

Distributions of Three- to Seven-Ring Polynuclear Aromatic Hydrocarbons on the Deep Sea Floor in the Central Pacific

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Three- to seven-ring parent and alkylated polynuclear aromatic hydrocarbons (PAHs) are determined in 20 deep sea surface sediments collected along a 175°E transect from 48°N to 15°S. The latitudinal distributions of PAHs except for perylene and retene show that they are low in the low latitudes (15°S–24°N) but remarkably increase from 27°N to 48°N. Concentrations of these PAHs at 48°N are 1–3 orders of magnitude higher than those of the lower latitudes. Similar latitudinal patterns of these PAHs suggest that they were transported as mixtures attached to some aerosol particles but not free forms.

Introduction

Polynuclear aromatic hydrocarbons (PAHs) are produced and released to the environment by combustion processes associated with industrial activities, power generation, woodburning, and automobile emissions which mainly occur in the midlatitude of the Northern Hemisphere (1–4). In contrast, biomass burning, another source of PAHs, occurs in the lower latitudes (5). In this study to understand the global fate of the PAHs we measured them in the deep sea surface sediments collected in the central Pacific from subarctic of the Northern Hemisphere to subtropical of the Southern Hemisphere. The deep sea sediments may reflect an averaged deposition pattern of PAHs during recent years, although some fraction of PAHs initially deposited to the ocean should have decomposed in the water column and sediments. Our primary purpose of this study is to reveal a latitudinal distribution of PAHs deposition on the deep sea floor. Based on the results we argue the processes and mechanisms to determine the distribution of PAHs.

Experimental Section

Sediment Samples. Twenty surface sediments were collected on a 175°E transect from 48°N to 15°S by a box-corer during the cruise of R/V *Hakurei-Maru* in 1992 and 1993 (Figure 1). Most sediments were recovered from water depths greater than 4500 m and are mainly composed of red clay (6). These sediments were stored in a freezer at –5 °C until analysis.

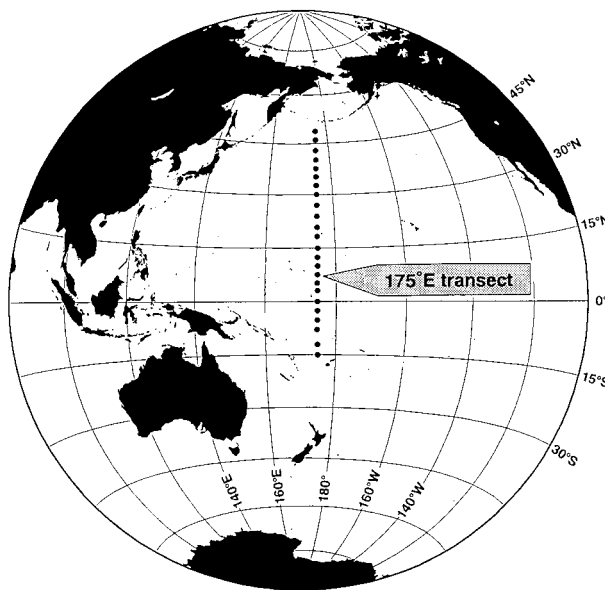


FIGURE 1. The location of surface sediments collected along the 175°E transect from 48°N to 15°S.

Sediments analyzed in this study are mostly surface 2 cm layers, but a few are mixtures of the uppermost 4 cm layers (Table 1).

Analytical Methods. The procedure used for extraction and isolation of PAHs from the sediments was described elsewhere (6). It is briefly summarized below. Prior to solvent extraction, internal standards (1.78 µg of *n*-C₁₉ fatty alcohol and 1.70 µg of iso-C₂₁ fatty acid) were spiked in the wet sediments. They were extracted by methanol and dichloromethane three times with a homogenizer and an ultrasonication. After they were saponified with 0.5 M KOH/methanol under reflux, neutral lipids were obtained from the combined extracts by extraction with hexane/dichloromethane (10:1). It was further divided into four subfractions on a Pasteur pipet column packed with silica gel (BIO-SIL A, 200–400 mesh) which was deactivated with 1% water.

