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ORGANIC POLLUTANTS IN THE COASTAL ENVIRONMENT OFF SAN DIEGO, CALIFORNIA. 2. PETROGENIC AND BIOGENIC SOURCES OF ALIPHATIC HYDROCARBONS

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Abstract—The results from the measurements of aliphatic hydrocarbons suggest that hydrocarbons in the Point Loma Wastewater Treatment Plant (PLWTP) effluents are mainly petroleum derived; those in the Tijuana River runoff have largely originated from terrestrial plants with visible petroleum contamination; and those in the sea surface microlayer, sediment traps, and sediments at various coastal locations off San Diego have mostly resulted from biogenic contributions with enhanced microbial products in the summer season. Rainfall in the winter season appeared to amplify the inputs from terrestrial higher plants to the coastal areas. The PLWTP discharged approximately 3.85 metric tons of n-alkanes (C_{10}–C_{35}) in 1994, well below the level (136 metric tons) estimated in 1979. The input of aliphatic hydrocarbons from the Tijuana River was about 0.101 metric tons in 1994. Diffusion, solubilization, evaporation, and microbial degradation seemed partially responsible for the difference in the concentrations and compositions of aliphatic hydrocarbons in different sample media, although the relative importance of each mechanism cannot be readily discerned from the available data. The results from analyses of aliphatic hydrocarbon compositional indices are generally consistent with those of polycyclic aromatic hydrocarbons.

Keywords—Aliphatic hydrocarbons   Petrogenic   Biogenic   Coastal marine environment   Compositional indices

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are known to be derived mainly from direct discharges, urban runoff, combustion of fossil fuels, and forest fires [1], but are not directly produced from biological sources at significant levels [2,3]. On the other hand, aliphatic hydrocarbons (AHs) in estuarine and marine environments may be derived from both biogenic and anthropogenic sources [4]. 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 metabolic activities or decomposition upon their death.

In the past, research efforts have been focused on the distributions of PAHs, mainly due to their potential adverse effects to a large number of invertebrates, fishes, birds, and mammals [2]. Less emphasis has been placed on AHs, primarily because they are relatively less harmful to living organisms [4]. However, understanding the characteristics of AHs should provide supplemental information useful for identifying the sources of hydrocarbons.

The composition of AHs found in the marine environment is often complex. Petroleum, in general, contains a complex suite of hydrocarbons with a wide range of boiling points [5]. By contrast, biogenic hydrocarbons generated by biosynthetic pathways usually exhibit relatively simple patterns [2]. Some hydrocarbon indices were thus developed and employed by several researchers in an effort to identify the possible sources of the contaminants [6–9].

In a previous article [10], we utilized the compositional patterns associated with PAH mixtures to identify and assess the sources of hydrocarbons found in the coastal marine environment off San Diego. In this article, the compositional patterns and molecular indices of AHs in these samples were used to further identify the petrogenic and biogenic sources of hydrocarbons. We also estimated the contributions of hydrocarbons from the Point Loma Wastewater Treatment Plant (PLWTP) and the Tijuana River, and assessed the dynamics of physical, geochemical, and biochemical processes affecting the organic contaminants during their residence in the marine environment.

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 (North Kingstown, RI, USA). 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 (Pointe Claire, PQ, Canada). Ultra-resi-analyzed-grade methylene chloride and hexane were obtained from J.T. Baker (Phillipsburg, NJ, USA).

