Watershed-based sources of polycyclic aromatic hydrocarbons in urban stormwater

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ABSTRACT

Previous studies have documented that polycyclic aromatic hydrocarbons (PAHs) from urban runoff accumulate in coastal estuarine and marine sediments. However, little is known about the sources and temporal patterns of PAH loading from stormwater. This study characterized the sources and temporal patterns of PAHs in urban stormwater by analyzing PAH concentrations and loads from a range of homogenous 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. 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. The magnitude of PAH loading was affected more by the period of the storm season than by the size of the storm. Early season storms repeatedly produced substantially higher loads than comparably sized late-season storms, and loading was not correlated with storm size. 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. The results of 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 stormwater runoff.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are associated with carcinogenic and mutagenic effects in humans and biota (Lehr and Jerina 1977, Bjorseth and Ramhal 1985, Crunkilton and DeVita 1997, Karahalil *et al.* 1998). These compounds are ubiquitous in the air and water of urban environments and have been shown to accumulate in coastal estuarine and marine sediments (Daskalakis and O'Connor 1995, Zeng and Vista 1997, Su *et al.* 1998, Menzie *et al.* 2002, Mai *et al.* 2003). 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) (Eaganhouse *et al.* 1981, Hoffman *et al.* 1984, Soclo *et al.* 2002). Recent studies have shown that pyrogenic sources predominate in urban settings and that the profile of PAHs in urban stormwater resembles that of atmospheric deposition (Hoffman *et al.* 1984, Burns *et al.* 1997, Gigliotti *et al.* 2002, Menzie *et al.* 2002, Larsen *et al.* 2003).

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 (Mobility Monitoring Program 2003). These mobile sources lead to exceedingly high PAH levels in the atmosphere (Naumova *et al.* 2002, Park *et al.* 2002, Sabin and Schiff 2004). 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 one hour (Ackerman and Weisberg 2003). 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 stormwater runoff (Hoffman *et al.* 1984, Crunkilton and DeVita 1997, Menzie *et al.* 2002, Mahler *et al.* 2004), little is known about the sources and temporal patterns in PAH loading from stormwater. Studies on other pollutants, such as pesticides (Schiff and Sutula 2004) and metals (Characklis and Wiesner 1997), 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 stormwater pollutants.

The objective of this study was to characterize temporal patterns and sources of PAH concentrations and loads in stormwater. 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 concentrations of total PAH vary within a storm season? Next, how does the concentration and load of total PAH vary within storm events? Last, what are the potential sources of PAH in stormwater 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.

METHODS

Sampling locations

The highly urbanized greater Los Angeles metropolitan area, in southern California, has a population of approximately 15 million residents (US Census Bureau 2000). Winter storms generally occur between December and March, with approximately 30 cm of total precipitation being distributed over 3 to 5 large and 8 to 10 small storms (Ackerman and Weisberg 2003). 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 6 developed and 2 undeveloped watersheds, ranging in size from 31 to 2,161 km^2 were sampled during the 2000-2001 storm season through 2003-2004 storm season (Table 1; Figure 1). In addition, 15 homogenous land use sites, representing 7 land use types, were sampled (Figure 1). Land use categories included high-density residential, low density residential, commercial, industrial, agricultural, recreational, and transportation.

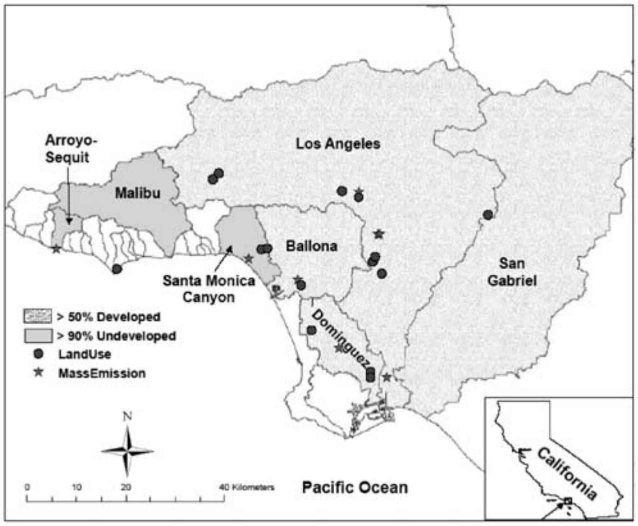

Figure 1. Map of in-river mass emission sampling sites and watersheds within the greater Los Angeles region, California, USA. Watersheds indicated in grey contained land use sites that drain catchments that are >90% undeveloped.

Sampling and analysis

A total of 10 discrete storms were sampled, with each site being sampled between 1 and 4 individual storms. Rainfall amounts ranged from 0.28 to 9.17 cm, and antecedent conditions ranged from 2 to 142 days without measurable rain. Rainfall was measured and recorded in 0.25 cm increments, using a standard tipping bucket at

Table 1. Stormwater polycyclic aromatic hydrocarbon mass emissions from in-river mass emission sampling locations in the Los Angeles, California, USA region. Annual loads are based on water year, as indicated in the footnotes below. SD = standard deviation, EMC = event mean concentration, PAH = polycyclic aromatic hydrocarbons.

