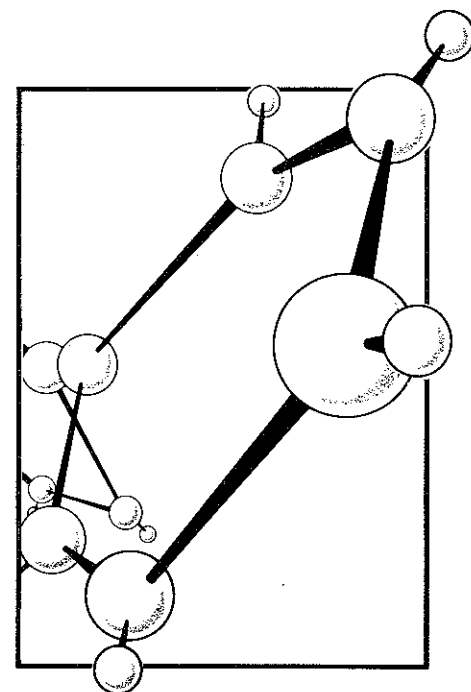


In a previous annual report (SCCWRP 1987), SCCWRP scientists described early efforts to measure polynuclear aromatic hydrocarbon (PAH) concentrations in marine sediments from offshore southern California. The purpose of that survey was to determine the composition and concentration of PAHs in *surface* sediments at a variety of coastal sites presumed to be receiving hydrocarbon inputs. Here are results from a study by Robert P. Eganhouse and Richard W. Gossett of PAHs in final effluent from the Joint Water Pollution Control Plant (JWPCP; Los Angeles County) and sediments cored from the Palos Verdes Shelf.

PAHs are toxic substances that originate from a multitude of sources and exhibit a wide range of physico-chemical properties. Although globally distributed, they are typically found in greater abundance near urbanized coastal areas. The major sources of PAHs to coastal and estuarine environments are believed to be municipal waste discharges, urban runoff, and atmospheric particulates. Unfortunately, published information concerning the composition and concentrations of PAHs in municipal wastewaters, particularly in southern California, is extremely limited (Barrick 1982, Grzybowski et al. 1983). This makes it difficult to evaluate the importance of municipal waste discharges compared with other inputs of PAHs to the Southern California Bight. One of the

objectives of the present study was to measure the concentrations of PAHs in the JWPCP's final effluent over the course of one year (1979). These data are used to estimate the mass emission rate of PAHs from this treatment plant as of 1979.

In addition to analyzing effluent samples, SCCWRP scientists examined sections of a sediment core collected from the Palos Verdes Shelf in connection with the County Sanitation District's coring program in 1981 (station 3C; 33°43.83 N, 118°24.01 W). Sediments from this core have been analyzed for elemental abundance, stable iso-



Polynuclear Aromatic Hydrocarbons in Waste Effluent and Sediments

topic composition and molecular markers by Eganhouse and Kaplan (1988) and for a variety of inorganic and organic trace constituents by the County Sanitation District. Because the core is so well characterized, we felt it would provide an opportunity to estimate the accumulation rate of PAHs at station 3C.

Figure 1 illustrates the PAH composition of the JWPCP final effluent collected on October 15, 1979. This sample is generally representative of those taken in other months; however, some of

the higher molecular weight PAHs found in low abundance in the October sample were not detected in effluent collected at other times during the year. The PAH distribution of the effluent is dominated by naphthalene, phenanthrene, and corresponding alkylated homologs. Higher molecular weight species (i.e., those having more than three fused rings) are in lower abundance. The alkyl homolog distributions (i.e., the relative abundances of parent and alkyl-substituted species) generally show a maximum for the C1- to

