Comparison of stormwater pollutant loading by land use type

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ABSTRACT

Urban stormwater is recognized as a major source of pollution to many of the nation's waterways. Managing stormwater is complicated by the extreme variability associated with runoff patterns from different land use (LU) types under different rainfall conditions. Models are an increasingly common tool for understanding the processes that influence variability in urban stormwater and incorporating this understanding into management decisions. Unfortunately, routine monitoring programs seldom provide the data necessary to adequately calibrate and validate watershed models. This study provides a regionally representative calibration data set by characterizing event mean concentrations (EMC) and fluxes of total suspended solids (TSS), metals, polycyclic aromatic hydrocarbons (PAHs), and bacteria from representative land-uses and investigates within-storm patterns in order to identify mechanisms that influence constituent loading. Pollutant concentrations and flow were measured over the entire storm duration from 8 different LU types over 11 storm events in 5 southern California watersheds for the 2000-01 through 2004-05 storm seasons. Mean TSS EMCs were significantly higher at recreational sites compared to all other LU sites. For trace metals, Cu, Pb, and Zn values were significantly higher at industrial sites than at other LU types. Despite some general variability among LUs, no significant differences in PAH concentration among LU types were observed. All LU sites had clear signatures of pyrogenic (combustion by-product) derived PAHs. Recreational LU sites had significantly higher levels of both *Escherichia coli* and enterococci, compared to other LU types. For all constituents, the greatest concentrations occurred during the rising limb of the storm hydrograph. Concentrations stayed high for relatively short periods and decreased back to base levels within one to two hours. Results of this study can be used to calibrate watershed models used for water quality assessments, contaminant load allocations, and TMDL development. These data sets can also assist stormwater engineers in the design of more effective monitoring programs and better performing treatment practices (i.e., BMPs) that address differences between LU types and specific rainfall/runoff conditions.

INTRODUCTION

Urban stormwater is recognized as a major source of pollution to many of the nation’s waterways (Characklis and Wiesner 1997, USEPA 2000, Davis *et al*. 2001). 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) into receiving waters (Novotny and Olem 1994).

Past monitoring and assessment efforts have provided important insight into the general patterns of stormwater loading. Previous studies have documented that the most prevalent metals in urban stormwater are Zn, Cu, Pb, and to a lesser degree Ni and Cd (Sansalone and Buchberger 1997, Davis *et al*. 2001). PAHs in urban stormwater have been shown to result mainly from atmospheric deposition (Hoffman *et al*. 1984, Menzie *et al*. 2002). Recent studies using *E. coli*, enterococci, and total coliform have documented freshwater outlets such as storm drains to be especially high contributors of bacterial contamination (Noble *et al*. 2003, Stein and Tiefenthaler 2005). These studies provide critical information for the general characterization of pollutants in urban stormwater. However, routine stormwater monitoring programs focus on quantification of average concentration or load at the terminal watershed discharge point. While important for regulatory compliance and overall status and trends assessment, such monitoring provides little insight into the mechanisms and processes that influence constituent levels in stormwater.

To effectively manage stormwater, managers need to gain a deeper understanding of factors that affect stormwater 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 LU types (i.e., commercial, residential, industrial, recreation, transportation, and open space). Decisions should also be influenced by knowledge of 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.

Information on pollutant runoff from various LU is critical for calibrating watershed models that can be used to design and evaluate proposed management measures (Ackerman and Stein 2008b). This is particularly important for larger watersheds where complex runoff patterns require the use of dynamic models such as Hydrological Simulation Program-FORTRAN (HSPF), Stormwater Management Model (SWMM), or the Generalized Watershed Loading Functions (GWLF) to describe pollutant load generation (Butcher 2003). Park and Stenstrom (2008) note that predicted stormwater loads are highly sensitive to LU designations and their associated EMC estimates, and one the greatest sources of model uncertainty arises from the lack of accurate EMC data. Because of this uncertainty, differences in predictions based upon EMC assumptions can be larger than the potential impact of applying BMPs.

The goal of this study was to quantify the sources and patterns of concentration and flux of trace metals, PAHs and fecal indicator bacteria from representative urban LU types. Results of this study can be used to establish profiles of ranges of expected pollutant types and levels associated with different LU types. These ranges can be used for watershed characterizations and for calibration of regional water quality models. In addition to quantifying differences between LU categories, our goal is to support model calibration by investigating within storm patterns in concentration and flux in order to identify mechanisms that influence constituent loading.