							Total PAHs					
							EMC			Mass Emissions		
	Watershed Size km^2	Date of Storm Event	Rainfall (cm)	Antecedent Dry Days	Mean Flow (cms)	Peak Flow (cms)	(ng/L)	SD	Flux (kg/km^2)	(kg)	SD	Annual Total PAH Load (kg/year)
LA River above Arroyo Seco	1460	11/12 - 11/13/2001	1.73	127	62.6	262.5	3256.8	846.7	0.0049	7.16	0.35	3.74[b]
LA River at Wardlow	2161	5/2 - 5/3/2003	3.56	4	209.9	756.7	470.7	453.2	0.0023	4.9	0.32	34.9[c]
		2/2/2004	1.14	29	90.4	375.6	3559.9	1185.5	0.0064	13.93	0.99	150.6[d]
									LA River	Mean Load		92.8 ± 81.8
Verdugo Wash	65	11/12 - 11/13/2001	1.83	11	68.5	368.2	4283.7	2043.2	0.2236	14.54	0.83	NA
		10/31 - 11/1/2003	1.74	30	56.5	155	4992.3	1093.3	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[a]
		4/6 - 4/7/2001	1.78	30	7.8	21.8	816.5	258.5	0.0016	0.2	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[a]
		11/24 - 11/25/2001	1.52	11	53.1	396.2	3118.9	1104.8	0.0246	8.3	1.78	17.3[b]
		5/2 - 5/3/2003	2.03	4	52.8	134.4	981.7	583	0.0032	1.08	0.12	20.0[c]
		10/31 - 11/1/2003	2.03	30	62	148.1	5821.2	1814.9	0.0233	7.87	0.54	72.9[d]
									Ballona Creek	Mean Load		32.7 ± 26.8
Dominguez Channel	187	3/17 - 3/18/2002	0.28	10	4.8	14	3293.4	791.8	0.0013	0.24	0.01	NA
		2/21 - 2/22/2004	1.52	18	14.7	35.5	2182.1	745.2	0.0123	2.31	0.09	NA
Santa Monica Canyon	41	4/6 - 4/7/2001	3.05	50	0.6	3	766.8	247.2	0.0002	0.01	0	NA
Open Space Arroyo Sequit	31	2/25 - 2/26/2004	9.17	2	3.4	21.9	137.6	0	0.0013	0.04	0	NA

[a] Water Year 2001 = October 2000 - September 2001.

[b] Water Year 2002 = October 2001 - September 2002.

[c] Water Year 2003 = October 2002 - September 2003.

each site. 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 minute 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 was transmitted to a data logger/controller upon query commands provided by in the data logger software.

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). 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. 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 pre-cleaned 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 United States Environmental Protection Agency (USEPA) method 625 (USEPA 1991).

Data analysis

Total PAH 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, 2 - 3 rings) and high molecular weight (HMW) PAH compounds (>230, 4 - 6 rings) for source analysis.

Four basic analyses were used to characterize temporal patterns and determine sources of PAH in stormwater. 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:

$$FWM = \frac{\sum_{i=1}^{n} C_i \bullet F_i}{\sum_{i=1}^{n} F_i} \qquad (1)$$

where:

FWM = 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 ith sample

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 p <0.05 significance level (Sokal and Rohlf 1969). 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 prior to 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

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, 2 - 3 rings) and high molecular weight (HMW) compounds (>230, 4 - 6 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[1,2,3-*cd*]pyrene	276	6
Fluorene	166	3	Methylanthracene	222	5
Naphthalene	128	2	Perylene	252	5
Phenanthrene	178	3	Pyrene	202	4

using a plot referred to as a pollutograph. A first flush in concentration from individual ME storm events was defined as the condition 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 (Bertrand-Krajewski *et al.* 1998). When these curves were close to unity, mass emission operated as a function of flow discharge. A strong first flush was defined when greater than or equal to 80% of the mass was discharged in the first 20% of runoff volume. A moderate first flush was defined as the condition when greater than or equal to 30% and less than or equal to 80% of the mass was discharged in the first 20% of runoff volume. No first flush was assumed when less than or equal to 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 investigated using a one-way analysis of variance, with $p < 0.05$ significance level (Sokal and Rohlf 1969). 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 predominated when F/P ratios approach 0.9 (Maher and Aislabie 1992). Pyrogenic sources predominated when P/A ratios ranged from 3 to 26 (Lake *et al.* 1979, Gschwend and Hites 1981).

RESULTS

Developed versus undeveloped watersheds

In-river total PAH loads, concentrations, and fluxes were higher for developed watersheds than for 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 those from undeveloped watersheds (2,655.0 ± 1,768.1 ng/L vs. 452.2 ± 444.9 ng/L; Tables 1 and 3). Flux of PAHs from developed watersheds was 47 times greater than that from undeveloped watersheds (Table 1). Mean PAH flux from the developed watersheds was 35.6 ± 69.8 g/km^2 and 0.75 ± 0.77 g/km^2 for the undeveloped watersheds. When the anomalously high fluxes from the Dominguez watershed were removed, flux from the developed watersheds was 7.8 ± 8.6 g/km^2, or greater than ten 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 and 6.11 ± 4.32 cm for storms in undeveloped watersheds).

