SOURCES, PATTERNS AND MECHANISMS OF STORM WATER POLLUTANT LOADING FROM WATERSHEDS AND LAND USES OF THE GREATER LOS ANGELES AREA, CALIFORNIA, USA

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EXECUTIVE SUMMARY

Storm water runoff and the associated contaminants from urban areas is one of the leading sources of water quality degradation in surface waters (US EPA 2000). Runoff from pervious and impervious areas (i.e., streets, parking lots, lawns, golf courses and agricultural land) carries accumulated contaminants (i.e., atmospheric dust, trace metals, street dirt, hydrocarbons, fertilizers and pesticides) directly into receiving waters (Novotny and Olem 1994). Because of the environmental effects of these contaminants, effective storm water monitoring and management requires identification and characterization of the sources, patterns, and mechanisms that influence pollutant concentrations and loads. Concentrations and loads of pollutants in urban storm water have been documented in some portions of the country (Hoffman et al. 1984; Buffleben et al. 2002; Simpson et al. 2002); however, little is known about the mechanisms and processes that influence spatial and temporal factors that affect the magnitude and patterns of constituent loading from specific land uses. Specifically, storm water managers need to understand how sources vary by land use type, how patterns of loading vary over the course of a single storm, how loading varies over the course of a storm season, and how applicable national or regional estimates of land use-based loading are to southern California.

To investigate these issues, the Southern California Coastal Water Research Project (SCCWRP) conducted a storm water sampling program over five seasons (2000-01 through 2004-2005). Constituent concentrations were measured over the entire storm duration from eight different land use types over 11 storm events in five watersheds in the greater Los Angeles, CA region (Figure ES-1). In addition, runoff samples were also collected from twelve mass emission sites (in-river) during 15 different storm events. A total of 71 site-events were sampled, comprised of 33 land use site-events and 38 mass-emission site events. These data were collected to better characterize contributions of specific land use types to loading of bacteria, trace metals, and organic compounds and to provide data for watershed model calibration. The specific goals of this study were (1) to examine constituent event mean concentrations (EMC), fluxes, and mass loadings associated with storm water runoff from representative land uses; (2) to investigate within storm and within season factors that affect constituent concentrations and fluxes; (3) to evaluate how constituent loadings compare to loadings from point sources, and (4) to assess how the concentrations of constituents in runoff compare to published data and water-quality criteria.

To understand the complex spatial and temporal patterns that affect storm water runoff in the greater Los Angeles region, runoff and constituent concentrations from a variety of land uses and mass emission sites were sampled over a range of different storm sizes and antecedent conditions. Between 10 and 15 discrete grab samples were collected for each site-event and the samples analyzed individually to provide time vs. concentration plots (i.e., pollutographs) for each site-event. Samples were analyzed for a broad range of constituents including trace metals, organic compounds and bacteria. Storms were targeted to capture early vs. late season conditions and large vs. small rainfall events. Understanding both intra-storm and inter-storm variability provides a more complete assessment of factors that influence constituent loading, and will allow us to develop dynamic watershed models that are able to predict pollutant runoff from specific land use types and watersheds under a variety of conditions.

General Conclusions

1. Storm water runoff from watershed and land use based sources is a significant contributor of pollutant loading and often exceeds water quality standards

Results of this study indicate that urban storm water is a substantial source of a variety of constituents to downstream receiving waters. Substantially high constituent concentrations were observed throughout the study at both mass emission (ME) and land use (LU) sites. Constituent concentrations frequently exceeded water quality criteria. Storm water concentrations of trace metals exceeded California Toxic Rule (USEPA 2000) water quality criteria in more than 80% of the wet weather samples collected at ME sites. This was partly due to industrial land use sites where 100% and 87% of runoff samples exceeded water quality criteria for zinc and copper, respectively. Furthermore, fecal indicator bacteria (FIB) at both ME and LU sites consistently exceeded California single-sample water quality standards. In fact levels of FIB at the recreational (horse) and agricultural LU sites were as high as those found in primary wastewater effluent in the U.S., with densities of 10^6-10^7 MPN/100mL.

2. All constituents were strongly correlated with total suspended solids

Land use had a strong influence on constituent concentrations. Total suspended solids (TSS) was strongly correlated with constituent EMCs at most land use sites, although not all correlations were statistically significant. This correlation was primarily influenced by highly urbanized land uses and a single undeveloped open space land use. High TSS loads in rivers contribute to water quality impairments, habitat loss and to excessive turbidity resulting in impairments in recreational, fish/wildlife, and water supply designated uses of the rivers. These results suggest that controlling TSS at specific land uses may result in reducing other particle-bound constituents.

3. Storm water EMCs, fluxes and loads were substantially lower from undeveloped open space areas when compared to developed urbanized watersheds

Storms sampled from less developed watersheds (i.e., Santa Monica Canyon and Arroyo Sequit) produced constituent EMCs and fluxes that were one to two orders of magnitude lower than comparably sized storms in urbanized watersheds (i.e., Los Angeles River and Ballona Creek) (Figure ES-2). Furthermore, the higher fluxes from developed watersheds were generated by substantially less rainfall than the lower fluxes from the undeveloped watersheds, presumably due to increased impervious surface area in developed watersheds. Stein and Yoon (2007) reported similar wet weather runoff results from undeveloped land uses while investigating pollutant contributions from natural sources. The contrasts between the different watershed scale mass-emission sites were also apparent at the small, homogeneous land use sites.

4. Land use based sources of pollutant concentrations and fluxes varied by constituent

No single land use type was responsible for contributing the highest loading for all constituents measured. For example industrial land use sites, contributed higher storm EMCs and fluxes of all trace metals than other land use types. (Figure ES-3). Recreational (horse) land use sites contributed significantly higher storm fluxes for *E. coli* while agricultural land use sites contributed the highest TSS fluxes. Substantially higher TSS fluxes were also observed at the industrial sites. PAHs were not preferentially generated by any one land use type, rather analyses of individual PAHs demonstrated a consistent predominance of high molecular weight (HMW) PAH compounds indicative of regional pyrogenic PAHs (i.e., atmospheric deposition) as a major source material of the PAHs found in urban storm water.

5. Storm water runoff contributed a similar range of constituent loading to regional point sources

Storm water runoff of trace metals from the urban watersheds in this study produced a similar range of annual loads as those from point sources; such as large publicly owned treatment plants (Table ES-1). Nevertheless, when combined with dry estimates of pollutant loading from Stein and Tiefenthaler (2005), the total non-point source contribution from all watersheds in the greater Los Angeles area far exceeds that of the point sources (Table ES-1).

6. The Los Angeles region contributed a similar range of storm water runoff pollutant loads as that of other regions of the United States

Comparison of constituent concentrations in storm water runoff from land use sites from this study reveal median EMCs that are comparable to current U.S. averages reported in the National Storm water Quality Database (NSQD; Pitt *et al*, 2003) (Figure ES-4). Comparison to the NSQD data set provides insight to spatial and temporal patterns in constituent concentrations in urban systems. Similarities between levels reported in the NSQD and this study suggest that land-based concentrations in southern California storm water are generally comparable to those in other parts of the country.

7. Storm water runoff concentrations improved over time when compared with the Nationwide Urban Runoff Program (NURP.

Results showed an improvement in water quality between constituent concentrations reported by NURP in 1983 and those observed in this study (Los Angeles River Watershed (LARW). Long-term overall trends of decreasing median constituent EMCs were observed at all land uses with the exception of total zinc, which showed an increase in median EMCs over the course of the studies (Figure ES-4). For example, lead concentrations have exhibited a 10-fold reduction over the last 20 years. Relatively low lead concentrations may reflect fate and transport characteristics of the particular systems sampled. However, a more likely explanation is that low concentrations of lead observed in these studies can be attributed to regulations banning the use of leaded gasoline.

8. Peak concentrations for all constituents were observed during the early part of the storm

Constituent concentrations varied with time over the course of storm events. For all storms sampled, the highest constituent concentrations occurred during the early phases of storm water runoff with peak concentrations usually preceding peak flow (Figure ES-5). In all cases, constituent concentrations increased rapidly, stayed high for relatively short periods and often decreased back to base levels within one to two hours. In contrast, the developed LU (recreational (horse) site; Figure ES 1-5c) had a peak concentration followed by intra-storm variable concentrations that mimicked flow. Although the pattern of an early peak in concentration was comparable in both large and small developed watersheds (Ballona Creek; Figure ES-5a, Los Angeles River Figure ES-5b), the peak concentration tended to occur later in the storm and persist for a longer duration in the smaller developed watersheds. Therefore monitoring programs must capture the early portion of storms and account for intra-storm variability in concentration in order 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.

9. The magnitude of a mass first flush effect at land use sites was a function of watershed size

Storm mass loading is a function of both concentration and magnitude of flow at various points during a storm. Cumulative mass loading of constituents from ME sites generally exhibited a weak “first flush” for trace metals and bacteria. For PAHs, a moderate first flush was observed where between 40% and 60% of the load was discharged during the first 25% of storm volume. In contrast to the ME sites, cumulative mass loading plots from small, homogenous land use sites exhibited moderate first flush for all constituents sampled. When all developed sites were analyzed together, the magnitude of the first flush effect decreased with increasing watershed size (Figure ES-6). The inverse relationship between first flush and catchment size has several potential mechanistic explanations including differences in relative pervious area, spatial and temporal patterns in rainfall, and pollutant transport through the catchment. Ultimately, the differences in first flush, whether due to imperviousness, travel time, or rainfall variability, suggest that management strategies aimed at capturing constituent loads should focus on more than just the initial portion of the storm at moderate to large catchments.

10. Highest constituent loading was observed early in the storm season with intra-annual variability driven more by antecedent dry period than amount of rainfall

Seasonal differences in constituent EMCs and loads were consistently observed at both ME and LU sites. In general, early season storms (October – December) produce significantly higher constituent EMCs and loads than late season storms (April-May), even when rainfall quantity was similar (Figure ES-7). This suggests that the magnitude of constituent load associated with storm water runoff depends, at least in part, on the amount of time available for pollutant build-up on land surfaces. The extended dry period that typically occurs in arid climates such as southern California maximizes the time for constituents to build-up on land surfaces, resulting in proportionally higher concentrations and loads during initial storms of the season. 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.

Further Research

This study establishes the relative contributions of land uses and watersheds to constituent loading in receiving water bodies. Having statistically significant data sets at regional, seasonal, and land use levels enables modelers to use the information for more sensitive calibration of models that may be used for contaminant load allocations. Similarly, these data sets can assist storm water engineers in the design of more effective monitoring programs and better performing treatment practices (i.e., BMPs) that address specific rainfall/runoff conditions.

Further research is needed to directly assess the relationship between constituent concentrations and particle-size distributions in storm water runoff from mass emission and land use sites to better understand the fate, transport and treatment of constituents in urban runoff.

Storm water borne metals, PAHs and (to a lesser extent) bacteria are typically associated with particulates to varying degrees depending on the constituent and the size distribution of suspended solids in the storm water runoff. Furthermore, the particle size distribution, and constituent partitioning can change over the course of a storm event (Furumai et al. 2002, Stein and Yoon 2007). Understanding the dynamic partitioning of constituents to various size particles is important to being able to estimate temporal and spatial patterns of constituent deposition in estuaries and harbors, and should be an area of future investigation.

Our understanding of the mechanisms of constituent loading from urban land uses could also be improved by estimating the percent of directly connected impervious area (DCIA) in each land use category (i.e., percent rooftop, sidewalks, paved driveways and streets) and its impacts on storm water runoff concentrations and loads. This could allow identification of critical source areas, which in turn could provide for more precise estimates of loading and more focused application of best management practices.

Table ES-1. Mean annual (± 95% confidence intervals) trace metal loading in the Los Angeles coastal region from different sources (mt = metric tons).

	Mean Annual Load / Year (mt ± 95% CI)		
Source	Total Copper	Total Lead	Total Zinc
Point Source Data[1,2] (2000-05)			
Large Publicly Owned Treatment Plants (POTWs)	10.9 ± 6.8	0.8 ± 0.8	13.9 ± 7.6
Low Volume Waste Power Generating Stations (PGS)	0.01	0.00	0.09
Wet Weather Runoff (2000-05)			
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**
2000-02 Dry Weather Urban Runoff [3,4]			
Los Angeles River	2.9 ± 19.9	0.1 ± 1.2	10.4 ± 80.6
Ballona Creek	0.2 ± 0.3	0.1 ± 0.4	0.7 ± 0.6
Total Annual Dry Weather Runoff	**3.1 ± 20.2**	**0.2 ± 1.6**	**11.1 ± 81.2**

[1] SCCWRP Biennial Report 2004-06 (Lyons G, Stein E).
[2] SCCWRP Biennial Report 2003-04 (Steinberger A, Stein E); PGS data represents year 2000 only.
[3] American Water Resources Association in Press (Stein E, Ackerman D).
[4] Water, Air and Soil Pollution, 2005. Vol. 164 (Stein E, Tiefenthaler L).

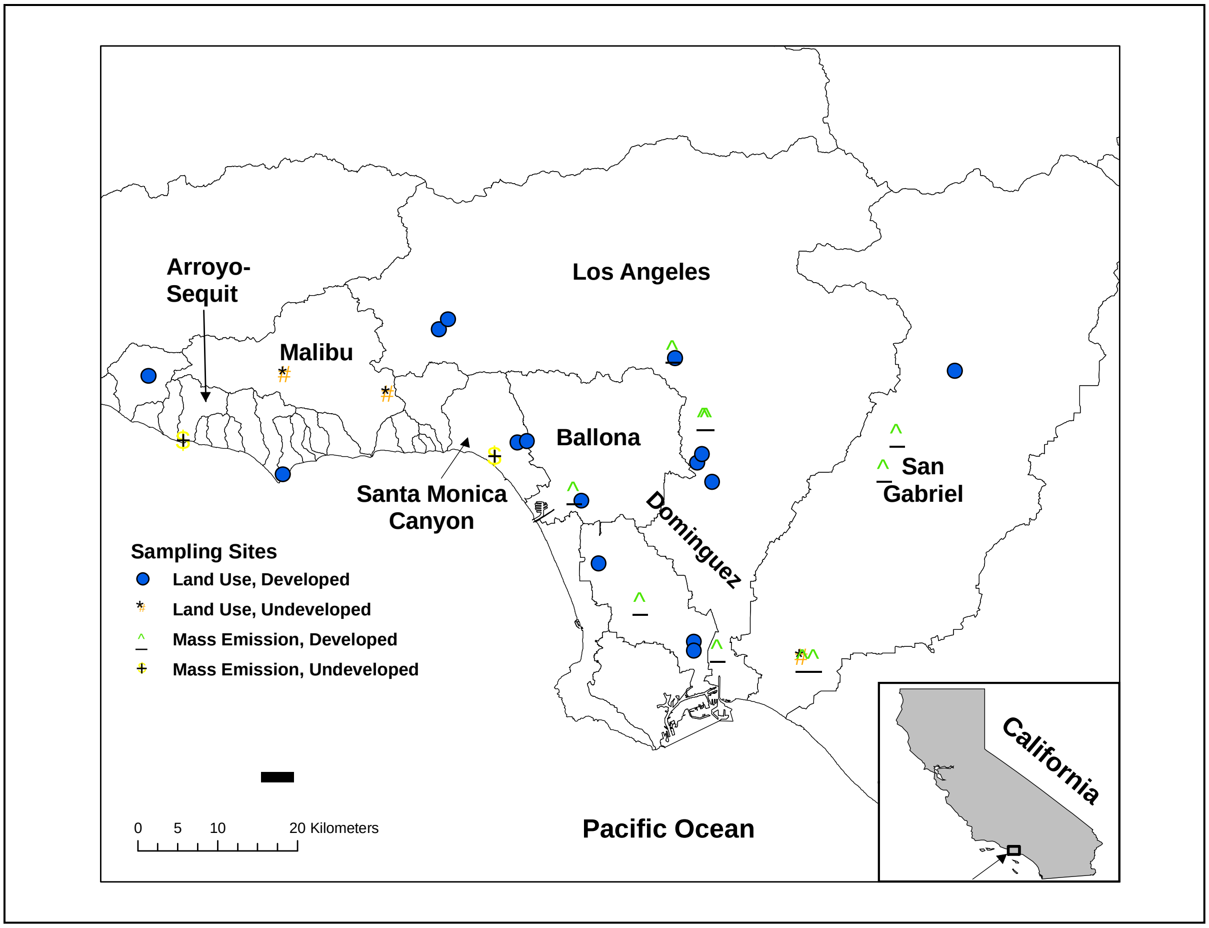


Figure ES-1. Map of in-river mass emission and land use sampling sites and watersheds within the greater Los Angeles region, California, USA.

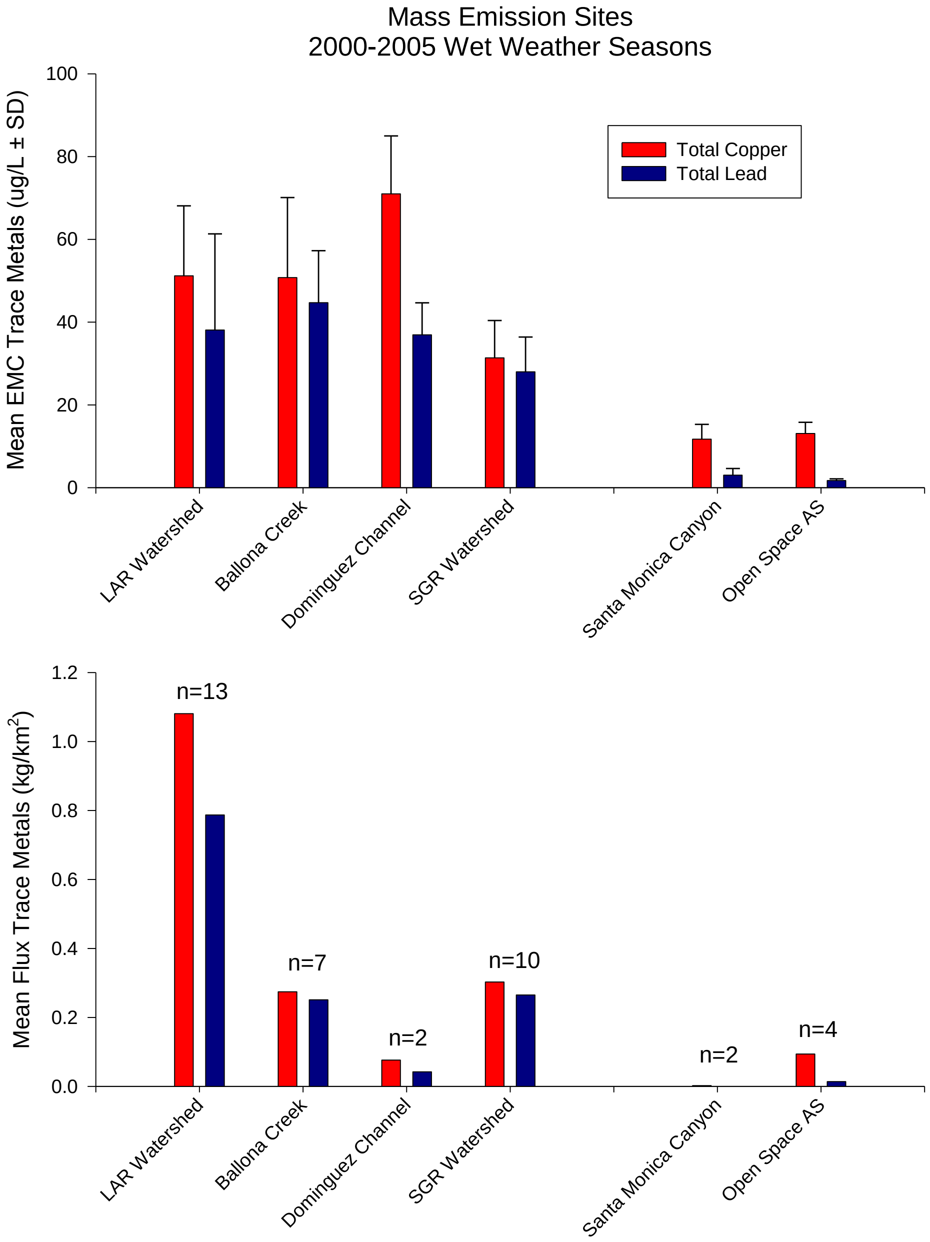
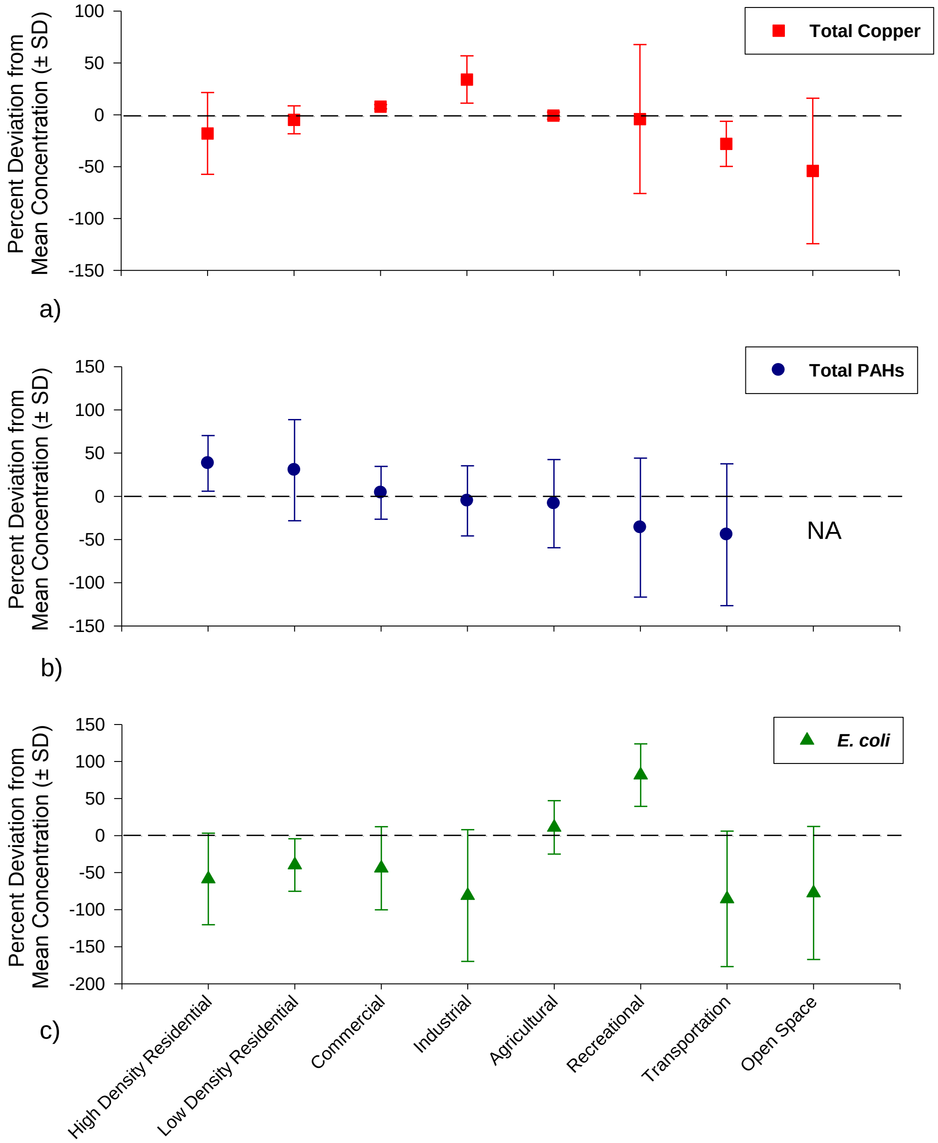


Figure ES-2. Average event mean concentrations (EMCs; a) and fluxes b) of total copper and lead loading from southern California watersheds during the 2000-2001 to –2004-2005 storm seasons. A similar pattern of higher loadings for the mass emission sites was observed for all other constituents measured in the study as well. Los Angeles River (LAR), San Gabriel River (SGR), and Arroyo Sequit (AS), number of storm events (n), and standard deviation (SD).



