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WATERSHED-BASED SOURCES OF POLYCYCLIC AROMATIC HYDROCARBONS IN URBAN STORM WATER

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Abstract—Polycyclic aromatic hydrocarbons (PAHs) are carcinogenic and mutagenic compounds, ubiquitous in the air and water of urban environments, and have been shown to accumulate in coastal estuarine and marine sediments. Although previous studies have documented concentrations and loads of PAHs in urban runoff, little is known about the sources and temporal patterns of PAH loading from storm water. This study characterized the sources and temporal patterns of PAHs in urban storm water by analyzing PAH concentrations and loads from a range of homogeneous land use sites and in-river mass emission sites throughout the greater Los Angeles, California, USA, region. Samples were collected at 30- to 60-min intervals over the course of a storm during multiple storm events over a four-year period in order to investigate PAH sources and inter- and intrastorm patterns in loading. Polycyclic aromatic hydrocarbon storm fluxes ranged from 1.3 g/km^2 for the largely undeveloped Arroyo Sequit watershed to 223.7 g/km^2 for the highly urbanized Verdugo Wash watershed, with average storm fluxes being 46 times higher in developed versus undeveloped watersheds. Early-season storms repeatedly produced substantially higher loads than comparably sized late-season storms. Within individual storms, PAHs exhibited a moderate first flush with between 30 and 60% of the total PAH load being discharged in the first 20% of the storm volume. The relative distribution of individual PAHs demonstrated a consistent predominance of high-molecular-weight compounds indicative of pyrogenic sources.

Keywords—Polycyclic aromatic hydrocarbons   Storm water   First flush   Source identification

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are associated with carcinogenic and mutagenic effects in humans and biota [1–4]. These compounds are ubiquitous in the air and water of urban environments and have been shown to accumulate in coastal estuarine and marine sediments [5–9]. Although some PAHs are naturally occurring, the majority are anthropogenic and enter the environment through release of petroleum products (petrogenic sources) or by combustion of organic matter (pyrogenic sources) [10–12]. Recent studies have shown that pyrogenic sources predominate in urban settings and that the profile of PAHs in urban storm water resembles that of atmospheric deposition [8,11,13–15].

The discharge of PAHs from urban watersheds is exacerbated in arid regions. Arid urban watersheds have a tremendous number of sources. For example, the average daily traffic in the Los Angeles, California, USA, region exceeds 81 million vehicle miles traveled per day ([16]; http://mobility.tamu.edu/mmp). These mobile sources lead to exceedingly high PAH levels in the atmosphere [17–19]. Moreover, the long antecedent periods without rain in arid regions potentially enhance the dry deposition of PAHs to urban landscapes from these atmospheric sources. When rainfall does occur, the precipitation is often short but intense. Storms flows in urban watersheds from the Los Angeles region can range from <0.5 cubic meters per second (cms) to >1,000 cms in less than 1 h [20]. Runoff from these largely impervious urban surfaces efficiently mobilizes deposited material, including PAHs, in the resulting surface runoff.

Although previous studies have documented concentrations and loads of PAHs in urban storm-water runoff [3,8,11,21],

little is known about the sources and temporal patterns in PAH loading from storm water. Studies on other pollutants, such as pesticides [22] and metals [23], have shown that concentrations can vary dramatically between individual storms as well as over the course of a single storm. However, this information has not been documented for PAHs. Because these temporal patterns can influence the ultimate fate of a pollutant, this knowledge is important for developing predictive models and management strategies for storm-water pollutants.

The objective of this study was to characterize temporal patterns and sources of PAH concentrations and loads in storm water. The goal was to answer the following four questions. First, how does the concentration and flux of total PAH differ between urban and arid watersheds? Second, how does the concentration of total PAH vary within a storm season? Third, how does the concentration and load of total PAH vary within storm events? Finally, what are the potential sources of PAH in storm-water runoff from urban watersheds? The first question was addressed by sampling at the mouth of various watersheds with differing levels of development. The second question was addressed by sampling multiple storm events with varying size, duration, intensity, and antecedent dry periods at the same watershed. The third question was addressed by measuring PAH concentrations over the course of entire storm events to construct time-versus-concentration plots. The fourth question was addressed in two fashions. First, concentrations and flux were compared among a variety of small, homogeneous land use types. Second, the relative distribution of individual PAHs were examined for source signatures indicative of pyrogenic versus petrogenic origin.

