

## ORGANIC POLLUTANTS IN THE COASTAL MARINE ENVIRONMENT OFF SAN DIEGO, CALIFORNIA. 3. USING LINEAR ALKYL BENZENES TO TRACE SEWAGE-DERIVED ORGANIC MATERIALS

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**Abstract**—Linear alkylbenzenes (LABs) were detected in the Point Loma Wastewater Treatment Plant (PLWTP) effluent, Tijuana River runoff, microlayer, water column particulates, and sediments collected off the coast of San Diego in 1994. The distributions of LABs in various media and sampling locations suggested that these compounds were essentially derived from domestic waste discharges. The PLWTP outfall is a major source for LAB inputs, while the Tijuana River runoff discharges much lower amounts of LABs. However, the contents of sewage-derived organics can be enhanced in the sea surface microlayer near the mouth of the Tijuana River. In addition, the I/E ratios indicated that 30–55% of the LABs were degraded in the water column particulates and sediments. Other processes (e.g., dilution, evaporation, bioaccumulation, etc.) may also be important in removing LABs from the discharge zone. Sewage-derived organic materials can be carried into remote areas via suspension of fine particulates.

**Keywords**—Linear alkylbenzenes      Sewage tracer      Transport and fate      Coastal marine environment

### INTRODUCTION

Since the mid-1960s, linear alkylbenzene sulfonates (LASs) have been widely used as surfactants in manufacture of detergents [1]. The LASs are synthesized from benzene via a two-step process [2]: Friedel–Crafts alkylation of benzene with either chloroalkane or alkene with the total number of carbons ranging from 10 to 14 to produce linear alkylbenzenes (LABs), followed by sulfonation of LABs at the phenyl ring using either H<sub>2</sub>SO<sub>4</sub> or SO<sub>3</sub>. Rearrangements taking place in the alkylation step yield an isomeric mixture of LABs for each alkyl group. Due to incomplete sulfonation, small amounts (1–3%) of unreacted LABs are carried into detergents [3] and into the aquatic environment via discharges of treated sewage. The presence of LABs has been found in various environmental media, including municipal wastewater effluent [4], sediment-trap particulates [5], riverine and marine sediments [6–11], and marine species [12,13]. Although LABs do not pose severe adverse effects to many marine organisms [3], LABs are useful tracers of domestic waste inputs in the environment [4,14–16], due to their limited sources.

In the two previous articles [17,18], we examined the distributions and sources of polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons (AHs) in the coastal marine environment off San Diego. Although qualitatively, the compositional patterns of these hydrocarbon compounds were useful in differentiating several sources of contaminant inputs, such as petrochemical products, biogenic residues, and combustion-induced remains. In this article, we will present the results from LAB measurements in the same samples. The objectives are (1) to assess the spread of domestic wastes discharged from the outfall of the Point Loma Wastewater Treatment Plant (PLWTP) and (2) to gain insights into the

mechanisms for the transport and fate of sewage-derived organic materials.

The LABs were first found in the marine environment off southern California in the late 1970s [5]. These compounds were further detected in the effluents of the four largest municipal wastewater treatment plants in Southern California [4]. Analyses of sediments collected near the outfall of the County Sanitation Districts of Los Angeles County indicated the presence of LABs and tetrapropylene-based alkylbenzenes (TABs), raw materials for detergent production before LABs [4]. The concentration profiles of these two types of compounds in the sediment column were consistent with their historical inputs from the wastewater treatment plant and U.S. surfactant usage [4,8]. Although LABs have often been discovered in various compartments and locations, TABs have been detected only in buried sediments in the Southern California Bight. Therefore, LABs are good indicators of presently discharged domestic wastes in the southern California marine environment [15].

In this paper, LABs are often labeled as C<sub>i</sub>-LAB-n, where *i* denotes the number of carbons in the alkyl chain and *n* is the position number of the phenyl ring (e.g., 1 indicates the terminal position of the alkyl chain). The isomeric distribution of C<sub>12</sub>-LABs may provide valuable information regarding the degree of biodegradation of LABs [19]. Specifically, the ratio of the concentrations of internal and external isomers, designated as I/E, is defined as:

$$I/E = \frac{\sum (C_{12}\text{-LAB-6} + C_{12}\text{-LAB-5})}{\sum (C_{12}\text{-LAB-4} + C_{12}\text{-LAB-3} + C_{12}\text{-LAB-2})}$$

A high I/E value indicates a high degree of LAB biodegradation, due to the selective biodegradation of the external isomers relative to the internal isomers [19].

