Environ Geochem Health
https://doi.org/10.1007/s10653-018-0122-z

ORIGINAL PAPER

Seasonal variability of anthropogenic indices of PAHs in sediment from the Kuala Selangor River, west coast Peninsular Malaysia

Najat Masood · Normala Halimoon · Ahmad Zaharin Aris · Mohamad Pauzi Zakaria · Vahab Vaezzadeh · Sami M. Magam · Shuhaimi Mustafa · Masni Mohd Ali · Mehrzad Keshavarzifard · Sadeq Abdullah Abdo Alkhadher · Chui Wei Bong · Murad Ali Alsalahi

Received: 14 November 2017 / Accepted: 8 May 2018

Abstract Rapid increase in industrialization and urbanization in the west coast of Peninsular Malaysia has led to the intense release of petroleum and products of petroleum into the environment. Surface sediment samples were collected from the Selangor River in the west coast of Peninsular Malaysia during four climatic seasons and analyzed for PAHs and biomarkers (hopanes). Sediments were soxhlet extracted and further purified and fractionated through first and second step column chromatography. A gas chromatography–mass spectrometry (GC–MS) was used for analysis of PAHs and hopanes fractions. The average concentrations of total PAHs ranged from 219.7 to 672.3 ng g^{-1} dw. The highest concentrations of PAHs were detected at 964.7 ng g^{-1} dw in station S5 in the mouth of the Selangor River during the wet inter-monsoonal season. Both pyrogenic and petrogenic PAHs were detected in the sediments with a predominance of the former. The composition of hopanes was homogeneous showing that petroleum hydrocarbons share an identical source in the study area. Diagnostic ratios of hopanes indicated that some of the sediment samples carry the crankcase oil signature.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10653-018-0122-z) contains supplementary material, which is available to authorized users.

N. Masood · N. Halimoon (✉) · A. Z. Aris ·
S. M. Magam · S. A. A. Alkhadher
Environmental Forensics Laboratory, Faculty of
Environmental Studies, Universiti Putra Malaysia,
43400 Serdang, Selangor, Malaysia
e-mail: mala_upm@upm.edu.my

M. P. Zakaria · V. Vaezzadeh · C. W. Bong
Institute of Ocean and Earth Sciences (IOES), University
of Malaya, 50603 Kuala Lumpur, Malaysia

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

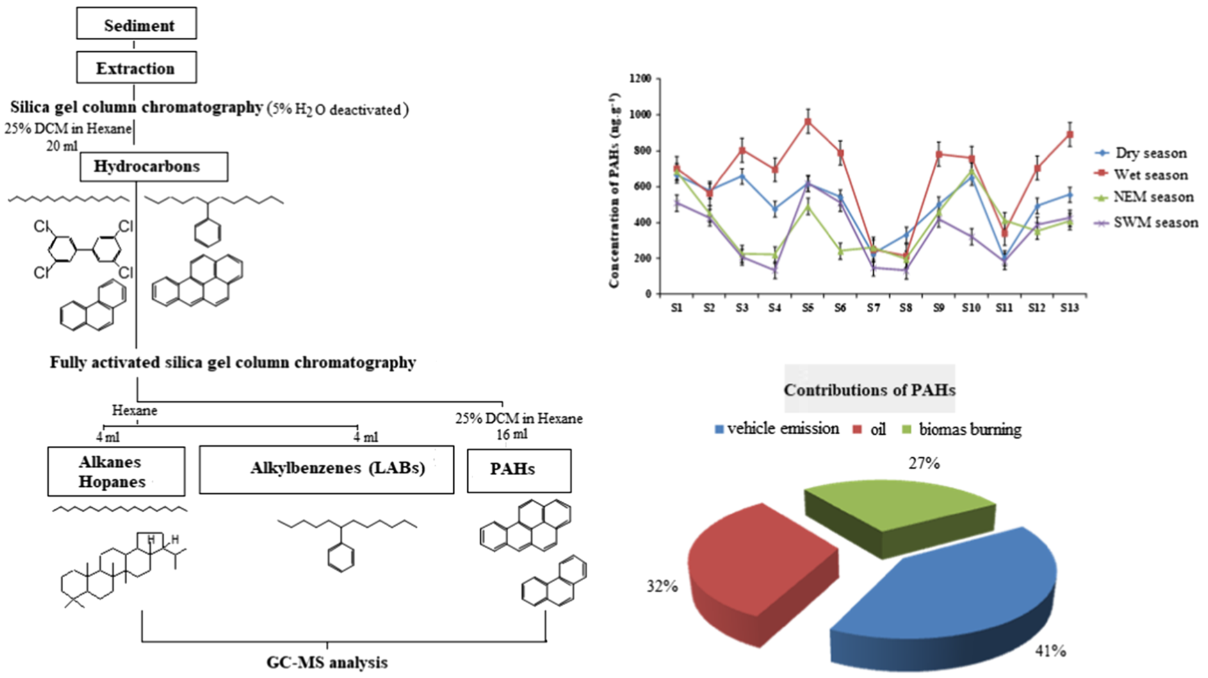
M. M. Ali
School of Environmental and Natural Resource Sciences,
Faculty of Science and Technology, Universiti
Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

M. Keshavarzifard
Department of Earth Sciences, Shiraz University, Shiraz,
Iran

C. W. Bong
Laboratory of Microbial Ecology, Institute of Biological
Sciences, University of Malaya, 50603 Kuala Lumpur,
Malaysia

M. A. Alsalahi
Department of Marine Chemistry and Pollution, Faculty
of Marine Science and Environment, Hodeidah
University, Hodeidah, Yemen

Graphical Abstract



Keywords Polycyclic aromatic hydrocarbons · Biomarkers · Riverine sediment · Pollution sources · Malaysia · Oil

