Compositional Indices of Polycyclic Aromatic Hydrocarbon Sources off San Diego, California

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The main sources of anthropogenic hydrocarbon compounds to the marine ecosystem off Southern California are 1) municipal and industrial waste discharge, 2) surface runoff, 3) inadvertent spills, and 4) aerial deposition. Only the hydrocarbons in the first two sources can be easily measured and regulated. In addition to these, in situ biochemical processes also produce significant amounts of hydrocarbons (Wakeham et al. 1980, Gassmann 1982, and references therein) of marine origin. The mixing of hydrocarbons from various sources yields a complicated assemblage that may not be readily recognized. Degradation of organic compounds primarily partitioned on particulates may occur in the water column before deposition. These factors affect efforts to evaluate the impact of wastewater discharges on the coastal marine environment.

The four major municipal wastewater dischargers in Southern California (City of Los Angeles Hyperion Treatment Plant, County Sanitation Districts of Los Angeles County (CSDLAC), County Sanitation Districts of Orange County, and City of San Diego Point Loma Wastewater Treatment Plant (PLWTP)) have made great

efforts to implement improved wastewater treatment technologies. As a consequence, the mass emission rates for a variety of contaminants from their sewage outfalls have steadily declined over the last 25 years (SCCWRP 1995). However, the discharge of a large quantity of numerous contaminants over the years has resulted in notable stresses in coastal marine sediments around the Southern California Bight (Bergen *et al.* 1995). Due to the slow degradation of many chemicals, contaminated sediments continue to impact the benthic community.

The compositional patterns of polycyclic aromatic hydrocarbon (PAH) and aliphatic

hydrocarbon (AH) assemblages have been used to discern the origins of hydrocarbon compounds found in the aquatic environment (Sporstøl *et al.* 1983, Colombo *et al.* 1989, and references therein). PAHs are sensitive indicators of petrogenic and pyrogenic inputs of hydrocarbons while nalkanes are useful in identifying biogenic- or petrogenicproducts. In general, PAHs from petrogenic-related sources are abundant in alkylated homologues relative to their parent compounds, while combustion of fossil fuels yields PAHs generally devoid of alkylated homologues.

These observations prompted the introduction of two useful indicators: 1) alkyl homologue distributions (AHDs) of naphthalene, phenanthrene/anthracene, and fluoranthene/ pyrene, etc.; and 2) parent compound distributions (PCDs) (Lake *et al.* 1979). Other individual ratios generally involving two PAH compounds (e.g., phenanthrene/anthracene (P/ A), methylphenanthrene/phenanthrene (MP/P), fluoranthene/pyrene (FL/PYR), and benz[a]anthracene/ chrysene (BZ[a]A/CHR)) have also been applied to source recognition. Similarly, several molecular indices derived from n-alkane components have been shown to be sensitive in differentiating biogenic and petrogenic inputs of hydrocarbons (Colombo *et al.* 1989, and references therein).

At present, little is known about the contributions of organic contaminants from various sources to the coastal marine environment off San Diego. To gain insight into this, we conducted a comprehensive study of their contributions



during the fiscal year 1993/94. The objectives of this study were to identify the possible origins or sources of hydrocarbons in the coastal region off San Diego and to evaluate the extent of organic contamination exerted by the point and nonpoint inputs. In addition, to further understand the lateral transport of urban pollutants into the ocean, we also measured linear alkylbenzenes (LABs). The methods for data analysis

utilized in this study for PAHs and AHs were similar to those employed by Sporstøl *et al.* (1983) and Colombo *et al.* (1989). In particular, we evaluated the molecular compositions and indices associated with the PAH and n-alkane assemblages in each sample. For LABs, the concentrations of the LAB compounds with 10 to 14 carbons in the alkyl chain were quantified. We also evaluated the LAB chemical compositions and the ratios of internal to external isomers (I/E ratio; Takada and Ishiwatari 1990) of phenyldodecanes in each sample. The data were used to further assess the input levels of these sewage-derived organic contaminants and their fate in the coastal marine environment. The results from this study are presented in three separate articles in this annual report. This first part in the series reports the results from PAHs.

STUDY SITE

The coast off San Diego begins at the United States-Mexico border and extends northwest approximately to Point La Jolla (Figure 1). A major municipal wastewater treatment facility, PLWTP, discharged treated sewage (advanced primary treatment) into the ocean in the area through a submarine outfall at a water depth of 60 m. An extension of the sewage outfall to a depth of 100 m began operation in November, 1993.

The Tijuana River (TJR) drains an area of 4,480 km², of which 27% lies in Mexico and 73% lies in the United States (Brownlie and Taylor 1981), and emerges into the ocean on the southern San Diego coast. Although discharges from TJR only accounted for 2% of total gauged runoff to the Southern California Bight in 1987 and 6% in 1988, it contained the highest concentrations of suspended solids, Cd, Cr, Cu, Ni, Pb, Zn, and total PCBs (Aroclor 1242 + Aroclor 1254) and second highest concentration of total DDTs (DDT and metabolites) among the eight largest creeks and rivers in Southern California (SCCWRP 1992).

San Diego Bay (SDB) is a southeast-northwest embayment; its widths vary from 1 to 4 km and its length is over 18 km with a maximum water depth of 21 m (Lenihan *et al.* 1990). Due to the highly elevated level of contamination in SDB, the National Benthic Surveillance Project (NBSP) under the National Oceanic and Atmospheric Administration National Status and Trends Program had established five sampling stations in the vicinity from 1984 to 1993 to monitor the distributions of contaminants in fish and sediments (Van Rhyn and Gauthier 1992).

Four stations were selected in the present study (Figure 1): A-17 ($32^{\circ}40.28$ ' N/117°17.03' W), R-61 ($32^{\circ}49.64$ ' N/117°19.67' W), SDB ($32^{\circ}43.53$ ' N/117°10.86'W), and MTJR ($32^{\circ}32.94$ ' N/117°08.81' W). In addition, effluent was collected from PLWTP and runoff was collected from TJR at Dairy Mart Road, about 6 km upstream from the ocean.

A-17 is located between the Y-shaped arms of the old PLWTP outfall with a water depth of 60 m. The reference station R-61, about 20 mi away from A-17 and at a water depth of 60 m, is near the northern San Diego coast off La Jolla and has little sediment contamination (SCCWRP 1993a). Station SDB in San Diego Bay is located at East Harbor Island at a depth of 7 m, close to a station used by NBSP (32°43.2' N/117°11.3' W; McCain *et al.* 1992). Station MTJR near the mouth of TJR is about 500 m from the coastline at a water depth of 16 m.

