	15	2.0	84
	23 Jun 2003	Spring	50	16	2.0	77

^a LA1, LA2, and LA3 = Los Angeles River (CA, USA); BC = Ballona Creek (CA, USA); DC = Dominguez Channel (CA, USA); SA = Santa Ana River (CA, USA); MA = Malibu Creek (CA, USA).

The goal of the present study was to provide empirical data regarding trace-metal atmospheric concentrations on large particles (diameter, $>6 \mu\text{m}$) and to estimate the mass loading of trace metals because of dry atmospheric deposition in coastal watersheds of the Los Angeles air basin. Ultimately, the purpose of the present study was to understand the importance of atmospheric deposition as a source of trace metals to contaminated waterbodies in this region. Four subsidiary questions also were asked to gain an understanding of the processes associated with dry deposition of trace metals in urban areas. First, do atmospheric concentrations and associated dry deposition vary spatially both within and between coastal watersheds? Second, do atmospheric concentrations and associated dry deposition vary temporally with season or other climatic factors? Third, how do estimates of direct dry atmospheric deposition to the surface of inland waterbodies compare with loadings of direct discharges to river systems from point sources? Fourth, how does the trace metal loading from dry deposition to the watershed compare with estimates of trace metal loading from wet-weather runoff?

MATERIALS AND METHODS

General approach

Measurements of trace-metal air concentrations on four coarse-particle size fractions (diameter, $>6 \mu\text{m}$) 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. Dry deposition fluxes were calculated using measured atmospheric concentrations and mod-

eled deposition velocities as a function of local meteorological conditions recorded at the time of sampling. Atmospheric concentrations and dry deposition fluxes were compared both among sites and among seasons and then correlated to meteorological factors. Finally, the trace-metal loading directly to the waterbody surface and the loading to the land surface of a watershed were compared to loading estimates from point sources and stormwater runoff to assess the relative magnitude of dry deposition as a potentially important nonpoint 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 (Fig. 1). These included three sites in the Los Angeles River watershed (LA1, LA2, and LA3), one in the Dominguez Channel watershed (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. Both BC and SA were located on rooftops, LA3 within the grounds of a water reclamation facility, and DC on the grounds of a university. We also sampled at one nonurban 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 (Champaign, IL, USA; <http://nadp.sws.uiuc.edu/lib/manuals/siteinst.pdf>) [16]. These criteria included the following: Areas generally representative of the region, with minimal impact of local point or area sources; areas a minimum distance of 100 m from major line sources; and all objects or structures



Fig. 1. Sampling sites in the coastal Los Angeles (CA, USA) air basin. LA1, LA2, and LA3 = Los Angeles River watershed sites; BC = Ballona Creek watershed site; DC = Dominguez Channel watershed site; SA = Santa Ana River watershed site; MA = Malibu Creek watershed site.

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 as well as 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; K. Noll, Chicago, IL, USA), which was designed to operate at high velocity and to collect particles directly from ambient air by impaction [17,18]. The NRI consists of a multistage rotary impactor that operates by simultaneously rotating four rectangular collector stages of different widths through the air. The instrument was operated at 320 rpm, producing cut diameters of 6, 11, 20, and 29 μm for the four collector stages. To prevent overloading, the smallest collector stage (stage A) was changed every 2 h during the day and every 4 h at night, whereas the next largest collector stage (stage B) was changed every 4 h during the day and every 8 h at night. The two largest collector stages (stages C and D) were not changed during the 24-h collection period. Mylar® strips, sized according to the desired cut point for each stage, were coated with a thin layer of Apiezon L grease (M&I Materials, Manchester, UK) and mounted onto each of the four collector stages. The NRI instrument has been used successfully to measure air concentrations in the upper range of the coarse-particle size distribution in other studies [9,18]. Metal concentrations were calculated for each NRI stage using the measured metal mass and the NRI rotation speed [17,19].

Meteorological data also were measured during each sampling period, including wind speed and direction, temperature, relative humidity, and barometric pressure, using a portable meteorological station (PortLog; Rain Wise, Bar Harbor, ME,

Table 2. Target trace metals and method detection limits

Trace metal	Method detection limit (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

USA). The 24-h means were used to characterize meteorological conditions during each sampling event.

Sample preparation

Before sampling, Mylar strips were cut to the desired size and cleaned by immersion 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 Apiezon L grease and mounted on the NRI stages 1 d before 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 was stored in a clean Petri dish before analysis.

