Petrogenic and Biogenic Sources of N-Alkanes off San Diego, California

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In a previous article (*Compositional Indices of Polycyclic Aromatic Hydrocarbon Sources off San Diego, California*, this annual report), we utilized the compositional patterns associated with polycyclic aromatic hydrocarbon (PAH) assemblages to identify and assess the sources of hydrocarbon inputs into the coastal marine environment off San Diego. Samples collected from a variety of media, including effluents from the Point Loma Wastewater Treatment Plant (PLWTP), Tijuana River (TJR) runoff, sea surface microlayer, sediment, and sediment trap materials were analyzed to obtain collective information. In this article, the compositional patterns and molecular indices of aliphatic hydrocarbons (AHs) determined in these samples were used to further identify the petrogenic and biogenic sources of hydrocarbons. Attempts were also made to estimate the relative contributions of hydrocarbons from various point sources (wastewater discharge, runoff, etc.), as well as to understand the dynamics of physical, geochemical and biochemical processes affecting the organic contaminants during their residence in the marine environment.

In the past, a great deal of attention has been focused on the distributions of PAHs, mainly due to the potential carcinogenic, mutagenic, and toxic effects to a large number of invertebrates, fishes, birds, and mammals from many of these compounds (Kennish 1992). Less emphasis has been placed on AHs, particularly n-alkanes, primarily because they are relatively less harmful to many living organisms as compared to other classes of petroleum hydrocarbons (Clark 1989). However, understanding the characteristics of AHs should provide supplemental information useful to identify the sources of petroleum hydrocarbons.

While PAHs are known to be derived mainly from direct discharges, urban runoff, combustion of fossil fuels, and forest fires (Neff 1979), they are not directly produced from biological sources at significant levels (Bird and Lynch 1974, Kennish 1992). On the other hand, AHs in the estuarine and marine environments were known to be derived from both biogenic and anthropogenic sources (Clark 1989). Significant amounts of AHs can be synthesized by many biochemical processes occurring in both terrestrial and marine organisms. These biosynthesized hydrocarbons can be released into the environment by the organisms through their metabolism or decomposition upon their death.

The composition of AHs found in the marine environment is often complex, due to a combination of inputs from various sources. To discern the sources, it is necessary to distinguish the anthropogenic hydrocarbons from those derived from the biogenic sources. Petroleum, in general, contains a rather complex suite of hydrocarbons with a wide range of boiling points (National Research Council 1985). By contrast, biogenic hydrocarbons generated by biosynthetic pathways usually exhibit relatively simple patterns (Kennish 1992). Some hydrocarbon indices thus were developed and employed by researchers in an effort to identify the possible origins of the contaminants. For instance, Clark and Blumer (1967) utilized the carbon preference index (CPI) and the concentration ratio of pristane/n-C_{17} (Pri/C_{17}) to identify the possible origins of paraffins in algae and sediments collected from the northeast coast of the United States. In a similar study, Gearing *et al.* (1976) differentiated various input sources for hydrocarbons in sediments obtained from the northeast Gulf of Mexico based upon several paraffin molecular markers, including the ratios of total odd-carbon alkanes/even-carbon alkanes (C_{odd}/C_{even}), C_{17}/Pri, n-C_{18}/phytane (C_{18}/Phy), and pristane/phytane (Pri/Phy). Recently, Colombo *et al.* (1989) applied seven AH indices, including the major hydrocarbon (MH), the low/high molecular weight hydrocarbons (LMW/HMW), n-C_{16} ratio (sum of all n-alkanes/n-C_{16}), CPI, C_{17}/Pri, and C_{18}/Phy, in conjunction with the molecular indicators derived from PAH constituents to identify the sources for the organic contaminants in the Rio de La Plata Estuary, Argentina. In another recent study, Serrazanetti *et al.* (1994) found that zooplankton samples collected in the Gulf of Trieste were partially contaminated with fossil hydrocarbons as indicated by CPI values close to 1. The satisfactory results from these studies in applying the AH compositional indices to differentiate biogenic and petrogenic inputs prompted us to utilize these molecular markers to identify the possible sources of pollutants in the Southern California Bight.

MATERIALS AND METHODS

Materials

Neat individual n-alkane standards, isoprenoid hydrocarbon standards (pristane and phytane), and internal standards (nitrobenzene-d_5 and chrysene-d_{12}) were obtained from Ultra Scientific, Inc. (North Kingstown, RI). Surrogate standards (n-$C_{12}D_{26}$, n-$C_{24}D_{50}$, and n-$C_{36}D_{74}$) were purchased from C/D/N Isotopes, Inc. (Quebec, Canada). Ultra resi-analyzed grade methylene chloride and hexane were obtained from J.T. Baker, Inc. (Phillipsburg, NJ). The standard solutions were all prepared in hexane.

Sample Collection and Extraction

Samples were collected in January and June 1994. Due to a contamination problem with the microlayer samples collected in January 1994, no measurements were made on these samples. Detailed information about the study site and abbreviations is given in *Compositional Indices of Polycyclic Aromatic Hydrocarbon Sources off San Diego, California* in this annual report.