Methods

Stormwater runoff was sampled from 21 different homogenous LU sites representing 8 distinct LU types in the greater Los Angeles region of California (Figure 1). The 19 homogenous LU sites represent the distribution of LU types in southern California as

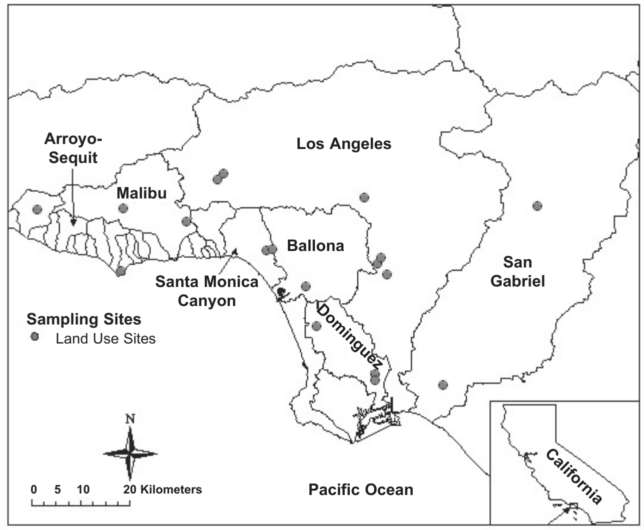

Figure 1. Land use sampling sites locations.

defined by the Southern California Association of Governments (http://scag.ca.gov/wags/index.htm; Table 1). The Southern California Association of Governments derived these LU types from year 2000 aerial photography surveys with a minimum resolution of 8 m^2. LU catchments ranged in size from 0.002 to 2.89 km^2 and the average LU catchment size was 0.75 ±1.0 km^2.

Pollutant concentrations, rainfall, and flow were measured for the entire storm duration over 11 storm events in 5 southern California watersheds for the 2000-01 through 2004-05 storm seasons. A total of 33 site events were sampled from homogenous LUs that included high density residential, low density residential, commercial, industrial, agricultural, recreational, transportation, and open space. Each site was sampled between one and four times.

Rainfall amounts ranged from 0.12 to 9.68 cm and antecedent conditions ranged from 0 to 142 days 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 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 within 20% of base flow. Between 10 and 15 discrete grab samples were collected per storm at approximately 30- to 60-minute intervals for each site-event based on optimal sampling frequencies in southern California described by Leecaster *et al*. (2001). All water samples were collected by

Table 1. Land use sites sampled, catchment size, and number of storms sampled for each site. Land use types as defined by the Southern California Association of Governments (SCAG) data sets.

Land Use Type	Watershed Size (km^2)	No. of Storms Sampled	SCAG Land Use Type Defined
High Density Residential (A #1)	0.52	3	Duplexes, Triplexes and 2- or 3-Unit Condominiums and Townhouses; High Density Single Family Residential; High Rise Apartments and Condominiums; Low Rise Apartments, Condominiums, and Townhouses; Medium Rise Apartments and Condominiums; Mixed Multi-Family Residential; Mixed Residential; Mobile Home Courts and Subdivisions, Low Density; Trailer Parks and Mobile Home Courts, High Density.
High Density Residential (A #2)	0.02	2	
High Density Residential (A #3)	1	2	
Low Density Residential (B #1)	0.98	3	Low Density Single Family Residential; Rural Residential, High Density; Rural Residential, Low Density.
Low Density Residential (B #2)	0.18	1	
Commercial (C #1)	NA	1	Attended Pay Public Parking Facilities; Base (Built-up Area); Colleges and Universities; Commercial Recreation; Commercial Storage; Correctional Facilities; Elementary Schools; Fire Stations; Government Offices; High Rise Major Office Use; Hotels and Motels; Junior or Intermediate High Schools; Low Rise and Medium Rise Major Office Use; Major Medical Health Care Facilities; Modern Strip Development; Non-Attended Public Parking Facilities.
Commercial (C #2)	2.45	1	
Commercial (C #3)	0.06	3	
Industrial (D #1)	0.004	1	Chemical Processing; Communication Facilities; Electrical Power Facilities; Harbor Facilities; Harbor Water Facilities; Improved Flood Waterways and Structures; Liquid Waste Disposal Facilities; Maintenance Yards; Major Metal Processing; Manufacturing; Manufacturing, Assembly, and Industrial Services; Marina Water Facilities; Mineral Extraction - Oil and Gas; Mixed Utilities; Motion Picture and Television Studio Lots; Natural Gas and Petroleum Facilities; Navigation Aids; Open Storage; Packing Houses and Grain Elevators; Petroleum Refining and Processing; Research and Development.
Industrial (D #2)	0.002	1	
Industrial (D #3)	2.77	3	
Industrial (D #4)	0.01	1	
Agricultural (E #1)	0.98	4	Dairy, Intensive Livestock, and Associated Facilities; Horse Ranches; Irrigated Cropland and Improved Pasture Land; Non-Irrigated Cropland and Improved Pasture Land; Nurseries; Orchards and Vineyards; Other Agriculture; Poultry Operations.
Agricultural (E #2)	0.8	1	
Recreational (F #1)	0.03	2	Developed Local Parks and Recreation; Developed Regional Parks and Recreation; Golf Courses; Undeveloped Regional Parks and Recreation.
Transportation (G #1)	0.01	1	Airports; Bus Terminals and Yards; Freeways and Major Roads; Mixed Transportation; Mixed Transportation and Utility; Park-and-Ride Lots; Railroads; Truck Terminals
Transportation (G #2)	0.002	1	
Open Space (H #1)	9.49	1	Abandoned Orchards and Vineyards; Air Field; Beach Parks; Beaches (Vacant); Cemeteries; Mineral Extraction - Other Than Oil and Gas; Other Open Space and Recreation; Specimen Gardens and Arboreta; Under Construction; Vacant Area; Vacant Undifferentiated; Vacant With Limited Improvements; Wildlife Preserves and Sanctuaries
Open Space (H #2)	2.9	1	

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. Discharge was measured as the product of the wetted cross-sectional area from where samples were collected and the flow velocity. Velocity was measured using an acoustic Doppler velocity (AV) meter that also measured stage and instantaneous flow data (SonTek/YSI, San Diego, CA).