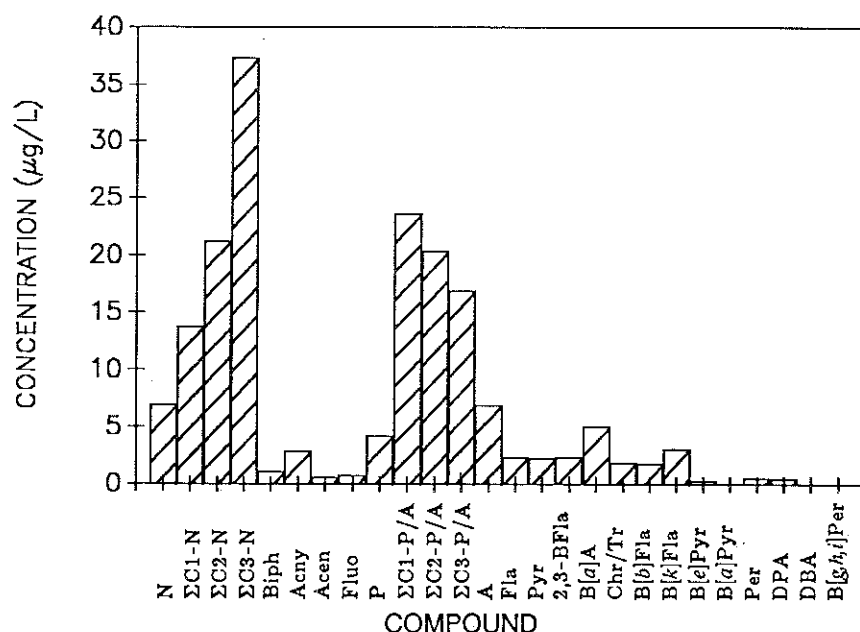


Figure 1. Distribution of PAHs in JWPCP final effluent, October 15, 1979.

Abbreviations: N, naphthalene; Biph, biphenyl; Acny, acenaphthylene; Acen, acenaphthene; Fluo, fluorene; P, phenanthrene; A, anthracene; Fla, fluoranthene; Pyr, pyrene; B, benzo group; Chr/Tr, chrysene/triphenylene; Per, perylene; DPA, 9,10-diphenylanthracene; DBA, dibenzo[a,h]anthracene.

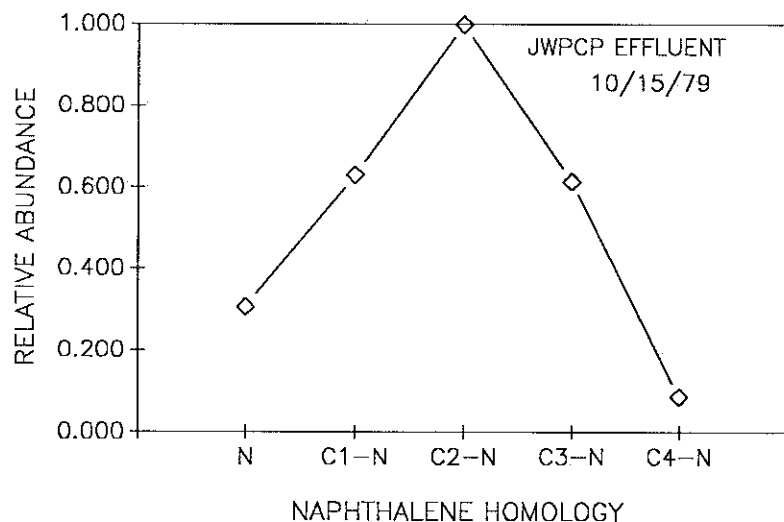


Figure 2. Alkyl homolog distribution of naphthalene series (C_nH_{2n-12}). N, Naphthalene.

C3-substituted naphthalenes and phenanthrene/anthracenes (Figure 2). In addition, the fluoranthene/pyrene series and other high molecular weight PAH groups exhibit dominance by the alkylated species. To-

gether these results suggest that the PAHs found in the effluent samples are derived from fossil fuels, not combustion sources.

Table 1 provides a summary of the mean concentrations of

PAHs in the effluents determined in this study along with data presented by Barrick (1982) for the Seattle METRO treatment plant (particulate concentrations) and Grzybowski et al. (1983) for waste effluent from Poland. Concentrations measured in the JWPCP effluent are approximately an order of magnitude greater than those determined for the METRO samples but generally fall within the range reported by Grzybowski et al. (1983). Some of this difference can be explained by the higher hydrocarbon concentrations of the California wastes. On average, the JWPCP hydrocarbon concentrations were five times greater than those reported for the Seattle METRO effluent. Despite the fact that the METRO plant receives inputs from storm water runoff, industrial contributions to the influent are relatively small. In contrast, the JWPCP receives substantial quantities of industrial wastes.

The JWPCP has monitored its effluent for the U.S. Environmental Protection Agency priority pollutants on an approximately quarterly basis since 1985. Non-detectable amounts have been reported for all PAHs except naphthalene and phenanthrene. In many cases, however, the reported detection limits are higher than the concentrations measured in this study.

There was an attempt by SCCWRP to measure priority pollutants in the JWPCP effluent

in 1978. The only PAHs reported to be present at measurable concentrations were naphthalene (29 $\mu\text{g/L}$) and acenaphthene (7 $\mu\text{g/L}$). These concentrations are approximately 5 to 7 times higher than those observed for samples taken in 1979.