Sample collection and extraction

Because the procedures for sample collection and extraction are detailed elsewhere [10], only a brief description is given here. Four stations around the San Diego coast were chosen. Sea surface microlayer, water column particulates, and sediments were sampled at A-17 (32°40.28′N, 117°17.03′W; water depth ∼60 m) near the PLWTP outfall and a reference station R-61 (32°49.64′N, 117°19.67′W; water depth ∼60 m) about 20 miles northwest from A-17. Microlayer and sediments were

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sampled at a station (32°43.53′N, 117°10.86′W; water depth ~7 m) in San Diego Bay (designated as SDB thereafter) near the East Harbor Island and a station (32°32.94′N, 117°08.81′W; water depth ~16 m) near the mouth of the Tijuana River (MTR). In addition, 24-h composite effluent was collected from PLWTP and runoff samples were taken from the Tijuana River at Dairy Mart Road, about 6 km above the ocean. Sampling was conducted in January and June 1994. All the samples were cooled with ice during transportation to the laboratory. Solid samples were frozen at −20°C and aqueous samples were refrigerated at 4°C prior to sample extraction.

Solid samples (sediments, sediment trap particulates, and filters loaded with particulates from aqueous samples) were extracted three times (16, 6, and 16 h) with methylene chloride using a roller table. The combined extract was cleaned, fractionated, and concentrated to 0.5 ml. Filtrates from aqueous samples were extracted three times with methylene chloride using the conventional neutral liquid–liquid extraction method. The extract was treated in the same manner as for the solid samples.

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 DB-1 and DB-5 (Folsom, CA, USA) (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, because it provided better chromatographic separation than did 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 microliters 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.

Quantitation was based on the internal standard method. 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 mean ± 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; n-$C_{36}D_{74}$, 61.4 ± 30.8. The concentrations of target compounds were not corrected for the recoveries of the surrogate standards.

The detection limits were 50 ng/g or ng/L for C_{10} to C_{18}, pristane, and phytane, 100 ng/g or ng/L for C_{19} to C_{25}, and 400 ng/g or ng/L for C_{26} to C_{36} based on 1 g of solid or 1 L of aqueous sample. These limits were set slightly higher than the method detection limits determined using the procedure given elsewhere [11], so that they were always achievable under our experimental conditions.

AH compositional indices

A total of seven compositional indices was employed in the present study to identify the sources of hydrocarbon inputs. 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 [12]. Hydrocarbons in benthic algae are generally predominated with either

n-C_{15}, n-C_{17}, or n-C_{19} [13]. In terrestrial vascular plants, odd-carbon n-alkanes in the range of C_{27} to C_{31} are often the major components [8,14].

The low-to-high molecular weight hydrocarbon ratio (LMW/HMW) is the concentration ratio of the n-alkane fractions with molecular weights $\leq C_{20}$ and $\geq C_{21}$. This ratio is usually near unity in petroleum products or in plankton and benthic algae [8,13] and commonly has lower values in higher plants [8]. The C_{16} ratio, defined as sum of all n-alkanes divided by n-C_{16}, is usually high (i.e., 50) for biogenic materials compared to relatively low values (i.e., 15) in petroleum-contaminated samples [8], because n-C_{16} is rarely found in biolipids [15].

Adjacent members of hydrocarbons in the same homologous series often appear at comparable concentrations in petroleum mixtures [2]. Consequently, the concentration ratios of petrogenic n-alkanes with odd- and even-numbered carbons are around unity. Biogenic samples, on the other hand, may exhibit different trends. Therefore, the value of carbon preference index (CPI), defined as $2(C_{27} + C_{29})/(C_{26} + 2C_{28} + C_{30})$, can be used to discern petrogenic and biogenic sources.

The last three indices, C_{17}/pristane (C_{17}/Pri), C_{18}/phytane (C_{18}/Phy), and pristane/phytane (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 [7,16]. In addition, zooplankton can convert ingested phytol to pristane, which may be the principal source of pristane found in other aquatic organisms [6,17,18]. Thus, high concentrations of pristane may be indicative of a high level of microbial degradation.

RESULTS

The measured concentrations of AHs and compositional indices are summarized in Table 1. The spatial and temporal distributions and compositions of AHs are described below.