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## MATERIALS AND METHODS

### Materials

Individual LAB standards, including C<sub>10</sub>-LAB-1, C<sub>12</sub>-LAB-1, and C<sub>13</sub>-LAB-1, were purchased from Aldrich (St. Louis, MO, USA) and C<sub>14</sub>-LAB-1 from Pfaltz and Bauer (Westbury, CT, USA). A mixture of LABs used as calibration standard, whose composition was determined previously [20], was generously provided by Dr. Robert Bowen (Science Applications International Corporation, Narragansett, RI, USA). The surrogate standard (phenanthrene-d<sub>10</sub>) and two internal standards (2-fluorobiphenyl and *p*-terphenyl-d<sub>14</sub>) were obtained from Ultra Scientific, Inc. (North Kingstown, RI, USA). The reason and validation for using these standards for LAB measurements were given previously [20]. Ultraresi-analyzed grade hexane and methylene chloride were purchased from J.T. Baker Inc. (Phillipsburg, NJ, USA).

### Sample collection and extraction

A detailed description of the sampling locations, sample collection, and sample extraction is given by Zeng and Vista [17]. Briefly, 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 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 (TRM). In addition, 24-h composite effluent was collected from PLWTP and runoff samples were taken from the Tijuana River (TR) 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.

### Instrumental analysis

Individual LAB compounds were identified using a Hewlett-Packard 5890 series II gas chromatograph equipped with a 5970 mass selective detector. Chromatographic separation was provided by a 60 m × 0.25-mm i.d. (0.25-μm film thickness) DB-5 column (J&W Scientific, Folsom, CA, USA). The LABs were measured simultaneously with PAHs and the general chromatographic conditions were detailed elsewhere [17]. Specific experimental techniques applicable to the LAB measurements were described previously [20]. The molecular ion used for quantitation was *m/z* 105 for C<sub>*i*</sub>-LAB-2 (*i* = 10–14) and *m/z* 91 for the other LAB compounds. Because the LAB mixture contains only C<sub>11</sub>-LAB to C<sub>14</sub>-LAB components, quantitation of C<sub>10</sub>-LAB-*n* (*n* = 2–5) was done using the relative response factor of C<sub>11</sub>-LAB-6.

The quantitation limit was 40 ng/g for solid samples based on 1 g of dry sample and 50 ng/L for aqueous samples based on 1 L of sample volume. These values were slightly higher than the method detection limits determined using the procedure described elsewhere [21], so they were always achievable under any circumstances.

All the samples were spiked with the surrogate standard at 2 μg/ml in the samples prior to extraction. The internal standards were spiked into the final extracts before instrument analysis. The mean ± 1 standard deviation of the surrogate standard recoveries in 31 field samples was 77 ± 13%. No correction was made for the concentrations of LABs in the samples. The general characteristics of the LAB assemblages obtained in these samples (Table 1) are described below.

## RESULTS

### PLWTP wastewater effluent

As expected, the LAB contents in the PLWTP wastewater effluent samples were the highest among all the field samples and as high as 2,760 ng/L for the particulate sample collected in June 1994. The large difference between the particulate concentrations (34,200 ng/g in January and 100,000 ng/g in June) was discussed previously and attributed to different samples used for total suspended solid and organics measurements [17]. The volume-based concentrations were much closer in these two samples (1,920 and 2,760 ng/L, respectively). The average LAB concentration in the PLWTP effluent (both dissolved and particulate) was 3,010 ng/L in 1994.

The distributional patterns of individual LABs detected in the PLWTP effluents did not exhibit substantial temporal variation or variation between the filtrate and particulate fractions (Fig. 1a–d). They all showed predominant components in the range of C<sub>11</sub>–C<sub>13</sub>. In addition, the I/E ratios were all less than 1 (from 0.77 to 0.87).

### Tijuana River runoff

The TR runoff samples contained much lower LAB concentrations compared to the PLWTP effluent. In addition, the LAB concentrations in the runoff filtrates were all below the detection limits. The particulate LAB concentration based on the aqueous volume was an order of magnitude greater in the January (714 ng/L) compared to June (57.4 ng/L) sample. However, the dry-weight based were closer (8,110 ng/g in January and 3,830 ng/g in June), again reflecting the large variation in the concentrations of suspended solids. The I/E ratios (5.8 in January and 2.6 in June) calculated from the LAB compositions in the particulate samples (Fig. 1e and f) were higher than unity.