After collection, water quality samples were stored in pre-cleaned glass bottles on ice with Teflon-lined caps until they were shipped to the laboratory for analysis. Samples were analyzed for TSS, trace metals, PAHs, *E. Coli*, and enterococci. Standard methods and protocols were used for all analysis (USEPA 1991); TSS was measured by filtration, metals by inductively coupled plasma mass spectroscopy (ICPMS), PAHs by capillary gas chromatography + mass spectroscopy, and *E. coli* and enterococci were measured by defined substrate colormetric analysis (IDEXX).

Using only those samples for a single storm, a flow-weighted EMC was calculated as:

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

where Ci = individual runoff sample concentration of i^{th} sample, Fi = 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. Differences in concentration between LU sites were investigated using a one-way ANOVA, with a $p < 0.05$ significance level followed by Tukey-Kramer post-hoc test for multiple comparisons (Sokal and Rohlf 1995).

Sources of PAHs were also assessed by analyzing the relative proportion of individual PAH compounds and their ratios to determine if a pyrogenic (i.e., combustion by-products) or petrogenic (i.e., unburnt petroleum) source signature was suggested. 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 ratio of fluoranthene to pyrene (F/P) and the ratio of phenanthrene to anthracene (P/A) were used to determine pyrogenic versus petrogenic sources of PAH. Pyrogenic sources predominate when F/P ratios approach 0.9 (Maher and Aislabie 1992). Pyrogenic sources predominate when P/A ratios ranged from 3 to 26 (Lake *et al*. 1979, Gschwend and Hites 1981).

Mechanisms of pollutant loading were investigated by analyzing patterns of 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 storm events was defined as a circumstance when the peak in concentration preceded the peak in flow. This was also 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 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.

Results

Pollutant Concentrations from Specific Land Use Types

Concentration and flux levels for specific LU types varied by constituent and no single LU type was responsible for contributing the highest loading for all constituents measured. Mean concentration values for TSS, metals, PAHs and bacteria for each LU category are summarized in Table 2 and discussed in detail below.

TSS and Metals

Industrial and agricultural LU sites contributed substantially higher fluxes of TSS compared to the other LU sites evaluated (Figure 2). For example, mean TSS flux from the industrial and agricultural LU sites were comparable around 3,150 kg/km^2 while mean TSS flux from recreational and high density residential LU was 2,211 kg/km^2 and 91 kg/km^2, respectively. Mean TSS flux from undeveloped LU sites were slightly higher than the remaining developed LU sites. For example mean TSS flux from open space LU sites was 514 kg/km^2 compared to 161 kg/km^2 and 94 kg/km^2 for low density residential and commercial LU sites, respectively. On a concentration basis, mean TSS EMCs were significantly higher at recreational sites (averaging 531 mg/L) compared to all other LU types ($p = <0.001 - 0.03$). Concentration of TSS from open space sites was comparable to that from industrial, agricultural and residential LUs and higher than transportation and commercial LU sites. These differences were not statistically significant, however.

Industrial LU sites had substantially higher concentration and flux of Cu and Zn compared to the other LU sites evaluated (Figure 2). Mean total Cu flux from the industrial LU was 1,238 g/km^2 while mean total Cu flux from high density residential and recreational LU was 101 g/km^2 and 190 g/km^2, respectively. Trace metal flux from undeveloped LU sites was lower than those observed in developed LUs. For example, mean Cu flux at open space LU sites was 24 g/km^2. In contrast to Cu and Zn, the mean flux of total Pb was greatest at agriculture, high density residential, and recreational LU sites (Figure 2). The mean flux of total Pb at these three LU sites was at least an order of magnitude greater than any other LU sampled.

On a concentration basis, Cu, Pb, and Zn values were significantly higher at industrial sites than at other LU types ($p <0.001$; Table 2). For example, Zn EMCs at the industrial LU averaged 599 mg/L compared to 362 mg/L and 208 mg/L for commercial and high density residential LU sites, respectively. High density residential also had a significantly higher Pb EMC relative to all other LU sites. Mean EMCs for all three metals from undeveloped LU sites were lower than those observed in developed LU sites. For example, mean Cu, Pb, and Zn EMCs from open space LU sites was 8 mg/L, 2 mg/L, and 23 mg/L, respectively.

Polycyclic Aromatic Hydrocarbons

For all LU sites sampled, mean PAH flux was between 0.33 and 140 g/km^2 (Figure 2). Flux from the industrial LU site was significantly greater than all other sites, which ranged from 0.33 to 8.9 g/km^2.