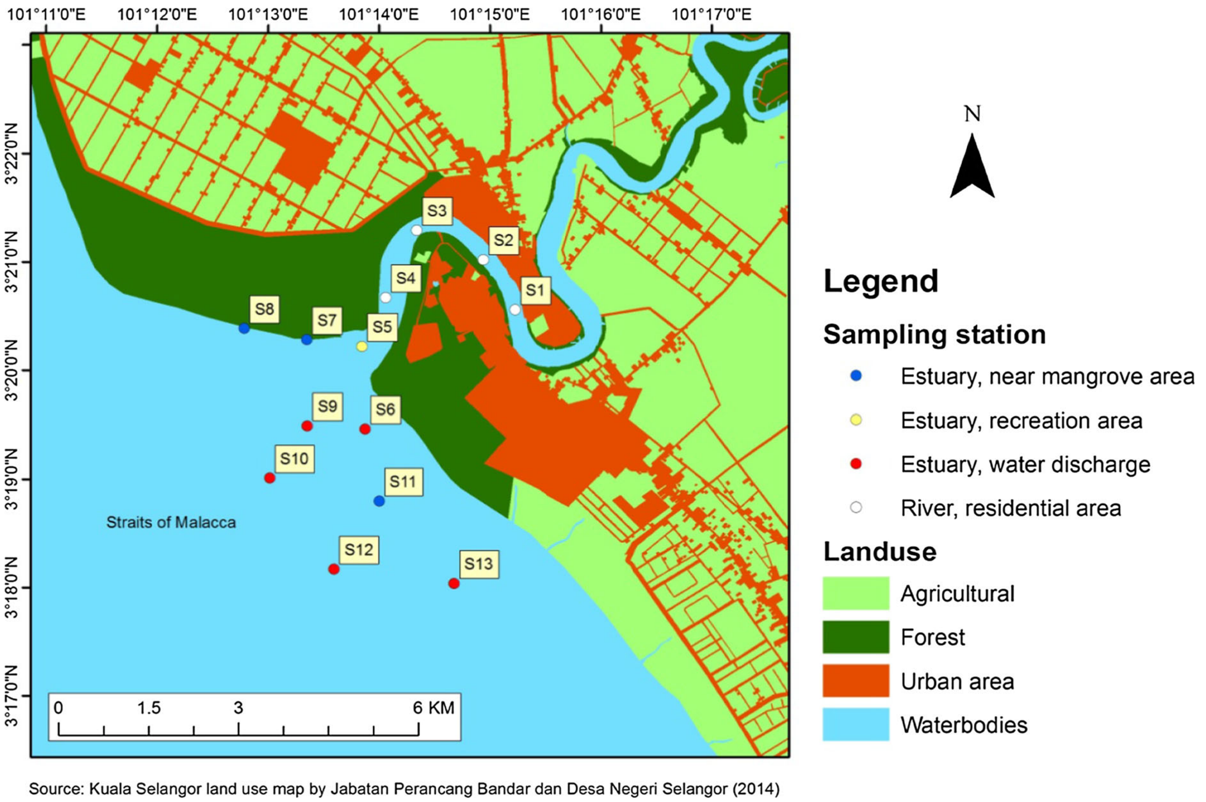
Introduction

Kuala Selangor is a fishing village located 67 km southeast of Kuala Lumpur. It has become a tourist location owing more to the red mangrove ecosystem along the river bank. The Kuala Selangor River is in fact one of the major river system in the Selangor state, draining into the Malacca Straits. It is 500 m wide at the mouth with a water depth of about 2.5 m during low tide, while the water depth can reach up to about 10 m at high tide. The coastal zone is characterized by a semidiurnal, macro-tidal regime with a mean spring tidal range of about 4.0 m depth (Tee and Mohamed 2005). There are four climatic seasons in this area including dry season, wet inter-monsoonal season, the northeast monsoon (NEM) and the southwest monsoon (SWM). The two latter show high rates of precipitation and are categorized as wet season. Seasonal variations of tropical climate have an enormous effect on transportation and fate of organic pollutants. During wet season, heavy tropical rainfall causes a great deal of pollutant washout which transports different types of pollutants into the rivers via runoffs (Liu et al. 2013). Furthermore, heavy rainfall during wet season intensifies the river flow resulting in further transportation of organic pollutants mainly attached to particulate organic matters from various potential input points along the river to the downstream and estuary (Chalov et al. 2015). High rate of precipitation during wet season also contributes to the deposition of atmospheric pollutants and consequently their direct and indirect transportation to the aquatic environment. The Kuala Selangor River also receives a lot of anthropogenic compounds, derived from terrestrial and atmospheric sources which increase the most recent inputs of pollutants. Among the pollutants, hydrocarbons such as polyaromatic hydrocarbons (PAHs) are among the most threatening ones which have been widely studied.

PAHs have been given more attention recently because of being among the most widespread organic pollutants and being toxic, mutagenic, and carcinogenic to humans and other organisms (Cao et al. 2009; Masiol et al. 2012; Karami et al. 2012). Additionally, they are subjected to bioaccumulation and bioconcentration in the aquatic food web. The sources of the PAHs can be classified into three groups: pyrogenic, petrogenic, and diagenic sources. The pyrogenic PAHs result from the incomplete combustion processes, while the petrogenic PAHs are produced by diagenic processes at low temperature over the geological time scale (Mai et al. 2002; Zakaria et al. 2002; Stout et al. 2004) and the diagenic PAHs derive from plant precursors (Gallon et al. 2005). The pyrogenic sources of the PAHs include vehicle emissions; industrial operations and power plants using fossil fuels; smelting; waste incinerators; and combustion of biomass (grass, wood, and coal), whereas the petrogenic sources include crude oil and petrochemicals, gasoline, diesel fuel, kerosene, lubricating oil, and asphalt (Boonyatumanond et al. 2006). Many studies have demonstrated that the sources of the anthropogenic PAHs can be distinguished by the ratio of low molecular weight (LMW) PAHs to high molecular weight (HMW) PAHs (Zakaria et al. 2002; Sakari et al. 2010; Mirsadeghi et al. 2013; Karyab et al. 2014; Nozar et al. 2014; Masood et al. 2016; Vaezzadeh et al. 2014; Vaezzadeh et al. 2015a; Keshavarzifard et al. 2017; Vaezzadeh et al. 2017a). The pyrolytic PAH compounds predominate in HMW PAHs; 4-, 5-, and 6-ring PAH compounds, whereas the petrogenic PAHs predominate in LMW PAHs; 2-ring and 3-ring PAH compounds (Irwin 1997; Mai et al. 2002; Bouloubassi et al. 2012; Masood et al. 2014).

Hydrocarbon compounds such as pentacyclic triterpenes (hopanes) have been proposed as molecular markers providing useful information about the sources of petroleum, original depositional environment, maturation, and diagenetic processes (Zakaria et al. 2001; Maioli et al. 2010). Due to their complex cyclic molecules, hopanes are rarely affected by photochemical and microbial degradation (Peters and Moldowan 1993; Suneel et al. 2014) enabling them to provide more confident discrimination in the analyses of sources and fate of chronic petroleum contamination. The relative composition of individual compounds of hopanes has recently been applied for identification of the source of petroleum pollution (Chandru et al. 2008; Wang et al. 2007; Keshavarzifard et al. 2017; Vaezzadeh et al. 2017b). They are widespread in oil and oil products such as heavy residual oils with high boiling points, lubricating oils, and asphalt. These compounds are resistant to environmental alteration and are routinely used to fingerprint petroleum contamination in sediments (Volkman 1986; Peters and Moldowan 1993; Prince et al. 1994; Wang et al. 1994; Zaghden et al. 2005; Harji et al. 2008; Hu et al. 2009). On account of this, the presence and source of petroleum compounds were substantiated in the present study by the presence and composition of hopanes. The source of hopanes, the depositional environment of the crude oil, and the maturity stage of the oil determine the compositions of hopanes (Volkman et al. 1997; Luellen and Shea 2003). The configuration of 17α(H), 21β(H) within the range of C_{27} to C_{35} is more thermodynamically stable than ββ and βα configuration, and, therefore, is a sign of petroleum hydrocarbons (PHCs). Hopanes of biological origin consist of high ββ configuration which shifts to the more thermodynamically stable αβ and βα configurations as a result of oil maturation, and are, thus, depleted in petroleum (Wang et al. 2006). The 18α(H)-22,29,30-trisnorneohopane (Ts) and 17α(H)-22,29,30-trisnorhopane (Tm) are sensitive indicators of thermal maturity when sediments originate from similar sources (Wang et al. 2006). As a result, hopanes with a predominance of the 17α(H), 21β(H) stereochemistry indicate significant petroleum inputs. In other respects, the hopanes are not categorized as environmental contaminants; however, they are useful biomarkers of oil pollution because of their persistence in the environment and various signatures in petroleum with different sources (Sakari et al. 2010).

Despite the Kuala Selangor River is located in the state of Selangor which is one of the most industrialized and urbanized states and probably the biggest source of pollution in the environment of Malaysia, petroleum pollution in this river has received little attention. The Kuala Selangor River receives large amounts of land-based pollutants from its developed surroundings in the form of runoffs and also via atmospheric deposition. Furthermore, the Kuala Selangor Estuary lies directly to the Straits of Malacca, one the world's busiest waterways with huge oil tanker traffic; therefore, the spillage of oil from the oil tankers and other vessels probably affects the Kuala Selangor Estuary. Thus, the focus of the current study is to investigate the concentrations and the origins of PAHs and hopanes as markers of oil pollution in the sediments of the Kuala Selangor River during four different climatic seasons. Diagnostic



Source: Kuala Selangor land use map by Jabatan Perancang Bandar dan Desa Negeri Selangor (2014)

Fig. 1 Landuse and landcover map for Kuala Selangor District

indices were used for source identification of PAHs and hopanes. Due to toxicity of PAHs for humans and other organisms, identification of their sources as the first measure to control the release of these pollutants into the environment is of high importance. In addition, the concentrations of LMW PAHs, HMW PAHs and total PAHs were compared with sediment quality guidelines (SQGs) to assess the potential adverse effects of PAHs to benthic organisms. Clustering analysis has rarely been used for source identification of PAHs in the riverine sediments of Malaysia and this study used hopanes for further investigation of petroleum hydrocarbon origins in the Kuala Selangor River. In addition, the effect of seasonal variation of tropical climate on PAH loads of riverine and estuarine sediments has not been well-documented and this study gives an indication of the magnitude, distribution and sources of petroleum pollution along the Kuala Selangor River and Estuary during four different tropical climates.