Gas Chromatography/Flame Ionization Detection (GC/FID) Analysis and Quantitation

A Varian 3500 GC equipped with two flame ionization detectors and two fused silica capillary columns, J&W Scientific (Folsom, CA) DB-1 and DB-5 (60 m × 0.25 mm i.d., 0.25 µm film thickness), was employed for sample analyses. The DB-1 column was used for quantitation, since it provided better chromatographic separation than DB-5 (for confirmation) in this particular application. The column temperature was programmed from 70°C (4-min hold) to 290°C (41-min hold) at a rate of 7°C/min. Helium was used as the carrier gas with a flow rate of 2 mL/min at 70°C. The total flow rate of the make-up gas (helium + nitrogen) was 20 mL/min. The flow rates of combustion gas H_2 and air were 24 mL/min and 280 mL/min, respectively. Two µL of each sample was manually injected into a split/splitless injector with 1-min solvent split time. The injector was maintained at 280°C and the detectors at 300°C.

Identification of the AHs was made by injecting a mixture of the AH standards, including pristane, phytane, and n-alkanes ranging from C_{10} to C_{36}. The concentrations of AHs were measured using the internal calibration technique. The internal standards, nitrobenzene-d_5 and chrysene-d_{12}, were introduced into the calibration standards and the final extracts prior to injection. Five levels of concentration, namely, 0.1, 0.4, 2.0, 5.0, and 10.0 µg/mL for the C_{10}-C_{29} components were chosen to establish the calibration curves. For the C_{30}-C_{36}, the corresponding concentrations in the calibration solutions were four times higher than those of C_{10}-C_{29}.

The method performance was assessed by the recoveries of surrogate standards, n-$C_{12}D_{26}$, n- $C_{24}D_{50}$, and n-$C_{36}D_{74}$, spiked into the standard solutions or the samples at 2 µg/mL prior to extraction. The means ± 1 standard deviation for the recoveries of the surrogate standards in 31 samples were as follows: n-$C_{12}D_{26}$ (37.1 ± 34.6); n-$C_{24}D_{50}$ (94.8 ± 26.5); and n-$C_{36}D_{74}$ (61.4 ± 30.8). The concentrations of target compounds were not corrected for the recoveries of the surrogate standards.

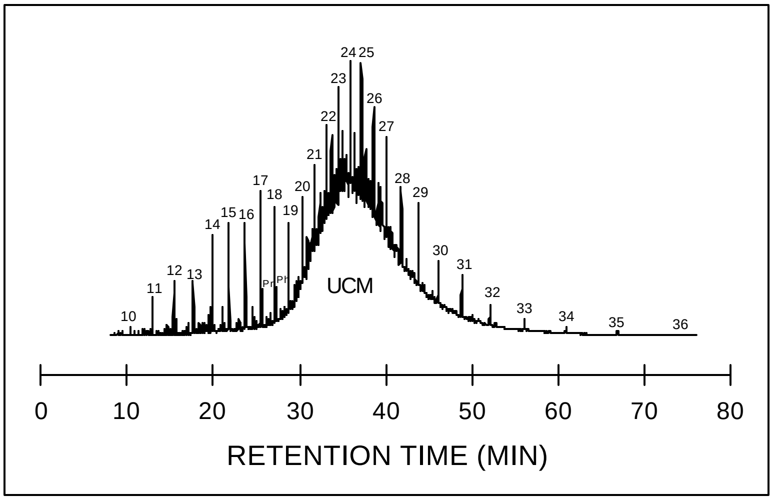

FIGURE 1. A typical gas chromatogram of the aliphatic hydrocarbon fraction in Point Loma Wastewater Treatment Plant effluent particulates collected in June 1994. The numbers close to the resolved peaks indicate the carbon numbers in n-alkanes. Pr = pristane; Ph = phytane; and UCM = unresolved complex mixture.

The method detection limits (MDLs) were determined using the procedure by Clesceri *et al.* (1989). Due to the difficulties of finding sediments with low levels of AHs, only the MDLs for aqueous samples were evaluated using distilled water. Quantitation of solid samples was also based on these MDLs. The detection limits, set slightly higher than the MDLs, were 50 ng/g or ng/L for C_{10}-C_{18}, pristane, and phytane, 100 ng/g or ng/L for C_{19}-C_{25}, and 400 ng/g or ng/L for C_{26}-C_{36} based on 1 g of solid or 1 L of aqueous sample.

RESULTS

PLWTP Wastewater Effluent

The chromatographic peaks of all the n-alkanes in the PLWTP effluent particulates are well resolved (Figure 1). While the AH assemblages were dominated by the n-alkane components, branched paraffins such as pristane and phytane were also detected. As previously mentioned, these isoprenoid hydrocarbons may be a diagnostic tool for identifying the possible sources of the organic contaminants. In addition, the presence of the unresolved complex mixture (UCM) in the sample suggests the presence of degraded petroleum products.

The concentrations of total AHs were higher in the particulates than in the filtrates (based on the aqueous sample volume) (Table 1). This may be attributed to the relatively low solubilities of AHs in the aqueous phase. Both particulate and filtrate samples were enriched with low molecular weight AH assemblages (Figures 2a and 2b). The total concentrations of AHs (in both particulates and filtrates) were 19.6 and 13.0 µg/L for the January and June effluents, respectively.