MATERIALS AND METHODS

Supplies used in the measurements of total organic carbon (TOC) and total nitrogen (TN) have been described previously (SCCWRP 1993b). GF/C 47-mm glass fiber

filters (1.2 µm pore size) were obtained from Whatman International Ltd. (Maidstone, England) and baked at 420°C for at least 4 h prior to use. A custom mixture of 12 PAHs was prepared by AccuStandard, Inc. (New Haven, CT) with 2000 µg/mL of individual PAHs in methylene chloride. An additional sixteen PAHs in a mixture were obtained from Ultra Scientific, Inc. (North Kingstown, RI). Internal (nitrobenzene-d_e, 2fluorobiphenyl, and p-terphenyl- d_{14}) and surrogate (naphthalene-d,, acenaphthalene-d₁₀, phenanthrene d_{10} , chrysene- d_{12} , and perylene- d_{12}) standards were purchased from AccuStandard, Inc. and Ultra Scien-





tific, Inc., respectively. A PAH reference standard (SRM 1491) was acquired from the National Institute of Standards and Technology (NIST; Gaitherburg, MD). Ultra resianalyzed grade hexane and methylene chloride were obtained from J.T. Baker Inc. (Phillipsburg, NJ) and used as supplied. All the standards were prepared in hexane.

Sample Collection

Sediment traps were deployed at 1 m and 5 m from the sea floor at both A-17 and R-61 in December 1993 and May 1994; they were retrieved 30 days after deployment. Surface sediments from A-17, R-61, SDB, and MTJR, microlayer samples from A-17 and R-61, effluent from PLWTP, and runoff from TJR were collected in January and June 1994.

The sediment traps used were designed to collect sinking particulates and are described in detail elsewhere (Hendricks and Eganhouse 1992). Three moorings were deployed at each of the A-17 and R-61 sites. Three and nine traps were used at the 1-m and 5-m depths, respectively. This sampling design was intended to obtain sufficient particulates for chemical analyses. All the traps deployed in December 1993 were recovered, while all three traps deployed at A-17 1-m, six traps at A-17 5-m, and one trap at R-61 5-m in May 1994 were lost. Upon retrieval, the traps were disassembled and water over the particles was decanted slowly. The sample bottles were capped with Teflon-lined caps.

Sediments were collected using a modified 0.1 m^2 Van Veen grab (Stubbs *et al.* 1987). Subsamples of the top 2 cm sediments were transferred into precleaned glass jars. Procedures for microlayer sample collection and handling were detailed previously (Cross *et al.* 1987). The upper 50 µm surface water samples were collected into precleaned 1-L amber glass bottles. Twenty-four-hour composite effluent samples were obtained from PLWTP and stored in precleaned 1-gal amber bottles. TJR runoff was collected by immersing a 1-gal glass bottle into the middle of the stream from a bridge. All the samples collected were immediately cooled with ice. Upon returning to the laboratory, the sediment and sediment trap samples were stored at -20°C and microlayer, effluent, and runoff samples were stored at 4°C until further treatment.

Sample Extraction

Sediments and Sediment Trap Particulates.

A weighed subsample was transferred into a 250-mL centrifuge bottle. The bottle was centrifuged at approximately 50 x g for 5 min and the top water layer was decanted. The sample was mixed with ~30 g of anhydrous sodium sulfate, spiked with surrogate standards, and ex-

tracted successively three times with methylene chloride (100 mL each) using a roller table. The combined extract was concentrated and solvent-exchanged to hexane using a rotary evaporator at 30°C and 650 mm Hg vacuum pressure. After sulfur removal with activated copper granules (overnight in the dark), the extract was further concentrated to $\sim 250 \ \mu L$ under gentle nitrogen flow. The extract was applied to a 1:2 alumina/silica gel glass column for separation of different fractions. The first fraction, containing AHs, was eluted with 15 mL of dry hexane. The second fraction, containing PAHs and LABs, was collected by eluting 5 mL dry hexane and 30 mL of a 30/70 mixture of methylene chloride and hexane through the alumina/ silica gel column. Each fraction was concentrated to ~ 0.5 mL using the rotary evaporator and transferred to a halfdram vial. The pear-shaped flask was rinsed with additional hexane and the solvent was also transferred to the half-dram vial. The final volume of the extract was adjusted to 500 µL under gentle nitrogen flow. Appropriate amounts of the internal standards were added to the extract prior to instrumental analysis.

Effluent, Runoff, and Microlayer. Particulates in each sample were separated with precleaned, preweighed GF/C filters. Sample bottles were shaken vigorously before filtration. A measured amount of the sample was gradually poured into the all-glass filtration assembly and filtered under vacuum. The filter was replaced when the flow dropped to approximately half of the initial speed. Each filter was transferred to a precleaned glass petri dish. The filters were cut in pieces with a clean, stainless steel blade and combined in a glass centrifuge bottle. The rest of the extraction procedure was the same as used for sediments and sediment trap particulates.

The filtrates were extracted three times with methylene chloride using the liquid-liquid extraction technique (Zeng and Khan 1995). The combined extract was concentrated and fractionated in the same fashion for the sediments and sediment trap particulates.

Total Suspended Solid (TSS), Moisture, TOC, and TN Measurements

An appropriate amount of an aqueous sample was filtered with a preweighed GF/C glass fiber filter. The loaded filter was placed in a petri dish and dried overnight at 60°C to constant weight. The difference in the weights of the filter before and after filtration with a specific sample volume was defined as the TSS concentration (in mg/L).

Moisture content was determined for sediments and sediment trap particulates. Approximately 10-15 g of

sample were transferred to a tared aluminum pan and weighed with an electronic balance (accuracy ~0.5 mg). The sample was dried at 60° C for 24 h, cooled in a dessicator, and weighed. The weight loss was defined as moisture content.

For sediments and sediment trap particulates, the TOC and TN contents were measured using a procedure in SCCWRP (1993b). For aqueous samples, particulates were filtered with GF/C filters. The loaded filters were treated in a same fashion as for sediment and sediment trap particulates. Analysis of blank glass fiber filters indicated no detectable TOC or TN.

Gas Chromatography/Mass Spectrometry (GC/MS) Analysis and Quantitation

Measurements of PAHs were made using an HP 5890 II GC with a 5970 mass selective detector (MSD); the experimental conditions are described in Zeng and Khan (1995).

Quantitation of PAH concentrations was performed using the internal calibration method. The internal standards were either prepared with the calibration standards or added to the final sample extracts. Twenty-six PAH compounds were measured in this study (Table 1). ΣC_1 -naphthalene consisted of 1-methylnaphthalene and 2-methylnaphthalene. C_2 -naphthalenes were quantified using the relative response factor of 2,6dimethylnaphthalene; C_3 -naphthalenes using 2,3,6trimethylnaphthalene; and C_1 -phenanthrenes using either 2-methylphenanthrene or 1-methylphenanthrene, depending on the closeness of their retention times.

