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Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Rivers and Estuaries in Malaysia: A Widespread Input of Petrogenic PAHs

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This is the first publication on the distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in riverine and coastal sediments in South East Asia where the rapid transfer of land-based pollutants into aquatic environments by heavy rainfall and runoff waters is of great concern. Twenty-nine Malaysian riverine and coastal sediments were analyzed for PAHs (3–7 rings) by gas chromatography mass spectrometry. Total PAHs concentrations in the sediment ranged from 4 to 924 ng/g. Alkylated homologues were abundant for all sediment samples. The ratio of the sum of methylphenanthrenes to phenanthrene (MP/P), an index of petrogenic PAHs contribution, was more than unity for 26 sediment samples and more than 3 for seven samples for urban rivers covering a broad range of locations. The MP/P ratio showed a strong correlation with the total PAHs concentrations, with an r^2 value of 0.74. This ratio and all other compositional features indicated that Malaysian urban sediments are heavily impacted by petrogenic PAHs. This finding is in contrast to other studies reported in many industrialized countries where PAHs are mostly of pyrogenic origin. The MP/P ratio was also significantly correlated with higher molecular weight PAHs such as benzo[a]pyrene, suggesting unique PAHs source in Malaysia which contains both petrogenic PAHs and pyrogenic PAHs. PAHs and hopanes fingerprints indicated that used crankcase oil is one of the major contributors of the sedimentary PAHs. Two major routes of inputs to aquatic environments have been identified: (1) spillage and dumping of waste crankcase oil and (2) leakage of crankcase oils from vehicles onto road surfaces, with the subsequent washout by street runoff. *N*-Cyclohexyl-2-benzothiazolamine (NCBA), a molecular marker of street dust, was detected in the polluted sediments. NCBA and other biomarker profiles confirmed our hypothesis of the input from street dust contained the leaked crankcase oil. The fingerprints excluded crude oil,

fresh lubricating oil, asphalt, and tire-particles as major contributors.

Introduction

Polycyclic aromatic hydrocarbons (PAHs), hydrocarbons containing two or more fused benzene rings, are one of the most important classes of anthropogenic organic contaminants (1). There are two types of anthropogenic sources of PAHs: petrogenic and pyrogenic sources. Crude and refined petroleum contains PAHs (i.e., petrogenic PAHs). They are introduced to aquatic environments through accidental oil spills, discharge from routine tanker operations, municipal and urban runoff, and so on. The combustion of fossil fuel (coal and petroleum) and biomass also produces PAHs (i.e., pyrogenic PAHs), which are released into the environment in the form of exhaust and solid residues. There are also natural sources of PAHs released to the environment. For example, perylene is believed to be produced through in situ conversion of perylenequinone pigment or some other organic matter during early diagenesis (2–4). PAHs are also derived from some other natural sources such as oil seeps and ancient sediment erosion. However, in many areas affected by human activities, natural sources are overwhelmed by anthropogenic sources except perylene. Many PAHs are persistent relative to many other organic compounds depending on depositional environment. Some are carcinogenic and mutagenic to animals (5). The endocrine disrupting activities of PAHs have been recently reported (6). Therefore, understanding the detailed biogeochemistry of PAH including their sources is very important.

The distributions of PAHs in sediments are the subject of intense studies from the middle 1970s to the present (Table S1, Supporting Information; see refs 2 and 7–65). They are distributed globally from inland lakes and urban rivers to the open ocean with a wide range of concentrations. Some of the most highly industrialized and urbanized locations, such as Boston, MA (9, 29), Sydney, Australia (18), Hamilton, Canada (13), and Long Island, NY (15), have extremely high concentrations of PAHs of more than 100 000 ng/g. Most studies of PAHs distribution in rivers and coastal/estuarine sediments have been conducted in the more industrialized areas of the world such as the United States, Canada, Europe, Australia, and Japan. However, in South East Asia, where industrialization and urbanization have proceeded rapidly during the past decade and the potential associated increase in PAHs input is of concern, no information on the environmental distribution of PAHs is available. The present paper is the first publication on environmental distribution and sources of PAHs in the riverine and coastal sediments of South East Asia. Climatic characteristics of this region (i.e., frequent and strong rainstorms) may wash out land-based pollutants to the aquatic environments more effectively than moderate and high latitudes. Therefore, the mix and magnitude of sources and transport mechanism of PAHs in South East Asia may be different as compared to other regions found at higher latitudes.

On a global basis, the widespread distribution of pyrogenic PAHs is obvious (Table S1, Supporting Information; see refs

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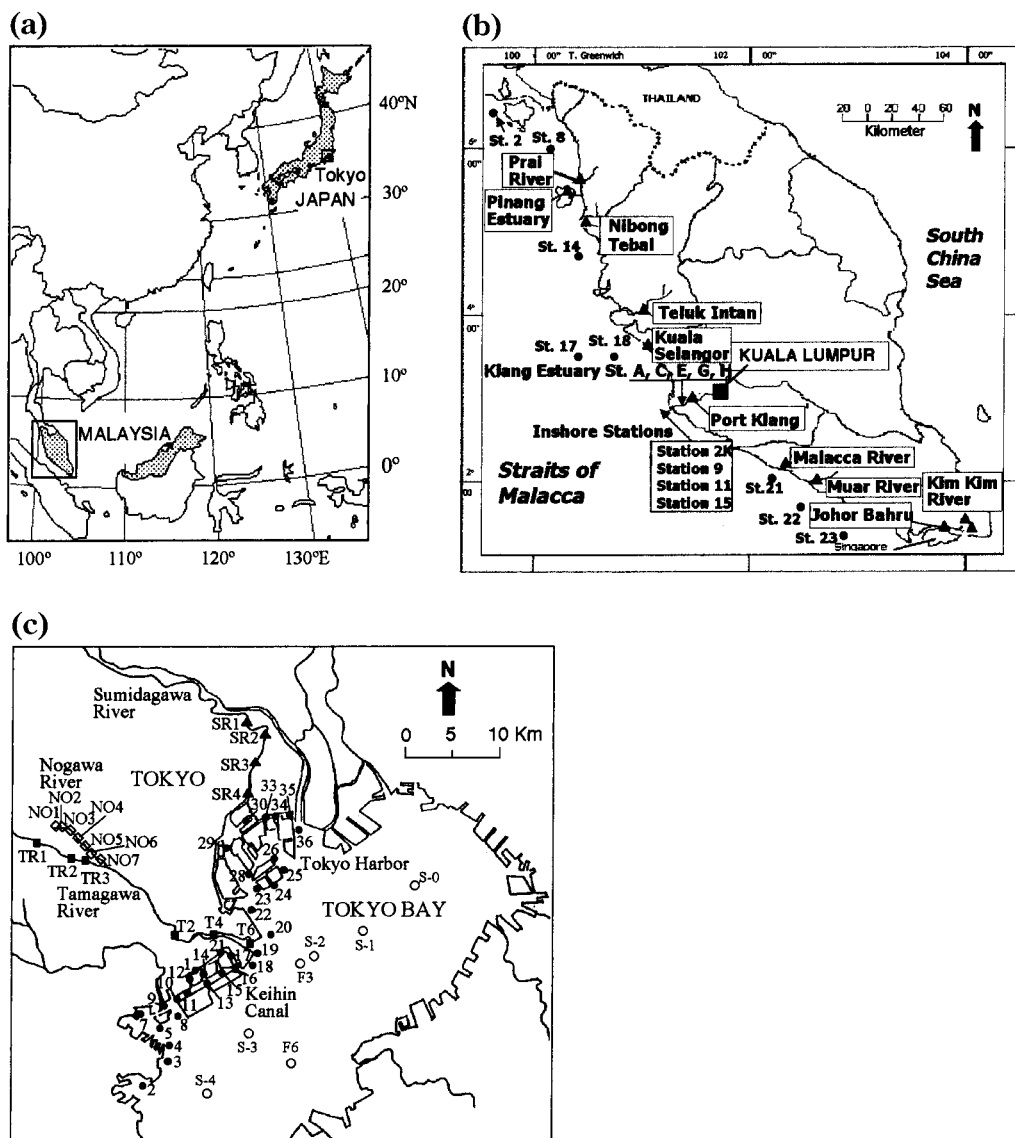


FIGURE 1. (a) Study areas. (b) Sampling locations for sediment on the west coast of peninsular Malaysia: (▲) river and estuary stations; (●) offshore locations. Individual locations for the Klang Estuary and Inshore stations are not indicated because of limited space on the map. (c) Sampling locations for sediment in Tokyo Bay and the adjacent canal, harbor, and rivers: (○) Tokyo Bay; (●) Keihin Canal and Tokyo Harbor; (▲) Sumidagawa River; (■) Tamagawa River; (◇) Nogawa River.