TJR Runoff

Similar to the PLWTP effluent samples, the TJR runoff particulate samples contained higher concentrations of alkane constituents than the filtrates and the total AH concentration was higher in the January samples (3.88 µg/L) than in the June samples (0.831 µg/L) (Table 1). The filtrates were relatively enriched with low molecular weight AHs (Figure 2c), while high molecular weight AHs were more abundant in the particulates (Figure 2d).

Microlayer

The microlayer samples, in general, contained fairly high AH concentrations, as compared to the PLWTP effluent and TJR runoff (Table 1). Among the four samples, the SDB sample had the highest AH content (1020 µg/g, dry weight) , followed by A-17 (553 µg/g, dry weight). The MTJR and R-61 samples contained almost equal amounts of AHs (211 µg/g and 195 µg/g, respectively). The AH compounds were highly concentrated in the particulate phase in all the microlayer samples. In addition, the ratio of AH concentrations between particulate and filtrate phases increased from the PLWTP effluent to TJR runoff and to microlayer.

The compositions of AHs in the microlayer samples (Figure 3) exhibited different patterns as compared to those found in the PLWTP effluent and TJR runoff (Figure 2). The microlayer particulates contained mostly AHs with C_{25} or longer alkyl chain; while the filtrate samples contained primarily low molecular weight AHs. In addition, these AH fractions are essentially dominated by the odd-carbon n-alkanes (Figure 3).

Sediments

The AH concentrations ranged from 0.1 to 1.3 µg/g in four sediment samples (Table 1), which was substantially lower than those found in PLWTP effluent, TJR runoff, and microlayer samples on a particle dry weight basis. Except for the SDB samples, all the other samples contained relatively low concentrations of short-chain AHs (n<25) (Figure 4). It is likely that the low-molecular weight AHs may eventually be removed by evaporation, dissolution, or biodegradation. In addition, the AH assemblages were dominated by the odd-numbered long-chain paraffins at n>25. While the AH compositional patterns at each sample did not reveal significant seasonal variation, the total concentrations were relatively higher in the January samples than in the June samples (Table 1; Figure 4).

The sediment samples collected from the reference station R-61 contained relatively low levels of AHs, as compared to those from the others. On the contrary, the SDB sediments had the highest total concentrations of AHs. This is likely a result of the relatively high level of waste disposal due to the maritime activities in the bay area in addition to a significant surface runoff contribution from the nearby San Diego Airport. Meanwhile, the MTJR sediments contained comparable concentrations of AHs to those in the R-61 sediments.

Sediment Trap Particulates

The sediment trap particulates collected from A-17 and R-61 contained much higher AH concentrations than those in the sediments (Table 1). The AH concentrations were quite different in the January and June samples at both the A-17 and R-61 5-m traps, apparently due to the high contents of pristane in the June samples (Figure 5).

The compositional patterns for AHs with C_{20} or longer chains (Figure 5) in the sediment trap samples are similar to those in the sediment counterparts (Figure 4). The high molecular weight components showed odd-numbered AH preference. All but the particulates at the A-17 1-m traps (January 1994) showed quite different distribution patterns of lower molecular weight AHs (C_{10}-C_{19}) from those in the sediments. All the sediment traps collected in June 1994 contained fairly high levels of pristane.

DISCUSSION

AH Compositional Indices

A total of eight compositional indices were determined in the samples analyzed in the present study (Table 1). The major hydrocarbon, MH, which is the alkane species with the highest concentration, is normally centered around C_{18} for specimens highly contaminated with petroleum (Clark and Finley 1973). Dominant hydrocarbons in benthic algae are generally either n-C_{15}, n-C_{17}, or n-C_{19} (Lytle *et al.* 1979). In terrestrial vascular plants, odd-carbon n-alkanes in the range of C_{27}-C_{31} are often the major aliphatic hydrocarbon components (Farrington and

Tripp 1977, Colombo *et al.* 1989). The MH found in the PLWTP effluents was C_{18} (Figures 2a and 2b, Table 1). This is in agreement with previous findings by Eganhouse and Kaplan (1982), who reported C_{14} and C_{16} as the major n-alkanes in the PLWTP effluents in 1979. As suggested by Eganhouse and Kaplan (1982), these results indicate a possible petrogenic origin for the hydrocarbons in the effluents. The TJR runoff samples, both filtrate and particulate, showed relatively high concentrations of C_{25}, C_{27}, C_{29}, and C_{31} (Figures 2c and 2d), implying that these hydrocarbon components may have originated biogenically from terrestrial plants. AH assemblages with the similar compositional pattern have been found in the external covers of stems, leaves, flowers, and fruits (Eglington and Hamilton 1967), which can easily be carried into the river. However, the filtrate samples appeared to have a second major component in the low molecular range (Figures 2c and 2d), which may indicate some degree of contamination by petroleum products. In most microlayer, sediment, and sediment trap particulate samples, the MHs were around C_{29} or C_{31} (Table 1). This may suggest that AHs from terrestrial high plants are the dominant hydrocarbon components in the coastal marine environment off San Diego.

LMW/HMW is the concentration ratio of the n-alkane fractions with molecular weights $\leq C_{20}$(LMW) and $\geq C_{21}$ (HMW). This ratio is usually near unity in petroleum products, or in plankton and benthic algae (Lytle *et al.* 1979, Colombo *et al.* 1989) and commonly has lower values in higher plants (Colombo *et al.* 1989). LMW/HMW ranged from 0.7 to 1.1 in the PLWTP effluent samples, further verifying a petrogenic source for hydrocarbons in the

TABLE 1. Concentrations and compositional indices[a] of aliphatic hydrocarbon (AH) compounds measured in samples collected off San Diego, California, in 1994.