Table 2. Mean event mean concentration (EMCs) of total suspended solids (TSS), total copper, total lead, total zinc, polycyclic aromatic hydrocarbons (Total PAHs), *Escherichia coli* (*E. coli*), and enterococci at land use sites in the Los Angeles, California region. Bolded values indicate significant differences among land use types (p <0.001 - 0.03). sd = standard deviation. NA = not analyzed.

Land Use Type (No. of Sites Sampled)	Mean EMC													
	TSS		Total Copper		Total Lead		Total Zinc		Total PAHs		*E. coli*		Enterococci	
	(μg/L)	sd	(μg/L)	sd	(μg/L)	sd	(μg/L)	sd	(ng/L)	sd	(MPN/100ml)	sd	(MPN/100ml)	sd
High Density Residential (4)	77.4	88.3	26.0	11.0	**28.4**	**16.6**	207.7	91.6	4.4E+03	2.6E+03	8.2E+03	7.7E+03	2.7E+04	3.6E+04
Low Density Residential (3)	105.0	142.9	29.9	18.1	6.0	8.4	87.1	60.7	1.4E+03	6.0E+02	3.0E+04	1.8E+04	5.5E+04	3.7E+04
Commercial (4)	49.6	67.8	38.1	18.4	20.4	14.0	362.2	135.6	1.2E+03	5.8E+02	1.1E+04	8.8E+03	7.7E+04	9.2E+04
Industrial (4)	92.2	50.9	**70.3**	**18.0**	**24.1**	**10.9**	**599.1**	**197.0**	1.5E+03	8.6E+02	3.8E+03	2.3E+03	2.1E+04	2.2E+04
Agricultural (1)	112.0	121.5	32.6	30.5	7.8	11.0	242.8	192.9	8.6E+02	1.0E+03	4.0E+04	1.4E+04	**1.2E+05**	**9.6E+04**
Recreational (1)	**530.0**	**339.4**	38.0	5.3	16.3	3.4	131.5	20.7	4.6E+02	3.0E+02	**5.3E+05**	**1.7E+05**	**1.4E+05**	**8.2E+04**
Transportation (2)	14.5	2.1	9.8	16.1	3.3	2.4	92.6	100.5	4.8E+02	2.8E+02	1.4E+03	2.7E+03	8.9E+03	4.4E+03
Open Space (2)	134.0	121.6	7.6	2.4	1.2	0.7	23.2	11.4	NA	NA	5.4E+03	3.1E+03	2.1E+04	2.7E+04

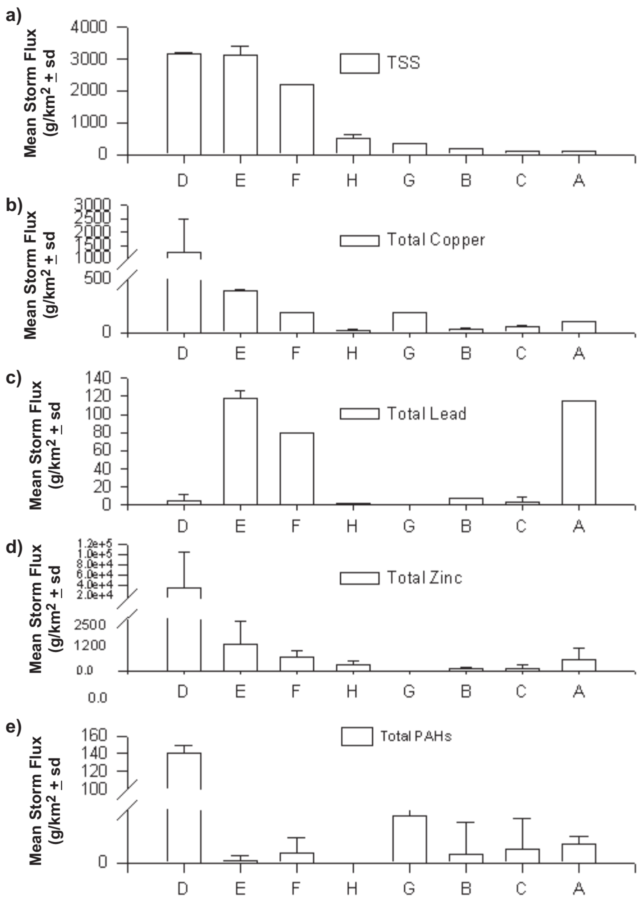

Figure 2. Mean storm flux of total suspended solids (TSS; a), total copper (b), total lead (c), total zinc (d), and total polycyclic aromatic hydrocarbons (PAHs; e) at land use sites for the 2000 to 2005 storm seasons. sd = standard deviation; D = industrial; E = agricultural; F = recreational; H = open space; G = transportation; B = low density residential; C = commercial; and A = high density residential.

Total PAH EMCs were between 4.6E ±02 and 4.4E ±03 ng/L (Table 2). Despite some apparent differences between LUs (e.g., high density residential having higher concentrations and industrial having higher flux), no significant differences were observed in PAH concentration among LU category (p = 0.94 and 0.60, analysis of covariance, with rainfall as a covariate).

