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WATERSHED AND LAND USE–BASED SOURCES OF TRACE METALS IN URBAN STORM WATER

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Abstract—Trace metal contributions in urban storm water are of concern to environmental managers because of their potential impacts on ambient receiving waters. The mechanisms and processes that influence temporal and spatial patterns of trace metal loading in urban storm water, however, are not well understood. The goals of the present study were to quantify trace metal event mean concentration (EMC), flux, and mass loading associated with storm water runoff from representative land uses; to compare EMC, flux, and mass loading associated with storm water runoff from urban (developed) and nonurban (undeveloped) watersheds; and to investigate within-storm and within-season factors that affect trace metal concentration and flux. To achieve these goals, trace metal concentrations were measured in 315 samples over 11 storm events in five southern California, USA, watersheds representing eight different land use types during the 2000 through 2005 storm seasons. In addition, 377 runoff samples were collected from 12 mass emission sites (end of watershed) during 15 different storm events. Mean flux at land use sites ranged from 24 to 1,238, 0.1 to 1,272, and 6 to 33,189 g/km^2 for total copper, total lead, and total zinc, respectively. Storm water runoff from industrial land use sites contained higher EMCs and generated greater flux of trace metals than other land use types. For all storms sampled, the highest metal concentrations occurred during the early phases of storm water runoff, with peak concentrations usually preceding peak flow. Early season storms produced significantly higher metal flux compared with late season storms at both mass emission and land use sites.

Keywords—Storm water Urban runoff Trace metals Land use First flush

INTRODUCTION

Urban storm water is recognized as a major source of trace metal pollution to many of the nations waterways [1–3]. Because metals typically are associated with fine particles in storm water runoff [2,4], they have the potential to accumulate in the sediments of downstream receiving waters. Williamson and Morrisey [5] reported that metals from urban watersheds accumulate in estuarine sediments, where they may contribute to the risk of toxicity. Schiff et al. [6] found that storm water plumes from Ballona Creek resulted in toxic effects to the endemic purple sea urchin. Subsequent toxicity identification studies identified zinc and, to a lesser extent, copper as being likely sources of the observed toxicity. In southern California, USA, several studies have documented trace metals as major constituents of concern in storm water runoff [1,7]. In fact, 64 bodies of water in the Los Angeles Basin are listed by the U.S. Environmental Protection Agency as impaired waterbodies because of trace metals under Section 303(d) of the Clean Water Act [8,9]; half of these are listed for more than one metal.

Because of the environmental effects of metals, a large emphasis on managing storm water has focused on the reduction and control of trace metals from urban watersheds. Storm water managers, however, need to understand the processes and mechanisms that affect runoff and associated metal loading before they can implement effective controls. To date, many of these mechanisms and processes remain unexplained. For example, managers need to understand how metal loading varies by land use type to target the most efficient locations for implementing controls. Another important mechanism is understanding how patterns of trace metal loading vary over the course of a single storm and how loading patterns vary over the course of a storm season. This information is extremely useful to managers who want to effectively target the times when loading is greatest. This is especially true in arid watersheds where storms are infrequent but intense, resulting in rapid changes of concentration and loading within minutes to hours. This forces managers to consider best-management practices that focus on a single storm—or even-within storm controls—for reducing trace metal contributions.

Existing data sets provide insight regarding land use–based loading, but they do not provide the mechanistic understanding needed by storm water managers. Between 1977 and 1983, the Nationwide Urban Runoff Program (NURP) compiled storm water runoff data from 81 different land uses representing 28 cities throughout the United States and included the monitoring of approximately 2,300 individual site events [10]. The utility of the NURP data set is somewhat limited because of its age (23 years). The National Stormwater Quality Database (NSQD) was created in 2003 to examine more recent storm water data from a representative number of National Pollutant Discharge Elimination System, municipal separate storm-sewer system storm water permit holders (http://www.cwp.org/NPDES_research_report.pdf) [11]. The NSQD includes phase one storm water monitoring data from 369 stations encompassing 17 states and a total of 3,770 individual site events between 1992 and 2003. The NSQD, however, does not contain any samples from the arid west. Neither the NURP nor the NSQD provides time-variable measurements that provide an understanding of the temporal processes that affect storm water loading. Several studies have documented spatial and temporal patterns of storm water loading from southern California land

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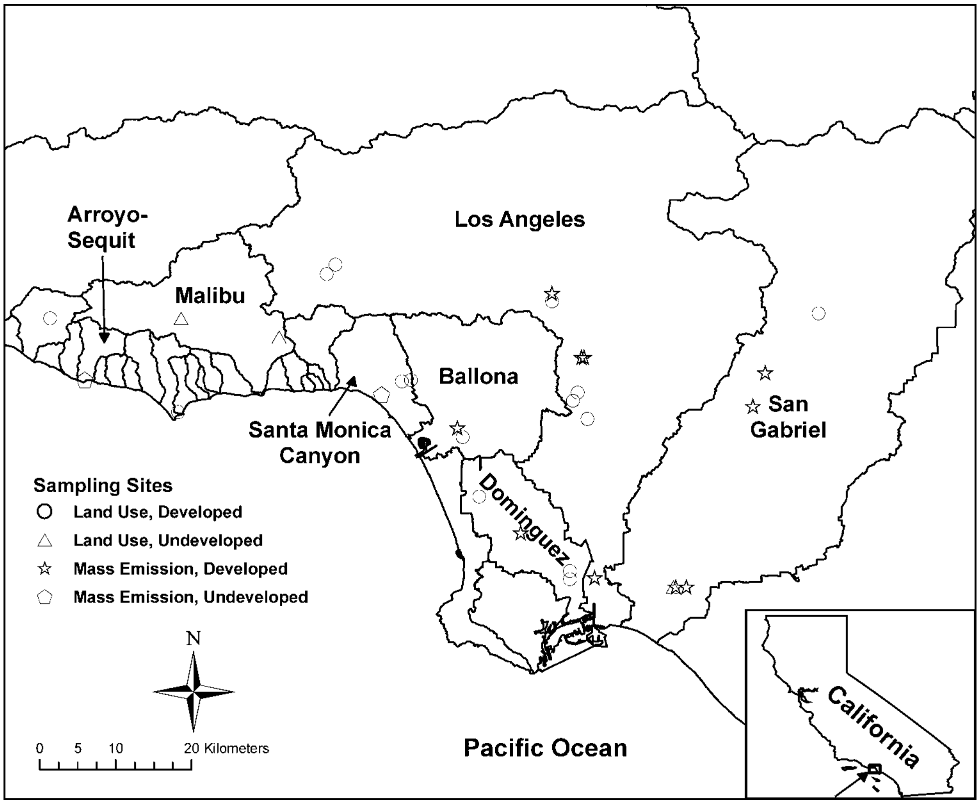

Fig. 1. Map of watersheds with land use and mass emission sampling sites within the greater Los Angeles region (CA, USA). Undeveloped sites have greater than 90% open space.

uses [12,13]; however, these studies examined organic compounds and did not include data on trace metals.