Materials and methods

Sample collection

The surface sediment samples were collected from the top 4 cm of sediments, representing recent inputs of pollution at 13 stations from the Kuala Selangor River. Surface sediment samples were collected using an Ekman dredge sampler and placed into previously solvent-rinsed stainless steel containers. A brief description of the sampling sites is provided in Table S1. The selected study area still has several patches of upland forest, swamp forest, and some mangroves. The major land use in the study area is agriculture, especially oil palm, paddy, and coconut plantation (Fig. 1). In this study, the sediment samples were collected from the river and its estuary during the rainy inter-monsoonal season, the dry inter-monsoonal season, the NEM, and the SWM since the samples are expected to contain varying amounts of pollutants during these seasons. The samples were transported to the laboratory on ice and stored at − 18 °C prior to further analysis.

Sample analysis

The procedures for extraction, purification, and fractionation were described elsewhere (Hartmann et al. 2000; Zakaria et al. 2002). Ten grams of freeze-dried sediment samples were placed in pre-cleaned cellulose thimbles and soxhlet extracted for about 8–10 h by distilled dichloromethane (DCM). The 50 µl of surrogate internal standards (SIS) mixture of PAHs was spiked into the solvents before extraction. The extract volume was then reduced using a rotary evaporator and copper treated. The extracts were transferred onto the top of 5% H_2O deactivated silica gel in a glass chromatographic column. This step is to separate polar compounds from non-polar ones. Exactly 20 ml of hexane/DCM (3:1, v/v) was used as an elution solvent for hydrocarbon fraction. The extracts were rotary evaporated and reduced to near dryness and sequentially fractionated with a fully activated silica gel column using 4 ml of high purity hexane to get alkanes and hopanes fraction, 4 ml of hexane again to get linear alkylbenzene (LABs) fraction which was discarded, and finally 16 ml of Hexane/DCM (3:1 v/v) to get PAHs fraction. 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, redissolved in internal injection standards (IIS) of hopanes and PAHs in 100 µl isooctane, respectively, and transferred to a 1.5 ml amber vial. The solution was analyzed with a 7890A Series Agilent gas chromatography (GC) equipped with the mass spectrometer (MS). A DB-5MS fused silica capillary column of 30 m length, 0.25 mm internal diameter (i.d.) and 0.25 µm film thickness (J&W Scientific, Folsom, CA, USA) was used.

Total organic carbon (TOC) analysis

The analytical procedure that was adopted by the researchers for assessment of the TOC content was the procedure described by Bakhtiari et al. (2010) and Vaezzadeh et al. (2015b). The sediment samples were dried overnight at 60 °C in an oven and then ground and homogenized using mortar and pestle. The inorganic carbon was removed prior to analysis. A mass of 1–2 g of each sediment sample was weighed and a volume of 1–2 mL of 1 M hydrochloric acid (HCl) solution was added until the sample was totally moist with HCl. After that, the samples were dried at 100 °C for 10 h to remove HCl. An aliquot of each sample was reweighed and then analyzed using LECO CR-412 Carbon Analyzer at 1350 °C for 60 s to determine the TOC, which is reported in this study in the mg g^{-1} unit.

Quality control (QC)

Quality control (QC) consists of professional laboratory practices, updated standard procedures, correct sample collection and calibration, standardization, instrument maintenance, reporting of generating forensic data analysis, continuous improvement program, and inspection and validation. In the present study, all standards (IIS, SIS, and native standards) used in the analysis were daily prepared. Each batch of samples (4 samples) was processed with a blank that contained all the chemicals and the standards present in the normal samples to determine any cross-contamination during the analytical procedure and contamination from the glassware. During instrumental analysis, a purge (i.e., capillary column solvent wash) was processed after each batch of six samples. Recovery of the surrogates generally ranged from 63 to 98% of the spiked concentration. The concentrations of the PAHs of interest were corrected using their recoveries (Pereira et al. 1999). The quality assurance for the hopane analyses was also conducted in this study. No recovery correction was made for the hopane analyses. Limits of detection (LOD) and limit of quantification (LOQ) of the analytical method were 0.12–1.30 and 0.41–4.07 ng g^{-1} for the PAH analytes, respectively. Also, LOD and LOQ of the hopanes were 1.6–2.9 and 5.4–9.9 ng g^{-1}, respectively.

Identification of PAHs sources

PAH diagnostic ratio is the preferred method for source identification due to its simplicity and validity by numerous studies. The five diagnostic ratios of PAHs: LMW/HMW, Ant/(Ant + Phe), Fluo/(Fluo + Pyr), BaA/(BaA + Chr), and InP/(InP + BgP) have been applied in order to identify the origins and sources of PAHs in the Selangor River (Table S2; Khalili et al. 1995; Mitchell et al. 1998;

Commendatore et al. 2000; Mai et al. 2002; Yunker et al. 2002; Guo et al. 2006; Vaezzadeh et al. 2014; Vaezzadeh et al. 2015a; Keshavarzifard et al. 2017).

Statistical analysis

IBM-SPSS software, v. 21.0 package was employed in the chemometric application using hierarchical agglomerative cluster analysis (HACA), principal component analysis (PCA), and correlation between TOC and total PAHs. These techniques were chosen to interpret and evaluate the organic contaminants dataset along Selangor River Basin. PCA has been applied in this study. Briefly, PCA is a statistical approach, which is often used to identify potential linear combinations of PAHs that may be useful to distinguish their sources. One-way ANOVA was performed to assess the differences of the PAHs dataset in different stations, where p value was < 0.05, the differences between PAHs datasets were considered as statistically significant.

Results and discussion

PAHs in the sediments of the Selangor River

Levels and composition of PAHs in the sediments of the Selangor River

Table 1 summarizes the concentrations of the individual and the total PAHs in the sediments at the various sampling stations, in addition to the mean concentrations and the respective standard deviations during the four climatic seasons. The results showed that the PAHs in the sediments ranged from 215.48 to 964.70 ng g^{-1} dw, with a mean of 651.64 ± 239.70 ng g^{-1} dw during the wet inter-monsoonal season, while ranged from 203.27 to 665.20 ng g^{-1} dw, with an average of 499.24 ± 155.70 ng g^{-1} dw during the dry inter-monsoonal season. PAHs ranged from 197.73 to 688.94 ng g^{-1} dw and from 133.90 to 618.90 ng g^{-1} dw with mean values of 341.30 ± 163.50 and 391.97 ± 165.30 ng g^{-1} dw during the NEM and the SWM seasons, respectively.

Temporally, the highest concentrations of PAHs were detected in the wet inter-monsoonal season at stations S5 and S13. The high concentrations of the PAHs during the wet inter-monsoonal season underline the role of surface runoffs in transportation of the PAHs to the rivers in Malaysia. This finding accords with that of Daka and Ugbomeh (2013) and Zhao et al. (2014) who reported that the concentrations of PAHs were higher during the wet season than the other seasons. The lowest PAHs (133.90 ng g^{-1} dw) were detected during the SWM season at station S8, which is located near a mangrove forest, while the highest PAHs (964.70 ng g^{-1} dw) were found during the wet inter-monsoonal season at station S5, which is situated in the estuary. In other respects, the outcomes of the one-way ANOVA indicated that the differences between the PAHs among the sampling stations were significant ($p < 0.05$). This can be ascribed to the presence of different anthropogenic sources of PAHs around each of the 13 sampling stations.

Overall, the concentrations of the various investigated PAHs were higher at the estuarine stations (S5–S12) than the other stations. One explanation can be the concentration of industrial activities, population and domestic runoffs in the vicinity of the estuary which can increase PAH levels. In this regard, Selangor City is located on the river's eastern side and significant urban runoffs from the city can contribute to the increase in the PAH concentrations. Moreover, heavy rainfall in Malaysia causes huge sediment washout; therefore, rivers carry large amounts of particulate matters containing hydrocarbons which will deposit in the estuary as the river enters the realm of salinity due to gravitational sedimentation and flocculation (Chalov et al. 2014). Malaysia is a tropical country covered by various types of vegetation; therefore, the particulate matters in the rivers abound in organic materials which can make strong bonds to organic pollutants and facilitate their transportation to the estuaries. Another reason for higher levels of PAHs in the estuarine stations can be the influence of sea-based petroleum pollution on the PAH loads of estuarine sediments. As mentioned earlier, the Kuala Selangor Estuary lies directly to the Straits of Malacca which is highly susceptible to oil spills from the heavy oil tanker traffic and other shipping activities. On the other hand, the lowest concentrations of the PAHs were observed at stations S7, S8, and S11 at 221.92 ± 50.18, 219.71 ± 82.49, and 285.31 ± 109.26 ng g^{-1} dw, respectively (Fig. S1).