Analysis of the distribution of PAHs within each storm event shows that HMW PAHs predominated regardless of LU, suggesting a pyrogenic source (Table 3). In most cases, 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. The exceptions to these patterns were for the industrial oil refinery and transportation gas station sites, where between 50 and 55% of the total PAHs consisted of HMW compounds.

As with the distribution of HMW versus LMW PAHs, the F/P and P/A ratios indicated a consistent pyrogenic source for all LUs. The F/P ratio was between 0.85 and 1.2 for most storms in this study, indicating a strong predominance of pyrogenic PAH sources (Table 3). Furthermore, the P/A ratio was nearly always less than 21, indicating a strong predominance of pyrogenic PAH sources. Again, the exception was at the industrial oil refinery and transportation gas station sites, where the P/A ratio was low until peak runoff occurred, at which time it rose to between 17 and 20.

Table 3. **Indicators of pyrogenic sources of PAHs for land use type. HMW = high molecular weight compounds; P/A = phenanthrene/anthracene ratio; F/P = fluoranthene/pyrene ratio; and NA = not analyzed.**

Land Use Type	Mean Storm Value		
	% HMW	P/A	F/P
High Density Residential	82	9.4	0.9
Low Density Residential	76	6.9	1
Commercial	79	8.7	0.9
Industrial	68	13	0.8
Agricultural	62	18.6	1.1
Recreation	85	4.4	1.2
Transportation	64	14.9	0.9
Open Space	NA	NA	NA

Bacteria

Comparison of bacteria concentrations for the storm events sampled for each LU category showed that recreational LU sites contributed significantly higher levels of both *E. coli* and enterococci; p <0.003) than other LU types. For example, *E. coli* concentrations at recreational LU sites were 5.3×10^5 MPN/100ml $\pm 1.7 \times 10^5$, while concentrations from other LUs ranged from 1.4×10^3 to 4.0×10^4 MPN/100ml (Figure 3). Agricultural LU sites contributed the second highest mean indicator bacteria EMCs, but the differences were statistically different from other LU sites only for enterococci (i.e., 1.2×10^5 MPN/100ml $\pm 9.6 \times 10^4$; p <0.008). Bacteria concentrations for open space sites were in the 10^2 range for E.Coli and enterococci, and 10^3 range for total coliforms.

Direct comparison of flux showed that stormwater from agricultural, recreational and industrial LU sites had the highest mean bacteria fluxes. Most of the developed LU types exhibited comparable fluxes of 10^{11} colonies/km^2. In contrast, the agricultural LU contributed substantially higher flux of both enterococci and total coliforms, with a mean enterococci flux in the range of 10^{14} colonies/km^2.

Pollutant First Flush

Pollutant concentrations varied with time over the course of storm events. For all storms and constituents sampled, the highest concentrations occurred during the early phases of stormwater runoff with peak concentrations usually preceding peak flow. 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. Figure 4 shows an example of this pattern of concentration change over the course of a storm for *E. coli*. This pattern was consistently observed for all constituents sampled for all LU types.

Although the pattern of an early peak in concentration was comparable in both undeveloped and developed catchments, peak concentration in the undeveloped catchments tended to occur later in the storm and persist for a longer duration (i.e., three to four hours; Figure 4). Furthermore, storm flow continued above base flow conditions for a longer duration in the undeveloped watersheds; however, concentrations steadily decreased following the early peak in storm. A similar pattern was observed for all constituents sampled.

A moderate mass first flush was generally observed from small, homogenous LU sites for all constituents sampled (Figure 5). The magnitude of first flush varied between storms and between individual sites, but the overall pattern was consistent. Highly impervious commercial and industrial sites exhibited a slightly stronger and more consistent first flush than the residential sites, which are more heterogeneous in terms of the distribution of pervious and impervious cover.

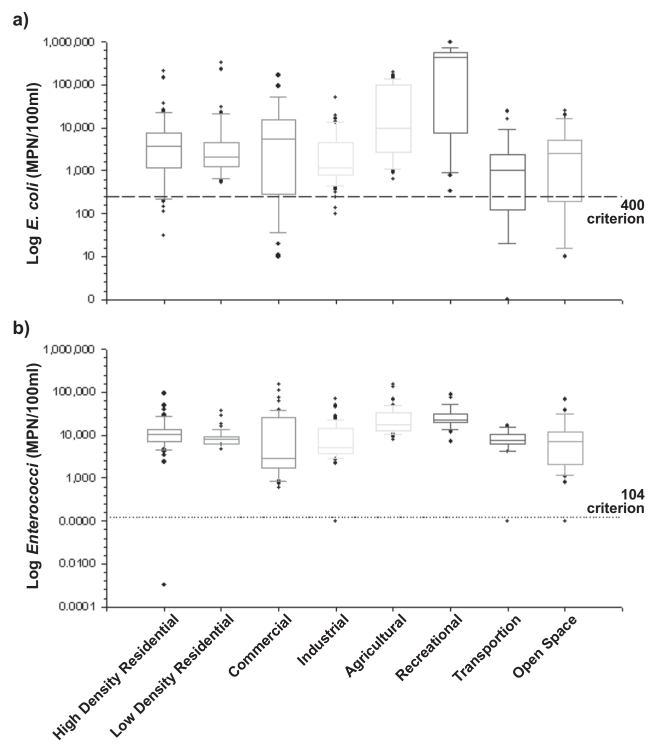

Figure 3. Distribution of *Escherichia coli* (*E. coli*; a) and enterococci (b) concentrations for the 2000 to 2005 wet seasons by land use type. Criterion lines = California State (single sample) water quality standards.