### Microlayer

None of the filtrate samples exhibited detectable levels of LABs. Only the microlayer particulates from MTR contained two LABs above the detection limits (Fig. 1g). The total LAB concentrations in this sample was 23.0 ng/L. The I/E ratio for this sample, however, could not be calculated due to the absence of several phenyl dodecanes (Fig. 1g).

### Sediments

All the sediments contained much lower LAB concentrations than those of the PLWTP effluent and TR runoff particulates on a particle dry weight basis. Samples collected at stations R-61 and MTR in both January and June 1994 contained no detectable LABs. Substantially low total LAB con-

Table 1. Linear alkylbenzene (LAB) concentrations in effluent, runoff, microlayer, sediment, and water-column particulate samples from the San Diego coast, California

Sample type	Total LABs					
	Dry wt based <sup>a</sup>		TOC based <sup>b</sup>		I/E ratio <sup>c</sup>	
	1/94	6/94	1/94	6/94	1/94	6/94
<b>PLWTP effluent</b>						
Filtrates	705	635	—	—	0.87	0.77
Particulates	34,200 (1,920)	100,000 (2,760)	99,600	281,000	0.85	0.78
<b>Tijuana River runoff</b>						
Filtrates	ND <sup>d</sup>	ND	—	—	N/A <sup>e</sup>	N/A
Particulates	8,110 (714)	3,830 (57.4)	79,600	46,900	5.8	2.6
<b>Microlayer</b>						
A-17 filtrates	NA <sup>f</sup>	ND	—	—	NA	N/A
A-17 particulates	NA	ND	NA	ND	NA	N/A
R-61 filtrates	NA	ND	—	—	NA	N/A
R-61 particulates	NA	ND	NA	ND	NA	N/A
MTR filtrates	NA	ND	—	—	NA	N/A
MTR particulates	NA	821 (23.0)	NA	8,290	NA	N/A
SDB filtrates	NA	ND	—	—	NA	N/A
SDB particulates	NA	ND	NA	ND	NA	N/A
<b>Sediments</b>						
A-17	35.3	39.2	6,540	7,640	1.6	2.3
R-61	ND	ND	ND	ND	N/A	N/A
MTR	ND	ND	ND	ND	N/A	N/A
SDB	1.61	ND	196	ND	N/A	N/A
<b>Sediment trap particulates</b>						
A-17 (1 m)	35.9	** <sup>g</sup>	1,900	**	4.2	**
A-17 (5 m)	24.8	10.9	1,110	371	4.4	N/A
R-61 (1 m)	ND	10.3	ND	403	N/A	N/A
R-61 (5 m)	5.1	60.4	187	1,880	N/A	2.3

<sup>a</sup> 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.

<sup>b</sup> In ng/g TOC for solid samples; TOC was not measured for aqueous samples.

<sup>c</sup> I/E ratio = ratio of internal and external isomers.

<sup>d</sup> ND, not detectable.

<sup>e</sup> N/A, not applicable because the LABs to calculate I/E were not detectable.

<sup>f</sup> NA, not analyzed; see text for reasons.

<sup>g</sup> A-17 1-m traps were not recovered in June 1994.

centration (1.61 ng/g dry weight) was detected in the SDB sediments collected in January. In contrast, the A-17 sediments contained the highest amounts of LABs (35.3 ng/g in January and 39.2 ng/g in June) as compared to those from other stations. The low LAB concentrations in the MTR sediments were consistent with the low PAH and AH concentrations in the same samples [17,18].

The LAB contents were too low in the R-61, MTR, and SDB sediments to calculate I/E ratios. The I/E ratios for the A-17 sediments collected in January and June, calculated from their LAB compositions (Fig. 2a and b), were 1.6 and 2.3, respectively.

#### *Sediment trap particulates*

The LAB concentrations in the A-17 sediment trap particulates were similar to those in the A-17 sediments. For comparison, the R-61 trap particulates contained detectable LABs, whereas the sediments contained none. In addition, the total LAB concentration collected in June from the R-61 sediment trap at 5 m was higher than those found in the A-17 sediment samples. The trap particulates collected in January from A-17 contained higher LAB concentrations than those collected in June. The coeluting C<sub>13</sub>-LAB-7 and C<sub>13</sub>-LAB-6 were the only detectable LABs in the sediment trap samples collected in June

at A-17 (5 m) and R-61 (1 m) and in January at R-61 (5 m). The total LAB concentrations in these three samples were 10.9, 10.3, and 5.1 ng/g.