PLWTP effluent

The chromatographic peaks of AHs in the PLWTP effluent particulates are well resolved (Fig. 1). Although the AH assemblages were dominated by the n-alkane components, branched paraffins such as pristane and phytane were also detected. In addition, the presence of an unresolved complex mixture in the sample was apparent. The total concentrations of AHs (in both particulates and filtrates) were 19.6 and 13.0 μg/L in the January and June effluents, respectively. Both particulate and filtrate samples were enriched with low molecular weight AH assemblages (Fig. 2a and b).

Tijuana River runoff

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 enriched with low molecular weight AHs (Fig. 2c) and the particulates had abundant high molecular weight AHs (Fig. 2d).

Microlayer

As previously noted, due to a contamination problem with the microlayer samples collected in January 1994 [10], no measurements were made on the January samples. The AH compounds were highly concentrated in particulates in all the microlayer samples. Among the four samples, the SDB sample had the highest AH concentration (1,020 μg/g), followed by A-17 (553 μg/g). The MTR and R-61 samples contained al-

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

Sample type	Total AHs (dry wt. based)[b]		Total AHs (TOC based)[c]		MH		LMW/HMW		n-C_{16} Ratio		CPI		C_{17}/Pri		C_{18}/Phy		Pri/Phy	
	January 1994	June 1994	January 1994	June 1994	January 1994	June 1994	January 1994	June 1994	January 1994	June 1994	January 1994	June 1994	January 1994	June 1994	January 1994	June 1994	January 1994	June 1994
PLWTP effluent																		
Filtrates	5.82	2.56	—[d]	—	C_{18}	C_{25}	1.6	0.96	12	14	4.1	2.1	2.4	2.7	4.5	4.0	1.1	2.8
Particulates	247	377	717	1,060	C_{18}	C_{17}	0.79	1.0	16	13	1.8	1.4	2.1	3.2	2.6	4.0	0.68	3.8
	(13.8)[e]	(10.4)																
Tijuana River runoff																		
Filtrates	0.237	0.337	—	—	C_{34}	C_{15}	1.7	1.9	10	13	—	—	2.7	3.7	3.1	1.2	0.52	1.2
Particulates	41.4	32.9	406	404	C_{29}	C_{25}	0.21	0.22	64	65	3.7	2.8	1.2	0.99	1.1	0.54	0.26	0.92
	(3.64)	(0.494)																
Microlayer																		
A-17 filtrates	—	0.054	—	—	—	C_{29}	—	0.69	—	—	—	—	—	—	—	—	—	—
A-17 particulates	—	553	—	4,290	—	C_{29}	—	0.065	—	—	—	14	—	3.6	—	1.2	—	2.1
		(6.36)																
R-61 filtrates	—	1.28	—	—	—	C_{34}	—	0.43	—	31	—	0	—	0.99	—	1.9	—	2.1
R-61 particulates	—	195	—	943	—	C_{31}	—	0.21	—	77	—	0	—	0.99	—	1.4	—	1.4
		(22.6)																
MTR filtrates	—	0.328	—	—	—	C_{29}	—	0.68	—	24	—	—	—	0.75	—	2.0	—	2.2
MTR particulates	—	211	—	2,130	—	C_{29}	—	0.025	—	490	—	4.1	—	0.55	—	1.3	—	2.5
		(5.91)																
SDB filtrates	—	0.206	—	—	—	C_{29}	—	0.42	—	21	—	—	—	—	—	—	—	—
SDB particulates	—	1,020	—	11,900	—	C_{33}	—	0.034	—	250	—	8.5	—	0.84	—	0.99	—	2.2
		(21.4)																
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	1.6	0.95	1.2	2.2
R-61	0.391	0.179	46.5	32.4	C_{29}	C_{31}	0.086	0.014	91	—	14	—	1.2	0	0.89	—	1.1	—
MTR	0.578	0.091	155	75.6	C_{29}	C_{29}	0.10	0.064	110	—	8.5	—	1.2	0.61	1.3	—	1.1	—
SDB	1.29	0.680	157	82.0	C_{31}	C_{31}	0.22	0.22	75	56	1.2	1.1	2.1	0.97	0.55	0.39	1.4	1.2
Sediment trap particulates																		
A-17 (1 m)	3.01	NR[f]	159	NR	C_{29}	NR	0.081	NR	200	NR	6.0	NR	0.29	NR	1.4	NR	2.9	NR
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	1.5	1.8	4.7	200
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	2.3	1.5	7.7	83
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	1.6	2.0	12	180

