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Historical Deposition and Biogeochemical Fate of Polycyclic Aromatic Hydrocarbons in Sediments Near a Major Submarine Wastewater Outfall in Southern California

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INTRODUCTION

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Over the last two decades a tremendous amount of research has been directed at understanding the environmental behavior and fate of polycyclic aromatic hydrocarbons (PAH), primarily because of their demonstrated carcinogenicity and global distribution.^{1,2} PAH have been found in many estuarine and coastal environments,³⁻¹⁰ and it has repeatedly been shown that the highest concentrations in and fluxes to sediments typically occur in areas adjacent to urban centers.¹¹⁻¹⁴ The possible sources of PAH near such urbanized sites include: atmospheric deposition,¹⁵ surface runoff,^{16,17} municipal waste effluents,^{18,19} industrial effluents,²⁰⁻²² spills and leakage during transport and production of fossil fuels.²³ natural seepage,^{10,24,25} and erosion of exposed shales ^{26,27} and coal seams.²⁸⁻³⁰ Whereas direct biosynthesis is generally believed to be insignificant, numerous PAH may be formed from biogenic precursors within relatively short periods of time (years to decades) during the early stages of diagenesis. Examples of the latter include retene, an alkylated phenanthrene derived from abietic acid,^{2,31} pervlene, a pentacyclic PAH whose diagenetic precursor(s) and pathway(s) remain controversial (cf. references in Venkatesan³²), and numerous tetra- and pentacyclic PAH derived from triterpenoidal precursors.2,33-35

One of the most consistent observations has been the similarity of PAH assemblages in many marine sediments from locations throughout the world.² The compositions indicate a dominantly pyrogenic (as opposed to uncombusted fossil fuel) origin and are presumed to reflect the widespread dispersal of combustion-derived PAH in the atmosphere.³⁶ Contributions of combustion PAH near urban centers are often augmented by inputs related to the use and disposal of fossil fuels. Offshore dispersal *via* currents is thought to be restricted,^{37,38} and many of the (lower molecular weight) PAH derived from uncombusted fossil fuels are relatively labile compared to those found in association with combustion particles.^{8,39-41} This explains the dominance of combustion-derived PAH in offshore sediments and the mixed compositions sometimes found in heavily urbanized

embayments and estuaries (e.g. Lake *et al.*⁷). Differences in the transport dynamics and susceptibility of individual PAH to biodegradation reflect variations in their physicochemical properties and phase associations, the latter of which may be established prior to introduction to the marine environment.^{11,42-45}

The vertical distribution of PAH in well-preserved, age-dated sediment cores typically show increasing concentrations in the post-1900 period.^{11,12,44,46,47} This parallels the rapid onset of modern industrialization and increased use of fossil fuels in the northern hemisphere.⁴⁸ Because similar profiles have been reported for both lacustrine and marine environments from widely separated locales, the depositional records would appear to document historical anthropogenic inputs on a regional, if not, global scale. The major caveat to this statement is that regional variations in anthropogenic activities related to fossil fuel consumption may cause minor differences in the character (e.g. rate of change, occurrence of subsurface maxima) of the downcore patterns.⁴⁹

Published information on the composition and abundance of PAH in municipal wastewater effluents and the fate of these compounds in receiving waters is relatively limited.^{18,19,50} This makes it difficult to evaluate the importance of such discharges vis a vis other inputs of PAH to coastal and estuarine environments. This paper extends previous studies^{19,51} aimed at describing the detailed organic chemical composition of municipal waste effluents in southern California. Here we present data on the composition and concentration of PAH in one of these effluents, that discharged by the Los Angeles County Sanitation District (LACSD). Because the LACSD receives a significant contribution of industrial (esp. petrochemical) waste to its influent, the emissions of petroleum hydrocarbons from this plant exceed those of any major treatment facility in the region.⁵² Our primary interest in investigating the LACSD effluent was to establish the origin of the PAH and estimate their rates of discharge to nearby coastal waters. Comparison of effluent PAH compositions with those of sediments deposited near the outfall system affords an opportunity to investigate the short-term fate of these compounds.

In this context, we have also examined sections of a sediment core collected from the Palos Verdes shelf during the LACSD's coring program in 1981. Sediments from this core have previously been analyzed for elemental abundance, stable isotopic composition, molecular markers and a variety of inorganic and chlorinated organic trace constituents.^{53,54} Because the core is so well characterized, we felt it would provide an opportunity to estimate the accumulation rate of PAH at this site and to draw some conclusions regarding the origin(s) and post-depositional fate of PAH in this waste-impacted environment.

STUDY AREA

Figure 1 shows the location of the LACSD plant, the outfall system from which its final effluent is released and the location of the sediment coring (station 3C1). In 1979 the LACSD discharged approximately 1.4×10^9 liters day⁻¹ of effluent, 100% of which received advanced primary treatment. The outflow of water, solids, oil and grease and hydrocarbons from this facility accounted for 35, 41, 45 and 39%, respectively, of the combined emissions by the four major treatment plants in southern California at that time.⁵² Mass emission rates of total hydrocarbons, saturated hydrocarbons and aromatic hydrocarbons were estimated at 8000, 4500 and 3500 metric tons yr⁻¹. The final effluent is discharged from two outfalls, the termini of which are located below the thermocline at a water depth of 60 m.

Sediments deposited on the shelf adjoining the Palos Verdes peninisula have for some time been heavily contaminated with DDT, and a complex assemblage of trace inorganic and organic substances (*cf.* refs in Eganhouse and Kaplan⁵³). Because the prevailing subsurface currents generally transport water and effluent particles along isobaths in a northwesterly direction, concentration isopleths of these contaminants tend to be centered on the 60 m depth contour and extend northward into Santa Monica Bay. The existence of the deepwater outfall system since the early 1950s has resulted in the accumulation of more than 60 cm of organic rich effluent-derived material near the outfalls. We chose to investigate a site 6 km downcurrent from the outfalls because of the

ability to collect material (by gravity coring) deposited before the onset of significant waste inputs.

EXPERIMENTAL

Sample Collection

Twelve monthly flow-proportioned 24-hour composites of final effluent were collected from the LACSD treatment plant (Carson, CA) during 1979. Details of the procedures used in these collections can be found elsewhere.⁵² Samples were returned to the laboratory and processed as described below. Results presented here pertain to unfiltered effluent samples extracted directly with chloroform.