The objective of the present study was to update and enhance the information on storm water trace metal mechanisms and processes for the arid west. The goals of the present study were to quantify trace metal event mean concentration (EMC), flux, and mass loading associated with storm water runoff from representative land uses; to compare EMC, flux, and mass loading associated with storm water runoff from urban (developed) and nonurban (undeveloped) watersheds; and to investigate within-storm and within-season factors that affect trace metal concentration and flux. The present study focused its work in the Los Angeles, California, USA, region. Despite Los Angeles being the largest metropolitan center on the west coast of the United States, with approximately 90 residents/km^2 (http://factfinder.census.gov/home/saff/main.html), no data from Los Angeles were compiled within the NURP or NSQD studies.

MATERIALS AND METHODS

Study area

Storm water runoff was sampled from 19 different homogenous land use sites (LU sites) and 12 mass emission sites (ME sites) that aggregate runoff from multiple land use types in the watershed (Fig. 1). The 19 homogenous LU sites represent the distribution of land use types in southern California as defined by the Southern California Association of Governments [14] (http://scag.ca.gov/wags/index.htm) (Table 1). The Southern California Association of Governments derived these land use types from year-2000 aerial photography surveys with a minimum resolution of 8 m^2. In the present study, LU sites are denoted as agricultural, commercial, high-density residential, industrial, low-density residential, open space, recreational, and transportation. The LU sites ranged in size from 0.002 to 2.89 km^2. In contrast to the smaller, homogeneous LU sites, ME sites had much larger catchments and consisted of heterogeneous land use distributions that commingle and, ultimately, discharge to recreational beaches and harbors along the Pacific Ocean. In the present study, 10 urban ME sites and two nonurban ME sites were sampled. Developed land use ranged from 49 to 94% of total watershed area in the 10 urban watersheds. Developed land use comprised less than 5% of the watershed area in the two nonurban watersheds. The 12 ME sites ranged in size from 31 to 2,161 km^2.

Rainfall

All the LU and ME sites were sampled during the 2000 through 2005 storm seasons. Winter storms typically occur between October and May, providing 85 to 90% of the annual average rainfall (38.4 cm) [15]; however, annual precipitation in Los Angeles can be highly variable. For example, the 2004-to-2005 rainfall season brought 94.6 cm of precipitation to downtown Los Angeles, making it the second wettest season in Los Angeles since records began in 1877 (http://www.wrh.noaa.gov/lox/). In contrast, the 2001-to-2002 rainfall season totaled a mere 11.2 cm (27 cm below the seasonal average). Consequently, the study period encompassed a representative range of precipitation conditions.

Sampling and analysis

Twenty discrete storms were sampled, with each site sampled for between one and seven individual storm events (Tables 2 and 3). Rainfall amounts ranged from 0.12 to 9.68 cm, and antecedent conditions ranged from 0 to 142 d without mea-

Table 1. Land use aggregation employed for the Southern California Association of Governments (SCAG) data sets[a]

Aggregated land use[b]	SCAG land use category
Agricultural (E)	Dairy, intensive livestock, and associated facilities; horse ranches; irrigated cropland and improved pasture land; nonirrigated cropland and improved pasture land; nurseries; orchards and vineyards; other agricultural; poultry operations
Commercial (C)	Attended pay public parking facilities; base (built-up area); colleges and universities; commercial recreation; commercial storage; correctional facilities; elementary schools; fire stations; government offices; high-rise major office use; hotels and motels; junior or intermediate high schools; low- and medium-rise major office use; major medical health care facilities; modern strip development; nonattended public parking facilities; older strip development; other public facilities; other special use facilities; police and sheriff stations; preschools/day care centers; regional shopping center; religious facilities; retail centers (nonstrip with contiguous interconnected off-street); senior high schools; skyscrapers; special care facilities; trade schools and professional training facilities
High-density residential (A)	Duplexes, triplexes, and two- or three-unit condominiums and townhouses; high-density, single-family residential; high-rise apartments and condominiums; low-rise apartments, condominiums, and townhouses; medium-rise apartments and condominiums; mixed multifamily residential; mixed residential; mobile home courts and subdivisions, low-density; trailer parks and mobile home courts, high-density
Industrial (D)	Chemical processing; communication facilities; electrical power facilities; harbor facilities; harbor water facilities; improved flood waterways and structures; liquid waste disposal facilities; maintenance yards; major metal processing; manufacturing; manufacturing, assembly, and industrial services; marina water facilities; mineral extraction, oil and gas; mixed utilities; motion picture and television studio lots; natural gas and petroleum facilities; navigation aids; open storage; packing houses and grain elevators; petroleum refining and processing; research and development; solid waste disposal facilities; water storage facilities; water transfer facilities; wholesaling and warehousing
Low-density residential (B)	Low-density, single-family residential; rural residential, high-density; rural residential, low-density
Open space (H)	Abandoned orchards and vineyards; air field; beach parks; beaches (vacant); cemeteries; mineral extraction other than oil and gas; other open space and recreation; specimen gardens and arboreta; under construction; vacant area; vacant undifferentiated; vacant with limited improvements; wildlife preserves and sanctuaries
Recreational (F)	Developed local parks and recreation; developed regional parks and recreation; golf courses; undeveloped regional parks and recreation
Transportation (G)	Airports; bus terminals and yards; freeways and major roads; mixed transportation; mixed transportation and utility; park-and-ride lots; railroads; truck terminals

[a] Southern California Association of Governments [14].
[b] Letters correspond to designations used in the present study.

surable rain. Rainfall at each site was measured using a standard tipping bucket that recorded in 0.025-cm increments. Antecedent dry conditions were determined as the number of days following the cessation of measurable rain. Water-quality sampling was initiated when flows were greater than of 20% of the base flow, continued through peak flows, and ended when flows subsided to less than 20% of base flow. Because watersheds in southern California have highly variable flows that may increase by orders of magnitude during storm events, these criteria are considered to be conservative. Flow at ME sites was estimated at 15-min intervals using existing, county-maintained flow gauges or stage recorders in conjunction with historically derived and calibrated stage-discharge relationships. At ungauged ME sites and previously unmonitored LU sites, stream discharge was measured as the product of the wetted cross-sectional area and flow velocity. Velocity was measured using an acoustic Doppler velocity meter (SonTek/YSI, San Diego, CA, USA). The acoustic Doppler velocity meter was mounted to the invert of the stream channel, and velocity, stage, and instantaneous flow data were transmitted to a data logger/controller on query commands found in the data logger software.

Between 10 and 15 discrete grab samples per storm were collected at approximately 30- to 60-min intervals for each site event based on optimal sampling frequencies in southern California as described by Leecaster et al. [16]. Samples were collected more frequently when flow rates were high or rapidly changing and less frequently during low-flow periods. All water samples were collected by either peristaltic pumps with Teflon® tubing and stainless-steel intakes that were fixed at the bottom of the channel or pipe pointed in the upstream direction in an area of undisturbed flow by direct filling of the sample bottle, by hand or affixed to a pole, or by indirect filling of intermediate bottles for securing large volumes. After collection, the samples were stored in precleaned glass bottles on ice with Teflon-lined caps until they were shipped to the laboratory for analysis.

Total suspended solids (TSS) were analyzed by filtering a 10- to 100-ml aliquot of storm water through a tared, 1.2-μm Whatman GF/C filter (Whatman International, Maidstone, Kent, UK). The filters plus the solids were dried at 60°C for 24 h, cooled, and weighed.