MATERIALS AND METHODS

Sampling locations

The highly urbanized greater Los Angeles metropolitan area in southern California has a population of approximately 15

million residents (U.S. Census Bureau 2000, http://factfinder. census.gov/home/saff/main.html?_lang=en). Winter storms generally occur between December and March, with about 30 cm of total precipitation being distributed over 3 to 5 large and 8 to 10 small storms [20]. Runoff from a range of residential, commercial, industrial, and other land uses drain to engineered flood control channels (highly modified rivers) and ultimately discharge to the Pacific Ocean. These flood control channels integrate runoff from all the land use types in their contributing watersheds and are termed mass emission (ME) sites. Eight different ME sites representing six developed and two undeveloped watersheds and ranging in size from 31 to 2,161 km^2 were sampled during the 2000–2001 through 2003–2004 storm seasons (Table 1 and Fig. 1). In addition, 15 homogeneous land use sites, representing seven land use types, were sampled (Fig. 1). Land use categories included high-density residential, low-density residential, commercial, industrial, agricultural, recreational, and transportation.

Sampling and analysis

A total of 10 discrete storms were sampled, with each site being sampled between one and four individual storms. Rainfall amounts ranged from 0.28 to 9.17 cm and antecedent conditions from 2 to 142 d without measurable rain. Rainfall was measured using a standard tipping bucket at each site that recorded at 0.025-cm increments. Antecedent dry conditions were determined as the number of days since 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 less than 20% of base flow. Since 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 land use sites, stream discharge was measured as the product of the channel cross-sectional area and the 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 were collected per storm at approximately 30 to 60 min intervals for each site-event based on optimal sampling frequencies in southern California described by Leecaster et al. [24]. Samples were collected more frequently when flow rates were high or rapidly changing and less frequently during lower-flow periods. All water samples were collected by one of three methods: 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, by direct filling of the sample bottle either by hand or affixed to a pole, or by indirect filling using an intermediate bottle for securing large volumes. After collection, the samples were stored in precleaned amber glass bottles on ice with Teflon-lined caps until they were shipped to the laboratory for analysis. Twenty-six specific PAHs were extracted, separated, and quantified by capillary gas chromatography coupled to mass spectrometry according to U.S. Environmental Protection Agency (U.S. EPA) method 625 [25].

Data analysis

Total PAH (ΣPAH) was computed as the sum of the 26 individual PAH compounds quantified (Table 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.

Four basic analyses were used to characterize temporal patterns and determine sources of PAH in storm water. First, event flow-weighted mean (FWM) concentrations, loading, and flux rates among undeveloped and developed ME sites were compared to determine if significant differences existed among watershed types. Using only those samples for a single storm, the event FWM was calculated according to Equation 1:

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

where FWM = flow-weighted mean for a particular storm, C_i = individual runoff sample concentration of ith sample, F_i = instantaneous flow at the time of ith sample, and n = number of samples per event. Mass loading was calculated as the product of the FWM and the storm volume during the sampling period. Flux estimates facilitated loading comparisons among watersheds of varying sizes. Flux was calculated as the ratio of the mass loading per storm and watershed area. Differences in concentration or flux between ME sites were investigated using a one-way analysis of variance, with a $p < 0.05$ significance level [26]. In all cases, nondetectable results were assigned a value of zero.

The second analysis compared seasonal patterns of total PAH concentration and load by plotting FWM concentration, load, and flux as a function of cumulative rainfall before the date of the storm being sampled. For this analysis, all ME sites were analyzed as a group to look for differences between early- and late-season storms across the sampling region. Annual total PAH loads per year (kg/year) for each site were calculated by summing mean daily flow data for all days with storm flow for the corresponding watershed water years to get an annual storm volume. The annual storm volume was multiplied by the storm-event mean concentration to produce an estimated annual load.

The third analysis compared flows and total PAH concentration within storm events. This comparison was evaluated by examining the time-concentration series relative to the hydrograph using a plot we term a pollutograph. A first flush in concentration from individual ME storm events was defined as when the peak in concentration preceded the peak in flow. This was quantified using cumulative discharge plots whereby cumulative mass emission was plotted against cumulative discharge volume during a single storm event [27]. When these curves are close to unity, mass emission is a function of flow discharge. A strong first flush was defined when ≥80% of the mass was discharged in the first 20% of runoff volume. A moderate first flush was defined when ≥30% and ≤80% of the mass was discharged in the first 20% of runoff volume. No first flush was assumed when ≤30% of the mass was discharged in the first 20% of runoff volume.

The fourth analysis examined sources of PAHs. First, the FWM concentrations from the homogeneous land use sites were compared. Differences between land use sites were in-