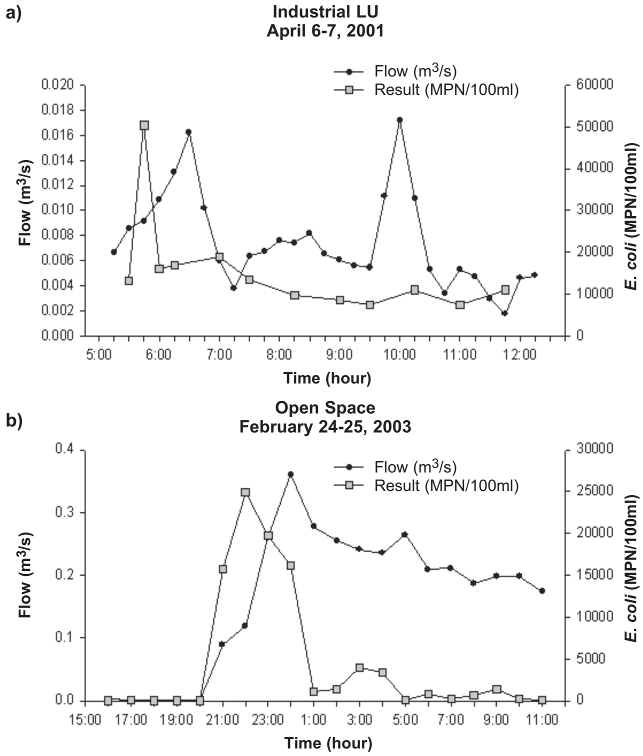

Figure 4. *Escherichia coli* (*E. coli*) concentrations with time for a storm event in the industrial (a) and open space (b) land use sites. Enterococci and total coliforms concentrations showed a similar pattern.

Discussion

Reliable data on relative pollutant loading from specific LUs is one of the most important parameters for calibration of water quality models and for evaluation of potential management actions (Arabi *et al*. 2006, Benham *et al*. 2006, Munoz-Carpena *et al*. 2006). The data compiled in this study suggest that the main sources of pollutants in urban stormwater vary by constituent class; models and management actions must account for these differences.

Trace metal concentrations and fluxes were highest at industrial LU sites. High metals flux from industrial sites observed in this study results, at least in part, from intrinsic properties of the industrial LUs themselves. These intrinsic properties include high impervious cover (typically greater than 70%) and on-site source generation such as washoff of metal debris from industrial processes. High metals flux is likely also related to the substantially higher TSS fluxes observed at the industrial sites. The City of Austin (1990) found Pb and Zn EMCs were related to the TSS EMCs and that controlling TSS at industrial sites also resulted in reduced metals loading. 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 (2008) used Bayesian networks to estimate pollutant loading from various LUs in southern California and concluded that Zn showed higher EMC values at commercial and industrial LUs. Bannerman *et al*. (1993) identified industrial LUs as a critical source area in Wisconsin stormwater producing significant Zn 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%.

Several lines of evidence implicate aerial deposition and subsequent wash-off of combustion by-products as the main source of PAH loading in stormwater. PAH flux was comparable between LU types, suggesting a regional source. 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 relative abundance of individual PAHs in runoff indicates a strong pyrogenic source indicative of combusted fossil fuels. In this study, HMW PAH consistently comprised greater than 70% of the total PAH concentration regardless of LU, suggesting a pyrogenic source. 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 stormwater 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 stormwater. Similarly, Soclo *et al*. (2002) found that high PAH loads associated with stormwater runoff to the Cotonou Lagoon in Benin were characterized by HMW PAHs that appear to be derived from atmospheric deposition. The exception to this pattern was for the industrial oil refinery and transportation gas station sites, where flux values were higher, and the signature of uncombusted PAHs was more pronounced. This makes sense given the obvious petrogenic source associated with these LU types.