2 and 7–65). In a limited number of locations, petrogenic-derived PAHs are dominant over pyrogenic (11, 19, 26, 31, 37, 39, 44, 49, 53, 55). Some of the locations are impacted by accidental oil spills (39, 44, 55) or effluents from petrochemical industries (53). However, widespread (i.e., nationwide) and continuous (i.e., nonaccidental) input of petrogenic PAHs has not been observed. On the other hand, frequent and strong rainstorms in South East Asia may continuously and extensively wash out petroleum PAHs from the land to the rivers and coastal zones.

The objectives of the present study are to investigate the distribution of sedimentary PAHs and to determine major sources of PAHs in one section of South East Asia, Malaysia. For comparison, sediment samples collected from rivers, estuaries, canals, and harbors in Tokyo, which is one of the most industrialized areas in the world, were analyzed. To help the source identification of PAHs, a molecular marker approach (66) has been employed. For source discrimination of petroleum-related sources, triterpanes (petroleum biomarkers) were measured. To examine the contribution from automobile-related sources, a molecular marker, *N*-cyclohexyl-2-benzothiazolamine (NCBA; ref 67) was utilized.

Experimental Section

Sample Collection. The map of the sampling location and the detailed description is described in Figure 1 and in Supporting Information Table S2, respectively.

Sediment Samples. Twelve sediment samples were collected from 10 rivers of the West Coast of Peninsular Malaysia in 1998 and 1999. The locations were selected as such to cover the whole West Coast including both rural (e.g., Teluk Intan, Nibong Tebal) and urban (e.g., Pinang Estuary, Port Klang, Malacca City, and Johor Bahru) areas. Five estuarine sediments (St.A, St.C, St.E, St.G, and St.H) were collected along the Klang Estuary in 1998 and in 2000. Klang River which runs through the capital city of Kuala Lumpur, is one of the most polluted rivers in Malaysia (68). Four inshore sediment samples (St.2K, St.9, St.11, and St.15) were collected off the Klang Estuary. Eight offshore sediment samples (St.2, St.8, St.14, St.17, St.18, St.21, St.22, and St.23) were collected in the Straits of Malacca. The sampling locations cover a broad range of the narrow Straits. Sixty-four sediment samples were collected in Tokyo Bay and adjacent rivers (Figure 1c) in 1996–1998. River and estuarine sediments were

collected using an Ekman Dredge. Collected cake of the sediments was placed on stainless steel pan, and the top 0–5 cm of sediments was taken using a precleaned stainless steel scoop. Because of both active input of terrestrial material to the rivers and estuaries and strong flushing of the bottom sediments caused by the frequent and strong rain in the tropical area, the top 5 cm layers of the sediments are thought to represent modern input. The coastal samples were collected using a Smith-McIntyre sampler. Immediately after the sampler was raised onto the boat, the top 0–2 cm layers were taken using a precleaned stainless steel scoop. When the sediment accumulation rate in the coastal area is considered, the coastal sediments are also expected to represent the accumulated modern pollution input (e.g., during last 10–20 years). For example, the sediment accumulation rate for the coastal area off the Klang Estuary was reported to be ~2 mm/year (69), indicating that the 0–2 cm layers of the inshore sediment samples correspond to the input of the last 10 years. The samples were placed in tightly sealed solvent-rinsed stainless steel containers and transported on ice to the laboratory. The samples were then stored at –35 °C until further analysis.

Crude Oil Samples. Crude oil samples including three Middle East oils and four South East Asian oils were kindly supplied by the Japan Coast Guard. The details are described elsewhere (70).

Street Dust Samples. Three street dust samples (KL-1, KL-2, KL-3) were collected from three heavy-trafficked streets in Kuala Lumpur in 1998. The details of the street dust samples are described elsewhere (70).

Asphalt Sample. Fresh asphalt samples (AS-1, AS-2) were obtained from two pieces of asphalt detached from the surface of asphalt-paved road in Kajang, a suburb of Kuala Lumpur. The samples were wrapped with aluminum foil, stored in a clean plastic Zip-Lock bag, transported to the laboratory, and stored in a freezer until further analysis.

Fresh Crankcase Oil. Two fresh crankcase oil samples (Petronas, BP) were randomly purchased from the Malaysian market (70).

Used Crankcase Oil. Four used crankcase oil samples were taken from storage tanks in a gas station, an automotive workshop, garages, and a motorcycle workshop in Malaysia. The samples were collected using a precleaned 10-mL glass pipet and placed in previously baked 30-mL amber vials. The samples were transported to the laboratory and stored in a freezer until further analysis.

Automobile Tire Rubber. Tire particles from four types of used tires were obtained by abrasion of their surfaces with a stainless steel file.

Analytical Procedure

PAHs and Triterpanes. The entire procedure for the extraction, purification, and fractionation is similar to those described by Hartmann et al. (71). Briefly, freeze-dried sediment samples, street dust samples, and tire particles were Soxhlet-extracted with dichloromethane (DCM). Oil and asphalt samples were dissolved into DCM. An appropriate volume of PAH surrogate internal standard mixture (naphthalene-*d*₈, anthracene-*d*₁₀, *p*-terphenyl-*d*₁₄, benz[*a*]anthracene-*d*₁₂, and perylene-*d*₁₄) was added to the sample extracts. The extracts were passed through a 5% H₂O-deactivated silica gel column to remove polar components. The hydrocarbon fraction obtained was further fractionated using a fully activated silica gel column following activated copper treatment for elemental sulfur removal. Altogether, three fractions were eluted. The first hexane fraction contained alkanes and triterpanes, while the second hexane fraction contained the alkylbenzenes and PCBs. PAHs with 3–7 benzene rings were eluted with hexane/DCM (3:1, v/v).

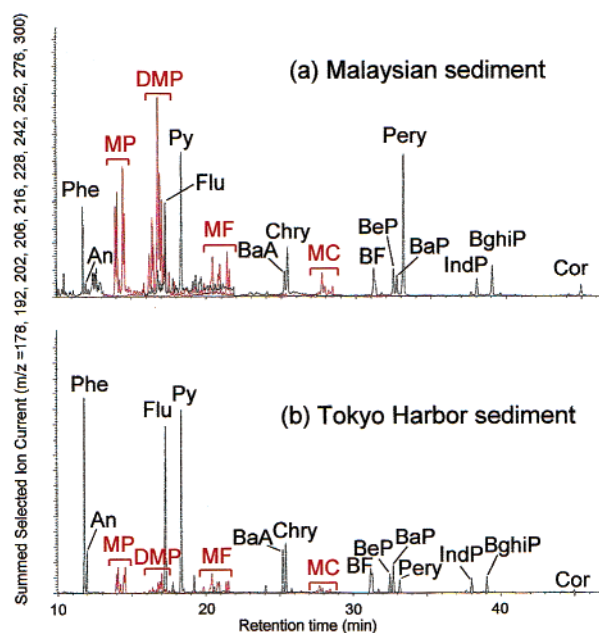


FIGURE 2. Gas chromatograms of PAHs in (a) Malaysian sediment and (b) Tokyo Harbor sediment: Phe, phenanthrene; An, anthracene; MP, methylphenanthrenes; (substitution position: 3, 2, 9, and 1 in the order of elution) DMP, C₂-phenanthrenes/anthracenes; Flu, fluoranthene; Py, pyrene; MF, C₁-fluoranthenes/pyrenes; BaA, benz[*a*]anthracene; Chry, chrysene; MC, C₁-chrysene/benz[*a*]anthracene; BF, benzofluoranthenes; BeP, benzo[*e*]pyrene; BaP, benzo[*a*]pyrene; Pery, perylene; IndP, indeno[1,2,3-*cd*]pyrene; BghiP, benzo[*ghi*]perylene; Cor, coronene.