Chemical analysis

Mylar strips were rinsed three successive times with 15 ml of *n*-hexane. The rinses were combined into a 50-ml centrifuge tube. The Mylar strips were then rinsed with 5% Optima-grade nitric acid, and the acid rinses were added to the combined hexane rinses. The hexane was evaporated in a 50°C water bath, and the remaining acidified sample was then heated to 65°C under sonication for a minimum of 24 h. The digested samples were transferred to a second centrifuge tube and analyzed for metals per U.S. Environmental Protection Agency Method 200.8 (<http://www.epa.gov/region09/qa/pdfs/200.8dqii1.pdf>) [20] using inductively coupled plasma–mass spectroscopy.

Target metals included chromium, copper, lead, nickel, and zinc. Method detection limits and minimum detectable air concentrations for these metals based on the typical air volumes sampled during the present study are given in Table 2. Laboratory blanks were analyzed with each batch of samples. All laboratory blanks had no detectable quantities of metals. 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 quantities of metals above the detection limits, so all samples were corrected for levels measured in their respective field blank.

Data analysis

Data analysis for atmospheric concentrations and dry deposition fluxes proceeded through the following three steps: Spatial comparisons among sites, temporal comparisons among seasons and meteorological variables, and watershed loading estimates. Dry deposition fluxes were calculated for each particle size fraction by multiplying the air concentration for a given particle size fraction by a modeled deposition velocity (Table 3) for that particle size fraction. The fluxes for each size fraction were then summed to estimate the total dry deposition flux during a sampling event. Meteorological data (wind speed, relative humidity, and temperature) measured during each sampling event were used as inputs to the model.

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

Particle size fraction	<i>n</i>	Deposition velocity (cm/s) ^a
6–11	26	0.44 ± 0.01
11–20	26	1.4 ± 0.01
20–29	26	3.4 ± 0.03
29–60	26	12 ± 0.1

^a Values are presented as the mean ± standard deviation.

More details regarding the model used to calculate the deposition velocities can be found elsewhere [21].

The spatial characterization focused on comparing atmospheric concentrations and dry deposition fluxes among sites using analysis of variance (ANOVA) [22]. In addition, sites were stratified into urban (LA1, LA2, LA3, BC, DC, and SA) and nonurban (MA) sites.

The temporal characterization focused on comparing the mean atmospheric concentrations and estimated dry deposition fluxes between seasons using ANOVA [22]. In an attempt to explain differences between sampling events, atmospheric concentrations and dry deposition fluxes 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 after measurable precipitation. Significant differences in concentrations/fluxes between rainfall strata were identified using a *t* test [22].

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 (~332 d for the 2002–2003 water-year in Los Angeles), and the area of the watershed. To understand the relative magnitude of these loadings, the annual dry deposition loadings 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 [23] for the same year as the present study. In addition, dry deposition directly to the surface of 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 [24].

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 to 3 m/s, mean temperatures from 1 to 24°C, and mean relative humidity 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 caused by 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 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 in fall, and the last 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 on the trace metal of interest (Table 4). No significant differences were found between urban sites for air concentrations of chromium and lead, whereas significant differences were observed for copper ($p = 0.02$), nickel ($p = 0.04$), and zinc ($p = 0.03$). Post hoc testing indicated that a single site, LA3, was responsible for the observed difference between urban sites for these three metals. This site had the lowest mean air concentrations for all five metals compared with the other urban sites. One explanation for this difference is that this site was located in a relatively suburban area of the San Fernando Valley and, compared with the other urban sites, was predominantly upwind of significant point and mobile sources.

Annual mean dry deposition fluxes of trace metals were within a factor of two for all urban sites except 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

Table 4. Mean trace metal air concentrations and dry deposition fluxes measured at seven sites in the Los Angeles coastal region (CA, USA)^a

	Urban sites ^b						All urban sites	Nonurban site (MA)
	LA1	LA2	LA3	BC	DC	SA		
Air concentration (ng/m ³)								
Chromium	1.6 ± 0.6	1.5 ± 0.7	1.1 ± 0.6	1.6 ± 0.1	2.4 ± 1	1.8 ± 0.4	1.7 ± 0.8	0.41 ± 0.03
Copper	7.8 ± 4	11 ± 4	5.2 ± 3	13 ± 3	7.5 ± 0.3	12 ± 2	9.3 ± 4	2.9 ± 1.0
Lead	4.0 ± 1.1	7.4 ± 3	2.2 ± 2	5.7 ± 2	4.7 ± 3	3.5 ± 1	4.8 ± 3	0.62 ± 0.1
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 ± 20	19 ± 10	35 ± 7	29 ± 9	68 ± 40	38 ± 20	4.5 ± 0.5
Flux (µg/m ² /d)								
Chromium	4.3 ± 1.3	5.2 ± 3	3.2 ± 2	5.0 ± 1.1	9.1 ± 4	4.8 ± 1.2	5.3 ± 3	1.1 ± 0.1
Copper	22 ± 7	34 ± 10	11 ± 5	31 ± 8	21 ± 3	23 ± 3	24 ± 10	3.7 ± 0.4
Lead	13 ± 4	29 ± 10	8.3 ± 9	17 ± 5	16 ± 10	9.9 ± 2	16 ± 10	1.4 ± 0.01
Nickel	5.0 ± 1.8	6.8 ± 4	3.8 ± 3	5.2 ± 1.1	8.8 ± 4	5.6 ± 1.2	5.9 ± 3	1.3 ± 0.4
Zinc	120 ± 30	150 ± 60	69 ± 50	120 ± 9	91 ± 30	230 ± 100	130 ± 70	15 ± 1

