Environ Sci Pollut Res
DOI 10.1007/s11356-015-4093-7

RESEARCH ARTICLE

Distributions and source apportionment of sediment-associated polycyclic aromatic hydrocarbons (PAHs) and hopanes in rivers and estuaries of Peninsular Malaysia

Mehrzad Keshavarzifard · Mohamad Pauzi Zakaria · Tan Shau Hwai · Ferdius Mohamat Yusuff · Shuhaimi Mustafa

Received: 22 October 2014 / Accepted: 8 January 2015

Abstract In this study, the distributions and sources of sediment-associated polycyclic aromatic hydrocarbons (PAHs) and hopanes in the Malaysian rivers and estuaries were evaluated. The concentrations of 16 USEPA PAHs varied from 225.5 to 293.9 (Perlis River), 195.2 to 481.2 (Kedah River), 791.2 to 1995.4 (Merbok River), 231.2 to 426.7 (Perak River), and 3803.2 to 7442.7 ng g^{-1} (Klang River) dry weight. PAHs can be classified as moderate in the Perlis, Kedah, and Perak Rivers, moderate to high in the Merbok River, and high to very high in the Klang River. The comparison of PAHs with sediment quality guidelines (SQGs) indicates that occasionally adverse biological effects may occur from total PAHs, low molecular weight (LMW), and high molecular weight (HMW) PAHs at stations 1, 2, and 3 of the Klang River and from total PAHs at station 2 of the Merbok River. The diagnostic ratios of individual PAHs indicate both petrogenic and pyrogenic origin PAHs with significant dominance of pyrogenic sources in the study areas. The results suggest that Malaysian sediments had hopane ratios (C29/C30) similar to MECO suggesting MECO as a major source of the petroleum hydrocarbons found in the sediments, which is consistent with results reported in previous studies. These findings demonstrate that effective and improved environmental regulations in Malaysia have shifted the source of petroleum hydrocarbons from petrogenic to pyrogenic origin.

Keywords Polycyclic aromatic hydrocarbons (PAHs) · Hopanes · Sources apportionment · Pyrogenic · Petrogenic · Sediment · Malaysia

Introduction

Malaysia is geographically situated in the heart of Southeast Asia. In the past decades, Malaysia has witnessed an accelerated growth in industrial development and number of registered vehicles that saw a tremendous increase of usage of oil and oil derivatives. By the end of 2012, there were 22.7 million vehicles (personal cars, commercial vehicles, public vehicles, and motorcycles) registered in Malaysia, compared to 10.6 million in 2000 (JPJ 2013), showing an increase of almost 12 million vehicles or 114 %. Moreover, the strategic location of the Malacca Strait has made it one of the busiest and largest shipping routes. A huge amount of petrol and petroleum products are transported from Middle-East countries to Japan, China, Korea, and other neighboring countries via the narrow Straits of Malacca. The oil tanker traffic in the Malacca Strait, the increase of population in Malaysia and Southeast Asia, and the increased usage of petroleum, growing urbanization, and industrialization along rivers and coastal

Responsible editor: Leif Kronberg

M. Keshavarzifard · M. P. Zakaria (✉)
Environmental Forensics Research Center (ENFORCE), Faculty of Environmental Studies, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
e-mail: mpauzi@upm.edu.my

T. S. Hwai
School of Biological Science, Universiti Sains Malaysia, 11800 Minden, Pulau Pinang, Malaysia

F. M. Yusuff
Department of Environmental Sciences, Faculty of Environmental Studies, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

S. Mustafa
Halal Products Research Institute, Universiti Putra Malaysia, 4300 Serdang, Selangor, Malaysia

zones have been major factors causing the increase of hydrocarbon contamination in Malaysian coastal ecosystems. The Malaysia's population size and density, and gross domestic product (GDP) have experienced continuous growth during the last 2 decades. In 2012, data on population rose from 18.4 million in 1991 to 29.51 million (DOSM 2014a; DOSM 2014b), demonstrating an increase of population (over 60 %) in Malaysia. In addition, the proportion of urban population in Malaysia increased to 71 % in 2010 compared to 50.7 % in 1991 (DOSM 2014c). Malaysia recorded an average GDP growth of 5.2 % from 2002 to 2012 (World Bank 2014). There is limited information on the environmental distribution of PAHs in tropical Asia including Malaysia; therefore, the associated increase in petroleum hydrocarbons is of concern in the Malaysian aquatic environment.

Petroleum chemicals are classified into many categories and compounds consisting of polycyclic aromatic hydrocarbons (PAHs), and aliphatic hydrocarbons and biomarkers (Head et al. 2006; Neff 1979; Wang and Stout 2010). PAHs are one of the most important classes of pollutants, widely distributed in the riverine, marine, and coastal environment and ecosystems (Neff 1979). PAH contamination is of great global concern due to their negative effects on aquatic organisms (Karami et al. 2012), human health (Masiol et al. 2012), and environmental consequences, such as their toxicity, mutagenic, carcinogenic, teratogenic, and hepatotoxic effects (Cao et al. 2009). Therefore, in terms of ecotoxicology, it is crucial to monitor their sources, pathways, distributions, and fate in the environment and ecosystems. Numerical sediment quality guidelines (SQGs) are introduced as useful tools for evaluating the potential toxicological impacts of sediment-associated pollutants on environmental receptors. Development methods of SQGs rely upon equilibrium partitioning models (theoretically) or upon the analysis of matching field-collected chemistry and biological affects data (empirically) (Ankley et al. 1994; Long et al. 1995; Macdonald et al. 1996).

Based on their source of release into natural environments, anthropogenic PAHs can be classified into two groups: pyrogenic and petrogenic. Pyrogenic PAHs are derived from incomplete combustion of organic matters such as combustion of fossil fuel, vehicular engines combustion, garbage incineration, and coal combustion (Dhammapala et al. 2007; Ergut et al. 2006). Pyrogenic sources of PAHs can be classified as stationary sources, i.e., industries (refineries), residential heating (furnace, making barbeque, and oil burnings), power and heat generation (coal, oil, and power plants), and agricultural burnings plus mobile sources including vehicles, airplanes, ships, and boats as well as from smoking cigarettes (Maliszewska-Kordybach 1999). Pyrogenic PAHs are partitioned with soot particles in the atmosphere, and they can be transported in a long-range atmospheric pathway (Gustafsson and Gschwend 1997; Takada et al. 1991). PAHs with petrogenic sources consist of unburned crude oil and its derivatives such as gasoline, diesel fuel, lubricating oil, and asphalt (Marchand et al. 2004; Ravindra et al. 2008). It was suggested that dumping of used crankcase oil is one of the major source of petrogenic PAHs in Malaysia (Zakaria et al. 2002). Using diagnostic ratios is one of the most effective techniques for PAH source appointment (Budzinski et al. 1997; Garrigues et al. 1995; Yunker et al. 2002). PAH ratio characteristics are controlled by differences in the relative stability of PAHs under low- and high-temperature regimes, which can provide important insight into PAH origins (Yunker and Macdonald 2003; Yunker et al. 2002). High molecular weight (HMW) PAHs (4-, 5-, and 6-ring PAHs) can indicate fossil and liquid fuel combustion, and biomass/coal (solid fuel) combustion PAH origins, while ratios for the low molecular weight (LMW) PAHs (2- and 3-ring PAHs) and ratios for several alkyl PAHs can indicate combustion from petroleum (Yunker et al. 2002). For ease of comparison, all parent PAH ratios have the combustion-dominated, thermodynamically less stable isomer in the numerator, so that ratios increase with an increase in combustion input (Yunker et al. 2002).

Hopanes, a group of pentacyclic triterpane hydrocarbons, are ubiquitous compounds in crude oil and petroleum products including lubricating oils, asphalt, and heavy residual oils with high boiling points. Their compositions depend on their origin in the crude oil (e.g., the sources of organic matter and the depositional environment) and the maturity stage of the oil (Luellen and Shea 2003; Volkman et al. 1997). Moreover, hopanes are resistant to environmental alternation and degradation due to their molecular structure (Prince 1994; Wang et al. 1994). These characteristics provide potential for hopanes to be used as biomarker. These molecular markers provide a fingerprint to determine the sources of oils (Chandru et al. 2008; Saha et al. 2009; Volkman et al. 1997; Zakaria et al. 2002). Hopanes with $\alpha\beta$ configuration (e.g., $17\alpha(H),21\beta(H)$-Hopanes) in the C_{27}–C_{35} range are characteristics of petroleum due to their greater thermodynamic stability compared to those with $\beta\alpha$ configuration (e.g., $17\beta(H),21\alpha(H)$-Hopanes) (Sakari et al. 2010). One of the tools which have been used to identify oil from nonpetroleum sources is the C_{29}/C_{30} ratio (ratio of $17\alpha(H),21\beta(H)$-norhopane to $17\alpha(H),21\beta(H)$-hopane) (Zakaria et al. 2000).

The objectives of the present study are to determine the contamination level and distribution of 16 USEPA PAHs and to investigate their major sources as well as to evaluate potential ecotoxicological impacts in the surficial sediments from the Perlis, Kedah, Merbok, Perak, and Klang Rivers and Estuaries. Several diagnostic and molecular ratios were used to identify the sources of sedimentary PAHs. The content of hopanes in surficial sediments was also monitored. The results of the present study will add new information to the global database and also provide data in order to improve the regulations and consequently the environmental quality of the selected rivers and estuaries.