	Total AHs (dry wt based)[b]		Total AHs (TOC based)[c]		MH		LMW/HMW		n-C_{16} Ratio		CPI		C_{17}/Pri	
Sample Type	1/94	6/94	1/94	6/94	1/94	6/94	1/94	6/94	1/94	6/94	1/94	6/94	1/94	6/94
PLWTP Effluent														
Filtrates	5.82	2.56	NA	NA	C_{18}	C_{25}	1.6	1.0	12	14	4.1	2.1	2.4	2.7
Particulates	247 (13.8)	377 (10.4)	717	1060	C_{18}	C_{17}	0.8	1.0	16	13	1.8	1.4	2.1	3.2
Tijuana River Runoff														
Filtrates	0.237	0.337	NA	NA	C_{34}	C_{15}	1.7	1.9	10	13	NA	NA	2.7	3.7
Particulates	41.4 (3.64)	32.9 (0.494)	406	404	C_{29}	C_{25}	0.21	0.22	64	65	3.7	2.8	1.2	0.99
Microlayer														
A-17 Filtrates	NA	0.054	NA	NA	NA	C_{29}	NA	0.69	NA	NA	NA	NA	NA	NA
A-17 Particulates	NA	553 (6.36)	NA	4290	NA	C_{29}	NA	0.065	NA	NA	NA	14	NA	3.6
R-61 Filtrates	NA	1.28	NA	NA	NA	C_{34}	NA	0.43	NA	31	NA	0	NA	0.99
R-61 Particulates	NA	195 (22.6)	NA	943	NA	C_{31}	NA	0.21	NA	77	NA	0	NA	0.99
MTJR Filtrates	NA	0.328	NA	NA	NA	C_{29}	NA	0.68	NA	24	NA	NA	NA	0.75
MTJR Particulates	NA	211 (5.91)	NA	2130	NA	C_{29}	NA	0.025	NA	490	NA	4.1	NA	0.55
SDB Filtrates	NA	0.206	NA	NA	NA	C_{29}	NA	0.42	NA	21	NA	NA	NA	NA
SDB Particulates	NA	1020 (21.4)	NA	11900	NA	C_{33}	NA	0.034	NA	250	NA	8.5	NA	0.84
Sediments														
A-17	0.928	0.666	172	130	C_{29}	C_{29}	0.083	0.084	120	150	3.8	4.2	1.1	0.78
R-61	0.391	0.179	46.5	32.4	C_{29}	C_{31}	0.086	0.014	91	NA	14	NA	1.2	0
MTJR	0.578	0.091	155	75.6	C_{29}	C_{29}	0.10	0.064	110	NA	8.5	NA	1.2	0.61
SDB	1.290	0.680	157	82.0	C_{31}	C_{31}	0.22	0.22	75	56	1.2	1.1	2.1	0.97
Sed. Trap Particulates														
A-17 (1 m)	3.01	**[d]	159	**	C_{29}	**	0.081	**	200	**	6.0	**	0.29	**
A-17 (5 m)	3.57	7.46	160	254	C_{29}	Pri	0.082	0.59	150	55	8.7	3.2	0.24	0.063
R-61 (1 m)	3.39	3.46	138	135	C_{29}	Pri	0.16	0.58	71	35	17	3.9	0.54	0.19
R-61 (5 m)	3.40	8.03	124	249	C_{29}	Pri	0.11	0.81	87	34	6.0	4.1	0.51	0.10

[a] See text for the definitions of the compositional indices.

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

[c] In µg/g TOC for solid samples; TOC was not measured for aqueous samples.

NA=not analyzed (see text).

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

PLWTP effluent. Although no firm conclusion can be drawn for the TJR runoff, the relatively low LMW/HMW values are consistent with the conclusion based on MHs, i.e., biogenic inputs derived from terrestrial plants are likely predominant sources. The lower LMW/HMW values in the January samples as compared to that of the June samples may be due to a larger amount of hydrocarbons from terrestrial plants carried into the river by the rainfalls in the winter. For the microlayer, sediment, and sediment trap samples, significantly low values of LMW/HMW found in January may have signaled a relatively high influx of decomposed organic matter derived from land plants in the previous fall. When the ocean begins to warm in the spring, the population of marine algae starts to increase (Serrazanetti *et al.* 1994). Since paraffins of either n-C_{15}, n-C_{17}, or n-C_{19} were found to be predominant in benthic algae (Clark and Blumer 1967, Youngblood *et al.* 1971), this mechanism perhaps accounted for the relatively higher values of LMW/HMW for the June samples as compared to those collected in January.