^a Detection limit was used for nondetects when calculating statistics. Values are presented as the mean ± standard deviation.

^b LA1, LA2, and LA3 = Los Angeles River; BC = Ballona Creek; DC = Dominguez Channel; SA = Santa Ana River; MA = Malibu Creek.

Table 5. Seasonal trace metal air concentrations and dry deposition fluxes at urban sites in the Los Angeles coastal region (CA, USA)^a

	Season			
	Summer	Fall	Winter	Spring
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 ± 3	11 ± 4	9.1 ± 5	8.1 ± 4
Lead	5.1 ± 3	5.5 ± 3	4.2 ± 1.3	4.2 ± 3
Nickel	2.0 ± 0.3	2.0 ± 0.6	2.0 ± 1.3	2.1 ± 1.0
Zinc	40 ± 5	44 ± 20	40 ± 40	29 ± 10
Flux (µg/m ² /d)				
Chromium	4.7 ± 1.8	6.2 ± 2	4.1 ± 1.1	6.0 ± 5
Copper	23 ± 10	30 ± 10	21 ± 8	21 ± 9
Lead	18 ± 10	19 ± 10	11 ± 5	15 ± 10
Nickel	7.4 ± 3	6.2 ± 3	4.8 ± 2	5.2 ± 2
Zinc	140 ± 30	140 ± 70	130 ± 120	100 ± 50

^a Detection limit was used for nondetects when calculating statistics. Values are presented as the mean ± standard error.

indicated that similar to air concentrations, this difference was caused primarily by a single site, LA3, which was located in a less urbanized area than the other sites and typically had lower fluxes than all the other sites.

Strikingly different air concentrations and fluxes were found between nonurban and urban sites (Table 4). Mean annual air concentrations were between three- and ninefold greater at urban sites than at the nonurban site, depending on the trace metal. Mean annual flux estimates were between 5- and 12-fold greater at urban sites compared to the nonurban site, depending on the trace metal.

Effect of seasonal trends and meteorological variables

Mean air concentrations and estimated dry deposition fluxes were similar among seasons (ANOVA, $p > 0.05$). On average, the range in air concentrations differed by less than a factor of two among seasons for all of the trace metals examined (Table 5), as expected, because the atmospheric emissions inventory in the Los Angeles air basin does not vary greatly by season. The range in dry deposition fluxes also differed by less than a factor of two, on average, among seasons for all the trace metals examined (Table 5). No significant correlations were found 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, also were 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 compared with that of seasonality (Fig. 2a). The lowest air concentrations were consistently observed within 5 d after a rain event compared to air concentrations measured more than 5 d after rainfall, regardless of season. For example, concentrations of lead averaged 1.5 ng/m³ within 5 d after rainfall but increased to 5.2 ng/m³ when more than 5 d separated 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 ($p = 0.01$). For chromium, although the lowest air concentrations were observed within 5 d after rainfall, the differences were not significant. The generally low atmospheric concentrations of chromium and the tight range