The variation in concentration of individual (or alkylated isomer groups of) PAHs found in all samples ranges from 46 to 74% (coefficient of variation), whereas the variation in total PAH concentrations (i.e., sum of 26 measured concentrations) is 53%. This is significantly greater than the variation in concentration of total hydrocarbons and extractable organics (Eganhouse and Kaplan 1982), possibly reflecting greater fluctuations of PAH inputs. Inspection of the data presented by Barrick (1982) indicates that similar levels of variation of individual PAH concentrations were observed in the Seattle effluent during 1978.

When the concentrations of total PAHs are applied to the mean monthly flows from the JWPCP, an annual mass emission rate of 110 metric tons is obtained. There are no known available data for other waste treatment plants or storm water drainage systems in southern California with which these figures can be compared for the year 1979. Recent studies at SCCWRP of a single storm in 1986 suggest that the total PAH emissions from the Los Angeles River during that event were 0.4

Table 1. Concentrations of PAHs in municipal wastewater effluent.

Analyte	Mean Concentration ($\mu\text{g/L}$)		
	This study ^a	Barrick (1982) ^b	Grzybowski et al. (1983)
Total hydrocarbons	16,300	3,000	NR ^c
Naphthalene	7.8	NR	NR
C1-naphthalenes	23.2	NR	NR
C2-naphthalenes	38.5	NR	NR
C3-naphthalenes	66.0	NR	NR
Phenanthrene	14.0	0.8	0.5-10.
Anthracene	0.9	NR	0.1-1.0
C1-phenanthrene/anthracenes	20.7	1.4	NR
C2-phenanthrene/anthracenes	20.5	1.6	NR
C3-phenanthrene/anthracenes	9.6	NR	NR
Fluoranthene	1.1	0.4	0.5-5.0
Pyrene	2.8	NR	11.-27.
Benz[a]anthracene	1.0	0.1	0.1-24
Chrysene/triphenylene	2.1	0.2	NR
Benzo[e]pyrene	0.5	0.1	1.-5.5
Benzo[a]pyrene	0.3	NR	0.6-6.5
Total PAH ^d	115.	NR	NR

^aMeasurements of unfiltered JWPCP effluent samples, 1979.

^bCalculated values based on particulate concentrations in METRO effluent; exception: total hydrocarbons = particulate + dissolved.

^cNR, Not reported.

^dTotal PAH is the sum of PAHs determined in this study.

metric tons (see p. 13). More data are required to develop yearly estimates for this and other drainage systems in the southern California region.

Figure 3 depicts the distribution of PAHs found in sediments at a depth of 2 to 4 cm below the sediment-water interface at station 3C. The PAH composition is somewhat variable in different sections of the core, but the pattern shown here is fairly representative of those seen at other depths. In contrast to the effluent PAH composition (Figure 1), sedimentary PAH distributions are dominated by higher

molecular weight species. Naphthalene, phenanthrene, and the corresponding alkylated homologs of these compounds were rarely seen and then only in low abundance. Because most of the hydrocarbons in this core down to depths of 24 cm are believed to be of sewage origin (Eganhouse and Kaplan 1988), it is likely that the lower molecular weight species so abundant in the effluent were lost via solubilization or biological degradation. The fact that the lower molecular weight species are not found in the uppermost section of the core indicates that alteration of the PAH assemblage occurs prior to