Procedural performance and matrix effects were monitored by recoveries of surrogate standards prepared with calibration standards or spiked to samples prior to extraction. The mean ± 1 SD (n=31) for the recoveries of the surrogate standards in field samples were as follows: naphthalene-d₈ -33.8 ± 12.6 , acenaphthalene-d₁₀ - 69.2 ± 14.5 , phenanthrene-d₁₀ - 82.0 ± 14.4 , chrysene-d₁₂ - 84.8 ± 24.4 , and perylene-d₁₂ - 98.6 ± 31.8 . Instrumental performance was checked for each batch of samples (less than 10) by analyzing the NIST SRM 1491 solution. The measured values were within $\pm 20\%$ of the certified values given by NIST for more than 80% of the PAH compounds (or times).

Concentrations of PAH compounds were expressed based on either particle dry weight for solid samples or volume for aqueous samples; they were not corrected for the recoveries of the surrogate standards. The detection limits (Table 1) were set slightly higher than the method detection limits determined using the procedure given previously (Clesceri *et al.* 1989). These detection limits were based on 1 g dry weight or 1 L volume for a sample. The actual detection limits for a sample with a different weight or volume were corrected accordingly.

RESULTS

Total Suspended Solids

Total suspended solid (TSS) concentration showed more than a 20-fold variation in PLWTP effluent, TJR runoff, and microlayer samples from four locations (Table 2).

TSS concentration was 56 and 27.5 mg/L in the PLWTP effluent samples collected in January and June 1994, respectively. In TJR runoff TSS was 88 mg/L in January 1994 and 15 mg/L in June 1994.

Microlayer samples showed a wide range of TSS concentrations at the same sampling site at different times or at different sites at the same time. TSS ranged from 11.5 mg/L (A-17 in June 1994) to 258 mg/L (A-17 in January 1994) with a mean value of 100 (±88) mg/L.

TABLE 1. Polycyclic aromatic hydrocarbon (PAH) analysis in samples collected off San Diego, California, in 1994. The method detection limits (MDLs) were based on 1 g of solid or 1 L of aqueous samples.

		Molecular Ion	MDL		
		for Quantitation	Solid	Aqueous	
Peak No.	PAH Compound	(m/z)	(ng/g)	(ng/L)	
1	Naphthalene	128	40	35	
2	ΣC Naphthalene	142	40	35	
3	Biphenyl	154	40	35	
4	ΣC_{a} -Naphthalene	156	40	35	
5	Acénaphthylene	152	40	35	
6	Acenaphthene	154	40	35	
7	ΣC_3 -Naphthalene	170	40	35	
8	Fluorene	166	40	35	
9	Phenanthrene	178	40	35	
10	Anthracene	178	40	35	
11	ΣC_1 -Phenanthrene	192	40	35	
12	3,6-Dimethylphenanthrene	206	40	35	
13	Fluoranthene	202	40	35	
14	Pyrene	202	40	35	
15	2,3-Benzofluorene	216	40	35	
16	Benzo[a]anthracene	228	40	35	
17	Chrysene	228	40	35	
18	Benzo[b]fluoranthene	252	40	35	
19	Benzo[k]fluoranthene	252	40	35	
20	Benzo[e]pyrene	252	40	35	
21	Benzo[a]pyrene	252	40	35	
22	Perylene	252	40	35	
23	9,10-Diphenylanthracene	330	200	200	
24	Indeno[1,2,3-cd]pyrene	276	200	200	
25	Dibenzo[a,h]anthracene	278	200	200	
26	Benzo[g,h,i]perylene	276	200	200	

TOC and TN

Particulates were higher in TOC and TN in PLWTP effluent than TJR runoff (Table 3). PLWTP effluent particulate TOC, TN, and C/N (TOC/TN) ratios were 34.4, 6.3, and 5.5% in the January sample and 35.7, 6.3, and 5.7% in the June sample, respectively. In TJR runoff particulates, TOC, TN, and C/N were 10.2, 2.18, and 4.7% in January and 8.15 %, 1.58, and 5.16% in June 1994. The difference probably results from mixing of raw sewage with other wastes or particles with less TOC and TN contents in TJR runoff.

Similar to the TSS results, TOC and TN in microlayer

particulates varied widely from sample to sample, ranging from 1.55 % (A-17 in January 1994) to 20.7 % (R-61 in June 1994) for TOC and from 0.108 % (A-17 from January) to 2.06 % (R-61 from June) for TN. C/N varied in a

TABLE 2. Concentrations of total suspended solids (TSS) in samples collected off San Diego, California, in 1994.

	TSS (mg/L)									
	1/	94	6/94							
Sample Type	Mean	SD	Mean	SD						
PLWTP Effluent	56	4 ^a	27.5	3.5						
TJR Runoff	88	22 ^b	15	1.4						
Microlayer A-17	258	20	11.5	2.1						
R-61	80.5	1.0	116	6						
MTJR	198	3	28	3						
SDB	87	12	21	5						
^a Three measurements. ^b Eleven measurements.										

relatively narrower range, from 3.6 (R-61 from January 1994) to 17 (A-17 from June 1994) (Table 3).

The A-17 and R-61 sediments contained fairly similar TOC and TN (TOC<1% and TN<0.1%), typical of relatively uncontaminated marine sediments. Sediments collected from MTJR contained the lowest TOC (0.374 % in January 1994 and 0.120 % in June 1994) and also relatively low TN. Overall, the SDB sediment samples contained the highest TOC and TN concentrations (0.82 % in January and 0.83 % in June for TOC; 0.069 % in January and 0.082 % in June for TN) among all the samples (Table 3).

The TOC concentrations in sediment trap particulates varied from 1.89 to 3.22 % with a mean of 2.58 (\pm 0.44) % and TN ranged from 0.180 to 0.352 % with a mean of 0.264 (±0.06) %. In general, R-61

	TOC (%)				TN (%)				C/N			
	1/94		6/94		1/94		6/94		1/94		6/94	
Sample Type	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PLWTP Effluent	34.4	3.5 ^ª	35.7	6.9	6.3	2.1	6.3	2.4	5.5	1.6	5.7	1.2
TJR Runoff	10.2	2.5 ^b	8.15	0.20	2.18	0.83	1.58	0.09	4.7	1.7	5.16	0.18
Microlayer												
A-17	1.55	0.74	12.9	1.1	0.108	0.092	0.77	0.24	14.4	8.5	17	7
R-61	1.63	0.13	20.7	0.8	0.45	0.17	2.06	0.31	3.6	1.2	10.0	1.1
MTJR	4.94	0.10	9.9	7.4	0.73	0.20	0.72	0.69	6.8	1.8	14	5
SDB	6.9	6.5	8.6	3.1	1.31	0.53	1.1	0.6	5.3	3.1	7.8	1.4
Sediments												
A-17	0.539	0.009	0.513		0.063	0.001	0.042		8.6	0.1	12.2	
R-61	0.841	0.006	0.554		0.063	0.002	0.019		13.3	0.5	29.2	
MTJR	0.374	0.008	0.120		0.046	0.002	0.045		8.1	0.2	2.67	
SDB	0.82	0.10	0.829		0.082	0.004	0.069		10.0	0.7	12.0	
Sediment Trap Particulates												
A-17 (1 m)	1.89	0.03 ^d	** ^C		0.180	0.010	**		10.5	0.6	**	
A-17 (5 m)	2.23	0.07 ^e	2.94		0.211	0.004		0.320	10.6	0.2	9.16	
R-61 (1 m)	2.46	0.05 ^d	2.56		0.244	0.012		0.259	10.1	0.3	9.87	
R-61 (5 m)	2.73	0.04 ^d	3.22		0.280	0.011		0.352	9.8	0.4	9.14	

TABLE 3. Concentrations of total organic carbon (TOC), total nitrogen (TN), and TOC/TN (C/N) ratio in samples (particulate portions only for effluent, runoff, and microlayer samples) collected off San Diego, California, in 1994.