C_{18}/Phy		Pri/Phy	
1/94	6/94	1/94	6/94
4.5	4.0	1.1	2.8
2.6	4.0	0.68	3.8
3.1	1.2	0.52	1.2
1.1	0.54	0.26	0.92
NA	NA	NA	NA
NA	1.2	NA	2.1
NA	1.9	NA	2.1
NA	1.4	NA	1.4
NA	2.0	NA	2.2
NA	1.3	NA	2.5
NA	NA	NA	NA
NA	0.99	NA	2.2
1.6	0.95	1.2	2.2
0.89	NA	1.1	NA
1.3	NA	1.1	NA
0.55	0.39	1.4	1.2
1.4	**	2.9	**
1.5	1.8	4.7	200
2.3	1.5	7.7	83
1.6	2.0	12	180

Since n-C_{16} is rarely found in biolipids (Thompson and Eglinton 1978), the C_{16} ratio, defined as sum of all n-alkanes/n-C_{16}, is usually high (i.e., 50) for biogenic materials compared to relatively low values (i.e., 15) in petroleum contaminated samples (Colombo *et al.* 1989). The C_{16} ratios are around 15 in the PLWTP effluent, relatively higher in the TJR runoff, and substantially higher in all the other samples (Table 1).

Geochemical processes produce petroleum that includes many homologous series. Adjacent members of hydrocarbons in the same homologous series often appear in the petroleum mixtures at comparable concentrations (Kennish 1992). Consequently, the concentration ratios of n-alkanes with odd- and even-numbered carbons are usually around unity. Biogenic samples, on the other hand, may exhibit different trends. For instance, the n-C_{25}, n-C_{27}, n-C_{29}, and n-C_{31} components predominate over even carbon homologues for land plants and spores (Farrington and Tripp 1977) and n-alkanes with 15, 17, 19, and 21 carbons predominate the corresponding paraffins of even carbons for marine algae, zooplankton, and phytoplankton (Clark and Blumer 1967, Blumer *et al.* 1971, Farrington and Tripp 1977). The values of CPI, defined as $2(C_{27}+C_{29})/(C_{26}+2C_{28}+C_{30})$, are all close to unity in the PLWTP effluent samples (Table 1), indicating a predominant petrogenic origin for the organic matter. CPI values in other samples, in general, range from 3 to 14, confirming biogenic inputs from terrestrial plants.

The last three indices, C_{17}/Pri, C_{18}/Phy, and Pri/Phy are related to the presence of isoprenoids in AH mixtures. In petroleum contaminated samples, the concentrations of pristane and phytane are nearly equal (Gearing *et al.* 1976, Keizer *et al.* 1978). In addition, zooplankton can convert ingested phytol to pristane, which may be the principal source of pristane found in other aquatic organisms (Blumer *et al.* 1964, Clark and Blumer 1967, Wakeham and Carpenter 1976). Thus, high concentrations of pristane may be indicative of high levels of microbial degradation. The Pri/Phy ratios for the PLWTP effluent samples collected in January are near unity, but higher in the June samples (2.8 and 3.8). The C_{17}/Pri ratio, in the range of 2.1-3.7, as found in the PLWTP effluents in the current study, are comparable to 1.7-2.2 as previously reported (Eganhouse and Kaplan 1982b). Overall, the C_{17}/Pri and C_{18}/Phy ratios are relatively higher in the PLWTP effluent and TJR runoff samples than those in the microlayer, sediment, and sediment trap samples. As will be discussed later, n-alkanes (e.g., n-C_{17} and n-C_{18}) are more likely subject to biodegradation than isoprenoids. This conclusion is corroborated by the general trend of lower C_{17}/Pri and C_{18}/Phy values in the June sediment and sediment trap samples relative to the January samples, probably due to the relatively higher level of microbial activities during the warmer months.

All the samples analyzed in the present study contained an unresolved complex mixture (UCM) as shown in the chromatogram of the PLWTP effluent particulate sample collected in June 1994 (Figure 1). UCM, composed of cyclic and branched alkanes, is known to resist microbial degradation more effectively than n-alkanes and thus has a greater tendency to remain in the environment after n-alkanes have degraded (Lee 1976, Lytle *et al.* 1979).

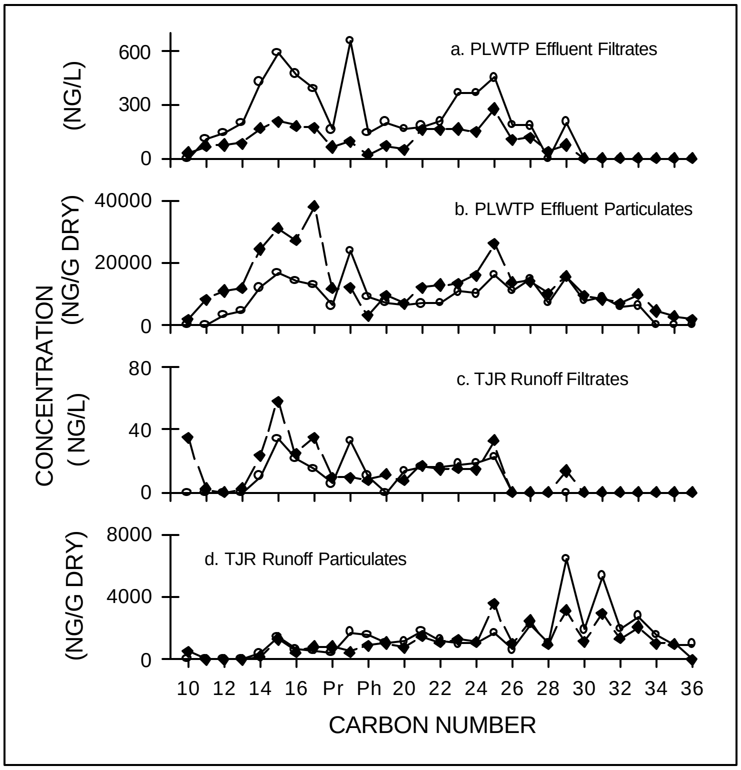

FIGURE 2. Compositional patterns of aliphatic hydrocarbon compounds in Point Loma Wastewater Treatment Plant effluent and Tijuana River runoff samples collected in January (O) and June (◆)1994. Concentrations are expressed in ng/g dry weight for particulate samples and in ng/L for filtrate samples. Pr = pristane and Ph = phytane.