Table 1. Storm–water polycyclic aromatic hydrocarbon mass emissions from in-river sampling locations in the Los Angeles, California, USA, region. Annual loads are based on water year, as indicated in the footnotes (cms = cubic meters per second; SD = standard deviation; PAH = polycyclic aromatic hydrocarbons; EMC = event mean concentration)

| | Watershed size (km²) | Date of storm event | Rainfall (cm) | Antecedent dry days | Mean flow (cms) | Peak flow (cms) | Total PAHs | | | | | | Annual total PAH load (kg/year) |
| | | | | | | | EMC | | Flux (kg/km²) | Mass emissions | | | |
							ng/L	SD		kg	SD		
Mass emission sites													
Los Angeles River above Arroyo Seco	1,460	11/12–11/13/2001	1.73	127	62.6	262.5	3,256.8	846.7	0.0049	7.16	0.35		3.74[a]
Los Angeles River at Wardlow	2,161	5/2–5/3/2003	3.56	4	209.9	756.7	470.7	453.2	0.0023	4.90	0.32		34.9[b]
		2/2/2004	1.14	29	90.4	375.6	3,559.9	1,185.5	0.0064	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	4,283.7	2,043.2	0.2236	14.54	0.83		NA[d]
		10/31–11/1/2003	1.74	30	56.5	155.0	4,992.3	1,093.3	0.1529	9.94	0.46		NA
Arroyo Seco	130	2/9–2/11/2001	3.56	12	2.9	13.5	788.8	177.8	0.0009	0.11	0.01		2.79[e]
		4/6–4/7/2001	1.78	30	7.8	21.8	816.5	258.5	0.0016	0.20	0.01		
Ballona Creek	338	4/6–4/7/2001	1.24	31	32.6	100.9	948.7	379.9	0.0054	1.81	0.13		20.5[e]
		11/24–11/25/2001	1.52	11	53.1	396.2	3,118.9	1,104.8	0.0246	8.30	1.78		17.3[a]
		5/2–5/3/2003	2.03	4	52.8	134.4	981.7	583.0	0.0032	1.08	0.12		20.0[b]
		10/31–11/1/2003	2.03	30	62.0	148.1	5,821.2	1,814.9	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	3,293.4	791.8	0.0013	0.24	0.01		NA
		2/21–2/22/2004	1.52	18	14.7	35.5	2,182.1	745.2	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.
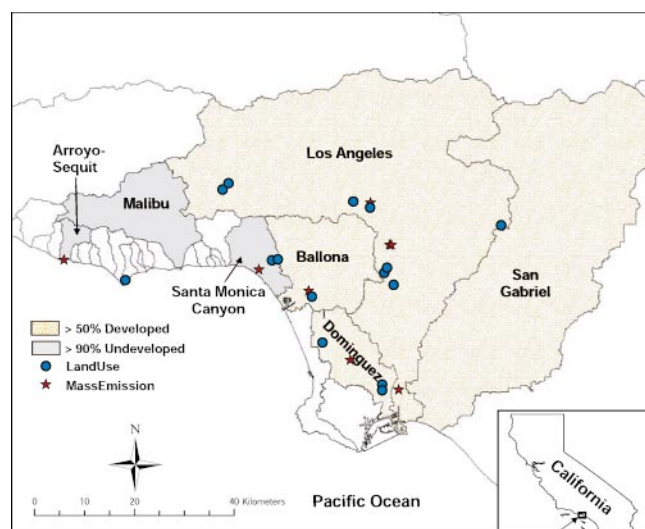[e] Water year 2001 = October 2000–September 2001.

Fig. 1. Map of in-river mass emission sampling sites and watersheds within the greater Los Angeles region, California, USA. Watersheds indicated in gray contained land use sites that drain catchments that are >90% undeveloped.

vestigated using a one-way analysis of variance, with a $p < 0.05$ significance level [26]. Next, 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 [28]. Pyrogenic sources predominate when P/A ratios ranged from 3 to 26 [29,30].

RESULTS

Developed versus 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 ($2,655.0 \pm 1,768.1$ ng/L vs 452.2 ± 444.9 ng/L; Tables 1 and 3). Flux of PAHs from developed watersheds was 46 times greater than that from undeveloped watersheds (Table 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).

The annual output rate of total PAHs in the Los Angeles River watershed during the 2002–2003 water year was approximately 34.9 kg/year (Table 1). During this same period, Ballona Creek had an 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; Fig. 2). 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 (Fig. 2).

PAH variability within storms

The greatest total PAH concentrations occurred during the rising limb of the storm hydrograph for nearly every storm

Table 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[*ghi*]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[1,2,4-*cd*]pyrene	276	6
Fluorene	166	3	Methylanthracene	222	5
Naphthalene	128	2	Perylene	252	5
Phenanthrene	178	3	Pyrene	202	4

Table 3. Total polycyclic aromatic hydrocarbons (PAHs) and selected polycyclic aromatic hydrocarbon ratios for the the watersheds in the Los Angeles, California coastal region, USA. EMC = event mean concentration; HMW = high-molecular-weight compounds