PAHs and triterpanes were analyzed by gas chromatography mass spectrometry (GC/MS) using a 30 m fused silica capillary column (HP-5MS) installed in a gas chromatograph (HP5890) interfaced with a Hewlett-Packard 5972A quadrupole mass selective detector (SIM mode). Detailed instrumental conditions were described previously (70, 72). PAHs concentrations were recovery-corrected using the spiked surrogates. The relative standard deviation (RSD; *n* = 4) of individual PAHs identified in sample extracts were <10%.

NCBA. The analytical procedure of NCBA is described in detail elsewhere (67). NCBA in sediment and street dust samples were Soxhlet-extracted with toluene/methanol (1:1) and purified using acid extraction and silica gel column chromatography. NCBA was analyzed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a flame photometric detector (FPD).

Results and Discussion

PAHs Compositions in the Malaysian Environment. Parent PAHs (i.e., PAHs with no alkyl substitutions) consisting of three or more benzene rings (i.e., phenanthrene to coronene) were identified in Malaysian sediment (Figure 2). The gas chromatogram also showed a distinct high abundance of alkylated homologues, which will be discussed in detail in subsequent sections. In almost all rural and offshore locations, perylene was a major PAHs. For instance, the perylene concentration in Teluk Intan sample represented 94% of the total PAHs (Table 1). The existence of perylene in high abundance in freshwater and marine sediments has been previously reported (2, 4, 73). Perylene is formed from biogenic precursors (e.g., perylenequinone pigments) during early diagenesis (2–4). Biogenic PAHs are beyond the focus of the present study; therefore, perylene is excluded from “total PAHs” in this paper.

Table 1 lists the PAHs concentrations in Malaysian sediments. The total PAHs in the sediment ranged from 4 to

TABLE 1. PAHs and Hopanes in Malaysian and Tokyo Sediment

sample	organic carbon (mg/g)	PAHs					Hopanes						homohopane index ^k (%)
		total PAHs ^a (ng/g)	perylene (ng/g)	PAHs/OC ^b (ng/mg)	H/L ratio ^c	MP/P ratio ^d	total hopanes ^e (ng/g)	C ₃₀ ^f (ng/g)	total PAHs/C ₃₀ ^g	C ₂₉ /C ₃₀ ^h	C ₃₁ –C ₃₅ /C ₃₀ ⁱ	Tm/Ts ^j	
Malaysia													
rivers													
Prai River	15.7	81	38	5	1.46	1.52	na ^l	na	na	na	na	na	na
Pinang Estuary	24.5	924	43	38	1.47	6.65	6515	1130	0.82	1.59	2.00	0.91	9.50
Nibong Tebal	16.8	62	40	4	1.09	2.21	na	na	na	na	na	na	na
Teluk Intan	32.5	20	884	1	1.10	2.59	264	9	2.13	6.75	8.73	2.29	1.30
Kuala Selangor	23.4	42	88	2	1.27	2.04	na	na	na	na	na	na	na
Port Klang	11.5	387	87	34	0.48	5.19	na	na	na	na	na	na	na
Malacca River (1998)	15.4	494	31	32	1.24	3.76	2779	451	1.09	1.64	2.28	0.88	10.2
Malacca River (1999)	15.8	262	47	17	0.94	3.01	na	na	na	na	na	na	na
Muar River	16.4	69	33	4	1.85	1.33	na	na	na	na	na	na	na
Johor Bahru (1998)	23.7	239	20	10	1.42	1.56	2404	416	0.58	1.41	2.14	0.82	9.8
Kim Kim River	6.6	41	1	6	0.82	2.47	na	na	na	na	na	na	na
Kim Kim Estuary	23.7	37	8	2	1.63	1.34	na	na	na	na	na	na	na
Klang estuary													
station A	10.9	378	124	35	0.47	5.38	na	na	na	na	na	na	na
station C	22.1	431	130	19	0.91	3.82	3213	561	0.77	1.61	1.83	0.81	8.30
station E	22.4	257	109	11	0.66	5.10	na	na	na	na	na	na	na
station G	10.0	82	45	8	1.41	1.41	1395	224	0.37	1.65	1.93	0.92	7.60
station H	15.2	19	6	1	0.64	0.39	98	15	1.21	1.67	2.4	0.89	8.9
Klang Coast (inshore)													
station 2K	14.2	27	17	2	1.09	1.44	323	47	0.58	1.69	2.60	0.97	5.70
station 15	11.7	21	19	2	1.60	1.20	220	31	0.68	1.71	2.41	0.93	5.30
station 11	2.7	9	11	3	1.80	1.09	81	10	0.91	1.71	3.12	1.33	3.30
station 9	13.0	39	36	3	1.79	1.08	270	35	1.12	1.79	2.73	1.07	5.30
Straits of Malacca (offshore)													
station 2	8.3	4	1	0	0.87	0.56	na	na	na	na	na	na	na
station 8	6.1	6	3	1	1.47	1.35	54	6	0.93	1.35	3.78	2.2	2.79
station 14	1.2	11	4	9	1.50	1.12	na	na	na	na	na	na	na
station 17	6.9	7	2	1	1.61	0.59	na	na	na	na	na	na	na
station 18	4.7	10	17	2	1.60	1.42	109	10	1.00	1.67	4.55	2.35	2.27
station 21	5.8	73	12	13	1.89	1.20	330	50	1.47	1.62	2.46	1.07	5.73
station 22	5.7	4	1	1	1.55	1.73	63	6	0.72	1.73	4.70	1.43	3.60
station 23	2.5	11	3	5	1.76	1.36	na	na	na	na	na	na	na
Tokyo													
	<i>n</i> = 64 ^m						<i>n</i> = 9 ⁿ						
average	25.3	9546	424	420	1.39	0.85	4214	884	6.66	1.47	1.25	1.18	6.01
SD	18.7	38770	1177	1490	0.37	0.24	3133	655	5.73	0.11	0.20	0.29	0.75
minimum	5.1	534	2	35	0.55	0.43	846	217	2.46	1.25	0.73	0.88	4.09
maximum	99.8	292370	9310	10118	2.24	1.55	8660	1763	17.60	1.60	1.39	1.79	6.63

^a Total PAHs = sum of concentrations of phenanthrene + anthracene + 3-methylphenanthrene + 2-methylphenanthrene + 9-methylphenanthrene + 1-methylphenanthrene + fluoranthene + pyrene + benz[*a*]anthracene + chrysene + benzo[*a*]fluoranthene + benzo[*e*]pyrene + benzo[*a*]pyrene + indeno[1,2,3-*cd*]pyrene + benzo[*ghi*]perylene. ^b PAH/OC = total PAHs concentration relative to the organic carbon content. ^c H/L ratio = a ratio of sum of benz[*a*]anthracene to benzo[*ghi*]perylene relative to sum of phenanthrene to pyrene. ^d MP/P ratio = a ratio of the sum of 3-methylphenanthrene, 2-methylphenanthrene, 9-methylphenanthrene, and 1-methylphenanthrene to phenanthrene. ^e Total hopanes = sum of triterpanes identified in Figure 6. ^f C₃₀ = 17 α ,21 β (*H*)-hopane. ^g Total PAHs/C₃₀ = a ratio of total PAHs relative to C₃₀ hopane. ^h C₂₉/C₃₀ = a ratio of 17 α ,21 β (*H*)-30-norhopane to 17 α ,21 β (*H*)-hopane. ⁱ C₃₁–C₃₅/C₃₀ = a ratio of sum of C₃₁ homohopane to C₃₅ homohopane relative to C₃₀ hopane. ^j Tm/Ts = a ratio of 17 α -22,29,30-trisnorhopane to 18 α -22,29,30-trisnorhopane. ^k Homohopane index = percent concentration of C₃₅ homohopanes relative to a sum of C₃₁–C₃₅-homohopane. ^l na = not analyzed. ^m Number of samples analyzed for PAHs; detailed values are available in the Supporting Information, Table S3. ⁿ Number of samples analyzed for hopanes.