Whole samples (particulate plus dissolved) were prepared by nitric acid digestion followed by analysis using inductively coupled plasma–mass spectroscopy according to U.S. Environmental Protection Agency Method 200.8 [17]. Target analyses included aluminum, antimony, arsenic, beryllium, cadmium, chromium, copper, iron, lead, mercury, nickel, selenium, silver, and zinc. Quality-assurance measurements indicated that all laboratory blanks were below the method detection limits, with duplicate samples being within a 10% reproducible difference.

Data analysis

Data analyses were broken into sections by comparison between LU sites, comparison between developed and undeveloped watersheds, and assessment of within-season and within-storm variability. Comparison between LU sites fo-

Table 2. Summary of storm events sampled at mass emission sites during the 2000–2001 to 2004–2005 storm seasons in Los Angeles (CA, USA)

Mass emission sites	Date of storm event	Watershed size (km^2)	Rainfall (cm)	Previous dry days (*n*)	Mean flow (cm/s)	Peak flow (cm/s)
Los Angeles River developed watersheds						
Los Angeles River above Arroyo Seco	1/26–27/2001	1,460	1.80	1	27.3	114.0
	2/9–11/2001		1.42	1	22.4	165.2
	2/12–13/2001		9.68	0	62.6	262.5
Los Angeles River at Wardlow	1/26–27/2001	2,161	1.80	1	15.0	50.9
	2/9–11/2001		1.42	1	1.4	6.0
	5/2–3/2003		3.56	4	209.9	756.7
	2/2–3/2004		1.14	6	90.4	375.6
Verdugo Wash	1/26–27/2001	65	1.80	1	15.0	50.9
	2/9–11/2001		1.42	1	13.9	90.2
	11/12–13/2001		9.68	0	68.5	368.2
	10/31/2003 to 11/1/2003		1.74	30	56.5	155.0
Arroyo Seco	2/9–11/2001	130	3.56	12	2.9	13.5
	4/7/2001		1.78	30	7.8	21.8
Ballona Creek	2/18–19/2001	338	1.50	3	38.1	107.0
	4/7/2001		1.24	31	32.6	100.9
	11/24–25/2001		1.52	11	53.1	396.2
	5/2–3/2003		2.03	4	52.8	134.4
	10/31/2003 to 11/1/2003		2.03	30	62.0	148.1
	2/2–3/2004		2.21	29	55.0	213.9
	2/21–22/2004		3.41	18	44.8	95.6
Dominguez Channel	3/17–18/2002	187	0.28	10	4.8	14.0
	2/21–22/2004		1.52	18	14.7	35.5
Undeveloped watersheds						
Santa Monica Canyon	2/9–11/2001	41	3.74	1	0.1	1.1
	4/7/2001		3.05	50	0.6	3.0
Open space, Arroyo Sequit	5/2–3/2003	31	5.03	3	0.0	0.0
	2/25–26/2004		4.12	1	3.4	21.9
	12/27–28/2004		5.05	17	0.0	0.2
	1/7/05		5.54	2	0.3	0.9

cused on EMCs, load, flux, and principal components analysis (PCA).

The EMC was calculated using Equation 1:

$$\mathrm{EMC} = \frac{\sum_{i=1}^{n} C_i F_i}{\sum_{i=1}^{n} F_i} \tag{1}$$

where C_i = individual runoff sample concentration of the *i*th sample, F_i = instantaneous flow at the time of the *i*th sample, and n = number of samples per event. Trace metal concentrations were log-transformed before calculations to improve normality. In all cases, nondetectable results were assigned a value of half the minimum detection limit based on the inability to log transform a value of zero. Mass loading was calculated as the product of the EMC and the storm volume. Flux estimates facilitated loading comparisons among watersheds of varying sizes. Flux was calculated as the ratio of the mass load per storm and watershed area. Differences in concentration or flux between LU sites were tested using a one-way analysis of variance (ANOVA), with a significance level of $p < 0.05$, followed by Tukey-Kramer post hoc test for multiple comparisons [18].

The PCA was used to identify the most important factors (i.e., groups of parameters, storm size, and storm season) controlling data variability with SAS® software (Vers 9.1; Statistical Analysis Systems Institute, Cary, NC, USA) [19]. As a multivariate data analysis technique, PCA reduces the number of dependent variables without sacrificing critical information [20]. The number of principal components (PCs) extracted (to explain the underlying data structure) was defined by using the Kaiser criterion [21], in which only the PCs with eigen (a symmetric matrix of covariance or correlation) values greater than unity are retained. Scores derived from the PCA were plotted along the first two PC axes and examined visually for relationships that differentiate constituent concentrations among subclasses (e.g., land use types). Principal components analysis and ANOVA were used in a two-step process in which the PCA was used to identify factors influencing variability and to group data into different sets based on the factors identified. Significant differences between the classes identified by the PCA were then tested by ANOVA.

The second analysis that compared developed and undeveloped ME sites followed an approach similar to that used for the LU sites, focusing on EMCs, load, and flux. Differences between watershed types were determined using ANOVA.

The third analysis bifurcated into two approaches. The first compared seasonal patterns of total metal loading by plotting mass emissions against storm season (early = October–December; mid = January–March; late = April–May) and cumulative annual rainfall. For this analysis, all ME sites were analyzed as a group to examine differences between early and late season storms across the sampling region using ANOVA. The second approach compared flow and total metal concentration of within-storm events. This comparison examined the time-concentration series relative to the hydrograph plots using a pollutograph. A first flush in concentration from individual ME storm events was defined as a circumstance when the peak in concentration preceded the peak in flow. This was quantified using cumulative loading plots in which cumulative mass emis-

Table 3. Summary of storm events sampled at land use sites in Los Angeles (CA, USA) during the 2000–2001 to 2004–2005 storm seasons. Numbers in parentheses indicate the number of sites sampled in that land use category

Land sites	Date of storm event	Watershed size (km^2)	Rainfall (cm)	Previous dry days (*n*)	Mean flow (cm/s)	Peak flow (cm/s)
High-density residential (1)	2/9–11/2001	0.52	1.93	2	0.082	0.563
	2/18–19/2001		0.61	4	0.060	0.233
	3/17–18/2002		0.20	10	0.000	0.003
High-density residential (2)	2/17/2002	0.02	0.89	19	0.001	0.006
	2/2–3/2004		1.19	29	0.004	0.025
High-density residential (3)	12/28/2004	1.0	3.25	0	0.009	0.080
	2/11/2005		1.35	13	0.004	0.016
Low-density residential (1)	2/18–19/2001	0.98	0.61	4	0.068	0.097
	3/4–5/2001		1.42	6	0.017	0.071
	2/2–3/2004		2.26	29	0.030	0.143
Low-density residential (2)	3/17–18/2002	0.18	2.13	19	0.008	0.116
Commercial (1)	2/17/2002	2.45	0.74	19	0.337	1.340
Commercial (2)	2/17/2002	NA[a]	0.89	19	0.002	0.008
	2/18–19/2001		0.81	4	0.003	0.008
Commercial (3)	4/7/2001	0.06	2.03	31	0.008	0.018
	3/17–18/2002		0.12	9	0.000	0.001
	2/9–11/2001		0.81	14	0.253	1.801
Industrial (1)	2/18–19/2001	2.77	0.41	3	0.205	0.774
	3/17–18/2002		0.25	27	0.000	0.003
Industrial (2)	2/17/2002	0.001	0.74	19	0.000	0.002
Industrial (3)	4/7/2001	0.004	2.06	25	0.008	0.017
Industrial (4)	3/15/2003	0.01	4.50	10	0.117	0.375
Agricultural (1)	2/18–19/2001	0.98	0.81	5	0.014	0.042
	3/4–5/2001		8.13	3	0.021	0.053
	3/17–18/2002		0.23	9	0.012	0.031
	2/2–3/2004		1.17	29	0.023	0.128
Agricultural (2)	4/7/2001	0.8	2.06	25	1.723	3.801
Recreational (1)	2/18–19/2001	0.03	0.61	4	0.015	0.044
	3/4–5/2001		1.42	6	0.003	0.014
Transportation (1)	4/7/2001	0.01	3.05	25	0.022	0.057
Transportation (2)	2/17/2002	0.002	0.74	19	0.001	0.006
Open space (1)	2/24–25/2003	9.49	3.00	11	0.160	0.360
Open space (2)	2/24–25/2003	2.89	2.57	11	0.180	0.680