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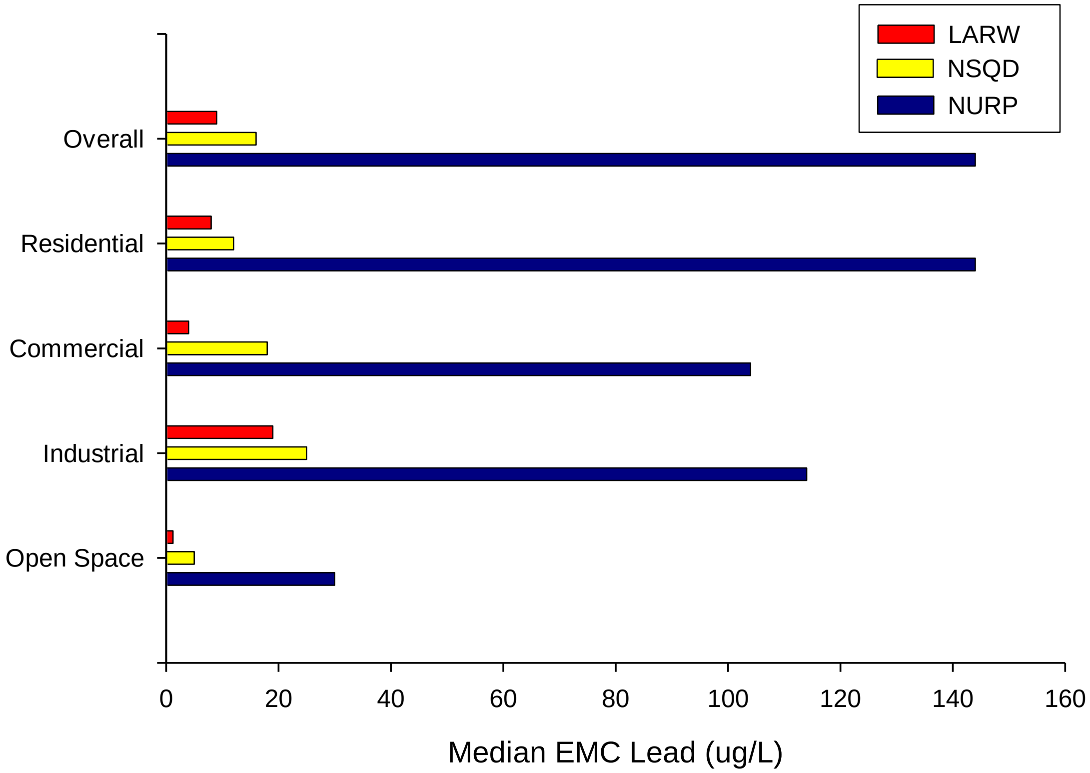

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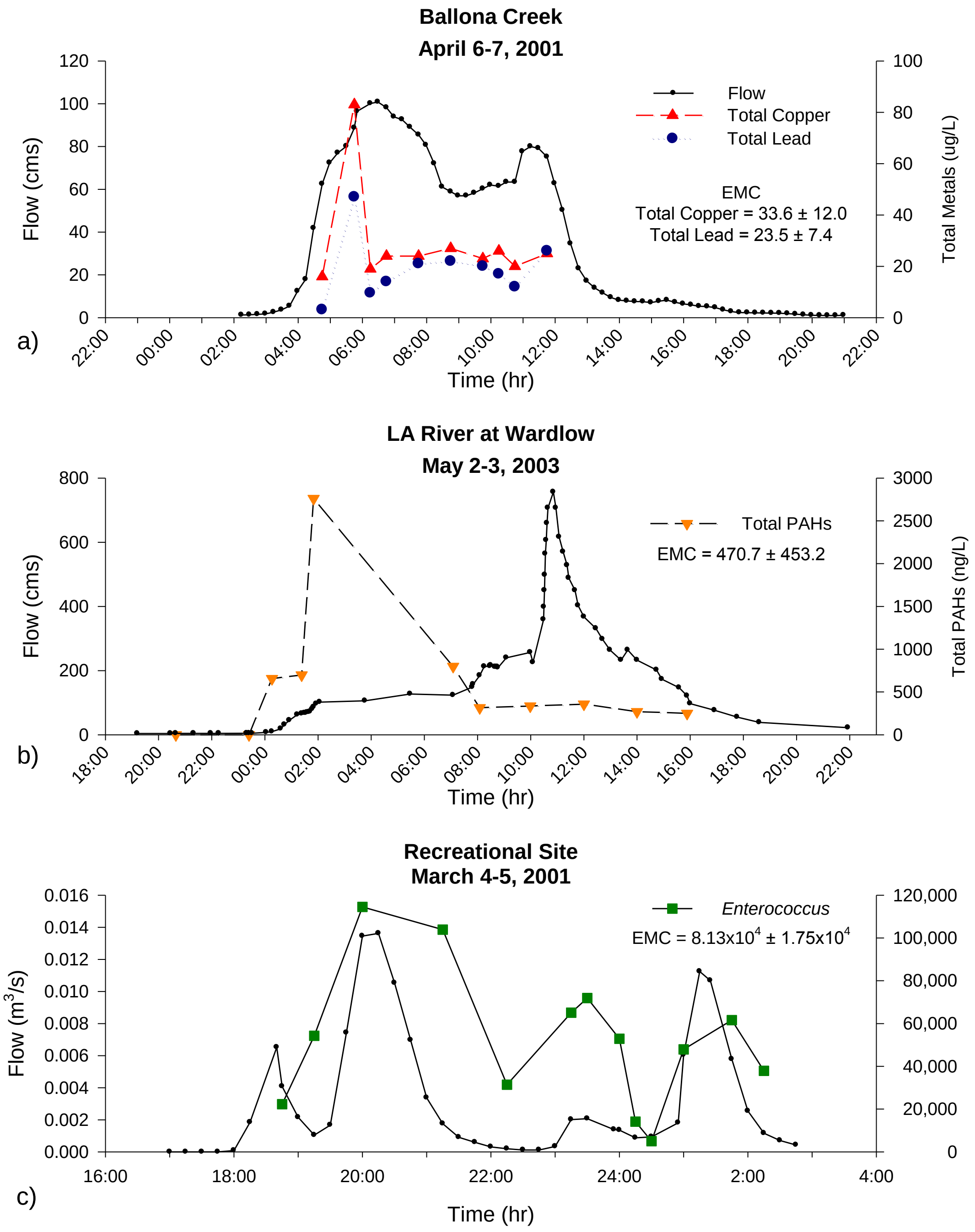
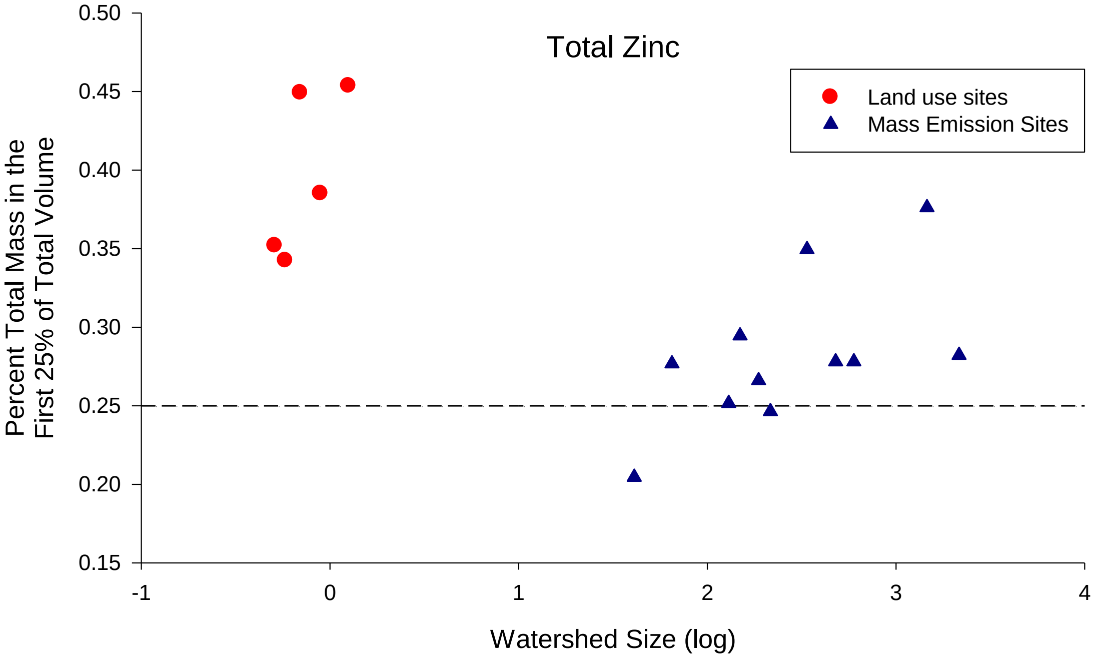


Figure ES-5. Variation in constituent concentrations with time for a storm event in the developed Ballona Creek a) and Los Angeles River watersheds b) and the developed recreational (horse) land use site c).



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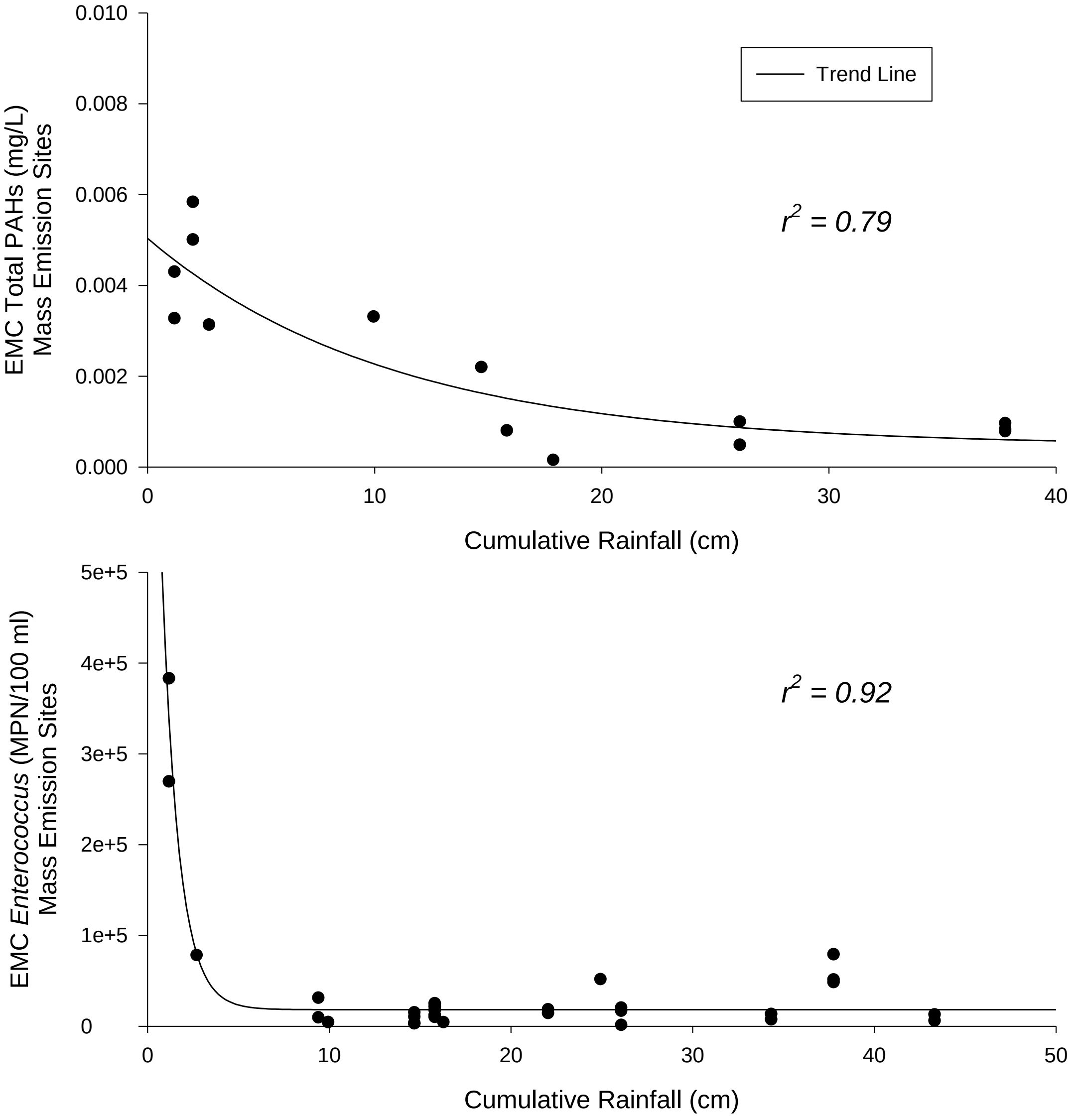

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LIST OF ACRONYMS

AV	Acoustic Doppler Velocity
BMP	Best Management Practices
BST	Bacterial Source Tracking
CDF	Cumulative Density Frequency
CTR	California Toxics Rules
DCIA	Directly Connected Impervious Area
E. coli	*Escherichia coli*
EMC	Event Mean Concentration
FIB	Fecal Indicator Bacteria
FWM	Flow Weighted Mean
HMW	High Molecular Weight
ICPMS	Inductively Coupled Plasma-Mass Spectroscopy
LARW	Los Angeles River Wet-weather
LMW	Low Molecular Weight
ME	Mass Emission
NPDES	National Pollutant Discharge Elimination System
NSQD	National Storm water Quality Database
NURP	National Urban Runoff Program
PAHs	Polycyclic Aromatic Hydrocarbons
PCs	Principal Components
PCA	Principle Component Analysis
SCCWRP	Southern California Coastal Water Research Project
TSS	Total Suspended Solids
USEPA	United States Environmental Protection Agency

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SECTION 1. INTRODUCTION

Urban storm water runoff has been identified as a major cause of degradation of surface water quality (Characklis and Wiesner 1997, Davis et al. 2001, Buffleben et al. 2002). Studies in southern California have documented trace metals, polycyclic aromatic hydrocarbons (PAHs) and fecal indicator bacteria (FIB) as major constituents of concern in storm water runoff (Buffleben et al. 2002, McPherson et al. 2002; Gigliotti 2000; Menzie et al. 2002). As a result numerous stream reaches in the greater Los Angeles Basin are listed as impaired waterbodies under Section 303(d) of the Clean Water Act for a range of constituents (LARWQCB 1998a and 2002).

Past monitoring and assessment efforts have provided important insight into the general patterns of storm water loading. Previous studies have documented that the most prevalent metals in urban storm water are zinc, copper, lead, and to a lesser degree nickel and cadmium (Sansalone and Buchberger 1997, Davis et al. 2001). Recent FIB studies using *Escherchia coli* (*E. coli*), *Enterococcus* spp. and total coliforms (Noble et al. 2003 and Stein and Tiefenthaler 2005) have documented freshwater outlets such as storm drains to be especially high contributors of bacterial contamination. Routine storm water monitoring programs focus on quantification of average concentration or load at the terminal watershed discharge point. While important for overall status and trends assessment, such monitoring provides little insight into the mechanisms and processes that influence constituent levels in storm water.

To effectively manage storm water, managers need to gain a deeper understanding of factors that affect storm water quality. In particular, managers need to understand the sources, processes and mechanisms that affect runoff and associated constituent loading. Specifically, managers need to understand how sources vary by land use (LU) type, how patterns of loading vary over the course of a single storm, how loading varies over the course of a storm season, and how applicable national or regional estimates of LU based loading are to southern California. Such information is critical to designing and implementing effective management strategies and for calibrating watershed models that can be used to evaluate proposed strategies.

The goal of this study is to quantify the sources, patterns of concentrations, fluxes, and loads of trace metals, PAHs and fecal indicator bacteria from representative land use types in the greater Los Angeles, California region. In addition to quantifying differences between land use categories, our goal is to investigate within storm and within season patterns in order to identify mechanisms that influence patterns of constituent loadings. Finally, we compare the estimates of storm water metals, total suspended solids (TSS) and *E. coli* loading to data from point and non-point sources and to existing water quality standards to provide context for the magnitude of importance of storm water to overall metals, TSS and *E. coli* loading for the region.

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SECTION 2. METHODS

Study Areas

Storm water runoff was sampled from 19 different land use (LU) sites and 12 mass emission (ME) sites throughout the greater Los Angeles area (Figure 2-1). The 19 LU sites represented homogeneous distributions of eight land use types including high density residential, low-density residential, commercial, industrial, agricultural, recreational (horse), transportation or open space. The LU sites ranged in size from 0.002 to 2.89 km^2 (see Appendix A for more detailed land use information). 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. There were 10 urban ME sites and two nonurban ME sites 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 non urban watersheds examined in this study. The 12 ME sites ranged in size from 31 to 2,161 km^2.

Rainfall

All of the LU and ME sites were sampled during the 2000–2001 through 2004–2005 storm seasons. Winter storms typically occur between October and May, providing 85% to 90% of the annual average rainfall (38.4 cm; Ackerman and Weisberg 2003). Annual precipitation in Los Angeles can be highly variable. For example, the 2004-2005 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 (National Weather Service; http://www.wrh.noaa.gov/lox/). In contrast, the 2001-2002 rainfall season totaled a mere 11.2 cm, 27 cm below the seasonal average. Consequently, the study period encompassed a wide range of precipitation conditions.

Sampling and Analysis

Twenty discrete storms were sampled, with each site sampled between one to seven individual storm events (Tables 2-1a and 2-1b). Rainfall amounts ranged from 0.12 to 9.68 cm and antecedent conditions ranged from 0 to 142 d without measurable 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 previous measurable rain. Water quality sampling was initiated when flows were greater than base flows by 20%, 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 orders of magnitude during storm events, these criteria are considered 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 (AV) meter. The AV 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 described by Leecaster et al. (2001). 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 one of three methods: 1) by 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, 2) by direct filling of the sample bottle either by hand or affixed to a pole, or 3) 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.

Chemical Analysis

Total Suspended Solids (TSS)

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

Trace Metal Analysis

Whole samples (particulate plus dissolved) were prepared by nitric acid digestion followed by analysis using inductively coupled plasma-mass spectroscopy (ICPMS) according to USEPA Method 200.8 (US EPA 1991). 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 method detection limits with duplicate samples within 10% reproducible difference.

Polycyclic Aromatic Hydrocarbon (PAHs) Analysis

Total PAH (∑PAH) was computed as the sum of the 26 individual PAH compounds quantified (Table 2-2). The individual PAHs were divided into low-molecular-weight (LMW) PAH compounds (<230, two to three rings) and high-molecular weight (HMW) PAH compounds (>230, four to six rings) for source analysis. The 26 specific PAHs were extracted, separated, and quantified by capillary gas chromatography coupled to mass spectrometry according to U.S. Environmental Protection Agency (US EPA) method 625 (US EPA 1991).

Fecal Indicator Bacteria Analysis

Concentrations of *E. coli* and *Enterococcus* spp.were measured by defined substrate technology using kits supplied by IDEXX Laboratories, Inc. (Westbrook, ME) according to the manufacturer's instructions. Briefly, 10-fold and 100-fold dilutions of the water samples were made with deionized water containing the appropriate media and sodium thiosulfate, mixed to dissolve, dispensed into trays (Quanti-Tray/2000), and heat sealed. *E. coli* was measured using the Colilert-18 reagents, while *Enterococcus* spp. were measured using Enterolert reagents. Samples were incubated overnight according to the manufacturer's instructions and inspected for positive wells. Conversion of positive wells from these tests to a most probable number (MPN) was done following Hurley and Roscoe (1983).

Data Analysis

Data analyses was broken into three sections; 1) comparison between LU sites; 2) comparison between developed and undeveloped watershed; and 3) assessment of within-season and within-storm variability. Comparison between LU sites focused on event mean concentrations (EMCs), load, flux, and principle components analysis (PCA). Prior to analysis constituent concentrations were log-transformed to improve normality. In all cases, non-detectable results were assigned a value of 1/2 the minimum detection limit, based on the inability to log transform a value of zero.

The EMC was calculated using Equation 1:

$$EMC = \frac{\sum_{i=1}^{n} C_i * F_i}{\sum_{i=1}^{n} F_i} \qquad \text{(Equation 1)}$$

where: EMC = flow-weighted mean for a particular storm; C_i = individual runoff sample concentration of *i*th sample; F_i = instantaneous flow at the time of *i*th sample; and n = number of samples per event. Constituent concentrations were log-transformed prior to calculations to improve normality. In all cases, non-detectable results were assigned a value of one-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 ANOVA, with a significance level $(p) < 0.05$, followed by Tukey-Kramer *post-hoc* test for multiple comparisons (Sokal and Rohlf 1969).

The PCA was used to identify the most important factors (i.e., groups of parameters, storm size and storm season) controlling data variability (Helene *et al*. 2000, SAS Inc. 2003, http://www.sas.com/textbook). As a multivariate data analysis technique, PCA reduces the number of dependent variables without sacrificing critical information (Qian et al. 1994). The number of principal components (PCs) extracted (to explain the underlying data structure) was defined by using the Kaiser criterion (Kaiser 1960) where only the PCs with eigenvalues 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). PCA and ANOVA were used in a two-step process: The PCA was used to identify factors influencing variability and to group data into different sets based on the factors identified. ANOVA was then used to test for significant differences between the classes identified by the PCA.

The second analysis that compared developed and undeveloped ME sites followed similar approach as 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 to December, mid = January to March, and late = April to 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 constituent concentration 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 emission was plotted against cumulative discharge volume during a single storm event (Bertrand-Krajewski et al. 1998). When these curves are close to unity, mass emission is a function of flow discharge. A strong first flush was defined as ≥75% of the mass was discharged in the first 25% of runoff volume. A moderate first flush was defined as ≥30% and ≤75% of the mass discharged in the first 25% of runoff volume. No first flush was assumed when ≤30% of the mass was discharged in the first 25% of runoff volume.

Further Analyses for Individual Constituents

Total Metal Comparison to The California Toxics Rules (CTR)

In order to investigate the percent of samples exceeding water quality standards total metals concentrations were compared to the California Toxics Rules (CTR) for inland surface waters (acute freshwater aquatic life protection standards, US EPA 2000). The standards for total copper, total lead and total zinc are 14.00, 81.65, and 119.82 respectively based on a hardness value of 100 mg/L.

The formula for calculating the acute objectives for copper, lead, and zinc in the CTR take the form of the following equation:

$$CMC = WER * ACF * \exp[(ma)(\ln(hardness)+ba]$$

Where: WER = Water Effects Ratio (assumed to be 1), ACF = Acute conversion factor (to convert from the total to the dissolved fraction), m_A = slope factor for acute criteria, and b_A = y intercept for acute criteria.

The CTR allows for the adjustment of criteria through the use of a water-effect ratio (WER) to assure that the metals criteria are appropriate for the site-specific chemical conditions under which they are applied. A WER represents the correlation between metals that are measured and metals that are biologically available and toxic. A WER is a measure of the toxicity of a material in site water divided by the toxicity of the same material in laboratory dilution water. No site-specific WER has been developed for any of the waterbodies in the Los Angeles River or San Gabriel River watersheds. Therefore, a WER default value of 1.0 was assumed. The coefficients needed for the calculation of objectives are provided in the CTR for most metals.

PAH Source Identification

PAHs were also analyzed to examine sources of PAHs. First, the FWM concentrations from the homogenous land use sites were compared. Differences between land use sites were investigated using a one-way analysis of variance (ANOVA) with a $p < 0.05$ significance level (Sokal and Rohlf 1969). Next, the relative proportion of individual PAH compounds and their ratios were evaluated to determine if the sources of PAHs suggested a pyrogenic (i.e., combustion by-products) or petrogenic (i.e., unburnt petroleum) signature. The ratio of fluoranthene (F) to pyrene (P; F/P) and the ratio of phenanthrene (P) to anthracene (A; P/A) were used to determine pyrogenic versus petrogenic sources of PAH. Pyrogenic sources predominate when F/P ratios approach 0.9 (Maher and Aislabe 1992). Pyrogenic sources predominate when P/A ratios ranged from 3 to 26 (Lake et al. 1979, Gschwend and Hites 1981).

Correlations between TSS, Flow and FIB

To explore the potential link between storm water runoff, TSS and FIB concentrations Spearman Rank correlation coefficients (a nonparametric measure of correlation) were computed between FIB, TSS and stream flow (Townsend 2002).

Cumulative Density Frequency Plots (CDFs) - Bacteria

Fecal indicator bacteria were used to assess whether storm water samples met State of California water quality thresholds by examining the relative frequency of exceedence for all storms combined at both ME and LU sites. Fecal indicator bacterial counts were plotted on logarithmic scales (a scale that minimizes differences and allows widely varying numbers to be shown) and compared to the CA single-sample criterion to estimate percent exceedances. The CA single-sample standard (assembly bill AB411) for ocean beaches has limits of 104 *Enterococcus* spp. bacteria in 100 ml of water, 400 *E. coli* colonies (400 MPN/100ml) and 10,000 total coliforms colonies (10,000 MPN/100mL). Cumulative density frequency plots (CDFs) were produced to compare observed bacterial concentrations to the CA quantitative standards and to calculate accumulated relative exceedance percentages.

An additional data analysis element examined the incidence of exceedences of California's AB411 water quality standards for fecal indicator bacteria compared to the size of the watershed. Watersheds were broken into small (<25 km^2), medium (20 km^2 - 99 km^2), and large (>100 km^2), with at least three watersheds falling into each category.

Constituent Comparison to Nationwide Results

Existing data sets provide insight into land use based loading, but do not provide the mechanistic understanding needed by storm water managers. Between 1977 and 1983 the U.S. EPA funded The Nationwide Urban Runoff Program (NURP), which compiled discharge data from separate storm sewers in different land uses to receiving waters. This project used 81 sites in 28 cities throughout the U.S. and included the monitoring of approximately 2,300 individual storm events (US EPA 1983a). The utility of the NURP data set is somewhat limited because it is 23 years old and only contains data from storm drains (vs. in-river measures). The National Storm water Quality Database (NSQD) was created in 2003 by the University of Alabama and the Center for Watershed Protection to examine more recent storm water data from a representative number of National Pollutant Discharge Elimination System (NPDES) municipal separate storm sewer system (MS4) storm water permit holders (Pitt et al. 2003). The NSQD includes Phase I storm water monitoring data from 369 stations from 17 states and 9 rain zones and a total of 3,770 individual storm events between 1992 and 2003. Unfortunately, the NSQD does not contain any samples from the arid west. Furthermore, neither the NURP nor the NSQD provides time variable measurements that provide an understanding of the temporal processes that affect storm water loading.

Table 2-1a. Summary of storm events sampled at mass emission sites during 2001-2005 in Los Angeles, CA, USA.