[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.
[c] In μg/g total organic carbon (TOC) for solid samples; TOC was not measured for aqueous samples.
[d] —, not analyzed (see text).
[e] The numbers in parentheses are concentrations based on the aqueous volumes, in μg/L.
[f] NR, not recovered. The A-17 1-m traps were not recovered in June 1994.
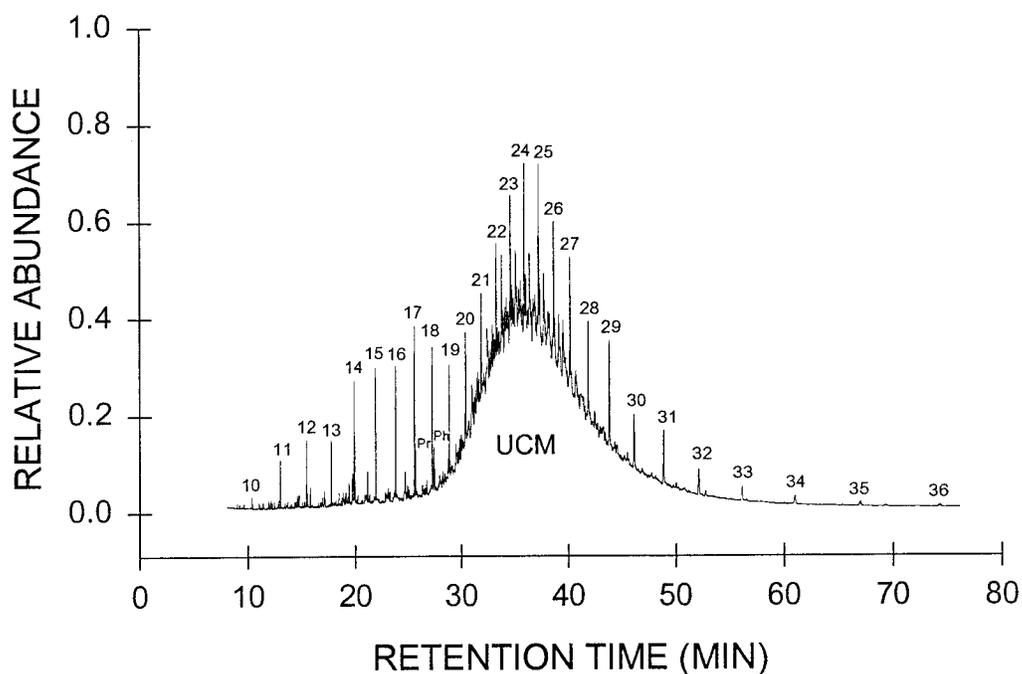
Fig. 1. A typical gas chromatogram of the aliphatic hydrocarbon fraction in Point Loma Wastewater Treatment Plant effluent particulates collected in June 1994. The numbers close to the resolved peaks indicate the carbon numbers in *n*-alkanes. Pr = pristane, Ph = phytane, UCM = unresolved complex mixture.

most equal amounts of AHs (211 μg/g and 195 μg/g for MTR and R-61, respectively).

The compositions of AHs in the microlayer samples (Fig. 3) exhibited different patterns as compared to those found in the PLWTP effluent and Tijuana River runoff (Fig. 2). All of the microlayer samples contained higher concentrations of

AHs with C_{25} or longer alkyl chains, although considerable amounts of low molecular weight AHs were also present in the filtrates.