Gas Chromatography/Mass Spectrometry Analysis. A fraction containing PAHs was analyzed by a ThermoQuest Voyager quadrupole mass spectrometer (EI mode, electron energy 70 eV) interfaced to a Carlo Erba 8060 gas chromatograph equipped with a split/splitless injector and a DB-5ms fused silica capillary column (30 m × 0.25 mm i.d.; 0.25 µm film thickness, J&W Scientific). Helium was used as a carrier gas. Temperatures of injector and ion source are maintained at 280 and 200 °C, respectively. Oven temperature was programmed at 50 °C for 2 min, 50–120 °C at 30 °C min^{–1}, and 120–300 °C at 6 °C min^{–1} and held at 300 °C for 15 min. Scan range and time of MS are 40–600 amu and 0.9 s, respectively. Data were acquired and processed with a MassLab version 1.4 data system.

A GC peak identification was conducted by comparing gas chromatographic retention times and mass spectra with those of authentic standards and/or those published in the literatures. In this study we identified and quantified 14 parent PAHs and five alkylated PAHs. Concentrations of most parent PAHs (PHEN, ANT, FLUO, PYR, B(a)A, TRP+CHRY, B(k)F, B(e)P, B(a)P, PERY, D(ah)A, and COR; for abbreviations see Table 1) were obtained from response factors of molecular ions generated by calibration with authentic standards. Concentrations of methylphenanthrenes and retene are tentatively determined by comparing the integrated peak

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TABLE 1. Blank and Sample Levels of PAHs Identified in the Deep Sea Sediments

compound	abbreviation	blank ^a (ng/expt)	sample range (ng/expt)
phenanthrene	PHEN	0.54 ± 0.26	2.85–43.7
anthracene	ANT	0.02 ± 0.04	0.06–0.98
3-methylphenanthrene	3-MP	0.04 ± 0.01	0.17–13.6
2-methylphenanthrene	2-MP	0.05 ± 0.02	0.15–20.8
9-methylphenanthrene	9-MP	0.04 ± 0.01	0.09–10.9
1-methylphenanthrene	1-MP	0.03 ± 0.01	0.09–9.44
fluoranthene	FLUO	0.11 ± 0.04	0.16–7.51
pyrene	PYR	0.06 ± 0.03	0.16–8.39
retene	RET	0 ± 0	0.00–2.17
benz[a]anthracene	B(a)A	0 ± 0	0.00–2.15
triphenylene+chrysene	TRP+CHRY	0.02 ± 0.02	0.07–6.54
benzo(b+k)fluoranthene	B(b+k)F	0.46 ± 0	2.17–26.4
benzo[e]pyrene	B(e)P	0 ± 0	0.00–15.2
benzo[a]pyrene	B(a)P	0 ± 0	0.00–5.11
perylene	PERY	0.04 ± 0.07	0.12–7.39
dibenz(a,h)anthracene	D(a,h)A	0 ± 0	0.00–23.3
coronene	COR	0 ± 0	0.00–15.8

^a Laboratory blank experiments were run three times.

area from summed selected ion monitoring ($m/z = 191 + 192$) and ($m/z = 234 + 219$), respectively, with the peak area of $m/z 178$ of phenanthrene.

Blank, Recovery, and Reproducibility. Procedural blank experiments were concurrently carried out three times through the sequential analysis of our samples to monitor the laboratory contaminations (Table 1). Compounds with mean blank levels larger than 0.1 ng per experiment are phenanthrene, fluoranthene, and benzo(b+k)fluoranthene. We subtracted the highest blank values from the analytical results of samples. We removed some samples which indicate extraordinarily high (> 30) phenanthrene:fluoranthene ratio, suggesting that contamination may be serious. Because total amounts of many PAH species extracted from the sediments between 27°N and 15°S are generally only 1 order of magnitude higher than those of laboratory blank experiments (Table 1), we do not discuss them in detail in the following section. Two independent recovery experiments for a standard mixture of 13 PAHs (phenanthrene to coronene spiked at 9.16 ng for each compound) indicate sufficiently high recoveries (higher than 94%) except for phenanthrene and anthracene which indicate relatively low recoveries of 84 and 77%, respectively. Therefore, some portion of latitudinal variabilities of phenanthrene and anthracene could reflect the variation of recovery. Internal standard recoveries for C₁₉ fatty alcohol and iso-C₂₁ fatty acid are $89.9 \pm 6.6\%$ (1σ , $n = 20$) and $73.1 \pm 4.9\%$ (1σ , $n = 20$), respectively. Based on triplicate analyses of perylene standard and duplicate analyses of standard mixtures containing 13 PAH species, analytical error of PAHs in this study was estimated to be $\pm 15\%$.