Mass Emission Sites	Date of Storm Event	Size (km^2)	Rainfall (cm)	Antecedant Dry Days	Mean Flow (cm/s)	Peak Flow (cm/s)
Los Angeles River Developed Watersheds						
LA River above Arroyo Seco	1/26 - 1/27/2001	1460	1.80	1	27.3	114.0
	2/9 - 2/11/2001		1.42	1	22.4	165.2
	2/12 - 2/13/2001		9.68	0	62.6	262.5
LA River at Wardlow	1/26 - 1/27/2001	2161	1.80	1	15.0	50.9
	2/9 - 2/11/2001		1.42	1	1.4	6.0
	5/2 - 5/3/2003		3.56	4	209.9	756.7
	2/2 -2/3/2004		1.14	6	90.4	375.6
Verdugo Wash	1/26 - 1/27/2001	65	1.80	1	15.0	50.9
	2/9 - 2/11/2001		1.42	1	13.9	90.2
	11/12 - 11/13/2001		9.68	0	68.5	368.2
	10/31 - 11/1/2003		1.74	30	56.5	155.0
Arroyo Seco	2/9 - 2/11/2001	130	3.56	12	2.9	13.5
	4/7/2001		1.78	30	7.8	21.8
Ballona Creek	2/18 - 2/19/2001	338	1.50	3	38.1	107.0
	4/7/2001		1.24	31	32.6	100.9
	11/24 - 11/25/2001		1.52	11	53.1	396.2
	5/2 - 5/3/2003		2.03	4	52.8	134.4
	10/31 - 11/1/2003		2.03	30	62.0	148.1
	2/2 -2/3/2004		2.21	29	55.0	213.9
	2/21 -2/22/2004		3.41	18	44.8	95.6
Dominguez Channel	3/17 - 3/18/2002	187	0.28	10	4.8	14.0
	2/21 -2/22/2004		1.52	18	14.7	35.5
Undeveloped Watersheds						
Santa Monica Canyon	2/9 - 2/11/2001	41	3.74	1	0.1	1.1
	4/7/2001		3.05	50	0.6	3.0
Open Space Arroyo Sequit	5/2 - 5/3/2003	31	5.03	3	0.0	0.0
	2/25 -2/26/2004		4.12	1	3.4	21.9
	12/27 -12/28/2004		5.05	17	0.0	0.2
	1/7/05		5.54	2	0.3	0.9

Table 2-1b. Summary of storm events sampled at land use sites in Los Angeles, California USA during 2000/01-2004/05 storm seasons.

Land-use Type	Date of Storm Event	Size (km^2)	Rainfall (cm)	Antecedant Dry Days	Mean Flow (cm/s)	Peak Flow (cm/s)
High Density Residential (#1)	2/9 - 2/11/2001	0.52	1.93	2	0.082	0.563
	2/18 - 2/19/2001		0.61	4	0.060	0.233
High Density Residential (#2)	3/17 - 3/18/2002	0.02	0.20	10	0.000	0.003
	2/17/2002		0.89	19	0.001	0.006
	2/2 -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 - 2/19/2001	0.98	0.61	4	0.068	0.097
	3/4 - 3/5/2001		1.42	6	0.017	0.071
	2/2 -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	0.89	19	0.002	0.008
Commercial (#3)	2/18 - 2/19/2001	0.06	0.81	4	0.003	0.008
	4/7/2001		2.03	31	0.008	0.018
	3/17 - 18/2002		0.12	9	0.000	0.001
Industrial (#1)	2/9 - 2/11/2001	2.77	0.81	14	0.253	1.801
	2/18 - 2/19/2001		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 - 2/19/2001	0.98	0.81	5	0.014	0.042
	3/4 - 3/5/2001		8.13	3	0.021	0.053
	3/17 - 3/18/2002		0.23	9	0.012	0.031
	2/2 -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 (horse)	2/18 - 2/19/2001	0.03	0.61	4	0.015	0.044
	3/4 - 3/5/2001		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

Table 2-2. List of the 26 individual polycyclic aromatic hydrocarbon compounds measured during the study. Compounds were divided into low-molecular-weight (LMW) compounds (<230, two to three rings) and high-molecular-weight (HMW) compounds (>230, four to six rings) for source analysis.

LMW Compounds	Weight	No. Rings	HMW Compounds	Weight	No. Rings
1-Methylnaphthalene	156+170	2	Benz[a]anthracene	228	4
1-Methylphenanthrene	192+206	3	Benzo[a]pyrene	252	5
2,3,5-Trimethylnaphthalene	155+170	2	Benzo[b]fluoranthene	252	5
2,6-Dimethylnaphthalene	156+170	2	Benzo[e]pyrene	252	5
2-Methylnaphthalene	156+170	2	Benzo[g,h,i]perylene	276	6
2-Methylphenanthrene	192+206	3	Benzo[k]fluoranthene	252	5
Acenaphthene	154	2	Chrysene	228	5
Acenaphthylene	152	3	Dibenz[a,h]anthracene	278	5
Anthracene	178	3	Fluoranthene	202	4
Biphenyl	154	2	Indeno[1,2,3-c,d]pyrene	276	6
Fluorene	166	3	Methylanthracene	222	5
Naphthalene	128	2	Perylene	252	5
Phenanthrene	178	3	Pyrene	202	4

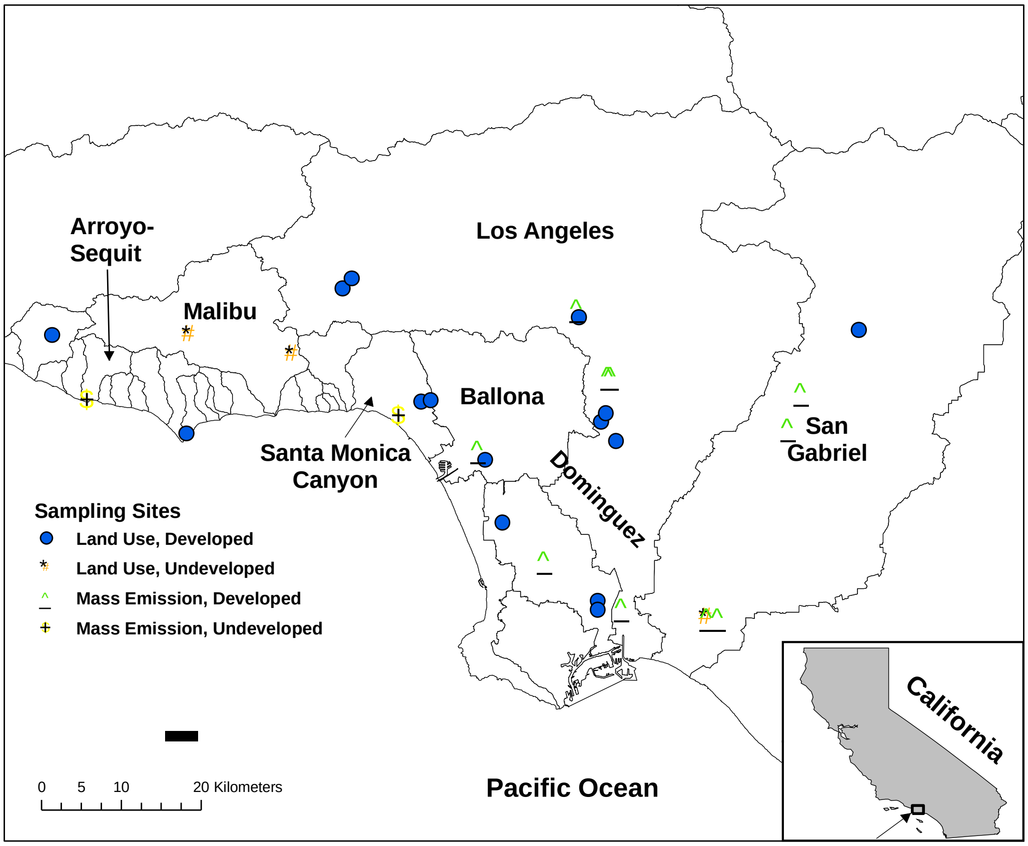

Figure 2-1. Map of watersheds with land use and mass emission sampling sites within the greater Los Angeles region, California USA. Undeveloped >90% open space.

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SECTION 3. TRACE METALS AND TOTAL SUSPENDED SOLIDS

Results

Comparison Between LU Sites

Industrial LU sites contributed a substantially higher flux of copper and zinc compared to the other LU sites evaluated (Figure 3-1). For example, mean total copper flux from the industrial LU was 1,238.0 g/km^2 while mean total copper flux from high density residential and recreational (horse) LU was 100.5 g/km^2 and 190.1 g/km^2, respectively. Trace metal flux from undeveloped LU sites was lower than those observed in developed LUs. 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 agriculture, high density residential, and recreational (horse) LU sites (Figure 3-1). The mean flux of total lead at these three LU sites was at least an order of magnitude greater than any other LU sampled.

Industrial LU had the greatest mean EMC for copper and zinc relative to all other LU sites (Figure 3-2). For example, zinc EMCs at the industrial LU averaged 599.1 μg/l compared to 362.2 μg/l and 207.7 μg/l for commercial and high density residential LU sites, respectively. High density residential had the greatest EMC for lead relative to all other LU sites (Figure 3-2). For example, lead EMCs at high density residential LU averaged 28.4 μg/l compared to 24.1 μg/l and 7.8 μg/l for industrial and agricultural LU sites, respectively. 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 was 7.6 μg/l, 1.2 μg/l, 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 (Figure 3-1). For example, mean TSS flux from the industrial and agricultural LU sites were comparable around 3,150.3 kg/km^2 while mean TSS flux from recreational (horse) and high density residential LU was 2,211.1 kg/km^2 and 91.1 kg/km^2, respectively. Mean TSS flux from undeveloped LU sites were comparable to 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 kg/km^2 and 94.0 kg/km^2 for low density residential and commercial LU sites, respectively.

Recreational (horse) LU had the greatest mean TSS EMC compared to all other LU sites. For example, TSS EMCs at the recreational (horse) LU averaged 530.7 mg/l compared to 111.1 mg/l 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 and industrial LU sites. TSS EMCs from open space LU sites averaged 134.8 mg/l.

Results of the PCA indicated that the land use was a predominate source of variability and that land use categories can be grouped based on differences in their intrinsic runoff and loading characteristics (Figure 3-3). Two Principal Components (PCs) had eigenvalues greater than one, with PC1 and PC2 accounting for 63% and 17% of the total variance, respectively. 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 (horse), and open space LU types were distinct from other LU types based on the concentrations of these constituents. Comparison of the PC scores (or eigenvectors) using a one-way ANOVA indicated that both industrial (group D) and recreational (horse) (group F) sites were significantly different ($p < 0.001$) than open space (group H) sites. All other LU types were indistinguishable.

Comparison Between Developed and Undeveloped Watersheds

The contrasts between the different small, homogeneous LU sites were also apparent at the watershed scale (Figure 3-4). Total copper, total lead and total zinc EMCs and fluxes were significantly greater at ME sites from developed compared to undeveloped watersheds (ANOVA, $p = < 0.001$). 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 copper, total lead and total zinc from undeveloped ME watersheds were 0.06 kg/km^2, 0.01 kg/km^2 and 0.1 kg/km^2 (Figure 3-1), respectively. 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 due to increased impervious surface area in developed watersheds. Similarly, total copper, total lead, and total zinc mean EMC concentrations from developed ME watersheds significantly exceeded those from undeveloped ME watersheds (46.1 ± 14.8 µg/L, 36.3 ± 15.3 µg/L, 251.9 ± 76.9 µg/L vs. 12.6 ± 3.0 µg/L, 2.2 ± 0.8 µg/L, and 27.0 ± 8.4 µg/L, respectively; ANOVA, $p = < 0.001$).

The TSS concentrations from less developed ME watersheds were within the same order of magnitude as those from more developed ME watersheds. For example, annual TSS EMCs for developed ME watersheds averaged 246.3 mg/L for Los Angeles River compared to 217.0 mg/L for the undeveloped ME watersheds. However, TSS fluxes 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/km^2 respectively, while mean TSS flux from undeveloped watersheds was 62.8 kg/km^2.

Within-Season and Within-Storm Variability

There were significant seasonal differences in total metal loading ($p < 0.001$). Early season storms had significantly higher total metal load than late season storms both within and between watersheds, even when rainfall quantity was similar (Figure 3-5). For example, the two early-season storms from Ballona Creek in water years 2001-2002 and 2003-2004 had total copper loadings that were approximately four times larger (ranging from 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 (Figure 3-6). 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 one to two hours. In contrast, the undeveloped watershed (Arroyo Sequit; Figure 3-6a) had appreciably lower peak concentrations than the developed watershed (Ballona Creek; Figure 3-6b). 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 persist for a longer duration in the undeveloped watersheds. Due to the small number of storms sampled in undeveloped watersheds, consistency of these patterns is inconclusive.

Cumulative mass loading of all trace metals from ME sites showed little variation over flow implying there was a weak “first flush” effect at these locations (Figure 3-7). In contrast, cumulative mass loading plots for total copper, lead and 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 (Figure 3-8). 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.

Discussion

Concentrations, flux, and loading in storm water runoff exhibited some key patterns with important implications for managers tasked with controlling trace metals. First, the magnitude of trace metal concentrations and loads were higher at industrial land uses than other land use types. High pollutant loading from industrial sites observed in this study results, at least in part, from intrinsic properties of the industrial land use themselves. These intrinsic properties include high impervious cover (typically greater than 70%) and on-site source generation. Other authors have reported similar results. Sanger et al. (1999) reported that total metal concentrations in runoff from industrial catchments tended to be higher than those from residential and commercial catchments. Park and Stenstrom (2004) used Bayesian networks to estimate pollutant loading from various land uses in southern California and concluded that zinc showed higher EMC values at commercial and industrial land uses. Bannerman et al. 1993 identified industrial land uses as a critical source area in Wisconsin storm water producing significant zinc loads. Bannerman *et al.* 1993 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 up to 75%. In this study high density residential sites had considerably higher lead EMCs than low density residential sites. This difference likely results from greater impervious cover and higher source generation at high density residential sites. High density sites typically have greater road surface and more vehicular use, resulting in more lead. In addition, higher impervious cover more effectively conveys accumulated pollutants to streams and creeks. Substantially higher TSS fluxes were also observed at the industrial sites, which may explain the high trace metal concentrations often associated with fine particles. The City of Austin (City of Austin 1990) found lead and zinc EMCs were related to the TSS EMCs. Consequently, controlling TSS at industrial sites may also 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 land use and mass emission 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 build-up 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 (PAHs) in the Los Angeles region (Sabin and K. 2004, Stein et al. 2006). Han et al. (2006) also reported that antecedent dry period was the best predictor of the magnitude of pollutant runoff from highways. Other researchers (Anderson and Rounds 2003, Ngoye and Machiwa 2004) 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 was also observed for PAHs in the greater Los Angeles area (Stein et al. 2006). Tiefenthaler et al. (2001) observed similar pollutographs that showed peak suspended-sediment concentrations preceding the peak in discharge for the Santa Ana River. Similar time vs. concentration relationships were observed by Characklis and Wiesner (1997), 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, lead and zinc at the small land use sites and a weak first flush at the larger mass emission sites. Lee et al. (2002) 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. (2006) reported that first flush characteristics increased with decreasing drainage area size. Characklis and Wiesner (1997) 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 mass emission catchments.

The inverse relationship between first flush and catchment size has several potential mechanistic explanations including relative pervious 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 that requires greater rainfall energy to washoff particles and associated contaminants. In our 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% impervious area. The undeveloped ME watersheds, which had the least within storm variability, were comprised of only 1% imperviousness. Pitt (1987) 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 our study, the time of travel in the larger ME watersheds like Ballona Creek or Los Angeles River was estimated in hours while travel times in the small LU catchments was 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 mass emission sites.

Spatial and/or temporal differences in rainfall further complicate first flush in large watersheds. Adams and Papa (2000) and Deletic (1998) 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 larger watersheds. When rainfall is distributed uniformly, then 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 (2003) 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 they were due to 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 goal is to capture a majority of metals load.

Urban storm water runoff from this study appeared worthy of management concern because it represented a large mass emission source that frequently exceeded water quality criteria (Table 3-1). Cumulatively, the annual average loading of total copper, lead, and 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 prior to 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 (Young *et al.* 1980), storm water concentrations of copper and zinc exceeded California Toxic Rule (US EPA 2000) water quality criteria in more than 80% of the wet weather samples collected at mass emission sites. This was partly due to 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% of its runoff samples, respectively. Only 8% to 9% of the runoff samples exceeded the water quality criterion for lead at commercial or industrial LU sites. Hall and Anderson (1988) concluded that industrial and commercial land use sites were the major source of trace metals most often considered toxic to aquatic invertebrates, with runoff from the commercial sites proving most frequently toxic to the test organism.

The focus on LU sites in this study enabled the comparison of median EMCs with data sets collected from other parts of the nation (Table 3-2). All of 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 (Pitt et al. 2004). With the exception of the open LU, all of the median EMCs for zinc were greater at LU sites in Los Angeles than median EMCs at LU sites reported in the NSQD. In contrast, all of the median EMCs for lead were lower at LU sites in Los Angeles than median EMCs at LU sites reported in the NSQD. Of the 15 LU – EMC combinations, all but one of the median EMCs (industrial zinc) were lower in Los Angeles than median EMCs reported by NURP (US EPA 1983; Table 3-2). Unlike the NSQD that was focused on data from the 1990's, NURP data was collected during the 1970's. Therefore, the differences between median EMCs from NURP and median EMCs from Los Angeles were also a function of time. Certainly this factor affected median EMCs for lead, which was phased out of gasoline in the mid-1980s (Marsh and Siccama 1997, Hunt et al. 2005).

Further research is needed to directly assess the relationship between trace metal concentrations and particle-size distributions in storm water runoff from mass emission and land use sites to better understand the fate, transport and treatment of trace metals in urban runoff. Storm water borne trace metals are typically 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 (Furumai et al. 2002). Understanding the dynamic partitioning of trace metals to various size particles is important to 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 of the mechanisms of metal loading from urban land uses could also be improved by estimating the percent of directly connected impervious area (DCIA) in each land use category (i.e., percent rooftop, sidewalks, paved driveways and streets) and its impacts on storm water runoff concentrations and loads. This could allow identification of critical source areas, which in turn could allow for more focused application of best management practices.

Table 3-1. Mean annual (± 95% confidence intervals) trace metal loading from different sources (mt = metric tons).

	Mean Annual Load / Year (mt ± 95% CI)		
	Total Copper	Total Lead	Total Zinc
Point Source Data[1,2] (2000-2005)			
Large Publicly Owned Treatment Plants (POTWs)	10.9 ± 6.8	0.8 ± 0.8	13.9 ± 7.6
Low Volume Waste Power Generating Stations (PGS)	0.01	0.00	0.09
Wet Weather Runoff (2000-2005) [3]			
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**

[1] SCCWRP Biennial Report 2004-06 (Lyons G, Stein E).
[2] SCCWRP Biennial Report 2003-04 (Steinberger A, Stein E); PGS data represents year 2000 only.
[3] This study

Table 3-2. Comparison of Nationwide Urban Runoff Program (NURP) and National Storm water Quality Database to trace metals concentrations from specific land uses in the Los Angeles, California USA region. Median event mean concentration (EMCs) are in µg/L .

	Constituent Median EMC (µg/L)		
Land use Type	Total Copper	Total Lead	Total Zinc
Overall			
LARW[1]	20	9	151
NSQD[2]	16	16	116
NURP[3]	34	144	160
Residential			
LARW[1]	18	8	103
NSQD[2]	12	12	73
NURP[3]	33	144	135
Commercial			
LARW[1]	17	4	156
NSQD[2]	17	18	150
NURP[3]	29	104	226
Industrial			
LARW[1]	33	19	550
NSQD[2]	22	25	210
NURP[3]	27	114	154
Open Space			
LARW[1]	8	1	23
NSQD[2]	5	5	39
NURP[3]	NA[4]	30	195

[1] 2001-2005 This Study

[2] The National Storm water Quality Database (NSDQ), Pitt et al. (2003)

[3] Nationwide Urban Runoff Program (USEPA 1983a)

[4] NA = Not analyzed

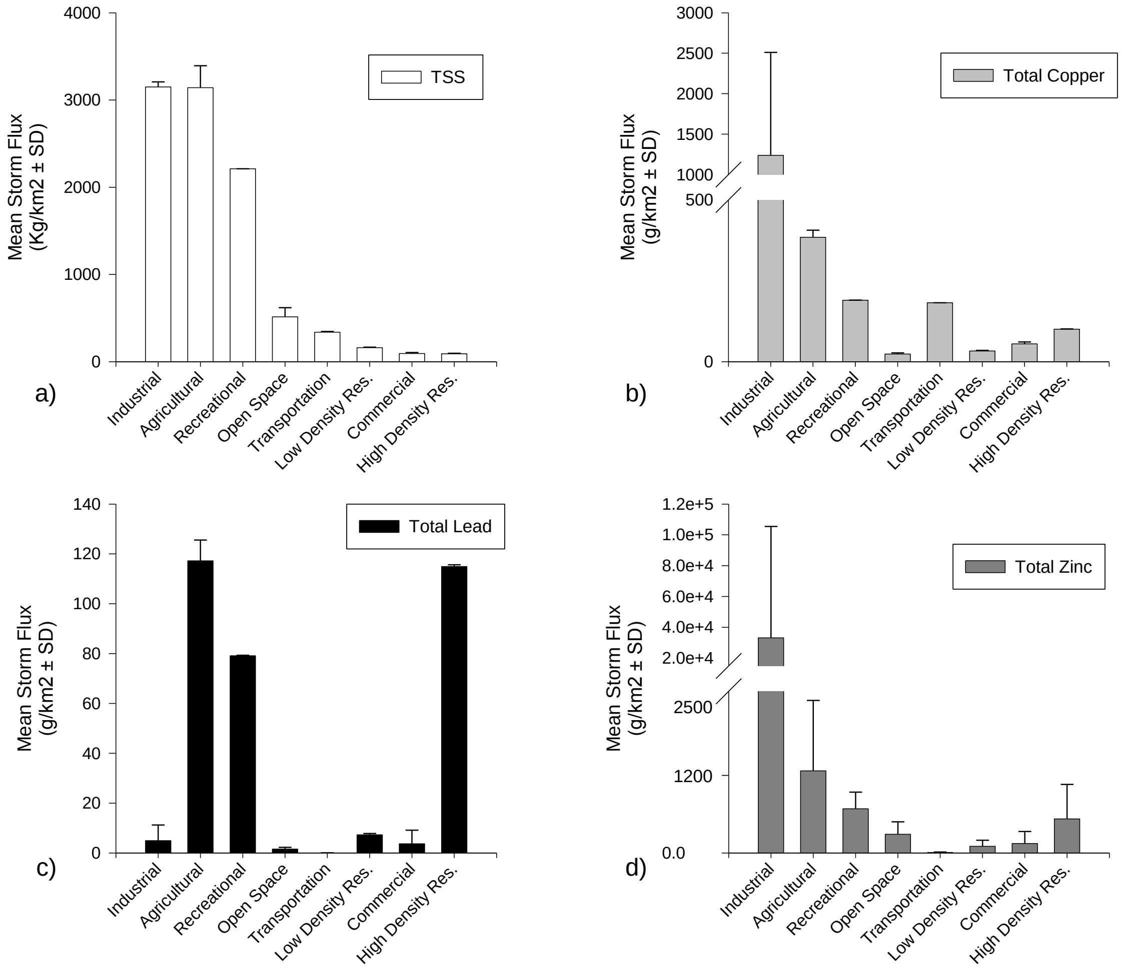

Figure 3-1. Mean storm flux of total suspended solids (TSS; a), total copper b), total lead (c), and total zinc (d) at land use sites during 2000/01-2004/05 storm seasons. Standard deviation (SD).

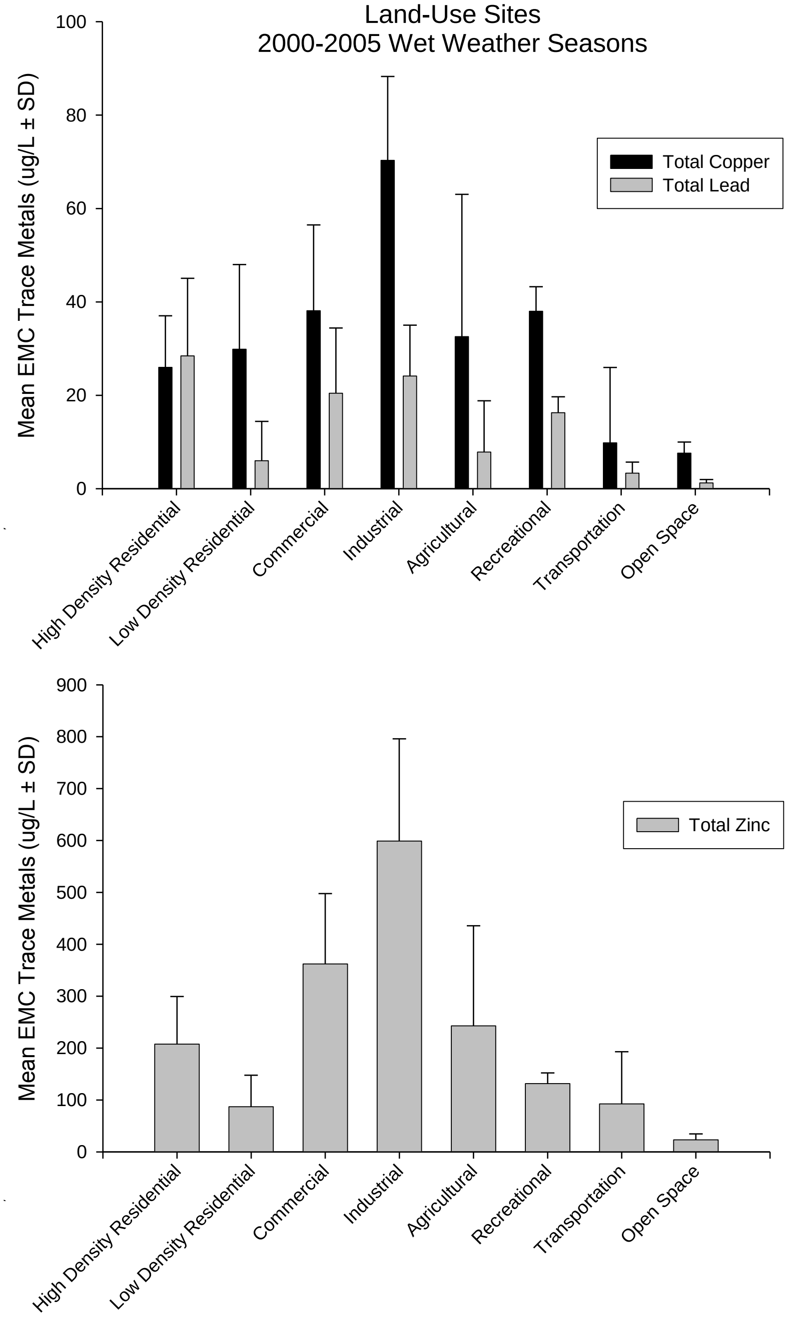

Figure 3-2. Mean storm EMCs of total copper and total lead (top) and total zinc (bottom) at specific land use sites during the 2000/01-2004/05 storm seasons. Standard deviation (SD).