The LAB compositions in three samples with the most abundant LABs are depicted in Figure 2c–e. Although the I/E ratio was not determinable for the LABs in the A-17 trap particulates collected in June, the corresponding ratios for the samples obtained in January at different depths were comparable (4.2 at 1 m and 4.4 at 5 m), indicating virtually no depth variation in the extent of biodegradation. The I/E ratio was 2.3 in the R-61 5-m sample, slightly lower than expected. However, the concentrations of individual LAB components detected were barely above the detection limits.

## DISCUSSION

### *Distribution and transport of LABs*

The results described above suggest two major point sources of LABs discharged into the study areas, i.e., the PLWTP outfall and TR. The concentrations of total LABs in the PLWTP effluent (2.6–3.4 µg/L; Table 1) were substantially lower than those obtained by Eganhouse et al. [4] for the CSDLAC effluent in 1979 (149 ± 69 µg/L). In the same study, only qualitative analyses of PLWTP effluent were reported [4].

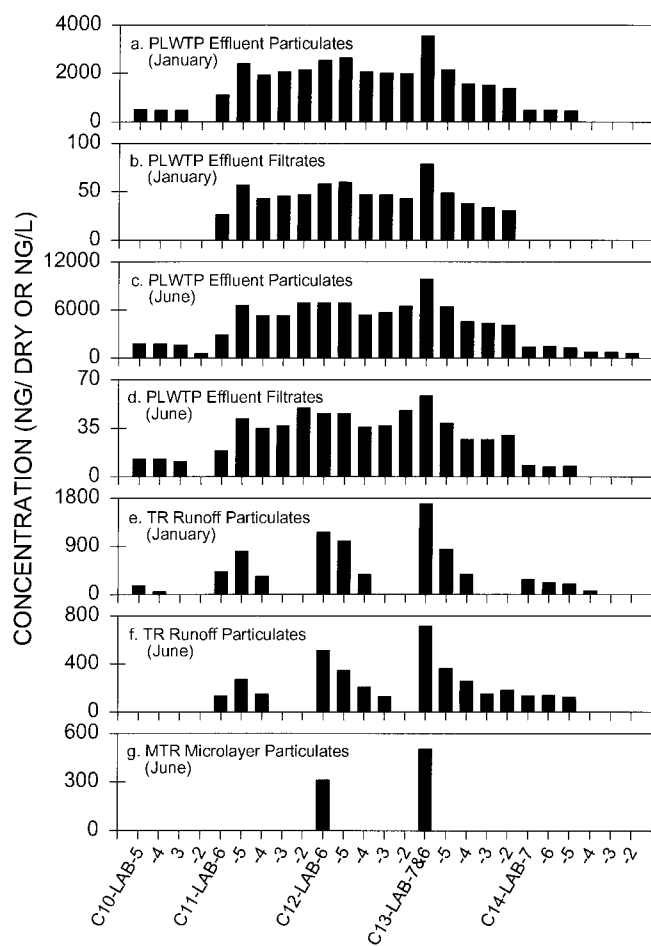


Fig. 1. Compositions of linear alkylbenzenes in the Point Loma Wastewater Treatment Plant (PLWTP) effluent, Tijuana River (TR) runoff, and mouth of the Tijuana River (MTR) microlayer samples (ng/g dry weight for particulates and ng/L for filtrates).

Thus, temporal changes could not be assessed. The particulate LAB concentrations (34–100  $\mu\text{g/g}$ ; Table 1) in the PLWTP effluent were slightly higher than those (18–34  $\mu\text{g/g}$ ) reported by Takada and Ishiwatari [14] in the effluent from one of the largest sewage treatment plants in the Tokyo Bay area.

The concentrations of total LABs in the TR runoff particulates were considerably lower (3.8–8.1  $\mu\text{g/g}$  dry weight or 0.057–0.714  $\mu\text{g/L}$  based on the aqueous volumes) compared to those in the PLWTP effluent particulates. Further, a detectable level of LABs found in the MTR microlayer particulates (0.82  $\mu\text{g/g}$ ) suggested a possible accumulation of sewage-derived organic matter at the nearshore sea surface water. However, the sediment collected from this location contained no detectable LAB contents. This, along with the low PAH [17] and AH [18] concentrations at the same location, indicates that tidal waves may effectively remove contaminants from this relatively shallow location into the deeper water.