Results and Discussion

Latitudinal Distributions of PAHs. Concentrations of total PAHs except for retene and perylene range from 60.6 ng g⁻¹ dry sediment to below blank level. They are low in the low latitudes (15°S–24°N) but remarkably increase from 27°N to 48°N (Table 2, Figure 2). Concentrations of these PAHs at 48°N are 1–3 orders of magnitude higher than those of the lower latitudes. Previous studies reported that the concentration of total three- to seven-ring PAHs in the pelagic deep sea floor from the North Atlantic (7–9) and Mediterranean Sea (10) showed equivalent or slightly higher range from 10 to 200 ng g⁻¹ dry sediment than our results. The PAH carbon comprises 10^{-5} – 10^{-7} of total organic carbon contents in the sediments with the latitudinal distribution similar with the

total PAH concentration (Figure 2). Total PAH concentration at 48°N where the PAH level shows the highest among our samples is 1 or 2 orders of magnitude lower than those of coastal marine sediments such as Beaufort Sea (11).

The latitudinal trend of all individual PAHs are evident, with the higher latitudes displaying higher concentrations than the lower latitudes (Figure 2). It should be noted that these three- to seven-ring PAHs show similar latitudinal distributions between them. Most PAHs show the highest concentrations at the northernmost site 48°N and gradually decrease to 27°N. Between 27°N and 15°S concentrations of PAHs generally show a relatively low level. One of the conspicuous features of the PAH composition is that phenanthrene exhibits the highest concentration. The averaged phenanthrene:fluoranthene ratio (PHEN/FLUO) is 5.4 ± 1.6 (1σ) for samples between 48°N and 19°N where a relatively large amount of PAHs were found. Our PHEN/FLUO ratio is significantly larger than those reported in the sediments from pelagic North Atlantic (~1 (9)), Mediterranean (0.4–1.3 (10)), and Buzzards Bay (0.3–0.7 (12)) but equivalent or smaller than those reported in sediments from Bransfield Strait near Antarctica (3–5 (13)) and Beaufort Sea (~6.4 (14)) and surface ice in Greenland (~15 (15)).

Perylene shows a noisy pattern and has a two-point maxima at 27°N and 7°N (Table 2). Retene, which is derived from soft combustion processes such as biomass burning (16) and transformation of sedimentary resin acids (17), shows a similar pattern with those of fuel combustion-derived PAHs. Dibenzothiophene and other lighter PAHs were not detected in significant amounts and were not reported here.

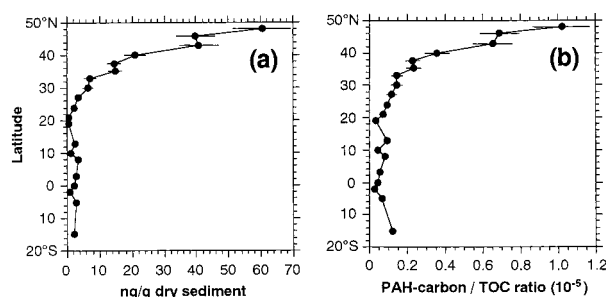
Origin of PAHs on the Deep Sea Floor. Relative abundances of alkylated to unsubstituted parent PAHs are useful in elucidating the origin of PAHs. Some PAH ratios such as the sum of methylphenanthrenes to phenanthrene (MP/PHEN) ratio have been proposed to elucidate the origin of environmental PAHs. The MP/PHEN ratios in petroleum range from 2 to greater than 6, whereas typical ratios in combustion PAH mixtures fall in a range from 0.5 to 1.0 (18, 19). The MP/PHEN ratios of our samples range from 1.7 to 0.15, with an increasing pattern from 24°N to 48°N (Figure 3). The carbon preference index of C₂₅–C₃₆ *n*-alkanes shows relatively high values in these samples (4.9–7.9, 48°N–24°N) without a correlation with MP/PHEN ratio (6). Furthermore, unresolved complex mixtures were not observed in both alkane and PAH fractions. Although some portion of PAHs in the higher latitudinal samples may be derived from petroleum, we consider that they primarily originated from pyrolytic sources.