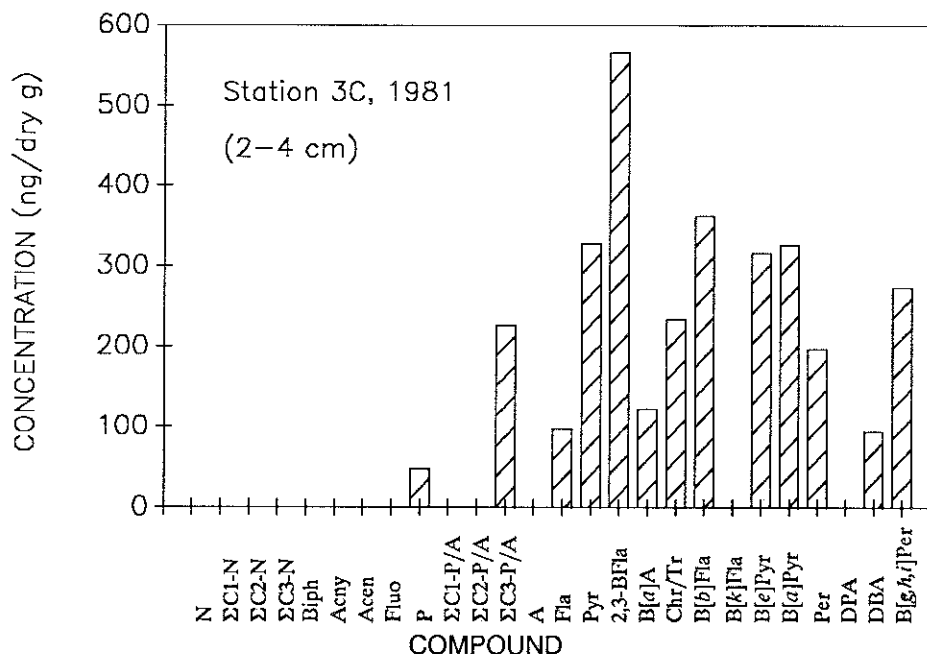


Figure 3. Distribution of PAHs in 2- to 4-cm section of sediment core at station 3C, 1981. Abbreviations are as in Figure 1.

sediment burial (i.e., in the water column and/or at the sediment-water interface).

Table 2 provides data for the sediment core along with results obtained from the literature. Although no measurements have yet been published for sediments from station 3C, Swartz et al. (1985) and Anderson and Gossett (1987) reported PAH data for whole grabs and surface sediments (0 to 2 cm), respectively, taken from the Palos Verdes Shelf in 1980 and 1986. Both surveys identified naphthalene and other lower molecular weight species at station 7C. The appearance of these relatively labile species at 7C and their absence at 3C may reflect differences in the sediment accumulation rates at these stations. Alkyl homolog distributions for the fluoranthene/pyrene series found in the highly contaminated

sediment sections show maxima among the higher molecular weight alkylated species. This suggests that petroleum, not fossil fuel combustion products, is the dominant source of these PAHs.

A comparison of effluent particulate PAH/organic carbon ratios with those observed in the sediment sections suggests that even the higher molecular weight PAHs found in low abundance in the effluent may be subject to extensive removal during the sedimentation process. Whether this reflects desorption/dissolution, degradation, or some combination is unclear. The resistance of higher molecular weight PAHs to environmental alteration appears to depend, in part, on their physico-chemical speciation upon introduction to the environment (Readman et al. 1984, Gschwend and Hites 1981)

with combustion-derived PAHs being more refractory than those occurring as petroleum residues. The present results are consistent with the hypothesis that the PAHs at station 3C are derived from petroleum.

Figure 4 illustrates the vertical concentration profile for total PAHs in the sediment core. Maximum concentrations are observed between depths (below the water-sediment interface) of 2 to 18 cm. With increasing depth below 18 cm, the PAH concentrations decline rapidly and appear to reach "background levels" at approximately 22 to 24 cm. At station 3C, the PAH distribution is similar to profiles observed for other waste-related contaminants, which typically exhibit a well-defined subsurface maximum at depths of 8 to 10 cm below the sediment-water interface (Eganhouse and Kaplan 1988, Stull et al. 1986). The appearance of high PAH concentrations over the same depth intervals as observed for other indicators of waste contamination (e.g., organic carbon and total hydrocarbons) strongly suggests that sewage is the dominant source of these compounds. The lack of a distinct subsurface maximum, however, indicates that changes in solids emissions alone (Eganhouse and Kaplan 1988) probably did not control accumulation rates of PAHs in these sediments.

Using tentative assignments for the ages of different depths of this core (Eganhouse and Kaplan 1988), one can calculate average accumulation rates of total and

Table 2. PAH concentrations in sediments of the Palos Verdes Shelf.