The annual output rate of total PAHs in the Los Angeles River watershed during 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 stormwater runoff discharge rate from Ballona Creek increased by a factor of 4 (72.9 kg/year). Notably, 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; 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 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 - 2003 and 2003 - 2004 had total PAH loadings that were approximately four times larger (ranging from 7.9 - 8.3 kg) than the two storms which 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 were analyzed together, PAH concentration and load decrease with increasing cumulative rainfall until approximately 10 cm (average annual rainfall = 33 cm), beyond which the effect is markedly less dramatic (Figure 2).

Polycyclic aromatic hydrocarbons 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 ng/L and 2,276 ng/L) occurred prior to the peak in flow (757 cms and 101 cms) in both the Los Angeles River and Ballona Creek, respectively (Figure 3). In the Los Angeles River example, peak total PAH concentrations occurred almost eight hours prior to 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 (Figure 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.

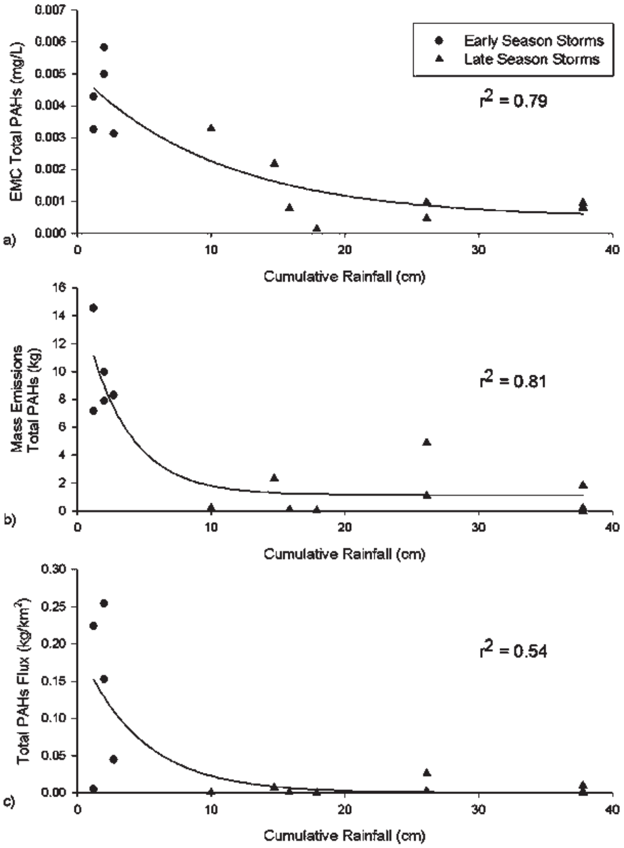

Figure 2: Cumulative annual rainfall versus polycyclic aromatic hydrocarbon (PAH) event mean concentration (EMC) (a), load (b), and flux (c). Plots show data for mass emission sites only.

Potential sources of PAHs

Sources of PAHs were investigated by comparing concentrations and loads in runoff from homogenous 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), there were no significant differences 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 were also used to determine the source of PAHs in stormwater. High molecular weight PAHs

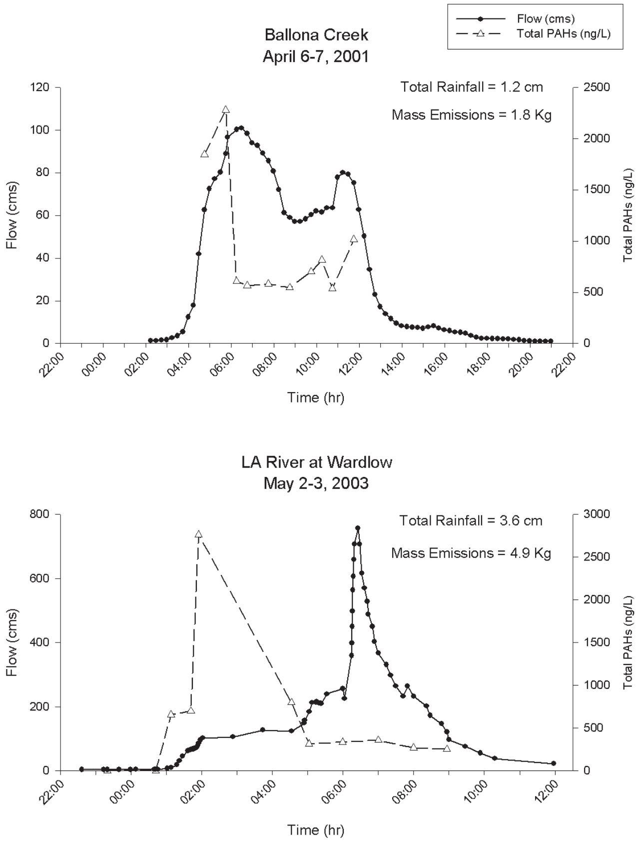

Figure 3: Variation in PAH concentrations with time for storm events in Ballona Creek (top) and LA River (bottom), California, USA.