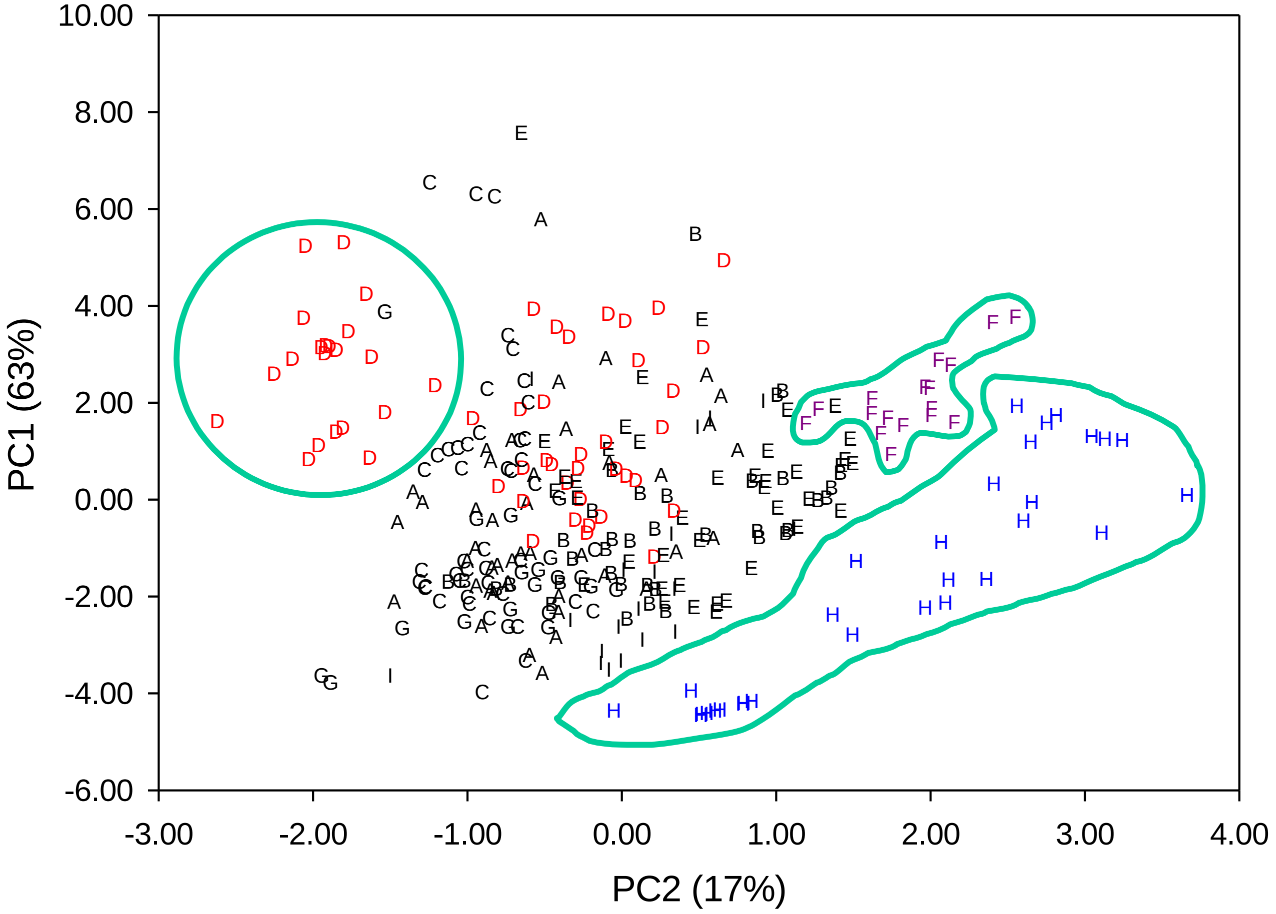

Figure 3-3. Plot of two principle components explaining 63% (y axis) and 17% (x axis) of the variation between trace metal concentrations at land use sites during 2000/01–2004/05 storm seasons. High density residential-Los Angeles River (A), Low density residential(B), C ommercial (C), Industrial(I) , Agricultural(E), Recreation (horse; F), Transportation(G), Open space(H), and High density residential-San Gabriel River (I).

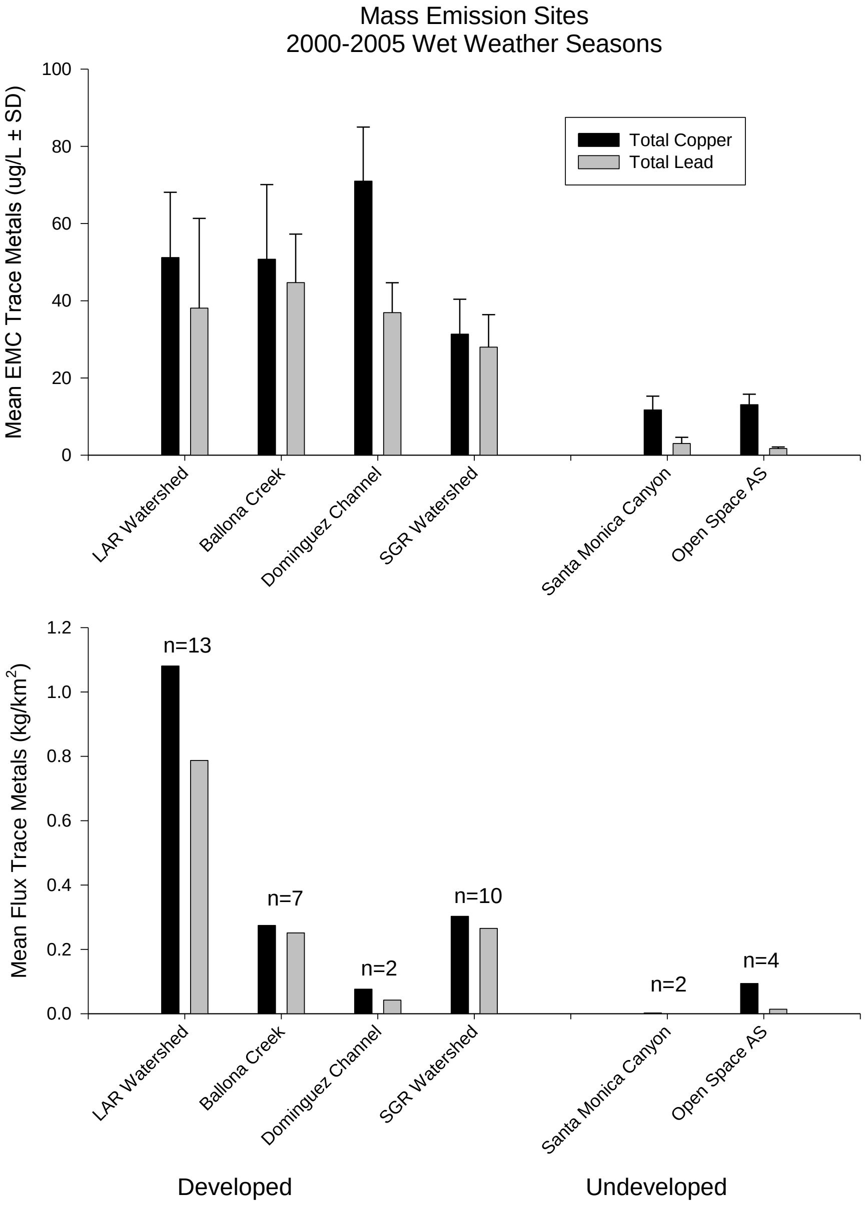

Figure 3-4. Average event mean concentrations (EMCs; top) and fluxes (bottom) of total copper and lead during the 2000/01 to 2004/05 storm seasons. Los Angeles River (LAR), San Gabriel River (SGR) and Arroyo Sequit (AS), number of storm events (n), and standard deviation (SD).

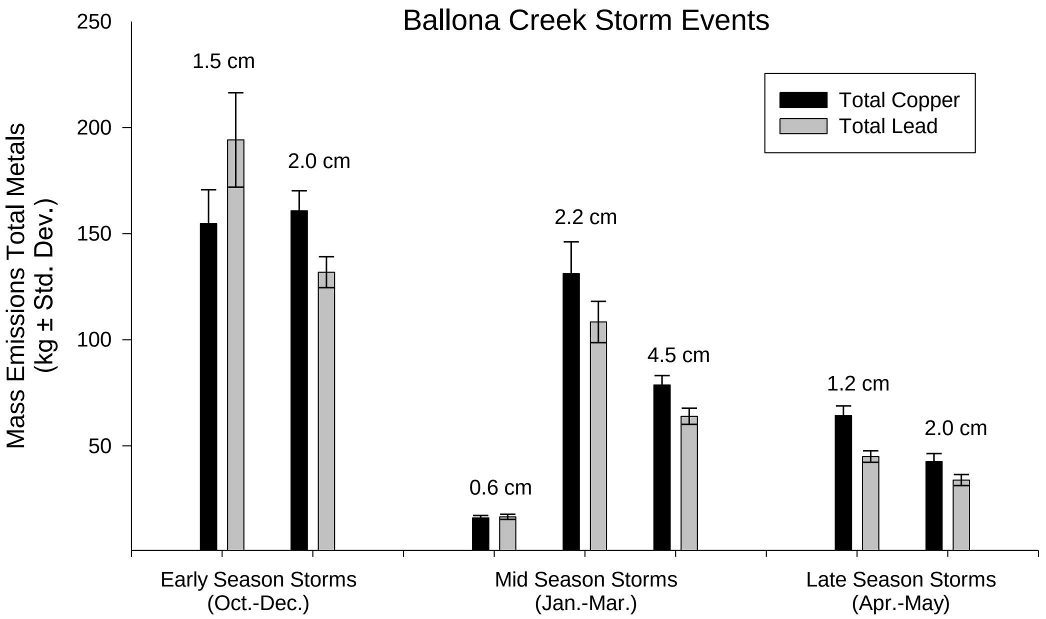

Figure 3-5. Metals loadings from early, mid, and late season storms in Ballona Creek during 2000/01 – 2004/05 storm seasons for total copper and total lead. The numbers above the bars in the graph indicate total event rainfall.

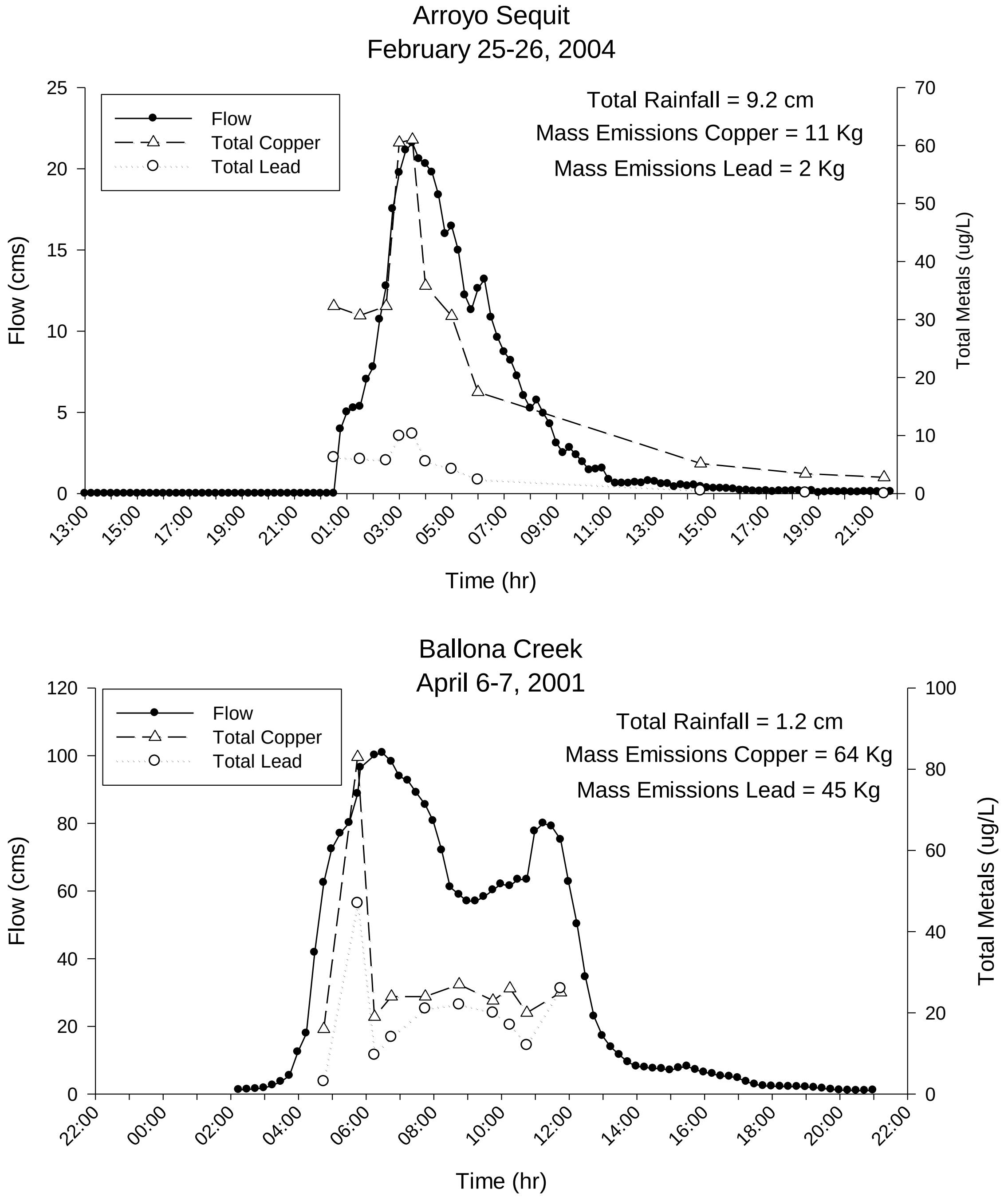

Figure 3-6. Variation in total copper and lead concentrations with time for a storm event in the undeveloped Arroyo Sequit watershed (top) and developed Ballona Creek watershed (bottom).

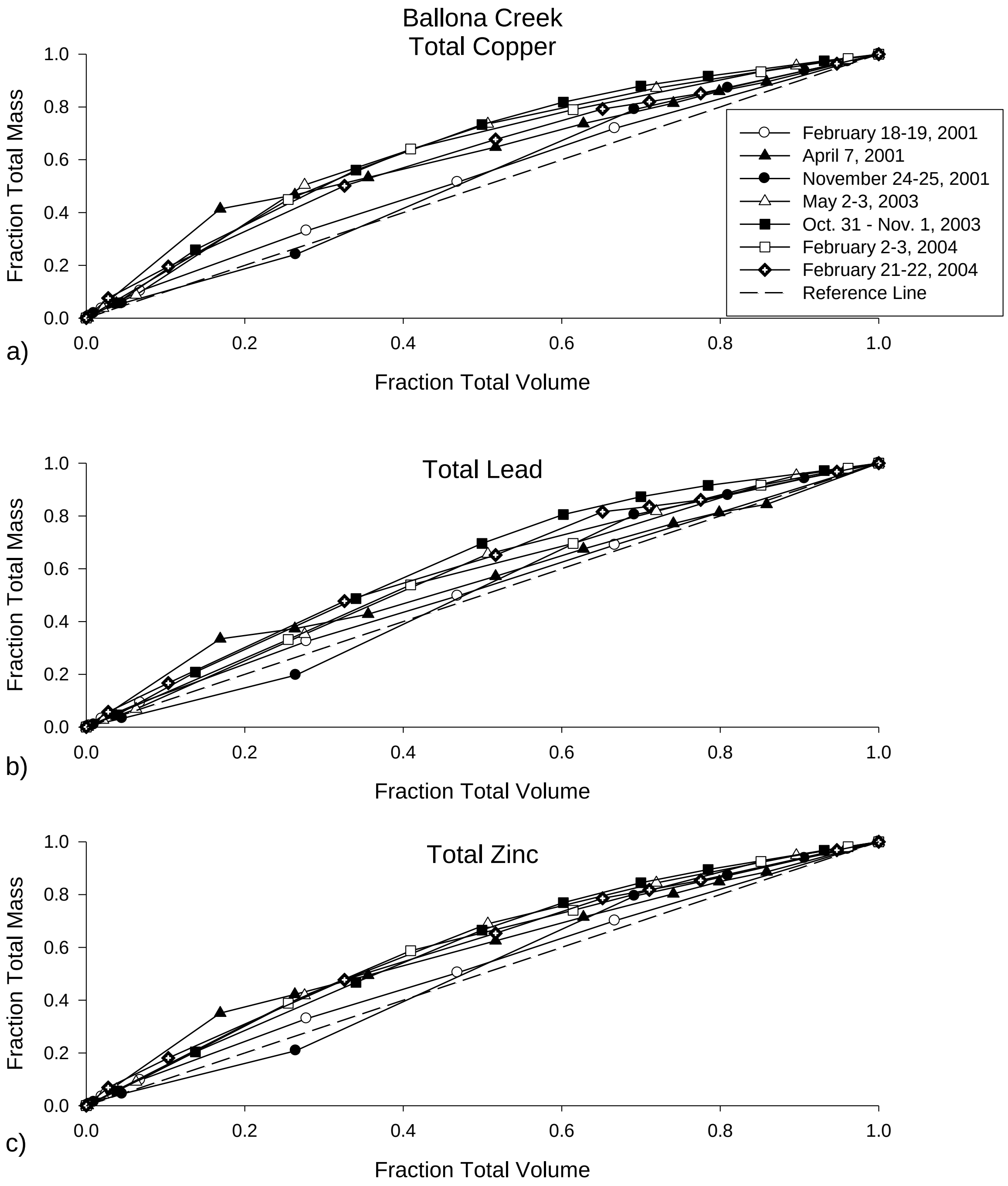

Figure 3-7. Cumulative load duration curves for total copper (a), total lead (b), and total zinc (c) for seven storms in the developed Ballona Creek watershed. Reference line indicates a 1:1 relationship between volume and mass loading. Portions of the curve above the line indicate proportionately higher mass loading per unit volume (i.e., first flush). Portions below the line indicate the reverse pattern.

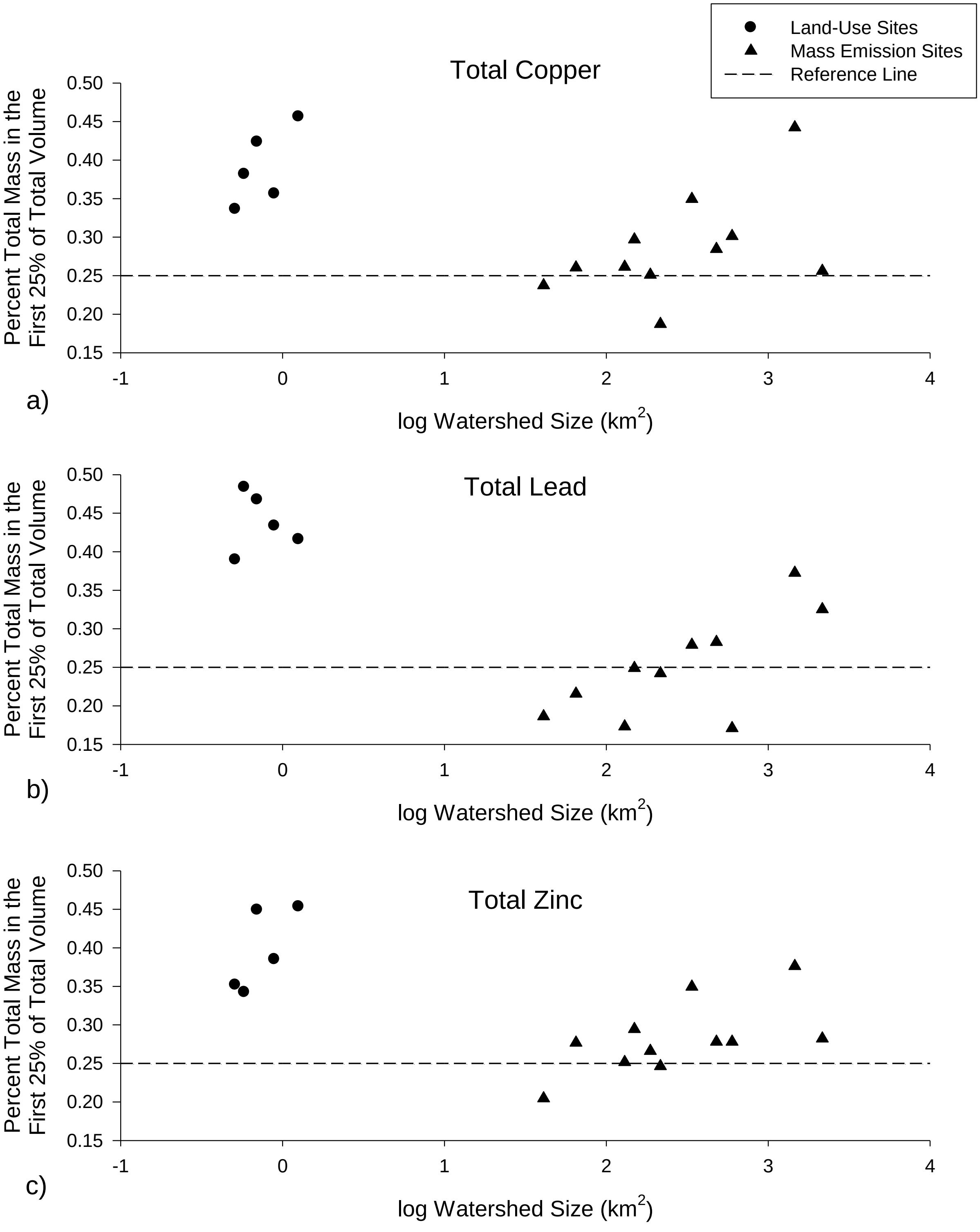

Figure 3-8. First flush patterns of total copper (a), total lead (b), and total zinc (c) in relation to watershed size. Dashed reference line indicates 25% of total mass loading in first 25% of total volume.

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SECTION 4. POLYCYCLIC AROMATIC HYDROCARBONS (PAHS)

Results

PAHs from Developed and Undeveloped Watersheds

In-river total PAH loads, concentrations, and fluxes were higher for developed versus undeveloped watersheds. For the 14 storm events measured, mean PAH load from developed watersheds was 5.6 ± 5.1 kg/storm, while mean load from undeveloped watersheds was 0.03 ± 0.02 kg/storm. Similarly, mean total PAH concentration from developed watersheds exceeded that from undeveloped watersheds (2,655.0 ± 1,768.1 ng/L vs 452.2 ± 444.9 ng/L; Tables 4-1 and 4-2). Flux of PAHs from developed watersheds was 46 times greater than that from undeveloped watersheds (Table 4-1). Mean PAH flux from the developed watersheds was 35.6 ± 69.8 g/km^2 compared to 0.75 ± 0.77 g/km^2 for the undeveloped watersheds. When the anomalously high fluxes from the Dominguez watershed are removed, flux from the developed watersheds was 7.8 ± 8.6 g/km^2, which is still greater than 10 times that of the undeveloped watersheds. Furthermore, the higher fluxes from developed watersheds were generated by substantially less rainfall than the lower fluxes from the undeveloped watersheds (1.85 ± 0.97 cm for storms in developed watersheds vs. 6.11 ± 4.32 cm for storms in undeveloped watersheds).

Annual PAH Loading in Storm water Runoff

The estimated annual output rate of total PAHs in the Los Angeles River watershed during the 2002–2003 water year was around 34.9 kg/year (Table 4-1). During this same period, Ballona Creek had an estimated annual output rate of approximately 20.0 kg/year into Santa Monica Bay. The following water year (2003–2004), the storm-water runoff discharge rate from Ballona Creek increased by a factor of four (72.9 kg/year). For comparative purposes, during the same time period, the Los Angeles River watershed discharged an estimated 150.6 kg/year of total PAHs into Santa Monica Bay. Annual output rates for undeveloped watersheds could not be estimated because those sites are not gauged, and consequently annual storm volumes are not available for estimation of annual PAH loads.