Sediments

The AH concentrations ranged from 0.1 to 1.3 μg/g in four sediment samples, substantially lower than those found in PLWTP effluent, Tijuana River 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 ($n < 25$) (Fig. 4). In addition, the AH assemblages were dominated by the odd-numbered long-chain
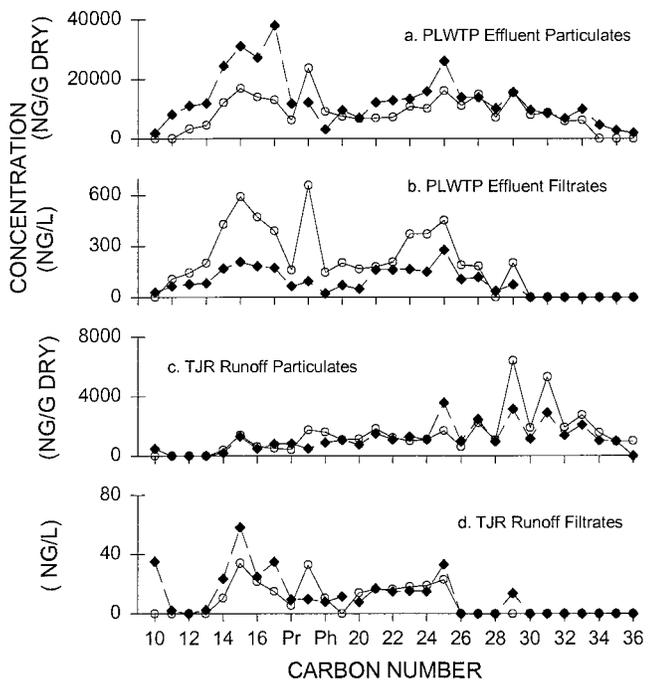

Fig. 2. Compositional patterns of aliphatic hydrocarbon compounds in Point Loma Wastewater Treatment Plant effluent and Tijuana River runoff samples collected in January (○) and June (♦) 1994. Concentrations are expressed in ng/g dry weight for particulate samples and in ng/L for filtrate samples. Pr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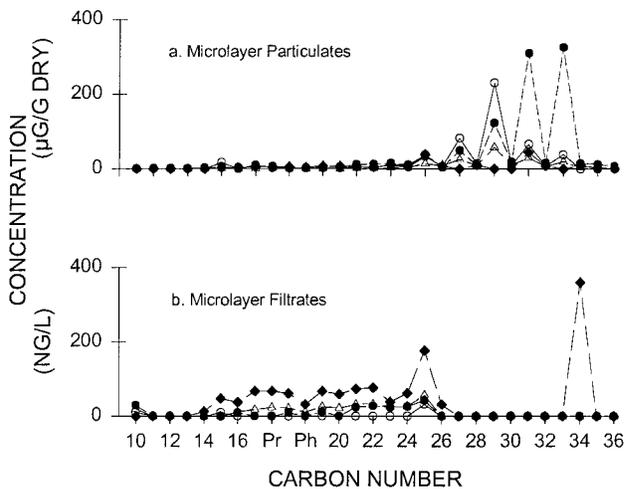