Although UCM alone may not be sufficient in confirming the presence of petroleum products (Keizer *et al*. 1978), additional evidence such as the presence of pristane and phytane with relatively low values of C_{17}/Pri and C_{18}/Phy (<3) in most cases indicate at least partial petrogenic contamination is likely in the study area. Therefore, samples collected from TJR runoff, microlayer, sediments, and sediment traps may contain relatively low levels of petrogenic hydrocarbons, in addition to those derived from the biogenic sources as previously discussed.

AH Inputs from Various Point Sources to the San Diego Coastal Marine Environment

The PLWTP and TJR constitute two major point sources of organic pollutants introduced into the coastal marine environment off San Diego. From the average daily flow of 6.5×10^8 L (City of San Diego 1994) for the PLWTP effluent discharge and the long-term annual mean flow of 43×10^6 m^3 from 1955 to 1988 for the TJR runoff (SCCWRP 1992), the estimated annual mass emission inputs of AHs from PLWTP and TJR were 3,860 kg/yr and 101 kg/yr, respectively, in 1994. The annual mass emission of total AHs from the PLWTP outfall was approximately ten times higher than that of total PAHs estimated in *Compositional Indices of Polycyclic Aromatic Hydrocarbon Sources off San Diego, California* in this annual report. For the TJR, however, the ratio of annual mass emissions of AHs/PAHs was nearly 40. The substantial difference in the annual mass emission ratios of AHs/PAHs in these two point sources may be attributed to a relatively high level of biogenic contributions from terrestrial sources in the TJR runoff. This is supported by the predominance of the odd n-alkanes in the C_{25}-C_{33} range (Figure 2d). On the other hand, the organic contaminants in the PLWTP effluents were mainly originated from petrogenic sources.

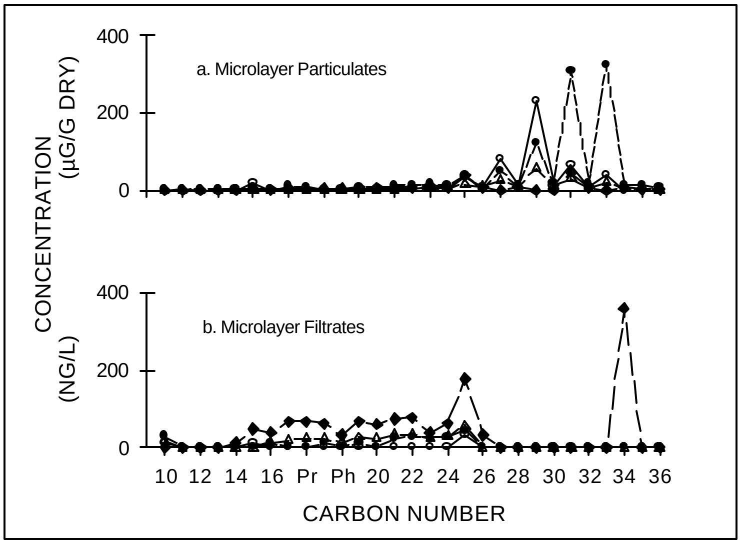

FIGURE 3. Compositional patterns of aliphatic hydrocarbon compounds in microlayer samples collected at stations A-17, R-61, MTJR, and SDB off San Diego, California, in June 1994. O: A-17; ◆: R-61; *D*: MTJR; ●: SDB. Concentrations are expressed in ng/g dry weight for particulate samples and in ng/L for filtrate samples. Pr = pristane and Ph = phytane.

The estimated mass emission of AHs from the PLWTP is much lower than those estimated for the effluents from other treatment plants. For instance, Barrick (1982) reported an annual mass emission of 30.6 mt/yr in 1978-79 for resolved AHs in the effluent from the Municipality of Metropolitan Seattle (METRO) sewage-treatment facility at Westpoint, Washington. The average daily flow volume

(458 million L) of effluent discharged by the METRO facility in 1978-79 was nearly three times as that reported by the PLWTP in 1994. However, the annual mass emission of AH inputs from the METRO plant to the Central Puget Sound was nearly eight times the corresponding input from the PLWTP to the Southern California Bight. Improving processing technologies, including advanced primary treatment, adopted at PLWTP apparently played an important role in removing most of the AH contaminants from the effluents. In another study, Eganhouse and Kaplan (1982) reported AH mass emission rates in the range of 1,100 to 4,500 mt/yr obtained in 1979 from various major municipal wastewater dischargers in Southern California. In particular, the AH mass emission of 1,110 mt/yr was estimated for the effluents discharged from PLWTP in 1979 (Eganhouse and Kaplan 1982). This level of mass emission is noticeably higher than the amount estimated in our current study, despite the lower total effluent flow in 1979 (484 million L/day) relative to 1994 (650 million L/day). This further confirms that improved sewage treatment and source control are lowering the inputs of organic contaminants into the Southern California marine ecosystem.