Particulate materials (e.g., clay, silt, sand, and shell fragments) in the water column may serve as sorptive sites for partitioning of hydrophobic organics [22,23]. Marine sediments, on the other hand, are the major sink of suspended particulates. Therefore, suspended particulates and sediments provide the means of transport and the ultimate reservoirs, respectively, for hydrophobic organic contaminants. The relative distributions of LABs in suspended particulates and sediments may thus be useful in assessing the possible modifi-

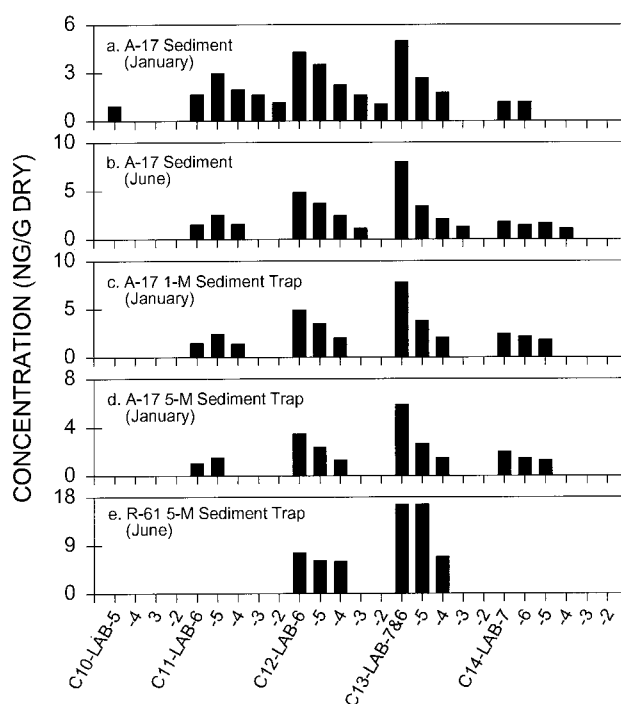


Fig. 2. Compositions of linear alkylbenzenes in A-17 sediments, 1-m and 5-m trap particulates, and R-61 5-m trap particulates, San Diego, California.

cations and alterations of sewage-derived contaminants during transportation to and residence in the sea floor.

The concentrations of total LABs in the A-17 trap particulates (0.011–0.036  $\mu\text{g/g}$ ) were substantially lower than those in the PLWTP effluent (34–100  $\mu\text{g/g}$ ). The concentrations of LABs in the A-17 sediments were also low (0.035–0.039  $\mu\text{g/g}$ ; Table 1). Similar spatial variations were also reported previously [14], that the total LAB concentrations in the sediments (0.01–15.8  $\mu\text{g/g}$ ) and in the suspended particles (4.2–31.3  $\mu\text{g/g}$ ) were lower than those in the wastewater effluents (8.7–36.3  $\mu\text{g/g}$ ). Eganhouse et al. [4] obtained total LAB concentrations of 21.4  $\mu\text{g/g}$  and 1,342  $\mu\text{g/g}$  in the sediments collected near the Joint Water Pollution Control Plant (JWPCP) outfall and in the JWPCP effluent, respectively. Obviously, dilution of particle-bound LABs in open ocean waters is mostly responsible for the decrease of LAB concentrations from PLWTP effluents to suspended particulates and sediments. As discussed in the following section, other mechanisms may also account for effectively removing LABs and/or altering their chemical compositions.

The total organic carbon (TOC) normalized concentration of LABs was lower in the A-17 trap particulates than in the A-17 sediments (Table 1), due to the higher TOC concentration in the trap particulates than in the sediments. This probably resulted from inputs of carbon-enriched materials (e.g., terrestrial high plants, etc.) and/or resuspended fine particulates enriched with TOC that effectively diluted the concentrations of sewage-derived organics in sewage particulates.

Three of the four traps at R-61, as well as those at A-17, contained detectable LABs, although the R-61 sediments virtually contained no LABs (Table 1). This indicated that fine particulates enriched with LABs or other organic compounds may stay in suspension long enough to be carried to remote locations, as first proposed by Zeng and Vista [17]. A large amount of LABs in the sinking particles is probably biode-

graded before reaching the sea floor. It should be noted that 5-phenylundecane and several isomeric secondary phenylalkanes with 10 to 13 carbons in the alkyl chains were previously detected in the sediment trap particulates collected in the Santa Monica and San Pedro basins [5], further verifying long-range transport of sewage-derived contaminants.