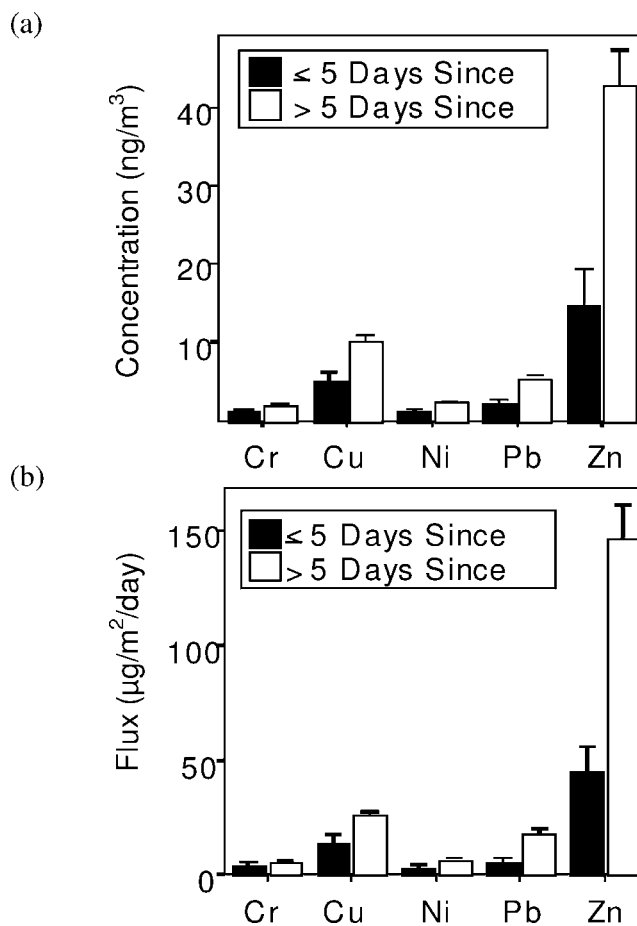


Fig. 2. Mean atmospheric concentrations (a) and fluxes (b) of trace metals on large particles (diameter, $>6 \mu\text{m}$) at urban sites in Los Angeles (CA, USA) with and without rainfall in the previous 5 d. Error bars represent the standard error of the mean.

we observed among sampling events may have limited our ability to detect significant differences because of the small number of samples.

Estimated dry deposition fluxes also were reduced within 5 d after rainfall (Fig. 2b). For example, the estimated dry deposition of lead averaged 5.4 µg/m²/d immediately following rainfall but increased to an average of 17 µg/m²/d 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, likely for the same reasons stated above regarding atmospheric concentrations.

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 that of the other urban watersheds. This mostly was a result of the Los Angeles River's large watershed area, which is an order of magnitude greater than the 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 the Ballona Creek, Dominguez Channel, or lower Santa Ana River watersheds, the nonurbanized Malibu Creek watershed

Table 6. Mean annual loadings of trace metals to watersheds in the Los Angeles coastal region (CA, USA)^a

	Chromium	Copper	Nickel	Lead	Zinc
Atmospheric deposition (metric tons/year)					
LA	3.0 (2.1–3.9)	16 (10–22)	3.7 (2.4–5.1)	12 (6–18)	80 (54–100)
BC	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)
DC	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)
SA	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)
MA	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 (metric tons/year) ^b					
LA	0.68	3.11	0.86	1.0	17
BC	0.17	0.72	0.21	0.23	3.7
DC	0.13	0.65	0.17	0.23	4.0
Watershed transmission efficiency (%) ^c					
LA	23	19	23	9	21
BC	30	21	35	11	28
DC	13	31	18	14	43

^a Values in parentheses represent the 95% confidence intervals expect for Malibu Creek, which represents the range. LA = Los Angeles River; BC = Ballona Creek; DC = Dominguez Channel; SA = Santa Ana River; MA = Malibu Creek.

^b From the watershed runoff model [21].

^c Stormwater/atmospheric deposition \times 100%.

experienced roughly an order of magnitude lower trace-metal loadings compared with its urbanized counterparts.

Deposition estimates versus stormwater loadings

Trace-metal loadings from dry atmospheric deposition to the land surface of the Los Angeles River, Ballona Creek, and Dominguez Channel watersheds were greater than the estimated trace metal loadings from urban stormwater runoff to these watersheds (Table 6). Loading from runoff in the Los Angeles River watershed comprised approximately 20% of the dry deposition loading for chromium, copper, nickel, and zinc and 10% of the loading for lead. In the Ballona Creek watershed, loading from runoff comprised only 10 to 20% of the dry deposition loading for copper and lead and 30 to 40% of the loading for chromium, nickel, and zinc. In the Dominguez Channel watershed, runoff comprised 10 to 20% of the chromium, nickel, and lead and 30 to 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 directly to the water surface of the Los Angeles River was negligible compared with the contribution from POTW discharges, as expected given the small surface area of the river (Table 7). The POTW discharges contributed one (lead and nickel), two (zinc), and three (copper) orders of magnitude more trace metals than direct dry deposition to the water surface. No data were available regarding POTW discharges of chromium.

Table 7. Mean annual loads (metric tons/year) of trace metals to the Los Angeles River (CA, USA)

	Trace metal (metric tons/year)				
	Chromium	Copper	Lead	Nickel	Zinc
Direct dry deposition ^a	0.001	0.003	0.002	0.001	0.01
POTW discharges ^b	N/A	2	0	1.2	10

^a Deposition to the surface of the waterbody.