²Eleven measurements.

^cTraps were lost. ^dFive measurements.

^eSix measurements.

SD = Standard deviation.

trap particulates contained higher TOC and TN than those from A-17 (Table 3).

Spatial and Temporal Distributions of PAHs

PLWTP Effluent. A large difference in particulate PAH concentration was observed between the effluent samples collected in January 1994 (5,920 ng/g) and in June 1994 (17,500 ng/g) (Table 4). In the present study, different subsamples were used in measuring TSS and organic compounds, due to the concern that some organic compounds might be lost if the same subsample processed for TSS measurement was also analyzed for organic compounds. Sample heterogeneity may be partially responsible for the large difference in the TSS concentrations (Table 2), resulting in elevated particle-based PAH concentrations in the effluent collected in June 1994. If the aqueous volumes were used, the particulate PAH concentrations were 332 ng/ L in the January sample and 481 ng/L in the June sample (Table 4). The PAH concentrations on a whole effluent basis were similar in both samples (1,780 ng/L in January vs. 1,550 ng/L in June).

TJR Runoff. The runoff samples were collected during low flows. The runoff filtrate collected in June 1994 carried higher PAH concentration relative to that collected in January 1994 (Table 4). This difference likely resulted from the different sample volumes used for analyses, as was in the case of the PLWTP effluent. The total PAH concentrations based on the aqueous volume were similar in the particulate and aqueous portions of the January sample, but much higher in the filtrates than in the particulates of the June sample (Table 4). Again, this discrepancy was partially due to the large differences in TSS (Table 2).

Microlayer. In processing the microlayer samples collected in January 1994 (the first batch in the present study), black ribbon filter papers were used to hold anhydrous sodium sulfate for removal of water content from extracts. Excessive, mostly unresolved peaks were found in the chromatograms of these samples, as well as in those of procedural blanks (pure solvent going through the extraction processes). GC/MS analyses indicated that ion fragments typical of hydrocarbon compounds (e.g., m/z 59, 71, 85, 99, etc.) were dominant. Due to the possible interference with sample quantitation, the analytical results for these samples were abandoned. Baked glass wool replaced the filter papers in the subsequent extraction of the other samples. The same interfering peaks did not appear in procedural blanks and samples.

No PAHs were detected in the microlayer filtrates at A-17 and R-61 and only a few PAHs were present in the microlayer particles (Table 4). The dry weight based concentrations of particulate PAHs were 1,770 ng/g in A-17 and 381 ng/g in R-61 sample. However, the concentrations based on the aqueous sample volume were similar in both samples (20.4 ng/L in A-17 and 44.2 ng/L in R-61). This drastic difference was clearly a result of the distinct concentrations of TSS in these two samples (11.5 mg/L in A-17 vs. 116 mg/L in R-61; Table 2).

The MTJR microlayer particulate sample contained a PAH concentration of 2,830 ng/g (dry weight); the filtrate sample had non detectable PAH content. The total PAH concentration based on the aqueous sample volume was similar in the MTJR microlayer (79.2 ng/L) and TJR runoff (80.1 ng/L) in June 1994.

The SDB microlayer particulates were highly enriched with PAHs (68,600 ng/g dry weight or 798,000 ng/g TOC based). On the other hand, the microlayer filtrates had a fairly low PAH concentration (42.2 ng/L) and only two PAH compounds, fluoranthene and pyrene, were detected. The total PAH concentration based on volume was 1,480 ng/L.

Sediments. The magnitude of sediment PAH contamination followed the order of SDB>A-17>R-61>MTJR. The PAH concentrations in A-17 sediments were 257 ng/g dry weight in January 1994 and 122 ng/g dry weight in June 1994; the temporal decline was possibly related to the initiation of the PLWTP outfall extension in November 1993. Similar trend was observed in R-61 sediment samples (23.9 *vs.* 7.1 ng/g dry weight).

Extremely low levels of PAHs were found in the sediment at MTJR, 16.5 ng/g dry wt. in January and these were nondetectable in June 1994. The PAH concentrations in SDB sediments were comparable in January (983 ng/g) and June (898 ng/g) 1994 (Table 4).

Sediment Trap Particulates. The A-17 sediment trap particulates contained slightly higher PAH concentrations than the R-61 particulates, but the difference was not as significant as in the case of sediments. The samples collected in January also contained slightly higher PAH concentrations than those collected in June. The PAH concentration decreased from the 1-m depth to 5-m depth at A-17, but increased at R-61. However, the variation at R-61 was not significant. Due to the higher TOC contents in sediment trap particulates than in sediments (Table 3), the TOC normalized PAH concentrations were higher in A-17 sediments than in sediment trap particulates, although the dry weight based concentrations were similar. TABLE 4. Concentrations of polycyclic aromatic hydrocarbons (PAHs) and percentages of 2,3-ring PAHs and fluoranthene+pyrene relative to total PAHs.

	Sample Size ^a		Total PAHs		Total PAHs (TOC based) ^c		%2 3-ring PAHs ^d		%FI +PYR ^e	
Sample Type	1/94	6/94	1/94	6/94	1/94	6/94	1/94	6/94	1/94	6/94
PLWTP Effluent										
Filtrates	2.4	10	1450	1070	_	_	100	99	0	1
Particulates	0.134	0.275	5920 (332)	17500 (481)	17200	49000	100	90	0	5
TJR Runoff			()	()						
Filtrates	10	30	10.8	78.5	_	_	38	92	62	8
Particulates	0.888	0.450	158 (13.9)	104 (1.6)	1550	1280	0	0	100	100
Microlayer			· · · · ·							
A-17 Filtrates	NA	5	NA	ND			NA	ND	NA	ND
A-17 Particulates	NA	0.0575	NA	1770 (20.4)	NA	13700	NA	0	NA	100
R-61 Filtrates	NA	5	NA	ND			NA	ND	NA	ND
R-61 Particulates	NA	0.580	NA	381 (44.2)	NA	1840	NA	33	NA	67
MTJR Filtrates	NA	5	NA	ND	—	—	NA	ND	NA	ND
MTJR Particulates	NA	0.140	NA	2830 (79.2)	NA	28500	NA	55	NA	32
SDB Filtrates	NA	5	NA	42.2			NA	0	NA	100
SDB Particulates	NA	0.105	NA	68600 (1440)	NA	798000	NA	18	NA	23
Sediments										
A-17	41.1	42.0	257	122	47600	23800	8	15	21	21
R-61	39.3	40.6	23.9	7.1	2840	1270	6	0	25	44
MTJR	41.9	44.1	16.5	ND	4690	ND	13	ND	43	ND
SDB	34.1	38.3	983	898	120000	108000	6	11	11	15
Sediment Trap Particulates		f								
A-17 (1 m)	47.6	**'	325	**	17200	**	13	**	15	**
A-17 (5 m)	46.8	4.58	270	224	12100	7650	17	13	16	22
R-61 (1 m)	5.61	6.96	145	120	5900	4690	7	6	29	29
R-61 (5 m)	9.60	6.96	163	130	5960	4030	7	12	23	31