[a] NA = not analyzed.

sion was plotted against cumulative discharge volume during a single storm event [22]. When these curves are close to unity, mass emission is a function of flow discharge. A strong first flush was defined as 75% or more of the mass being discharged in the first 25% of runoff volume. A moderate first flush was defined as between 30 and 75% of the mass being discharged in the first 25% of runoff volume. No first flush was assumed when 30% or less of the mass was discharged in the first 25% of runoff volume.

RESULTS

Comparison between LU sites

Industrial LU sites contributed a substantially higher flux of copper and zinc compared to the other LU sites evaluated (Fig. 2). For example, mean total copper flux from the industrial LU sites was 1,238.0 g/km^2, whereas mean total copper flux from high-density residential and recreational LU sites was 100.5 and 190.1 g/km^2, respectively. Trace metal flux from undeveloped LU sites was lower than that observed in developed LU sites. For example, mean copper flux at open-space LU sites was 23.6 g/km^2. In contrast to copper and zinc, the mean flux of total lead was greatest at agricultural, high-density residential, and recreational LU sites (Fig. 2). The mean flux of total lead at these three LU sites was at least an order of magnitude greater than that of any other sampled LU site.

Industrial LU sites had the greatest mean EMCs for copper and zinc relative to all other LU sites (Fig. 3). For example, zinc EMCs at the industrial LU sites averaged 599.1 μg/L, compared to 362.2 and 207.7 μg/L for commercial and high-density residential LU sites, respectively. High-density residential and industrial sites had the greatest EMCs for lead relative to all other LU sites (Fig. 3). For example, lead EMCs at high-density residential and industrial LU sites averaged 28.4 and 24.1 μg/L, respectively, compared to less than 20 μg/L for other LU sites. Mean EMCs for all three metals from undeveloped LU sites were lower than those observed in developed LU sites. For example, mean copper, lead, and zinc EMCs from open-space LU sites were 7.6, 1.2, and 23.2 μg/L, respectively.

Both industrial and agricultural LU sites contributed substantially higher fluxes of TSS compared to the other LU sites evaluated (Fig. 2). For example, mean TSS flux from the industrial and agricultural LU sites were comparable at around 3,150.3 kg/km^2, whereas mean TSS flux from the high-density residential LU sites was 91.1 g/km^2. Mean TSS flux from undeveloped LU sites was comparable to that of the remaining developed LU sites. For example, mean TSS flux from open-space LU sites was 513.8 kg/km^2, compared to 160.8 and 94.0 kg/km^2 for low-density residential and commercial LU sites, respectively.

Recreational LU sites had the greatest mean TSS EMC compared to all other LU sites. For example, TSS EMCs at the recreational LU sites averaged 530.7 mg/L, compared to 111.1 and 92.0 mg/ L for agricultural and industrial LU sites, respectively. Mean TSS EMCs from undeveloped LU sites were comparable to those observed in developed agricultural

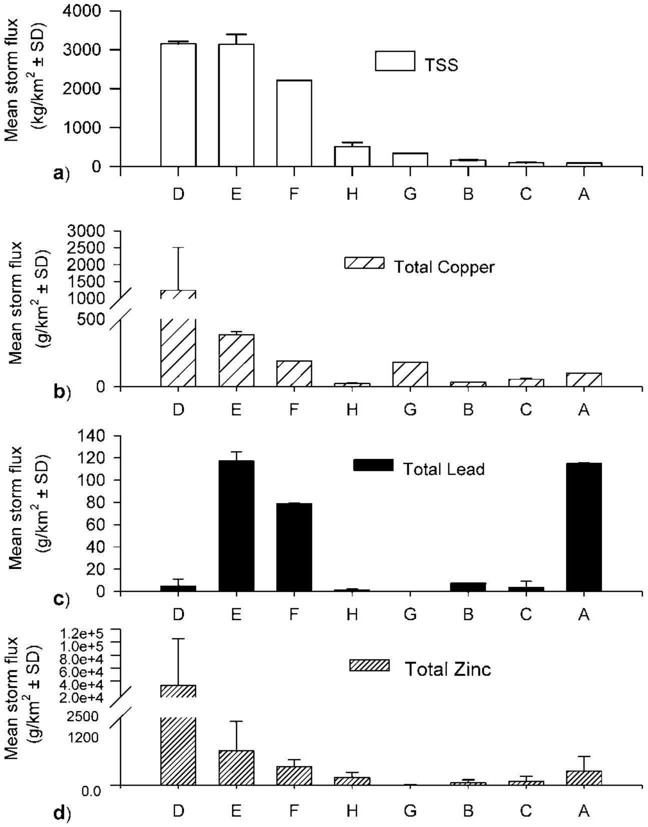

Fig. 2. Mean storm flux of total suspended solids (TSS) (**a**), total copper (**b**), total lead (**c**), and total zinc (**d**) at land use sites in Los Angeles (CA, USA) during 2000–2001 to 2004–2005 storm seasons. A = high-density residential; B = low-density residential; C = commercial; D = industrial; E = agricultural; F = recreation; G = transportation; H = open space; SD = standard deviation.

and industrial LU sites. The TSS EMCs from open-space LU sites averaged 134.8 mg/L.

Results of the PCA indicated that the land use is a predominant source of variability and that land use categories can be grouped based on differences in their intrinsic runoff and loading characteristics (Fig. 4). Two PCs had eigen values of greater than one, with PC1 and PC2 accounting for 63 and 17%, respectively, of the total variance. Factor loadings indicated that PC1 and PC2 described concentrations of copper, cadmium, lead, nickel, zinc, and TSS. The two-dimensional plot of scores from PC1 and PC2 revealed that industrial, recreational, and open-space LU types were distinct from other LU types based on the concentrations of these constituents. Comparison of the PC scores (or eigen vectors) using a one-way ANOVA indicated that both industrial and recreational sites were significantly different ($p < 0.001$) than open-space sites. All other LU types were indistinguishable.