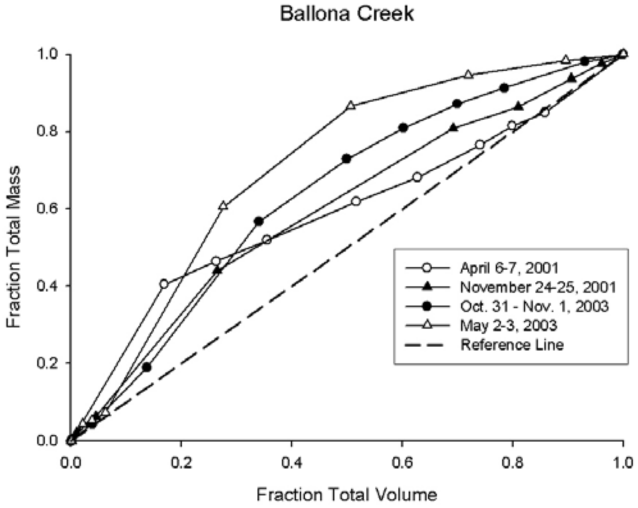

Figure 4: Cumulative polycyclic aromatic hydrocarbon mass loading for four storms in Ballona Creek, California, USA. Plots show percent of mass washed off for a given fraction of the total runoff. Reference line indicates a 1:1 relationship between volume and mass loading. Portions of the curve above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

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 5; 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 F and P 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 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 low molecular weight 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; Lake *et al.* 1979, Gschwend and Hites 1981, Maher and Aislabie 1992). Only one storm, March 17, 2002 to March 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 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 (Figure 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 (Figure 5).