^aIn g (gram) for solid (particulates and sediments) and L (liter) for aqueous samples (filtrates).

^b In ng/g dry weight for solid samples and ng/L for aqueous samples; the numbers in parentheses are concentrations based on the aqueous volumes, in ng/L.

^cIn ng/g TOC for solid samples; TOC was not measured for aqueous samples.

^dPercent of the concentrations from naphthalene to 3,6-dimethylphenanthrene (see Table 1) relative to total PAHs.

^ePercent of the concentrations of fluoranthene and pyrene relative to total PAHs.

¹A-17 1-m traps were not recovered in June 1994.

NA=not analyzed; see text for reasons.

ND=not detectable.

PAH Compositions

High molecular weight PAHs were relatively more abundant in the PLWTP effluent particulates than in the filtrates (Figures 2a and 2b). Both effluent filtrates and particulates contained mostly 2,3-ring PAHs and extremely low concentrations of fluoranthene/pyrene (Table 4). The particulates from TJR runoff contained only one PAH component (pyrene), while the filtrates were enriched with low molecular weight PAHs (Figures 3a and 3b; Table 4).

The number of PAH compounds detected was normally small for microlayer samples except for the SDB sample, which contained a large number of PAHs (Figure 3d). PAHs with more than three benzene rings were dominant in this sample (Table 4).

A common feature in the sediments and sediment trap particulates was the low percentage (from 0 to 15%) of the 2,3-ring PAHs, as opposed to the dominance (from 90 to 100%) of these low molecular weight PAHs in the PLWTP effluent (Table 4). There was a substantial difference in PAH compositions between the PLWTP effluent and A-17 sediment and sediment trap particulate samples (Figure 2). Although not shown, PAH compositions in R-61 sediments and sediment trap particles were similar to those in A-17 samples.

The alkyl homologue distributions (AHDs) of naphthalene and parent compound distributions (PCDs) for a selected and representative group of samples varied somewhat between samples (Figures 4 and 5). Due to the generally low PAH concentrations in our samples, other AHD series (e.g., phenanthrene/anthracene, fluoranthene/ pyrene, etc.) could not be determined accurately. Therefore, any conclusions regarding PAH origins derived from AHDs only refer to low molecular weight PAHs.

Vertical Fluxes of Organic Materials at A-17 and R-61

The fluxes of particulates, TOC, TN, and total PAHs at A-17 and R-61 varied spatially and temporally (Table 5).



FIGURE 2. Polycyclic aromatic hydrocarbon (PAH) compositions in the Point Loma Wastewater Treatment Plant (PLWTP; City of San Diego) effluent, A-17 (near old PLWTP outfall) sediments, and A-17 sediment trap particulates collected in January 1994. Peak numbers are defined in Table 1.

The flux of particulates at each depth was the average of multi-trap measurements. Fluxes of TOC, TN, and PAHs were calculated directly from the concentrations of TOC, TN, and PAHs (Tables 4 and 5) and the fluxes of particulates. PAH concentrations were possibly underestimated in

these samples, due to insufficient sample amounts for the PAH measurements in the May -June 1994 sediment trap particulates.

The maximum flux of particulates was 255.2 g/m²d at the A-17 1-m traps deployed between December 21, 1993 and January 20, 1994. The A-17 1-m traps were lost in the second sampling during May -June 1994, hence no temporal comparison could be made at this depth. A substantial decline in fluxes of particulates between January and June was obvious at all other traps. They decreased from 89.4 to 22.0 g m^{-2} d⁻¹ for the A-17 5-m traps, from 87.8 to 34.7 g m⁻² d⁻¹ for the R-61 1-m traps, and from 55.8 to



FIGURE 3. Polycyclic aromatic hydrocarbon (PAH) compositions in the Tijuana River (TJR) runoff, mouth of Tijuana River (MTJR) microlayer particles, San Diego Bay (SDB) microlayer particles, and SDB sediment collected off San Diego, California in June 1994. Peak numbers are defined in Table 1.

14.6 g m⁻² d⁻¹ for the R-61 5-m traps. Since TOC, TN, and PAH contents were only slightly higher in the sediment trap particulates collected in June 1994 than those collected in January 1994 (Tables 4 and 5), the temporal variation in the fluxes of TOC, TN, and PAHs followed the same pattern as



FIGURE 4. Alkyl homologue distributions (AHDs) of naphthalene in selected samples collected off San Diego, California.

did the fluxes of particulates. For the samples collected in the winter of 1993/94, the PAH fluxes varied from 82.9 to 24.1 μ g m⁻² d⁻¹ at A-17 and from 12.7 to 9.1 μ g m⁻² d⁻¹ at R-61 in going from 1-m to 5m traps (Table 5).

DISCUSSION PAH Origins: Compositional Indices

The PAH assemblages in the samples analyzed in the present study can be divided into two distinct groups based on their PAH compositional patterns. The first group includes PLWTP effluent, TJR runoff, and MTJR



FIGURE 5. Parent compound distributions (PCDs) in selected samples collected off San Diego, California.

microlayer particulates which were dominated by low molecular weight PAHs, i.e., high proportion of 2,3-ring PAHs (38-100%, Table 4). The PAH compositions in the second group of samples were characterized by the predominance of 4,5-ring PAH compounds, generally considered combustion-related products. This type of PAH assemblages has been observed in most marine sediments around the world (Laflamme and Hites 1978) and is believed to derive mainly from incomplete combustion of fossil fuels.

Alkylated naphthalenes were more abundant than the parent compound in both the PLWTP effluent filtrate and particulate samples, although the patterns were slightly different (Figures 4a and 4b). The AHD pattern of the filtrate sample was similar to that of a crude oil sample (Sporstøl *et al.* 1983), while the relative abundance of alkyl substituted naphthalenes in the particulate sample showed an almost linear increase with increasing alkyl carbon number. Nevertheless, the relatively high abundance of alkylated naphthalenes suggested that PAHs (especially those with low molecular weights) received by the PLWTP were mostly petroleum-related.