	Date of storm event	EMC ΣPAHs (ng/L)	EMC pyrene (ng/L)	Pyrene/ ΣPAHs (%)	Fluoranthene/ pyrene ratio	Phenanthrene/ anthracene ratio	EMC Phenanthrene (ng/L)	Phenanthrene/ ΣPAHs (%)	HMW (%)	Dominant sources of origin
Mass emission sites										
Los Angeles River above Arroyo Seco	11/12–11/13/2001	3,256.8	427.9	13.1	1.1	8.0	291.3	8.9	76.4	Pyrogenic
Los Angeles 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
	2/2/2004	3,559.3	401.0	11.3	1.0	7.5	278.1	7.8	71.8	Pyrogenic
Verdugo Wash	11/12–11/13/2001	4,283.7	593.8	13.9	1.1	7.8	373.0	8.7	83.5	Pyrogenic
	10/31–11/1/2003	4,992.3	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	3,118.9	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	5,821.2	786.2	13.5	1.1	10.2	473.0	8.1	82.7	Pyrogenic
Dominguez Channel	3/17–3/18/2002	3,293.4	534.6	16.2	0.9	74.9	508.2	15.4	77.5	Petrogenic
	2/21–2/22/2004	2,182.1	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	12.6	61.0	Pyrogenic
Mean ΣPAHs (ng/L)		2,300								

Fig. 2. 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.
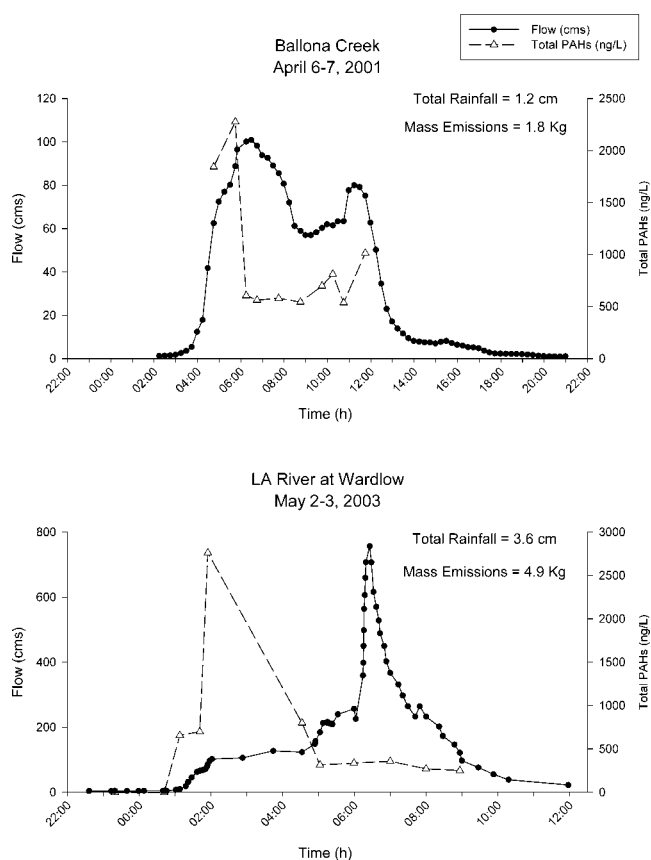

Fig. 3. Variation in polycyclic aromatic hydrocarbon (PAH) concentrations with time for storm events in Ballona Creek (top) and Los Angeles River (bottom), California, USA.

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 (Fig. 3). 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 30 and 60% of the total PAH load was discharged in the first 20% of storm volume for the storms examined in this study. The mass loading plots for Ballona Creek (Fig. 4) 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.

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). 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 also 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
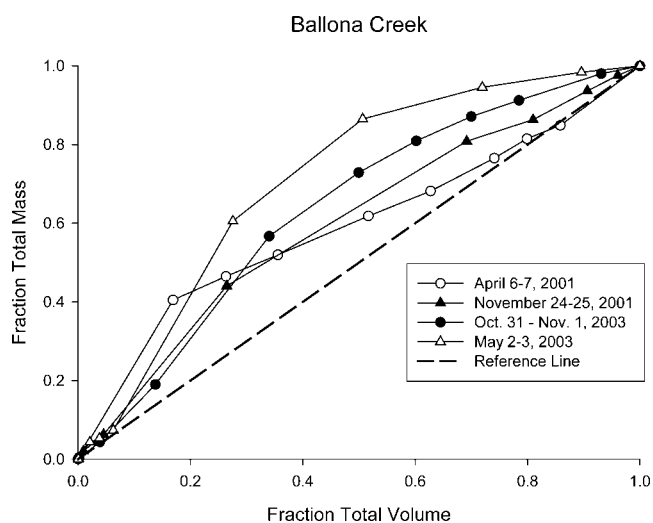

Fig. 4. Cumulative polycyclic aromatic hydrocarbon mass loading for four storms in Ballona Creek, California, USA. Plots show percent of mass washed off for a given fraction of the total runoff. Reference line indicates a 1:1 relationship between volume and mass loading. Portions of the curve above the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