924 ng/g. The concentration of PAHs in sediments collected near major townships (Georgetown, Malacca City, Port Klang, and Johor Bahru) are generally 1 order of magnitude higher than those of rural samples (Table 1). Figure 3 shows Malaysian sedimentary PAHs concentration in comparison with global and Tokyo concentrations. The global PAHs concentrations were derived from previous studies obtained from literature (2, 7–65) cited in Supporting Information Table S1, while Tokyo data were derived from the present study and are listed in Supporting Information Table S3. Global rivers, lakes, estuaries, harbors, and coastal areas showed different levels of PAHs concentrations ranging from 1 to 760 000 ng/g with modal concentration of 1000–10 000

ng/g. PAHs concentrations in Malaysian sediments can be categorized as low to moderate, whereas those in Tokyo Bay can be categorized as moderate to high. The lower concentration of PAHs in Malaysian sediments are probably due to less impact by human activities. However, increased dilution of sedimentary PAHs due to excessive sediment load from anthropogenic activities and river-borne suspended particles from heavy and frequent down-pour may have partially contributed the lower PAHs concentrations. This dilution effect has been discussed in detail elsewhere (74).

Ubiquitous Input of PAHs with Petrogenic Signature. Figure 2 shows gas chromatograms of PAHs in sediments collected from a polluted river in Malaysia (top panel) and

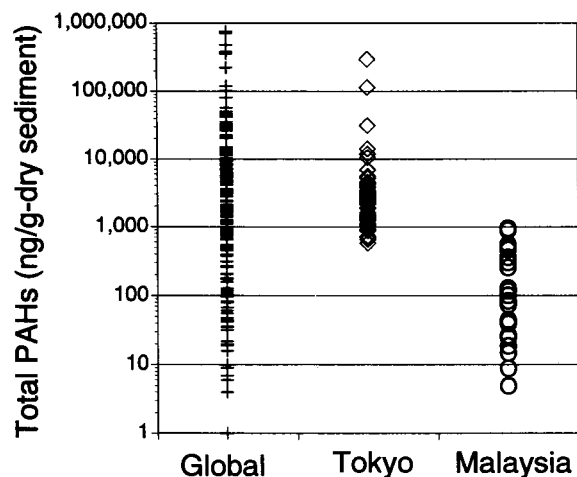


FIGURE 3. PAHs concentrations in Malaysian and Tokyo sediments in comparison to those of the reported concentrations for world rivers, lakes, and coastal zones. Data for global sediments are derived from the references cited in Table S1.

a polluted river in Tokyo (bottom panel). PAHs profile in the Tokyo Harbor is a typical representation of gas chromatograms of industrialized countries (37, 40, 47, 50, 59, 75–80) with severe depletion in alkylated PAHs, indicating that sedimentary PAHs in Tokyo are largely of pyrogenic source. In contrast, the alkyl PAHs are in great abundance for the Malaysian sediment. As shown in Figure 2, Malaysian sediments are more abundant in alkyl phenanthrenes/anthracenes, alkyl fluoranthene/pyrenes, and alkyl chrysenes/benz[a]anthracenes than are Tokyo sediments. The abundance in alkyl PAHs is characteristic signature for PAHs generated via low-temperature diagenesis, that is, petrogenic sources including crude oil and the refined products (e.g., gasoline, diesel fuel, and fuel oil). PAHs for all sediments collected in Malaysian urban locations bear the similar petrogenic signature, indicating they are heavily impacted by petrogenic input. Normally, petrogenic-source PAHs (e.g., crude and fuel oil) contain lower molecular weight (LMW) PAHs with a severe depletion of higher molecular weight (HMW) PAHs, while pyrogenic sources are abundant in HMW PAHs. Malaysian urban river sediments contained a considerable abundance of HMW PAHs, although they are also abundant in LMW PAHs, indicating the input of both petrogenic and pyrogenic sources.

To quantitatively express the abundance of alkyl homologues, an MP/P ratio has been proposed (81). The relative abundance of methylphenanthrenes/phenanthrene (MP/P) ratio has been used to distinguish petrogenic and pyrogenic sources of PAHs. MP/P ratios measured in combustion mixtures are generally <1 , whereas unburned fossil PAHs mixtures typically display a range of values from 2 to 6 (81, 82). Figure 4 shows MP/P ratio of Malaysian sediments in comparison to those from Tokyo. Tokyo's MP/P ratios ranged from 0.4 to 1.6 with the most frequent occurrence around unity, and these are typical for industrialized countries (e.g., see refs 16, 21, 23, 42, 51, 57, and 82), indicating that the major PAHs source in Tokyo is pyrogenic. On the other hand, Malaysian MP/P ratios showed a much higher range and much higher values than those observed in Tokyo sediments, although there is some overlapping of values between the two countries. An MP/P ratio of greater than unity was found for more than 26 samples and greater than 2 for 11 out of 29 samples of Malaysian sediments. A higher MP/P ratio of greater than 3 was observed in urban rivers spanning from North to South of the west coast of Peninsular Malaysia (i.e., Pinang Estuary, Klang Estuary, and Malacca River). A higher MP/P ratio for the Malaysian sediments indicates that the

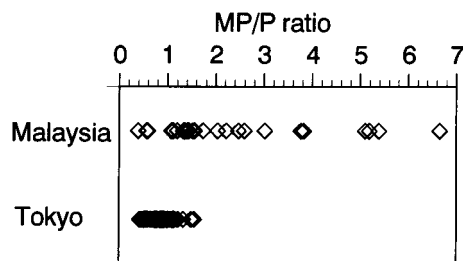


FIGURE 4. MP/P ratios for Malaysian and Tokyo sediments (MP/P ratio: a ratio of the sum of 3-methylphenanthrene, 2-methylphenanthrene, 9-methylphenanthrene, and 1-methylphenanthrene to phenanthrene).

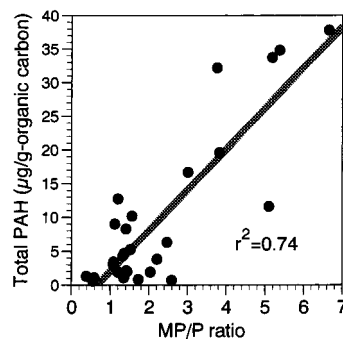


FIGURE 5. Relationship between the total PAH concentration and the MP/P ratio. See Table 1 for the definition of "total PAHs".

Malaysian aquatic environments have been more heavily impacted by petrogenic input than have those of the industrialized countries.

The higher MP/P ratios were mostly observed in samples that have been collected in the urban rivers where relatively higher PAHs concentrations were observed, suggesting that petrogenic input is a major control on the PAHs contamination in Malaysia. Thus, the correlation between sedimentary PAHs concentrations and their MP/P ratio is examined. PAH concentrations are initially normalized to organic carbon contents before any calculations are made because organic carbon content is an important controlling factor of the sorption of PAHs on sediment (83). In addition, a positive correlation between PAHs and sedimentary organic carbon has been previously reported by many researchers (e.g., see refs 28 and 48). Figure 5 shows a correlation of total PAHs and MP/P ratio for Malaysian rivers, estuaries, and coastal sediments. The positive correlation ($r^2 = 0.74$) indicates that Malaysian sedimentary PAHs concentrations are strongly controlled by petrogenic input. Furthermore, the MP/P ratio is significantly correlated not only with total PAHs but also with HMW PAHs. For example, chrysene, benzo[a]pyrene, and benzo[ghi]perylene showed good correlation with the MP/P ratio with r^2 values of 0.69, 0.56, and 0.60, respectively. These strong correlations of the MP/P ratio with HMW PAHs mean that there are sources with a petrogenic signature which also bring HMW PAHs to Malaysian urban sediments together with LMW PAHs.