Effect of Rainfall Patterns

Antecedent dry period (expressed as cumulative rainfall) was strongly correlated with total PAH concentration, load, and flux in an exponentially nonlinear manner (r^2 = 0.54–0.81; Figure 4-1). Early-season storms have significantly higher PAH loads than late-season storms both within and between watersheds, even when rainfall quantity is similar. For example, the two early-season storms from Ballona Creek in water years 2002 and 2003 had total PAH loadings that were approximately four times larger (ranging from 7.9–8.3 kg) than the two storms that occurred at the end of the rainy season (1.1–1.8 kg), despite the early- and late-season storms resulting from comparable rainfall. When all watersheds are analyzed together, PAH concentration and load decrease with increasing cumulative rainfall until approximately 10 cm (average annual rainfall is 33 cm), beyond which the effect is markedly less dramatic (Figure 4-1).

PAH Variability Within Storms

The greatest total PAH concentrations occurred during the rising limb of the storm hydrograph for nearly every storm sampled. For example, peak concentrations (2,761 and 2,276 ng/L, respectively) occurred before the peak in flow (757 and 101 cms) in both the Los Angeles River and Ballona Creek (Figure 4-2). In the Los Angeles River example, peak total PAH concentrations occurred almost 8 h before the peak in storm flow. In the Ballona Creek example, a second peak in flow (75 cms) was also preceded by a second peak in total PAH concentration (1,015 ng/L).

Despite a strong and consistent pattern of first flush in concentration, cumulative mass loading plots exhibited only a moderate first flush of PAHs. Between 40% and 60% of the total PAH load was discharged in the first 25% of storm volume for the storms examined in this study. The mass loading plots for Ballona Creek (Figure 4-3) illustrate a consistent pattern of higher mass loading in the early portions of the storm, with a slightly stronger first flush in late-season storms. Land use sites showed a similar pattern of higher mass loading in the early portions of the storm however mid season storms (i.e., January-March) exhibited the strongest first flush.

Potential Sources of PAHs

Sources of PAHs were investigated by comparing concentrations and loads in runoff from homogeneous land uses sites. For all land use sites samples, mean PAH flux was between 0.33 and 140 g/km^2, while FWM concentration was between 4.6E ± 02 and 4.4E ± 03 ng/L (Table 4-3). Despite some apparent differences between land uses (e.g., high-density residential having higher concentrations and industrial having higher flux), no significant differences were observed in either concentration or flux among land use category ($p = 0.94$ and 0.60, analysis of covariance, with rainfall as a covariate).

The relative proportion of individual PAH compounds can be used to determine the source of PAHs in storm water. The HMW PAHs dominated LMW PAHs in runoff from all storms analyzed, suggesting a pyrogenic source. During the May 2–3, 2003, storm, HMW PAHs in runoff from the Los Angeles River and Ballona Creek accounted for 72% of the total PAH concentrations from these watersheds (Figure 4-4 and Table 4-2). Similarly, HMW PAHs in runoff from the Dominguez channel watershed in Los Angeles County, California, USA, accounted for 74% of the total PAH concentrations from its watershed. Even in the undeveloped Arroyo Sequit watershed, HMW PAHs accounted for 63% of the total PAH concentrations. In all storms and at all sites, the HMW compounds fluoranthene and pyrene were the dominant HMW PAHs. Analysis of the distribution of PAHs within each storm event shows that HMW PAHs are predominant uniformly throughout each storm regardless of land use (Figure 4-5). The exceptions were the industrial oil refinery and the agricultural sites, where the proportions of HMW and LMW PAHs were comparable throughout the storm. In all cases (except the oil refinery and agricultural sites), the relative contribution of LMW PAH compounds averaged 14 to 30% of the total PAH mass. Phenanthrene was the most dominant LMW PAH, comprising 7 to 21% of the total PAH contribution (Table 4-2).

The F/P ratio was between 0.9 and 1.2 for all storms in this study, indicating a strong predominance of pyrogenic PAH sources (Table 4-2). Furthermore, the P/A ratio was nearly always less than 21, once again indicating a strong predominance of pyrogenic PAH sources

(Table 4-2). Only one storm, March 17–18, 2002, at the Dominguez channel site, had a potential petrogenic source; the F/P ratio was 0.9, but the P/A ratio was .74. This result is consistent with the data from the land use sites, as the Dominguez watershed contains four major oil refineries. As with the distribution of HMW versusLMW PAHs, the F/P and P/A ratios indicate a consistent pyrogenic source for all lands use and mass emission sites regardless of the point within the storm (Figure 4-6). Again, the exception was at the industrial oil refinery, where the P/A ratio is low until the peak runoff occurs, at which time it rises to between 17 and 20. For both Ballona Creek and the Los Angeles River, a moderate, transient increase in the P/A ratio occurs coincident with the time of peak flow (Figure 4-4).

Discussion

Anthropogenic sources of total PAHS in storm-water runoff from urbanized coastal watersheds appears to be a significant source of PAHs to the southern California Bight. Estimates from this study based on FWM concentrations and gauged annual discharge volume indicate that during the study period approximately 92.8 and 32.7 kg/year of total PAH were discharged annually from the Los Angeles River and Ballona Creek watersheds, respectively. Over the same time period, the combined treated wastewater discharge from the city and county of Los Angeles (~2.8 x 10^6 m^3/d) discharged an estimated 740 kg of PAHs to the southern California Bight (Steinberger et al. 2003). The main difference between the two types of discharges is the delivery of the load to the coastal oceans; the treated wastewater discharge occurs in small, steady doses that occur daily, while storm-water loading occurs over the 10 to12 precipitation events that this region averages annually. The impact of the total PAHs in storm water discharged from urbanized watersheds is also reflected in receiving waterbody impacts. Regional monitoring of the southern California Bight revealed that the highest concentrations of PAHs were associated within bay and harbor areas that receive inputs from urbanized coastal watersheds (Noble et al. 2003). Bays and harbors only accounted for 5% of the total area of soft-bottom habitat but contained approximately 40% of the total PAH mass residing in southern California Bight surficial sediments. A second concern is the cost of remediating PAH in dredged materials. Total PAH is one of the most commonly occurring contaminants in dredged materials from San Pedro Bay (Steinberger and Schiff 2003). While some of these contaminants likely arise from port and industrial activities, they are colocated at the mouths of the Los Angeles River and Dominguez Channel watersheds, which is likely a contributing source.

The impact of PAH contributions on receiving waters from urbanized watersheds are not constrained to the southern California Bight. The National Status and Trends Program, which samples sediments and tissues in estuaries and coastal areas nationwide, repeatedly finds elevated PAHs near urban centers (Daskalakis and O'Conner 1995). San Pedro Bay (CA, USA) ranked third nationwide in total PAH concentration in mussel tissue during 2002. The top two locations are Elliott Bay (WA, USA) and Puget Sound (WA, USA), both located near urban centers. On the East Coast, Long Island Sound (NY, USA) adjacent to New York City was ranked fourth.

The annual watershed loading of PAHs estimated from this study are lower than those estimated from two studies in the eastern United States. Hoffman et al. (1984) estimated 680 kg/year of PAH loading from the 4,081 km^2 Narragansett Bay watershed in Rhode Island, USA. Similarly, Menzie et al. (2002) estimated 640 kg/year of PAH loading from the 758 km^2

Massachusetts Bay, USA, watershed. This difference may be explained by several factors. First, PAH loading relies on washoff of aerially deposited materials (the process by which airborne toxic contaminants enter coastal waters via aerial fallout). Watersheds in the western United States typically experience less than one-third rainfall and runoff volumes than comparably sized watersheds in the eastern United States. The lower volumes of annual runoff likely translate to lower loads. This may seem counter-intuitive; however, if the primary pollutant source to the land surface is aerial deposition (vs. being generated by activities within the land use), there is a practical limit to the amount of material that can accumulate. Previous studies have shown that physical processes such as wind or turbulence from traffic can limit pollutant accumulation on roads and other impervious surfaces (Pitt and Shawley 1981, Asplund et al. 1982, Kerri et al. 1985). Chemical processes, such as volatilization or oxidation can also limit the accumulation of potential pollutants on impervious surfaces (Hewitt and Rashad 1992). Because of the asymptotic nature of PAH buildup, loading to receiving waters is controlled by the frequency and magnitude of runoff events that "cleanse" impervious surfaces and provide subsequent opportunity for additional material to accumulate. A second reason for higher estimated PAH loading in the eastern United States is that PAHs are generated predominantly from concentrated point sources, such as coal-fired power plants. Southern California does not have coal-fired power plants; rather, PAHs are predominantly from mobile sources (cars, trucks, and trains), which discharge more diffusely across the region.

Concentrations in runoff from land use sites in this study were between 0.03 and 7.84 µg/L; these values are similar to those observed in previous studies by others. For example, Mahler et al. (2004) reported PAH concentrations between 5.1 and 8.6 µg/L in parking lot runoff, and Menzie et al. (2002) reported concentrations between 1 and 14 µg/L from a broad range of land uses.

In contrast to the results of this study, storm-water monitoring by local municipalities in southern California consistently report no detectable PAHs in storm water. This discrepancy is likely attributable to two factors. First, the practical PAH detection limit used by local municipalities is typically between 1 and 5 µg/L, which is acceptable by U.S. EPA regulatory guidelines. However, the mean FWM concentrations in storm water during this study were often lower than this level. The second factor is the sampling design used for regulatory-based monitoring. Most local municipalities are mandated to collect a storm composite sample that do not emphasize (and may completely miss) the first flush of total PAH that was observed. We almost always observed the greatest peaks in total PAH concentrations during initial storm flows, up to 8 h before peak flow. This pronounced first flush suggests that in highly urbanized watersheds, particle-bound PAHs may be rapidly mobilized from impervious land surfaces during the early portions of storms. Similar first-flush patterns in PAH concentrations during storms were observed by Hoffman et al. (1984) and (Smith et al. 2000). Furthermore, (Buffleben et al. 2002; University of California, Los Angeles, Los Angeles, CA, USA, unpublished data) also observed that peak PAH concentrations in Ballona Creek occur up to 14 h before peak flow.

Seasonal flushing at mass emissions sites was one phenomenon not previously reported by others. Seasonal flushing occurred when early-season storms consistently discharged higher PAH loads than storms of a similar size or larger later in the season. This seasonal effect was correlated with the length of antecedent dry condition but not with rainfall quantity. The lack of a meaningful relationship between rainfall quantity and PAH loading has been reported in several other studies (Eaganhouse et al., Hoffman et al. 1984). Hoffman et al. (1984) suggested that the lack of a clear relationship was due to the complex spatial and temporal dynamics associated with rain patterns, which may affect runoff patterns more than the total amount of rainfall during a given storm. In addition, differential particle wash-off from land surfaces may mask any differences associated with total rainfall. The strong relationship between PAH flux and antecedent dry period suggests that storm-event PAH loads are a function primarily of the amount of time available for PAHs to build up on the land surfaces between subsequent rain events. The PAH loads from land surfaces during later-season storms (i.e., after 10 cm of accumulated rainfall) may reflect contributions from wet deposition or from localized accumulation; however, we currently lack the data to answer this question definitively. Analysis of PAH concentration in wet deposition would help improve our understanding of the sources of PAHs during the latter part of the storm season. Environmental managers can use this knowledge of temporal patterns of PAH loading to focus efforts on storm capture or treatment during the early portions of storms and during the earliest storms of the year.

Sources of PAHs in Storm water

Several lines of evidence implicate aerial deposition and subsequent wash-off of combustion by-products as the main source of PAH loading in storm water. First, the flux of total PAHs among large developed watersheds were similar throughout the urbanized region of Los Angeles, suggesting a similar regional source of PAHs. If urban land use distribution strongly influenced PAH loadings, then flux would have differed by watershed based on differential urban land use practices. In fact, no difference was observed in PAH concentrations in runoff between various urban land uses, which differs from the findings of previous studies from the eastern United States (Ngabe et al. 2000). Menzie et al. (2002) concluded that residential and commercial land uses generated higher PAH concentrations than other land use types because of secondary petrogenic sources that enhanced the regional pyrogenic source of PAHs. Hoffman et al. (1984) found that runoff from industrial and highway sites had higher PAH concentrations than residential runoff but accounted for these differences in runoff dynamics as opposed to unique sources.

Second, the relative abundance of individual PAHs in runoff indicates a strong pyrogenic source indicative of combusted fossil fuels. The typical distribution of PAHs observed from mass emission sites (Figure 4-7) was similar to the distribution of PAHs observed in dry deposition collected in Los Angeles by Sabin et al. (2004). Furthermore, in this study, HMW PAH consistently comprised approximately 73% of the total PAH concentration regardless of land use. Hoffman et al. (1984) reported comparable results in their study of urban runoff in Rhode Island’s Narragansett Bay watershed, where HMW PAHs accounted for 71% of the total inputs to Narragansett Bay. A more recent study by Menzie et al. (2002) of PAHs in storm-water runoff in coastal Massachusetts identified similar HMW PAH compounds as observed in this study (chrysene, fluoranthene, phenanthrene, and pyrene) as the primary PAH compounds in storm water. Similarly, (Soclo et al. 2002) found that high PAH loads associated with storm-water runoff to the Cotonou Lagoon in Benin were characterized by HMW PAHs that appear to be derived from atmospheric deposition. The consistent predominance of HMW PAHs throughout all storms, even during the period of first flush, further indicates a consistent regional source, such as aerial deposition. If specific land uses were generating secondary petrogenic wash-off as suggested by Menzie et al. (2002), the distribution of PAHs would have changed during the storm; however, we did not observe any differences within storms. The exception to this pattern was for the industrial oil refinery site, where the signature of petrogenic PAHs was more pronounced. This makes sense given the obvious petrogenic source associated with this land use type. Nevertheless, the pyrogenic signature was still prevalent at this land use, especially during the latter portions of the storm.

The PAH sources can also be inferred by examining ratios of particular PAHs in runoff samples. We used both the fluoranthene/pyrene (F/P) and phenanthrene/anthracene (P/A) ratios. Small F/P ratios close to 0.9 suggest that individual PAHs are associated with combustion products (Maher and Aislabie 1992); in contrast, large F/P ratios suggest petrogenic sources of PAHs (Colombo et al. 1989;Table 4-4). Both the F/P and the P/A ratios observed in this study indicate that aerial deposition of combustion by-products is likely the dominant source of PAHs in the watersheds that drain to the greater Los Angeles coastal region, and this source is consistent during all portions of storm-water runoff. Several additional ratios have been used to assess the different sources of PAHs. Takada et al. (1990) used methylated/parent PAH ratios as indicators of PAH sources. Results showed that PAHs in runoff from residential streets had a more significant contribution from atmospheric fallout of other combustion products. Zakaria et al. (2002) explained their low ratios of methylphenanthrene to phenanthrene (MP/P; <0.6) to mean that combustion- derived PAHs are transported atmospherically for a long distance and serve as background contamination. The ratios of methylphenanthrene to phenanthrene in our study (0–0.2) also suggest a strong contribution of aged urban aerosols to overall PAH loads (Nielsen 1996, Simo et al. 1997, Hwang et al. 2003)**.** Watersheds in the greater Los Angeles area are heavily urbanized; therefore, ample opportunity exists for combustion-derived aerosols that generate particulate matter to be deposited on land surfaces. The petrogenic signature seen in the Dominguez Channel can be explained by the presence of slightly different sources in this watershed. The Dominguez watershed contains a high density of oil refineries and other industrial land uses that drain directly to the Ports of Los Angeles and Long Beach. The presence of multiple oil refineries discharging to a single stream explains the concentration of petrogenic PAHs in this area.

Conclusions based on ratios of specific PAH compounds should be used with some caution, especially because a relatively limited set of PAHs were analyzed in this study. Furthermore, if reference (or source) samples were not analyzed, it is always a good idea to use these ratios on a relative basis. Nevertheless, the preponderance of evidence from this study, combined with the well-documented fact that atmospheric deposition (both wet and dry) is the major source of contamination in arid and semiarid climates, such as that existing in southern California (Sabin et al. 2004, Gunther et al. 1987), supports the conclusions of this study: The predominant source of PAHs in urban storm water in the greater Los Angeles area is from aerial deposition and subsequent wash-off of PAHs associated with combustion byproducts.

Table 4-1. Storm-water polycyclic hydrocarbon mass emissions from in-river sampling locations. Annual loads are based on water year, as indicated in the foot notes. Cubic meters per second(cms); Standard deviation (SD); Polycyclic aromatic hydrocarbons (PAH); and Event mean concentration(EMC).

							Total PAHs					
Mass Emission Sites	Size km^2	Date of Storm Event	Rainfall (cm)	Antecedant Dry Days	Mean Flow (cms)	Peak Flow (cms)	EMC ng/L	EMC SD	Flux (kg/km^2)	Mass Emissions (kg)	Mass Emissions SD	Annual Total PAH (kg/year)
LA River above Arroyo Seco	1460	11/12 - 11/13/2001	1.73	127	62.6	262.5	3,256.80	846.70	0.0049	7.16	0.35	3.74[a]
LA River at Wardlow	2161	5/2 - 5/3/2003	3.56	4	209.9	756.7	470.70	453.20	0.0023	4.90	0.32	34.9[b]
		2/2/04	1.14	29	90.4	375.6	3,559.33	1,185.50	0.0	13.93	0.99	150.6[c]
										Mean Load:		92.8 ± 81.8
Verdugo Wash	65	11/12 - 11/13/2001	1.83	11	68.5	368.2	4,283.70	2,043.20	0.2236	14.54	0.83	NA[d]
		10/31 - 11/1/2003	1.74	30	56.5	155.0	4,992.30	1,093.30	0.1529	9.94	0.46	NA
Arroyo Seco	130	2/9 - 2/11/2001	3.56	12	2.9	13.5	788.80	177.80	0.0009	0.11	0.01	2.79[e]
		4/6 - 4/7/2001	1.78	30	7.8	21.8	816.50	258.50	0.0016	0.20	0.01	
Ballona Creek	338	4/6 - 4/7/2001	1.24	31	32.6	100.9	948.70	379.90	0.0054	1.81	0.13	20.5[e]
		11/24 - 11/25/2001	1.52	11	53.1	396.2	3,118.90	1,104.80	0.0246	8.30	1.78	17.3[a]
		5/2 - 5/3/2003	2.03	4	52.8	134.4	981.70	583.00	0.0032	1.08	0.12	20.0[b]
		10/31 - 11/1/2003	2.03	30	62.0	148.1	5,821.20	1,814.90	0.0233	7.87	0.54	72.9[c]
										Mean Load:		32.7 ± 26.8
Dominguez Channel	187	3/17 - 3/18/2002	0.28	10	4.8	14.0	3,293.40	791.80	0.0013	0.24	0.01	NA
		2/21 - 2/22/2004	1.52	18	14.7	35.5	2,182.10	745.20	0.0123	2.31	0.09	NA
Santa Monica Canyon	41	4/6 - 4/7/2001	3.05	50	0.6	3.0	766.8	247.2	0.0002	0.01	0.00	NA
Open Space Arroyo Sequit	31	2/25 - 2/26/2004	9.17	2	3.4	21.9	137.6	0.0	0.0013	0.04	0.00	NA

[a] Water year 2002 = October 2001-September 2002
[b] Water year 2003 = October 2002-September 2003
[c] Water year 2004 = October 2003-September 2004
[d] NA = annual storm volumes not available; consequently, annual loads could not be estimated
[e] Water year 2001 = October 2000-September 2001

Table 4-2. Total polycyclic aromatic hydrocarbons (PAHs) and selected polycyclic aromatic hydrocarbon ratios. Event mean concentration (EMC); High-molecular-weight compounds (HMW).

Mass Emission Sites	Date of Storm Event	EMC ∑PAHs (ng/L)	EMC Pyrene (ng/L)	Pyrene/ ∑PAHs (%)	Fluoranthene/ Pyrene Ratio	Phenanthrene/ Anthracene Ratio	EMC Phenanthrene (ng/L)	Phenanthrene/ ∑PAHs (%)	HMW (%)	Dominant Sources of Origin
LA River above Arroyo Seco	11/12 - 11/13/2001	3256.8	427.9	13.1	1.1	8.0	291.3	8.9	76.4	Pyrogenic
LA River at Wardlow	5/2 - 5/3/2003	470.7	133.5	28.4	1.1	20.9	97.3	20.7	69.7	Pyrogenic
	2/2/04	3559.3	401.0	11.3	1.0	7.5	278.1	7.8	71.8	Pyrogenic
Verdugo Wash	11/12 - 11/13/2001	4283.7	593.8	13.9	1.1	7.8	373.0	8.7	83.5	Pyrogenic
	10/31 - 11/1/2003	4992.3	677.9	13.6	0.9	11.6	341.8	6.8	82.0	Pyrogenic
Arroyo Seco	2/9 - 2/11/2001	788.8	131.9	16.7	1.0	8.6	101.2	12.8	81.7	Pyrogenic
	4/6 - 4/7/2001	816.5	135.0	16.5	1.1	7.2	101.9	12.5	84.6	Pyrogenic
Ballona Creek	4/6 - 4/7/2001	948.7	177.9	18.8	0.9	4.9	89.6	9.4	88.7	Pyrogenic
	11/24 - 11/25/2001	3118.9	428.8	13.8	1.0	8.1	302.9	9.7	71.8	Pyrogenic
	5/2 - 5/3/2003	981.7	237.4	24.2	1.0	4.3	122.3	12.4	74.6	Pyrogenic
	10/31 - 11/1/2003	5821.2	786.2	13.5	1.1	10.2	473.0	8.1	82.7	Pyrogenic
Dominguez Channel	3/17 - 3/18/2002	3293.4	534.6	16.2	0.9	74.9	508.2	15.4	77.5	Petrogenic
	2/21 - 2/22/2004	2182.1	308.8	14.2	1.1	6.4	210.5	9.6	69.7	Pyrogenic
Santa Monica Canyon	4/6 - 4/7/2001	766.8	134.9	17.6	1.0	4.1	73.8	9.6	86.5	Pyrogenic
Open Space Arroyo Sequit	2/25 - 2/26/2004	137.6	14.3	10.4	1.2	10.2	17.2	12.5	63.0	Pyrogenic
	Mean ∑PAHs (ng/L)	2,300.00								

Table 4-3. Event mean concentration (EMC) and mass loading of polycyclic aromatic hydrocarbons (PAHs) from land use sites. Site numbers indicate different sites within a given land use category. SD = standard deviation; NA = watershed size not available.

							Total PAHs		
Land-use Type	Size (km^2)	Date of Storm Event	Rainfall (cm)	Dry Days	Mean Flow (cms)	Peak Flow (cms)	Flux (kg/km^2)	EMC	
								(ng/L)	SD
High Density Residential #1	0.02	2/17/02	0.89	21	0.001	0.006	1.8E-03	1.92E+03	7.03E+02
High Density Residential #1	0.02	2/2/04	1.19	2	0.0042	0.0251	2.0E-02	3.31E+03	1.00E+03
High Density Residential #2	0.52	3/17 - 3/18/2002	0.20	27	0.000	0.003	1.1E-05	7.84E+03	5.99E+03
High Density Residential #3	1.0	12/28/04	3.25	0	0.009	0.080	2.45E-06	7.11E+00	2.97E+00
High Density Residential #3	1.0	2/11/05	1.35	13	0.004	0.016	5.4E-08	5.06E-01	1.28E-01
Mean High Density Residential #1							***7.2E-03***	***4.4E+03***	***2.6E+03***
Mean High Density Residential #3							**1.2E-06**	**3.8E+00**	**1.6E+00**
Low Density Residential #1	0.98	3/4 - 3/5/2001	2.67	3	0.017	0.071	7.2E-05	1.55E+02	5.54E+01
Low Density Residential #1	0.98	2/2/04	2.26	2	0.030	0.143	3.3E-03	3.3E+03	1.6E+03
Low Density Residential #2	0.18	3/17 - 3/18/2002	2.13	9	0.008	0.116	1.7E-03	8.86E+02	1.82E+02
Mean Low Density Residential							***1.7E-03***	***1.4E+03***	***6.0E+02***
Commercial #1	NA	2/17/02	0.89	20	0.002	0.008	NA	2.27E+02	1.63E+02
Commercial #2	2.45	2/17/02	0.74	20	0.337	1.340	7.7E-03	4.43E+03	2.05E+03
Commercial #3	0.06	4/6 - 4/7/2001	2.03	31	0.008	0.018	8.2E-05	3.00E+01	1.95E+01
Commercial #3	0.06	3/17 - 3/18/2002	0.12	9	0.000	0.001	2.9E-06	2.08E+02	6.93E+01
Mean Commercial							***2.6E-03***	***1.2E+03***	***5.8E+02***
Industrial #1	0.004	4/6 - 4/7/2001	2.06	31	0.008	0.017	5.7E-03	1.36E+02	6.85E+01
Industrial #2	0.001	2/17/02	0.74	20	0.000	0.002	2.9E-03	6.31E+02	3.42E+02
Industrial #3	2.77	3/17 - 3/18/2002	0.25	9	0.000	0.003	6.6E-06	4.41E+03	2.29E+03
Industrial #4	0.01	3/15/03	4.50	9	0.117	0.375	5.6E-01	8.89E+02	7.55E+02
Mean Industrial							***1.4E-01***	***1.5E+03***	***8.6E+02***

Table 4-3. Continued

Land-use Type	Size (km^2)	Date of Storm Event	Rainfall (cm)	Dry Days	Mean Flow (cms)	Peak Flow (cms)	Total PAHs Flux (kg/km^2)	Total PAHs EMC (ng/L)	Total PAHs EMC SD
Agricultural #1	0.98	3/4 - 3/5/2001	2.74	3	0.021	0.053	4.3E-04	6.83E+02	7.77E+02
		3/17 - 3/18/2002	0.23	10	0.012	0.031	2.0E-05	4.55E+02	1.72E+02
		2/2/04	1.17	2	0.0228	0.128	5.3E-04	1.43E+03	2.09E+03
Mean Agricultural							***3.3E-04***	***8.6E+02***	***1.0E+03***
Recreational (horse)	0.03	3/4 - 3/5/2001	1.42	3	0.003	0.014	1.8E-03	4.58E+02	2.97E+02
Mean Recreational							***1.8E-03***	***4.6E+02***	***3.0E+02***
Transportation #1	0.01	4/6 - 4/7/2001	3.05	31	0.022	0.057	1.4E-02	3.63E+02	2.53E+02
Transportation #2	0.002	2/17/02	0.89	47	0.001	0.006	3.7E-03	5.95E+02	3.16E+02
Mean Transportation							***8.9E-03***	***4.8E+02***	***2.8E+02***

Table 4-4. Selected polycyclic aromatic hydrocarbon ratios and their source signature ranges.