Among the sediment and sediment trap samples from A-17 and R-61, only the A-17 1-m sediment trap sample collected in January 1994 contained a recognizable AHD pattern (Figure 4c-4e; R-61 samples not shown), which was similar to those in the PLWTP effluent samples, i.e., low molecular PAHs were likely derived from petroleum related sources. On the other hand, PCDs determined in these samples (Figures 5c-5e; R-61 samples not shown) were similar to those found in the sediments from Narragansett Bay (Rhode Island) believed to be contaminated by combustion-generated PAHs (Lake et al. 1979). Biodegradation and desorption of low molecular weight PAHs during transport and deposition was a possible mechanism for the PAH compositional difference in the effluent and sediment (and sediment trap) samples. However, the TOC normalized PAH concentrations in sediments (47,600 ng/g in January and 23,800 ng/g in June; Table 4) were comparable to those in the PLWTP effluent particulates (17,200 ng/g in January and 49,000 ng/g in June; Table 4). If the PLWTP outfall was a sole source for PAH inputs, biodegradation of sewage-derived PAHs would yield a much lower TOC normalized concentration of total PAHs. In addition, dilution of the effluent particulates by particles from other sources may also be possible. Apparently, PAH assemblages in the water column particles and sediments at A-17 and R-61 originated from both combustion and petroleum related sources. For the microlayer samples collected at A-17 and R-61, only a few mid range molecular weight PAHs were detected in the particulates. Thus, no AHDs and PCDs could be accurately determined. As also discussed in the following section, nonpoint source inputs, presumably produced by combustion-related processes, may have exerted a greater impact on the microlayer than the PLWTP outfall.

Both AHD and PCD (Figures 4f and 5f) in the TJR runoff filtrate sample collected in June 1994 suggested a petrogenic source for PAHs. As noted previously (SCCWRP 1992), a large percentage of the TJR discharge has reportedly been raw sewage and industrial and agricultural wastes, whose composition may be comparable to that of the wastes received by the PLWTP. In addition, only 3% of the drainage land of TJR on the U.S. side is urban and suburban (Brownlie and Taylor 1981). Therefore, combustion-derived PAHs that normally dominate urban riverine runoff (Hoffman *et al.* 1984,

Level off Bottom Particulates TOC ΤN Total PAHs (g/m²/d) Site Collection Date $(\mu g/m^2/d)$ (m) $\left(\frac{g}{m^2}\right)$ A-17 12/21/93-1/20/94 1 (3 traps) 255.2 4.82 0.459 82.9 0.189 5 (9 traps) 89.4 1.99 24.1 5/30/94-6/29/94 1 (traps lost) 5 (3 traps) 22.0 0.65 0.070 4.9 87.8 R-61 12/21/93-1/20/94 1 (3 traps) 2.16 0.214 12.7 5 (9 traps) 55.8 1.52 0.156 9.1 5/30/94-6/29/94 1 (3 traps) 34.7 0.89 0.090 4.2 5 (8 traps) 0.47 0.051 14.6 1.9

TABLE 5. Fluxes of particulates, total organic carbon (TOC), total nitrogen (TN), and total polycyclic aromatic hydrocarbons (PAHs) at A-17 and R-61 (outfall and reference) off San Diego, California, in 1993-1994.

Prahl *et al.* 1984, Anderson and Gossett 1987) should not be the major components in TJR runoff.

Unlike the other microlayer samples, the MTJR microlayer particulates contained high concentrations of low molecular weight PAHs (Figure 3c), indicating a predominant petrogenic origin for PAH compounds. This observation was collaborated by the patterns of AHD and PCD in this sample (Figures 4g and 5g). By contrast, the MTJR sediment displayed low proportion of 2,3-ring PAHs (Table 4); its AHD and PCD patterns were indicative of predominant pyrogenically produced PAHs, showing little or no effect from the TJR runoff.

The relative abundance of four to six-ring PAHs in SDB sediments ranged from 89 to 94% (Figure 3e and Table 4), similar to the result (~90% were four to six-ring PAHs) of McCain et al. (1992). This may indicate a consistent source, predominantly combustion-related, of PAH inputs into the study site. However, the AHD (Figure 4i) showed possible petrogenic PAH inputs, at least for low molecular weight PAHs. On the other hand, the PCD (Figure 5i) in the sample was similar to those in sediments contaminated with pyrogenic PAHs (Lake et al. 1979). Apparently, PAHs in this sediment may have derived from both petroleum and combustion sources. The microlayer particulate sample was clearly contaminated with PAHs of combustion origin, as indicated by the similar PCD patterns (Figure 5j) and reported by Lake et al. (1979) for sediments containing predominant combustion-derived PAHs. The AHD in this sample (Figure 4j) also pointed to a similar conclusion. The microlayer filtrate sample contained extremely low PAH concentrations and therefore neither AHD nor PCD was determined. The only PAHs detected in the filtrate sample were fluoranthene and pyrene, indicating a combustionrelated origin for PAHs.

A major source of PAH inputs into the SDB site may be a large storm runoff outfall draining the San Diego International Airport, engine exhausts from boats and ships, and accidental oil spills. Without detailed analyses of samples collected from these sources, it is impossible to quantify their individual contributions of PAHs from each of these sources. Since the proportion of 2,3-ring PAHs in the SDB sediment and microlayer samples were all less than 20% (Table 4), PAHs from combustion sources appeared to prevail. This might effectively disqualify oil spills from contributing significant amounts of PAHs. Automobile exhausts, probably similar to boat engine exhausts, were known to contain both petroleum residues and incomplete combustion products (Simoneit 1985, Takada *et al.* 1990).

It may be concluded from the above discussions that PAHs in the PLWTP effluent and TJR runoff were predominantly derived from petroleum-related sources. Sediments and water-column particulates near the PLWTP outfall received PAHs mostly from combustion sources, with minor inputs of low molecular weight PAHs from petrogenic sources, probably the PLWTP outfall and natural oil seepage. Despite heavy shipping activities in San Diego Bay, oil spills did not appear to be the significant source for the PAH contamination in the sediment and microlayer. Instead, combustion-related sources, e.g., engine exhausts and urban surface runoff, seemed to contribute significant amounts of PAHs to San Diego Bay.

To corroborate the above conclusions, we calculated ratios of MP/P, P/A, FL/PYR, and BZ[a]A/CHR in the same samples (Figure 6). These ratios have been used extensively to distinguish petrogenic and pyrogenic sources of PAHs (Colombo *et al.* 1989). In general, petroleum-contaminated samples contain higher MP/P, FL/PYR, and P/A and lower BZ[a]A/CHR than combustion contaminated samples (Colombo *et al.* 1989).