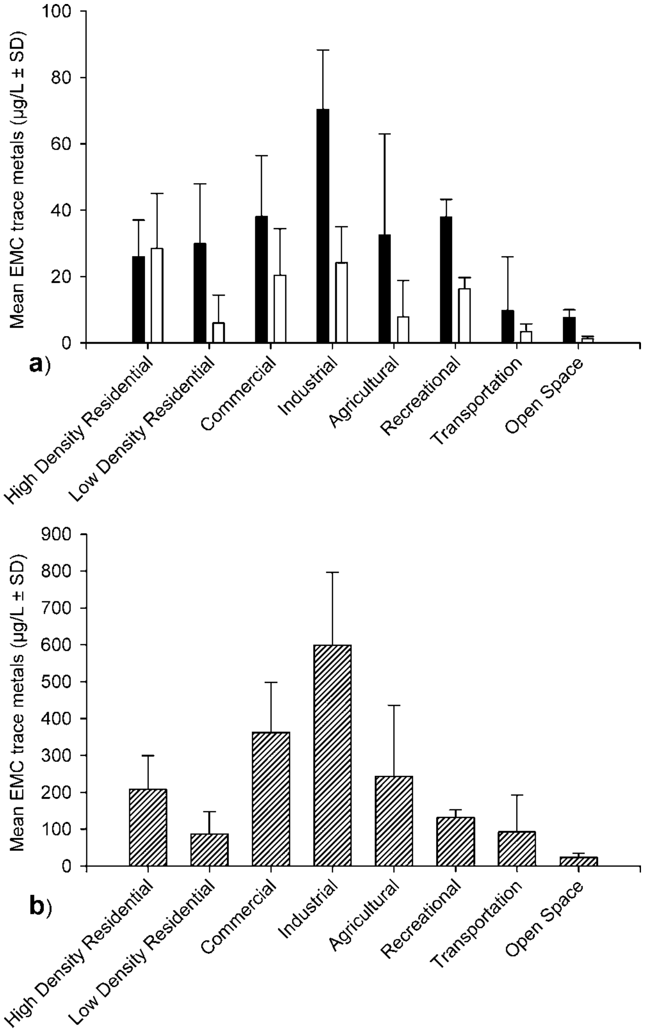

Fig. 3. Mean storm event mean concentrations (EMCs) of total copper (■) and total lead (□) (**a**) and total zinc (▨; **b**) at specific land use sites during the 2000–2001 to 2004–2005 storm seasons in Los Angeles (CA, USA). SD = standard deviation.

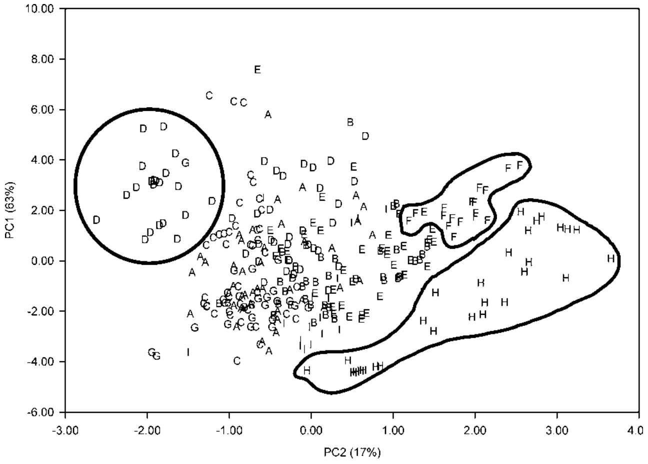

Fig. 4. Plot of two principal components (PCs) explaining 63% (*y*-axis) and 17% (*x*-axis) of the variation between trace metal concentrations at land use sites in the Los Angeles River (CA, USA) watershed during 2000–2001 to 2004–2005 storm seasons. A = high-density residential Los Angeles River watershed; B = low-density residential; C = commercial; D = industrial; E = agricultural; F = recreation; G = transportation; H = open space; I = high-density residential San Gabriel River watershed.

Comparison between developed and undeveloped watersheds

The contrasts between the different small, homogeneous LU sites also were apparent at the watershed scale (Fig. 5). Total copper, total lead, and total zinc EMCs and fluxes were significantly greater at ME sites from developed compared to undeveloped watersheds (ANOVA, $p \leq 0.001$). For the 15 storm events measured, the mean flux of total copper, total lead, and total zinc from developed ME watersheds was 0.6, 0.5, and 3.0 kg/km^2, respectively. The mean flux of total cop-

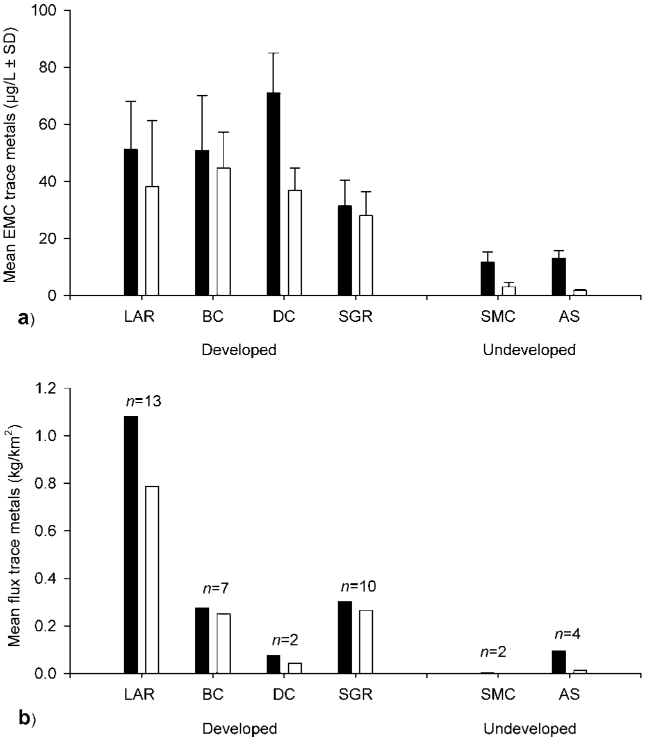

Fig. 5. Average event mean concentrations (EMCs) (**a**) and fluxes (**b**) of total copper (■) and total lead (□) from southern California (USA) watersheds during the 2000–2001 to 2004–2005 storm seasons. LAR = Los Angeles River; BC = Ballona Creek; DC = Dominguez Channel; SGR = San Gabriel River; SMC = Santa Monica Canyon; AS = Arroyo Sequit; *n* = number of storm events; SD = standard deviation.

per, total lead, and total zinc from undeveloped ME watersheds were 0.06, 0.01, and 0.1 kg/km², respectively (Fig. 2). Furthermore, the higher fluxes from developed ME watersheds were generated by substantially less rainfall than the lower fluxes from the undeveloped ME watersheds (2.8 ± 0.8 cm for storms in developed ME watersheds vs 4.4 ± 0.8 cm for storms in undeveloped ME watersheds), presumably because of increased impervious surface area in developed watersheds. Similarly, total copper, total lead, and total zinc mean EMCs from developed ME watersheds significantly exceeded those from undeveloped ME watersheds (46.1 ± 14.8, 36.3 ± 15.3, and 251.9 ± 76.9 μg/L, respectively, vs 12.6 ± 3.0, 2.2 ± 0.8, and 27.0 ± 8.4 μg/L, respectively; ANOVA, $p \leq 0.001$).