Table 4. Event mean concentration (EMC) and mass loading of polycyclic aromatic hydrocarbons (PAHs) from land use sites in the Los Angeles, California, USA, region. Site numbers indicate different sites within a given land use category. SD = standard deviation; NA = watershed size not available

|	Watershed size (km^2)	Date of storm event	Rainfall (cm)	Dry days	Sampling duration (h)	Mean flow (cms)	Peak flow (cms)	Flux (kg/km^2)	Total PAHs EMC ng/L	Total PAHs EMC SD
High-density residential 1	0.02	2/17/2002	0.89	21	3	0.001	0.006	1.8E − 03	1.92E + 03	7.03E + 02
High-density residential 1	0.02	2/2/2004	1.19	2	5	0.004	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	1	0.000	0.003	1.1E − 05	7.84E + 03	5.99E + 03
Mean high-density residential								7.2E − 03	4.4E + 03	2.6E + 03
Low-density residential 1	0.98	3/4–3/5/2001	2.67	3	31	0.017	0.071	7.2E − 05	1.55E + 02	5.54E + 01
Low-density residential 1	0.98	2/2/2004	2.26	2	5	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	3	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	2/17/2002	0.89	20	4	0.002	0.008	NA	2.27E + 02	1.63E + 02
Commercial 2	2.45	2/17/2002	0.74	20	3	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	6	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	1	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	6	0.008	0.017	5.7E − 03	1.36E + 02	6.85E + 01
Industrial 2	0.001	2/17/2002	0.74	20	3	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	1	0.000	0.003	6.6E − 06	4.41E + 03	2.29E + 03
Industrial 4	0.01	3/15/2003	4.50	9	10	0.117	0.375	5.6E − 01	8.89E + 02	7.55E + 02
Mean industrial								1.4E − 01	1.5E + 03	8.6E + 02
Agricultural 1		3/4–3/5/2001	2.74	3	32	0.021	0.053	4.3E − 04	6.83E + 02	7.77E + 02
	0.98	3/17–3/18/2002	0.23	10	1	0.012	0.031	2.0E − 05	4.55E + 02	1.72E + 02
		2/2/2004	1.17	2	5	0.023	0.128	5.3E − 04	1.43E + 03	2.09E + 02
Mean agricultural								3.3E − 04	8.6E + 02	1.0E + 03
Recreational 1	0.03	3/4–3/5/2001	1.42	3	32	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	5	0.022	0.057	1.4E − 02	3.63E + 02	2.54E + 02
Transportation 2	0.002	2/17/2002	0.89	47	3	0.001	0.006	3.7E − 03	5.95E + 02	3.16E + 02
Mean transportation								8.9E − 03	4.8E + 02	2.8E + 02
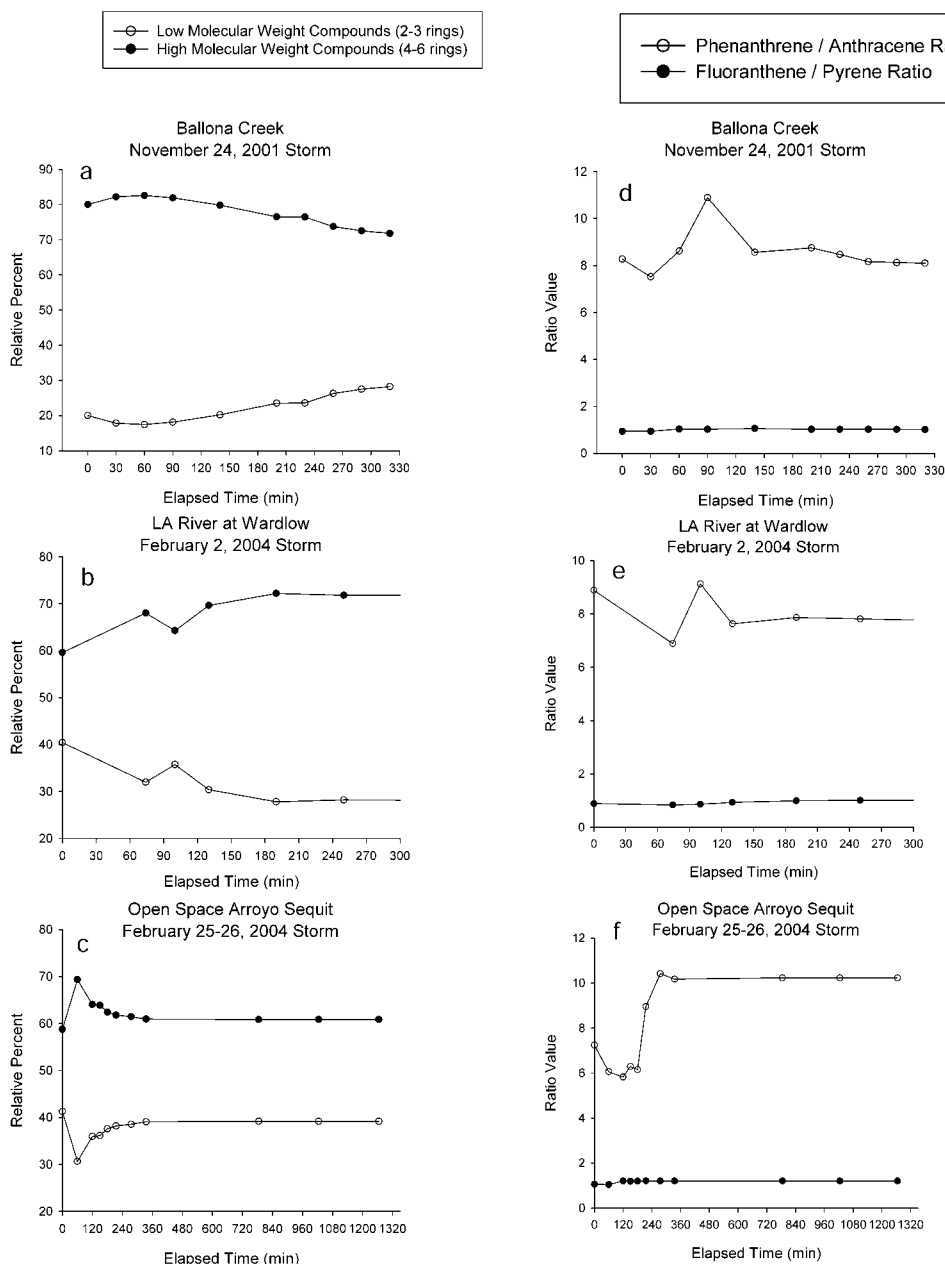
Fig. 5. Distribution of polycyclic aromatic hydrocarbons (PAHs) within storms for mass emission sites located in the Los Angeles region, California, USA. Plots on the left (**a**–**c**) show distribution of high- versus low-molecular-weight PAHs throughout individual storms. Plots on the right (**d**–**f**) 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.