Methodology

Study area and sampling

Top 4-cm surface sediment samples were collected at 15 stations from the Perlis, Kedah, Merbok, Perak, and Klang Rivers and Estuaries, located on the west of Peninsular Malaysia, in January 2013. The location of the sampling sites is shown in Fig. 1 and Table 1. All samples comprised of top sediment cakes (to indicate modern input of target pollutants) collected using an Ekman dredge. At each station, the shell debris and organisms were carefully removed, and the samples were then transferred into previously cleaned aluminum foil and double pre-cleaned Ziploc bag and then placed in the cooler box with dry ice (Keshavarzifard et al. 2014). Afterward, the samples were transported to the laboratory and stored at −20 °C before analysis. Prior to analysis, the samples were freeze-dried and undergone next step of analysis.

Chemical, extraction, and separation

The procedures of extraction, purification, and fractionation were described elsewhere (Keshavarzifard et al. 2014; Zakaria et al. 2002). This method relies upon homogenization, extraction, two-step silica gel column chromatography, and gas chromatography–mass spectrometry (GC-MS). Briefly, 8 g of freeze-dried sediment was precisely weighed and then placed in a cellulose thimble in the soxhlet glass chamber. Each sample was spiked with 50 μL of 10 μg/g of a surrogate internal standard mixture containing naphthalene-d_8, anthracene-d_{10}, chrysene-d_{12}, and perylene-d_{12} for the recovery correction calculations of PAH compounds. The sample was extracted using 300 mL high purity dichloromethane (DCM) for 8–10 h. Following activated copper treatment to remove elemental sulfur, the extract was rotary evaporated followed by a gentle drying using pure nitrogen gas until near dryness. The concentrated extract was carefully transferred onto the top of the first step glass column (0.9-cm i.d.×9-cm height), which were previously packed with 5 % H_2O-deactivated silica gel (60–200 mesh size, Sigma Chemical Company, USA) to remove polar compounds. In this step, the nonpolar components, including hydrocarbons were eluted by using 20 mL of hexane/DCM (3:1, *v*/*v*). Then, the hydrocarbon eluent obtained from the first step column was further separated and fractionated by second step column chromatography using a fully activated silica gel column (0.47-cm i.d×18-cm height) to obtain alkanes and hopanes, linear alkylbenzenes (LABs), and PAH fractions. The first hexane (4 mL) fraction contained alkanes and hopanes, while the third fraction contained PAHs using 16 mL hexane/DCM (3:1, *v*/*v*). PAHs with two to six aromatic rings were fractionated in the third fraction using 16 mL high purity hexane/DCM (3:1, *v*/*v*). The volume of hopanes and PAH fractions was reduced to approximately 1 mL using a rotary evaporator and concentrated using a gentle stream of pure nitrogen gas to near dryness. The PAH fraction was then redissolved in 200 μL isooctane containing 10-ppm internal injection standard (IIS), *p*-terphenyl-d_{14}. The hopane fraction was firstly redissolved in 50 μL containing 10-ppm IIS, 17β,21β(H)-hopane C_{30}. Hopanes and PAHs were analyzed by gas chromatography–mass spectrometry (GC-MS) Shimadzu QP5050A model and BPX-5MS fused-silica capillary column (30-m by 0.25-mm i.d., 0.25-μm film thickness). The carrier gas was of high purity helium (He) with a constant pressure at 60 kg/cm^2.

GC-MS analysis of PAHs and hopanes

The 16 USEPA priority PAHs (include PAHs with two-ring, naphthalene (Nap); three-ring, acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant); four-ring, fluoranthene (Fluo), pyrene (Py), benzo[a]anthracene (BaA), chrysene (Chr); five-ring, benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP); and six-ring, indeno[1,2,3-cd]pyrene (InP), dibenzo[a, h]anthracene (DBA), and benzo[ghi]perylene (BgP)) were analyzed using GC-MS Shimadzu QP5050A model and BPX-5MS fused-silica capillary column (30-m by 0.25-mm i.d., 0.25-μm film thickness). A 1-μL aliquot of purified samples was introduced into the GC-MS injector. The GC-MS temperature program started at 70 °C for 2 min, with a ramp of 30 °C per minute until 150 °C. The temperature was further increased to 310 °C with an increasing rate of 4 °C/min for 15 min. The analysis was done using selected ion monitoring (SIM) mode with splitless injection.

Individual hopanes were monitored in SIM mode at (mass/charge ratio) $m/z=191$. The oven temperature was held at 70 °C for 2 min, then continued at 30 °C/min to 150 °C, 5 °C/min to 310 °C and held for 6 min. The capillary column HP-5MS (30 m, 0.25-mm i.d., containing a 0.25-μm film thickness bonded phase of DB-5MS) was interfaced directly to the ion source of the mass spectrometer. The mass spectrometer was scanned repeatedly at an ionization potential of 70 ev with the source at 200 °C and electron multiplier voltage at ~2000 ev. We used 17α(H)-22,29,30-trisnorhopane (Tm), $C_{29}17\alpha$, 17β(H),21α(H)-norhopane ($C_{29}17\beta$), $C_{30}17\alpha$, and 17β(H),21α(H)-hopane ($C_{30}17\beta$) as analytical standards. Detailed qualitative and quantitative analyses of hopanes are discussed elsewhere (Zakaria et al. 2000).

Quantification of target compounds of PAH and hopanes was carried out based on external calibration curves using

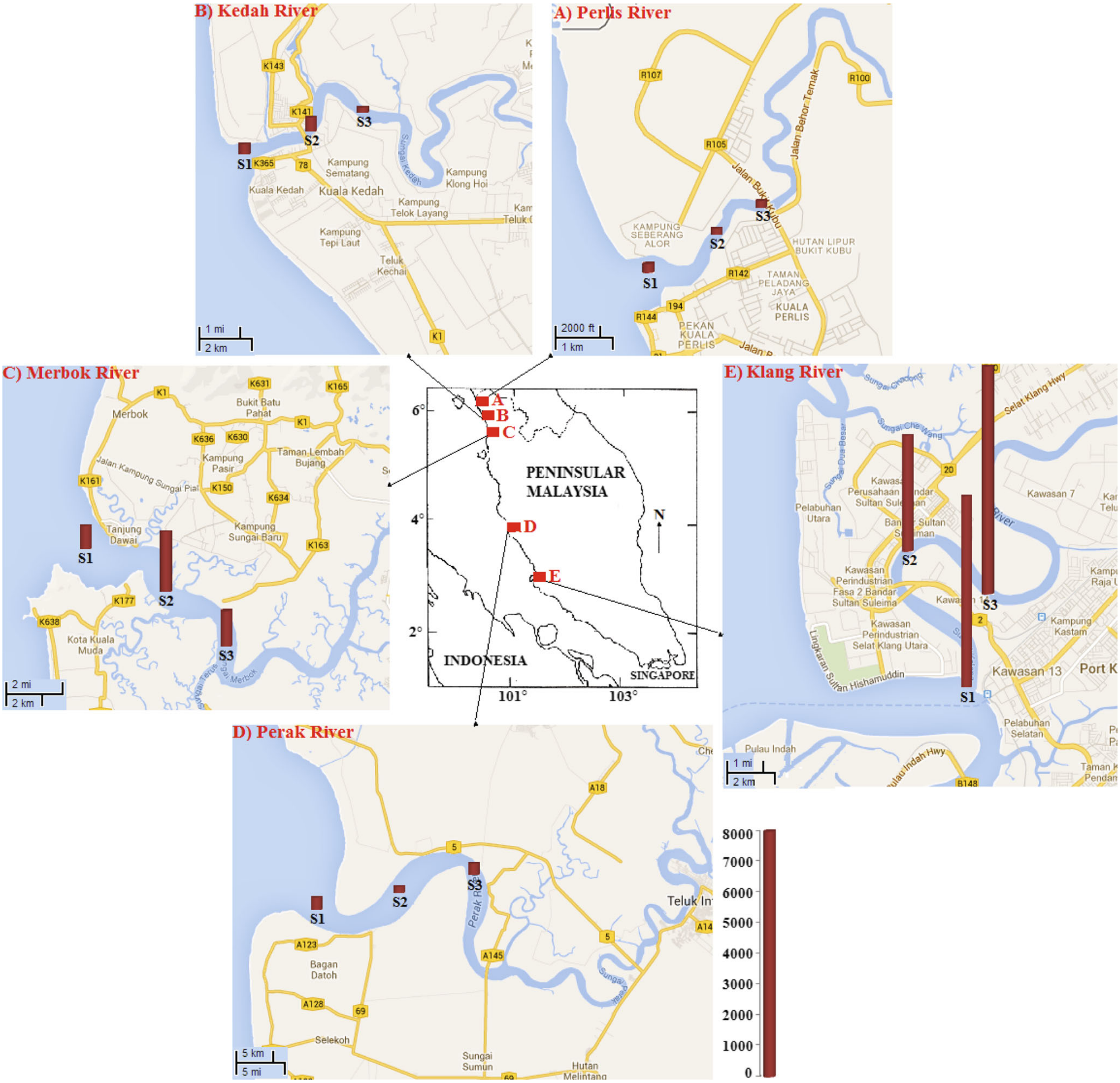


Fig. 1 Location of sampling areas: **a** Perlis River, **b** Kedah River, **c** Merbok River, **d** Perak River, and **e** Klang River

standard mixtures of PAH and hopane. Determination of target compounds was achieved based on matching their compound ionization and retention times with the standard mixture of PAHs and hopanes. Nondetectable compounds (<0.01 ppm) were treated as no value in calculation of the total PAH, LMW, and HMW PAHs. All of PAHs and hopanes in sediment samples were calculated based on dry weight (dw).