The TSS concentrations from less developed ME watersheds were similar to those from more developed ME watersheds. For example, annual TSS EMCs for developed ME watersheds averaged 246.3 mg/L for the Los Angeles River, compared to 217.0 mg/L for the undeveloped ME watersheds. The TSS fluxes, however, were substantially higher for developed ME watersheds. For the 15 storm events measured, mean TSS flux from the developed Los Angeles River and San Gabriel River watersheds were 3,116.8, and 398.8 kg/km², respectively, whereas mean TSS flux from undeveloped watersheds was 62.8 kg/km².

Within-season and within-storm variability

Significant seasonal differences were found in total metal loading ($p < 0.001$). Early season storms had significantly higher total metal load compared with late season storms both within and between watersheds, even when rainfall quantity

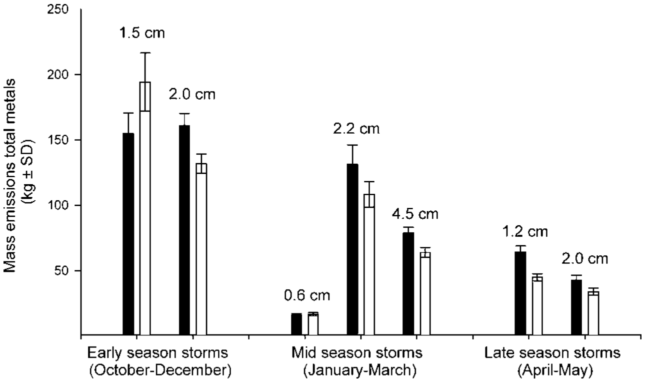

Fig. 6. Metals loadings from early, mid, and late season storms in Ballona Creek during 2000–2001 to 2004–2005 storm seasons in Los Angeles (CA, USA) for total copper (■) and total lead (□). Numbers above the bars in the graph indicate total event rainfall. SD = standard deviation.

was similar (Fig. 6). For example, the two early season storms from Ballona Creek in water years 2001 to 2002 and 2003 to 2004 had total copper loadings that were approximately fourfold larger (range, 154.7 ± 16.0 to 160.8 ± 9.4 kg) than the two storms that occurred at the end of the rainy season (42.6 ± 3.8 to 64.2 ± 4.6 kg), despite the early and late season storms resulting from comparable rainfall. The results for total lead and total zinc showed a similar pattern.

Trace metal concentrations varied with time over the course of storm events (Fig. 7). For all storms sampled, both the highest trace metal concentrations and the peak flow occurred in the early part of a storm event. In all cases, metal concentrations increased rapidly, often preceding peak flow. Concentrations stayed high for relatively short periods and often decreased back to base levels within 1 to 2 h. In contrast, the

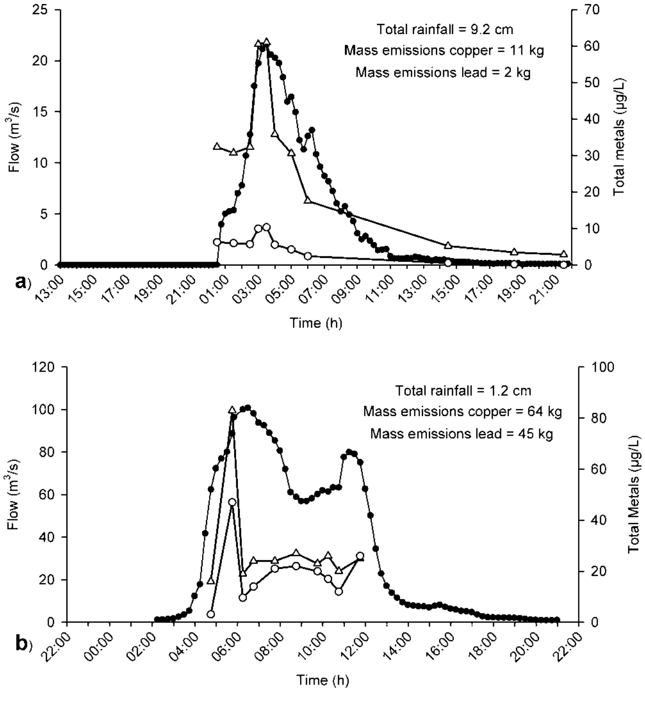

Fig. 7. Variation in flow (●), total copper (△), and total lead (○) concentrations with time for a storm event in the undeveloped Arroyo Sequit watershed (**a**) and developed Ballona Creek watershed (**b**) in Los Angeles (CA, USA).

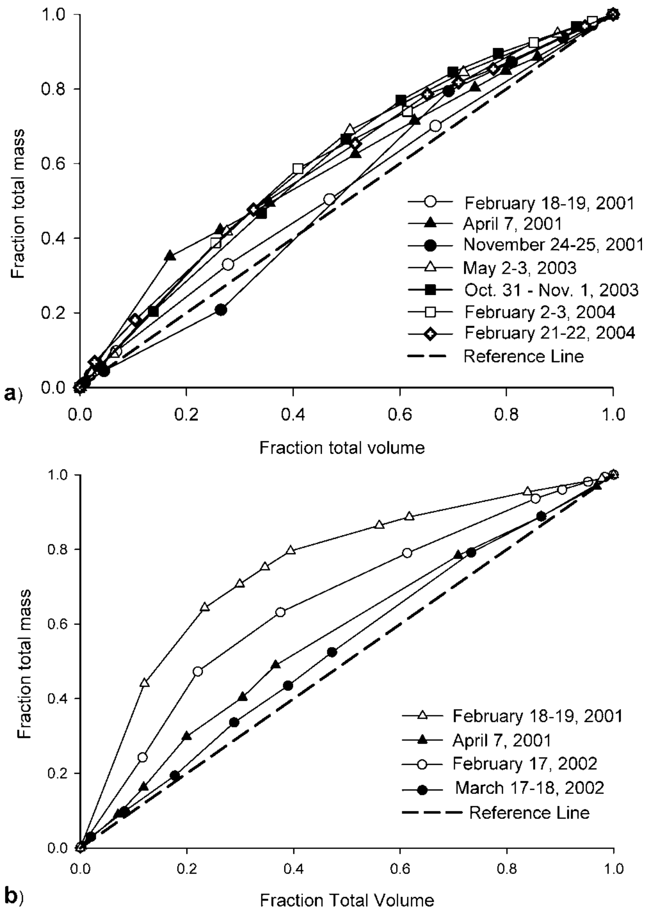

Fig. 8. Cumulative load duration curves for total zinc for seven storms in the developed Ballona Creek watershed (**a**) and for four storms in the commercial land use (**b**) in Los Angeles (CA, USA). Reference line indicates a 1:1 relationship between volume and mass loading. Portions of the curve above the line indicate proportionately higher mass loading per unit volume (i.e., first flush). Portions below the line indicate the reverse pattern.

undeveloped watershed (Arroyo Sequit) (Fig. 7a) had appreciably lower peak concentrations than the developed watershed (Ballona Creek) (Fig. 7b). Although the pattern of an early peak in concentration was comparable in both undeveloped and developed watersheds, the peak concentration tended to occur later in the storm and to persist for a longer duration in the undeveloped watersheds. Because of the small number of storms sampled in undeveloped watersheds, the consistency of these patterns is inconclusive.