Compound	Concentration (ng/dry g)		
	This study ^a (3C; 1981)	Swartz et al. (7C; 1985)	Anderson and Gossett (7C; 1986)
Naphthalene	-- ^b	--	87
C1-naphthalenes	--	NR ^c	104
C2-naphthalenes	--	NR	415
C3-naphthalenes	--	NR	462
Biphenyl	--	NR	22
Acenaphthylene	--	160	57
Acenaphthene	--	NR	--
Fluorene	--	NR	16
Phenanthrene	--	290	197
Anthracene	--	623	52
C1-phenanthrene/anthracenes	--	NR	773
C2-phenanthrene/anthracenes	--	NR	1193
C3-phenanthrene/anthracenes	--	NR	701
Fluoranthene	17	294	157
Pyrene	127	838	401
2,3-Benzofluoranthene	149	NR	842
Benz[a]anthracene	36	1330	166
Chrysene/triphenylene	88	606	274
Benzofluoranthene	207	633	746
Benzo[e]pyrene	217	NR	317
Benzo[a]pyrene	212	NR	323
Perylene	105	NR	353
9,10-Diphenylanthracene	--	NR	4
Dibenz[a,h]anthracene	38	NR	NR
Benzo[g,h,i]perylene	205	NR	217
Total PAH	1,400	--	7,300
μg Total PAH/g organic carbon ^d	23.5	--	154.

^aData are for 0- to 2-cm section.^bBelow detection limit.^cNR, Not reported.^dElemental analysis from Eganhouse and Kaplan (1988).

individual PAHs in the sediments. Table 3 presents estimated average accumulation rates based on such calculations. It is clear that the average accumulation rates of total PAHs for sections occurring after about 1950 (i.e., <24 cm) are an order of magnitude greater than those for the pre-1950 period. Moreover, the average accumulation rates appear not to have changed significantly during the three decades since 1950. The estimated accumulation rates for

deeper sections of the core (i.e., >24 cm) are similar to those made by Gschwend and Hites (1981) for sediments near urban centers such as Boston Harbor and Buzzards Bay, MA. These are, nevertheless, at least an order of magnitude higher than those found at remote locations where sedimentary fluxes are dominated by atmospheric deposition. This suggests that even the deeper sections of the 3C core may have been heavily influenced by local inputs (in-

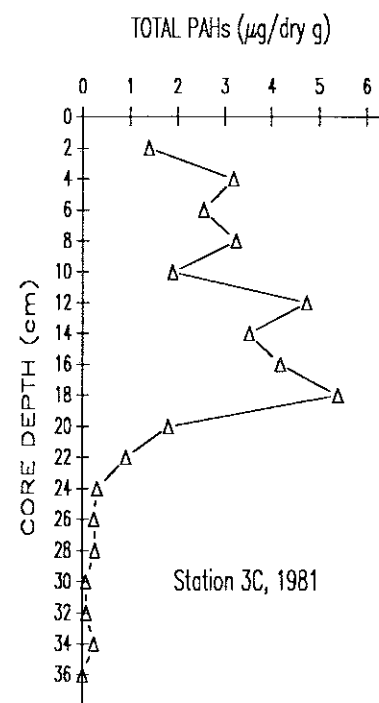


Figure 4. Vertical concentration profile of total PAHs at station 3C, 1981.

cluding natural oil seepage) with direct atmospheric deposition playing only a minor role. Such a hypothesis is consistent with stable isotopic and molecular evidence at this site and in San Pedro Basin.

The results discussed here demonstrate the need for further study of municipal wastewater inputs of PAHs to the coastal ecosystem. In recent years, there has been a marked reduction in the mass emission rates of suspended solids, oil and grease, and other trace constituents from the JWPCP (Stull and Haydock 1988). It is, therefore, important to determine if similar reductions have occurred for PAH inputs. Because these toxic compounds appear to be accumulating in nearshore sediments at rates far in excess of "natural" fluxes, information regarding the bio-

Table 3. Average accumulation rates of PAHs in sediments at station 3C, 1981.

Depth Interval (cm)	Approx. Date Interval	Accumulation rate (ng cm ⁻² yr ⁻¹) for:						
		Fla	Pyr	B[a]A	Chr/Tr	B[e]Pyr	B[a]Pyr	Tot. PAH
0-8	1971-81	77	273	89	173	227	274	2640
8-14	1962-71	65	335	76	135	316	200	2970
14-24	1950-62	117	283	80	124	333	276	2870
24-34	1937-50	18	28	8	11	25	22	240
Boston Harbor ^a		37	39	19	23	14	17	NR ^b

^aFrom Gschwend and Hites (1981).^bNR, Not reported.

geochemical fate and chemical speciation of sewage-derived PAHs is also of interest. Current evidence clearly indicates that the dominant source of PAHs to the JWPCP effluent (as of 1979) is petroleum. A large, but unknown, fraction of these PAHs appears to have been lost during the early stages of diagenesis. Hence, only the more resistant, higher molecular weight PAH species tend to accumulate in waste-impacted sediments. Whether the presence of these carcinogenic substances represents a threat to the health of indigenous marine life remains to be investigated.

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