Quality assurance and quality control

The quality assurance (quality control and quality assessment) was conducted during the experimental analysis of this study. Quality control for the PAHs analyses was performed by monitoring the recovery of surrogate standards (naphthalene-d_8, anthracene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) prior to solvent extraction. The recovery of surrogates was >83 % of the spiked concentration. The samples with the recovery of the surrogate standards lower than the accepted range were reanalyzed. PAH concentrations were recovery-corrected against the surrogate standards (deuterated PAHs) spiked (Cortazar et al. 2008). All standards were freshly prepared prior to analysis and procedural blanks for PAHs, and hopanes were run with every batch of samples (Arias et al. 2009). The analysis of a reagent blank demonstrated that the analytical

Table 1 Detailed water quality data of sampling sites

Sampling location	Latitude (° N)	Longitude (° E)	DO (mg/L)	Conductivity (ms/cm)	Turbidity	Salinity (ppt)	Temperature (°C)	PH
Perlis River S1	6° 24′	100° 7′	5.5	45.5	19.7	29.3	30	8
Perlis River S2	6° 24′	100° 8′	5.8	19	20.3	19	29	8
Perlis River S3	6° 26′	100° 9′	6.8	9.2	16.1	5	30.1	7.6
Kedah River S1	6° 6′	100° 16′	4.9	39.78	17.4	25.2	31.1	7.5
Kedah River S2	6° 6′	100° 19′	2.1	25.56	14.5	15.5	29.8	7.03
Kedah River S3	6° 7′	100° 20′	2.2	13.11	10.3	7	31	6.83
Merbok River S1	5° 39′	100° 24′	12.1	39.26	3.56	24.29	30	8.5
Merbok River S2	5° 38′	100° 26′	14.1	37.14	5.01	23.4	31	8.45
Merbok River S3	5° 41′	100° 29′	7.8	25.53	13	14	30.3	7.33
Perak River S1	4° 0′	100° 45′	5.05	40.14	6.41	22.6	32.10	7.57
Perak River S2	4° 2′	100° 51′	5.41	6.31	12.3	3.1	31.5	7.72
Perak River S3	3° 57′	100° 55′	4.5	20.44	23.6	0.9	31	7.43
Klang River S1	2° 59′	101° 23′	3.8	45.77	21.7	26.5	30.3	7.56
Klang River S2	3° 3′	101° 25′	4.98	41.37	36.2	16.6	30.5	7.69
Klang River S3	3° 2′	101° 27′	1.45	12.10	43.9	6.2	30.2	7.51

system and glassware were free of contamination. The quality assurance for the hopane analyses was also conducted in this study. No recovery correction was made for the hopane analyses.

Analysis of TOC

Total organic carbon (TOC) was measured according to a method described by Nelson and Sommers (1996). A total of 1 or 2 g of the homogenized and freeze-dried sample was added by 1 or 2 mL of 1 M HCl and then dried at 100 °C overnight to eliminate inorganic carbons. Thereafter, a LECO CR-412 Carbon Analyzer (with the furnace temperature of 1350 °C and O_2 boost time of 1 min) was used to determine the TOC percentage.

Results and discussion

Concentrations, distribution pattern, and composition profiles of PAHs

Table 2 and Fig. 2 summarized the spatial distribution patterns of PAHs. The concentrations of total PAH varied from 225.5 to 293.9 with a mean value of 255.3 (the Perlis River), 195.2 to 481.2 with a mean value of 344.5 (the Kedah River), 791.2 to 1995.4 with a mean value of 1320 (the Merbok River), 231.2 to 426.7 with a mean value of 350.1 (the Perak River), 3803.2 to 7442.7 with a mean value of 5834.3 (the Klang River) all on nanograms per gram dry weight basis. In addition, the minimum and maximum concentrations of PAHs in the collected sediments were 195.2 and 7442.7 ng g^{-1}, respectively, which were recorded at the station 3 of the Kedah River and the station 3 of the Klang River, respectively. In general, the Klang River was the most polluted river among the study sites, followed by the Merbok River, the Perak River, and the Kedah River. The Perlis River, however, was the least polluted river. The levels of sediment contamination by PAHs can be classified as low (0–100 ng g^{-1}), moderate (100–1000 ng g^{-1}), high (1000–5000 ng g^{-1}), and very high (>5000 ng g^{-1}) to the level of pollution (Baumard et al. 1998). Based on this classification, PAHs can be classified as moderate in the Perlis, Kedah, and Perak Rivers, moderate to high in the Merbok River, and high to very high in the Klang River.

For the purpose of determining the concentration trend of PAHs in the Klang River and Estuary, we compare the average concentrations of total PAH in sediments from the Klang River and Estuary in the present study with those of Zakaria et al. (2002) and Bakhtiari et al. (2010) where the average concentrations of total PAH were 233.4 and 1804 ng g^{-1}, respectively (Table 3). A significant increase in the levels of PAHs was observed in the sediment samples of the present study compared to those results reported by the workers. However, more studies are needed to confirm this statement. There are two reasons for the increment: first, the sedimentation input by land-based activities such as land-clearing has increased since the previous studies which results in more input of contaminants carried by suspended sediments from upper and middle areas of the Klang River. Second, Malaysia has experienced a dramatic increase in population, industrialization,

Table 2 PAHs in selected major rivers of the Malaysian sediments

Study area	Station	TOC %	Total PAHs	LMW PAHs	HMW PAHs	LMW/HMW	Py/Fluo	Fluo/ (Fluo+Py)	BaA/ (BaA+Chr)	InP/ (Inp+BgP)	MP/P
Perlis	S1	2.44	293.9	86.6	207.3	0.42	1.1	0.49	–	0.41	0.89
	S2	5.53	225.5	89.5	136	0.66	0.84	0.54	0.74	0.41	1.3
	S3	2.17	246.5	125.3	121.2	1.03	1.55	0.39	0.71	0.49	2.6
Kedah	S1	1.64	357.1	81.7	275.4	0.3	0.6	0.62	0.5	0.49	1.9
	S2	1.9	481.2	188.4	292.8	0.64	0.95	0.51	0.91	0.19	2.01
	S3	2.19	195.2	22.6	172.6	0.13	–	–	0.61	–	0.3
Merbok	S1	7.06	791.2	114.9	676.3	0.17	–	–	0.18	–	0.99
	S2	2.04	1995.4	368.1	1627.3	0.23	0.99	0.5	0.48	0.45	1
	S3	3.31	1173.3	229	944.3	0.24	0.96	0.51	0.54	0.45	1.2
Perak	S1	5.97	426.7	106.5	320.2	0.33	0.99	0.5	1	–	0.4
	S2	1.82	231.2	73.3	157.9	0.46	0.97	0.51	1	0.5	0.94
	S3	1.26	392.5	118.3	274.2	0.43	1.2	0.46	0.46	0.54	0.76
Klang	S1	1.54	6257.1	1118.3	5138.8	0.2	0.9	0.52	0.39	0.46	0.87
	S2	2.07	3803.2	761.7	3041.5	0.25	0.5	0.66	1	0.35	0.77
	S3	1.75	7442.7	2051.2	5391.5	0.38	0.91	0.52	0.33	0.52	0.99
ERL	–	–	4000	552	1700	–	–	–	–	–	–
ERM	–	–	45000	3160	9600	–	–	–	–	–	–
TEL	–	–	1684	–	–	–	–	–	–	–	–
PEL	–	–	16770	–	–	–	–	–	–	–	–

TOC total organic carbon, *Total PAHs* sum of the concentrations of 16 USEPA priority PAHs, *LMW PAHs* sum of low molecular weight PAHs concentrations from naphthalene to fluoranthene, *HMW PAHs* sum of high molecular weight PAHs concentrations from pyrene to benzo [ghi]perylene, *LMW/HMW* the ratio of LMW PAH to HMW PAHs, *Py/Fluo* the ratio of pyrene to fluoranthene, *Fluo/Fluo+ Py* the ratio of fluoranthene to fluoranthene + pyrene, *BaA/(BaA+ Chr)* the ratio of benzo(a)anthracene to benzo(a)anthracene + chrysene, *InP/(Inp+ BgP)* the ratio of ideno(1,2,3-cd)pyrene to ideno(1,2,3-cd)pyrene + benzo(ghi)perylene, *MP/P* the ratio of 3-methylphenanthrene, 2-methylphenanthrene, 9-methylphenanthrene, and 1-methylphenanthrene to phenanthrene, *ERL* effects range-low value (Long et al. 1995), *ERM* effects range-median value (Long et al. 1995), *TEL* threshold effect levels (Macdonald et al. 1996), *PEL* probable effect levels (Macdonald et al. 1996)

and urbanization resulting in the significant increase of the pollution load into the river. For example, the Klang River runs through the capital city of Kuala Lumpur, a highly industrialized city, and its GDP and population evidently increased during the last few decades. It is reasonable to assign these high concentrations of PAHs to the increment of using oil and coal as energy sources and traffic-related source of PAHs in Kuala Lumpur and