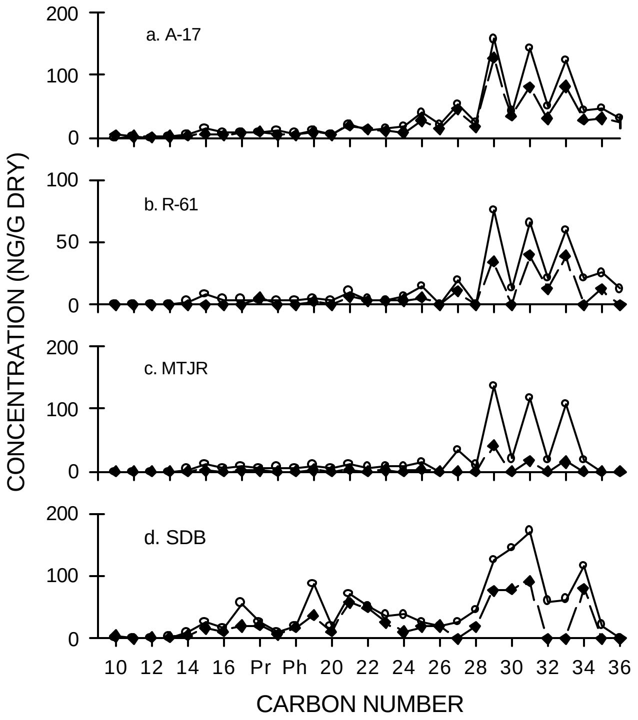

FIGURE 4. Compositional patterns of aliphatic hydrocarbons compounds in sediments collected at stations A-17, R-61, MTJR, and SDB off San Diego, California, in January (O) and June (◆)1994. Concentrations are expressed in ng/g dry weight. Pr = pristane and Ph = phytane.

The annual mass input of AHs for the TJR runoff was estimated to be 101 kg/yr in 1994. This figure was comparable to the total mass emission of 130 kg/yr reported by Mackenzie and Hunter (1979) for total petroleum hydrocarbons drained to the Delaware River during three storm events in 1975. These values are significantly lower than that (2,401 mt/yr) from the Los Angeles River as estimated by Eganhouse and Kaplan (1981). The estimation by Eganhouse and Kaplan (1981), however, was based on the results obtained during storm events in November 1978 that efficiently removed petroleum products on pavements.

Fate of Petrogenic and Biogenic Aliphatic Hydrocarbons

The results in the present study indicate that the molecular compositions of AHs in the coastal marine environment are significantly different from those of wastewater effluent and riverine runoff. In addition to several possible sources of inputs as previously discussed, these differences may also result from geophysical, geochemical, and biological processes that take place in the marine waters.

Upon entering the marine environment, AHs rapidly undergo various redistributions into four different areas: atmosphere, sea surface, upper water column, and bottom sediments (Kennish 1992). Depending on the corresponding partition coefficients, each constituent may exist in each medium at different concentrations. Hydrocarbons with low to medium molecular weights are more volatile and have a higher tendency to evaporate into the atmosphere. Significantly lower concentrations of C_{10} to C_{24} in the microlayer samples as compared to those in the PLWTP effluent and riverine runoff samples (Figures 2 and 3) may thus be partially attributed to evaporation. In fact, evaporation losses accounted for the largest initial change in composition of oil spilled at sea (Kennish 1992).

Despite their hydrophobic nature, a small fraction of petroleum pollutants still dissolves in the water column. Similar to the evaporation rate, the solubility is inversely related to the molecular weights of the AHs (Kennish 1992). In addition, the degree of dissolution of each AH component also depends on the environmental conditions such as sea turbulence, wind, wave action, temperature, etc. In any event, dissolution is the primary step that leads to degradation of AHs by either abiotic or biotic processes. It has been reported that microbial degradation by marine bacteria plays a key role in the destruction of petroleum hydrocarbons (Kennish 1992, and references therein). The relative rates of microbial degradation, in general, are in the order of n-alkanes > branched alkanes > cyclic alkanes >