The SDB sediment sample contained extremely low LAB contents, possibly derived from the storm runoff draining through the San Diego International Airport.

#### *Fate of LABs in the coastal marine environment*

Upon entering the ocean waters, LABs may be redistributed into various phases, which may account partially for the large discrepancy between the TOC-normalized concentrations of LABs in the PLWTP effluent particulates and A-17 sediments (and trap particulates). Air, water, sediment particles, and biota are the likely compartments for redistribution of sewage-derived LABs [3]. The TOC-normalized concentrations of LABs in the A-17 trap particulates and sediments were about 0.13 to 1.9% and 2.7 to 6.6%, respectively, of those in the PLWTP effluent particulates (calculated from Table 1). Apparently, most LABs in the effluent particulates are probably dispersed into different compartments when they reach the water column and sediment at this location.

Another important way of removing LABs from the aquatic environment is biodegradation. As demonstrated experimentally by Takada and Ishiwatari [19] and Bayona et al. [24], aerobic degradation by microbes preferably eliminates external LAB isomers, resulting in high I/E ratios. Therefore, by examining I/E ratios, one may be able to estimate the degree of biodegradation of LAB compounds.

The I/E ratios in the PLWTP effluent are all less than 1 (Table 1), suggesting little biodegradation during the treatment process. By contrast, the I/E ratios (1.6–4.4) in A-17 trap particulates and sediments are substantially greater than 1. Based on the relationship between the degradation of LABs and I/E [19], 30 to 55% of the LABs are degraded before they incorporate into the suspended particles and bottom sediments. It is clear that, in addition to biodegradation, other processes, such as dilution with nonsewage-derived particles, dissolution into water, evaporation to the atmosphere, and accumulation by marine organisms, may effectively dissipate sewage-related organic materials from the discharge zone. However, relatively less attention has been given to these possible mechanisms.

Relatively high I/E ratios in the particulates (5.8 in June and 2.6 in January; Table 1) of the TR runoff also indicated substantial biodegradation of LABs occurring during riverine transport.

#### *Overview of organic pollutant inputs into the coastal marine environment off San Diego*

The information presented thus far may allow a general assessment of the pollutant inputs into the coastal marine environment off San Diego. Based on the measured concentrations of PAHs (1,780 and 1,550 ng/L in the PLWTP effluent and 24.7 and 80.1 ng/L in the TR runoff [17]), AHs (19.6 and 13.0 ng/L in the PLWTP effluent and 3,880 and 831 ng/L in the TR runoff [18]), and LABs (Table 1) in the PLWTP effluent and TR runoff, the mass emission rates of these compounds are estimated (Table 2). The vertical fluxes of PAHs, AHs, and LABs in the water column at A-17 and R-61 (Table 3) were calculated using the procedure described in [17].

The PLWTP outfall is a major point source for organic

Table 2. Mass emission rates of total polycyclic aromatic hydrocarbons (PAHs), aliphatic hydrocarbons (AHs), and linear alkylbenzenes (LABs) from the Point Loma Wastewater Treatment Plant (PLWTP) outfall and Tijuana River in 1994

Compounds	Annual mass emission (kg/year)	
	PLWTP outfall	Tijuana River
PAHs <sup>a</sup>	395	2.2
AHs <sup>b</sup>	3,860	101
LABs	710	17

<sup>a</sup> Estimated in Zeng and Vista [17].

<sup>b</sup> Estimated in Tran et al. [18].

pollutants found in the area, as indicated by the substantially higher sediment concentrations of LABs (35.3 and 39.2 ng/g; Table 1) and PAHs (257 and 122 ng/g [17]) in A-17 than in R-61 (ND for LABs in Table 1 and 23.9 and 7.1 ng/g for PAHs [17]). The sediment concentrations of AHs in these two locations, however, were not so different (928 and 666 ng/g at A-17 and 391 and 179 ng/g at R-61 [18]). Because AHs can be produced by in situ biological processes, their background level in the marine environment may be fairly high, compared to inputs from PLWTP. This was further verified by considerably high AH concentrations in MTR sediments (578 and 91 ng/g [18]), although sediment PAH (16.5 ng/g and ND [17]) and LAB (ND, Table 1) concentrations were extremely low at this location.