Fig. 2 Concentrations of total PAH, LMW, and HMW PAHs in sediments collected from the Perlis, Kedah, Merbok, Perak, and Klang Rivers (please see the legend of Table 2 for the definition of "Total PAHs, LMW, and HMW 16 PAHs")

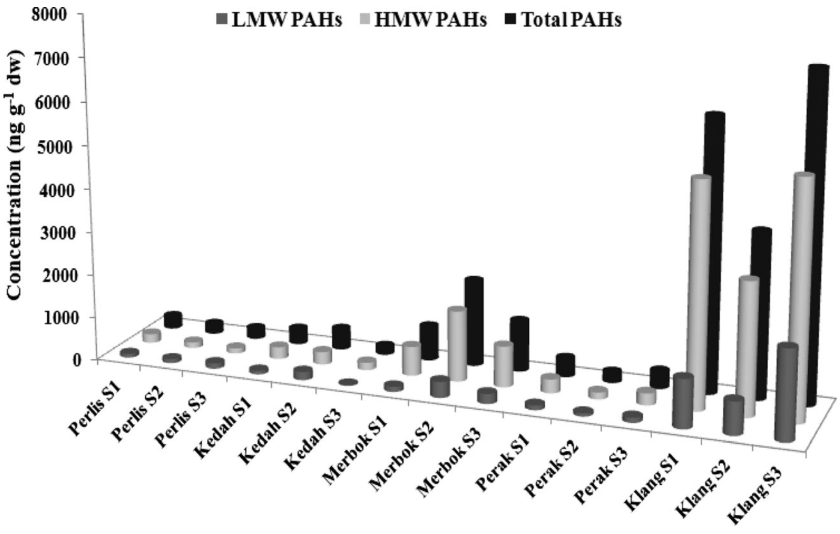


Table 3 Total PAH concentrations in sediments from different locations around the world

Location	Total PAHs (ng g^{-1})	Number of PAH compounds	Contamination Level[a]	References
Boston Harbor, USA	7300–358000	16	Very high	(Wang et al. 2001)
Barcelona Harbour, Spain	1740–8420	14	High to very high	(Baumard et al. 1998)
Guanabara Bay, Brazil	91–8035	20	Low to very high	(Meniconi et al. 2002)
Patos Lagoon Estuary, Brazil	37–11779.9	23	Low to very high	(Medeiros et al. 2005)
Rybinsk Reservoir, Russia	178–5203	11	High to very high	(Siddall et al. 1994)
Yangtze estuary, China	76.9–2936	16	Low to high	(Wang et al. 2012)
Hangzhou, China	132.7–7343	10	Moderate to very high	(Chen et al. 2004)
Hyeongsan River, Korea	5.30–7680	16	Low to very high	(Koh et al. 2004)
The Northern Persian Gulf	55.3–1231	16	Low to high	(Nozar et al. 2014)
Gorgan Bay, Caspian Sea	107.9–516	16	Moderate	(Araghi et al. 2014)
Jakarta Bay, Indonesia	191–1252	18	Moderate to high	(Rinawati et al. 2012)
Canals, Rivers, Lake, and Coastal Environments of Southeast of Asia including: Thailand, Vietnam, Cambodia, Laos, the Philippines and Indonesia	1020–1760	26	High	(Saha et al. 2009)
Malaysia	206	26	Moderate	(Saha et al. 2009)
Prai River, Malaysia	81	15	Low	(Zakaria et al. 2002)
Pinang Estuary, Malaysia	924		Moderate	
Malacca River (1998), Malaysia	494		Moderate	
Malacca River (1999), Malaysia	262		Moderate	
Rivers and Estuaries in Malaysia	4–924		Low to moderate	
Klang Estuary, Malaysia	19–431	15	Low to moderate	(Zakaria et al. 2002)
Klang River, Malaysia	1304–2187	19	High	(Bakhtiari et al. 2010)
West Coast of Peninsular Malaysia	19–481	19	Low to moderate	(Mirsadeghi et al. 2013)
Prai River, Malaysia	1102–7938	16	High to very high	(Keshavarzifard et al. 2014)
Malacca River, Malaysia	716–1210	16	Moderate to high	
Merambong River, Malaysia	38.6–122.8	16	Low to moderate	(Vaezzadeh et al. 2014)
Muar River, Malaysia	15.5–165.7		Low to moderate	
Kuala Selangor River, Malaysia	563–1037	16	Moderate to high	(Masood et al. 2014)
Perlis River, Malaysia	225.5–293.9	16	Moderate	This study
Kedah River, Malaysia	195.2–481.2		Moderate	This study
Merbok River, Malaysia	791.2–1995.4		Moderate to high	This study
Perak River, Malaysia	231.2–426.7		Moderate	This study
Klang River, Malaysia	3803.2–7442.7		High to very high	This study

[a] Scale of level of contamination: low: 0–100; moderate: 100–1000; high: 1000–5000; very high: >5000 (Baumard et al. 1998)

Selangor States. It is important to point out that the current study has demonstrated one of the highest PAH concentrations found in any sediments of the Malaysian aquatic environment.

Compared with other areas in Malaysia, the total PAH concentrations in the present study were comparable or lower than those presented in the Prai and Malacca Rivers (Keshavarzifard et al. 2014), in the Langat River (Bakhtiari et al. 2009), and in aquaculture areas in Peninsular Malaysia (Retnam et al. 2013), but were higher than those observed in the Merambong and Muar Rivers (Vaezzadeh et al. 2014), in the Selangor River (Masood et al. 2014) in the surface sediments in rural and urban areas of Malaysia (Saha et al. 2009), and in aquacultures located in intertidal mudflats of the west coast of Peninsular Malaysia (Mirsadeghi et al. 2013).

Most of the PAH values can be widely categorized in range over tens of thousands of nanograms per gram (developed countries) up to thousands of nanograms per gram (fast-growing countries, including Brazil, Russia, India, China, and South Korea) and in the range from tens to hundreds of nanograms per gram (developing countries) (see Table 3). PAH concentrations in the Perlis, Kedah, and Perak Rivers were comparable to those of developing countries, while in the Merbok and Klang Rivers were comparable to those of fast-growing countries. For comparison, total PAH levels in Boston

Harbor, USA (7300–358,000 ng g^{-1}) are many folds higher than those in Malaysian riverine and estuaries.

Evaluation of ecotoxicological risk of PAHs

Sediment quality guidelines (SQGs) can be used for assessment of contamination in freshwater, estuarine, and marine sediments (Long et al. 1995; Macdonald et al. 1996), and based on the results, the environmental regulation and policy can effectively protect aquatic life. In this study, four widely used sets of SQGs, including effects range-low value (ERL), effects range-median value (ERM), probable effects level (PEL), and threshold effects level (TEL), were applied to evaluate the ecological toxicity of the individual and total PAH levels in the sediments of the study areas. Long et al. (1995) suggested that, based on SQGs, adverse biological effects are considered to occur rarely (PAH concentrations < ERL and < TEL), occasionally (PAH concentrations ≥ ERL, ≥TEL, <ERM, and < PEL), and frequently (PAH concentrations ≥ ERM and ≥ PEL). The results of this study (total PAH, LMW PAHs, and HMW PAHs) were compared with the ERL, ERM, PEL, and TEL SQGs (Table 2). The results found that the concentrations of 16 PAHs at the stations 1 and 3 of the Klang River were higher than the ERL value. Moreover, the total PAH concentrations at station 2 of the Merbok River and stations 1, 2, and 3 of the Klang River were higher than the TEL value. The levels of LMW and HMW PAHs at stations 1, 2, and 3 of the Klang River were higher than the ERL value. The concentrations of total PAH, LMW PAHs, and HMW PAHs in the rest of the samples were lower than the SQGs values. Based on these results, occasionally adverse biological effects may occur from total PAH, LMW, and HMW PAHs at stations 1, 2, and 3 of the Klang River and from total PAH at station 2 of the Merbok River.

Composition of PAHs

The composition pattern of PAHs (the mean values of different ring PAHs in three sampling stations of each river) by ring size is described in more detail in the collected surface sediments. As displayed in Fig. 3, PAHs in the Perlis River was dominated by three-ring PAHs (38 %), followed by four-ring PAHs (29 %), while PAHs in the Merbok River were dominated by six-ring PAHs (29 %), followed by five-ring PAHs (27 %). The composition pattern of PAHs in both the Kedah and Perak Rivers was dominated by four-ring PAHs (32 and 28 %, respectively), followed by three-ring PAHs (23 and 22 %, respectively), but in the Klang River, PAHs were dominated by five-ring PAHs (35 %), followed by four-ring PAHs (23 %). Two-ring PAHs had the smallest portion of PAHs in the sediment samples of all stations, ranging from 0.00 ng g^{-1} at station 3 of the Perlis River and station 1 of the Perak River to 491.1 ng g^{-1} at station 3 of the Klang River. Overall, both higher molecular compounds and lower molecular compounds were representative of the total PAH compounds in the collected sediments from all rivers and estuaries (Fig. 3). As it is shown in Figs. 2 and 3, LMW PAHs (two- and three-ring PAHs) were depleted in the estuaries (station 1) of all study areas. This depletion can be due to the high salinity and low velocity of the water in the estuaries (Table 1), which may have increased the degradation of LMW PAHs.