Another striking feature is that the cluster of low PAHs concentrations with low MP/P ratios includes the inshore and offshore locations. For example, station 17, located about 60 km in the Straits of Malacca off the northwest coast (Figure 1b), has an MP/P ratio of 0.59. This can be explained by a mechanism where combustion-derived PAHs are transported atmospherically for a long distance and serve as background contamination as reported by many researchers (e.g., see refs 9, 14, 40, 62, 65, 77, 84, and 85). The prevailing wind pattern of the Straits of Malacca could facilitate the atmospheric transport of PAHs from the Klang River Valley

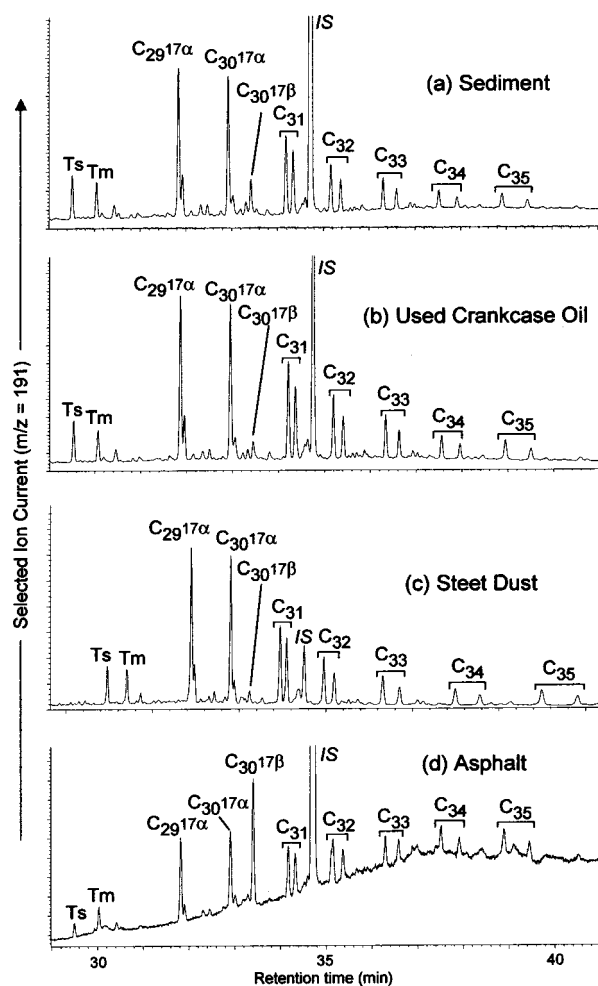


FIGURE 6. Gas chromatograms of triterpanes in Malaysian urban sediment and source materials: (a) sediment, Klang Estuary St.C; (b) used crankcase oil, Home Auto Mechanics; (c) street dust, KL-1; (d) asphalt: Asphalt-1; Ts, 18 α (H),21 β (H),22,29,30-trisnorhopane; Tm, 17 α (H),21 β (H),22,29,30-trisnorhopane; C₂₉ 17 α , 17 α (H),21 β (H)-norhopane; C₃₀ 17 α , 17 α (H),21 β (H)-hopane; C₃₀ 17 β , 17 β (H),21 α (H)-hopane; C₃₁–C₃₅, homohopanes consisting of C₃₁–C₃₅ carbons with S and R stereoisomers at the 22 carbon; IS, Internal Injection Standard (17 β (H),21 β (H)-hopane).

and the city of Kuala Lumpur to the Straits, especially in the month of January (86). This is consistent with a low MP/P ratio (0.60–1.21) for aerosol samples collected in a few coastal locations (e.g., Petaling Jaya and Port Dickson) in Malaysia (87).

Determination of PAHs Sources in Malaysian Sediments

Homogeneous Hopane Composition in Malaysian Urban Sediments. In the previous section, widespread input of PAHs bearing a petrogenic signature in the urban areas of Malaysia was explored. A more specific identification of the sources is made in this section. On the basis of the PAH concentration–MP/P ratio relationship (Figure 5 and Table 1), urban stations (i.e., Klang Estuary, Pinang Estuary, Malacca City, and Johor Bahru) are thought to be mostly affected by the petrogenic input. Therefore, in this section, we compare various compositional indices of hydrocarbons between the urban stations and possible sources. To help with the identification, petroleum biomarker compositions (hopanes) are utilized. Figure 6 shows an example of gas chromatograms of hopanes in Malaysian urban sediments. Hopane compositions of all of the urban sediments are very similar to each other and are characterized by a predominance of 17 α ,-

21 β (H) C₃₀ hopane (C₃₀ 17 α) and 17 α ,21 β (H) C₂₉ hopane (C₂₉ 17 α) with stair-step progression of C₃₁–C₃₅ homohopanes. In general, hopane compositions vary in petroleum, depending on their origins and maturity; therefore, hopane fingerprints are different among different petroleum (88). However, the chromatographic profiles of hopanes observed in the Malaysian urban sediments were remarkably constant. This may imply the existence of a single diffuse source.

Crude Oil. As indicated in Table 2, crude oil contains significant amounts of PAHs, and its spillage from oil refineries and some other facilities may contribute to sedimentary PAHs. However, the PAHs profiles of the crude oil samples examined were abundant in LMW PAHs, showed severe depletion of HMW PAHs, and were quite different from those of the urban sediments (Table 1 and Figure 7). The abundance of HMW PAHs is parametrized as an H/L ratio (see definition in Table 1). An H/L ratio for crude oils ranged from 0.02 to 0.13 (Table 2), whereas the ratios for Malaysian urban sediments were 0.47–1.47 (Table 1). Such large differences suggest that Malaysian sedimentary PAHs are probably not derived from crude oil spillage as the only or major source. However, molecular weight distribution of PAHs (i.e., the H/L ratio) can be modified by various processes following their discharge to the environments. For example, LMW PAHs are more susceptible to microbial degradation (89) and volatilization and dissolution into the water column (5). As a result of those environmental alterations, higher H/L ratios could be seen in sediments in comparison to crude oil. Therefore, using only the H/L ratio to exclude crude oil from major sources of the sedimentary PAHs is inadequate. More conservative indicators are necessary for source discrimination.

Hopanes are one of the conservative markers found to be useful for this purpose (88), and their compositions provide further supportive evidence that the crude oil spillage is only minor contributor. In the previous paper (70), we proposed that abundances of C₂₉ 17 α and C₃₁–C₃₅ homohopanes relative to C₃₀ 17 α (the C₂₉/C₃₀ and C₃₁–C₃₅/C₃₀ ratios, respectively) were useful indicators to identify petroleum sources. Both the C₂₉/C₃₀ and C₃₁–C₃₅/C₃₀ ratios of South East Asian crude oil (SEACO) were significantly lower than those of the Malaysian sediments (Tables 1 and 2 and Figure 8), hence excluding SEACO as contributor to the sedimentary petroleum. On the other hand, Middle East crude oil (MECO) had C₂₉/C₃₀ and C₃₁–C₃₅/C₃₀ ratios very similar to those in the sedimentary hopanes (Figure 8). This may suggest a contribution from MECO to the sedimentary petroleum hydrocarbons. However, MECO is imported from the Middle East, and only a limited number of oil refineries in Malaysia process MECO. Therefore, spillage of MECO would not have been widespread. Actually, there is no oil refinery dealing with MECO in Pinang Estuary, Klang Estuary, or Johor Bahru. Furthermore, MECO showed wide variability in some maturity indices of petroleum biomarkers depending on their maturity. For example, the 17 α -22,29,30-trisnorhopane to 18 α -22,29,30-trisnorhopane (Tm/Ts) ratio varies from 0.35 to 2.31 among MECO (Table 2 and Figure 8), whereas the Tm/Ts ratios for the polluted sediments were remarkably constant (0.81–0.92; Table 1 and Figure 8). The homogeneous hopane composition among the Malaysian sediments indicates the existence of a common diffuse source.