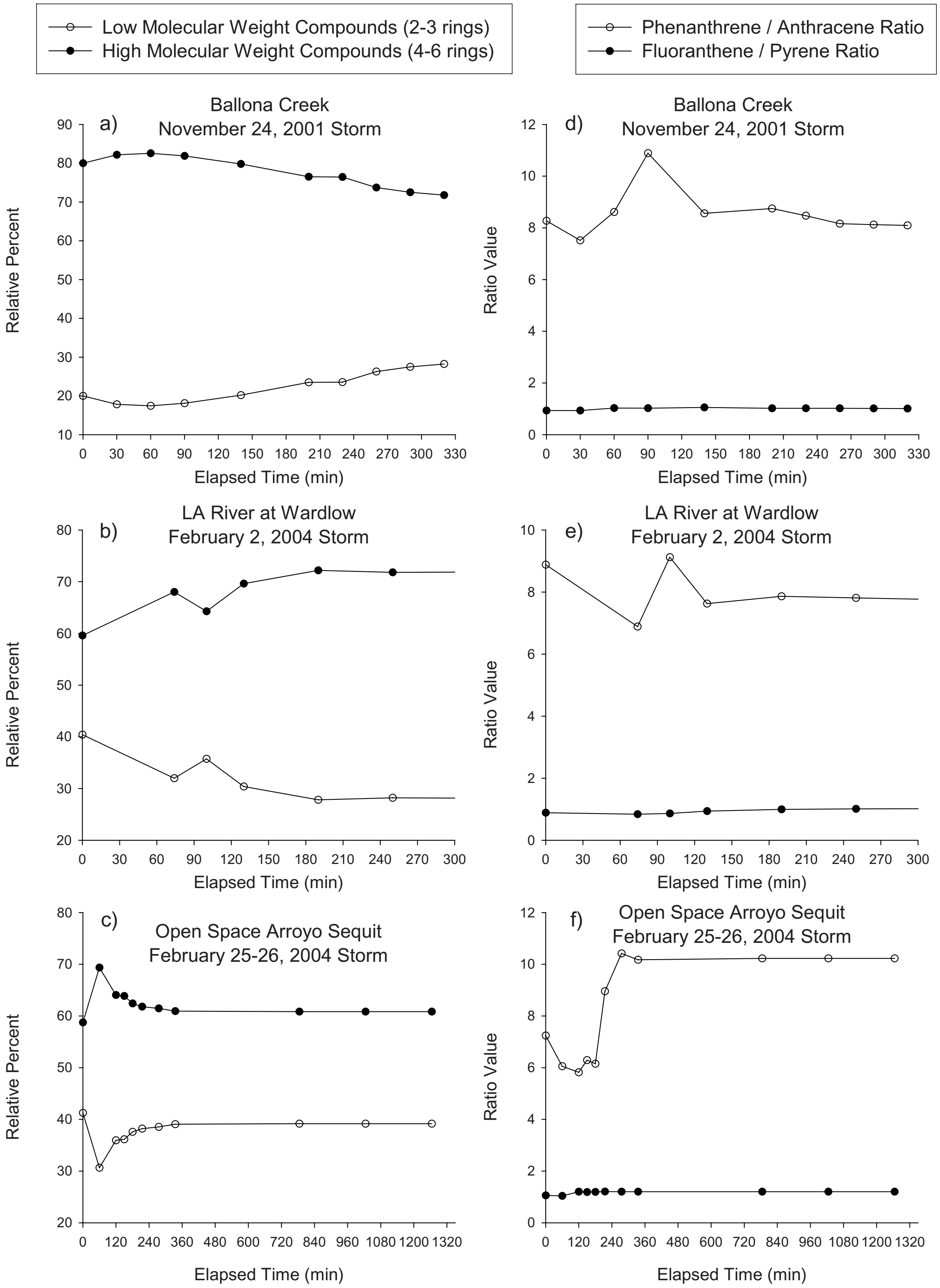

Figure 5: Distribution of polycyclic aromatic hydrocarbons (PAHs) within storms for mass emission sites located in the Los Angeles Region, California, USA. Plots on the left (a - c) show distribution of high versus low molecular weight PAHs throughout individual storms. Plots on the right (d - f) show Phenanthrene/Anthracene (P/A) and Fluoranthene/Pyrene (F/P) ratios throughout individual storms. Peaks in the P/A ratio correspond to peak storm flows.

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

	Storm Event Dates	EMC Total PAHs (ng/L)	EMC Pyrene (ng/L)	Pyrene/ Total PAHs (%)	Fluoranthene/ Pyrene Ratio	Phenanthrene/ Anthracene Ratio	EMC Phenanthrene (ng/L)	Phenanthrene/ Total PAHs (%)	HMW (%)	Dominant Origin Sources
LA River above Arroyo Seco	11/12 - 11/13/2001	3256.8	427.9	13.1	1.1	8	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
	2/2/2004	3559.3	401	11.3	1	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	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	Pyrogenic
Arroyo Seco	2/9 - 2/11/2001	788.8	131.9	16.7	1	8.6	101.2	12.8	81.7	Pyrogenic
	4/6 - 4/7/2001	816.5	135	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	8.1	302.9	9.7	71.8	Pyrogenic
	5/2 - 5/3/2003	981.7	237.4	24.2	1	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	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	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	61	Pyrogenic
	Mean Total PAHs	**2300**								