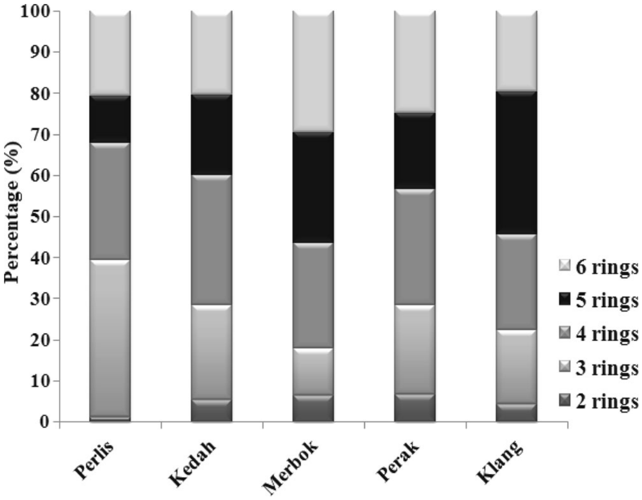
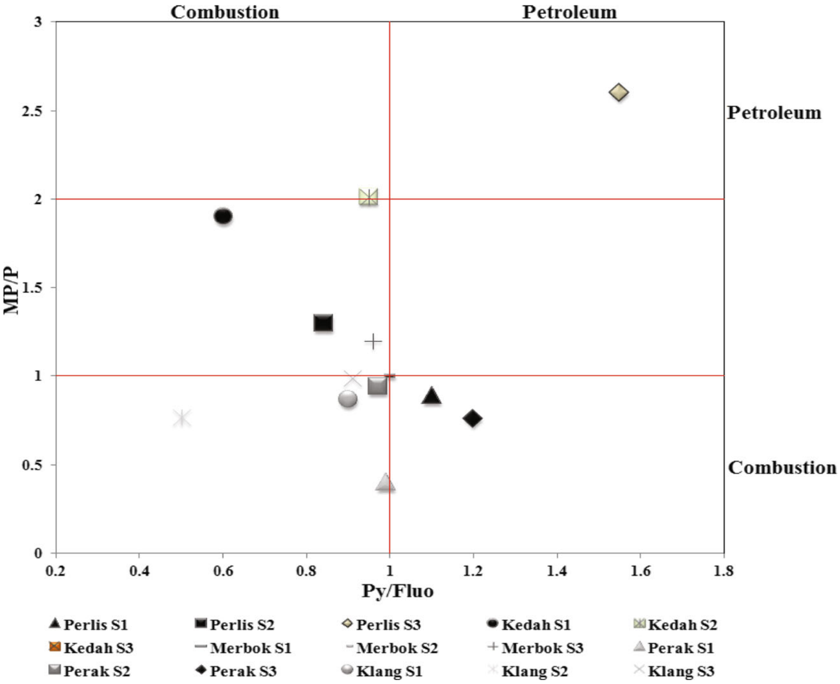


Fig. 3 The composition pattern of PAHs mean values by ring size in surface sediments of the Perlis, Kedah, Merbok, Perak, and Klang Rivers

Source diagnostics and apportionment

Identifying PAH sources is necessary for controlling their input into the environment and ecosystems and also for remedial activities. PAH isomeric ratios, which is based on the relative abundance of individual PAH or groups of PAHs, including Py/Fluo, Fluo/(Fluo+Py), InP/(Inp+BgP), BaA/(BaA+Chr), and MP/P (methylphenanthrenes (3-methylphenanthrene, 2-methylphenanthrene, 9-methylphenanthrene, and 1-methylphenanthrene) to phenanthrene) have been practically used for differentiation of petrogenic and pyrogenic sources of PAHs (Keshavarzifard et al. 2014; Mirsadeghi et al. 2013; Yunker et al. 2002; Zakaria et al. 2002). Pyrene and fluoranthene are different in terms of thermodynamics, of which pyrene is more stable than fluoranthene. Therefore, the high abundance of this ratio indicates petrogenic origins, while the lower abundance indicates pyrogenic origins (Budzinski et al. 1997). Stations which exhibited a Py/Fluo ratio of more than 1 mean that the source of PAHs is related to a petrogenic origin, while a ratio of lower than 1 predominantly indicates pyrogenic origins (Sicre et al. 1987). In this study, the Py/Fluo ratios in all samples were lower than 1, except for samples from stations 1 and 3 of the Perlis River and station 3 of the Perak River (Table 2 and Fig. 4), suggesting dominance of pyrogenic PAHs at most of the stations. This is confirmed by LMW/HMW ratios (LMW/HMW ratios ranged from

Fig. 4 Plots of PAH isomer pair ratios for source identification: Py/Fluo versus MP/P



0.13 to 1.03), which demonstrate the dominance of HMW PAHs (combustion derivative PAHs) (Table 2).

Parent PAHs are thermodynamically more stable than alkylated PAHs. In high-temperature combustion-derivative PAHs, the alkylated PAHs are depleted, whereas in petroleum products, they are in high abundance. Therefore, the ratio of alkylated PAHs to parent PAHs has been used for source identification of PAHs (Garrigues et al. 1995; Youngblood and Blumer 1975). Some studies have suggested that an MP/P ratio lower than 1 indicates combustion origin PAHs, while an MP/P ratio higher than 2 implies fresh petroleum origin PAHs (Garrigues et al. 1995; Yang et al. 2009). The MP/P ratios in the sediment samples at station 3 of the Perlis River (MP/P was 2.6) and station 2 of the Kedah River (MP/P was 2.01) indicate fresh petroleum contribution, while at station 2 of the Perlis River, station 1 of the Kedah River and station 3 of the Merbok River the MP/P ratios were between 1 and 2. Moreover, MP/P ratios in the sediment samples at the other stations were lower than 1 (Table 2 and Fig. 4), and these imply that the PAHs have mainly originated from combustion.

A ratio of Fluo/(Fluo+Py)<0.4 indicates typical petroleum contamination, whereas Fluo/(Fluo+Py)>0.5 suggests that PAHs are mainly from biomass and coal combustion, and 0.4<Fluo/(Fluo+Py)<0.5 implies petroleum combustion (Mitchell et al. 1998). As shown in Table 2 and Fig. 5, the ratios of Fluo/(Fluo+Py) at station 3 of the Perlis River was lower than 0.4, indicating fresh petroleum input, while at station 1 of the Perlis River, station 1 of the Merbok River, and stations 1 and 3 of the Perak River, the ratios were between 0.4 and 0.5, meaning that the PAHs were mainly from petroleum combustion. Fluo/(Fluo+Py) ratios at the rest of stations were higher than 0.5, implying biomass and coal combustion.

For a more specific identification of the contamination sources, BaA/(BaA+Chr) and InP/(InP+BgP) ratios (Table 2 and Fig. 5) were also calculated to distinguish between petroleum, petroleum combustion, biomass burning, and coal combustion. BaA/(BaA+Chr) ratio<0.2 is attributed to petrogenic source, 0.2<BaA/(BaA+Chr)<0.35 suggests either petroleum or combustion, and BaA/(BaA+Chr)>0.35 corresponds to pyrogenic origin. In the present study, the ratios of BaA/(BaA+Chr) were 0.18 at station 1 of the Merbok River, 0.33 at station 3 of the Klang River, and ranged from 0.39 to 0.91 at the other stations, which is evidence of petroleum-derived pollution, petroleum- and combustion-derived PAHs, and pyrogenic origin PAHs, respectively. As shown in Table 2 and Fig. 5, InP/(InP+BgP) ratio values lower than 0.2, from 0.2 to 0.5, and higher than 0.5 were used as indicators of petroleum, petroleum combustion, and coal and biomass combustion, respectively. All stations had values of the ratio InP/(InP+BgP) between 0.35 to 0.5, except for both station 3 of the Perak River (InP/(InP+BgP) was 0.54) and the Klang River (InP/(InP+BgP) was 0.52) and lastly, station 2 of the Kedah River (InP/(InP+BgP) was 0.19), which implied that PAHs originated mainly from vehicle emissions related to fossil oil combustion, biomass and coal combustion, and fresh petroleum input, respectively.