Indicator	Pyrogenic	Petrogenic	Reference
Fluoranthene / Pyrene Ratio	0.9 - ≤1	>1	Maher and Aislabie, 1992
Phenanthrene / Anthracene Ratio	3 - 26	>26	Gschwend and Hites, 1981; Lake et al., 1979
Methylphenanthrene / Phenanthrene Ratio	<1.0	2 - 6	Hwang et al., 2003

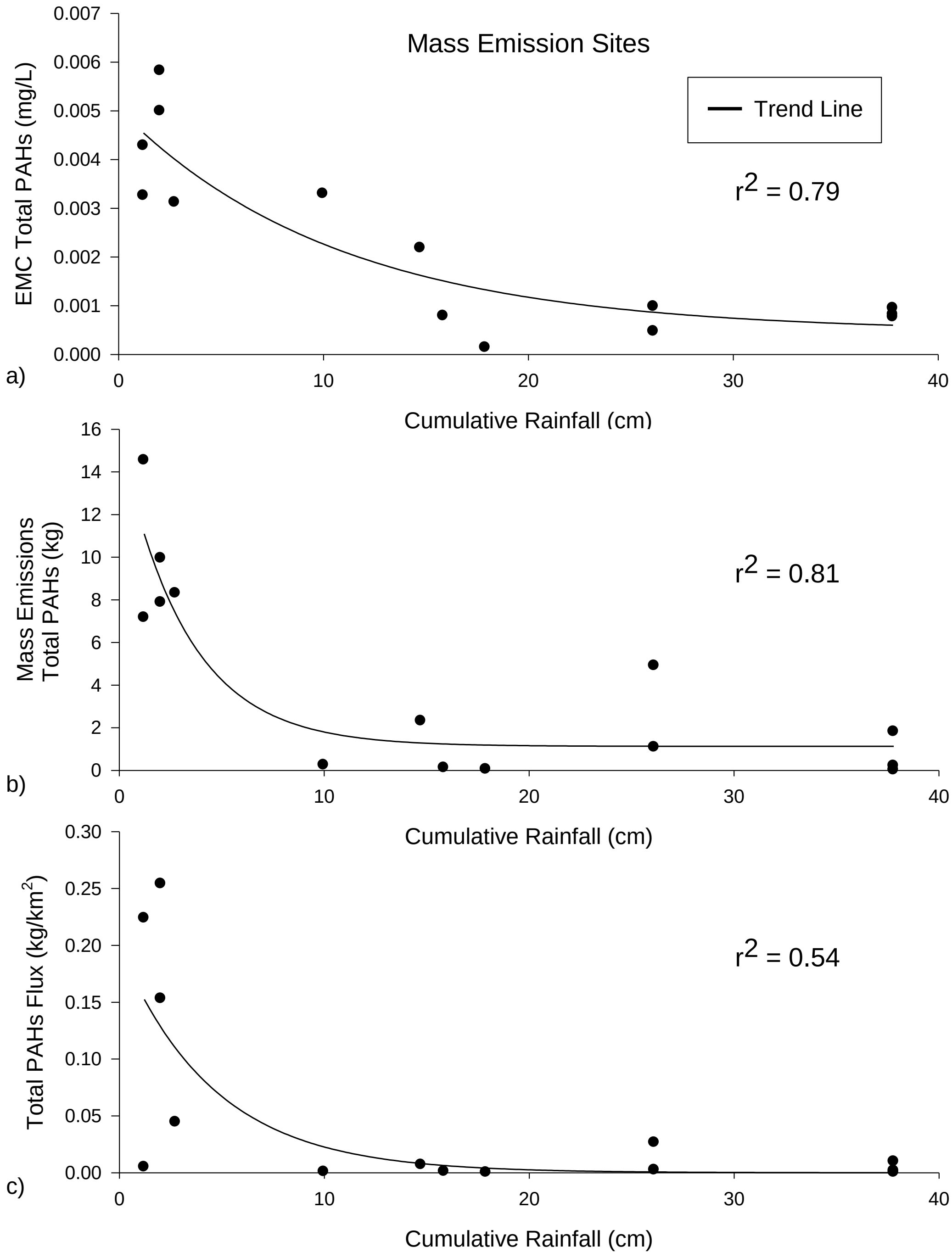

Figure 4-1. Cumulative annual rainfall versus polycyclic aromatic hydrocarbon (PAH) event mean concentration (EMC; a), load (b), and flux (c). Plots show data for mass emission sites only.

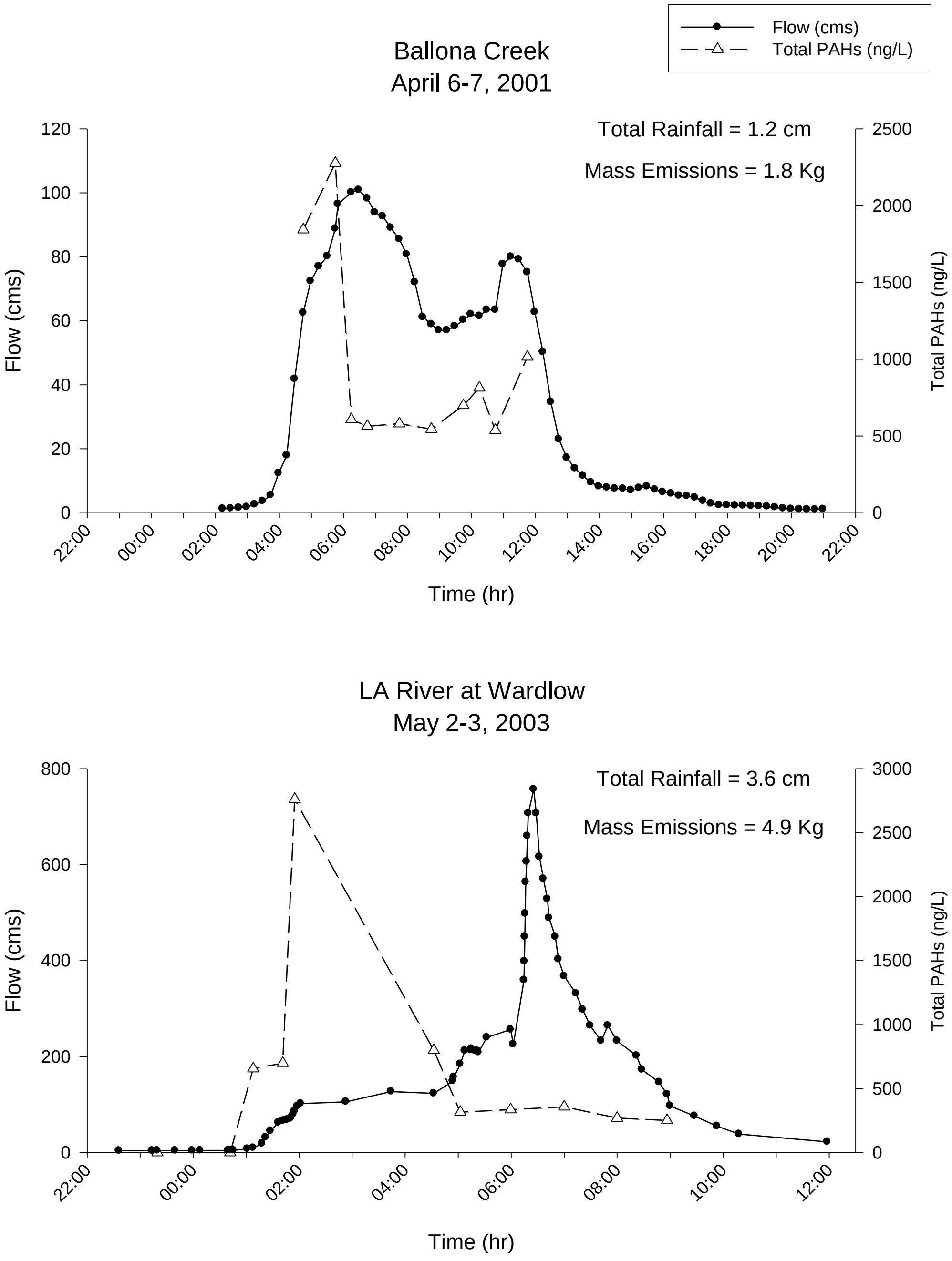

Figure 4-2. Variation in polycyclic aromatic hydrocarbon (PAH) concentrations with time for storm events in Ballona Creek (top) and Los Angeles River (bottom).

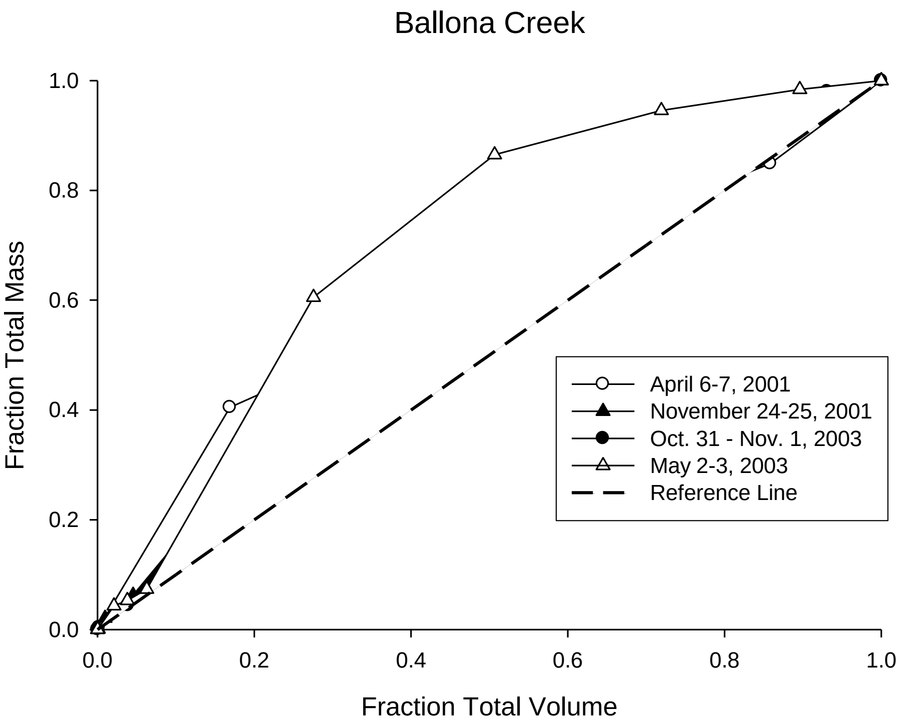

Figure 4-3. Cumulative polycyclic aromatic hydrocarbon mass loading for four storms in Ballona Creek. Plots show percent of mass washed off for a given fraction of the total runoff. Reference line indicates a 1:1 relationship between volume and mass loading. Portions of the curve above the line indicate proportionately higher mass loading per unit volume (i.e., first flush). Portions below the line (if any) indicate the reverse pattern.

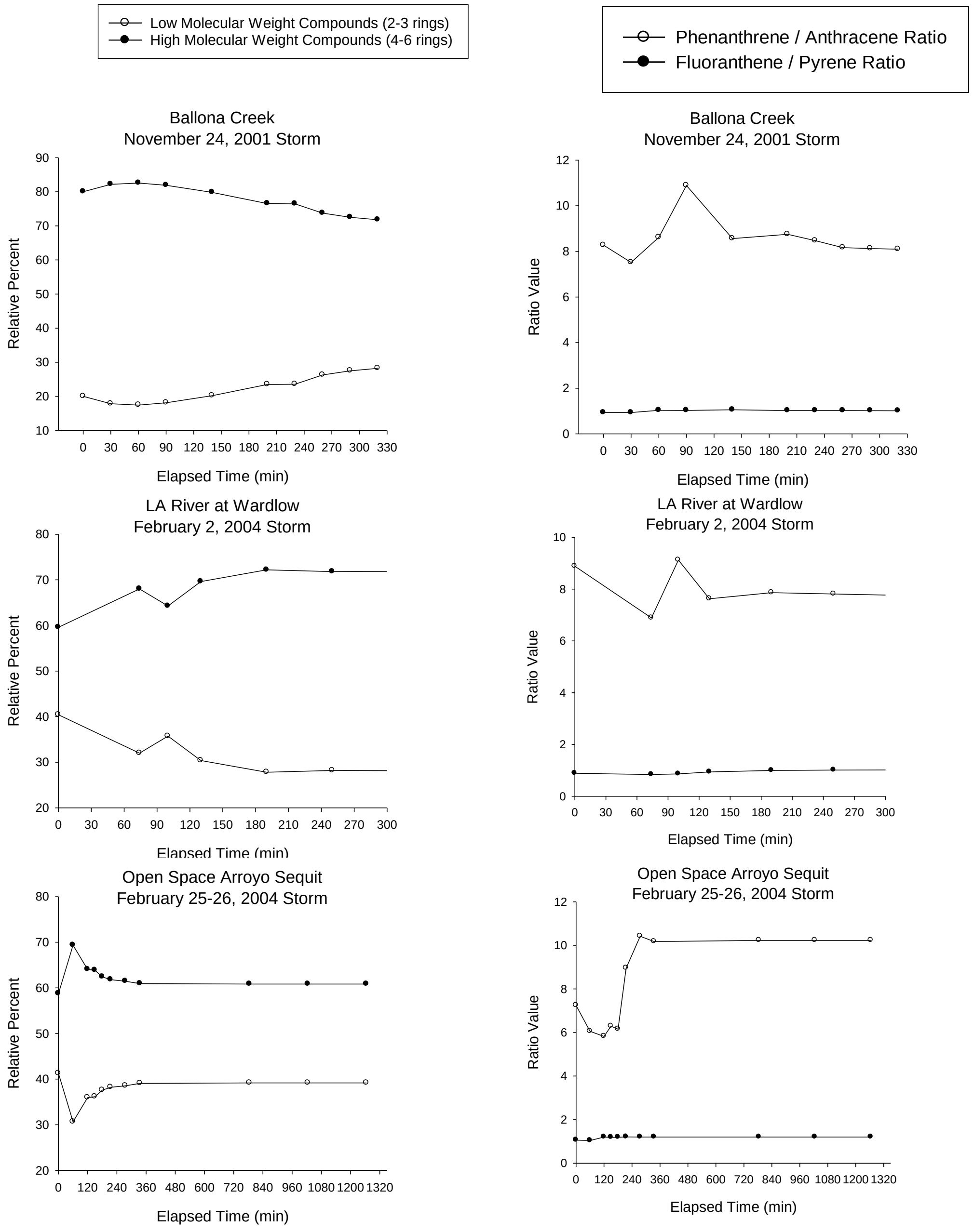

Figure 4-4. Distribution of polycyclic aromatic hydrocarbons (PAHs) within storms for mass emission sites. Plots on the left (a–c) show distribution of high- versus low-molecular-weight PAHs throughout individual storms. Plots on the right (d–f) show phenanthrene/anthracene (P/A) and fluoranthene/pyrene (F/P) ratios throughout individual storms. Peaks in the P/A ratio correspond to peak storm flows.

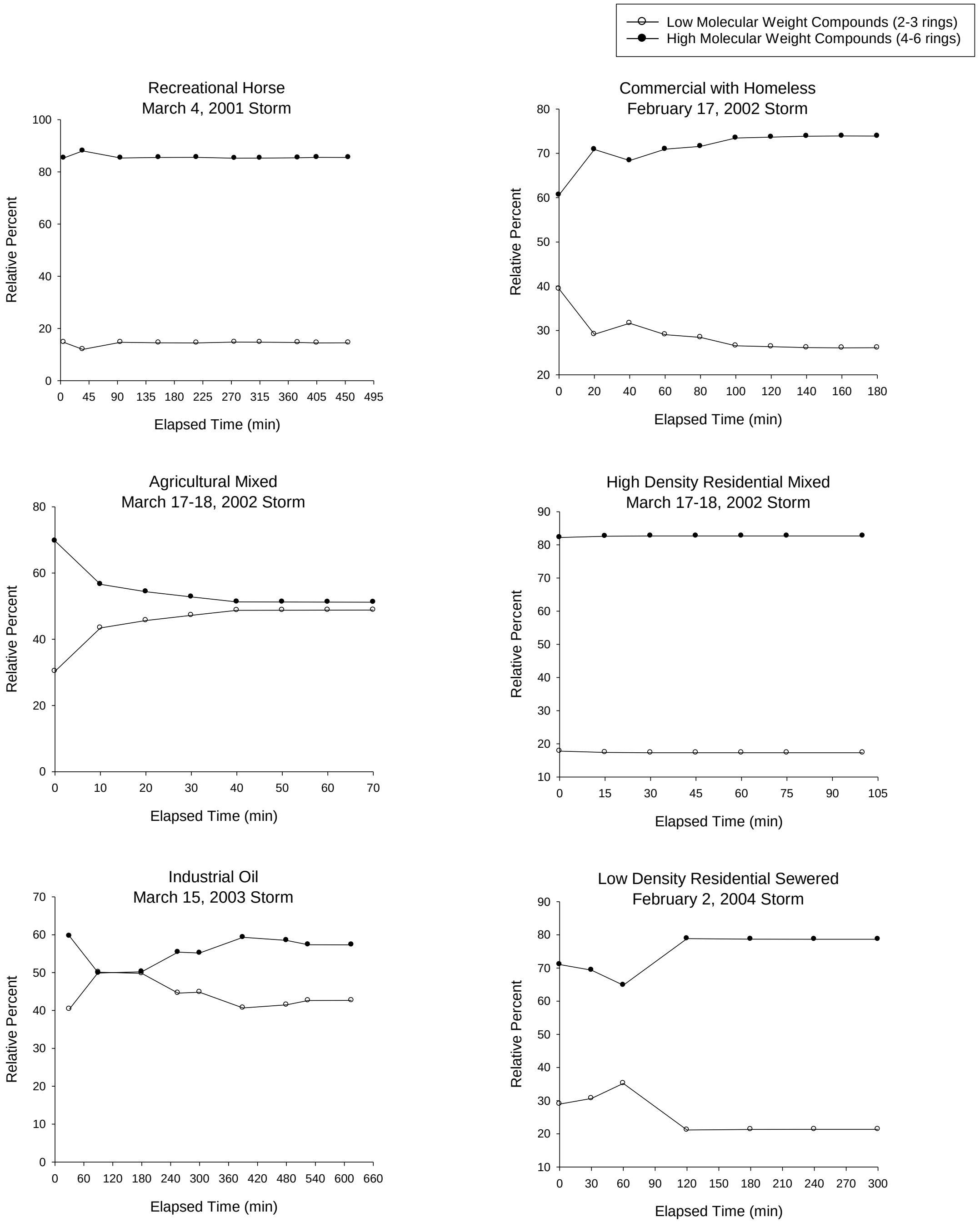

Figure 4-5. Distribution of polycyclic aromatic hydrocarbons (PAHs) within storms for representative land use sites (a–f). Plots show distribution of high- versus low-molecular-weight PAHs throughout individual storms. Data are shown for six sites that represent the results observed for the 15 land use sites where data were collected.

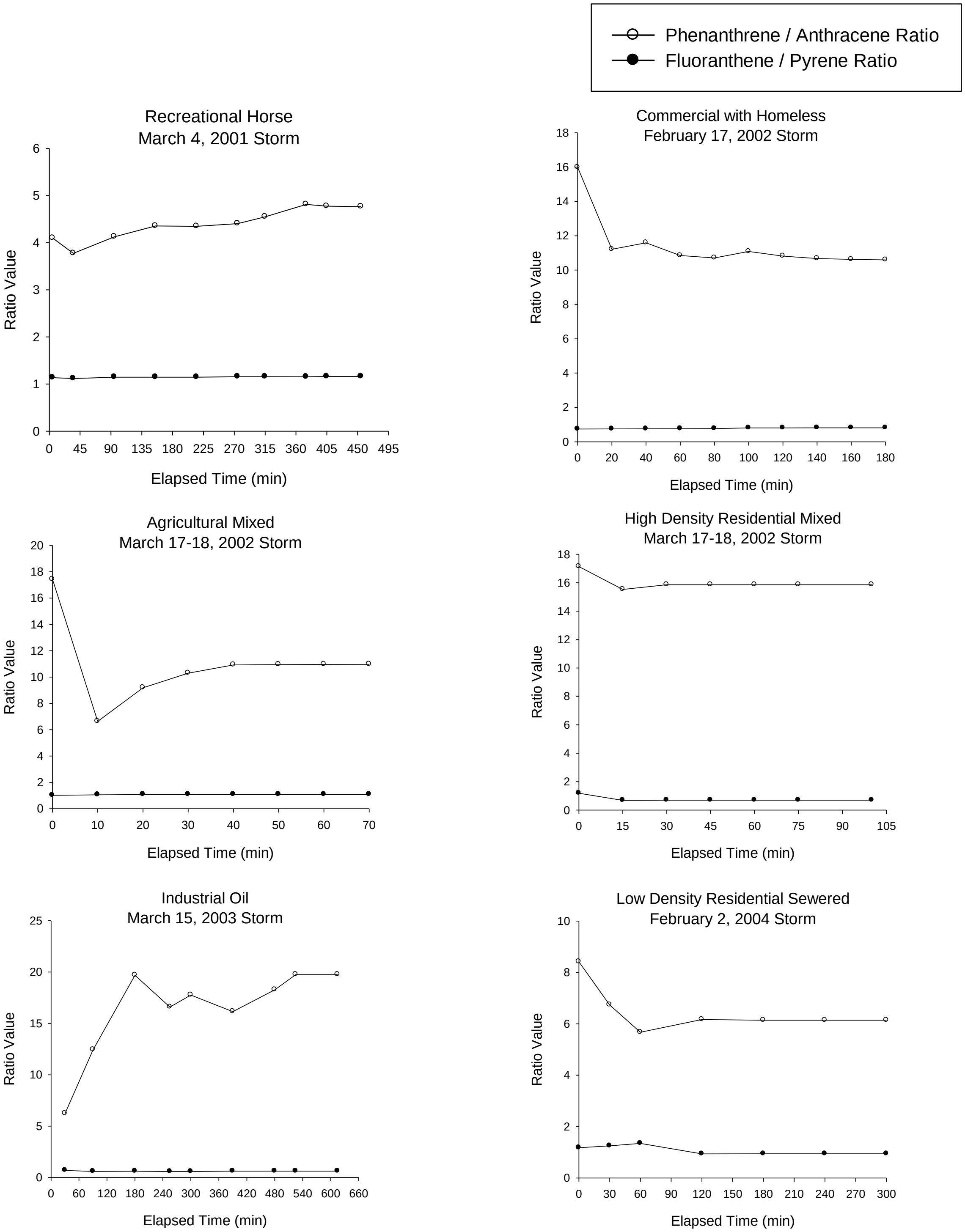

Figure 4-6. Distribution of polycyclic aromatic hydrocarbons within storms for representative land use sites. Plots (a–f) show phenanthrene/anthracene (P/A) and fluoranthene/pyrene (F/P) ratios throughout individual storms. Data are shown for six sites that represent the results observed for the 15 land use sites where data were collected.