Fig. 3. Compositional patterns of aliphatic hydrocarbon compounds in microlayer samples collected at stations A-17, R-61, MTR, and SDB off San Diego, California, USA, in June 1994. ○: A-17; ♦: R-61; △: MTR; ●: SDB. Concentrations are expressed in ng/g dry weight for particulate samples and in ng/L for filtrate samples. Pr = pristane, Ph = phytane.
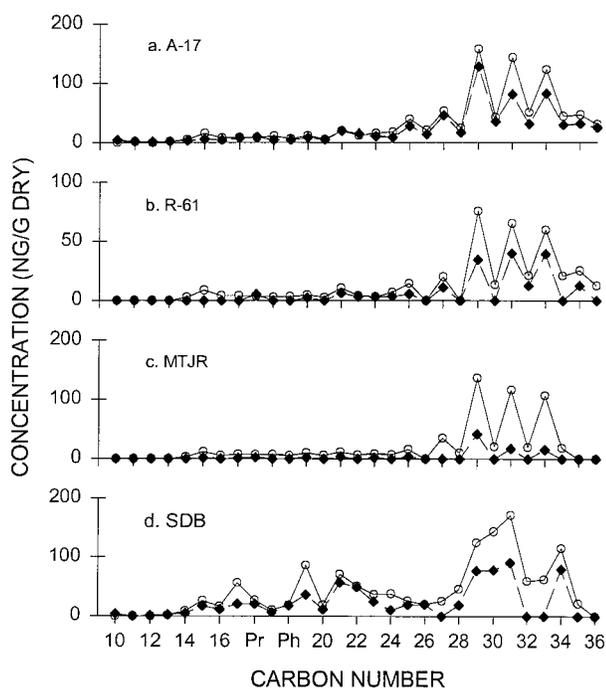
Fig. 4. Compositional patterns of aliphatic hydrocarbon compounds in sediments collected at stations A-17, R-61, MTR, and SDB off San Diego, California, USA, in January (○) and June (♦) 1994. Concentrations are expressed in ng/g dry weight. Pr = pristane, Ph = phytane.
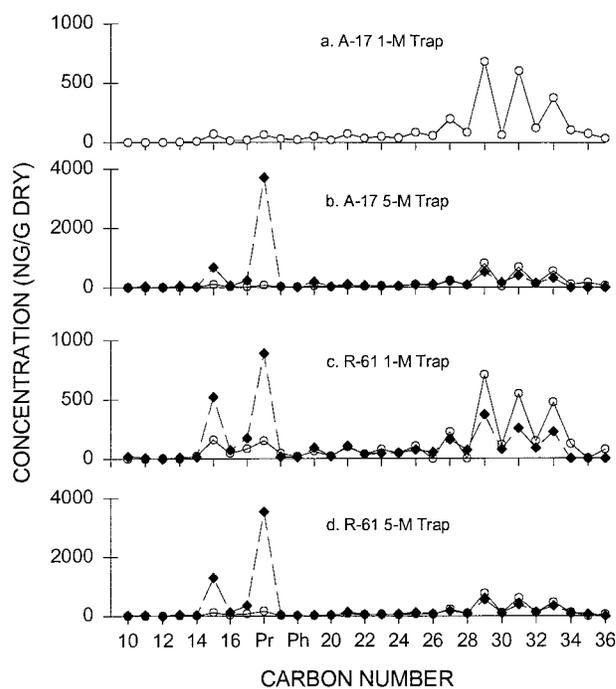

Fig. 5. Compositional patterns of aliphatic hydrocarbon compounds in sediment trap particulates collected at stations A-17 and R-61 off San Diego, California, USA, in January (○) and June (♦) 1994. Concentrations are expressed in ng/g dry weight. Pr = pristane, Ph = phytane.

paraffins at $n > 25$. Although 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 (Fig. 4).

Sediment trap particulates

The sediment trap particulates collected from A-17 and R-61 contained much higher AH concentrations than those found in the sediments. The AH concentrations were substantially 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 (Fig. 5). The compositional patterns for AHs with C_{20} or longer chains (Fig. 5) in the sediment trap samples are similar to those in the sediment counterparts (Fig. 4), which showed odd-numbered AH preference for the high molecular weight components.