Many studies in industrialized countries reported a pyrogenic input of PAHs in aquatic sediments (Cardellicchio et al. 2007; He et al. 2014; Hites et al. 1980; Notar et al. 2001; Pereira et al. 1999; Stout et al. 2004; Wakeham 1996; Zhang

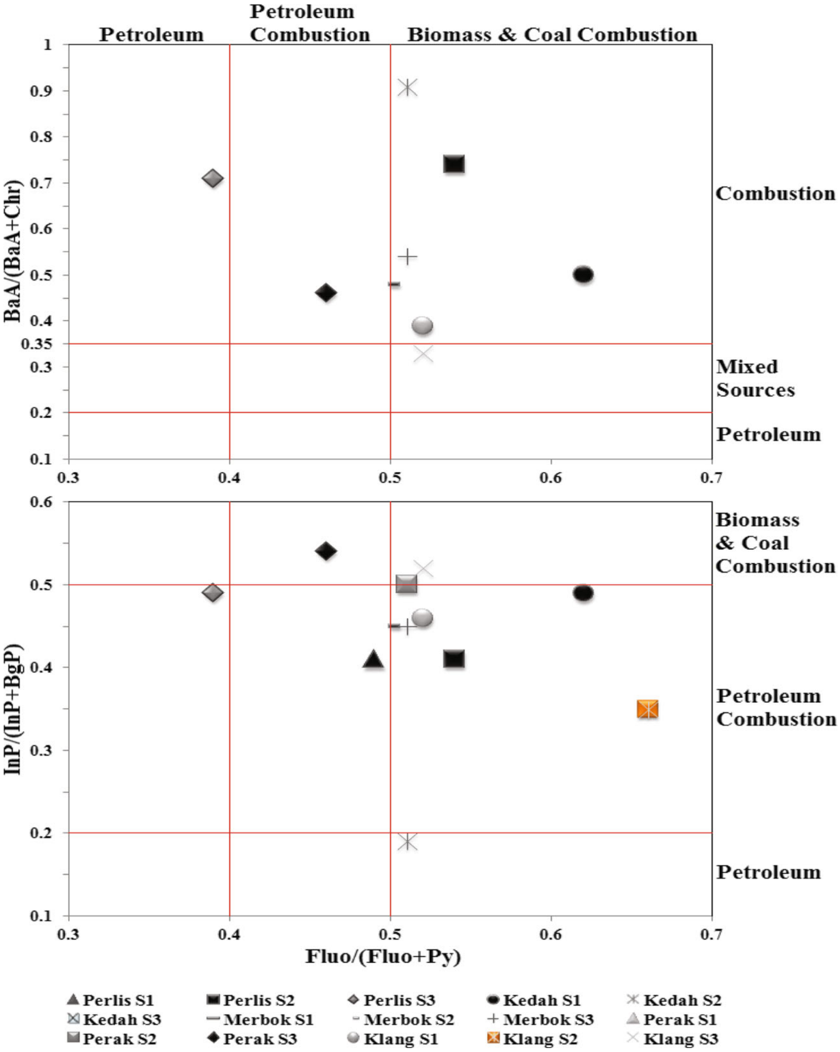


Fig. 5 Plots of PAH isomer pair ratios for source identification: Fluo/(Fluo+Py) versus InP/(InP+BgP) and BaA/(BaA+Chr)

et al. 2012). In comparison to the industrialized countries, our finding of widespread inputs of pyrogenic PAHs in surficial sediments of Malaysian Rivers and Estuaries is consistent. On the other hand, Zakaria et al. (2002) reported that PAHs in the surface sediments collected from major rivers and estuaries throughout Malaysia in 1998–2000 were significantly petrogenic, which is in contrast with our findings. Therefore, it can be concluded that PAH sources of Malaysian aquatic environment have shifted from petrogenic to pyrogenic. However, it would require further sampling in the future to confirm this apparent shift.

PAHs from mobile sources, including exhaust emission from vehicles, cargo vessels, ships, ferries, and fishing boats may have been the main reasons for the recent increase of HMW PAHs input into Malaysian aquatic sediments. Besides that, widespread episodes of smoke and haze that originated from biomass burning and forest fires in Malaysia and Sumatra, Indonesia, in the past decade can also be responsible for pyrogenic PAHs in the Malaysian environment. Population as well as a proliferation of urban sprawl has had continuous growth in Malaysia during the past few decades, which caused increased road traffic. This statement is consistent with Van Metre et al. (2000) who reported that population growth with increase of urban sprawl had a significant correlation with increase of traffic activities. In addition, Okuda et al. (2002), Omar et al. (2002), and Omar et al. (2006) suggested road traffic emissions as the main source of PAHs in atmospheric aerosols in Kuala Lumpur, the capital city of Peninsular Malaysia.

In some countries, there are policies to regulate biomass burning activities but, in developing countries, is introduced as one of the major sources of PAHs (Okuda et al. 2002). For instance, a large forest fire that occurred in Indonesia in 1997 emitted considerable amounts of carbonaceous materials into the atmosphere of neighboring regions, including Malaysia (Okuda et al. 2002). Moreover, the enhanced concentrations of benzofluoranthenes (BFs) compared to HMW PAHs were recorded in Kuala Lumpur during a hazy episode to those during clear days by Omar et al. (2006), which can be attributed to biomass burning process. This is supported by Omar et al. (2002) and Abas et al. (2004) who demonstrated that the measured PAH concentrations in Kuala Lumpur during a hazy episode were found to be many folds higher than those recorded on clear days. However, Okuda et al. (2002) recorded that local wood-burning contribution to Malaysian atmospheric PAHs ranges from 25 to 35 %. A portion of PAHs in Malaysian sediments can be attributed to coal and natural gas combustion (Yang and Chen 2004) in coal-fired power plants located along the West coast water of Malaysia, coal combustions in Perak (Manjung), Negri Sembilan (Lukut),

Table 4 Hopanes in Malaysian sediments

		Total hopanes[a]	C_{30}[b]	Total PAHs/C_{30}	C_{29}/C_{30}[c]	Reference
MECO (Middle East Crude Oil)						(Zakaria et al. 2002)
Arabian Light		1,680,000	295,000	0.65	2.01	
Umm Shaif		899,000	143,000	4.90	1.56	
Marban		333,000	54,000	6.28	1.41	
SEACO (South East Asian Crude Oil)						(Zakaria et al. 2002)
LABUAN		760,000	161,000	19.01	0.98	
MIRI		1,540,000	366,000	1.31	0.85	
TAPIS		626,000	145,000	6.52	1.16	
Sumatra		773,000	197,000	3.55	0.85	
Used Crankcase Oil						(Zakaria et al. 2002)
Petronas Gas Station		884,000	135,000	12.74	2.04	
Yong Motor Workshop		1,770,000	243,000	4.73	2.66	
Home Auto Mechanic		2,550,000	423,000	3.14	1.81	
Motorcycle Workshop		2,690,000	474,000	1.09	1.56	
Malaysian Sediment						(Zakaria et al. 2002)
Straits of Malacca (offshore), Malaysia		54–330	6–50	0.72–1.47	1.35–1.73	
Straits of Malacca, (Near Shore), Malaysia		81–323	10–47	0.58–1.12	0.87–1.71	
Johor Bahru, Malaysia		2404	416	0.58	1.41	
Klang Estuary, Malaysia		98–3213	15–561	0.37–1.21	1.61–1.67	
Pinang Estuary, Malaysia		6515	1130	0.82	1.59	
Present Study						
Perlis	S1	307.5	68.2	4.31	2.2	–
	S2	243	34.3	1.74	2.4	–
	S3	213	27.6	8.94	2.3	–
Kedah	S1	133.6	24.4	14.64	1.9	–
	S2	310.9	68.9	6.98	1.8	–
	S3	64.1	13.3	14.73	2.1	–
Merbok	S1	257.9	35.85	22.07	2.65	–
	S2	232.83	45.79	43.58	1.82	–
	S3	364.5	25	46.88	2	–
Perak	S1	69.4	14.5	29.51	2.6	–
	S2	42.9	8	29.06	2.2	–
	S3	40.53	13.86	28.32	1.23	–
Klang	S1	2749.8	379.2	16.50	2.19	–
	S2	2633.2	367.2	10.36	2.13	–
	S3	2317.6	288.4	25.81	1.79	–

[a] Sum of the concentrations of 17α(H)-22,29,30-trisnorhopane, 17α(H),21β(H)-norhopane (C_{29}17α), 17β(H),21α(H)-norhopane (C_{29}17β), 17α(H),21β(H)-hopane (C_{30}17α), and 17β(H),21α(H)-hopane (C_{30}17β)

[b] 17α(H),21β(H)-hopane

[c] The ratio of 17α(H),21β(H)-norhopane to 17α(H),21β(H)-hopane

and Selangor (Kapar), and natural gas combustion in Selangor (Klang, Serdang, and Kuala Langat), Perak (Pantai Remis), Kedah (Kulim), Negeri Sembilan (Port Dickson), and Perlis (Kuala Sungai Baru).

The primary sources of PAHs for the urban rivers in our study relate to atmospheric deposition of combustion products within the watershed, while in some parts of the study area such as station 3 of the Perlis River, petrogenic PAHs may contribute as major PAH contaminations, which could come from crude and refined petroleum and also oily sewage discharges. Effective monitoring and improved environmental regulations in Malaysia that has been conducted throughout the country during the last decade may explain why the PAH signatures of the Perlis, Kedah, Merbok, Perak, and Klang Rivers and Estuaries have shifted from a petrogenic (fresh petroleum input) to pyrogenic origin (combustion and background input).