Nonpoint sources contribute greatly to the PAH inputs, as discussed previously [17]. This is corroborated by the higher concentrations of PAHs (122–257 ng/g [17]) than those of LABs (35.3–39.2 ng/g) in A-17 sediments. Because the mass emission of LABs was almost twice as much as that of PAHs from the PLWTP outfall (Table 2) and the degree of biodegradation of LABs was about 30 to 55% in A-17 sediments as inferred from the I/E ratios (Table 1), the large difference between the PAH and LAB concentrations in A-17 sediments can only be accounted for by other non-point inputs of PAHs. Additional evidence is the higher vertical fluxes of PAHs than those of LABs at A-17 and R-61 (Table 3). If no biodegradation

Table 3. Comparison of fluxes of total polycyclic aromatic hydrocarbons (PAHs), aliphatic hydrocarbons (AHs), and linear alkylbenzenes (LABs) at A-17 and R-61 off San Diego, California

Site	Collection date	Level off bottom (m)	Fluxes (ng/m <sup>2</sup> /d)		
			PAHs <sup>a</sup>	AHs <sup>b</sup>	LABs
A-17	12/21/93–1/20/94	1 <sup>c</sup>	82.9	770	9.2
		5 <sup>d</sup>	24.1	320	2.2
	5/30/94–6/29/94	1 <sup>e</sup>	—	—	—
R-61	12/21/93–1/20/94	5 <sup>c</sup>	4.9	160	0.24
		1 <sup>c</sup>	12.7	300	NA <sup>g</sup>
	5/30/94–6/29/94	5 <sup>d</sup>	9.1	190	0.28
		1 <sup>c</sup>	4.2	120	0.36
		5 <sup>f</sup>	1.9	120	0.88

<sup>a</sup> [17].

<sup>b</sup> [18].

<sup>c</sup> Three traps.

<sup>d</sup> Nine traps.

<sup>e</sup> Traps lost.

<sup>f</sup> Eight traps.

<sup>g</sup> NA, not applicable because the corresponding LABs were not detectable.

was assumed during the transport of PAHs from the PLWTP outfall to the sediments, approximately half of the PAHs found in the sediments would be introduced from sources other than the PLWTP outfall. Actual inputs from nonpoint sources should be more significant because PAH biodegradation is likely to happen.

Bottom currents may transport fine suspended particles enriched with sewage-derived organic materials from the discharge zone to remote areas. This transport mechanism likely has resulted in fairly high PAH [17] and LAB concentrations in R-61 trap particulates, despite the long distance (~20 miles) between these two locations.

The TR discharges relatively low amounts of organics into the ocean waters (Table 2). However, a great deal of sewage-related organic matter may be accumulated in the sea surface microlayer near the mouth of the river. Sewage-related organic materials can be transported toward the nearby beaches and pose potential health hazard to swimmers. By contrast, extremely low concentrations of PAHs and LABs were determined in the sediments at the same location, suggesting effective removal of contaminants from the runoff into deeper waters. Therefore, the impact of the TR runoff on the quality of the nearshore sediments should be minimal.

The microlayer particulates at SDB contained the highest PAH [17] and n-alkane [18] concentrations as compared to other microlayer samples. Combustion-generated hydrocarbons were the predominant components in the SDB samples, as implied by the molecular indices associated with the compositions of PAH and AH assemblages. The storm runoff draining the San Diego International Airport and boat engine exhausts are probably the major sources of hydrocarbon inputs.