Cumulative mass loading of all trace metals from ME sites was relatively linear with flow, implying that no strong first flush effect existed at these locations (Fig. 8). In contrast, cumulative mass loading plots for total copper, total lead, and total zinc from LU sites exhibited moderate first flush patterns in the residential, commercial, industrial, agricultural, and open-space LU categories. When all developed catchments were analyzed together, the magnitude of the first flush effect decreased with increasing watershed size (Fig. 9). For the developed LU sites that had catchments generally less than 3 km^2 in size, between 30 and 50% of the total copper, total lead, and total zinc load was discharged during the first 25% of storm volume. For the ME sites, where runoff was integrated across larger and more diverse landscapes, between 15 and 35% of the total mass of copper, lead, and zinc was discharged during the first 25% of storm volume.

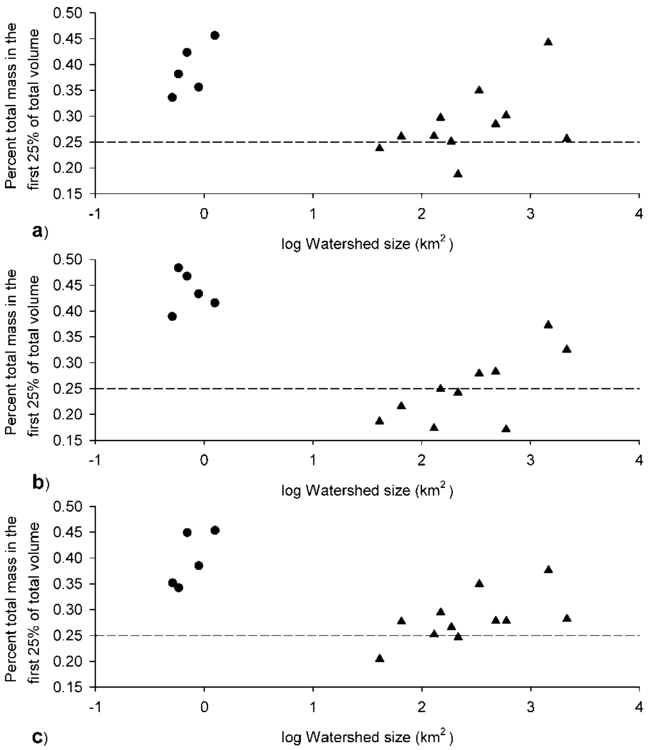

Fig. 9. First flush patterns of total copper (**a**), total lead (**b**), and total zinc (**c**) in relation to watershed size in Los Angeles (CA, USA). Dashed reference line indicates 25% of total mass loading in first 25% of total volume. Watershed size is in log scale. ● = land use sites; ▲ = mass emission sites.

DISCUSSION

Concentrations, flux, and loading in storm water runoff exhibited some key patterns having important implications for managers tasked with controlling trace metals. First, the magnitude of trace metal concentrations and loads were higher at sites with industrial land uses than at sites with other land use types. The high pollutant loading from industrial sites observed in the present study results, at least in part, from intrinsic properties of the industrial land use. These intrinsic properties include high impervious cover (typically >70%) and on-site source generation. Other authors have reported similar results. Sanger et al. [23] reported that total metal concentrations in runoff from industrial catchments tended to be higher than those from residential and commercial catchments. Park and Stenstrom [24] used Bayesian networks to estimate pollutant loading from various land uses in southern California and concluded that zinc showed higher EMCs at sites with commercial and industrial land uses. Bannerman et al. [25] identified industrial land uses as a critical source area in Wisconsin, USA, storm water, producing significant zinc loads. Bannerman et al. [25] further suggested that targeting best-management practices to 14% of the residential area and 40% of the industrial area could significantly reduce contaminant loads by as much as 75%. Substantially higher TSS fluxes also were observed at the industrial sites, which may explain the high trace metal concentrations often associated with fine particles. The City of Austin [26], Texas, USA found that lead and zinc EMCs were related to the TSS EMCs. Consequently, controlling TSS at industrial sites also may result in reducing other constituents with the same particle sizes.

A second key conclusion that may affect storm water management is that seasonal flushing was consistently observed at both LU and ME sites. This suggests that the magnitude of trace metal loads associated with storm water runoff depends, at least in part, on the amount of time available for buildup on land surfaces. The extended dry period that typically occurs in arid climates, such as southern California, maximizes the time for trace metals to build up on land surfaces, resulting in proportionally higher concentrations and loads during initial storms of the season. Similar seasonal patterns were observed for polycyclic aromatic hydrocarbons in the Los Angeles region [13,27]. Han et al. [28] also reported that the antecedent dry period was the best predictor for the magnitude of pollutant runoff from highways. Other researchers [29,30] have reported corresponding temporal trends for other particle-bound contaminants. This seasonal pattern suggests that focusing management actions on early season storms may provide relatively greater efficiency than distributing lower-intensity management actions throughout the season.

A third key conclusion is that trace metal concentrations varied throughout the duration of storm hydrographs. The greatest total metal concentrations occurred at or just before the peak in flow of the storm hydrograph for nearly every storm sampled. This hydrograph/pollutograph pattern also was observed for polycyclic aromatic hydrocarbons in the greater Los Angeles area [13]. Tiefenthaler et al. [31] observed similar pollutographs that showed peak suspended-sediment concentrations preceding the peak in discharge for the Santa Ana River. Similar time-versus-concentration relationships were observed by Characklis and Wiesner [2], who reported that the maximum concentrations of zinc, organic carbon, and solids coincided with early peak storm water flows. The early occurrence of peak concentrations indicates that monitoring programs must capture the early portion of storms to generate accurate estimates of EMC and contaminant loading. Programs that do not initiate sampling until a flow threshold has been surpassed may severely underestimate storm EMCs.

Despite a strong and consistent pattern of high metal concentrations early in the storm hydrograph, cumulative mass loading plots exhibited only a moderate first flush of total copper, total lead, and total zinc at the small LU sites and no appreciable first flush at the larger ME sites. Lee et al. [32] also found that the magnitude of first flush varied by constituent, with metals generally showing the weakest first flush. Furthermore, first flush phenomena were strongest for small catchments and generally decreased with increasing catchment size. Han et al. [28] also reported that first flush characteristics increased with decreasing drainage area size. Characklis and Wiesner [2] reported that storm water runoff of trace metals from the urban areas of Houston exhibited no discernable first flush effect; however, these measurement were from larger ME site catchments.

The inverse relationship between first flush and catchment size has several potential mechanistic explanations, including relative impervious area, spatial and temporal patterns in rainfall, and pollutant transport through the catchment. Smaller LU catchments have increased impervious area that allows contaminants to be easily washed off relative to larger ME watersheds with less impervious area, which requires greater rainfall energy to wash off particles and associated contaminants. In the present study, industrial, commercial, and high-density residential LU sites were comprised of 72, 72, and 33% imperviousness, respectively. In contrast, the larger ME watersheds (>40 km^2) ranged from 32 to 59% imperviousness. The undeveloped ME watersheds, which had the least within-storm variability, were comprised of only 1% imperviousness. Pitt [33] also found a first flush on relatively small paved areas that he associated with washoff of the most available material.