Downcore profiles of PAHs in coastal sediments from northeast United States and Greenland ice core showed that the accumulation rates of PAHs have dramatically increased during the last 100 years (11, 15). These results suggested that most PAHs found in the deep sea surface sediments in the higher latitude of the Northern Hemisphere are originally formed in the fossil fuel combustion and/or biomass burning which have recently been intensified. Thus, we think that the parent PAHs except for perylene and retene reported in this study are most likely derived from combustion sources and the long-range transported in the atmosphere.

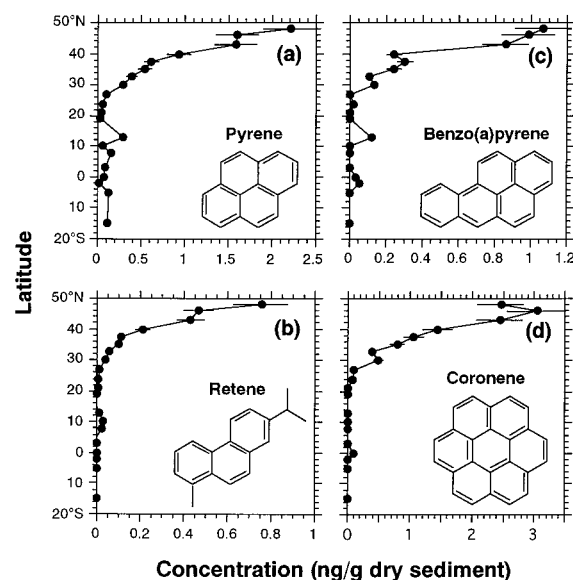
The photolytic reaction rate of benzo[a]pyrene is higher than that of benzo[e]pyrene (20). In our sediments the B(a)P/B(e)P ratio from 48°N to 30°N is around 0.3 with a strong spike at 40°N (as high as 1.6) and nearly zero from 27°N to 15°S with two large spikes (Figure 3b). Low values of the B(a)P/B(e)P ratio suggest that they were transported in the atmosphere for a relatively long time. We do not discuss the ratio further, because concentrations of both B(a)P and B(e)P especially from 30°N to 15°S are too low to verify the ratio.

TABLE 2. Results of PAH Analyses of Deep Sea Sediments from 175°E Transect

latitude	water depth (m)	organic carbon (mg/g dry sed)	concentrations (ng/g dry sediment)						
			total PAHs	PHEN	FLUO	B(a)A	B(b+k)F	PERY	D(a)hA
48.10°N	5334	560	60.6	12.6	1.58	0.55	5.06	2.81	4.86
45.97°N	5317	550	39.9	6.46	1.42	0.42	5.02	1.08	4.50
43.00°N	5906	590	40.8	8.45	1.24	0.42	3.61	1.43	3.39
40.00°N	4854	561	21.2	4.94	0.89	0.18	2.91	0.41	1.98
37.50°N	5065	607	14.7	2.90	0.68	0.15	2.58	0.45	1.20
35.25°N	4952	596	14.9	2.74	0.65	0.12	2.11	0.34	0.96
33.00°N	4633	470	7.16	1.57	0.51	0.10	1.26	0.27	0.56
30.00°N	5410	434	6.64	1.41	0.39	0.06	1.35	0.12	0.53
27.07°N	5814	280	3.47	0.78	0.13	0.02	0.45	0.83	0.08
24.00°N	5741	238	2.40	0.54	0.09	0.01	0.35	0.53	0.07
21.00°N	2505	109	0.81	0.33	0.06	0.00	0.14	0.02	0.00
19.00°N	4026	221	0.81	0.29	0.04	0.01	0.25	0.03	0.00
12.90°N	5640	264	2.63	0.58	0.35	0.08	0.36	0.06	0.15
9.98°N	5461	321	1.44	0.45	0.03	0.00	0.39	0.19	0.00
7.93°N	5338	429	3.67	0.73	0.12	0.03	0.50	1.07	0.12
3.00°N	5005	502	2.93	1.17	0.05	0.03	0.79	0.12	0.00
0.00°	4881	481	2.39	0.68	0.05	0.01	0.48	0.16	0.16
2.00°S	4720	360	0.97	0.37	0.03	0.00	0.25	0.00	0.00
5.00°S ^a	5438	435	3.06	0.93	0.06	0.02	0.62	0.07	0.12
14.98°S	3022	161	2.12	0.67	0.17	0.00	0.22	0.43	0.00