Sediments were collected using a gravity corer during April, 1981 as described by Eganhouse *et al.*⁵⁵ Although the design and method of deploying the coring device were intended to minimize disruption of the sediment surface and avoid unnecessary compaction, it is probable that the some portion of the flocculent surface layer was lost. The sediments were extruded while frozen, cut into 2 cm intervals, trimmed of the outer 2 cm and stored in a freezer until analyses could be performed.

Analyses

Details of the procedures used to isolate hydrocarbons from effluent and sediment samples can be found elsewhere.^{52,55} Briefly, the effluents were extracted with chloroform; the sediments were extracted with a $CH_2Cl_2/MeOH$ solution. These extracts were treated for removal of water and elemental sulfur after which they were analyzed gravimetrically for total extractable organic matter. Following esterification of fatty acids, an aliquot of the extract was applied to thin layers of silica gel for isolation of the total hydrocarbon fraction (THC). In some cases, total saturated hydrocarbon and total aromatic hydrocarbon (TAH) fractions were also separated by thin layer chromatography. Yields of these fractions were subsequently determined by microgravimetry.

Aromatic hydrocarbon sub-fractions suitable for instrumental analysis were obtained from the THC fraction using adsorption chromatography on activated silica gel as described in Anderson and Gossett.⁵⁶ Recovery surrogates (12.5 μ g l⁻¹ of naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂ and perylene-d₁₂ in hexane) were added to the column along with the THC fraction, and the PAH were collected (f₂: hexane/benzene, 60:40) following elution of a fraction corresponding to the saturated hydrocarbons (f₁: hexane). Fraction 2 was concentrated under a stream of N₂ gas, amended with a measured volume of the internal standard solution (anthracene-d₁₀) and adjusted to a known volume by addition of hexane for subsequent instrumental analysis.

Measurement of individual PAH concentrations was accomplished using a Hewlett-Packard 5970 MSD. A 30 m x 0.25 mm I.D. capillary column coated with DB-5 (0.25μ m film thickness) was used with splitless injection at 50°C. The column was temperature programmed to 275°C at 4°C min⁻¹ with an isothermal hold at the upper temperature. Mass spectra were acquired by scanning from 50-400 amu sec⁻¹ at an ionizing voltage of 70 eV. Peak identifications were based on relative retention times of authentic standards coupled with positive confirmation of the mass spectra. Quantitation of individual PAH was performed by comparison of the integrated peak areas of selected ions for each PAH using the internal standard method. In the case of alkylated homologs of naphthalene and phenanthrene/anthracene, the summed areas of individual homolog peaks were used for quantitation following mass spectral verification. With the exception of naphthalene-d₈, recoveries generally exceeded 90%. Consequently, no correction of PAH concentrations has been made for recovery. Naphthalene recoveries averaged 73 and 43%, respectively, for effluent and sediment samples. Precision is estimated at $\pm 20\%$.⁵⁶

RESULTS AND DISCUSSION

PAH in Wastewater Effluent

Compositional Features

Table 1 provides data on the concentrations of 19 parent PAH and six alkylated homolog groups in the LACSD effluent. When summed, the PAH determined by gas chromatography/mass spectrometry comprise <2% of the total hydrocarbons and $\leq 6\%$ of the total aromatic hydrocarbons measured gravimetrically (following thin layer chromatographic separation).⁵² High resolution gas chromatography confirms that the TAH fraction consists largely of an unresolved complex mixture (UCM) with resolved PAH representing, at most, a minor component of the total.¹⁹ The vast majority (>90%) of the resolved PAH contain 2-3 rings, and naphthalene + (C_{1-3}) alkylated homologs make up 50-75% of the total (Table 1). Hoffman et al.¹⁷ report finding similar results for sewage effluents from Rhode Island. The dominance of the PAH assemblage by di- and tricyclic species is consistent with the hypothesis that most of the hydrocarbons in these effluents are derived from petroleum^{3,19} and not from the thermal alteration of organic matter. The LACSD treatment plant receives wastes from all but one of the petrochemical plants in the Los Angeles basin, and it is presumed that these inputs represent a primary source of hydrocarbons and PAH to the plant. The major PAH having 4-5 rings are fluoranthene, pyrene (and alkylated homologs) and chrysene/triphenylene. Other compounds, including benzo[ghi]perylene, were observed variably and generally at low concentrations $(< 1 \mu g l^{-1})$, an exception being the benzopyrenes, which were found at concentrations exceeding 2 μ g liter⁻¹ during the month of September. Notable for their absence, even in the September sample, are 9,10-diphenylanthracene and benzo[k] fluoranthene (see below). Analyses performed by the LACSD⁵⁷ on effluent collected in 1987 indicate that some of these higher molecular weight PAH are consistently present in the effluent (e.g. benzo[a]pyrene, benzo[e]pyrene, benzofluoranthenes and perylene). However, the

concentrations they determined were typically at or below the detection limit of the methodology used here (*ca.* 0.05 μ g l⁻¹; *cf.* Table 1).

Figure 2 illustrates the alkyl homolog distributions (AHD) of the naphthalene (C_nH_{2n-12}) , phenanthrene/anthracene (C_nH_{2n-18}) , dibenzothiophene $(C_nH_{2n-16}S)$ and fluoranthene/pyrene (C_nH_{2n-22}) series for the September effluent sample. The compositions depicted in this figure are representative of all of the samples with some minor exceptions discussed below. In all cases, the AHDs are dominated by the C2-3 homologs rather than the parent compounds. This agrees with findings of Barrick¹⁸ and further supports an uncombusted fossil fuel origin for the majority of these compounds.³⁶ The naphthalene series is either absent or in low abundance in combustion particles,^{58,59} whereas the phenanthrene/anthracene series represents an overlap between the two sources. In contrast, the fluoranthene/pyrene series is typically found in small quantities in crude oil, while it often represents the most abundant PAH in soot, atmospheric particles and marine sediments.^{11,47,59,60} For this reason, Sporst ϕ l et al.⁵⁹ have suggested that the fluoranthene/pyrene series is a more definitive indicator of combustion vs. fossil sources for the higher molecular weight PAH. Based on the relatively low abundance of these tetracyclic compounds (F/P + C_{1-3} -homologs $\leq ca.$ 2% total PAH) in the effluent and the prevalence of their higher alkylated homologs, contributions of combustion products to the higher molecular weight PAH pool in these effluent samples would appear to be small. Similar conclusions were reached by Baird et al.⁵⁷ who examined the LACSD effluent in 1987.