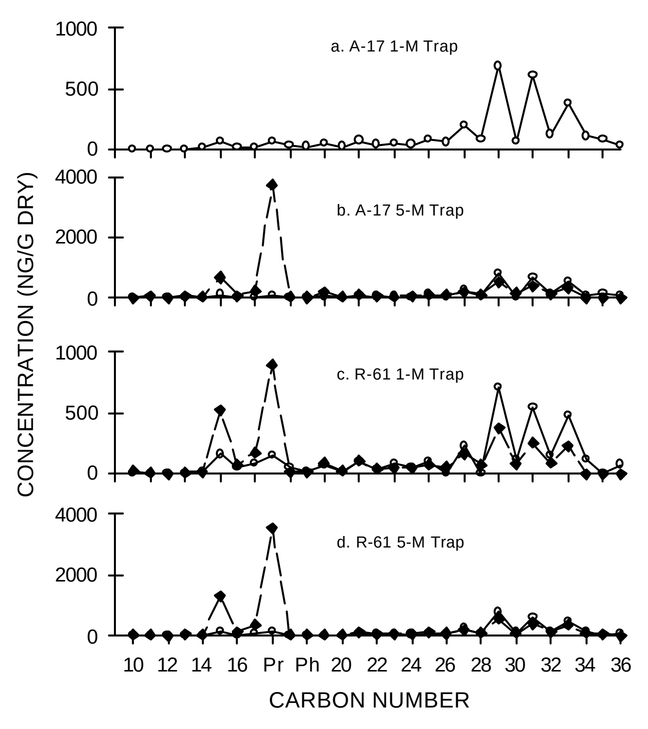

FIGURE 5. Compositional patterns of aliphatic hydrocarbons compounds in sediment trap particulates collected at stations A-17 and R-61 off San Diego, California, in January (○) and June (◆)1994. Concentrations are expressed in ng/g dry weight. Pr = pristane and Ph = phytane.

aromatics (Wakeham and Farrington 1980). However, hydrocarbons of relatively long chain lengths, due to their strong hydrophobicity, tend to adsorb to particulate materials such as clay, sand, organic material, etc. These suspended particulates may undergo several cycles of resuspension and redeposition before finally being incorporated into "permanent" sediments (SCCWRP 1986). Most of the samples collected by the sediment traps contained significantly lower concentrations of the low molecular weight n-alkanes (<C_{25}) (Figure 5), suggesting a significant loss of these hydrocarbons due to either evaporation, and/or degradation. This is further supported by the high concentrations of pristane in the samples collected at stations A-17 (5 m) and R-61 (1 and 5 m). The presence of relatively high concentrations of pristane as compared to phytane has often been taken as an indication for biological input resulting from degradation of ingested phytol by zooplankton as previously noted (Blumer *et al.* 1964). At both A-17 and R-61, the concentrations of total AHs in January 1994 were comparable at different depths (1 and 5 m). In June, however, the concentration of total AHs was significantly higher at 5 m than that at 1 m at R-61 (the 1-m traps at A-17 were lost in June). Interestingly, the concentration of total AHs at 1-m traps of R-61 was comparable to those at 1-m and 5-m traps of both A-17 and R-61 in January. Since aquatic organisms were more active during the warmer months (Serrazanetti *et al.* 1994), the seasonal variation in the total AHs may be attributed to the change in the hydrocarbon contributions derived from microbial production. For PAHs, on the other hand, their total concentration at A-17 decreased as the distance from the sea floor increased from 1 to 5 m (*Compositional Indices of Polycyclic Aromatic Hydrocarbon Sources off San Diego, California* in this annual report). This reverse trend may be a result of different bioconversion processes taking place in different marine organisms in addition to other effects induced by many abiotic factors. As discussed in the preceding article, PAHs in the study area were mainly derived from sewage and industrial effluents, combustion of fossil fuel, petroleum spills, etc. The change in the PAH concentrations within the aquatic environment was thus more likely due to their biological degradation or current circulation rather than due to additional biogenic input from marine organisms.

Acting as the ultimate repositories, sediments incorporate organic materials whose molecular compositions have been modified by various processes. During their residence in the sediments, organic contaminants continue to undergo further alterations. Benthic organisms can effectively alter the compositions of the organic contaminants via their active mixing of the deposited contaminants with the above resuspended particles and their ingestion and metabolism of hydrocarbons (Wakeham and Farrington 1980, and references therein). In addition, many animals and microorganisms living in the sediments also produce biogenic AHs that are eventually accumulated in the sediments (Clark and Blumer 1967). The overall concentrations of AHs in the sediments were much lower than those found in the sediment trap particulates (Table 1), possibly reflecting the importance of degradation and/or resuspension of components derived from biological activities.

CONCLUSIONS

The results obtained from the measurements of AHs in the PLWTP effluent, TJR runoff, and microlayer, sediment traps, and sediments at various locations in the coastal marine environment off San Diego suggest that these contaminants were largely derived from both biogenic and anthropogenic petroleum sources. Several mechanisms, including diffusion, solubilization, evaporation, and microbial degradation are believed to be responsible for the difference in the concentrations and compositions of AHs in different sample media. The relative importance of each mechanism, however, can not be readily discerned from the available data. Nevertheless, it is evident that petroleum-derived contaminants still persist in the coastal environment. In addition to the contributions by the effluent and surface runoff, hydrocarbon contaminants may also be airborne from terrestrial sources to the coastal waters. Thus, similar studies focusing on nonpoint source inputs in the area should be conducted before any attempt can be made to elucidate the relative importance of each pathway by which organic pollutants are introduced to this coastal environment.

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ACKNOWLEDGMENTS

The authors would like to thank Harold Stubbs, Dario Diehl, Andrew Jirik, and Larry Cooper of SCCWRP and Tim Rothans, Jack Russell, Richard Mange, and Mike Kelly of City of San Diego Metropolitan Wastewater Department (CSDMWWD) for sample collection; CSDMWWD for the use of R/V *Monitor III*; M. Indira Venkatesan (University of California, Los Angeles, CA) and Dave Young (United States Environmental Protection Agency, Newport, OR) for critically reviewing the manuscript, and Cherrie Vista and Azra Khan of SCCWRP for technical assistance.