Table 1 The total concentrations of PAHs (ng g^{-1} dw) in the sediments of Selangor River

Station	PAHs (ng g^{-1} dw)					
	DIMP	RIMP	NEM period	SWM period	Mean	STD
S1	665.2	703.4	685.6	510.3	641.1	88.6
S2	576.4	563.2	450.5	426.9	504.3	76.5
S3	658.2	804.7	226.1	208.9	474.5	302.8
S4	475.7	696.8	221.7	136.6	382.7	254.2
S5	615.4	964.7	490.1	618.8	672.3	203.9
S6	541.1	790.5	242.4	509.6	520.9	224.2
S7	225.4	251.4	260.8	150.1	221.9	50.2
S8	331.7	215.5	197.7	133.9	219.7	82.5
S9	500.5	782.5	458.9	421.2	540.8	164.4
S10	649.9	758.8	688.9	322.8	605.1	193.5
S11	203.3	341.5	411.3	185.1	285.3	109.3
S12	492.3	705.2	352.9	388.2	484.7	158.5
S13	555.1	893.1	408.6	425.0	570.5	224.9
Mean	499.3	651.6	391.9	341.3	471.1	137.2
± STD	155.7	239.7	165.3	163.5	181.1	39.3

DIMP the dry inter-monsoon period, *RIMP* the rainy, or wet, inter-monsoon period, *STD* standard deviation

The levels of PAHs can be classified according to the ranges of the detected concentrations. In this regard, Baumard et al. (1998) categorized the levels of PAHs as low if the PAH concentration is < 100 ng g^{-1} dw, moderate if the PAH concentration is within the range of 101–1000 ng g^{-1} dw, high if the PAH concentration is within the range of 1001–5000 ng g^{-1} dw, and very high if the PAH concentration is > 5000 ng g^{-1} dw. According to Wang et al. (2010), the PAH concentration in the range of 500–1000 ng g^{-1} dw can be indicative of moderately high PAH pollution. The average concentrations of the studied PAHs in the sediments of the Selangor River ranged from 219.71 to 672.26 ng g^{-1} dw. In consequence, six of the sampling sites (S3, S4, S7, S8, S11, and S12) are moderately polluted with PAHs, whereas the other seven sites have moderately high levels of pollution with PAHs. These findings are in line with the previously reported results for sediments from the rivers along the west and east coasts of Peninsular Malaysia as well as in some other developing countries (e.g., Sanger et al. 1999; Zakaria et al. 2002; Feng et al. 2007; Ma et al. 2007; Sakari et al. 2008a, b; Bakhtiari et al. 2009; Vaezzadeh et al. 2014).

The PAH composition profile is useful for tracking down the sources of PAHs and elucidating their fate and transport in the environment (El Nemr et al. 2013). The composition pattern of PAHs according to ring numbers in the sediment samples of the Selangor River in the four study seasons is shown in Fig. 2. The average percentages of the individual 2-, 3-, 4-, 5-, and 6-ring PAHs in the sediments of the 13 stations in the Selangor River were 5% ± 2.44, 36% ± 4.77, 27% ± 8.61, 24% ± 6.24, and 8% ± 2.92, respectively. Moreover, the composition of the PAHs was dominated by the four-ring PAHs (40%), followed by the three-ring PAHs (33%) during the dry season, while dominated by the three-ring PAHs (38%), followed by the four-ring PAHs (29%) during the wet season. As shown in Fig. 2, the dominant PAHs in the NEM season were the three-ring PAHs (40%), followed by the four-ring PAHs (31%). Similarly, the PAHs with the highest proportions in the SWM season

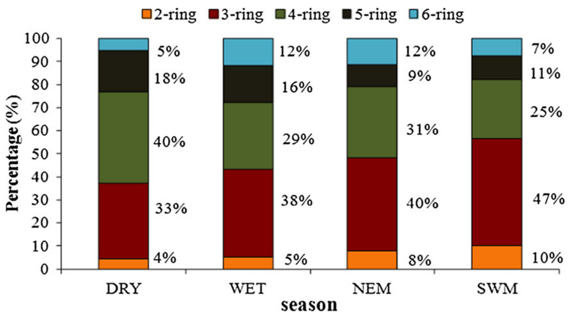


Fig. 2 Percentages of the 2-ring PAHs to the 6-ring PAHs in the sediments according to sampling period ($n = 52$). *NEM* northeast monsoon, *SWM* southwest monsoon

were the three-ring and four-ring PAHs with 47 and 25% of total PAHs, respectively. The two-ring PAHs had the lowest percentage during all four climatic seasons (Fig. 2).

Sources of PAHs based on the composition of PAHs in the sediments

The PAHs typically occur in complex mixtures and their composition may be used to characterize and identify their sources. Identification of the sources of the PAHs is crucial for reducing their inputs into the environment and developing environmental pollution control strategies. The frequently adopted method for source identification of PAHs is use of diagnostic ratios (typically isomers). This method is based on the hypothesis that paired chemicals are diluted to a similar extent and that the ratios remain constant en route from sources to receptors (Katsoyiannis et al. 2007).

LMW to HMW PAH ratio higher than 1.0 indicates a pollution of petrogenic origin, while a ratio lower than 1.0 indicates pyrogenic origin of PAHs (Magi et al. 2002; Qiao et al. 2006; Chen and Chen 2011). In the present study, the average range of the values of the LMW/HMW PAHs during the four climatic seasons ranged from 0.51 to 0.97 (Table 2). The values of LMW/HMW PAHs in the sediment samples during the four climatic seasons were < 1.0, except for the stations S6 (1.17) and S7 (1.06) in the dry intermonsoonal season; station S12 (1.53) in the NEM season; and the stations S2, S8, S10, S11, S12, and S13 in the SWM season. At the latter stations, the ratios were 1.32, 1.72, 1.73, 2.16, 2.14, and 1.10, respectively (Table 2). In fact, the data indicated that 78% of the samples had PAHs from combustion origin, while the PAHs in the remainder of the samples are of petrogenic origin. These results spotlight domination of the HMW PAHs and indicate that these stations were heavily impacted by the combustion-derived PAHs which are present in the urban atmospheric particles and are rich with HMW PAHs. The pyrogenic PAHs may have been transported to the Selangor River by the prevailing SWM winds, although more studies are needed to confirm this presumption.

A comparison with the relevant literature demonstrates that the values of LMW/HMW PAHs obtained in this study are consistent with those reported by Bakhtiari et al. (2009) for the sediments of Langat River, which ranged from 0.17 to 0.39. Dominance of the HMW PAHs in the riverine sediments in the west coast of Peninsular Malaysia has been also reported recently by Raza et al. (2013) and Vaezzadeh et al. (2015a). The HMW PAHs have even been found to be the most common PAHs in the sediments of the east coast of Peninsular Malaysia (Tahir et al. 2011). On the other hand, higher percentages of LMW PAHs were reported in sediments collected from urban areas in Peninsular Malaysia, hence indicating high inputs of petrogenic PAHs (Zakaria et al. 2002). High inputs of LWM PAHs to the riverine systems were also reported in sediments in Bangkok, Thailand, implying dominance of petrogenic sources of PAHs (Boonyatumanond et al. 2006).