Close examination of the ΣC_1 -phenanthrene/phenanthrene ratio, however, suggests that lower values are generally found for samples having higher relative abundances of the 4-5 ring PAH (Table 1). In the case of the July and October samples, the ratios are less than 1.0. These particular samples also exhibit fluoranthene + pyrene concentrations that exceed 2% of total PAH and are only slightly less abundant than the higher alkylated homologs (Table 1). Although the effect is minor, these trends indicate that some

combustion-derived PAH are present in the effluent and constitute a variable component of the higher molecular weight species. Unlike treatment systems such as the METRO in Seattle,¹⁸ the LACSD plant is largely decoupled from inputs due to surface runoff. Consequently, pyrogenic PAH are unlikely to arise from contributions by surface runoff. (This may also account for the lack of any discernable seasonal pattern in the PAH composition and/or concentrations.) Products of high temperature catalytic cracking or other industrial pyrolytic processes,^{61,62} on the other hand, might reasonably be expected to be entering the system. Another possible source are the wastes generated by car washes, gasoline stations and other vehicular service industries.⁶³

It is also interesting to note that the fluoranthene/pyrene ratio is, with one exception (sample taken 12/79), less than unity in all effluent samples (mean $\pm 1\sigma = 0.40 \pm$ 0.27). In 1987, Baird *et al.*⁵⁷ reported similar ratios for the LACSD effluent (mean $\pm 1\sigma =$ 0.65 \pm 0.49). The fluoranthene/pyrene ratio is almost universally near or greater than one in combustion particles, atmospheric aerosols and sediments contaminated by pyrogenic sources.^{1,2,11,14,15,22,34,37,38,48} In contrast, crude oils and refined petroleum products typically show ratios less than 1.0.^{11,64} This again signals a dominantly petroleum origin for the high molecular weight PAH in the effluent. Comparable data for municipal wastewater effluents were reported by Grzybowski *et al.*⁵⁰ who found fluoranthene and pyrene concentrations within ranges of 0.5-5.0 and 11.0-27.0 µg l⁻¹, respectively.

Estimation of Mass Emission Rates

Table 2 presents a summary of the mass emission rates of the individual and Σ PAH from the LACSD plant for the year 1979. These data were developed by applying the concentrations determined for each monthly sample to the flow for that date. The daily mass emissions were then multiplied by the number of days in each month, and the monthly estimates were summed to produce an annual figure. Also provided are estimates reported by Barrick¹⁸ for the Seattle METRO treatment plant during the period 1977-

1979. With the exception of phenanthrene, these data represent particulate concentrations. The particulate-based data are comparable with those reported here (i.e. total concentrations) because the vast majority of the higher molecular weight PAH in municipal wastes and urban runoff^{17,57} are associated with filterable (0.45-1.2 μ m) particulate matter.

If one computes the ratio of annual mass emissions of individual PAH for the LACSD and METRO effluents, it is apparent that the LACSD discharge rate greatly exceeds that of the METRO (LACSD/METRO: range-8-50, mean-33.4). Normalization of mass emissions to the population served reduces the difference to factors ranging from 1.0 to 6.4 (mean LACSD/METRO=4.3). By comparison, the average ratio (of daily per capita mass emissions) for total hydrocarbons is 5.9/3.12 = 1.89.^{18,52} Thus, the LACSD effluent would appear to have been discharging significantly greater amounts of hydrocarbons and, especially, PAH to coastal waters of the southern California Bight during 1979 than the METRO plant was to Puget Sound. This probably reflects the large petrochemical input to the former. Recent work by Baird et al.⁵⁷ has revealed significantly lower concentrations of PAH in the LACSD effluent (Table 1). With the exception of naphthalene, individual PAH and associated alkylated homolog groups appear to have been present in lower concentrations in 1987 than they were in 1979 by more than an order of magnitude. This is probably due to a combination of industrial source control and improvements in treatment. Between 1979 and 1987, the fraction of effluent that received full secondary treatment at the LACSD changed from 0 to 54%. However, it is more likely that the reduction in PAH emissions during this period was achieved by aggressive source control measures as evidenced by the nearly parallel decreasing trends in influent and effluent oil and grease mass inputs starting in the late 1970s.65

PAH in Sediments

PAH Composition and Sources

Table 3 summarizes the PAH composition of surficial (0-2 cm) sediments collected from station 3C1 (*cf.* Figure 1) on the Palos Verdes Shelf. Data are also provided from two investigations^{56,66} in which surficial sediments were analyzed for PAH at station 7C, in close proximity to the outfall termini (*cf.* Figure 1).

In the case of the 3C1 sediments, di- and tricyclic PAH were not detected in the 0-2 cm section, and Σ PAH concentrations were 1.25 μ g dry g⁻¹. By comparison, significant amounts of di- and tricyclic PAH were found in sediments collected at station 7C, and the concentration of Σ PAH in these sediments is more than a factor of five greater (7.04 μ g g⁻¹). These differences probably reflect variations in sediment accumulation rates of waste-derived particles at the two sites (see below; Kettenring⁶⁷). Deeper sections of the 3C1 core were found to contain small, but measurable, quantities of phenanthrene, anthracene and their alkylated homologs. However, the lower molecular weight species (e.g. naphthalene, biphenyl, etc...) were generally below detection limits. Gas chromatograms of the f2 fractions of all core sections reveal an unresolved complex mixture similar to that reported by Venkatesan et al.¹⁰ for sediments from San Pedro Basin. The resolved PAH represent only a small fraction of the total aromatics isolated in the f2 fraction. Examination of the AHDs for the fluoranthene/pyrene series in the 3C1 sediments (Figure 3) typically show increasing amounts of higher alkylated homologs up to at least the C₄-substituted species, indicating a petroleum origin. Similar trends have been reported by Venkatesan et al.³⁸ for surface (0-5 mm) sediments from the San Pedro Basin floor. Moreover, the F/P ratios in the 3C1 sediments range from 0.13 to 0.75 (mean $\pm 1\sigma =$ 0.42 ± 0.22) and are essentially indistinguishable from ratios reported in Table 1 for the LACSD effluent (mean $\pm 1\sigma = 0.40 \pm 0.27$). Because of the occurrence of submarine oil seepage in this region,^{68,69} however, the PAH in these sediments probably originate from a combination of petroleum residues discharged from the LACSD outfall system and natural oil seepage. Similarities between the distribution of higher molecular weight PAH found in

the effluent and near surface sediments at 3C1 (Figure 4) are suggestive of a linkage between the waste discharge and the sedimentary PAH.