^a Surface 4 cm was analyzed.FIGURE 2. Latitudinal distribution of (a) concentrations of total parent and alkylated PAH species and (b) PAH carbon to total organic carbon (PAH-carbon/TOC) ratio. Error bars indicate an estimated analytical error of $\pm 15\%$.

Factors Controlling the Distribution of PAHs in the Deep Sea Sediments. Concentration of PAHs in the sediments is a function of water content, dry bulk density of the sediments, sedimentation rate, and mass accumulation rate (MAR) of PAHs. Water content of our sediments ranged from 36 to 72%. We think that dry bulk density of our samples does not vary much, because our samples are mainly composed of red clays except for samples from the equator, 2°S, and 12°S, and dry bulk density of deep sea sediments is generally a simple function of CaCO_3 content (21). As for the sedimentation rate, previous studies estimated the sedimentation rate of red clay in the central Pacific (175°N \pm 25°) of 0.39–1.6 cm/k yr (22, 23). Therefore, we consider that the latitudinal variation of total PAHs with 2 orders of magnitude found in our samples could not be explained by the variabilities of porosity, dry bulk density, and sedimentation rate. Bioturbation is also an important factor to determine the apparent concentration of a given compound in the surface sediments. Bioturbation generally mixes surface 5–10 cm sediments (24). Unfortunately, we cannot estimate the depth of bioturbation zone and mixing rate in our samples, because of the lack of chronological information in them. Here, we assume that the bioturbation depth and frequency are the same between the sampling sites. Under this assumption, the concentration in surface sediments are primarily controlled by the “accumulation rate”, because most PAHs found in our sediment samples should have deposited in the same period of time (during the 19th and 20th centuries). On the

FIGURE 3. Latitudinal distribution of diagnostic PAH ratios. (a) Total methylphenanthrene to phenanthrene (MP/PHEN) ratio and (b) benzo[a]pyrene to benzo[e]pyrene (B(a)P/B(e)P) ratio. Error bars indicate an estimated analytical error of $\pm 15\%$.

basis of above considerations, we conclude that our latitudinal profile of PAH concentrations principally reflects that of PAH accumulation rates on the deep sea floor.

For any PAH species, latitudinal distribution of PAHs in the deep sea floor has been expected to be a complex function of emission parameters, physicochemical properties, atmospheric residence time, seawater solubility, and microbial degradability of the species. The latitudinal patterns of PAHs are not correlated with that of annual mean precipitation, which is high (>2500 mm/yr) in the intertropical convergence zone and low (<1000 mm/yr) in the subtropical (around 20°N) and polar regions (25). This suggests that the deposition of PAHs is not primarily controlled by the wet deposition process but other process(es) prevailing in the higher latitudes. It was recently suggested that the water solubility and octanol–water partitioning coefficient (K_{OW}) play important roles to determine the global distribution of organic pollutants (26). However, in this study we do not observe