Homogeneous hopanes composition in Malaysian Riverine sediments

In the previous section, widespread input of PAHs bearing a pyrogenic signature in the sediments of Malaysian Rivers on the basis of the PAH diagnostic ratios was suggested. Petroleum biomarker compositions (hopanes) were utilized to identify the source of PAHs in Malaysian Riverine sediments. In general, hopane compositions are different in petroleum, based on their origin and maturity, which cause different hopane fingerprints in different types of petroleum (Volkman et al. 1997). However, the profiles of hopanes recorded in the Malaysian Riverine sediments were mostly constant. This may imply the existence of a single diffuse source. Hopane compounds are the biomarkers found to be useful for source discrimination (Volkman et al. 1997; Zakaria et al. 2000), and their compositions provide further supportive evidence that the crude oil spillage is only a minor contributor (Zakaria et al. 2002). Hopane compositions of all of the collected sediments are mostly similar to each other. The C_{29}/C_{30} ratios of Southeast Asian crude oil (SEACO) were lower than those of the Malaysian sediments (Table 4), therefore excluding SEACO as a contributor to the Malaysian sedimentary petroleum. On the other hand, Middle East crude oil (MECO) had C_{29}/C_{30} similar ratios to those in the Malaysian sedimentary hopanes (Table 4). It can be proposed that MECO significantly contributed to the Malaysian sedimentary petroleum hydrocarbons, which is consistent with Zakaria et al. (2002) who reported the same results in Malaysian Urban sediments. However, hopane composition and total PAH/C_{30} ratios for some samples show crankcase oil signature (Table 4).

Conclusion

The concentrations of total PAH varied from 225.5 to 293.9, 195.2 to 481.2, 791.2 to 1995.4, 231.2 to 426.7, and 3803.2 to 7442.7 ng g^{-1} in sediments from the Perlis, Kedah, Merbok, Perak, and Klang Rivers, respectively. The minimum and maximum concentrations of PAHs were 195.2 and 7442.7 ng g^{-1} at station 3 of the Kedah River and Klang River, respectively. PAHs can be classified as moderate in the Perlis, Kedah, and Perak Rivers, moderate to high in the Merbok River, and high to very high in the Klang River. The comparison of the concentrations of PAH in the sediments from the selected rivers with sediment quality guidelines (SQGs) indicates that adverse biological effects are expected to occur at stations 1, 2, and 3 of the Klang River and at station 2 of the Merbok River. Compositional parameters of PAHs revealed that HMW-PAHs were dominant in the study area. The utility of PAHs diagnostic ratios revealed both petrogenic and pyrogenic sources derived from combustion (atmospheric input) and fresh petrogenic input (via lateral or horizontal transport) with a dominance of pyrogenic PAHs. Furthermore, the C_{29}/C_{30} hopanes ratios of Southeast Asian crude oil (SEACO) were lower than those of the Malaysian sediments. The results suggest that SEACO can be excluded as a contributor to the Malaysian sedimentary petroleum. On the other hand, Middle East crude oil (MECO) had C_{29}/C_{30} similar ratios to those in the Malaysian sedimentary hopanes. Therefore, we proposed that MECO is a major contributor to the Malaysian sedimentary petroleum hydrocarbons, which is consistent with results reported in Zakaria et al. (2002). The use of a multimodal approach for source identification in this study had also shown that hopane composition for some samples carried used crankcase oil signature. Further study needs to be done in order to determine the amount of PAH contamination resulting from transboundary input. Elucidating such input is important to managing hydrocarbon pollution on a regional and global scale.

Acknowledgments The research was funded by Inisiatif Putra Berkumpulan Grant (IPB) through Universiti Putra Malaysia (Grant no. 9412401). The authors are very grateful to the chief editor and the reviewers of this article for their valuable contribution.

References

Abas M et al (2004) Organic composition of aerosol particulate matter during a haze episode in Kuala Lumpur, Malaysia. Atmos Environ 38:4223–4241

Ankley GT et al (1994) Assessing potential bioavailability of metals in sediments: a proposed approach. Environ Manag 18:331–337

Araghi PE, Bastami KD, Rahmanpoor S (2014) Distribution and sources of polycyclic aromatic hydrocarbons in the surface sediments of Gorgan Bay, Caspian Sea Marine Pollution Bulletin

Arias AH, Spetter CV, Freije RH, Marcovecchio JE (2009) Polycyclic aromatic hydrocarbons in water, mussels (Brachidontes sp., Tagelus sp.) and fish (Odontesthes sp.) from Bahía Blanca Estuary, Argentina. Estuarine. Coastal and Shelf Sci 85:67–81

Bakhtiari AR, Zakaria MP, Yaziz MI, Lajis MNH, Bi X (2009) Polycyclic aromatic hydrocarbons and n-alkanes in suspended particulate matter and sediments from the Langat River, Peninsular Malaysia. Environ Asia 2:1–10

Bakhtiari AR et al. (2010) Distribution of PAHs and n-alkancs in Klang River surface Sediments, Malaysia. Pertanika J Sci Technol 18

Baumard P, Budzinski H, Garrigues P, Sorbe J, Burgeot T, Bellocq J (1998) Concentrations of PAHs (polycyclic aromatic hydrocarbons) in various marine organisms in relation to those in sediments and to trophic level. Mar Pollut Bull 36:951–960

Budzinski H, Jones I, Bellocq J, Pierard C, Garrigues P (1997) Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. Mar Chem 58:85–97

Cao B, Nagarajan K, Loh KC (2009) Biodegradation of aromatic compounds: current status and opportunities for biomolecular approaches. Appl Microbiol Biotechnol 85:207–228

Cardellicchio N, Buccolieri A, Giandomenico S, Lopez L, Pizzulli F, Spada L (2007) Organic pollutants (PAHs, PCBs) in sediments from the Mar Piccolo in Taranto (Ionian Sea, Southern Italy). Mar Pollut Bull 55:451–458

Chandru K, Zakaria MP, Anita S, Shahbazi A, Sakari M, Bahry PS, Mohamed CAR (2008) Characterization of alkanes, hopanes, and polycyclic aromatic hydrocarbons (PAHs) in tar-balls collected from the East Coast of Peninsular Malaysia. Mar Pollut Bull 56:950–962

Chen B et al (2004) Distributions of polycyclic aromatic hydrocarbons in surface waters, sediments and soils of Hangzhou City, China. Water Res 38:3558–3568

Cortazar E, Bartolomé L, Arrasate S, Usobiaga A, Raposo J, Zuloaga O, Etxebarria N (2008) Distribution and bioaccumulation of PAHs in the UNESCO protected natural reserve of Urdaibai, Bay of Biscay. Chemosphere 72:1467–1474

Dhammapala R, Claiborn C, Simpson C, Jimenez J (2007) Emission factors from wheat and Kentucky bluegrass stubble burning: comparison of field and simulated burn experiments. Atmos Environ 41: 1512–1520

DOSM (2014) Department of Statistics Malaysia, Population and Demography, Report No. 4; Demographic Indicators, Malaysia.

DOSM (2014) Department of Statistics Malaysia; Population and Demography, Report No. 1; Intercensal Mid-Year Population Estimates.

DOSM (2014) Department of Statistics Malaysia; Population Distribution and Basic Demographic Characteristic Report 2010.

Ergut A, Granata S, Jordan J, Carlson J, Howard JB, Richter H, Levendis YA (2006) PAH formation in one-dimensional premixed fuel-rich atmospheric pressure ethylbenzene and ethyl alcohol flames. Combustion and Flame 144:757–772

Garrigues P, Budzinski H, Manitz M, Wise S (1995) Pyrolytic and petrogenic inputs in recent sediments: a definitive signature through phenanthrene and chrysene compound distribution. Polycycl Aromat Compd 7:275–284

Gustafsson O, Gschwend PM Soot as a strong partition medium for polycyclic aromatic hydrocarbons in aquatic systems. In: ACS Symposium Series, 1997. ACS Publications, pp 365-381

He X, Pang Y, Song X, Chen B, Feng Z, Ma Y (2014) Distribution, sources and ecological risk assessment of PAHs in surface sediments from Guan River Estuary, China. Mar Pollut Bull 80:52–58

Head IM, Jones DM, Röling WF (2006) Marine microorganisms make a meal of oil. Nat Rev Microbiol 4:173–182

Hites RA, Laflamme RE, Windsor JG, Farrington JW, Deuser WG (1980) Polycyclic aromatic hydrocarbons in an anoxic sediment core from the Pettaquamscutt River (Rhode Island, USA). Geochim Cosmochim Acta 44:873–878

JPJ (2013) Road Transport Department Malaysia www.jpj.gov.my/en/utama. 2014

Karami A, Christianus A, Ishak Z, Shamsuddin ZH, Masoumian M, Courtenay SC (2012) Use of intestinal Pseudomonas aeruginosa in fish to detect the environmental pollutant benzo [a] pyrene. J Hazard Mat

Keshavarzifard M et al (2014) Baseline distributions and sources of Polycyclic Aromatic Hydrocarbons (PAHs) in the surface sediments from the Prai and Malacca Rivers, Peninsular Malaysia. Mar Pollut Bull 88:366–372

Koh C-H, Khim J, Kannan K, Villeneuve D, Senthilkumar K, Giesy J (2004) Polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) and 2, 3, 7, 8-TCDD equivalents (TEQs) in sediment from the Hyeongsan River, Korea. Environ Pollut 132:489–501

Long ER, MacDonald DD, Smith SL, Calder FD (1995) Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ Manag 19:81–97

Luellen DR, Shea D (2003) Semipermeable membrane devices accumulate conserved ratios of sterane and hopane petroleum biomarkers. Chemosphere 53:705–713

Macdonald DD, Carr RS, Calder FD, Long ER, Ingersoll CG (1996) Development and evaluation of sediment quality guidelines for Florida coastal waters. Ecotoxicology 5:253–278

Maliszewska-Kordybach B (1999) Sources, concentrations, fate and effects of polycyclic aromatic hydrocarbons (PAHs) in the environment. Part A: PAHs in air Polish. J Environ Studies 8:131–136