The most possible sources of PAHs in the environment can be identified by the use of indices that employ certain ratios of the concentrations of various PAHs in the environment (Soclo et al. 2000; Tsymbalyuk et al. 2011; Yunker et al. 2002). Parent PAH ratios as well as alkylated ones, which are based on the relative abundance of individual PAH or groups of PAHs, have been practically developed for identifying and differentiating the petrogenic and pyrogenic sources of PAHs (Yunker et al. 2002; Zakaria et al. 2002; Vaezzadeh et al. 2015a; Keshavarzifard et al. 2015, 2017). On the basis of thermodynamic stability, each of Phe/Ant and Flu/Pyr has been widely used to distinguish petrogenic origin PAHs from those of pyrolytic origins (Yang et al. 2005; Liang et al. 2007; Karacik et al. 2009). In this respect, the Fluo is less favored than Pyr under fossil fuel formation conditions (Iqbal et al. 2008). As a result, Fluo/Pyr ratios higher than 1 indicate petrogenic origins, whereas the ratios lower than 1 indicate pyrogenic sources (Sicre et al. 1987; Budzinski et al. 1997). In the current study, the average ratios of Phe/Ant and Flu/Pyr in the sediments of the Selangor River during the four climatic seasons ranged from 0.45 ± 0.39 to 1.32 ± 0.90 and 0.31 ± 0.16 to 4.15 ± 6.90, respectively. As Phe/Ant < 10 and Fluo/Pyr > 1, it was concluded that the PAHs detected in the sediments originated from both pyrolytic and petrogenic sources (Fig. 3). This is confirmed by the LMW/HMW ratios which ranged from 0.55 to 1.17.

The ratio of Fluo/(Fluo + Pyr) is frequently used to identify the sources of PAHs (Mitchell et al. 1998; Liu et al. 2008). A Fluo/(Fluo + Pyr) ratio within the

Table 2 Average values of different diagnostic ratios of PAHs in the sediments of Selangor River

Station	LMW/HMW[a]	MP/P[b]	Fluo/(Fluo + Pyr)[c]	BaA/(BaA + Chr)[d]	(InP/(InP + BgP)[e]
1	0.52	1.57	0.49	0.65	0.65
2	0.54	0.80	0.54	0.30	0.57
3	0.54	1.00	0.63	0.40	0.39
4	0.71	1.15	0.62	0.43	0.37
5	0.72	0.36	0.76	0.46	0.51
6	0.91	1.15	0.66	0.46	0.34
7	0.92	1.04	0.69	0.63	0.50
8	0.61	1.39	0.78	0.49	0.63
9	0.65	1.34	0.75	0.38	0.38
10	0.76	0.57	0.70	0.50	0.22
11	0.97	0.70	0.78	0.55	0.40
12	0.81	0.50	0.65	0.63	0.58
13	0.51	1.35	0.72	0.64	0.59

[a] *LMW/HMW* The ratio of the sum of the concentrations of PAHs (from Naphthalene to Anthracene) divided by the sum of the concentrations of PAHs (Fluoranthene to Benzo[ghi]perylene)

[b] *MP/P* The ratio of methylphenanthrenes/phenanthrene

[c] *Fluo/Fluo + Pyr* The ratio of fluoranthene/(fluoranthene + pyrene)

[d] *BaA/BaA + Chry* The ratio of benzo(a)anthracene/(benzo(a)anthracene + chrysene)

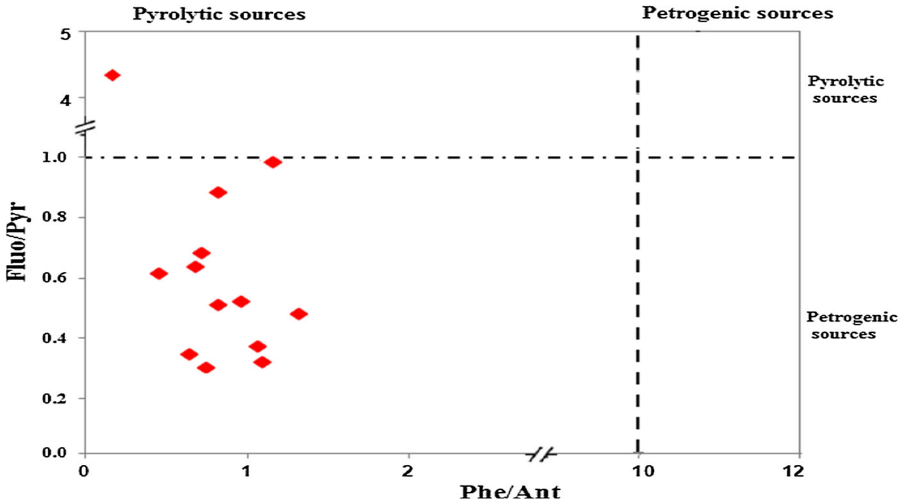
[e] *InP/InP + BgP* The ratio of Indeno[1,2,3-cd]pyrene/(Indeno[1,2,3-cd]pyrene + Benzo[g,h,i]perylene)

range of 0.4–0.5 was attributed to combustion of liquid fossil fuels (vehicle and crude oil), whereas a ratio < 0.4 corresponds to petroleum contamination and a ratio > 0.5 corresponds to combustion of biomass; grass, wood, or coal (Yunker et al. 2002; Zemo 2009). As shown in Table 2 and Fig. 4, the average ratios of Fluo/(Fluo + Pyr) in the sediment samples of the Selangor River varied from 0.49 ± 0.31 to 0.78 ± 0.16 during the four climatic seasons. The values of this ratio, which were all > 0.4, indicated biomass and coal combustion origins of the PAHs.

A value of the InP/(InP + BgP) ratio that is < 0.20 indicates a petroleum source, whereas a value > 0.50 discloses contribution of biomass and coal combustion. Meanwhile, a value in the range of 0.20–0.50 indicates petroleum combustion as the source (Yunker et al. 2002). On the other hand, a BaA/(BaA + Chr) value < 0.20 implies a petroleum source of the PAHs, while a value within the range of 0.20–0.35 points to petroleum combustion, especially liquid fossil fuel, and vehicle and crude oil. Meantime, a BaA/(BaA + Chr) value > 0.35 reveals combustion of coal, grass, and wood (Yunker et al. 2002). As Fig. 4 shows, the average InP/(InP + BgP) ratios during the four climatic seasons of this study ranged from 0.22 ± 0.16 to 0.65 ± 0.36. These results imply a petroleum source and a range of combusted materials that include coal, wood, and grass as the major sources of the PAHs in the sediments of the Selangor River. Lastly, for the stations S3, S4, S6, S7, S9, S10, and S11, the InP/(InP + BgP) values fell within the range of 0.20–0.50, suggesting fossil fuel (vehicle and crude oil) combustion as the main PAH origin at these stations. At the rest of the stations, however, the (InP/(InP + BgP) values were higher than 0.5, implying biomass and coal combustion as source of PAHs. In this study, the values of the BaA/(BaA + Chr) ratio ranged from 0.30 ± 0.06 to 0.65 ± 0.36 during the four climatic seasons and were > 0.35, except for S2 where this ratio lied in the range 0.20–0.35. These findings indicated petroleum combustion, especially liquid fossil fuel, and vehicle and crude oil as major PAH origins. Furthermore, the BaA/(BaA + Chr) values were higher than 0.35 at the rest of the sediment sampling stations, which indicated predominance of pyrogenic sources of PAHs (Fig. 4).

The MP/P ratio, originally proposed by Youngblood and Blumer (1975), is another ratio used for

Fig. 3 The Phe/Ant versus Fluo/Pyr ratios in the surface sediments of Selangor River and their associations with PAH sources



PAH source identification (Prahl et al. 1984; Barrick and Prahl 1987; Takada et al. 1991; Yunker et al. 2002). It has been employed to distinguish between petrogenic and pyrogenic sources of PAHs in many previous studies (e.g., Zakaria et al. 2002; Boonyatumanond et al. 2006; Keshavarzifard et al. 2017; Saha et al. 2009; Bakhtiari et al. 2010). The MP/P ratio is generally lower than 1.0 for the PAHs of pyrogenic origins but ranges from 2 to 6 in the case of a fresh petroleum origin (Garrigues et al. 1995; Yang and Hofmann 2009). The average values of the MP/P ratio in the sediment samples of the Selangor River ranged from 0.36 ± 0.32 to 1.57 ± 0.55 during the four climatic seasons. The values were in general < 2, with the majority of the sediments having values less than unity, which is a sign of pyrogenic sources of PAHs. The values of the MP/P ratio were higher than 2 at S4 and S9 in the wet inter-monsoonal season, S8 in the dry inter-monsoonal season and S13 in the NEM season indicating fresh petroleum inputs of PAHs (Fig. 4).