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 (Fig. 5 and Table 3). 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 (Fig. 6). 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 3).

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 3). Furthermore, the P/A ratio was nearly always less than 21, once again indicating a strong predominance of pyrogenic PAH sources (Table 3) [28–30]. 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 versus
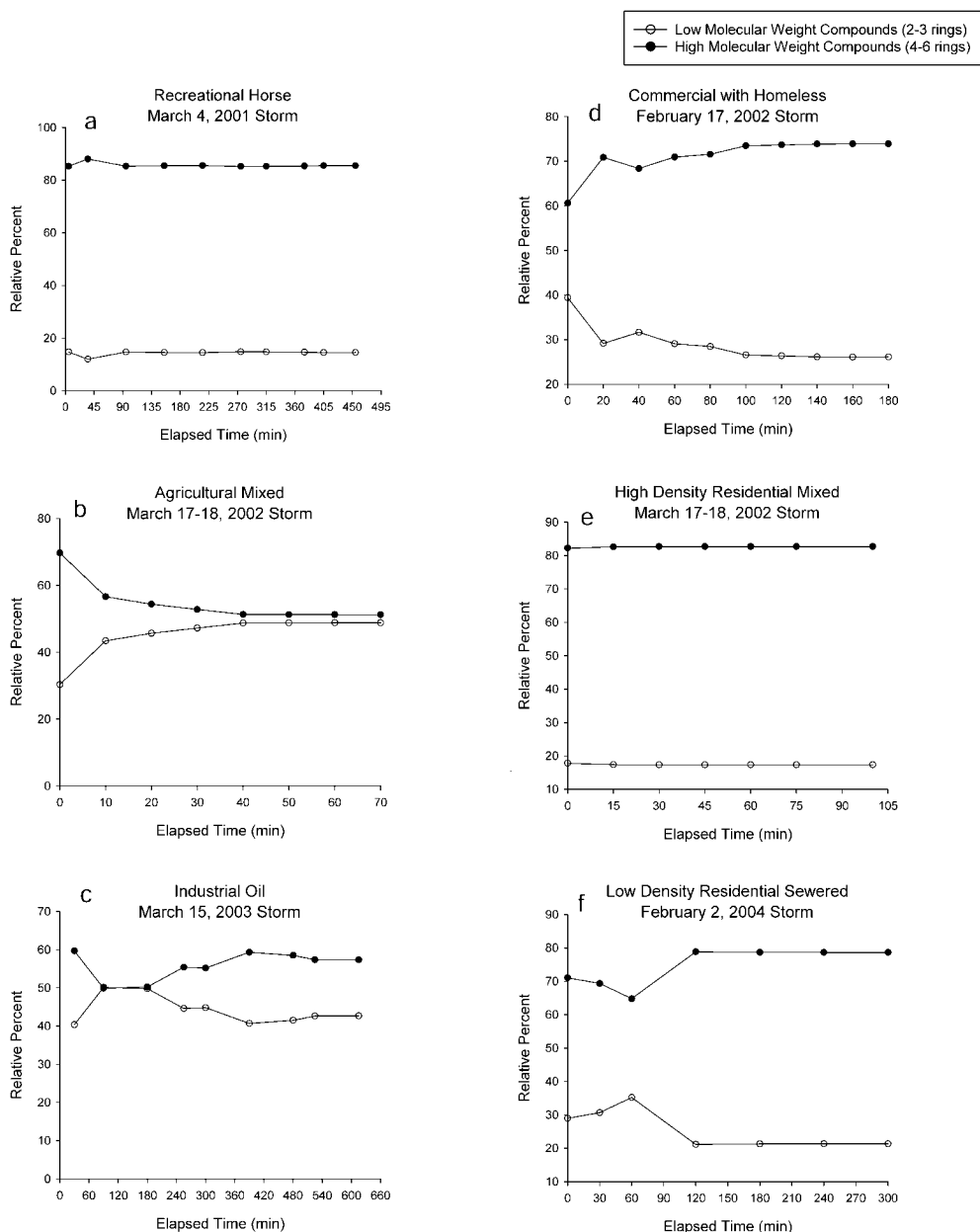
Fig. 6. Distribution of polycyclic aromatic hydrocarbons (PAHs) within storms for representative land use sites (**a–f**). Plots show distribution of high- versus low-molecular-weight PAHs throughout individual storms. Data are shown for six sites that represent the results observed for the 15 land use sites where data were collected.