DISCUSSION

Implications of the AH compositional indices

The MH found in the PLWTP effluents was C_{18} (Fig. 2a and b). This is in agreement with previous findings by Eganhouse and Kaplan [19] who reported C_{14} and C_{16} as the major *n*-alkanes in the PLWTP effluents in 1979. The LMW/HMW ranged from 0.8 to 1.6 in the PLWTP effluents. As shown in Table 1, the C_{16} ratios are around 15 in the PLWTP effluent, indicating a predominant petrogenic origin for the organic matter. The C_{17}/Pri ratios, in the range of 2.1 to 3.2, are comparable to 1.7 to 2.2, as previously reported [19]. Overall, the C_{17}/Pri and C_{18}/Phy values are relatively higher in the PLWTP effluents (and Tijuana River runoff samples) than those in the microlayer, sediment, and sediment trap samples. Finally, the Pri/Phy values are between 0.68 and 3.8. These results suggested

a possible petrogenic origin for hydrocarbons in the PLWTP effluents.

The Tijuana River runoff samples, both filtrate and particulate, showed relatively high concentrations of C_{25}, C_{27}, C_{29}, and C_{31} (Fig. 2c and d), implying that these hydrocarbon components may be biogenically originated from terrestrial plants. Aliphatic hydrocarbon assemblages with a similar compositional pattern have been found in the external covers of stems, leaves, flowers, and fruits [20], which can easily be carried into the river. However, the filtrate samples appeared to have a second major component in the low molecular range (Fig. 2c and d), which may indicate some degree of petroleum contamination. The relatively low LMW/HMW values are consistent with the conclusion based on MHs, that is, biogenic inputs derived from terrestrial plants are likely the predominant sources. The lower LMW/HMW values in the January samples as compared to those of the June samples may be due to a larger amount of hydrocarbons from terrestrial plants carried into the river by rainfall in the winter. The CPI values are generally higher in the Tijuana River runoff than in the PLWTP effluent. By contrast, C_{17}/Pri and C_{18}/Phy values are generally lower in the Tijuana River runoff than in the PLWTP effluent. The Pri/Phy ranges from 0.26 to 1.2, slightly lower than those found in the PLWTP effluents.

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 higher plants are the dominant hydrocarbon components in the coastal marine environment off San Diego. Notably, the MH was pristane in all the sediment trap particulates collected in June 1994; but the second highest component was C_{15} (Fig. 5). This is also consistent with the higher values of LMW/HMW in the June samples than in the January samples. Relatively high influxes of decomposed organic matter may be 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 [9]. This perhaps accounts for higher values of LMW/HMW for the June samples, because $n\text{-}C_{15}$, $n\text{-}C_{17}$, or $n\text{-}C_{19}$ were found to be predominant in benthic algae [6].

The C_{16} ratios are substantially higher in microlayer, sediment, and sediment trap particulate samples (from 21 to 490) than in the PLWTP effluents and Tijuana River runoff (from 12 to 65), suggesting a dominant biogenic source for the marine samples. The CPI values are also slightly higher in microlayer, sediment, and sediment trap particulate samples relative to the PLWTP effluents and Tijuana River runoff, except for the SDB sediments. The SDB sediments also showed higher LMW/HMW values compared to other sediment samples. This may indicate a certain level of petroleum contamination in San Diego Bay.

Both C_{17}/Pri and C_{18}/Phy values are relatively low in the microlayer, sediment, and sediment trap samples. As will be discussed later, n-alkanes (e.g., $n\text{-}C_{17}$ and $n\text{-}C_{18}$) are more likely subject to biodegradation than are isoprenoids. This 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 activity during the warmer months. The Pri/Phy values are all greater than 1 in these samples and higher than those in the PLWTP effluents and Tijuana River runoff, further indicating the effects of microbial degradation.

AH mass emissions from the PLWTP and Tijuana River

The PLWTP outfall and Tijuana River constitute two major point sources of organic pollutants discharged into the coastal region off San Diego. From the average daily effluent flow of 6.50×10^8 L in the PLWTP [21] and the long-term annual mean flow of 4.29×10^{10} L from 1955 to 1988 for the Tijuana River runoff [22], the estimated mass emissions of AHs from the PLWTP outfall and Tijuana River were 3.86 and 0.101 metric tons, respectively, in 1994.