Figure 4 confirms predominance of the pyrogenic over the petrogenic sources of PAHs in the sediments of the Selangor River. As shown in this figure, all sampling stations fall within the pyrogenic and mixed sources zone of the diagram. It is also noteworthy that the ratios employed in this study highlighted grass, wood, and coal combustion as sources of PAHs at most of the 13 sampling stations.

In summary, various diagnostic ratios indicated that the PAHs in the sediments of the Selangor River were mainly derived from combustion sources, including petroleum, coal, and biomass combustion. He et al. (2010) reported that the PAHs produced by biomass burning during a haze episode can be transported by air masses during the monsoon. Moreover, the aerosols in Peninsular Malaysia were found to be dominated by pyrogenic PAHs originating from automotive exhaust emissions (Okuda et al. 2002) and biomass burning particularly from the southern Sumatra, Indonesia (Omar et al. 2006; Bahry et al. 2009). PAH pollution in urban and remote areas has been reported to be transported by long-range atmospheric transport (e.g., Okuda et al. 2002; Yang et al. 2007; He et al. 2010). Furthermore, the Selangor estuary, which faces the Straits of Malacca, is vulnerable to the pollution caused by oil spills from tanker operation (Zakaria et al. 2001; Abas et al. 2004; Mirsadeghi et al. 2011; Keshavarzifard et al. 2016). Thus, the petrogenic sources of PAHs in the Selangor River can be ascribed to ship and fishery boat activities as well as to oil spills and land-based runoffs from the residential areas near the Straits of Malacca coastal areas.

A proportion of the PAHs found in the Malaysian sediments can be attributed to coal burning and natural gas combustion (Yang and Chen 2004) in coal–fired power plants located along the West coast of Malaysia, such as Perak (Manjung), Negeri Sembilan (Lukut), and Selangor (Kapar) in the cases of coal combustion, and Selangor (Klang), Selangor (Kuala Langat), Perak (Pantai Remis), Kedah (Kulim), Negeri Sembilan (Port Dickson), Selangor (Serdang), and Perlis (Kuala Sungai Baru) in the cases of natural

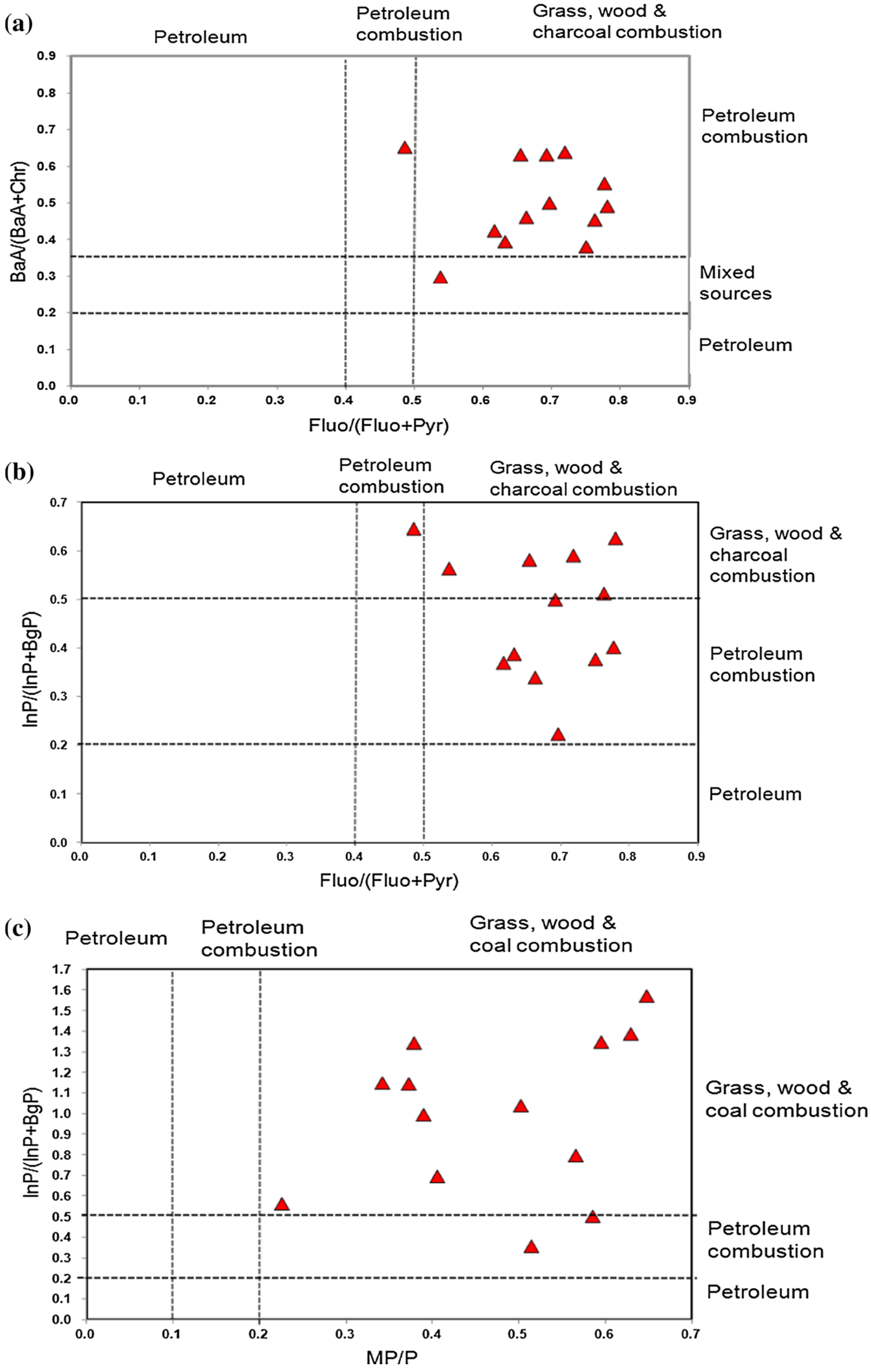


Fig. 4 Relations between PAH ratios and their associations with PAH sources: **a** BaA/(BaA + Chr) versus Fluo/(Fluo + Pyr), and **b** InP/(InP + BgP) versus Fluo/(Fluo + Pyr), and **c** InP/(InP + BgP) versus MP/P

gas combustion. Considering continuous monitoring in the region, a shift in the sources of PAHs in the sediments of the west coast of Peninsular Malaysia has taken place since the last decade (Zakaria et al. 2002; Zakaria and Mahat 2006; Bakhtiari et al. 2009; Raza et al. 2013; Retnam et al. 2013; Sakari and Zakaria 2013; Keshavarzifard et al. 2014, 2016; Vaezzadeh et al. 2015a). One major reason for this shift from petrogenic to pyrogenic sources as the dominant sources of PAHs can be effective measures to control release of PAHs from petrogenic sources such as oil spills, while the pyrogenic sources of PAHs, such as automobile exhaust, are active and growing.

Identification of the sources of PAHs using clustering analysis

Clustering analysis was performed to identify the homogeneous groups of PAHs in the sediment samples. The results of this analysis are presented in a hierarchical dendrogram (Fig. 5).

Three distinct clusters were obtained. The first group includes FTH, PYR, PHE, ANT, MANT, and RET, most of which are 4-ring PAHs. These PAHs usually come from pyrogenic sources, e.g., combustion of coal and wood (Zakaria et al. 2002; Wang et al. 2007). The second group consists of BbF, CHR, BaA, BkF, BaP, and BghiP, which are mostly HMW PAHs with 5–6 benzene rings. Clustering of these PAHs in this group indicates combustion, mainly of vehicle fuel, as their main source (Wang et al. 2007). The third major group consists of the 2–3 ring PAHs NAP, ACE, ACY, and DBT, which derive from unburned fossil fuels, and petroleum (Dobbins et al. 2006; González et al. 2006; Ye et al. 2006; Luo et al. 2008).

Identification of the sources of PAHs using principal components analysis (PCA)

The purpose of Principal Components Analysis (PCA) is to represent the total variability in the original PAH data with the minimum number of principal components (PCs). By critically analyzing the PAHs loading on each extracted component, the common sources for these PAHs can be identified (Larsen and Baker 2003). In this study, the PCA was applied to the normalized data revealing three PCs responsible for 66% of the total variation of PAHs in the surface sediments of the Selangor River (Table 3).