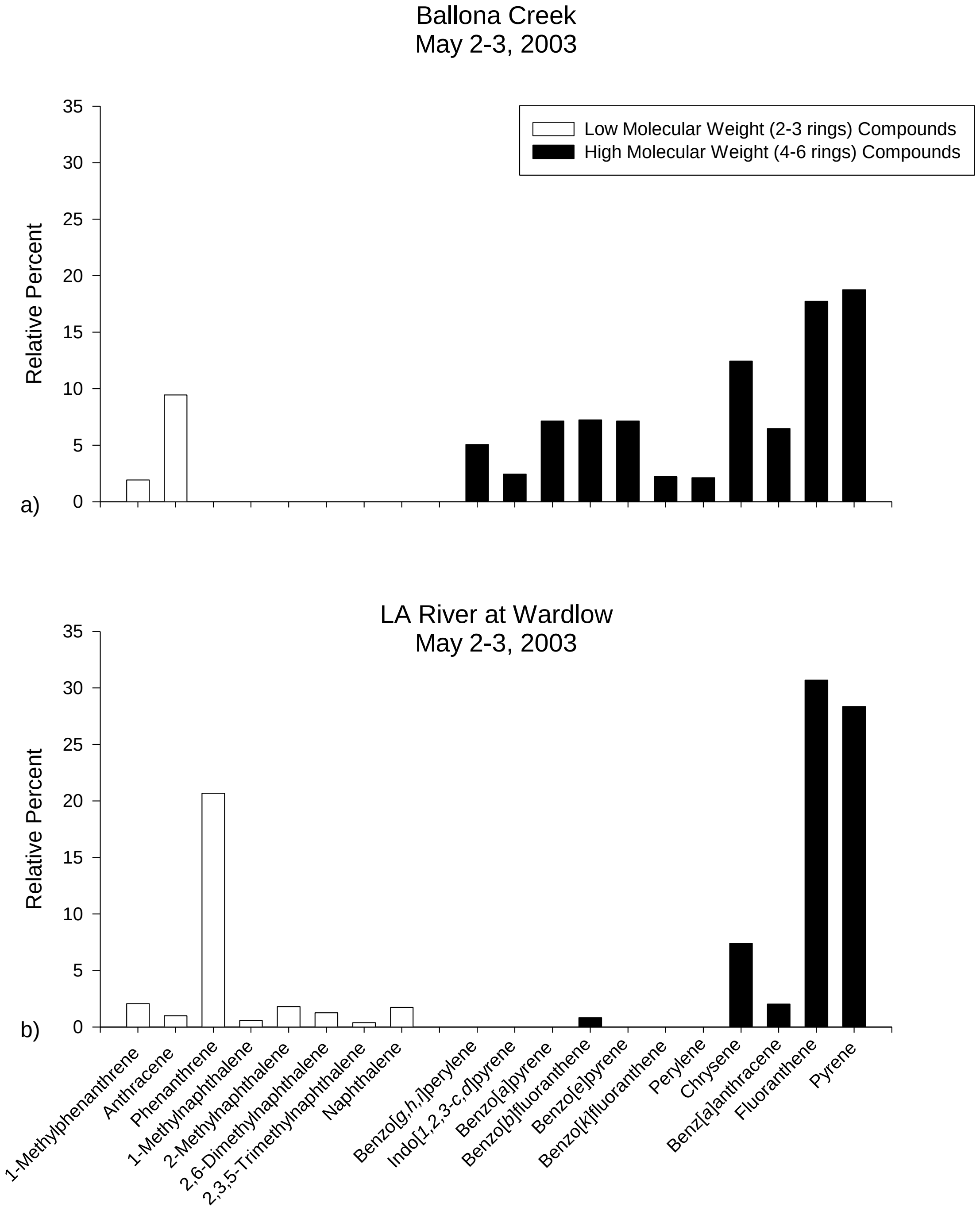

Figure 4-7. Relative distribution of individual polycyclic aromatic hydrocarbon compounds for Ballona Creek (a) and Los Angeles River (b) on May 2–3, 2003.

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SECTION 5. FECAL INDICATOR BACTERIA (FIB)

Results

FIB from Developed and Undeveloped Watersheds

E. coli, *Enterococcus* spp. and total coliforms occurred at all ME sites at concentrations that consistently and uniformly exceeded CA water quality standards (Figure 5-1). Mean *E. coli*, *Enterococcus* spp. and total coliforms EMCs and fluxes were significantly greater at ME sites from developed compared to undeveloped watersheds (ANOVA, $p = 0.006$). For example the mean EMC at the developed Ballona Creek watershed was two orders of magnitude higher than at the undeveloped Open Space Arroyo Sequit watershed (10^4 MPN/100 mL vs. 10^2 MPN/100 mL, respectively; Fig. 5-1a). Bacteria EMCs were typically higher in the Los Angeles River compared to the other watersheds sampled.

Bacterial flux from ME sites exhibited a similar pattern as that observed for the EMCs. For example, *E. coli* fluxes were two orders of magnitude higher at the developed Ballona Creek watershed versus the undeveloped Arroyo Sequit watershed (i.e., 10^{12} colonies/km^2 vs. 10^{10} colonies/km^2, respectively; ANOVA, $p = 0.02$, Figure 5-1b). Similarly, *Enterococcus* spp., and total coliforms fluxes were substantially higher for the developed watersheds versus the undeveloped watershed, but these differences were not statistically significant. Furthermore, the higher fluxes from developed watersheds were generated by substantially less rainfall than the lower fluxes from the undeveloped watersheds (2.07 ±1.22 cm for storms in developed watersheds vs 6.49 ±3.79 cm for storms in undeveloped watersheds).

FIB Concentration and Flux from Specific Land-use Types

Figure 5-2 shows the median FIB concentrations for the storm events sampled for each LU category. Mean *E. coli*, EMCs from the recreational LU site were significantly higher than the commercial, high density residential, industrial and transportation LU sites (i.e., $5.3\text{x}10^5$ MPN/100mL ± $1.7\text{x}10^5$, p=0.004, Appendix B-15) and were an order of magnitude higher than mean EMCs observed at ME sites. Agricultural LU sites contributed the second highest mean indicator bacteria EMCs but were not statistically different from all other LU sites (i.e., $4.0\text{x}10^4$ MPN/100mL ± $1.4\text{x}10^4$ *E. coli*, $1.2\text{x}10^5$ MPN/100mL ± $9.6\text{x}10^4$ *Enterococcus* spp. and $6.4\text{x}10^5$ MPN/100mL ± $9.6\text{x}10^4$ total coliforms).

Direct comparison of flux showed that storm water from agricultural, recreational and industrial LU sites had the highest mean FIB fluxes. Most of the developed LU types exhibited comparable fluxes of 10^{11} colonies/km^2 (Appendix B-15). In contrast, the agricultural LU contributed substantially higher flux of both *Enterococcus* spp. and total coliforms (e.g. mean *Enterococcus* flux = 10^{14} colonies/km^2 (Appendix B-15). Mean FIB fluxes at the open space LU were comparable to those observed at developed LU sites (e.g. 10^{12} colonies/km^2; Appendix B-15).

Correlation between FIB and TSS Concentration

A simple Spearman's correlation matrix (Table 5-1) of TSS, stream flow and FIB indicates that *E. coli* was significantly positively correlated ($p < 0.0001$) with TSS from agricultural, recreational and open LU sites. *E. coli* concentration from low-density residential and industrial LU sites were weakly correlated with TSS. *Enterococcus* spp. was significantly correlated (p <0.0001) with total suspended solids from low-density residential, agricultural, recreational and transportation LU sites and all correlations with the exception of the low-density residential site were positive. *Enterococcus* spp. counts from commercial and open LU sites were weakly and positively correlated with TSS. Both *E. coli* and *Enterococcus* spp. had correlation coefficients (Spearman's *rho* or ρ) between 0.5 and 0.8, indicating that similar processes may have controlled the effect of TSS on each of these parameters. FIB concentrations were only significantly correlated (p <0.0001) with stream flow at the commercial, high-density residential and agricultural LU sites.

California Bacterial Water Quality Standards

Bacteria concentrations exceeded the California beach water quality single-sample water quality standard in almost all of the samples collected during this study. Concentrations of FIB at many LU sites were as high as those found in primary wastewater effluent (10^6-10^7 MPN/100ml). Cumulative density frequency plots showed 98%, 94% and 92% of the in-river storm water samples for *Enterococcus* spp., *E. coli* and total coliforms bacteria exceeded CA ambient water quality standards (Figure 5-3). Similar results were observed at LU sites. Approximately 80% of all samples exceeded water quality thresholds at LU sites for at least one indicator (i.e., *E. coli* exceedence = 83%; Figure 5-3). The above comparisons are based on receiving water quality standards. If compared to the proposed freshwater standards, which are approximately 60% lower than the receiving water standards, the exceedances would be slightly higher.

Large-sized watersheds (>100 km^2) exhibited the greatest frequency of water quality threshold exceedences (Figure 5-4). More than any other indicator, concentrations of *Enterococcus* spp. were responsible for the majority of water quality threshold exceedences across all three watershed size categories, exceeding thresholds 98% of the time for both large and medium-sized watersheds (25-100 km^2), and 96% of the time for small-sized watersheds. *E. coli* and total coliform concentrations followed a decreasing frequency of exceedences in terms of watershed size (i.e., large > medium > small).

Temporal Patterns in Indicator Bacteria Loading

Effect of Rainfall Patterns: Indicator bacteria from LU sites showed little variation when evaluated for seasonal differences between early- and late- season storms. In contrast, antecedent dry period (expressed as cumulative annual rainfall) was strongly correlated with FIB concentrations from ME sites in an exponentially non-linear manner (r^2 = 0.67-0.92; Figure 5-5). Early-season storms generally had higher *Enterococcus* spp. and total coliforms EMCs than late-season storms both within and between watersheds with an inflection point at approximately 10 cm, even when rainfall quantity was similar. For example, the early-season storm from Ballona Creek in water year 2004 had an *Enterococcus* spp. EMC two times larger (3.0 x 10^4 MPN/100mL) than the storm that occurred at the end of the rainy season in water year 2003 (1.6 x 10^4 MPN/100mL), despite the early- and late-season storms resulting from comparable rainfall (approx. 3.0 cm). The results for *E. coli* EMCs from early- and late- season storms were comparable. When all watersheds are analyzed together *E. coli*, *Enterococcus* spp. and total coliforms concentrations decrease with increasing cumulative annual rainfall until approximately

10 cm (average annual rainfall is 33 cm), beyond which the effect is markedly less dramatic (Figure 5-5).

With-in Storm Variability

FIB concentrations varied with time and as a function of flow over the course of storm events. Figures 5-6 and 5-7 show the pattern of change throughout storm events for *E. coli* and *Enterococcus* spp.. In all cases, bacterial concentrations increased markedly preceding peak flow (compared to base flow level). *Enterococcus* spp. concentrations stayed high for a relatively short period at the developed Ballona Creek site (2.4 x 10^5 MPN/100mL) and then decreased back to base levels within two hours (Figure 5-6a). In contrast, *E. coli* concentrations were more variable exhibiting two separate peaks around 2.6 x 10^4 MPN/100mL and an order of magnitude lower than *Enterococcus* spp. concentrations (Figure 5-6b)[1]. Although the pattern of an early peak in concentration was comparable in both undeveloped and developed watersheds, in the undeveloped watersheds the peak concentration tended to occur later in the storm and persist for a longer duration (i.e., three to four hours; Figure 5-7). Furthermore, flow continued above base flow conditions for a longer duration in the undeveloped watersheds however FIB concentrations steadily decreased following the early peak in storm. We cannot make conclusions about the consistency of these patterns given the small number of storms sampled at undeveloped watersheds.

Discussion

The relatively higher bacteria concentrations from recreational and agricultural LU sites may be due to several sources. Sources of bacteria include domestic pet and wildlife wastes that are deposited, stored, or applied to the land, a fact that may account for the high *E. coli* and *Enterococcus* spp. EMCs, and overall mean flux of 1.4 x 10^{13} and 1.1 x 10^{14} colonies/km^2, respectively observed at the agricultural sites during this study. In contrast, land use sites, such as industrial areas and built-out residential areas, have proportionately less direct sources of fecal material and have lower sediment concentrations in storm water than do mixed LU and developing areas (i.e., recreational, Mallin 1998, Burnhart 1991). This difference in source material may be a factor that accounts for why these LU sites had lower indicator bacteria EMCs and fluxes.

The association of bacteria with storm water particles may also explain differences in *E. coli* and *Enterococcus* spp. concentrations from different LU sites. Correlations of FIB with TSS from recreational and agricultural LU sites indicate associations with particulate material, but it is unclear if that particulate material resulted from soils transported to the stream from these LU sources or from erosion and resuspension of sediment already in the streambed from upland sources. Other studies have implicated streambed sediment and its resuspension (Matson et al. 1978, Francy et al. 2000, Embrey 2001) as sources and principal transport vectors for bacteria. The higher indicator bacterial concentrations at the recreational and agricultural land use sites indicate that bacteria associated with these areas may be directly associated with sources at those sites. Another possible explanation for the high FIB concentrations at agricultural sites may be

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[1] Unfortunately FIB samples were not collected prior to 3:30 AM due to failure to be on site when storm commenced.

due to the regular application of fertilizers, algaecides and fungicides (Niemi 1991, Cook and Baker 2001). Assessing particle size distribution over the entire storm duration at these LU sites may provide a clearer or consistent particle source association. Interestingly, indicator bacteria concentrations were only significantly correlated ($p<0.0001$) with stream flow at the commercial and high-density residential LU sites even though bacteria in streams are commonly associated with suspended particles (Schillinger and Gannon, 1985, Hunter et al. 1999), either because they were transported to the streams attached to the particles, they were bound to streambed sediment (Matson et al.1978) that has been resuspended (Grimes 1975, Matson et al.1978, Hunter et al. 1999) or because of specific bacterial affinities for sediment particles (Scholl and Harvey 1992, Bolster et al. 2001) that may occur in the water column. Although bacterial transport has been correlated with stream stage (Hunter et al. 1992) and stream flow during storms and also tends to be associated with the transport of suspended sediment (Davis et al. 1977), these associations are not always evident (Qureshi and Dutka 1979). In the Los Angeles River watershed the lack of correlations at specific LU sites with stream flow may indicate that contributing sources or processes for bacteria were different from storm to storm.

Comparison of FIB concentrations in runoff from LU sites from this study reveal median *E. coli* EMCs that are comparable to current U.S. averages reported in the National Stormwater Quality Database (NSQD; Maestre et al. 2003), but lower than concentrations reported in the Nationwide Urban Runoff Program (NURP) database (U.S. EPA 1983a; Figure 5-8). The exception is that median total coliform values from all LU sites in Los Angeles, CA are substantially higher than those observed in the rest of the U.S. (Table 5-2). The similarities in median event-mean *E. coli* concentrations from LU sites across the U.S. measured since 1992 (reported by the NSQD) and those observed 13 years later during this study demonstrate that the issue of fecal bacteria contamination in urban watersheds is not improving over time.

Seasonal comparisons of wet weather FIB concentrations to dry weather concentrations from the urbanized Ballona Creek watershed during 2002-03 revealed that contributions from wet weather far exceeded those from dry weather (Table 5-3). Freshwater outlets such as storm drains are found to be especially high contributors of indicator bacteria contamination (Stein and Tiefenthaler 2005, Noble et al. 2000, Bay and Schiff 1998). Nevertheless, the highest mean dry-weather *E. coli* concentrations (7,457 MPN/100 ml) found in samples from Ballona Creek were still an order of magnitude lower than the lowest mean *E. coli* storm EMC from this study (43,305 MPN/100 ml; Table 5-3, $p<0.03$ E. coli; $p<0.04$ *Enterococcus* spp.; $p<0.02$ total coliforms). Wet versus dry sampling events have been compared by other studies in the southern California region (Noble et al. 2006, Schiff et al. 2003, Noble et al. 2003). These studies also found a higher number of exceedences of water quality standards during wet weather for all indicators, especially at storm water outflows and storm drains.

Consistently higher bacteria levels during early season storms likely reflect bacteria buildup during dry periods that "flushes" to rivers during early season storms. Bacteria concentrations in rivers were strongly influenced by the length of antecedent dry condition but not with amount of rainfall. The strong relationship between indicator bacteria EMC and antecedent dry period suggests that the magnitude of bacterial load associated with storm water runoff depends on the amount of time available for build up on land surfaces, and that storm size is a less reliable predictor of the magnitude of bacterial loading. Since indicator bacteria continue to reproduce in the environment and reproduction is favored in aerobic temperate waters, low flow and high temperature conditions that typically occurs in southern California between May and October likely allows indicator bacteria concentrations to build-up on land surfaces, resulting in proportionally higher bacteria concentrations and loads during the initial storms of the season. A similar seasonal pattern (i.e., 10 cm cumulative annual rainfall threshold) was observed for polycyclic aromatic hydrocarbons (PAHs) and trace metals in the Los Angeles region (Stein et al. 2006, Sabin et al. 2004, Tiefenthaler et al. in press). Han et al. (2006) also reported that antecedent dry period was the best predictor of the magnitude of pollutant runoff from highways. Other researchers (Anderson and Rounds 2003, Ngoye and Machiwa 2004) 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.

FIB concentrations in storm water were highly variable, with concentrations often ranging by factors of 10 to 100 during a single storm. The greatest bacteria concentrations occurred at or just before the peak in flow of the storm hydrograph for nearly every storm sampled. This hydrograph/pollutograph pattern was also observed for PAHs (Stein et al. 2006) and trace metals (Tiefenthaler et al. in press) in the greater Los Angeles area. Tiefenthaler et al. (2001) observed similar pollutographs that showed peak suspended-sediment concentrations preceding the peak in discharge for the Santa Ana River. Similar time vs. concentration relationships were observed by Characklis and Wiesner (1997), who reported that the maximum concentrations of zinc, organic carbon and solids coincided with early peak storm water flows. Bacterial counts typically vary by up to five orders of magnitude on daily, seasonal, and inter-annual scales. The extreme variability in FIB makes storm water bacteria concentrations difficult to accurately estimate. Furthermore, as living organisms, many processes that do not influence other constituents, such as re-growth of environmentally adapted strains, die-off, and random fluctuations in population size, may affect bacterial counts (Ferguson et al. 2005). Therefore, more frequent monitoring over longer time periods and for the entire duration of storms is necessary in order to make assessments of “typical” bacterial counts and accurate estimates of EMC and FIB loading.

Further research is needed to directly assess the relationship between indicator bacteria concentrations and particle-size distributions in storm water runoff from mass emission and LU sites to better understand the fate, transport and treatment of indicator bacteria in urban runoff. Storm water borne bacteria are typically associated with particulates to varying degrees depending on the indicator bacteria and the size distribution of suspended solids in the storm water runoff. Furthermore, the particle size distribution, and bacteria partitioning can change over the course of a storm event (Furumai et al. 2002). Understanding the dynamic partitioning of indicator bacteria to various size particles is important to being able to estimate temporal and spatial patterns of bacterial deposition in estuaries and harbors, and should be an area of future investigation. Our understanding of the mechanisms of indicator bacteria loading from urban LU sites could also be improved by estimating the percent watershed impervious surface coverage in each LU category (i.e., percent rooftop, sidewalks, paved driveways and streets) and its impacts on storm water runoff concentrations and loads. This could allow identification of critical source areas and allow for more targeted application of best management practices.

Table 5-1. Correlations between total suspended solids (TSS) and stream flow with respect to fecal indicator bacteria (FIB) during storm condition. Within a table cell, the upper row shows Spearman's correlation coefficient (ρ), the middle row shows probability (p) that the null hypothesis of no correlation is true, and the lower row shows number of samples (n). Numbers in bold indicate correlations that are significant (p <0.04).

	Total Suspended Solids			**Stream Flow**		
	E. coli	*Enterococcus* spp.	Total Coliforms	*E. coli*	*Enterococcus* spp.	Total Coliforms
High Density Residential	-0.0815	0.0226	-0.0196	0.6110	-0.0564	0.0656
	0.6060	0.8860	0.9010	**<0.0001**	0.7050	0.66
	42	42	42	42	42	42
Low Density Residential	-0.3640	-0.6030	-0.1800	0.2390	0.0400	-0.2690
	0.0268	**<0.0001**	0.2850	0.1280	0.8000	0.0851
	37	37	37	37	37	37
Commercial	0.2460	0.3540	0.4160	0.7720	0.8190	0.7960
	0.0958	**0.0149**	**0.0038**	**<0.0001**	**<0.0001**	**<0.0001**
	47	47	47	47	47	47
Industrial	-0.3890	-0.3040	-0.1300	-0.2510	-0.2480	-0.1330
	0.0035	**0.0244**	0.3440	**0.0421**	**0.0447**	0.285
	55	55	55	55	55	55
Agricultural	0.5530	0.6160	0.3560	0.2810	0.4360	0.6880
	<0.0001	**<0.0001**	**0.0178**	**0.0440**	**0.0015**	**<0.0001**
	44	44	44	44	44	44
Recreational (horse)	0.6940	0.7670	0.7320	-0.0162	0.5870	-0.0921
	<0.0001	**<0.0001**	**<0.0001**	0.9370	**0.0027**	0.664
	20	20	20	20	20	20
Transportation	0.5190	0.7410	0.6720	-0.7120	0.3920	-0.3470
	0.0190	**<0.0001**	**0.0011**	**0.0080**	0.1970	0.253
	20	20	20	20	20	20
Open	0.6700	0.4610	0.1740	0.2550	0.2230	-0.1990
	<0.0001	**0.0106**	0.3550	0.0980	0.1490	0.198
	30	30	30	30	30	30

Table 5-2. Comparison of Nationwide Urban Runoff Program (NURP) and National Stormwater Quality Database data to fecal indicator bacteria concentrations from specific land uses in the Los Angeles, California, USA region. Median event mean concentration (EMCs) are in (MPN/100mL). NA = not analyzed.

Land Use Type	Median EMC (MPN/100mL)	
	E. coli	Total Coliform
Overall		
LARW[1]	3,922	40,559
NSQD[2]	5,091	11,000
NURP[3]	20,000	NA
Residential		
LARW[1]	6,331	55,426
NSQD[2]	8,345	5,467
NURP[3]	17,000	NA
Commercial		
LARW[1]	3,939	22,291
NSQD[2]	4,300	NA
NURP[3]	16,000	NA
Industrial		
LARW[1]	1,546	39,595
NSQD[2]	2,500	12,500
NURP[3]	14,000	NA
Open Space		
LARW[1]	5,374	25,565
NSQD[2]	7,200	NA
NURP[3]	NA	NA

[1] 2001-2005 Los Angeles River Watershed Wet Weather Study
[2] The National Stormwater Quality Database (NSDQ), Pitt et al. (2003)
[3] Nationwide Urban Runoff Program (U.S. EPA 1983a)

Table 5-3. Comparison of seasonal concentrations of fecal indicator bacteria (FIB) from the Ballona Creek watershed. Event mean concentration (EMCs) in MPN/100mL.

	Ballona Creek					
Fecal Indicator Bacteria	Dry Weather[1] EMC (MPN/100 mL)			Wet Weather EMC (MPN/100 mL)		
	Min	Max	n	Min	Max	n
E. coli	693	7,457	3	8,304	43,305	6
Enterococcus spp.	727	2,173	3	14,438	78,368	6
Total Coliforms	21,763	40,556	3	127,635	678,973	6

[1] Data summarized from Water, Air and Soil Pollution, 2005. Vol. 164 (Stein E, Tiefenthaler L)

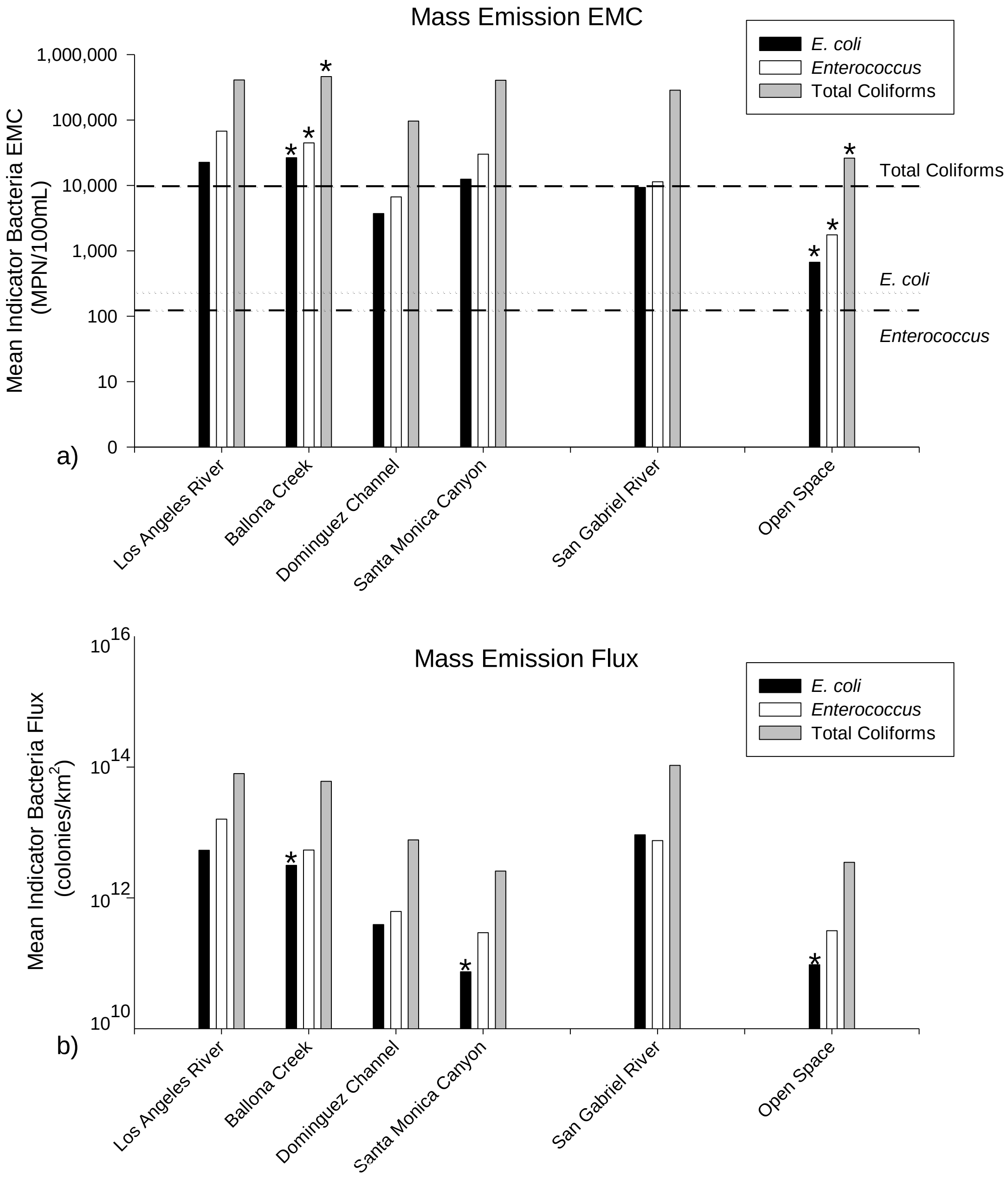

Figure 5-1. **Mean storm EMCs (a) and fluxes (b) of *E. coli*, *Enterococcus* spp. and total coliform concentrations at specific southern California watersheds during the 2000/01-2004/05 storm seasons. Dotted lines indicate California beach water quality standards.**