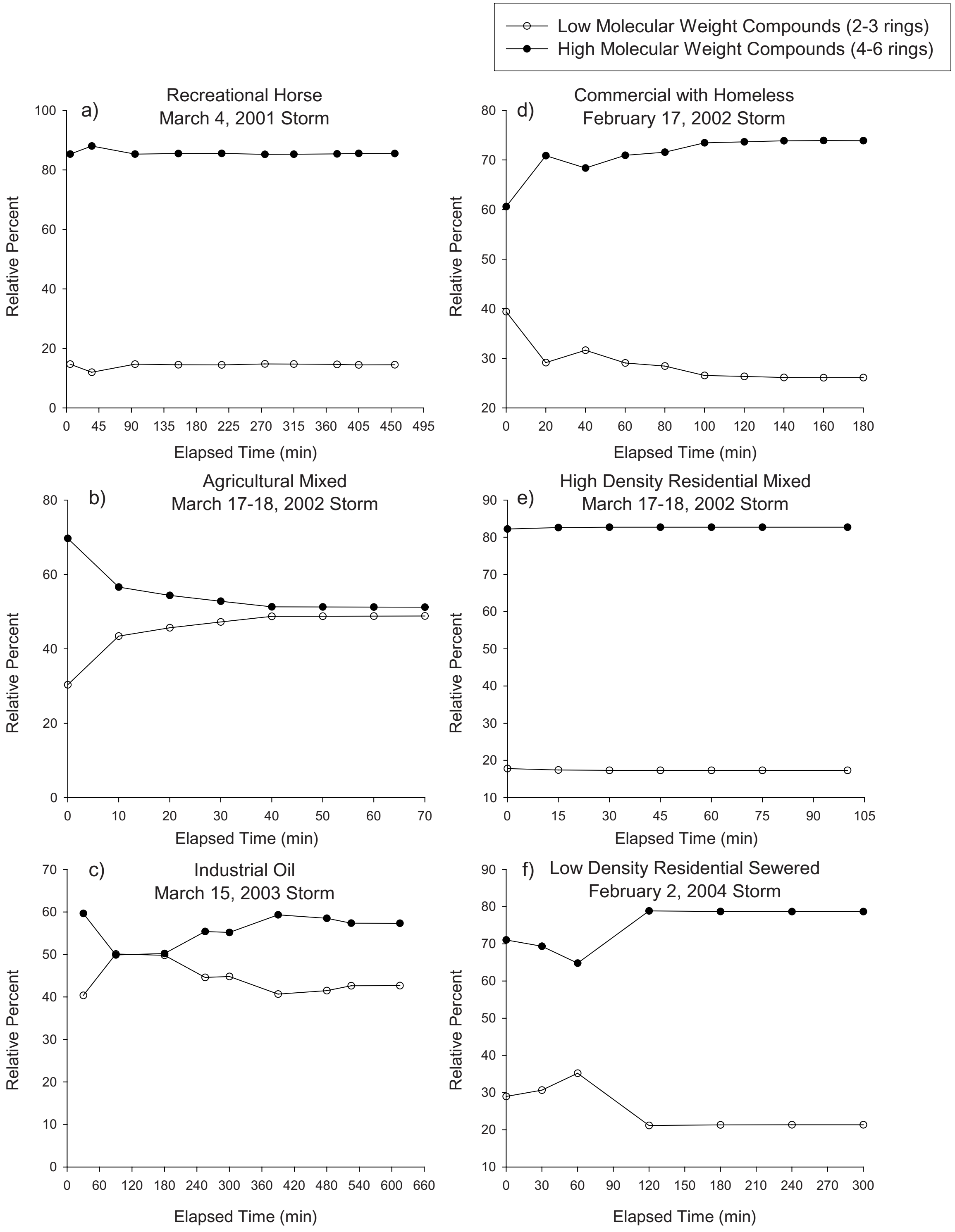

Figure 6: Distribution of polycyclic aromatic hydrocarbons (PAHs) within storms for representative land use sites. Plots show distribution of high versus low molecular weight PAHs throughout individual storms. Data is shown for six sites that represent the results observed for the 15 land use sites where data was collected.

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.

								Total PAHs		
									EMC	
	Watershed Size (km$^{2)}$	Storm Event Date	Rainfall (cm)	Dry Days	Sampling Duration (hrs)	Mean Flow (cms)	Peak Flow (cms)	Flux (kg/km^2)	(ng/L)	SD
High Density Residential 1	0.02	2/17/2002	0.89	21	3	0.001	0.006	1.80E-03	1.92E+03	7.03E+02
High Density Residential 1	0.02	2/2/2004	1.19	2	5	0.004	0.0251	2.00E-02	3.31E+03	1.00E+03
High Density Residential 2	0.52	3/17 - 3/18/2002	0.2	27	1	0	0.003	1.10E-05	7.84E+03	5.99E+03
Mean High Density Residential								7.20E-03	4.40E+03	2.60E+03
Low Density Residential 1	0.98	3/4 - 3/5/2001	2.67	3	31	0.017	0.071	7.20E-05	1.55E+02	5.54E+01
Low Density Residential 1	0.98	2/2/2004	2.26	2	5	0.03	0.143	3.30E-03	3.30E+03	1.60E+03
Low Density Residential 2	0.18	3/17 - 3/18/2002	2.13	9	3	0.008	0.116	1.70E-03	8.86E+02	1.82E+02
Mean Low Density Residential								1.70E-03	1.40E+03	6.00E+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	1.34	7.70E-03	4.43E+03	2.05E+03
Commercial 3	0.06	4/6 - 4/7/2001	2.03	31	6	0.008	0.018	8.20E-05	3.00E+01	1.95E+01
Commercial 3	0.06	3/17 - 3/18/2002	0.12	9	1	0	0.001	2.90E-06	2.08E+02	6.93E+01
Mean Commercial								2.60E-03	1.20E+03	5.80E+02
Industrial 1	0.004	4/6 - 4/7/2001	2.06	31	6	0.008	0.017	5.70E-03	1.36E+02	6.85E+01
Industrial 2	0.001	2/17/2002	0.74	20	3	0	0.002	2.90E-03	6.31E+02	3.42E+02
Industrial 3	2.77	3/17 - 3/18/2002	0.25	9	1	0	0.003	6.60E-06	4.41E+03	2.29E+03
Industrial 4	0.01	3/15/2003	4.5	9	10	0.117	0.375	5.60E-01	8.89E+02	7.55E+02
Mean Industrial		3/4 - 3/5/2001	2.74	3	32	0.021	0.053	1.40E-01	1.50E+03	8.60E+02
								4.30E_04	6.83E+02	7.77E+02
Agricultural 1	0.98	3/17 - 3/18/2002	0.23	10	1	0.012	0.031	2.00E-05	4.55E+02	1.72E+02
		2/2/2004	1.17	2	5	0.023	0.128	5.30E-04	1.43E+03	2.09E+03
Mean Agricultural								3.30E-04	8.60E+02	1.00E+03
Recreational 1	0.03	3/4 - 3/5/2001	1.42	3	32	0.003	0.014	1.80E-03	4.58E+02	2.97E+02
Mean Recreational								1.80E-03	4.60E+02	3.00E+02
Transportation 1	0.01	4/6 - 4/7/2001	3.05	31	5	0.022	0.057	1.40E-02	3.63E+02	2.53E+02
Transportation 2	0.002	2/17/2002	0.89	47	3	0.001	0.006	3.70E-03	5.95E+02	3.16E+02
Mean Transportation								8.90E-03	4.80E+02	2.80E+02