The PAH sources can also be inferred by exam-

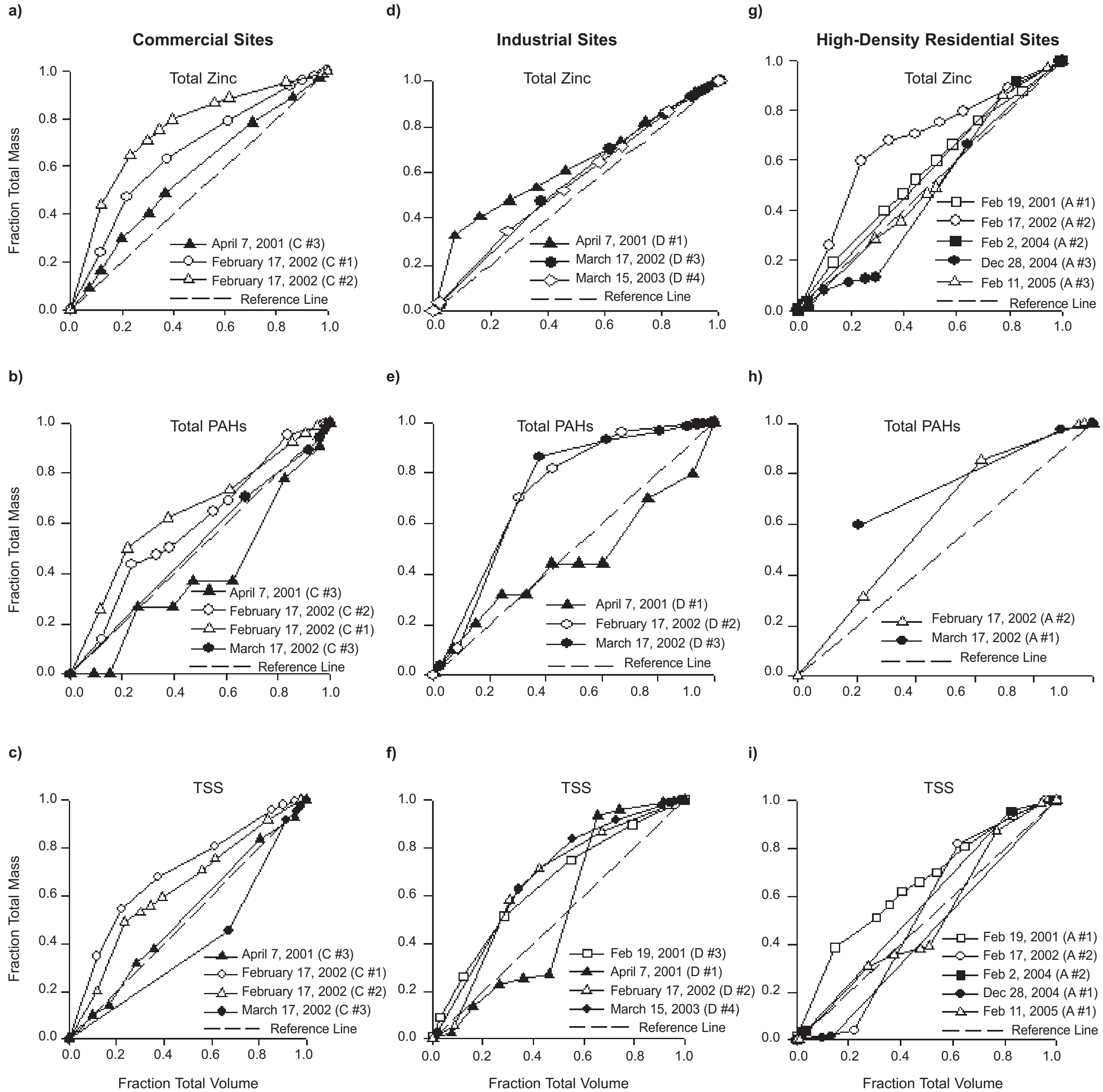

Figure 5. Cumulative mass loading for total zinc (a - c), total polycyclic aromatic hydrocarbons (PAHs; d - f), and total suspended solids (TSS; g - i) as a fraction of total storm volume for commercial, industrial, and residential land use sites.

ining ratios of particular PAHs in runoff samples. The present study used both F/P and 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). 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. 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 show 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).

The highest concentration of bacteria was observed from recreational and agricultural LU sites. This 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 enterococci EMCs observed at the agricultural sites during this study. In contrast, LU sites, such as industrial areas and built-out residential areas, have proportionately less direct sources of fecal material and have lower sediment concentrations in stormwater than do mixed LU and developing areas (Burnhart 1991, Mallin and Wheeler 2000). 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 stormwater particles may also explain differences in *E. coli* and enterococci concentrations between different LU sites. 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 LU 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 the regular application of fertilizers, algaecides, and fungicides (Niemi and Niemi 1991, Cook and Baker 2001). Future assessment of particle size distribution over the entire storm duration at these LU sites may help clarify the association of bacteria with suspended particles (Schillinger and Gannon 1985, Hunter *et al*. 1999).

Understanding the relative contribution of various LUs to overall pollutant loading is an important first step in model development. However, model calibration requires quantified LU EMCs, and the resolution and reliability of model output is directly related to the precision of the EMC data. Because of the expense associated with collecting LU EMC data, many models are calibrated using either regional or national data sets, such as the National Storm Water Quality Database (NSQD; Pitt *et al*. 2003).

To investigate the implications of using data sets collected at broader spatial scales for model calibration we compared our data to LU EMCs from the NSQD and from two regional data sets. The NSQD includes stormwater 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 (Pitt *et al*. 2003). Unfortunately, the NSQD does not contain any samples from the arid west. We also compared our results to two regional data sets. The first regional data set was consisted of data from municipal stormwater permit monitoring collected across three southern California counties from 667 site events distributed between 45 distinct sites (Ackerman and Schiff 2003). The second regional data set was from a project conducted by the Oregon Association of Clean Water Agencies (ACWA; 1997) that evaluated data collected from LU based stormwater monitoring conducted during the 1990s. The ACWA database includes information from 39 monitoring stations and with up to 15 sampling events per station, and almost 320 monitoring data points.