Used Crankcase Oil. Motorvehicles (automobiles, trucks, buses, and motorcycles) could potentially carry a uniform petroleum signature on a nationwide basis. Among various automobile-related hydrocarbon sources, used crankcase oil has been suspected as a significant source of sedimentary hydrocarbons (90). The PAHs profile for “fresh” crankcase oil displays severe depletion of HMW PAHs (Figure 7). The H/L ratio for the fresh crankcase oil was 0.06 and 0.23 (Table 2). These values are extremely low relative to the range of

TABLE 2. PAH and Hopanes in Crude Oil, Fresh Crankcase Oil, Used Crankcase Oil, Street Dust, and Asphalt^a

	PAHs				Hopanes						homo-hopane index (%)
	total PAHs (ng/g)	perylene (ng/g)	H/L ratio	MP/P ratio	total hopanes (ng/g)	C ₃₀ (ng/g)	total PAHs/C ₃₀	C ₂₉ /C ₃₀	C ₃₁ –C ₃₅ /C ₃₀	Tm/Ts	
MECO (Middle East Crude Oil)											
Arabian Light	192 000	1 030	0.08	3.39	168 000	295 000	0.65	2.01	1.80	2.31	10.1
Umm Shaif	700 000	0	0.05	4.34	899 000	143 000	4.90	1.56	2.30	0.76	11.2
Marban	339 000	1 850	0.06	3.88	333 000	54 000	6.28	1.41	1.86	0.35	9.20
SEACO (South East Asian Crude Oil)											
LABUAN	3 060 000	9 170	0.02	2.43	760 000	161 000	19.01	0.98	0.48	2.2	0.00
MIRI	480 000	14 600	0.05	2.45	1 540 000	366 000	1.31	0.85	0.41	1.49	1.50
TAPIS	946 000	5 390	0.04	3.17	626 000	145 000	6.52	1.16	0.89	1.43	2.00
Sumatra	700 000	1 970	0.13	2.24	773 000	197 000	3.55	0.85	0.78	0.52	2.90
Fresh Crankcase Oil											
Petronas	8 390	49	0.06	5.30	3 960 000	619 000	0.01	1.52	3.00	0.70	9.80
BP	6 990	285	0.23	1.28	5 360 000	874 000	0.01	1.32	2.93	1.00	11.5
Used Crankcase Oil											
Petronas Gas Station	1 720 000	12 100	0.77	6.55	884 000	135 000	12.74	2.04	1.69	0.92	7.14
Yong Motor Wkshop	1 150 000	4 430	0.23	5.01	1 770 000	243 000	4.73	2.66	1.2	0.62	5.93
Home Auto Mechanic	1 330 000	5450	0.28	4.61	2 550 000	423 000	3.14	1.81	1.87	0.71	9.32
Motorcycle Wkshop	518 000	2 500	0.29	3.99	2 690 000	474 000	1.09	1.56	2.08	0.72	9.61
Street Dust											
KL-1	4 550	45	0.30	4.14	21 200	3 420	1.33	1.64	2.47	1.12	12.3
KL-2	1 080	12	0.62	1.97	6 740	1 070	1.01	1.62	2.75	1.41	13.8
KL-3	2 690	23	0.56	0.81	5 030	830	3.24	1.57	2.55	1.33	14.0
Asphalt											
Asphalt-1	1 540	36	0.34	4.41	29 200	3 800	0.41	1.66	3.2	1.58	16.9
Asphalt-2	1 340	44	0.53	3.63	10 800	1 390	0.96	1.66	3.6	2.04	16.5

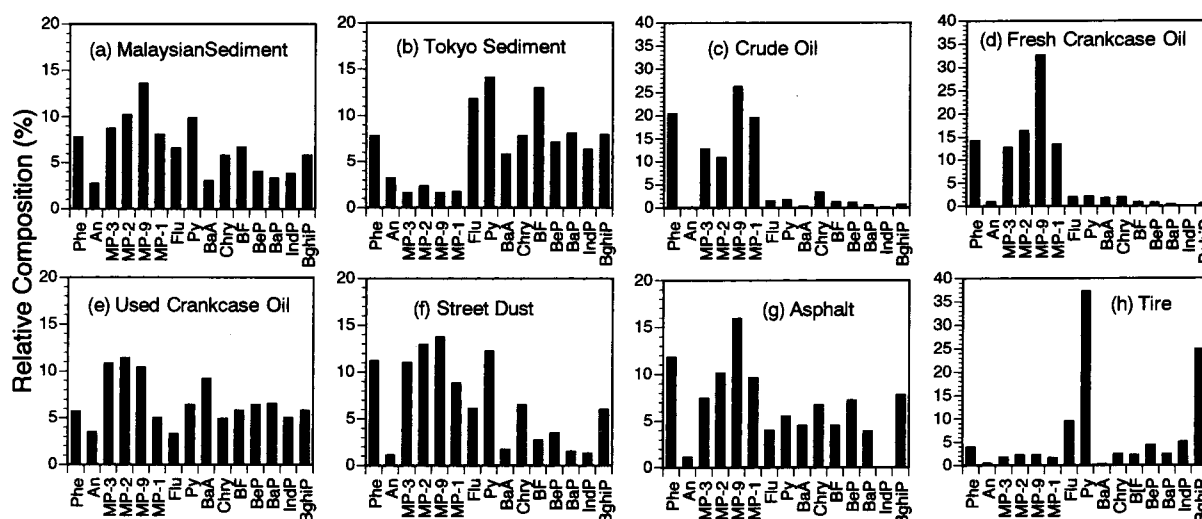
^a See legend of Table 1 for the definition of PAHs and Hopane indices.

FIGURE 7. PAHs profiles of the urban sediment and the source materials: (a) Malaysian sediment, Port Klang; (b) Tokyo Harbor sediment, st.25; (c) crude oil, Arabian light; (d) fresh crankcase oil, Petronas; (e) used crankcase oil, Petronas Gas Station; (f) street dust, KL-1; (g) asphalt, Asphalt-1; (h) tire, Bridgestone. See the caption of Figure 2 for compound abbreviations.

values for the urban sediments (0.47–1.47; Table 1), indicating that Malaysian sedimentary PAHs could not have originated from fresh crankcase oil (Figure 8). On the other hand, the concentration of PAHs in used crankcase oil is 3 orders of magnitude higher than that in fresh crankcase oil. The concentrations (total PAHs: 518 000–1 719 000 ng/g; Table 2) are comparable to those reported previously (90–92). These extremely elevated concentrations of PAHs are thought to be derived both from the accumulation of PAHs generated in the combustion chamber in the engine and from the incorporation of PAHs in unburned fuel (gasoline or diesel) into the crankcase oil. To compare the PAHs concentration in sediments and used crankcase oil, PAHs concentrations are normalized to C₃₀ 17 α hopane. The PAH/C₃₀-hopane ratio

in used crankcase oil ranged from 1.1 to 12.7 (Table 2). As shown in Figure 8, this is approximately 1 order of magnitude greater than those in urban sediments (0.58–1.09; Table 1), indicating that used crankcase oil could be an important source of sedimentary PAHs.