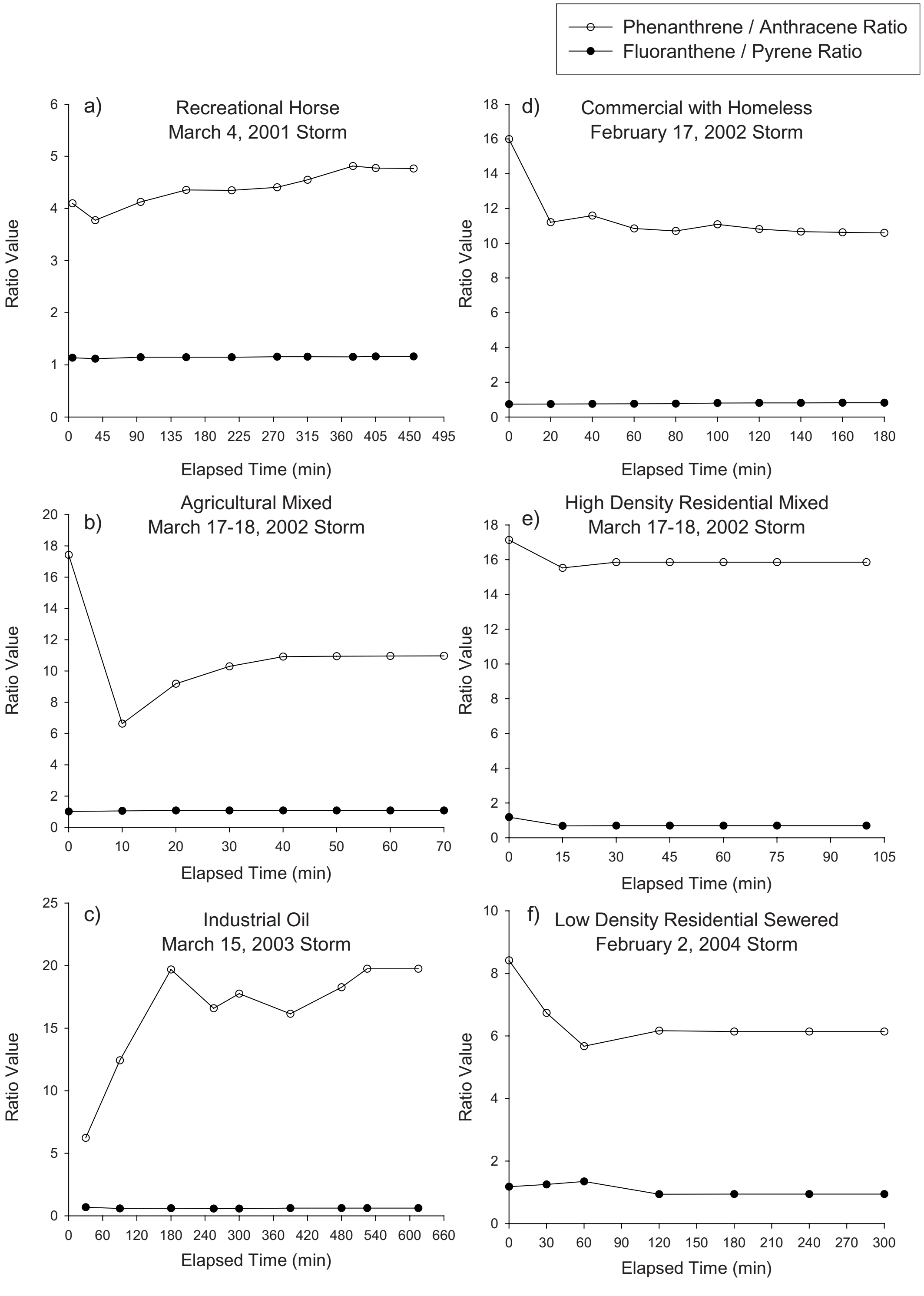

Figure 7: Distribution of polycyclic aromatic hydrocarbons within storms for representative land use sites. Plots show Phenanthrene/Anthracene (P/A) and Fluoranthene/Pyrene (F/P) ratios throughout individual storms. Data is shown for six sites that represent the results observed for the 15 land use sites where data was collected.

DISCUSSION

Anthropogenic sources of total PAHs in stormwater runoff from urbanized coastal watersheds appears to be a significant source of PAHs to the Southern California Bight (SCB). Estimates from this study based on FWM concentrations and gauged annual discharge volume indicate that approximately 92.8 kg/year 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 (~ 2.8 x 10^6 m^3/day) discharged an estimated 740 kg of PAHs to the SCB (Steinberger and Schiff 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 stormwater loading occurs over the 10 to 12 precipitation events that this region averages annually.

The impact of the total PAHs in stormwater discharged from urbanized watersheds is also reflected in receiving waterbody impacts. Regional monitoring of the SCB revealed that the highest concentrations of PAHs were associated within bay and harbor areas that receive inputs from urbanized coastal watersheds (Noblet *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 SCB 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 *et al.* 2003). While some of these contaminants likely arise from port and industrial activities, they are co-located 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 SCB. 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'Connor 1995). San Pedro Bay, California, USA, ranked third nationwide in total PAH concentration in mussel tissue during 2002. The top two locations are Elliott Bay and Puget Sound, Washington, USA, both located near urban centers. On the east coast, Long Island Sound, New York, USA, adjacent to New York City was ranked fourth (Noblet *et al.* 2003).