Marchand N, Besombes J, Chevron N, Masclet P, Aymoz G, Jaffrezo J (2004) Polycyclic aromatic hydrocarbons (PAHs) in the atmospheres of two French alpine valleys: sources and temporal patterns. Atmos Chem Phys 4

Masiol M, Hofer A, Squizzato S, Piazza R, Rampazzo G, Pavoni B (2012) Carcinogenic and mutagenic risk associated to airborne particle-phase polycyclic aromatic hydrocarbons: a source apportionment. Atmos Environ

Masood N et al. (2014) Distribution of Petroleum Hydrocarbons in Surface Sediments from Selected Locations in Kuala Selangor River, Malaysia. In: A.Z. Aris et al. (eds.), From Sources to Solution. pp 351-356. doi:10.1007/978-981-4560-70-2_64, 351-356

Medeiros PM, Bícego MC, Castelao RM, Del Rosso C, Fillmann G, Zamboni AJ (2005) Natural and anthropogenic hydrocarbon inputs to sediments of Patos Lagoon Estuary, Brazil. Environ Int 31:77–87

Meniconi MFG, Gabardo IT, Carneiro MER, Barbanti SM, da Silva GC, Massone CG (2002) Brazilian Oil Spills Chemical Characterization–Case Studies. Environ Forensic 3:303–321

Mirsadeghi SA, Zakaria MP, Yap CK, Gobas F (2013) Evaluation of the potential bioaccumulation ability of the blood cockle (*Anadara granosa L.*) for assessment of environmental matrices of mudflats. Sci Total Environ 454:584–597

Mitchell PKK, Mills G, Fisher–NIWA G, Eason-Landcare C (1998) Technical paper No. 37 Toxic

Neff JM (1979) Polycyclic aromatic hydrocarbons in the aquatic environment. Sources, fates and biological effects Applied Science Publishers Ltd London,(15 A NEF):274

Nelson D, Sommers L (1996) Total carbon, organic carbon and organic matter. In 'Methods of soil analysis. Part 3: chemical methods'.(Ed. DL Sparks) pp. 961–1010 Soil Science Society of America: Madison, WI

Notar M, Leskovšek H, Faganeli J (2001) Composition, distribution and sources of polycyclic aromatic hydrocarbons in sediments of the Gulf of Trieste, Northern Adriatic Sea. Mar Pollut Bull 42:36–44

Nozar SLM, Ismail WR, Zakaria MP (2014) Distribution, sources identification, and ecological risk of PAHs and PCBs in coastal surface sediments from the Northern Persian Gulf. Human Ecol Risk Assess: Int J

Okuda T, Kumata H, Zakaria MP, Naraoka H, Ishiwatari R, Takada H (2002) Source identification of Malaysian atmospheric polycyclic aromatic hydrocarbons nearby forest fires using molecular and isotopic compositions. Atmos Environ 36:611–618

Omar NYM, Abas M, Ketuly KA, Tahir NM (2002) Concentrations of PAHs in atmospheric particles (PM-10) and roadside soil particles collected in Kuala Lumpur, Malaysia. Atmos Environ 36:247–254

Omar NYM, Mon TC, Rahman NA, Abas M (2006) Distributions and health risks of polycyclic aromatic hydrocarbons (PAHs) in atmospheric aerosols of Kuala Lumpur, Malaysia. Sci Total Environ 369:76–81

Pereira WE, Hostettler FD, Luoma SN, van Geen A, Fuller CC, Anima RJ (1999) Sedimentary record of anthropogenic and biogenic polycyclic aromatic hydrocarbons in San Francisco Bay, California. Mar Chem 64:99–113

Prince RC, Elmendorf, D.L., Lute, J.R., Hsu, C.S., Halth, C.E., Senlus, J.D., Dechert, G.J., Douglas, G.S., Butler, E.L. (1994) 17a(H), 21a(H)-Hopane as a conservative internal marker for estimating the biodegradation of cruce oil. Environmental Science and Technology:142–145

Ravindra K, Sokhi R, Van Grieken R (2008) Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmos Environ 42:2895–2921

Retnam A, Zakaria MP, Juahir H, Aris AZ, Zali MA, Kasim MF (2013) Chemometric techniques in distribution, characterisation and source apportionment of polycyclic aromatic hydrocarbons (PAHS) in aquaculture sediments in Malaysia. Mar Pollut Bull 69:55–66

Rinawati et al (2012) Distribution, source identification, and historical trends of organic micropollutants in coastal sediment in Jakarta Bay, Indonesia. J Hazard Mater 217:208–216

Saha M et al (2009) Sources of sedimentary PAHs in tropical Asian waters: differentiation between pyrogenic and petrogenic sources by alkyl homolog abundance. Mar Pollut Bull 58:189–200

Sakari M et al (2010) Urban vs. Marine based oil pollution in the strait of Johor, Malaysia: a century record. Soil Sediment Contam 19:644–666

Sicre M, Marty J, Saliot A, Aparicio X, Grimalt J, Albaiges J (1987) Aliphatic and aromatic hydrocarbons in different sized aerosols over the Mediterranean Sea: occurrence and origin. Atmos Environ 21:2247–2259

Siddall R, Robotham P, Gill R, Pavlov D, Chuiko G (1994) Relationship between polycyclic aromatic hydrocarbon (PAH) concentrations in bottom sediments and liver tissue of bream (Abramis brama) in Rybinsk Reservoir, Russia. Chemosphere 29:1467–1476

Stout SA, Uhler AD, Emsbo-Mattingly SD (2004) Comparative evaluation of background anthropogenic hydrocarbons in surficial sediments from nine urban waterways. Environ Sci Technol 38:2987–2994

Takada H, Onda T, Harada M, Ogura N (1991) Distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in street dust from the Tokyo Metropolitan area. Sci Total Environ 107:45–69

Vaezzadeh V et al. (2014) Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Sediment from Muar River and Pulau Merambong, Peninsular Malaysia. In: A.Z. Aris et al. (eds.), From Sources to Solution, . pp 451-455. doi:10.1007/978-981-4560-70-2_81, 451-455

Van Metre PC, Mahler BJ, Furlong ET (2000) Urban sprawl leaves its PAH signature. Environ Sci Technol 34:4064–4070

Volkman JK, Revill AT, Murray AP (1974) Applications of biomarkers for identifying sources of natural and pollutant hydrocarbons in aquatic environments. In: ACS Symposium Series, 1997. Washington, DC: American Chemical Society, pp 110-132

Wakeham SG (1996) Aliphatic and polycyclic aromatic hydrocarbons in Black Sea sediments. Mar Chem 53:187–205

Wang Z, Stout S (2010) Oil spill environmental forensics: fingerprinting and source identification. Academic Press

Wang Z, Fingas M, Sergy G (1994) Study of 22-year-old Arrow oil samples using biomarker compounds by GC/MS. Environ Sci Technol 28:1733–1746

Wang X-C, Zhang Y-X, Chen RF (2001) Distribution and partitioning of polycyclic aromatic hydrocarbons (PAHs) in different size fractions in sediments from Boston Harbor, United States. Mar Pollut Bull 42:1139–1149

Wang Y, Li X, Li BH, Shen ZY, Feng CH, Chen YX (2012) Characterization, sources, and potential risk assessment of PAHs in surface sediments from nearshore and farther shore zones of the Yangtze estuary, China. Environ Sci Pollut Res 19:4148–4158

World Bank (2014) Gross Domestic Product (GDP) Growth (Annual %). http://data.worldbank.org/indicator/NY.GDP. Accessed 2014

Yang H-H, Chen C-M (2004) Emission inventory and sources of polycyclic aromatic hydrocarbons in the atmosphere at a suburban area in Taiwan. Chemosphere 56:879–887

Yang Z, Wang L, Niu J, Wang J, Shen Z (2009) Pollution assessment and source identifications of polycyclic aromatic hydrocarbons in sediments of the Yellow River Delta, a newly born wetland in China. Environ Monit Assess 158:561–571

Youngblood W, Blumer M (1975) Polycyclic aromatic hydrocarbons in the environment: homologous series in soils and recent marine sediments. Geochim Cosmochim Acta 39:1303–1314

Yunker MB, Macdonald RW (2003) Alkane and PAH depositional history, sources and fluxes in sediments from the Fraser River Basin and Strait of Georgia, Canada. Org Geochem 34:1429–1454

Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org Geochem 33:489–515

Zakaria M, Takada H, Hironouchi A, Tanabe S, Ismail A, Shariff M (2000) Source identification of oil pollution using molecular markers in the Straits of Malacca. In: Towards sustainable management of the Straits of Malacca. Proceedings of the International Conference on the Straits of Malacca, 19-22 April 1999, Malacca, Malaysia. Universiti Putra Malaysia, Malacca (Malaysia)

Zakaria MP, Takada H, Tsutsumi S, Ohno K, Yamada J, Kouno E, Kumata H (2002) Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in Malaysia: a widespread input of petrogenic PAHs. Environ Sci Technol 36:1907–1918

Zhang K, Liang B, Wang J-Z, Guan Y-F, Zeng EY (2012) Polycyclic aromatic hydrocarbons in upstream riverine runoff of the Pearl River Delta, China: an assessment of regional input sources. Environ Pollut 167:78–84