LMW 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 (Fig. 7). 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 (Fig. 5).

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 approximately 92.8 and 32.7 kg/year of total PAH are 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 ($\sim$2.8 $\times$ 10^6 m^3/d) discharged an estimated 740 kg of PAHs to the southern California Bight [31]. 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 to 12 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 water-body 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 ([32]; http://www.sccwrp.org).
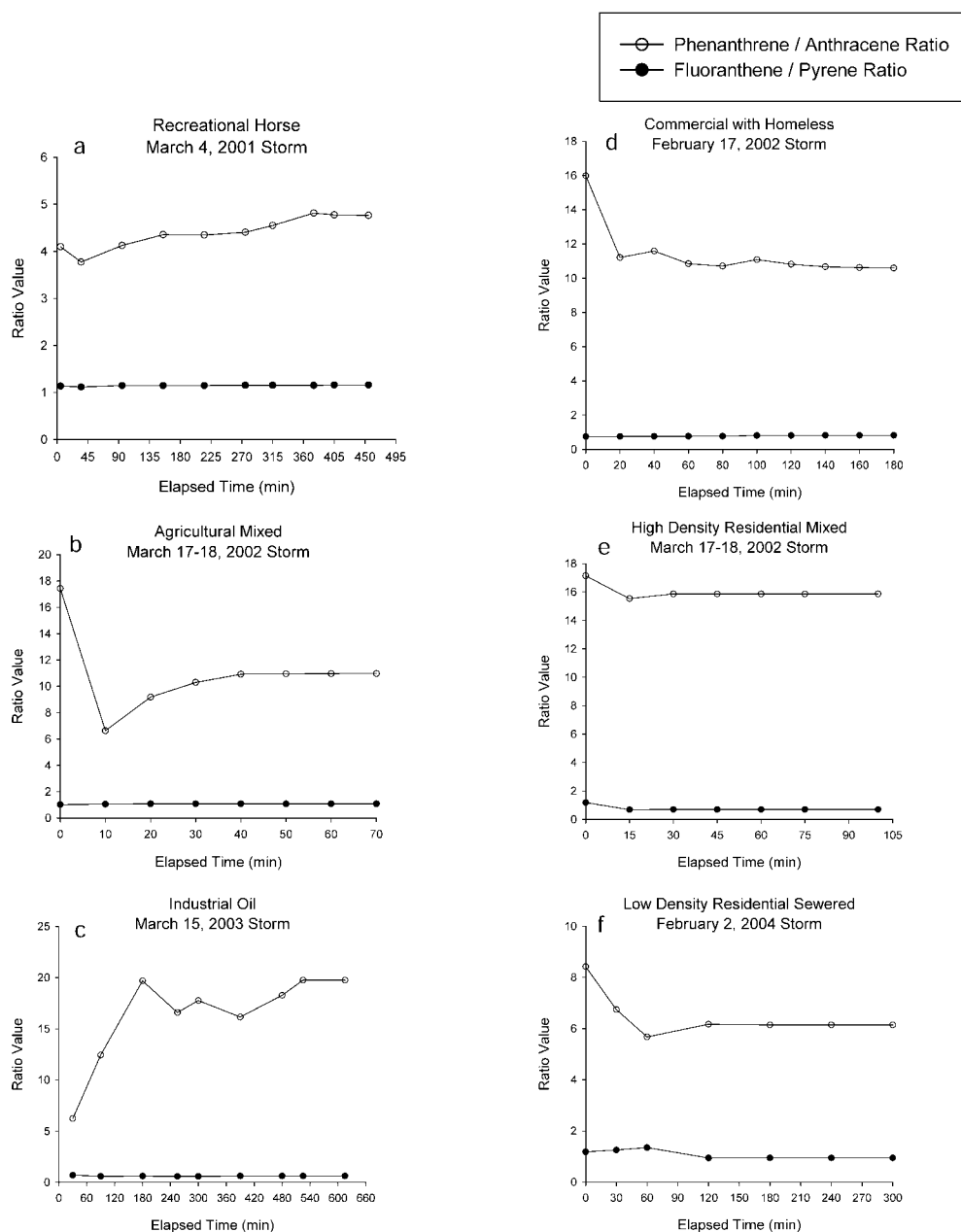
Fig. 7. Distribution of polycyclic aromatic hydrocarbons within storms for representative land use sites. Plots (**a–f**) show phenanthrene/anthracene (P/A) and fluoranthene/pyrene (F/P) ratios throughout individual storms. Data are shown for six sites that represent the results observed for the 15 land use sites where data were collected.