The first PC is responsible for 26.6% of the total variance. It receives high loadings from 5-ring and 6-ring PAHs (BkF, BaP, BghiP, and DahA) and moderate loadings from BeP and IcdP. The major source in this PC appears to be road dust from the urban areas of Selangor and vehicular fuel (gasoline and diesel) combustion. According to Khalili et al. (1995), gasoline combustion produces NAP, FLU, BEP, ACY, and PYR. Meanwhile, the BghiP, BkF, and Coronene have been identified as tracers for gasoline engines, with IcdP and PYR being present in both the diesel-, and gasoline-powered engines (Larsen and Baker 2003). Owing to that, diesel and gasoline emissions could not be differentiated by PCA in this study and generally PC1 was described as vehicular emission component.

Outputs of PCA bring to notice that the second extracted component (PC2) explains 21.2% of total variation in the PAH concentrations. It receives high loadings from 2-ring and 3-ring PAHs that are dominated by NAP, FLU, and DBT. The runoffs from oil-burning power-generation plants are characterized by 2-ring and 3-ring PAHs, specifically methylnaphthalenes and phenanthrenes (Larsen and Baker 2003). In view of this, PC2 was categorized as a petroleum component. The two major sources of petroleum pollution in the Malaysian environment are dumping of used crankcase oil and the washout of oil products due to strong storms in this tropical country (Zakaria et al. 2002).

The third extracted component alone is responsible for 17.8% of the total variance in the levels of PAHs in the sediments. This component received loadings from alkylated PHE, ANT, FTH, PYR, and RET (4-ring PAHs) and moderate loading from MANT. The alkylated PHE, ANT, FTH, PYR, and RET are associated with coal combustion (Simoneit 2002), while RET, which is mostly linked to wood combustion, is derived from diterpenoids resin acid and abietic acid, which are constituents of conifers resin (Ramdahl 1983; Fang et al. 1999; He et al. 2010). The RET found in the lakes and oceans sediments was traced back mainly to natural degradation of abietic acid (Ramdahl 1983) and pulp and paper mill effluents (Mandalakis et al. 2004). In this study, the RET detected as one of the major sedimentary PAHs comparable with some parent PAHs such as FTH and PYR. In Malaysia, a profound proportion of the PAHs originates from uncontrolled biomass combustion of domestic and garden wastes and smoke from regional forest fires (Omar et al. 2002, 2006). The RET and its precursors are not produced during combustion of tropical woods (Abas et al. 1995; Fang et al. 1999) and, as such, they did not contribute to PC3. In conclusion, the first PCA uncovers that there are three sources for the PAHs in the sediments of the Selangor River, namely, vehicle emissions (PC1), petroleum oil (PC2), and biomass combustion (PC3).

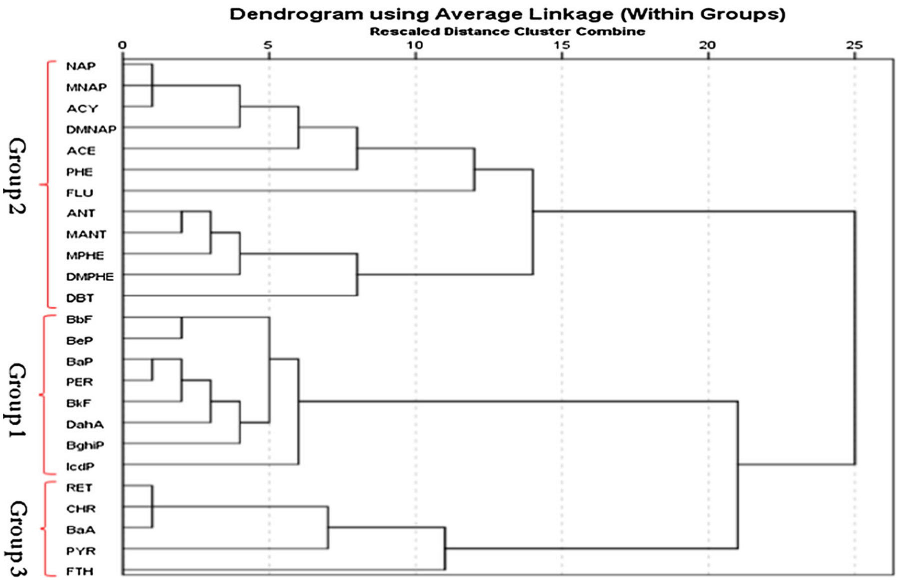


Fig. 5 Hierarchical dendrogram for PAHs in Selangor River sediments

Assessment of PAH toxicity in the sediments of the Selangor River

The potential toxicological impacts of the PAHs in the sediments of the Selangor River were assessed by comparing their concentrations with the numerical effect-based sediment quality guideline (SQG) values (Table 4) which are commonly developed based upon adverse effects of the pollutants on benthos since they are constantly in direct contact with the pollutants in the sediments (Burton 2002). Based upon different thresholds, the SQGs are divided into two general categories:

1. Concentrations which are less than those at which adverse effects occasionally happen to biological units, such as the threshold effect level (TEL), the screening level contamination (SLC), and the effects range low (ERL).
2. Concentrations which commonly cause adverse effects to biological units, including the probable effects level (PEL) and the effect range median (ERM).

The values of total PAHs, LMW PAHs, and HMW PAHs reported in the current study were compared with the ERL, SCL, ERM, PEL, and TEL SQGs (Table 4). Based on this comparison, it was found that the total PAHs in the surface sediments of the Selangor River were below the ERL value (4000 ng g^{-1} dw) in the four climatic seasons. The maximum total PAHs in the surface sediments in the four climatic seasons was 964.70 ng g^{-1} dw, which is also much lower than the ERL value. Therefore, the PAH levels in the surface sediments of the Selangor River comply with the minimal-effects range. Consequently, the PAHs are unlikely to cause any adverse biological effects to the aquatic organisms in the Selangor River. The comparison of the levels of LMW PAHs and HMW PAHs in the sediments of the Selangor River with the SQGs demonstrated that these concentrations are far less than the ERL, SCL, ERM, PEL, and TEL values. Thus, the probability for the PAHs in the Selangor River to have adverse effects on the aquatic biota including those that are closely associated with sediments is low.

Percentages of TOC in the sediments

Overall, the concentrations of TOC in the sediments of the Selangor River ranged from 1.16 to 1.98% in the four climatic seasons with a mean concentration of 1.41% ± 0.25 (Schumacher 2002). There was no significant correlation ($p > 0.05$) between TOC and total PAHs in the sediments of the study area. This finding contrasts with the findings of some other studies (e.g., Witt and Trost 1999; Liu et al. 2008; Jiang et al. 2009) which reported that the concentrations of hydrocarbons in sediments are highly related to their organic matter content. However, the present finding is in agreement with the findings of some other studies (e.g., Phelps 2000; Ouyang et al. 2006; Cailleaud et al. 2009) which did not find any significant relationship between total PAHs and organic matter content. A possible explanation for this result is that the PAHs are introduced to the environment from industrial and shipping ports and routes, while the organic carbon (OC) is mostly naturally present in the environment (Ouyang et al. 2006). As a result, this inconsistency might be because of the differences in the sources of OC and PAHs in the study area. Based on this finding, the total PAHs in the sediments of the Selangor River were not normalized by TOC and are reported in the present study on a dry weight basis (dw).