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.* (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. Watersheds in the western United States typically experience less than one third rainfall and runoff volumes than comparably sized watershed 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.* (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, stormwater monitoring by local municipalities in southern California consistently report no detectable PAHs in stormwater. 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 USEPA regulatory guidelines. However, the FWM mean concentrations in stormwater 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 this study observed. The greatest peaks in total PAH concentrations were almost always observed during initial storm flows, up to eight hours prior to 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 hours 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.* (unpublished data, University of California, Los Angeles, Los Angeles, CA, USA) also observed that peak PAH concentrations in Ballona Creek occur up to 14 hours prior to 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 the 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.* 1981, 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 washoff 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 primarily a function of the amount of time available for PAHs to build up on 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, there is insufficient data to answer this question definitively. Analysis of PAH concentration in wet deposition would help improve understanding of the sources of PAHs during the latter part of the storm season. Environmental managers can use this knowledge of the temporal patterns of PAH loading to focus efforts on storm capture or treatment during the early stages of storms and during the earliest storms of the year.

Sources of PAH in stormwater

Several lines of evidence implicate aerial deposition and subsequent washoff of combustion by-products as the main source of PAH loading in stormwater for most watersheds. First, the flux of total PAHs among large developed watersheds were similar throughout the urbanized region of Los Angeles, California, 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, there was no difference in PAH concentrations in runoff between various urban land uses, which differs from the findings of previous studies in 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 due to 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 attributed these differences to runoff dynamics, as opposed to unique sources.

Second, the relative abundance of individual PAHs in runoff suggests a strong pyrogenic source indicative of combusted fossil fuels. The typical distribution of PAHs observed from mass emission sites (Figure 8) was similar to the distribution of PAHs observed in dry deposition collected in Los Angeles, California, by Sabin and Schiff (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 high molecular weight PAHs accounted for 71 % of the total inputs to Narragansett Bay. A more recent study of PAHs in stormwater runoff in coastal Massachusetts (Menzie *et al.* 2002) identified similar high molecular weight 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 high molecular weight 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 washoff, as suggested by Menzie *et al.* (2002), the distribution of PAHs would have changed during the storm; however, no

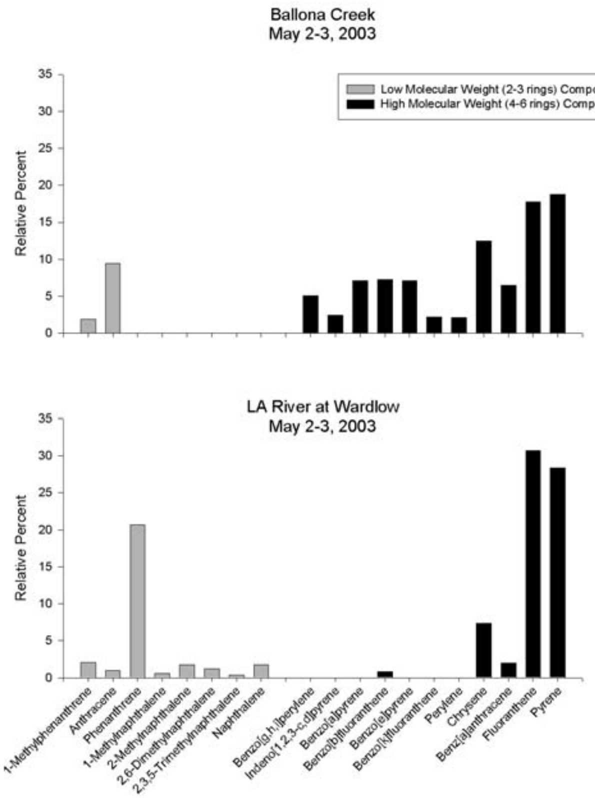

Figure 8: Relative distribution of individual polycyclic aromatic hydrocarbon compounds in California watersheds.

differences were observed within storms. The exception to this pattern was for the industrial oil refinery site, where the signature of petrogenic PAHs was more pronounced. These findings are considered reasonable, given the obvious petrogenic source associated with this land use type. Nevertheless, the pyrogenic signature was still prevalent for this land use, especially during the latter stages of the storm.

Polycyclic aromatic hydrocarbon sources can also be inferred by examining ratios of particular PAHs in runoff samples. For this study, both F/P and P/A ratios were used. 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 5). Both the F/P and 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 (with the exception of Dominquez channel), and this source is consistent for all portions of stormwater 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 methylphenanthrene to phenanthrene (MP/P) ratios (<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 this study (0 - 0.2) also suggest a strong contribution of aged urban aerosols to overall PAH loads (Nielsen 1996, Simo *et al.* 1997). Watersheds in the greater Los Angeles area are heavily urbanized; therefore, there is ample opportunity for combustion derived aerosols, which 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, California. 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

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

Indicator	Pyrogenic	Petrogenic	Reference
Fluoranthene / Pyrene Ratio (F/P)	0.9.-≤1	>1	Mahler et al. 2004
Phenanthrene / Anthracene Ratio (P/A)	3 - 26	>26	Lake et al. 1979, Gschwend and Hites 1981
Methylphenanthrene / Phenanthrene (M/P)	<1.0	2 - 6	Hwang et al. 2003

source) samples have not been 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 semi-arid climates, such as those which exist in southern California (Gunther *et al.* 1987, Sabin and Schiff 2004), supports the conclusions of this study: The predominant source of PAHs in urban stormwater in the greater Los Angeles area is from aerial deposition and subsequent washoff of PAHs associated with combustion by-products.

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