For MP/P, the highest ratios were found in the PLWTP effluent particulates and TJR runoff filtrates. In addition, the PLWTP effluent filtrates also showed a fairly high MP/P ratio. Nondetectable methylphenanthrene in MTJR microlayer particles and sediments yielded a zero MP/P ratio for these samples. SDB microlayer particulates also had a small MP/P ratio. Similarly, the highest value of P/A

ratio occurred in the PLWTP effluent particulates. Since anthracene was not detectable in the PLWTP effluent filtrates, TJR runoff filtrates, and MTJR microlayer particulates, a very high P/A ratio would be expected for these samples. The SDB microlayer particles and sediments had the smallest P/A ratios. For BZ[a]A/CHR, both benz[a]anthracene and chrysene were not detectable in the PLWTP effluent (both filtrates and particulates) and TJR runoff filtrates. Benz[a]anthracene was not found in the MTJR microlayer particulates. Since benz[a]anthracene and chrysene are normally abundant in samples contaminated with combustion-derived PAHs, the low levels of these compounds indicated a predominantly petroleum-related origin. As a comparison, the A-17 and MTJR sediments and A-17 sediment trap particulates displayed relatively large BZ[a]A/CHR ratios. The trend of the BZ[a]A/CHR ratios was consistent with those observed for MP/P and P/A. These results are generally in agreement with the conclusions drawn above based on the patterns of AHDs and PCDs.

By contrast, the FL/PYR ratio did not show any consistent trend among the samples examined. In particular, the PLWTP effluent particulate and TJR runoff filtrate samples had relatively low FL/PYR ratios, while the SDB microlayer particulate and sediment samples possessed high FL/PYR ratios. A s observed by Colombo *et al.* (1989), the range of the FL/PYR ratio did not vary much (0.5 to 0.9) for a variety of sediments.

It should be noted that the generally low levels of PAHs found in the sample media limit the applicability of compositional indices in the identification of PAH origins. Many other factors, such as solubility, extent of biodegradation,



etc., may also contribute to the alteration of PAH assemblages after they are released into the environment. In this sense, the above compositional analyses are qualitative at best. If possible, other molecular indices should be combined to enhance the confidence of source identification. For instance, n-alkanes have also been found useful for source identification (Colombo *et al.* 1989).

C/N ratios also have been used to determine the sources of organic matter. Typically, high C/N ratios indicate terrestrial origins, while marine *in situ* processes generate organic materials with low C/N values. PLWTP effluent and TJR runoff particulates had C/N ratios around 5 (Table 3). In addition, sediment trap particulates at A-17 and R-61 also had a narrow range of C/N ratios around 10. By contrast, the range of C/N ratios was quite broad for microlayer particulates and sediments. For microlayer samples, this may underscore the dynamic nature of the sea surface microlayer, as also observed in the TSS data. For sediments, this may mean that the usefulness of the C/N ratio as a source indicator for organic matter inputs is limited.

Assessment of PAH Inputs from Point and Nonpoint Sources

There are two major point sources of PAHs in the study area: PLWTP sewage outfall and TJR. Nonpoint sources may include aerial fallout, inadvertent oil spills, and marine oil seepage. PAH inputs from PLWTP and TJR may be estimated from this study and relevant information in the literature. Contributions from nonpoint sources, however, are difficult to quantify; only a qualitative assessment can be made.

FIGURE 6. Ratios of methylphenanthrene/ phenanthrene (MP/P), phenanthrene/ anthracene (P/A), fluoranthene/pyrene (FL/ PYR), and benzo[a]anthracene/chrysene (BZ[a]A/CHR) in selected samples collected off San Diego, California. The sample number follows the same order as used in Figures 4 and 5.

^aConcentrations of methylphenanthrenes were below detection limits.

^bConcentrations of anthracene were below detection limits.

^cConcentrations of both fluoranthene and pyrene were below detection limits.

^dConcentrations of both benz[a]anthracene and chrysene were below detection limits.

^eConcentration of benz[a]anthracene was below detection limit.

From the PAH concentrations in the PLWTP effluent (Table 4) and the average effluent flow of 172 mgd (6.5×10^8 L) in 1994 (City of San Diego 1994), the average mass emission of total PAHs from the PLWTP outfall is estimated to be 395 kg in 1994. An estimate of the PAH mass emission from TJR is somewhat difficult, as the samples were collected during low flows and the total water discharge in 1994 is unavailable. If a long-term annual mean flow of 42.9×10^6 m³ from 1955 to 1988 (SCCWRP 1992) is used, the average mass emission of PAHs during 1994 was roughly 2.2 kg. This estimate may still be in the same order of magnitude even if data during storm events were applied, since PAH concentrations might be slightly lower during storms as in the case of oil and grease measured in Los Angeles River runoff (SCCWRP 1973).

Eganhouse and Gossett (1991) estimated the mass emission of a similar suite of total PAHs to be 110.5 metric tons (MT) for the Joint Water Pollution Control Plant (JWPCP) of the CSDLAC in 1979. If a mass emission ratio of 3.4:1 for aromatic hydrocarbons determined in the effluents of JWPCP and PLWTP in 1979 (Eganhouse and Kaplan 1982) was used to correct for PAHs, the PAH mass emission from PLWTP was approximately 32.5 mt in 1979. Thus, it appears that PAH emissions from the PLWTP outfall have been reduced by a large factor over the last 15 years, probably attributable to dramatic source reduction from petrochemical inputs and improved treatment processes. For comparison, our results suggest that the PAH contribution from TJR appeared to be insignificant.

Since the microlayer reflects recent inputs of contaminants, the microlayer data may be useful in identifying the in-situ sources of contaminants. The percentages of fluoranthene + pyrene relative to total PAHs were 100% and 67% in the A-17 and R-61 microlayer, respectively; these were much higher than those found in the PLWTP effluent (Table 4). Since fluoranthene and pyrene are generally considered as combustion-related PAHs (Hites et al. 1980, Prahl et al. 1984), the dominance of fluoranthene + pyrene in the A-17 and R-61 microlayer suggests that aerial fallout might have a greater impact on the sea surface microlayer than the inputs from the PLWTP outfall, even though A-17 is close to the outfall. However, without the knowledge of atmospheric PAH deposition rates in the area, the relative importance of the contributions from the PLWTP outfall and aerial deposition cannot be quantified.

By contrast, the PAH compositions were similar in MTJR microlayer and TJR runoff (both contained relatively high portions of 2,3-ring PAHs), underscoring the impact of TJR. The higher PAH concentration (2,830 ng/g) in MTJR microlayer particulates, compared to those in TJR runoff (158 and 104 ng/g) (Table 4), confirmed a significant enrichment of PAHs in the sea microlayer (Hardy *et al.* 1990, Kucklick and Bidleman 1994). It seems that PAHs remaining in the area after being discharged are possibly localized mostly in the sea surface microlayer. This speculation is consistent with the extremely low PAH concentrations in the sediment at the same sampling location (Table 4) and enhanced TOC content in the microlayer particulates (Table 3).