Recent work by Eganhouse and Kaplan⁵³ has shown that the vast majority (85-100%) of the hydrocarbons found in the upper 24 cm of this core are derived from municipal effluent. These authors found correlations between the vertical distribution of specific molecular markers of the LACSD effluent (e.g. linear alkylbenzenes, DDT) and oil seepage $(17\alpha(H), 18\alpha(H), 21\beta(H), 28, 30$ -bisnorhopane) and the historical discharge of wastes from the LACSD treatment plant. Some of these results are summarized in Figure 5, where vertical concentration profiles of Σ PAH, total hydrocarbons and the $17 \propto$ (H), $18 \propto$ (H), 21β (H)-28, 30-bisnorhopane/hopane ratios are provided. The bisnorhopane (C_{28}^{*}) is a pentacylcic triterpane found abundantly in the Monterey shale and California oils (cf. references in Simoneit and Kaplan⁶⁸) but only in trace quantities in the LACSD effluent.^{19,53} Because of the restricted occurrence of this compound in other (non-California) oils and its pervasive distribution in sediments in this region, the bisnorhopane has been proposed as a unique molecular indicator of natural seepage in the southern California Bight.⁶⁸ Hopane, on the other hand, is an ubiquitous constituent of fossil organic matter and is used here as a normalizing factor to distinguish between the effluent (C_{28}^* /hopane ratio < 0.09) and seepage oil (C_{28}^* /hopane ratios > 1.0).⁵³

In this figure, the concentration of total hydrocarbons exhibits a distinct maximum at a sub-bottom depth of 6-8 cm, declines rapidly at greater depth and reaches apparent background levels at *ca*. 24 cm. The subsurface maximum has been assigned a tentative date of *ca*. 1971 because this corresponds to the year of maximum solids emissions from the LACSD,⁶⁵ whereas the 22-24 cm horizon is believed to correspond to *ca*. 1950, a period when waste discharges to the shelf began to become important.^{55,65,70} Other effluentderived contaminants show subsurface maxima at the same depth in these sediments,^{55,56} and Eganhouse and Kaplan⁵³ have demonstrated strong correlations among concentrations of organic carbon, organic nitrogen, extractable organics and THC. Together, these results

support the hypothesis that the sediment profiles record the history of waste emissions to the Palos Verdes Shelf. By comparison, the Σ PAH concentration appears to increase irregularly downcore to ca. the 16-18 cm section. Thereafter, concentrations decline with increasing depth until near-background levels are reached, again at ca. 24 cm. The elevated **DPAH** concentrations in the upper 24 cm of this core approximate the trends for total hydrocarbons and organic carbon, indicating that these related organic compound groups probably originate from the same source. However, a well-defined subsurface maximum is not apparent for the PAH, and the highest concentration is found at a greater sub-bottom depth than the THC maximum. Assuming these discrepancies cannot be ascribed to diagenetic effects, the patterns suggest that historical changes in the emissions of solids from the LACSD plant alone did not control the accumulation rates of PAH in these sediments. The trend for the C_{28}^* /hopane ratio (Figure 5) is essentially the reverse of that exhibited by the PAH and THC, with highest ratios (i.e. greatest seepage inputs) found within the 34-36 cm section. This is consistent with the hypothesis that the input of wastewater hydrocarbons (and, therefore, the PAH) has dominated contributions made by natural seepage over the time period represented by the upper 34 cm of this core.⁵³

Figure 4 shows PAH distributions for the LACSD effluent (9/79), the 2-4 cm section of core 3C1 and a sample of the Redondo oil seep⁶⁹ (for sampling locations see Figure 1). Differences between the seep and effluent PAH distributions include: 1) the absence of benzo[k]fluoranthene and 9,10-diphenylanthracene in the effluent (*cf.* Table 1) the absence of dibenz[*a,h*]anthracene from the seep material, and 3) the greater relative abundance of perylene in the seep oil. Examination of the PAH distribution in the core sediments indicates that both benzo[k]fluoranthene and 9,10-diphenylanthracene were undetected, dibenz[*a,h*]anthracene is present in approximately the same amount (relative to benzo[*ghi*]perylene) as found in the effluent sample, and perylene is less abundant than the benzopyrenes, unlike the seep oil. These relations strongly suggest that the PAH in nearsurface sediments at 3C1 are dominated by waste, not seepage, inputs. The same patterns

are found throughout the core with one exception: the abundance of perylene relative to the benzopyrenes is somewhat variable.

Short-term Biogeochemical Fate of Waste-derived PAH

The behavior and fate of PAH in aquatic environments may depend upon the phases with which these compounds become associated during formation.^{42,43} For example, it has recently been suggested that PAH present in combustion particles may be occluded within the ash or soot matrix and thereby be prevented from release to surrounding waters.⁴² This is thought to account for the extreme uniformity of PAH composition in a sediment core collected in the Tamar Estuary.⁴⁴ Oil-derived PAH, on the other hand, are expected to be largely adsorbed to surfaces of particles or present as agglomerations where they are more readily available for release and metabolism. Based on the earlier discussions, it is clear that the PAH associated with the LACSD effluent particles (including the four-six ring compounds) are largely petroleum derived. It is, therefore, likely that these PAH would be subject to exchange during and after sedimentation.

Comparison of data provided in Tables 1 and 3 indicates that virtually all of the two and three ring PAH which dominate effluent compositions are absent in surficial sediments at station 3C1. These compounds are sufficiently soluble in water that a significant portion would be expected to be present in the dissolved phase of the effluent. This expectation is, in fact, met.⁵⁷ However, the absence of two and three ring PAH in the sediments indicates that the particle-bound fraction of these compounds are effectively removed prior to incorporation of waste particles into the sediments at station 3C1. The higher molecular weight PAH (four-six rings) have very low solubilities in water and strongly sorb to particulate matter.⁶² Not surprisingly, they are found entirely in the filterable particulate phase (i.e. < ca. 0.5μ m) of the effluent.⁵⁷ and they are the dominant PAH in the sediments.

One means of estimating the magnitude of PAH removal during sedimentation is by

comparing the particulate organic carbon-normalized concentrations of PAH in the effluent and in surficial sediments. Because of the difficulty of detecting all of the 4-6 ring PAH in many of the effluent samples, we have selected the September 1979 sample (which exhibited the highest concentrations of high molecular weight PAH) for purposes of comparison. As noted earlier, these compounds are entirely associated with filterable particulate matter. Thus, it is reasonable to compute POC-normalized concentrations for the effluent sample. The organic carbon-normalized concentrations for each compound (sediments) exhibited no discernible trend with depth, and given the time period over which the sediments in this core were presumbably deposited, the variation was surprisingly low. One exception is that the concentrations of all compounds tended to maximize at a depth of 16-18 cm. As noted earlier, this may correspond to a period of intense PAH input to the LACSD plant.