Median EMCs from this study were generally within 20% of those reported in the NSQD and the two regional studies (Table 4). The most notable exceptions were higher EMCs for Cu and Zn at the industrial LU sites and higher TSS at the open space sites in this study as compared to the other data sets. The similarity between these data sets suggests that for general estimates of pollutant loading using simple models, national or regional data sets are sufficient. However, when possible, region-specific LU EMCs should be used as the sources may vary with specific local LU practices.

Although storm EMCs (such as those contained in the NSQD) may be sufficient for estimating overall pollutant loading using simple models, time variable data is necessary to calibrate dynamic models. These models provide more refined estimates of pollutant washoff and can be used to simulate within-storm patterns, such as first flush. Output from dynamic models can also be used to assist stormwater engineers in the design of more effective monitoring programs and better performing treatment practices (i.e., BMPs) that address specific rainfall/runoff conditions.

For all constituents, the highest concentrations occurred at or just before the peak in flow of the storm hydrograph. Tiefenthaler *et al*. (2001) observed similar pollutographs that showed peak suspended-sediment concentrations preceding the

Table 4. Comparison of EMCs for specific land uses for the present study (Stein *et al.*), the southern California regional study (Ackerman and Schiff), Oregon Association of Clean Water Agencies (ACWA) data, and National Stormwater Quality Database (NSQD), for TSS, metals, and *E. coli*. Values are 50th percentile. In addition, where data were available, the 10th and 90th percentiles are shown.

Land Use Type	Research	Median EMC				
		TSS (mg/L)	Copper	Lead (µg/L)	Zinc	*E. coli* (MPN/100ml)
Residential	Stein *et al*.[1]	19, 28, 238	14, 18, 55	4, 8, 67	47, 103, 240	6,331
	Ackerman and Schiff[2]	13, 60, 220	6, 16, 51	0, 5, 37	0, 100, 255	NA
	ACWA[3]	64	14	NA	108	8,345
	NSQD[4]	48	12	12	73	NA
Commercial	Stein *et al*.[1]	13, 18, 115	11, 24, 80	2, 5, 54	130, 156, 699	3,939
	Ackerman and Schiff[2]	15, 58, 179	8, 23, 59	0, 4, 28	65, 157, 437	NA
	ACWA[3]	92	32	NA	168	4,300
	NSQD[4]	43	17	18	150	NA
Industrial	Stein *et al*.[1]	58, 73, 145	29, 33, 181	16, 19, 38	369, 550, 878	1,546
	Ackerman and Schiff[2]	22, 86, 329	9, 30, 89	0, 7, 45	76, 218, 580	NA
	ACWA[3]	102	24	NA	274	2,500
	NSQD[4]	77	22	25	210	NA
Agricultural	Stein *et al*.[1]	19, 88, 238	12, 24, 56	3, 10, 13	102, 234, 472	6,160
	Ackerman and Schiff[2]	798, 1191, 4871	64, 96, 547	17, 49, 117	93, 304, 628	NA
	ACWA[3]	NA	NA	NA	NA	NA
	NSQD[4]	NA	NA	NA	NA	NA
Open Space	Stein *et al*.[1]	65, 135, 203	5, 8, 10	1, 1, 2	20, 23, 27	5,374
	Ackerman and Schiff[2]	3, 18, 788	0, 7, 51	0, 0, 16	0, 0, 148	NA
	ACWA[3]	58	4	NA	25	7,200
	NSQD[4]	78	5	5	39	NA

[1]2001-2005 Los Angeles River Watershed Wet Weather Study (Stein *et al*. 2007).

[2]The southern California regional study (Ackerman and Schiff 2003).

[3]Assessment of Urban Stormwater Pollution in Oregon (ACWA 1997).

[4]The National Stormwater Quality Database (NSDQ; Pitt *et al*. 2003).

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 stormwater flows. Shinya *et al*. (2000) reported a prounounced first flush for TSS, Fe, Zn, and PAHs in runoff from urban highways. However, the magnitude of first flush varied by constituent, with the strongest first flush observed for pollutants that tend be transported in the particulate phase. In contrast, constituents where a substantial portion of washoff occurs in the dissolved phase show a more linear relationship with flow. 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. Similarly, models must be run at short enough time steps to capture these early, transient peaks in concentration.

First flush patterns were also variable within specific LU categories. Although some of this variability can be attributed to differences between storms sampled, EMCs for individual LU sites within a given category often differed by 20 to 40%. However, within LU variability was always less than the variability between LU categories. The amount of within LU variability is not surprising given that a given LU category can contain a diversity of specific LU types. For example, commercial developments can include retail shops, schools, and office buildings. Ackerman and Stein (2008a) showed that impervious cover estimates can vary by between 20 and 40% within a given LU category, leading to differences in runoff and pollutant loading patterns. Future refinement of pollutant washoff properties based on components of LU sites (e.g., roads, rooftops, lawns) could improve the resolution of EMCs and in turn increase model precision.

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