A corollary to the relationship between imperviousness and catchment size is travel time. Travel time becomes a factor because contaminants are rapidly delivered to the point of discharge within smaller, more impervious catchments relative to larger, less impervious catchments. In the present study, the travel time in the larger ME watersheds like Ballona Creek or the Los Angeles River was estimated in hours, whereas that in the small LU catchments were in minutes. As a result, not all first flush in smaller catchments upstream arrive at a ME site at the same time, effectively diluting short peaks in concentration. Hence, the different times of concentration (i.e., travel times) from various portions of the watershed may obscure first flush patterns at larger ME sites.

Spatial and/or temporal differences in rainfall further complicate first flush in large watersheds. Adams and Papa [34] as well as Deletic [35] both concluded that the presence of a first flush depends on numerous site and rainfall characteristics. In smaller catchments, rainfall distribution is more uniform compared to that in larger watersheds. When rainfall is distributed uniformly, particles and associated pollutants are potentially washed off at the same time. In larger catchments, rainfall lags between various parts of the watershed may take hours, and rainfall quantity and/or duration may not be similar between subwatersheds. Ackerman and Weisberg [15] quantified rainfall temporal and spatial variability and determined that these factors were an important consideration in hydrologic inputs to the coastal ocean of southern California. Ultimately, the differences in first flush, whether resulting from imperviousness, travel time, or rainfall variability, suggest that management strategies at most moderate to large catchments should focus on more than just the initial portion of the storm if the hope is to capture a majority of metal loads.

Urban storm water runoff from the present study appeared to be worthy of management concern, because it represented a large mass emission source that frequently exceeded water-quality criteria (Table 4) [36,37]. Cumulatively, the annual average loading of total copper, total lead, and total zinc from the Los Angeles River, Ballona Creek, and Dominguez Channel exceeded the mass emissions from industrial point sources, such as power-generating stations and oil refineries, by orders of magnitude. Annual storm water loading from these three watersheds also rivaled—or exceeded—trace metal emissions from point sources, such as publicly owned treatment works. One significant difference between these point sources and urban storm water is that southern California has a completely separate sanitary sewer collection system, and urban storm water receives no treatment before discharge into estuaries or the coastal ocean. Assuming a hardness of 100 mg/L and that 15% of the total metals in storm water occur in the dissolved fraction [38], storm water concentrations of copper and zinc would have exceeded California Toxic Rule [39] water-quality criteria in more than 80% of the wet-weather samples collected at ME sites. This resulted, in part, from industrial LU sites, where 100 and 87% of runoff samples exceeded water-quality criteria for zinc and copper, respectively. Commercial LU sites exceeded water-quality criteria in 79 and 72%, respectively, of its runoff samples. Only 8 to 9% of the runoff samples exceeded the water-quality criterion for lead at commercial or industrial LU sites. Hall and Anderson [40] concluded that

Table 4. Annual trace metal loadings (mean ± 95% confidence intervals) in the Los Angeles (CA, USA) coastal region from different sources

Research	Mean annual load (mt/year)[a] Total copper	Total lead	Total zinc
Point-source data[bc] (2000–2005)			
Large, publicly owned treatment plants	10.9 ± 6.8	0.8 ± 0.8	13.9 ± 7.6
Low-volume waste power-generating stations	0.01	0.00	0.09
Wet weather runoff[d] (2000–2005)			
Los Angeles River	1.6 ± 1.2	1.4 ± 1.5	9.8 ± 9.4
Ballona Creek	0.7 ± 0.4	0.6 ± 0.3	4.3 ± 2.5
Dominguez Channel	0.4 ± 2.4	0.2 ± 1.1	2.1 ± 11.0
Total annual wet weather runoff	2.7 ± 4.0	2.2 ± 2.9	16.2 ± 22.9

[a] mt/year = metric tons per year.
[b] Lyon et al. [36].
[c] Steinberger and Stein [37]. Power-generating station data represent year 2000 only.
[d] Present study.

industrial and commercial LU sites were the major source of trace metals most often considered to be toxic to aquatic invertebrates, with runoff from the commercial sites most frequently proving toxic to the test organism.

The focus on LU sites in the present study enabled the comparison of median EMCs with data sets collected from other parts of the nation (Table 5). All the median EMCs for total copper at LU sites from Los Angeles were greater than or equal to median EMCs at LU sites reported in the NSQD [11]. With the exception of the open-space LU sites, all the median EMCs for zinc were greater at LU sites in Los Angeles than at the LU sites reported in the NSQD. In contrast, all the median EMCs for lead were lower at the LU sites in Los Angeles than at the LU sites reported in the NSQD. Of the 15 LU site–EMC combinations, all but one of the median EMCs (industrial zinc) were lower in Los Angeles than then median EMCs reported by the NURP [10] (Table 5). Unlike the NSQD, which was focused on data from the 1990s, the NURP data were collected during the 1970s. Therefore, the differences between median EMCs from NURP and median EMCs from Los Angeles also were a function of time. Certainly, this factor affected median EMCs for lead, which was phased out of gasoline during the mid-1980s [41,42].

Table 5. Comparison of Nationwide Urban Runoff Program (NURP) and National Stormwater Quality Database (NSQD) to trace metals concentrations from specific land uses in the Los Angeles (CA, USA) region[a]

Land use type	Median EMC (μg/L) Total copper	Total lead	Total zinc
Overall			
LARW[a]	20	9	151
NSQD[b]	16	16	116
NURP[c]	34	144	160
Residential			
LARW	18	8	103
NSQD	12	12	73
NURP	33	144	135
Commercial			
LARW	17	4	156
NSQD	17	18	150
NURP	29	104	226
Industrial			
LARW	33	19	550
NSQD	22	25	210
NURP	27	114	154
Open space			
LARW	8	1	23
NSQD	5.3	5	39
NURP	NA[d]	30	195

[a] LARW = Los Angeles River watershed. Values from the present study (2001–2005).
[b] Pitt et al. [11].
[c] U.S. Environmental Protection Agency [10].
[d] NA = not analyzed.

Further research is needed to directly assess the relationship between trace metal concentrations and particle-size distributions in storm water runoff from ME and LU sites to better understand the fate, transport, and treatment of trace metals in urban runoff. Storm water–borne trace metals typically are associated with particulates to varying degrees, depending on the metal and the size distribution of suspended solids in the storm water runoff. Furthermore, the particle-size distribution and metal partitioning can change over the course of a storm event [43]. Understanding the dynamic partitioning of trace metals to particles of various size is important for being able to estimate temporal and spatial patterns of trace metal deposition in estuaries and harbors and should be an area of future investigation. Our understanding about the mechanisms of metal loading from urban land uses also could be improved by estimating the percentage of directly connected impervious area in each land use category (i.e., percentage rooftop, sidewalk, paved driveway, and street) and its impacts on storm water runoff concentrations and loads. This could allow identification of critical source areas, which in turn could reduce the amount of land use area needing best-management practices.

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