When one compares the PAH concentrations in the 2-4 cm sediment section with those obtained for the September effluent sample (Table 4) and then computes the difference as a percentage, apparent "losses" of 40-96% are obtained for individual PAH. This computation assumes that the organic carbon is refractory, which is clearly not the case. Investigating the short-term decomposition of LACSD effluent particles in coastal waters, Myers⁷⁰ found organic carbon concentration to decrease by approximately 25% within a period of *ca*. 1 week. If such a correction is applied to the present data to account for loss of particulate organic carbon, one finds that the "apparent losses" range from 47-112%. Given the uncertainties associated with use of the September effluent sample and Myers' estimates for the decomposition of organic carbon, the corrected losses fall within an acceptable range. More importantly, however, the magnitude of the lost fraction appears to be inversely related to the log solubility of the compound (Figure 6). The data depicted in this figure suggest that PAH having solubilities lower than approximately 10⁻⁷ moles liter⁻¹ are lost during the earliest stages of sedimentation.

A similar exercise can be performed using the total hydrocarbon concentration as normalizing factor (Table 5, Figure 6). In this case, one must assume that the character of the hydrocarbons discharged by the LACSD through time has not changed significantly. Judging from the uniformity of the high resolution gas chromatographic profiles of the total hydrocarbon fractions of effluent samples taken over a 12 month period¹⁹ and from sediments throughout the 3C1 core,⁵³ this assumption seems tenable. The estimated fraction of "lost" PAH ranges from 21-95%. Agreement between estimates based on OCnormalized and THC-normalized concentrations is quite good for the more soluble compounds. In the extreme case of benzo[ghi]perylene, differences in estimates of the lost fraction fall within a factor of 1.9. The discrepancy may indicate a greater relative lability of the hydrocarbons (compared with total organic carbon). Although the magnitude of the "lost fraction" of the high molecular weight PAH remains uncertain, it is systematically related to the solubility of the individual PAH. Examination of Figures 2 and 3 shows that the fluoranthene/pyrene AHDs of effluent and sediments are different. The effluent exhibits a maximum at the C₃-alkyl homolog, whereas the sediment AHD more typically shows a monotonic increase in abundance with degree of alkylation.³⁸ Because the log solubilities of PAH within a homology decrease linearly with increasing molar volume,⁷¹ this difference is another manifestation of solubility-controlled removal.

Several processes may be responsible for the compositional changes that take place between the time of discharge and the accumulation of effluent-derived PAH in bottom sediments. The most important of these are: desorption and biological degradation. Photochemical oxidation is unlikely to be significant because the wastewater effluent is discharged below the thermocline, and, except under unusual circumstances during nonstratified conditions, effluent particles do not enter the photic zone. Numerous studies of the the desorption kinetics of hydrophobic organic compounds have demonstrated that sorbate release occurs in two phases: a rapid desorption step in which 25-60% of the sorbate is released within minutes to hours and slow desorption of the remainder over a

time scale of days to months.⁷²⁻⁷⁵ Once discharged, the effluent experiences rapid dilution with seawater in the range of 100:1 to 300:1. Consequently, rapid desorption of the PAH from effluent particles during initial dilution could account for release of as much as 25-60% of the PAH. The fact that virtually all of the two and three ring PAH in the effluent are absent from sediments heavily impacted by the discharge indicates that if desorption were the only process involved during sedimentation of effluent particles, it must have taken place over time scales in excess of hours. This is consistent with estimates of the average time that effluent particles require to reach the bottom on this part of the shelf (days) and the likelihood that once deposited, most of the particles experience repeated resuspension and redeposition prior to incorporation into the permanent sediments. In effect, this would act to increase their residence time in the water column.

Karickhoff⁷² and Karickhoff and Morriss⁷³ presented a sorption kinetics model consisting of "labile" and "non-labile" compartments that simulated the results of laboratory desorption experiments. They showed that the slow desorption step could be characterized by a rate constant, k_d , that was inversely related to the equilibrium partition coefficient, K_p , of a given hydrophobic organic substance. Rate constants ranging from 0.49 hr⁻¹ (naphthalene) to 0.031 hr⁻¹ (pyrene) were reported. Similar results were obtained by Wu and Gschwend⁷⁴ who developed a radial diffusion model to simulate sorption-desorption kinetics. In the latter case, experimental data could be fitted using a single effective diffusivity parameter, D_{eff} , which again was inversely related with K_p . The common conceptual feature of these two models is the requirement that desorption (and adsorption) rates are limited by diffusive processes occurring within particle pores, the sorbent matrix and/or intraggregate pore spaces. Regardless which mechanism(s) or matrix is most important, the experimental data suggest that the more hydrophobic (i.e. less soluble) PAH should desorb more slowly from particles. Thus, desorption kinetics could explain the trend of increasing PAH loss with increasing solubility (Figure 6).

At the same time, numerous microcosm studies have demonstrated that the rate at which PAH are degraded by microorganisms in the water column and sediments increases with decreasing molecular size (i.e. increasing solubility).^{39,41,76,77} Within the water column higher molecular weight PAH are particularly susceptible to photodegradation,^{76,78} whereas the lower molecular weight species (e.g. naphthalene, phenanthrene, anthracene) are removed primarily by evaporation and microbial degradation. Hinga et al.⁷⁹ reported little biodegradation of benz[a]anthracene within the water column of a marine mesocosm. Rather, metabolism was found to occur in surface (0-1 cm) sediments; degradation was apparently slowed in deeper anoxic layers. Herbes³⁹ was unable to establish degradation of 4 and 5-ring PAH (i.e. benzo[a]pyrene and dibenz[a,h]anthracene) in incubated sediments taken downstream of a coal-coking plant, whereas 2 and 3-ring compounds showed measurable degradation in both water and sediment compartments. Gardner et al.⁸⁰ also noted that rate of PAH removal in sediments decreases with increasing molecular weight and reduced oxygen availability. This effect of redox conditions has been confirmed by others.⁸¹ Together these results suggest that the lower molecular weight species are probably rapidly removed during sedimentation by a combination of desorption and biodegradation. Transport times for effluent particles through the water column are expected to be on the order of days. Judging from the results of previous microcosm experiments (which were conducted on similar time scales), the residence time of effluent particles in the water column is probably insufficient to bring about the complete physical release of the high molecular weight PAH. Consequently, the partial losses of 4-, 5- and 6ring PAH largely occur after initial deposition during the period when the particles reside within the oxidizing layer of the surface sediments.