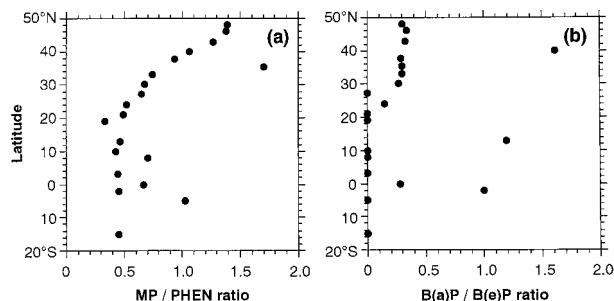


FIGURE 4. Latitudinal distributions of (a) total methylphenanthrene/phenanthrene ratio (MP/PHEN ratio) and (b) benzo[e]pyrene/benzo[a]pyrene ratio (B(e)P/B(a)P ratio).

significant differences in latitudinal distribution of three- to seven-ring PAHs whose water solubilities and K_{OW} range from 6.62×10^{-3} (PHEN) to 4.66×10^{-7} mol/m³ (COR) and $10^{4.57}$ (PHEN) to $10^{7.64}$ (COR), respectively (27). Therefore, some other parameters may be fundamentally important for the deposition of PAHs.

Because of their wide range of vapor pressures, in the temperate atmosphere three- to four-ring PAHs are distributed in both gas and particle phases, whereas five- to seven-ring PAHs are exclusively associated with particles (28). For most PAHs not containing cyclopenta fused rings, the important atmospheric gas-phase reactions are with OH radical and N_2O_5 (29), whereas PAHs with cyclopenta fused rings such as fluoranthene and some PAHs such as B(a)P react with O_3 in the atmosphere (20). Above photochemical reactions proceed so fast that the atmospheric lifetimes of gas-phase PAHs are generally within a few hours or less. Since it takes at least a few days for PAH molecules to migrate from source regions such as East Asia to the Central Pacific, the major portion of PAHs found in our sediments could not be transported as free forms. On the other hand, the PAHs associated with particles such as soot (carbon black) have much longer lifetimes (30, 31) and lower gas-phase concentrations than predicted from the vapor pressures of compounds, suggesting that a fraction of the soot PAHs is nonexchangeable with gas phase. Recent studies suggested that most PAHs found in the coastal marine sediments are associated with soot (32). However, PAHs in soot particles have a relatively low concentration of phenanthrene (33), suggesting that an additional or alternative mechanism may be required for explaining high phenanthrene concentrations in our sediments.

Once PAH molecules associated with some aerosol particles are scavenged from the atmosphere to the surface ocean, some adsorb on the suspended particulate matter, while others dissolve in seawater. We do not know a precise mechanism for transporting PAHs from the surface ocean to the underlying sediments. However, in the Washington coastal region fecal pellets of zooplankton were reported to contain relatively large amount of PAHs, which suggests them as a major agent to transport PAHs downward (34). In the course of sinking in the water column, PAHs are attacked by microbes, and some fraction should be decomposed, although they show remarkably enhanced resistance to microbial degradation when PAHs are adsorbed onto soot particles (35, 36). In the Greenland ice core the concentrations of lower molecular weight PAHs such as dibenzothiophene or phenanthrene are much higher than those of the higher molecular weight PAHs (15). Therefore, a major portion of PAHs especially for lighter molecular weight may have been dissolved in seawater and decomposed in the water column and sediments. Unfortunately, we still have little information on the degradation rate constants of PAHs. Thus we cannot estimate the precise fraction preserved in the sediments of

PAHs initially added to the ocean. However, because dissolved oxygen concentration, one of the possible controlling factors of the rate constants of PAH degradation, is not much different between sampling sites (37), we may say that the decomposition of PAHs in the water column and sediments did not significantly change the original trend for the latitudinal distribution of air-to-sea deposition of PAHs.

Based on the above arguments, we conclude that the primary factor controlling the concentration of PAHs in the deep sea sediments from the central Pacific is deposition flux from the atmosphere to the ocean. The reason PAHs preferentially deposit in the higher latitude ($>30^\circ N$) is an important problem to be solved, but processes prevailing in latitudinal transport from East Asia or in low-temperature environments is important in understanding the distribution of PAHs in the central Pacific Ocean.

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