Used crank case oil was abundant in alkylated PAHs with an MP/P ratio of 3.99–6.55 and also abundant in HMW PAHs as shown in Figure 7. That is, used crankcase oil is a mixture of petrogenic PAHs, with an abundance in alkyl homologues, and pyrogenic PAHs, with an abundance in HMW species. Unburned fuel brings the petrogenic signature while high-temperature combustion in the engine introduces a pyrogenic signature to the used crankcase oil. Used crankcase oil is a unique source because it has both pyrogenic (i.e., abundant

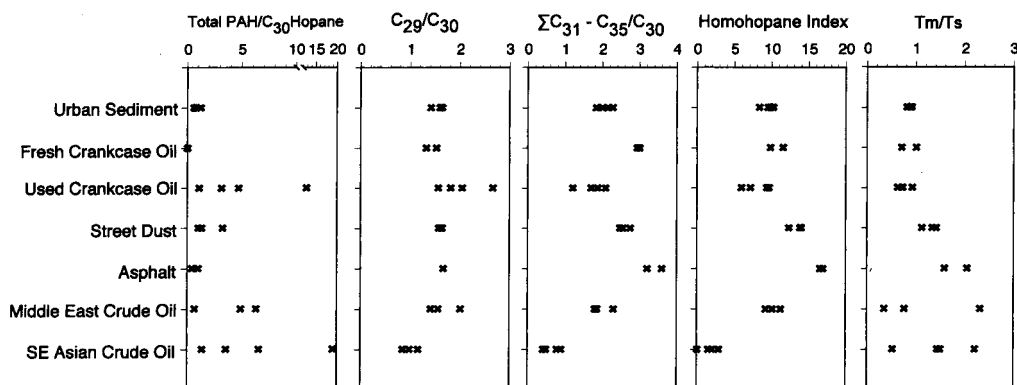


FIGURE 8. Hopane-normalized PAHs concentrations and hopane indexes in Malaysian urban sediment and the source materials. See Table 1 for the definitions of the indices.



FIGURE 9. Photos of improper handling of used crankcase oils in automotive workshops and garages: (left) August 12, 2001, automotive workshop, Serdang, Selangor; (center) and June 7, 2001, garage, Kajang, Selangor; (right) August 19, 2001, garage, near Malacca City.

HMW PAHs) and petrogenic (i.e., abundant alkyl homologues) signatures. When the chromatographic pattern of PAHs of the used crankcase oil samples is compared to those of the polluted sediment samples, very similar characteristics are revealed (Figure 7). Used crankcase oil is abundant in alkyl PAHs to a similar degree to those in the urban sediments. The MP/P ratios in the used crankcase oil (3.99–6.55) well overlapped the range of MP/P in the sediments (1.56–6.65). The abundance in the HMW PAHs was also similar to those in the urban sediments. The H/L ratios for the used crankcase oil samples overlapped with those of the polluted sediment samples (Tables 1 and 2). Furthermore, hopane fingerprints of the used crankcase oil were very similar to those in polluted sediments (Figure 6). The range of the C₂₉/C₃₀ ratio, (C₃₁–C₃₅)/C₃₀ ratio, and homohopane index of the used crankcase oil (1.56–2.66, 1.2–2.08, and 5.9–9.6, respectively) have also well overlapped with those in the urban sediments (1.41–1.64, 1.83–2.28, and 8.3–10.2, respectively), as shown in Tables 1 and 2 and Figure 8. In addition to these source indexes, maturation indexes (i.e., Tm/Ts ratio) were constant among the used crankcase oil data, and the range (0.71–0.92) covers the range of urban sediments (0.81–0.91). This is in contrast to the case of crude oil where Tm/Ts varied quite significantly. All of these fingerprints of used crankcase oil, in addition to their high PAHs content, indicate that used crankcase oil is one of the major contributors of PAHs in Malaysian sediments. The unique character of crankcase oil (i.e., a mixture of petrogenic and pyrogenic PAHs) can explain why the MP/P ratio is correlated with not only LMW PAHs concentrations but also HMW PAHs concentrations in Malaysian sediments.

Several other researchers have previously reported the input of used crankcase oil in aquatic environments (90, 93–98). Volkman et al. (93) have estimated the contribution of crankcase oil to sedimentary petroleum hydrocarbons using biomarker fingerprints. In an effort to provide a better understanding of petroleum hydrocarbons in urban runoff,

Latimer et al. (94) analyzed petroleum products and source materials for hydrocarbons. The study found that the hydrocarbon content in runoff had originated primarily from used crankcase oil. A questionnaire survey of residents in Providence, RI, observed that approximately 10% of the used crankcase oil generated by those residents who changed oil themselves was dumped onto roads or into storm sewers (99). Although evidence of the contribution of used crankcase oil to sedimentary hydrocarbons have been reported for “aliphatics” (90, 93–98), very limited evidence for “PAHs” has, however, been reported (100). This is probably due to pyrogenic PAHs profiles which are derived from combustion sources masking the petrogenic signature of used-crankcase-derived PAHs. In these contexts, the results of the present study are unique.

Used crankcase oil is listed under “Scheduled Wastes from Specific Sources—S012” in the Malaysian Environmental Quality Act and Regulations (101). Under the provision of the Act, the dumping of waste crankcase oil is punishable by law. Unlike in industrialized countries where recycling systems are more organized and established and a high degree of willingness to participate in recycling programs (e.g., see ref 94) and strict law and enforcement could minimize the input of the oil, Malaysia has no recycling program for used crankcase oil to date. Most of the used crankcase oils were improperly stored, allowing for indiscriminate spillage to the ground and streets or even for oils to be poured directly to drains, as shown in Figure 9. Heavy rainstorms that occur almost everyday in the tropics and equatorial regions can easily wash the spilled oil out to drains, rivers, and estuaries without enough time to undergo degradation/evaporation on the grounds or to receive cleanup activities. We believe that the combination of the improper storage of waste crankcase oil and frequent rainstorms is one of the main factors for the widespread input of crankcase oil PAHs.

Input from Street Dust and Traffic Sources. Another route for used crankcase oil to reach river sediment is the

TABLE 3. *N*-Cyclohexyl-2-benzothiazolamine (NCBA) Concentrations in Malaysian Sediments and the Source Materials

	NCBA (ng/g)	total PAHs ^a (ng/g)	PAH/NCBA ratio
Tire Rubber			
T-1	1 410	43 100	30.6
T-2	12 800	48 300	3.8
T-3	13 800	80 500	5.8
T-4	7 130	52 300	7.3
average	8 785	56 050	11.9
Malaysian Street Dust			
KL-1	74	4 547	61
KL-2	42	1 085	26
KL-3	12	2 686	224
average	43	2 773	104
Malaysian Sediment			
Pinang Estuary	2.48	924	373
Klang Estuary (St. A)	5.20	378	73
Malacca River	0.81	262	323
Procedural Blank	0.15		

^a See legend of Table 1 for the definition of "total PAHs".

leakage of the engine oil from vehicles onto road surfaces during driving and the incorporation into street dust and subsequent flushing by rainstorms. The contribution of street dust to sedimentary PAHs has been the subject of many studies (10, 15, 95, 102, 103). Street dust is normally transported into the sediments via street runoff and could be an important source of PAHs in tropical regions due to high and intense rainfall events. Our measurements have confirmed high concentrations of PAHs in street dust (1080–4550 ng/g; Table 2). These concentrations are 1 order of magnitude higher than those in the urban sediments (Table 1), and street dust could be a significant contributor to sedimentary PAHs.

The PAHs profiles of the street dust samples resembled those of the polluted sediments (Figure 7). The MP/P ratio and H/L ratio in the street dust samples ranged from 0.81 to 4.14 and from 0.30 to 0.62, respectively (Table 2). These values are similar to those for the urban sediments (Table 1), suggesting a significant contribution of street dust to the sedimentary PAHs. Hopane compositions of the street dust samples were also similar to those of the urban sediments (Figure 6). The range of the hopane indices, the C_{29}/C_{30} ratio, $(C_{31}-C_{35})/C_{30}$ ratio, homohopane index, and Tm/Ts ratio, were 1.57–1.64, 2.47–2.75, 12.3–14.0, and 1.12–1.41 (Table 2), and these ranges are similar to those for the Malaysian urban sediments (Table 1).