Post-depositional Alteration

The foregoing discussion points to differential rates of removal for the higher molecular weight PAH within the surface layers of the sediments on the Palos Verdes

Shelf. If kinetically-controlled removal (i.e. coupled desorption and metabolism) of 4-, 5and 6-ring PAH were to continue following incorporation and burial of effluent particles, one would expect to see systematic changes in PAH composition with increasing subbottom depth. (This assumes, of course, that the quality of the source PAH has not changed significantly with time.) Such systematic changes over time have been reported for lower molecular weight species (i.e. naphthalenes and phenanthrenes) introduced to intertidal sediments during a fuel oil spill²³ and in microcosm studies.⁷⁷ However, Readman *et al.*⁴⁴ observed uniform higher molecular weight PAH compositions throughout a 50 cm core from the Tamar Estuary. In the latter case, the lack of compositional variation with depth was attributed to the occlusion of (predominantly) pyrogenic PAH in the source particles. Examination of downcore variations in PAH composition at station 3C1 should reveal whether kinetically-controlled removal continues after burial.

Table 6 presents a Pearson correlation matrix for sediment concentrations of ten 4-, 5- and 6-ring PAH in the 3C1 core. All correlations are significant (p value ≤ 0.001). High correlation coefficients are found for many pairs. However, the best coefficients were generally obtained when both PAH were present in higher concentrations, presumably the result of improved analytical precision. In general, these correlations suggest that kinetically-controlled, compound-specific removal of these higher molecular weight PAH is not occurring during burial. This is nicely illustrated in Figure 7 which shows a scatterplot of pyrene *vs.* benzo[*ghi*]perylene. As discussed earlier (Tables 4 and 5, Figure 6), these two compounds represent extremes with respect to apparent PAH removal rates during the earliest stages of sedimentation. Nevertheless, the relative abundances of these PAH are maintained throughout the core. Although no data are available on the variation of redox conditions with sub-bottom depth at 3C1, it is known that the presence of hydrogen sulfide in surface sediments has varied in response to wastewater solids emissions and advances by the echiuran, *Listriolobus pelodes*.⁸² Because of the high depositional flux of labile organic matter at this site, it is presumed that the sediments are anoxic only a short distance below

the sediment-water interface. Under these conditions, the resistance of all PAH to biodegradation would be enhanced.⁷⁹⁻⁸¹ In contrast to the findings of Readman *et al.*⁴⁴ for sedimentary PAH in the Tamar Estuary, the PAH in these sediments are derived primarily from uncombusted petroleum. Consequently, the compositional uniformity of the PAH cannot be attributed to occlusion within combustion particles. Exchange of the high molecular weight PAH between porewaters and the overlying water column (or deeper in the core) by molecular diffusion and/or tranport in association with porewater colloids is limited by the hydrophobicity of these compounds and the lack of significant porewater advection at depth.⁸³ Thus, the virtual cessation of PAH degradation, presumably in response to the onset of reducing conditions within the sediment, is the most plausible explanation for the uniformity of PAH composition in these sediments.

Historical Accumulation Rates of PAH

Using tentative assignments for the ages of different depths of this core,⁵³ one can calculate average accumulation rates of total and individual PAH on the Palos Verdes Shelf. Table 7 presents estimates based on such calculations. Although approximate, these estimates show that the average accumulation rates of individual and total PAH after *ca*. 1950 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 subsequent to 1950. The rates determined for deep sections of the core (i.e. >24 cm) are similar to those reported by Gschwend and Hites¹¹ for sediments near urban centers such as Boston Harbor and Buzzards Bay, MA and by Barrick¹⁸ for a site within Central Puget Sound near the Seattle METRO wastewater outfall (Table 7). They are, however, at least an order of magnitude higher than those found at remote locations where sedimentary fluxes are dominated by atmospheric deposition.^{11,15} This suggests that even the deeper sections of the 3C1 core, predating 1950, may have been heavily influenced by local inputs of fossil PAH, with direct atmospheric deposition playing only a minor role.

CONCLUSIONS

The LACSD treats and discharges wastes originating from a multitude of domestic and industrial sources. To the extent that it receives an unusually large proportion of petrochemical wastes and little surface runoff, it may be considered an uncommon municipal treatment plant. These factors undoubtedly influence the composition and quantity of PAH in its effluent. We estimate that as of 1979 the LACSD discharged approximately 110 metric tons PAH yr⁻¹. Present indications suggest that the LACSD may have reduced emissions of PAH to the ocean by more than order of magnitude during the period 1979-87, mostly as a result of source control. This reinforces the effectiveness of source control measures (as opposed to treatment upgrades) in large centralized urban treatment systems.

The vast majority of the PAH in the LACSD effluent are of petroleum origin and consist of lower molecular weight species (2- and 3-ring PAH) and their alkylated homologs. Upon discharge to the ocean, these compounds are apparently rapidly removed such that little, if any, evidence of them are found in heavily contaminated surficial sediments 6 km downcurrent from the outfall system. The effluent particles are probably buried too rapidly for complete release/removal of the higher molecular weight PAH (4-, 5- and 6-ring compounds). Nevertheless, a fraction of these compounds appears to be lost prior to incorporation into the permanent sediments. The extent of removal is directly related to (the logarithm of) their aqueous solubility. Thus, the 6-ring PAH tend to survive better than the 4- and 5- ring PAH. It is unclear whether these changes are brought about by simple physical release (desorption), microbial degradation processes or both. However, once incorporated into the sediments, the composition of the high molecular weight PAH does not change with time. Either they are metabolized at identical rates or not metabolized at all. Evidence from other microcosm studies suggests that under the reducing conditions that prevail below the sediment-water interface at this site, the latter

hypothesis is more likely. Because the PAH in these sediments are of petroleum (rather than a combustion) origin, physical occlusion (as proposed for pyrogenic PAH) should not be regarded as a unique prerequisite for preservation in the sedimentary column.

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- Figure 1. Location of the LACSD outfall system, sediment sampling stations (3C1 and 7C) and the Redondo oil seep.
- Figure 2. Distribution of naphthalene (C_nH_{2n-12}), phenanthrene/anthracene (C_nH_{2n-18}), dibenzothiophene ($C_nH_{2n-16}S$) and fluoranthene/pyrene (C_nH_{2n-22}) alkyl homolog series for LACSD effluent sample taken 9/13/79. Abundances are based on summation of integrated molecular ion current for each level of alkylation.
- Figure 3. Distribution of fluoranthene/pyrene alkyl homolog series for sediment sections from core 3C1. Abundances are based on summation of integreated molecular ion current for each level of alkylation.
- Figure 4. Composition of PAH in LACSD final effluent (9/79), near surface sediments (2-4 cm) from station 3C1 and a sample of the Redondo oil seep. For compound names see Table 1.
- Figure 5. Vertical concentration profiles of total PAH and total hydrocarbons and the 17 (H),18 (H),21 (H)-28,30-bisnorhopane/hopane ratio in the 3C1 core.
- Figure 6. Per cent PAH lost during early sedimentation vs. log molar solubility of 4-,5and 6-ring PAH in sediments of core 3C1.
- Figure 7. Scatter diagram of pyrene vs. benzo[ghi]perylene concentration in sediments of core 3C1. Line and equation represent results of linear regression analysis.