The annual mass emission of AHs from the PLWTP outfall was approximately 10 times higher than that of total PAHs estimated in [10]. On the other hand, the ratio of annual mass emissions of AHs to PAHs from the Tijuana River was nearly 40. The substantial difference in these two ratios may be attributed to a relatively high level of terrestrial plant contributions to the Tijuana River. This is supported by the predominance of the odd n-alkanes in the C_{25} to C_{33} range in the Tijuana River runoff particulates (Fig. 2d).

Eganhouse and Kaplan [23] reported aliphatic hydrocarbon (different from the definition in the present study) mass emission rates in the range of 1,100 to 4,500 metric tons/year obtained in 1979 from four major municipal wastewater dischargers in Southern California. In particular, the n-alkane (C_{10}–C_{35}) concentrations in the unfiltered PLWTP wastewater effluents collected in January, April, July, and October 1979 were 781, 277, 305, and 1,710 µg/L, respectively [19]. From the total daily effluent flow of 4.84×10^6 L [23], the 1979 annual n-alkane mass emission for the PLWTP was approximately 136 metric tons. This figure is significantly higher than the 1994 annual mass emission of 3.85 metric tons as obtained for n-alkanes (C_{10}–C_{35}) in the current study. This confirms that better sewage treatment and source control are lowering the inputs of organic contaminants into the Southern California marine ecosystem.

The AH mass emission from the Tijuana River was comparable to that (0.130 metric tons) reported by MacKenzie and Hunter [24] for total petroleum hydrocarbons drained to the Delaware River during three storms in 1975. These values are much lower than that estimated by Eganhouse and Kaplan [25](2,401 metric tons) from the Los Angeles River in 1978.

Fate of petrogenic and biogenic AHs

The molecular compositions of AHs in the coastal marine environment are 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 redistribution into four compartments: atmosphere, sea surface, upper water column, and bottom sediments [2]. Depending on the partition coefficients, each constituent may exist in each medium at different concentrations. For instance, low concentrations of C_{10} to C_{24} in the marine samples as compared to those in the PLWTP effluent and riverine runoff samples (Figs. 2 to 5) may be partially attributed to evaporation.

Hydrocarbons with short alkyl chains (therefore low molecular weights) dissolve in the aqueous phase to a greater extent than those with longer alkyl chains. The later compounds tend to adsorb on suspended particles and eventually incorporate into the ''permanent'' sediments [26]. Because dissolution enhances the availability of chemicals to microorganisms, dissolved hydrocarbons are more readily subjected to biodegradation by marine bacteria [2]. The relative rates of microbial degradation generally are in the order of n-alkanes > branched alkanes > cyclic alkanes > aromatics [27], consistent with their solubility trend. As shown in Figure 5, most of the sediment trap samples contained fairly low concentrations of the low molecular weight n-alkanes ($<C_{25}$), suggesting a substantial loss of these hydrocarbons due to evaporation and/or preferential degradation. The degradation mechanism is further corroborated by the high concentrations of pristane in the samples collected in June (Fig. 5).

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 alteration. Benthic organisms can effectively alter the compositions of the organic contaminants via actively mixing the deposited contaminants with the above resuspended particles, and by ingestion and metabolism of hydrocarbons [27]. In addition, many animals and microorganisms living in the sediments also produce biogenic AHs that are eventually accumulated in the sediments [6]. As shown in Table 1, the overall concentrations of AHs in the sediments were much lower than those found in the sediment trap particulates, possibly reflecting the importance of degradation and/or resuspension of components derived from biological activities.

It should also be noted that in addition to the contributions by the effluent and surface runoff, hydrocarbons may also be airborne from terrestrial sources to the coastal waters. Thus, similar studies focusing on the non-point source inputs in the area should be conducted before attempting to elucidate the relative importance of each pathway by which organic pollutants are introduced to this coastal environment.

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