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 [33]. 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 [7]. 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 loadings of PAHs estimated from this study are lower than those estimated from two studies in the eastern United States. Hoffman et al. [11] estimated 680 kg/year of PAH loading from the 4,081 km^2 Narragansett Bay watershed in Rhode Island, USA. Similarly, Menzie et al. [8] 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. 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. Second, PAH in the eastern United States are 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. [21] reported PAH concentrations between 5.1 and 8.6 µg/L in parking lot runoff, and Menzie et al. [8] 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 FWM mean 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. [11] and Smith et al. [34]. Furthermore, Buffleben et al. (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 [10,11]. Hoffman et al. [11] 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
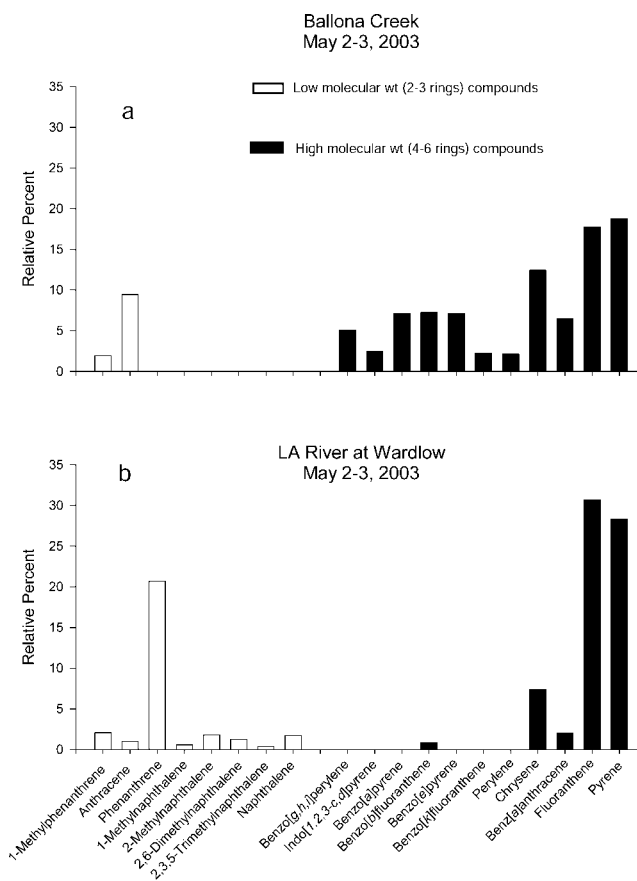

Fig. 8. Relative distribution of individual polycyclic aromatic hydrocarbon compounds for Ballona Creek (**a**) and Los Angeles River (**b**), California, USA, on May 2–3, 2003.

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 PAH 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 [35]. Menzie et al. [8] 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. [11] 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 (Fig. 8) was similar to the distribution of PAHs observed in dry deposition collected in Los Angeles by

Table 5. Selected polycyclic aromatic hydrocarbon ratios and their source signature ranges

Indicator	Pyrogenic	Petrogenic	Reference
Fluoranthene/pyrene ratio (F/P)	0.9 to ≤1	>1	[21]
Phenanthrene/anthracene ratio (P/A)	3–26	>26	[29–30]
Methylphenanthrene/phenanthrene (M/P)	<1.0	2–6	[42]

Sabin and Schiff [17]. Furthermore, in this study, HMW PAH consistently comprised approximately 73% of the total PAH concentration regardless of land use. Hoffman et al. [11] 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. [8] 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, Socolo et al. [12] 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. [8], 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 [28]; in contrast, large F/P ratios suggest petrogenic sources of PAHs [36] (Table 5). 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. [37] 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. [38] 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 [39,40,41]. 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 [17,42], 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 by-products.

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