Compound ^a	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Dec	Mean	1987 ^b
Naph	7.0	3.7	1.7	16.3	7.4	1.7	17.8	13.0	8.1	6.9	2.0	7.8	3.92
ΣC ₁ -Naph	16.2	15.5	22.2	53.3	19.3	12.6	21.3	7.5	22.8	13.7	10.6	23.2	4.85
ΣC_2 -Naph	30.1	26.6	46.7	81.5	25.3	29.4	24.9	75.8	45.3	21.2	16.3	38.5	
ΣC ₃ -Naph	45.9	38.2	90.0	134.4	46.4	54.4	40.4	121.0	87.8	37.3	30.6	66.0	
Biphenyl	1.8	1.2	4.6	5.7	2.8	2.5	5.9	6.6	2.9	2.9	4.4	3.7	
Aceny	c						2.3			0.6		0.3	
Acenaph			1.3	2.0			1.8	2.0	1.3	0.7		0.8	0.03
Fluorene	1.4	0.7	2.6	3.3	1.2	1.8	5.4	3.6	2.7	4.2	1.1	2.5	
Phen	7.1	5.4	15.3	17.5	7.8	9.6	21.0	19.7	18.0	23.6	5.8	13.7	0.99
ΣC_1 -Phen/A	13.7	11.4	22.3	37.4	12.4	19.3	15.8	36.6	37.8	20.4	9.8	21.5	
ΣC ₂ -Phen/A	11.3	8.4	48.8	34.9	10.7	16.3	10.9	35.4	55.8	16.6	8.4	23.4	
ΣC ₃ -Phen/A	3.6	1.9	6.1	15.6	5.2	7.6	4.3	17.3	36.8	6.9	2.6	9.8	
Anthracene			0.8	1.4			2.3	1.2	1.0	2.2	0.9	0.9	
Fluoran	0.4		1.1	1.0	0.7	0.5	2.3	0.9	1.4	2.4	1.3	1.1	0.03
Pyrene	1.5	0.6	2.4	2.7	1.3	1.6	4.7	3.8	5.5	5.0	1.2	2.8	0.04
B[a]Anthr				0.7	0.4	0.6	1.4	1.1	3.8	1.8	0.8	1.0	0.09
Chrys/Tri	0.5		0.2	1.4	1.4	1.4	2,4	2.9	9.6	3.1		2.1	
B[b]Fluoran						0.3		2.0	0.3		0.2	0.02	
B[k]Fluoran													
B[e]Pyrene				0.3		0.3	0.6	0.5	2.7	0.5		0.4	0.06
B[a]Pyrene							0.6	0.2	2.5	0.4		0.3	0.02
Perylene				•					0.7	1		<0.1	0.01
9,10-DPA										1			
DB[a,h]Anthr									0.3			<0.1	
B[ghi]Peryl									0.7	1	·	<0.1	
ΣPAH ^d	138.7	112.5	261.6	403.6	139.4	157.1	180.5	382.5	346.8	167.7	91.4	216.5	•••• ¹¹ • •
% 2,3-ring ^e	98.3	99.5	98.6	98.5	97.3	97.2	93.2	97.5	91.5	92.0	96.5	96,4	
% Naph+f	71.5	74.7	61.4	70.8	70.6	62.5	57.8	67.2	47.3	47.2	65.1	63.3	
ΣC_1 -Phen/Phen	1.9	2.1	1.5	2.1	1.6	2.0	0.8	1.9	2.1	0.9	1.7	1.7	1.26
Fluoran/Pyrene	0.24	0.00	0.45	0.38	0.51	0.31	0.49	0.23	0.25	0.47	1.09	0.40	0.65

Table 1. Concentration of PAH in LACSD final effluent (µg liter⁻¹) during 1979, 1987.

Naph = Naphthalene; Aceny = Acenaphthylene; Acenaph = Acenaphthalene; Phen = Phenanthrene; Fluoran = Fluoranthene; B[a]Anthr = Benz[a]Anthracene; Chrys/Tri = Chrysene/Triphenylene;
B[b]Fluoran = Benzo[b]Fluoranthene; B[k]Fluoran = Benzo[k]Fluoranthene; B[a]Pyrene = Benzo[b]Fluoran = Benzo[a]Pyrene; 9,10-DPA = 9,10-Diphenylanthracene;

DB[a,h]Anthr = Dibenz[a,h]Anthracene; B[gh]Peryl = Benzo[gh]Perylene.

b Data for 1987 mean concentrations reported by Baird et al.⁵⁷

c Not detected.

^d Σ PAH=Summation of individual PAH excluding biphenyl.

e 2,3-ring=Naphthalene, phenanthrene, anthracene + alkylated homologs.

^f Naph + = Naphthalene + alkylated homologs.

· · · · · · · · · · · · · · · · · · ·	MER	(mta)	Per cap (mg ca	ita MER p ⁻¹ d ⁻¹)
Compound ^a	LACSDb	METRO	LACSD	METRO
Naph	3.99		2.99	
ΣC_1 -Naph	11.9		8.94	
ΣC_2 -Naph	19.7 -		14.8	
ΣC ₃ -Naph	33.8		25.4	
Biphenyl	1.91		1.44	
Aceny	0.13		0.10	
Acenaph	0.43		0.32	
Fluorene	1.30		0.98	
Phen	7.00	0.18	5.26	0.9
ΣC_1 -Phen/A	11.0	0.22	8.24	1.2
ΣC_2 -Phen/A	11.9	0.25	8.94	1.4
ΣC_3 -Phen/A	4.92		3.70	
Anthracene	0.45		0.34	
Fluoran	0.55	0.067	0.41	0.4
Pyrene	1.40		1.05	
B[a]Anthr	0.94	0.014	0.36	0.08
Chrys/Tri	0.48	0.028	0.78	0.2
B[b]Fluoran	0.11	_	0.08	
B[e]Pyrene	0.22	0.013	0.17	0.07
B[a]Pyrene	0.17		0.12	
Perviene	0.03		0.02	
DB[ah]Anthr	0.01		0.01	
B[ghi]Peryl	0.03		0.02	
ΣPAH ^d	110.5		83.0	

Table 2. Mass emission rates (metric tons yr⁻¹) of individual PAH from the LACSD and Seattle METRO wastewater treatment plants.