Baker *et al.* (1995) estimated that 3% of sewage particles rose to the surface in a laboratory experiment within 24 h, while 22% settled onto the bottom and 75% remained in suspension. If these results are applicable in the coastal marine environment, then the water column dynamics must be evaluated before a better understanding of the point and nonpoint inputs can be obtained.

The fluxes of particulates at A-17 (both 1-m and 5-m depths) were greater than those at R-61 (Table 5). In addition, the particulate fluxes at both A-17 and R-61 were greater in January 1994 than in June 1994. Fluxes of particulates, TOC, TN, and PAHs at the 5-m depth of A-17 were similar to those at the 5-m depth of R-61 measured in June 1994. As mentioned previously, discharge from the PLWTP sewage outfall extension began in November 1993, which increases the distance between the discharge site and station A-17. All these suggest that the PLWTP sewage outfall was an important source of particulates and organic matter in the surrounding water column. It should be noted that the particulates may also carry materials from nonpoint sources into the sediment traps (more discussions below), thus amplifying organic matter fluxes.

Water Column Dynamics

Sedimentation processes in the water column can be extremely complex. As noted previously by Eganhouse and Gossett (1991), petroleum-generated PAHs, enriched on the surfaces of sewage-derived particles, were more vulnerable to biodegradation and/or desorption in the water column during deposition. Therefore, sinking organic materials may undergo rapid degradation or desorption (especially for low molecular PAH compounds), leading to depleted TOC and PAH concentrations in sediments compared to water column particulates. On the other hand, resuspension of selective fractions of sediment particulates may magnify or compromise this effect.

From the results obtained in the present study, several observations can be summarized: (1) PAH compositions in the sediments and sediment trap particulates were similar, but substantially different from those of the PLWTP effluent (e.g., 0 to 17% of the PAHs were 2,3-ring PAHs in sediments and trap particulates, compared to 90 to 100% in

the PLWTP effluent); (2) A-17 sediment trap particulates contained higher TOC, TN, and PAH concentrations (dry weight) than the respective sediments, but the TOC normalized PAH concentrations were higher in sediments than in the sediment trap particulates; (3) R-61 sediment trap particulates contained higher TOC, TN, and PAH concentrations (both dry weight and TOC normalized) than the respective sediments; (4) there was a trend of increasing TOC and TN contents from 1-m trap to 5-m trap particulates for both A-17 and R-61; (5) PAH concentrations (both dry weight and TOC normalized) decreased from 1-m trap to 5-m trap at A-17, but they were similar in the 1-m and 5m traps at R-61. These observations may have reflected the water-column dynamics related to a number of processes, e.g., mixing and transport of organic matter from point and nonpoint sources, bottom sediment resuspension, and biochemical degradation.

Observation (1) implies that sources other than the PLWTP outfall contribute significantly to the PAH presence in the water column and sediment, or that degradation and/or desorption of PAHs may occur rapidly in the water column. The following information supports the first mechanism. The sediment PAH concentrations (dry weightbased) in A-17 sediments and trap particulates were about 20 to 150 times lower than those found in the PLWTP effluent particulates, while the TOC-normalized concentrations in these samples were comparable (Table 4). If PAHs in the water column or sediments were solely from the PLWTP effluent, degradation or desorption would yield lower TOC normalized concentrations of PAHs in the water column particulates and sediments, assuming TOC is the main component for partitioning of PAH in particles. On the other hand, the similar PAH compositions in A-17 and R-61 sediments and sediment trap particulates (Figure 2) may underscore the influence on the depth dependence of particle fluxes from sediment resuspension by near-bottom currents (Table 5) (Hendricks and Eganhouse 1992). Resuspension of sediment particulates occurs over a short vertical distance magnifying the flux of sinking particles near the bottom.

Observation (2) suggests that at station A-17, the sediment traps collected sinking sewage-derived, highdensity particulates. Organic materials settling with particulates from the upper water column may undergo rapid degradation, resulting in depleted TOC and TN concentrations in the sediments (Hendricks and Eganhouse 1992). The higher TOC normalized PAH concentrations in the sediments were mainly a result of much lower TOC contents in the sediments than in the sediment trap particulates. This might indicate that PAHs degraded much slower than sewage-derived organic carbon, due to the rapid deposition associated with the high-density particulates. Observation (3) probably pointed to a long-range transport mechanism that carried the sewage-derived organic matter to remote locations, such as R-61. Low-density sediment particulates highly enriched with PAHs (Prahl and Carpenter 1983, Saliot *et al.* 1985) (presumably also enriched with TOC and TN) may tend to stay in suspension and are transported by currents to adjacent areas. These particulates may eventually aggregate with each other or with highdensity particulates from other sources and finally sink to the sea floor. Since the sedimentation process is relatively slow for low-density particles, organic materials may experience biodegradation, fractionation, and transformation.

Observation (4) further supports the hypotheses of rapid degradation for organic materials during sedimentation or that the settling particles normally contain low contents of organic matter. Prahl and Carpenter (1983) suggested that combustion-derived PAHs did not preferentially stay in finer grained sediment particles of greater surface area; therefore, they were not easily subject to biodegradation or desorption from the particles. Hence, observation (5) might be due to a combination of slow degradation of sinking combustionderived PAHs and resuspension of low-density particles enriched with PAHs from the bottom sediments.

CONCLUSIONS

The magnitude of PAH contamination in the coastal marine environment off San Diego has declined significantly over the last decade or so, apparently attributable to improved waste treatment techniques and source control. For instance, the mass emission rate of PAHs from the PLWTP outfall in 1994 (~395 kg/yr), estimated from the present study, was approximately 1.2% of that in 1979. Sediment PAH contamination at a specific site in San Diego Bay also declined to one third of the level as measured almost a decade ago.

Partially due to the decline of PAH emission from the PLWTP outfall as noted above, PAHs found in the sea surface microlayer, sediments, and water column particulates near the PLWTP outfall were predominantly derived from nonpoint sources. The sea surface microlayer near the mouth of TJR appeared to accumulate enhanced amounts of PAHs, TOC, and TN, probably discharged from the river, although they were in extremely low abundance in the sediments at the same location. Surprisingly, PAHs detected in the microlayer and sediments in San Diego Bay were mainly derived from combustion sources rather than oil spills, despite the heavy shipping activities in the area.

Low-density particles enhanced with organic materials may tend to stay in suspension or continue to be resus-

pended from the sea floor. Sewage-derived organic materials settling along with high density particulates may undergo rapid degradation in the water column. These hypotheses could explain the trend of increasing TOC, TN, and PAH concentrations from bottom sediments to water column particulates. However, this needs to be corroborated by additional parameters. Sediment resuspension caused by near-bottom currents may result in similar PAH compositions in water column particulates and sediments. Settling of resuspended particulates may enhance the flux of particles, as well as the fluxes of organic materials, near the sea floor.

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