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#### REFERENCES

1. Myers, D. 1992. *Surfactant Science and Technology*, 2nd ed. VCH, New York, NY, USA.
2. Hinds, G.E. 1976. Petroleum-based raw materials for anionic surfactants. In W.M. Lindfield, ed., *Surfactant Science Series—Anionic Surfactants*, Vol. 7. Marcel Dekker, New York, NY, USA, pp. 11–86.
3. Gledhill, W.E., V.W. Saeger and M.L. Trehy. 1991. An aquatic environmental safety assessment of linear alkylbenzene. *Environ. Toxicol. Chem.* **10**:169–178.
4. Eganhouse, P.R., D.L. Blumfield and I.R. Kaplan. 1983. Long-chain alkylbenzenes as molecular tracers of domestic wastes in the marine environment. *Environ. Sci. Technol.* **17**:523–530.
5. Crisp, P.T., S. Brenner, M.I. Venkatesan, E. Ruth and I.R. Kaplan. 1979. Organic chemical characterization of sediment-trap particulates from San Nicolas, Santa Barbara, Santa Monica and San Pedro Basins, California. *Geochim. Cosmochim. Acta* **43**:1791–1801.
6. Ishiwatari, R., H. Takada, S.J. Yun and E. Matsumoto. 1983. Alkylbenzene pollution of Tokyo Bay sediments. *Nature* **301**:599–600.
7. Murray, A.P., C.F. Gibbs and P.E. Kavanagh. 1987. Linear alkyl benzenes (LABs) in sediments of Port Phillip Bay (Australia). *Mar. Environ. Res.* **23**:65–76.
8. Eganhouse, P.R. and I.R. Kaplan. 1988. Depositional history of recent sediments from San Pedro Shelf, California: Reconstruction using elemental abundance, isotopic composition and molecular markers. *Mar. Chem.* **24**:163–191.
9. Raymundo, C.C. and M.R. Preston. 1992. The distribution of linear alkylbenzenes in coastal and estuarine sediments of the western north sea. *Mar. Pollut. Bull.* **24**:138–146.
10. Chalaux, N., J.M. Bayona, M.I. Venkatesan and J. Albaigés. 1992. Distribution of surfactant markers in sediments from Santa Monica basin, Southern California. *Mar. Pollut. Bull.* **24**:403–407.
11. Chalaux, N., H. Takada and J.M. Bayona. 1995. Molecular markers in Tokyo Bay sediments: Sources and distribution. *Mar. Environ. Res.* **40**:77–92.
12. Albaigés, J., A. Farrán, M. Soler, A. Gallifa and P. Martín. 1987. Accumulation and distribution of biogenic and pollutant hydrocarbons, PCBs, and DDT in tissues of western Mediterranean fishes. *Mar. Environ. Res.* **22**:1–18.
13. Serrazanetti, G.P., C. Pagnucco, L.S. Conte and R. Artusi. 1994. Aliphatic hydrocarbons and linear alkylbenzenes in zooplankton from the Gulf of Trieste. *Chemosphere* **28**:1119–1126.
14. Takada, H. and R. Ishiwatari. 1987. Linear alkylbenzenes in urban riverine environments in Tokyo: Distribution, source and behavior. *Environ. Sci. Technol.* **21**:875–883.
15. Eganhouse, R.P., D.P. Olaguer, B.R. Gould and C.S. Phinney. 1988. Use of molecular markers for the detection of municipal sewage sludge at sea. *Mar. Environ. Res.* **25**:1–22.
16. Takada, H. and R. Ishiwatari. 1991. Linear alkylbenzenes (LABs) in urban riverine and coastal sediments and their usefulness as a molecular indicator of domestic wastes. *Water Sci. Technol.* **23**:437–446.
17. Zeng, E.Y. and C.L. Vista. 1997. Organic pollutants in the coastal marine environment off San Diego, California. 1. Source identification and assessment by compositional indices of polycyclic aromatic hydrocarbons. *Environ. Toxicol. Chem.* **16**:179–188.
18. Tran, K., C.C. Yu and E.Y. Zeng. 1997. Organic pollutants in the coastal marine environment off San Diego, California. 2. Petrogenic and biogenic sources of n-alkanes. *Environ. Toxicol. Chem.* **16**:189–195.
19. Takada, H. and R. Ishiwatari. 1990. Biodegradation experiment of linear alkylbenzenes (LABs): Isomeric composition of C<sub>12</sub> LABs as an indicator of the degree of LAB degradation in the aquatic environment. *Environ. Sci. Technol.* **24**:86–91.
20. Zeng, E.Y. and C.C. Yu. 1996. Measurements of linear alkylbenzenes by GC/MS with interference from tetrapropylene-based alkylbenzenes: Calculation of quantitation errors using a two-component model. *Environ. Sci. Technol.* **30**:322–328.
21. American Public Health Association, American Water Works Association, and Water Pollution Control Federation. 1980. *Standard Methods for the Examination of Water and Wastewater*, 15th ed. American Public Health Association, Washington, DC.
22. Karickhoff, S.W., D.S. Brown and T.A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Res.* **13**:241–248.
23. Wakeham, S.G. and J.W. Farrington. 1980. Hydrocarbons in contemporary aquatic sediments. In R.A. Baker, ed., *Contaminants and Sediments. IV: Fate and Transport, Case Studies, Modeling, Toxicity*. Ann Arbor Science, Ann Arbor, MI, USA, pp. 3–32.
24. Bayona, J.M., J. Albaigés, A.M. Solanas and M. Grifoll. 1986. Selective aerobic degradation of linear alkylbenzenes by pure cultures. *Chemosphere* **15**:595–598.