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Compound names given in Table 1. This study. Effluent samples collected 1979. Data from Barrick¹⁸ for effluent collected 1977-1979. Σ PAH=Summation of individual PAH excluding biphenyl. d

	PA	ry g ')		
Compound ^a	This study ^b (3C1; 1981)	Swartz et al. ⁶⁶ (7C; 1980)	Anderson and Gossett ⁵⁶ (7C; 1986)	
Naph	c	29	87	
ΣC1-Naph		NRd	104	
ΣC_2 -Naph		NR	415	
ΣC_3 -Naph	#	NR	462	
Biphenyl		NR	22	
Aceny		160	57	
Acenaph		NR		
Fluorene		NR	16	
Phen		290	197	
ΣC ₁ -Phen/A		NR	773	
ΣC_2 -Phen/A		NR	1193	
ΣC_3 -Phen/A		NR	701	
Anthracene		623	52	
Fluoran	17	294	157	
Pyrene	127	838	401	
B[a]Anthr	36	1330	166	
Chrys/Tri	- 88	606	274	
B[b]Fluoran	207	633	746	
B[e]Pyrene	217	NR	317	
B[a]Pyrene	212	NR	323	
Perylene	105	NR	353	
9,10-DPA		NR	4	
DB[a,h]Anthr	38	NR	NR	
B[ghi]Peryl	205	NR	217	
ΣΡΑΗ	1252		7037	

Table 3. PAH concentrations (ng dry g ⁻¹) in s	sediments of the Palos Verdes Shelf
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Compound names given in Table 1. Data are for 0-2 cm section. а

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С Below detection limit.

d Not reported.

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	Concentration (μ g g OC ⁻¹)						
Compound ^a	Effluent	Sediments	"% PAH Lost" ^b				
Fluoran	13.8	1.55	88.8				
Pyrene	54.8	5.25	90.4				
B[a]Anthr	37.8	1.95	94.8				
Chrys/Tri	95.7 *	3.74	96.1				
B[b]Fluoran	19.6	5.79	71.4				
B[e]Pyrene	26.9	5.06	81.2				
B[a]Pyrene	24.5	5.22	78.7				
Perylene	7.3	3.15	56.8				
DB[a,h]Anthr	3.2	1.5	53.0				
B[ghi]Peryl	7.3	4.37	40.2				
ΣΡΑΗ	3459	42.0	98.8				

Table 4. Organic carbon normalized PAH concentrations (μ g g OC⁻¹) in LACSD effluent (9/13/79) and near surface sediments (2-4 cm) from core 3C1.

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Compound names given in Table 1. % PAH lost is caculated as {1-[Conc.sed/Conc.eff]} • 100.

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Compound ^a	Effluent	Sediments	"% PAH Lost" ^b	
Fluoran	76.5	11.3	85.3	
Pyrene	303	38.1	87.4	
B[a]Anthr	209	14.2	93.2	
Chrys/Tri	530 ~	27.2	94.9	
B[b]Fluoran	108	42.0	61.2	
B[e]Pyrene	149	36.7	75.4	
B[a]Pyrene	136	37,9	72.1	
Perylene	40.3	22.9	43.2	
DB[a,h]Anthr	17.7	10.9	38.3	
B[ghi]Peryl	40.4	31.7	21.5	
ΣΡΑΗ	19300	304.6	98.4	

Table 5. Total hydrocarbon normalized PAH concentrations (mg g THC⁻¹) in LACSD effluent (9/13/79) and near surface sediments (2-4 cm) from core 3C1

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Compound names given in Table 1. % PAH lost is caculated as {1-[Conc.sed/Conc.eff]]} • 100.

	Fluoran	Pyrene	B[a]Anthr	Chrys/Tri	B[b]Fluoran	B[e]Pyrene	B[a]Pyrene	Perylene	DB[a,h]Anthr
Fluoran	1.000	*	*	*	*	*	* :	*	*
Pyrene	.921	1.000	*	*	*	*	*	*	*
B[a]Anthr	.936	.961	1.000	*	*	*	*	*	*
Chrys/Tri	.836	.909	.897	1.000	*	*	*	*	*
B[b]Fluoran	.894	.959	.909	.898	1.000	*	*	*	*
B[e]Pyrene	.904	.950	.901	.910	.979	1.000	*	*	*
B[a]Pyrene	.842	.924	.886	.905	.967	.982	1.000	*	*
Perylene	.800	.942	.855	.849	.972	.929	.933	1.000	*
DB[a,h]Anthr	.860	.751	(.731)	(.707)	.805	.865	.828	(.695)	1.000
B[<i>ghi</i>]Peryl	.878	.944	.924	.863	.979	.940	.931	.952	(.730)

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Table 6. Pearson correlation matrix for PAH concentrations in core sediments.^a

p = <.001 for all values except for those in parentheses which were p = .001. Compound names given in Table 1. а

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Depth Ap Interval (cm)	Approximate	Accumulation rate (ng cm ⁻² yr ⁻¹)							
	Date Interval	Fluoran	Pyrene	B[a]Anthr	Chrys/Tri	B[e]Pyrene	B[a]Pyrene	ΣΡΑΗ	Site
0-8	1971-81	77	273	89	172	285	274	2280	Palos V.
8-14	1962-71	65	335	76	134	316	304	2660	
14-24	1950-62	117	283	80	124	333	276	2550	N
24-34	1937-50	18	28	8	12	25	23	228	Ŵ
Urban 1	900-present	37	39	19	23	14	17	_0	Boston H.
sites ^{a,b}	modern	46		19	30	23			Puget Snd.
Remote	present	3	2	0.8	1.5	1.5	0.8	•	Average
Sites(avg.) ^a	ca. 1950	4	ʻ 3	1.5	2.5	3	1.5		for 5
	ca. 1900	0.4	0.3	0.1	0.2	0.5	0.1		lacustrine sites
Atmospheric	1980	0.6	0.4				0.9		Seguim
Deposition ^d	1980	0.6	0.5				1.1		Quillayute

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Table 7. Average accumulation rates of PAH in sediments at station 3C1, 1981, and other sites.

After Gschwend and Hites.¹¹ After Barrick.¹⁸ а

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Not reported. After Prahl *et al.*¹⁵ d



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Relative Abundance