To estimate the contribution of PAHs in the street dust, NCBA, a molecular marker of tire particles and street dust, was also measured. NCBA is an impurity of a vulcanization accelerator (*N*-cyclohexyl-2-benzothiazolesulfenamide (CBS)) for automobile tire rubber and is specific to tire particles and street dust (67, 104). NCBA has been detected in tire-wear particles, street dust, and river sediments in Tokyo and has been proven as a powerful molecular marker of vehicle-derived pollution (67, 104). In the present study, Malaysian street dust and three of the polluted river sediments (Pinang Estuary, Klang Estuary St. A, and Malacca River) were analyzed for NCBA. Concentrations of NCBA in the Malaysian street dust ranged from 12 to 74 ng/g (Table 3), which are similar to those observed in Tokyo (67). As is obvious from Table 3, NCBA was significantly detected in all of the sediment samples analyzed. This has clearly indicated that street dust particles are contributing to Malaysian urban sediments. To quantitatively estimate their contribution to sedimentary PAHs, a PAHs/NCBA ratio is used. The PAHs/NCBA ratio in

the street dust ranged from 26 to 224, with an average of 104 (Table 3). By multiplying the averaged PAHs/NCBA ratio of the street dust by the NCBA concentrations in the sediments, street-dust-derived PAHs concentrations were estimated at 255, 535, and 84 ng/g for Pinang Estuary, Klang Estuary St. A, and Malacca River, respectively. They represent 28%, 141%, and 32% of the total PAHs observed in the sediments. In this calculation, NCBA and PAHs were assumed to behave similarly (i.e., no fractionation) during the transport of street dust to the aquatic environments. This assumption has been extensively examined by Kumata et al. (104). Using this assumption and the large variability of the PAHs/NCBA ratio in the street dust, the estimation carries significant uncertainties. However, this calculation suggests that street dust can significantly contribute to sedimentary PAHs in Malaysia.

To determine the major sources of PAHs in street dust, we examined asphalt, leakage of crankcase oil from vehicles, and tire-wear particles. Faure et al. (105) reported that road asphalts contribute to river sediments through their analysis of triterpane biomarkers (e.g., hopanes and terpanes). However, the results from this study show that hopane-normalized PAHs concentrations in the asphalt samples (PAH/ C_{30} -hopane: 0.41–0.97) were lower than those of street dust (1.01–3.24), although PAHs composition of the asphalt samples was similar to those in street dust (Figure 7 and Table 2). The lower PAHs concentrations indicate that asphalt could play a minor role in the contribution of PAHs in street dust. Furthermore, the hopane fingerprint of asphalt match poorly with that of the street dust. Mass fragmentograms (m/z 191) of asphalt showed a hump and a predominance of $17\beta,21\beta(H)$ C_{30} hopane (C_{30} 17β), which were normally minor in the urban sediments and street dust, over C_{30} 17α (Figure 6). These chromatographic patterns are different from those in the street dusts. Also, the hopane composition of asphalt was shifted to higher molecular weight as compared to street dust. Asphalt samples have a higher $C_{31}-C_{35}/C_{30}$ (3.2–3.6) and homohopane index (16.5–16.9) as compared to those in the street dust (2.5–2.8 and 12.3–14.0, respectively) and those in the urban rivers. These compositional features indicate that asphalt is not a major contributor of PAHs in street dust and in urban sediments. Because NCBA was detected in street dust and the sediment samples, tire particles may contribute to PAHs in the street dust and the sediments. However, the PAH composition of tire particles is characterized by an extremely high abundance of pyrene and benzo[ghi]perylene (Figure 7) and is quite different from that of the street dust and the river sediments. Calculation using the PAH/NCBA ratio has also indicated that the contribution of tire particles to street dust PAHs is less than 50%. Thus, these data concluded that tire particles are not the main contributor to street dust PAHs.

Last, the contribution of PAHs by leakage of engine oil from driven vehicles to road surface was examined. PAHs and hopane fingerprintings are found to be very similar between used crankcase oil and street dust (Figure 7). Also, the hopane-normalized PAH concentration of the used crankcase oil (PAH/ C_{30} -hopane: 1.1–12.7) was significantly higher than those in street dust (1.0–3.2). These results indicate that the leakage of engine oil could be a major contributor of PAHs in street dust, although asphalt and tire particles could be minor contributors. This result is different from the findings reported by Takada et al. (103) in that engine oil was a minor source of PAHs in street dusts in the Tokyo area. We hypothesized that the leakage of engine oil from an automobile could be more severe in Malaysia and other similar South East Asian countries. Unlike in Japan where automobile lifecycles are normally very short (5–9 years; see ref 106), South East Asian automobile lifecycles are relatively longer. For example, Malaysian automobile lifecycles are between 9 and 20 years (Anonymous officer, Road Transport

Department (JPJ), Ministry of Transport, Malaysia. Personal communication, 2001), which led to increase the possibility of engine oil leakage to the streets. Furthermore, the maintenance of automobiles appears to be generally poor in South East Asian countries, including Malaysia, and this will increase the chances of engine oil leakage to the streets, although no study has been done to confirm this suggestion.

In conclusion, used crankcase oil is the major source of sedimentary PAHs in Malaysia urban areas. These PAHs reach aquatic sediments by two main routes: (1) indiscriminate dumping and poor management in service stations and garages, and (2) leakages from poorly maintained vehicles to road surfaces, followed by incorporation into street dust, and subsequent wash-out as stormwater runoff to streams and rivers. We conclude that the road asphalt and tire-particle contribution to the Malaysian sedimentary PAHs play only a minor role. Levels of sedimentary PAHs in Malaysia are low to moderate when compared with other industrialized countries. Nonetheless, concern about the effects of PAHs accumulation on the aquatic and benthic ecosystems exists because Malaysian sedimentary PAHs are heavily impacted by petrogenic PAHs. It has been suggested that petrogenic PAHs are more available for biological uptake (107, 108), unlike pyrogenic PAHs which are less available to equilibrium partitioning as a result of presumed strong associations with combustion particles (27, 109–111). Also, pyrogenic PAHs in the crankcase oil may be macerated with the "oil" to be more bioavailable than those in soot without crankcase oil. In addition, the input of used crankcase oil poses a wide range of potential hazards to aquatic organisms because it contains heavy metals and other toxic chemicals in addition to PAHs (90). Furthermore, their adverse effects on aquatic biota have been documented (112, 113).

The present paper focused on Malaysia. However, similar situations could also be happening in other countries of the South East Asian region, because many have similar climatic and socioeconomic conditions. Heavy rain in the region caused surface erosion, contributing large amounts of soils to rivers and coastal zones, which dilute PAHs in the aquatic environments. However, frequent rainfall and fast flushing would transfer the pollutants to the aquatic environments before they undergo various removal processes in terrestrial environments such as photodegradation, the blowing away and atmospheric transport of particulate PAHs by wind, and in-stream degradation, among others. Also, public cleaning of pollutants on land (e.g., sweeping of road surfaces) is ineffective due to the frequent rain in the region. All of these processes may supply large amounts of PAHs to the aquatic environments. In the past decade, South East Asian countries have seen an exponential increase in motorization and industrialization. This change will bring a tremendous increase in the usage of crankcase oil resulting in a potential increase in the discharge of used crankcase oil into the South East Asian region. Because of the complexity of the climatic and socioeconomic conditions of the South East Asian region, the input, behavior, distribution, and fate of PAHs could be altogether different from those in the higher latitude zone. Through demonstrating the significant contribution of used crankcase oil to sedimentary PAHs, this study has afforded an important benchmark for future studies in this region. More studies should be done to cover a whole range of the South East Asian region and to understand the sociobiogeochemistry of PAHs inherent to this area.

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Supporting Information Available

Tables of the global distribution of sedimentary PAHs (Table S1); sample description for Malaysian sediments, crude oil, fresh lubricating oil, street dust, asphalt, and used crankcase oil (Table S2); and sedimentary PAHs in rivers, canals, harbors, and the bay in Tokyo (Table S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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