^b POTW = publicly owned treatment works; Ackerman et al. [24].

DISCUSSION

Urban watersheds had greater air concentrations of trace metals and, subsequently, greater estimated dry deposition than the nonurban watershed in the coastal Los Angeles air basin during the present study. These results are not surprising, because these urban areas have a greater proportion of air emissions from mobile, point, and area sources [15]. In the case of our study sites, the nonurban Malibu Creek watershed is upwind of the Los Angeles metropolitan area, which further removes it from an urban influence. In addition, we observed similar mean air concentrations among the remaining six urban sites, as expected because of similar emission sources throughout Los Angeles. The urban areas of coastal Los Angeles accounted for in the present study are extensive, covering an area of no less than 3,000 km². Increased sample density may have documented greater differences among urban sites and may illustrate one limitation of the present study. Regardless, we expect that differences between urban sites would not have been as extreme as those between any of the urban sites and the nonurban site.

Furthermore, whereas little research has focused on dry deposition of trace metals in urban areas, our estimates were of the same order of magnitude as those reported in previous studies of Chicago (IL, USA) (Table 8). Moreover, dry deposition fluxes reported in the literature for nonurban areas typically were an order of magnitude lower than the fluxes reported for urban Los Angeles, similar to the differences observed between nonurban and urban sites in the present study (Table 8). These similarities were observed despite differences in the sampling methodologies used in the various studies and the wide geographic areas covered by the different studies.

In addition, it was apparent from our data that rain had a large effect on urban air concentrations and fluxes, as expected based on visibility data and other ambient air measurements [1]. Rainfall scavenging of particles has been documented in other studies [4,7,25], but to our knowledge, differences in air concentrations and fluxes of trace metals on coarse particles before and after rainfall in urban air have not been reported previously. The effect was so significant that atmospheric concentrations/fluxes at urban sites following rainfall resembled

Table 8. Comparison of estimates of dry deposition fluxes of trace metals

	Year	Flux ($\mu\text{g}/\text{m}^2/\text{d}$)				
		Chromium	Copper	Lead	Nickel	Zinc
Urban						
Los Angeles (CA, USA)	2002–2003	5.3	24	16	5.9	130
Chicago (IL, USA) ^a	1994		60	70		200
Chicago (IL, USA) ^b	1993–1995	5.7	63	38		120
Nonurban						
Malibu (CA, USA)	2003	1.1	3.7	1.4	1.3	15
South Haven (MI, USA) ^a	1994		7	4		4
Lake Superior (MI, USA) ^c	1993–1994	0.36	6.6	2.5	1.6	15
Lake Michigan (MI, USA) ^c	1993–1994	0.36	3.6	2.6	0.88	4.9
Chesapeake Bay (MD, USA) ^d	1990–1993		0.90	2.0		5.8

^a Paode et al. [10].^b Shahin et al. [30].^c Sweet et al. [31].^d Baker et al. [6].

atmospheric concentrations/fluxes at the nonurban site during other times of the year. The effect of rainfall was more significant than any seasonal or other meteorological components examined. The lack of seasonality may result both from the temperate climate experienced in southern California (daily mean temperature, wind speed, and humidity typically do not vary widely between seasons) and from the atmospheric emission sources of trace metals within the air basin (e.g., vehicle-miles traveled) not varying widely between seasons.

Stormwater runoff provides one mechanism for the removal of metals from urban areas, and the present study provides evidence that 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 mobilized easily by surface flows during storms, because rainfall in impervious urban areas is more likely to run off than that in nonurban areas. This may be especially significant in the Los Angeles area, because 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 these watersheds, similar to the findings in other studies [26,27]. The watershed transmission efficiencies of 10 to 20% that we estimated for the Los Angeles River watershed are similar to those estimated by Riedel et al. [27] in their discussion of sources of trace metals in the Patuxent River, which drains the highly urbanized area between Washington, DC (USA), and Baltimore (MD, USA).

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 [28] estimated that 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. [29] 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, because the estimates of dry deposition rates used by Davis et al. were an order of magnitude lower than those measured in the present study, these percentages likely underestimate the contribution

from dry deposition in semiarid regions, such as Los Angeles. Few studies have investigated the contribution from dry atmospheric deposition on the watershed and subsequent runoff 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 particular, a better understanding of the sequestration of deposited trace metals within urban watersheds is needed to quantify better the amount of deposited metals that are removed in stormwater runoff.

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 reflects 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 [24], and this contribution overwhelms most other direct sources to the river during dry weather.

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