~~Will be updated~~

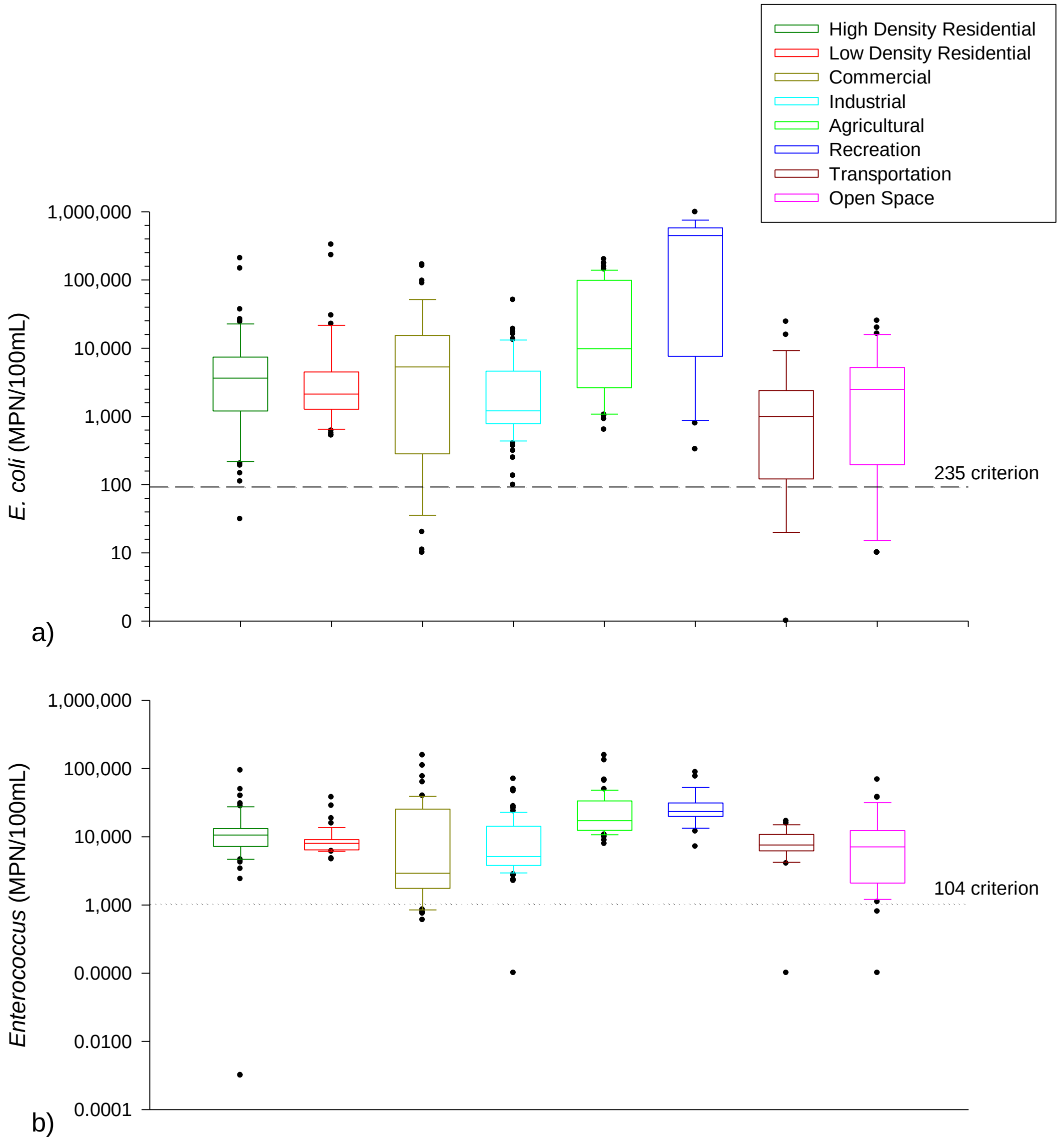

Figure 5-2. Distribution of *E. coli* (a) and *Enterococcus* spp. (b) concentrations during the 2000-2005 wet seasons from land use (LU) sites.

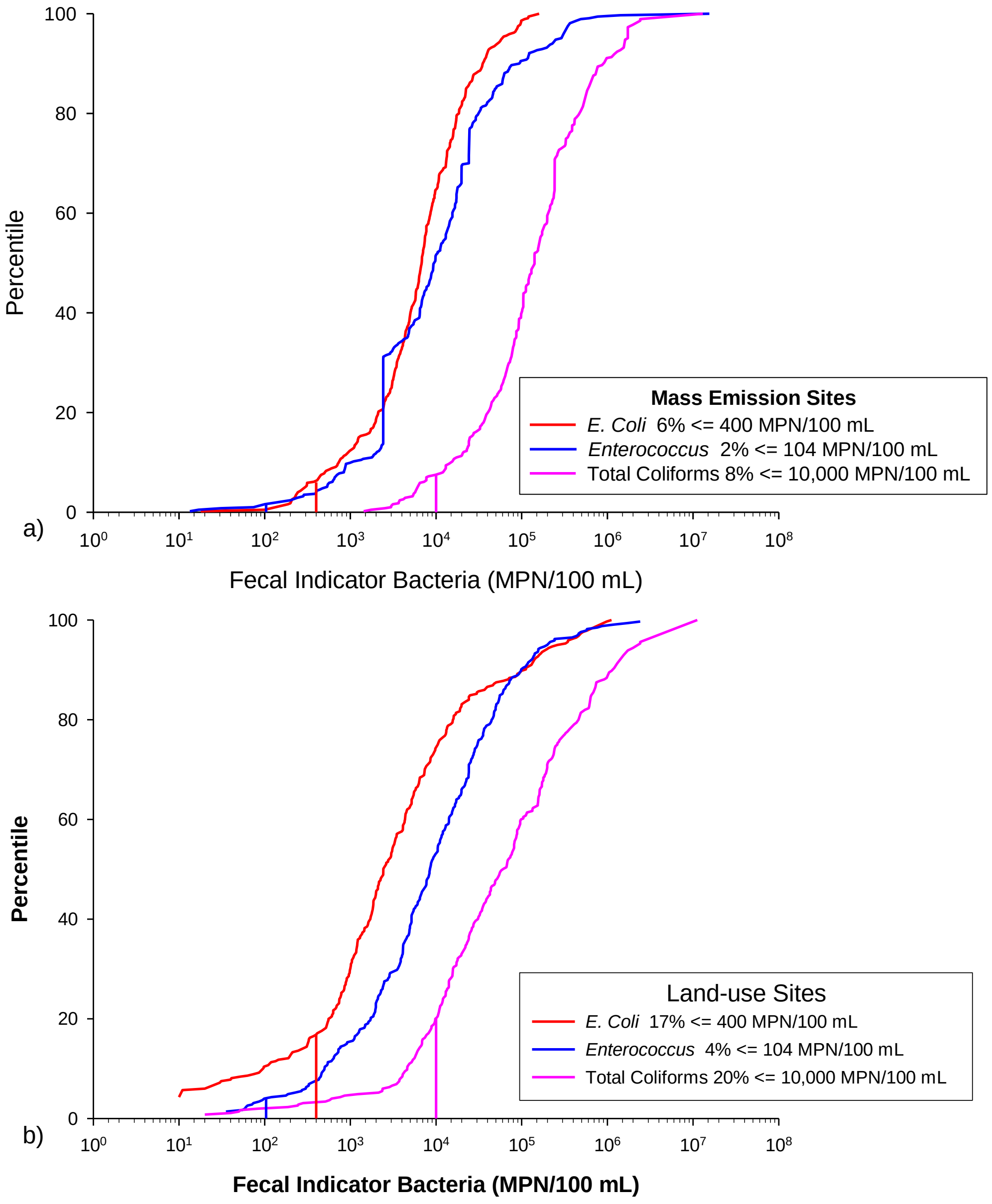

Figure 5-3. Cumulative density frequency plots (CDFs) of mass emission (ME; a) and land use (LU) sites (b) relative to beach water quality standards.

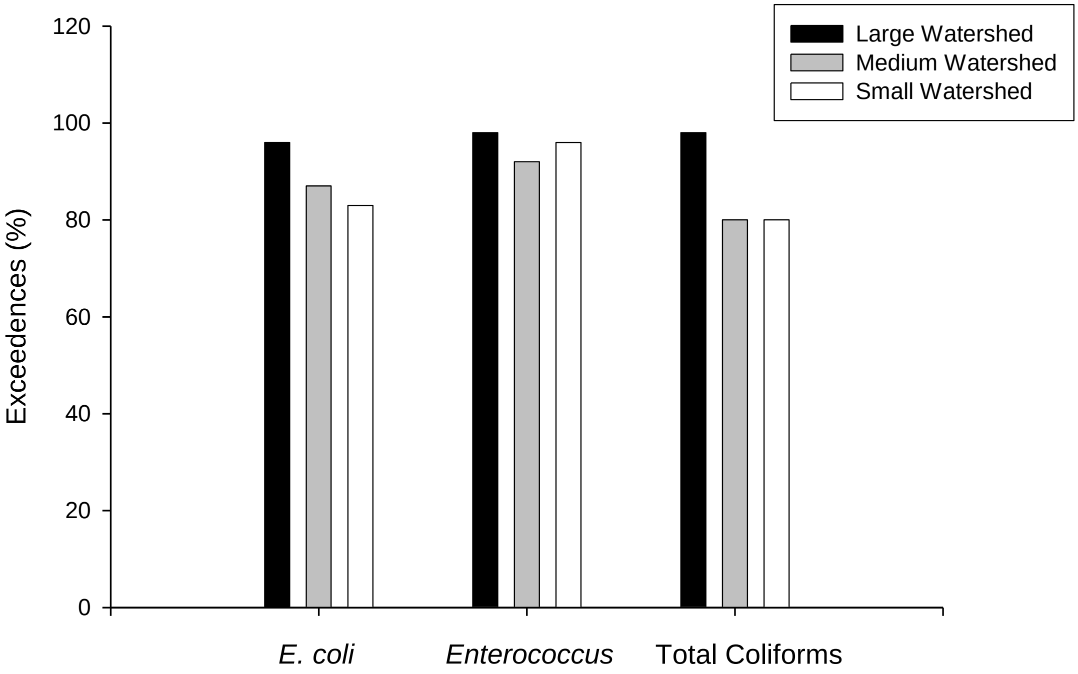

Figure 5-4. Comparison of water quality threshold exceedences at mass emission (ME) and land use (LU) sites with watershed size (small: <25 km^2, 25-100 km^2, >100 km^2).

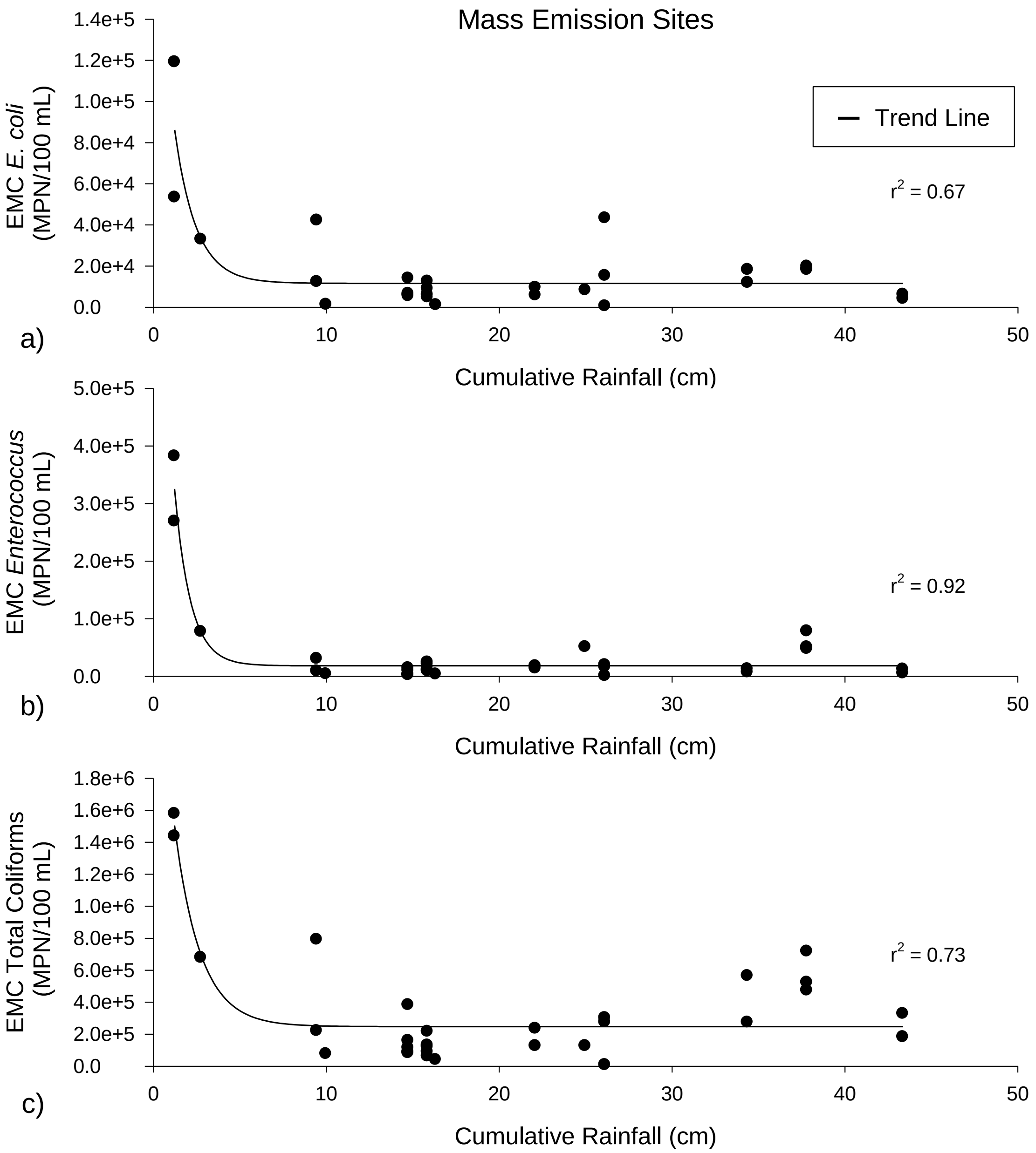

Figure 5-5. Cumulative annual rainfall versus event mean concentration (EMC) for *E. coli* (a), *Enterococcus* spp. (b), and total coliforms (c) during 2000-2005 storm seasons for mass emission (in-river) sites only.

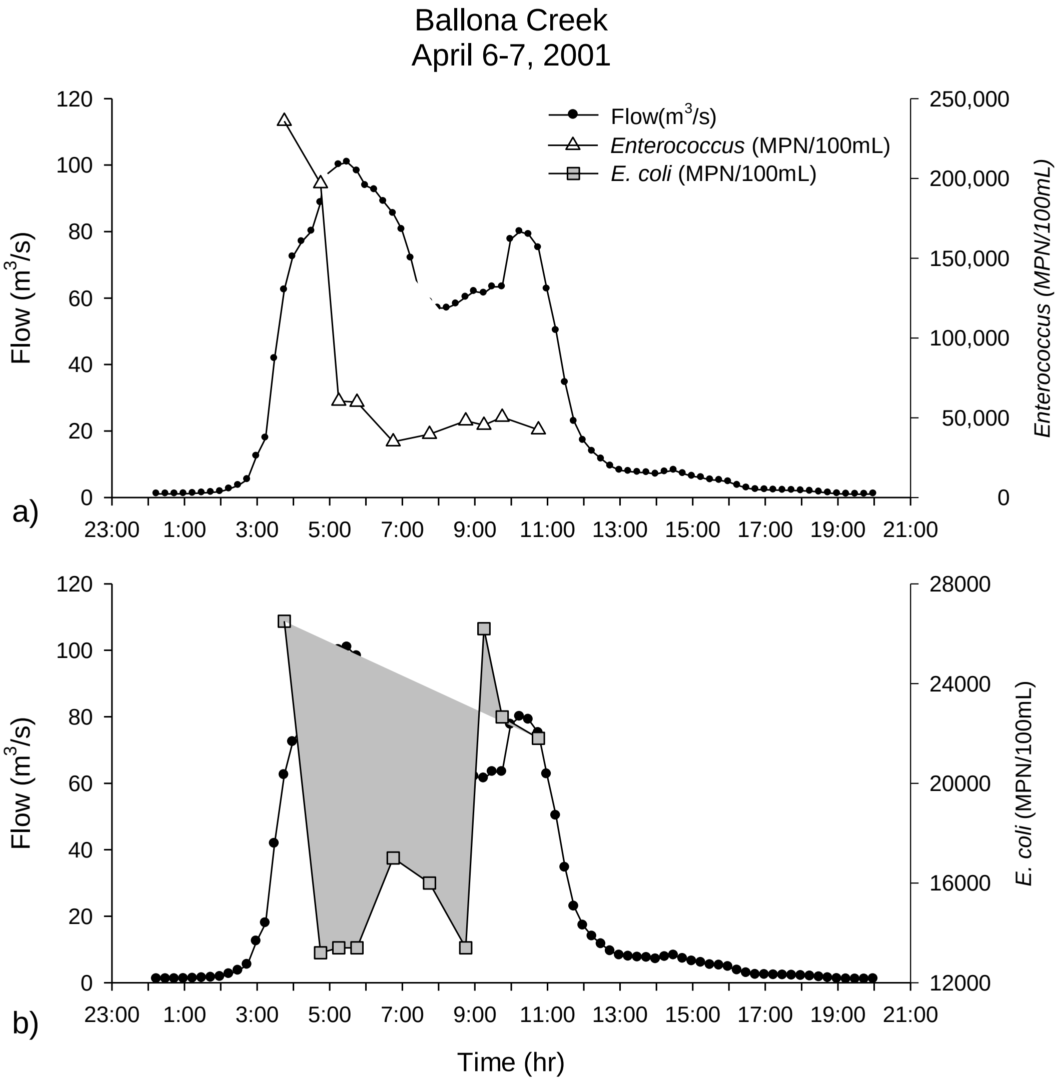

Figure 5-6. *Enterococcus* spp. (a) and *E. coli* (b) concentrations with time for a storm event from the developed Ballona Creek watershed.

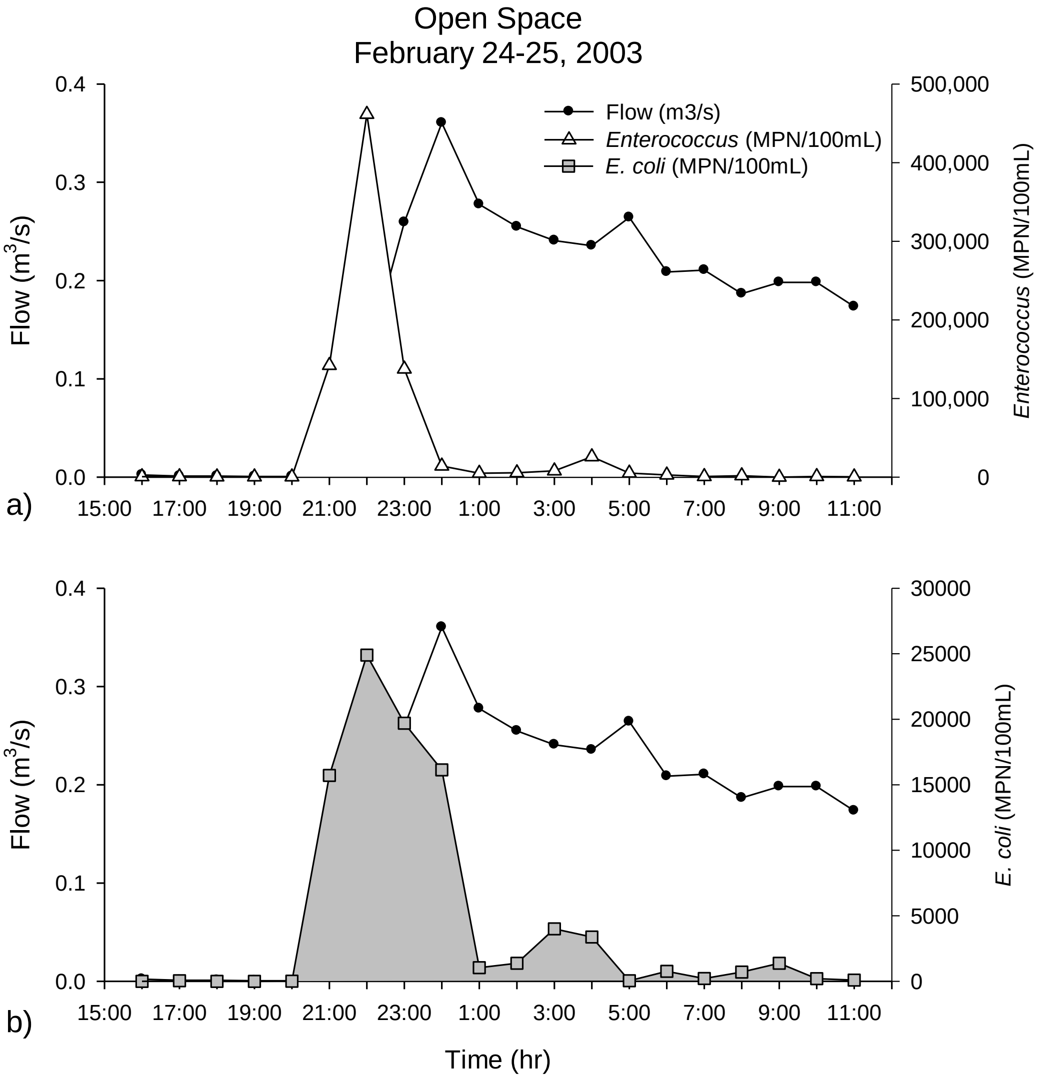

Figure 5-7. ***Enterococcus*** **spp. (a) and** ***E. coli*** **(b) concentrations with time for a storm event from the open space land use site.**

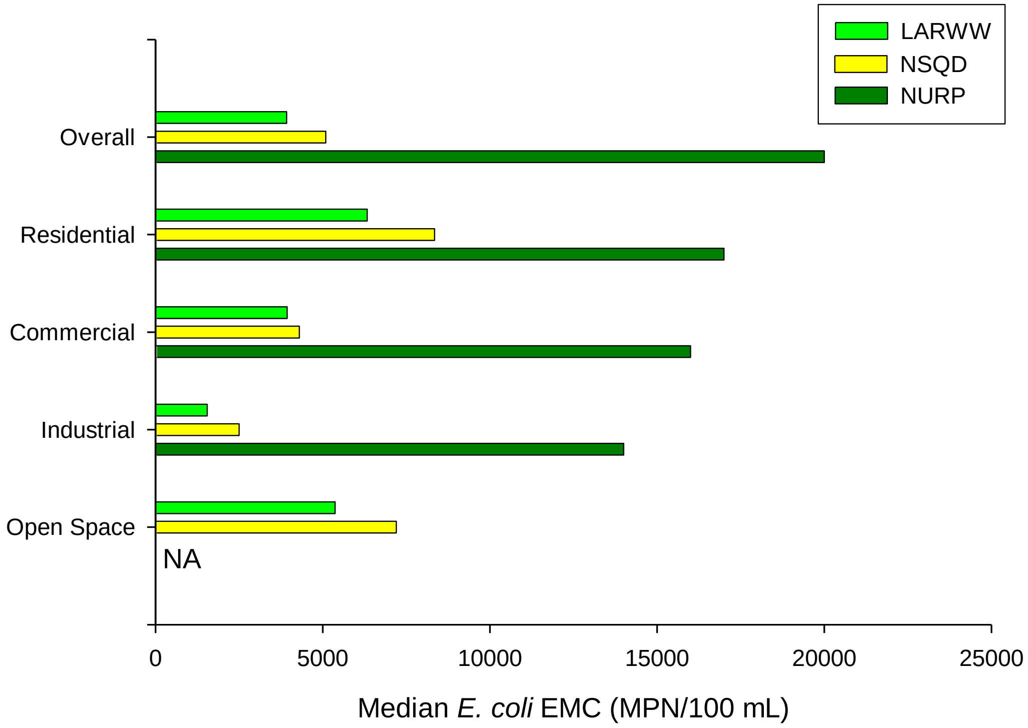

Figure 5-8. Comparison of median *E. coli* event mean concentration (EMCs) at specific land use (LU) sites during the 1983 Nationwide Urban Runoff Program (NURP, U.S. EPA 1983a), to the 1990 National Stormwater Quality Database (NSQD, Pitt et al. 2003) monitoring study and the 2001-2005 Los Angeles River Wet Weather (LARWW) study. Median EMCs are in (MPN/100mL). NA = not analyzed.

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APPENDIX A: Detailed Description of Land Use Categories

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/510_APPENDIX_A.pdf

APPENDIX B: Trace Metal, TSS and Bacteria EMCs, Fluxes and Loadings at Mass Emission and Land Use Sites

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/510_APPENDIX_B.pdf

APPENDIX C: First Flush Patterns of Trace Metals at Mass Emission and Land Use Sites

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/510_APPENDIX_C.pdf

APPENDIX D: Probability Density Frequency Plots (PDFs) of Fecal Indicator Bacteria at Land Use Sites in the Greater Los Angeles, CA Region

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/510_APPENDIX_D.pdf