Table 3 Rotated component matrix of PAHs in Selangor River sediments (High loadings (> 0.65) shown in bold)

No.	PAHs	Principal component (PC)[a]		
		1	2	3
1	NAP	0.194	**0.857**	0.168
2	MNAP	0.060	− 0.126	0.005
3	ACY	0.149	0.247	− 0.053
4	DMNAP	0.016	0.224	− 0.020
5	ACE	0.098	0.319	0.136
6	FLU	− 0.277	**0.748**	0.178
7	DBT	0.428	**0.697**	-0.079
8	PHE	− 0.203	0.194	**0.820**
9	ANT	0.024	− 0.037	**0.917**
10	MPHE	− 0.478	− 0.084	0.119
11	MANT	0.100	0.256	0.611
12	DMPHE	0.568	− 0.070	0.068
13	FTH	0.290	0.010	**0.874**
14	PYR	0.165	0.192	**0.763**
15	RET	0.207	− 0.076	**0.691**
16	BaA	− 0.206	0.091	0.281
17	CHR	0.059	0.095	0.158
18	BkF	**0.871**	− 0.109	0.279
19	BbF	− 0.055	0.075	0.509
20	BaP	**0.806**	− 0.033	0.122
21	BeP	0.548	0.109	0.031
22	PER	0.174	0.036	-0.074
23	BghiP	**0.747**	0.432	0.212
24	DahA	**0.734**	0.225	0.332
25	IcdP	0.513	0.025	0.048
Eigenvalue		8.55	4.19	3.63
Variability (%)		26.6	21.2	17.8
Cumulative (%)		26.6	47.8	65.5
Estimated source		Vehicle	Oil	Biomass

Abbreviations for PAHs compounds in this study: *NAP* naphthalene, *MNAP* methylnaphthalene, *ACY* acenaphthylene, *DMNAP* dimethylnaphthalene, *ACE* acenaphthene, *FLU* fluorene, *DBT* dibenzothiophene, *PHE* phenanthrene, *ANT* anthracene, *MPHE* methylphenanthrene, *MANT* methylanthracene, *DMPHE* dimethylphenanthrene, *FTH* fluoranthene, *PYR* pyrene, *RET* retene, *BaA* benza(a)anthracene, *CHR* chrysene, *BkF* benzo(k)fluoranthene, *BbF* benzo(b)fluoranthene, *BaP* benzo(a)pyrene, *BEP* benzo(e)pyrene, *PER* perylene, *BghiP* benzo(ghi)perylene, *DahA* dibenzo(ah)anthracene, *IcdP* indeno(cd-23)pyrene

[a] Rotation method: Varimax with Kaiser Normalization

Hopanes in the sediments of the Selangor River

Levels of hopanes in the Selangor River sediments

As it was reported earlier, the sediments of the Malaysian Rivers are highly impacted by pyrogenic PAHs as was evidenced by the PAH diagnostic ratios. Previously, petroleum biomarker compositions (hopanes) were applied to identify the source of PAHs in Malaysian riverine sediments and constant hopane profiles were detected in the riverine sediments of Malaysia, indicating a similar diffuse source. Hopanes have been used as biomarkers for discrimination of the sources of petroleum (e.g., Volkman et al. 1997; Zakaria et al. 2000; Vaezzadeh et al. 2017b), and their compositions provided further supportive evidence on the sources of crude oil spillage in the aquatic environment (Zakaria et al. 2002).

In order to identify the origins of the petroleum hydrocarbon, the current study investigated the concentrations and sources of hopanes including (17α(H)-22,29,30-trisnorhopane (Tm), 17α(H),21ß(H)-norhopane (C_{29}17α), 17ß(H),21α(H)-norhopane (C_{29}17ß), 17α(H),21ß(H)-hopane (C_{30}17α), and 17ß(H),21α(H)-hopane (C_{30}17ß)) in the Selangor River. The average concentrations of total hopanes in the sediments ranged from 235 to 1044 ng g^{-1}, with a mean concentration of 442.05 ± 218.81 for all stations (Table 5). In addition, the minimum and maximum concentrations of hopanes in the collected sediments were 235 and 1044 ng g^{-1}, respectively, which were recorded at station S3 and station S9, respectively. These results indicated large variations among the different sediment sampling stations.

Table 4 Proposed sediment quality guidelines (SQGs) in terms of PAH content (Long et al. 1995; Macdonald et al. 1996; Burton 2002)

Station	Total PAHs				LMW PAHs				HMW PAHs			
	Dry	Rainy	NEM	SWM	Dry	Rainy	NEM	SWM	Dry	Rainy	NEM	SWM
S1	665.2	703.4	685.6	510.3	121.7	318.6	238.6	193.5	543.5	384.8	446.9	316.8
S2	576.4	563.2	450.5	426.9	139.4	111.5	213.5	242.9	436.9	451.7	237.1	184.1
S3	658.2	804.7	226.1	208.9	126.8	364.5	110.7	65.2	531.4	440.3	115.4	143.7
S4	475.7	696.8	221.7	136.6	132.6	357.5	87.8	56.5	343.1	339.2	133.9	80.1
S5	615.4	964.7	490.1	618.9	246.1	447.4	151.1	278.9	369.3	517.3	339.0	340.0
S6	541.1	790.5	242.4	509.6	291.2	360.2	112.6	226.9	249.9	430.3	129.8	282.7
S7	225.4	251.4	260.8	150.1	116.0	124.1	121.9	64.5	109.4	127.3	138.9	85.6
S8	331.7	215.5	197.7	133.9	51.5	104.7	92.0	84.6	280.2	110.8	105.7	49.3
S9	500.5	782.5	458.9	421.2	155.3	361.9	173.6	160.6	345.2	420.6	285.3	260.6
S10	649.9	758.8	688.9	322.8	320.6	204.2	312.8	204.6	329.2	554.6	376.1	118.2
S11	203.3	341.5	411.3	185.1	95.1	142.4	196.8	126.5	108.1	199.2	214.5	58.7
S12	492.3	705.2	352.9	388.2	175.1	215.2	213.7	264.6	317.3	489.9	139.3	123.6
S13	555.1	893.1	408.6	425.0	236.2	156.4	153.0	222.5	318.9	736.8	255.6	202.6
ERL	–	4000	–	–	–	–	552	–	–	1700	–	–
ERM	–	45,000	–	–	–	–	3160	–	–	9600	–	–
TEL	–	1684	–	–	–	–	–	–	–	–	–	–
PEL	–	16,770	–	–	–	–	–	–	–	–	–	–
SLC	–	4090	–	–	–	–	–	–	–	–	–	–

DIMP the dry inter-monsoonal period, *RIMP* the rainy inter-monsoonal period, *NEM* the northeast monsoon period, *SWM* the southwest monsoon period, *ERL* effects range low value, *ERM* effects range median value, *TEL* threshold effect levels, *PEL* probable effect levels, *SLC* screening level contamination

Identification of the sources of hopanes in the Selangor River

Based on previous data on composition of hopanes provided by Zakaria et al. (2001), signatures of the Southeast Asia and Middle East crude oils (SEACO and MECO, respectively) were found in environmental samples in Malaysia. MECO is highly used for production of engine and lubricating oil. Both 17α,21β(H) C_{30} hopane (C_{30} 17α) and 17α,21β(H) C_{29} hopane (C_{29} 17α), as well as 17α,21β(H), 22S, and 22R homohopanes from C_{31} to C_{35}, are present in MECO and SEACO. However, hopanes of higher plant origin are abundant in SEACO. Since SEACO comes from non-marine (i.e., lacustrine and deltaic) shale rocks, the ratios of C_{29}/C_{30} and C_{31}-C_{35}/C_{30} are lower in the SEACO than in the MECO oil. However, the MECO has higher ratios of C_{29}/C_{30} and C_{31}-C_{35}/C_{30} due to having marine carbonate rock origin.

Values of three hopane indices employed in this study, namely, C_{29}/C_{30}, ΣC_{31}–C_{35}/C_{30}, and Tm (17α(H)-22,29,30-trisnorhopane)/Ts (18α(H)-22,29,30-trisnorneohopane) are shown in Table 5. The ratio of Tm/Ts can be used as a measure of the thermal maturity of different samples from the same source (Wang et al. 2006). This ratio has a wide range of values (Table 5), both in MECO (0.35–2.31) and SEACO (0.52–2.20). In the present study, the range of T_m/T_s ratio was 0.71–1.98 in the Selangor River. Table S3 shows the values of C_{29}/C_{30}, ΣC_{31}–C_{35}/C_{30}, and the Tm/Ts ratios for the crude oil, fresh and used crankcase oil, street dust, and asphalt (Zakaria et al. 2002).

The ratios of C_{29}/C_{30} and ΣC_{31}–C_{35}/C_{30} can be used to distinguish MECO from SEACO as a source of hopanes. The ratio of C_{29}/C_{30} ranges from 1.41 to 2.01 and from 0.85 to 1.16 in MECO and SEACO oil, respectively (Zakaria et al. 2002). On the other hand,

Table 5 Hopane concentrations (ng g^{-1}) and relative ratios in the sediments of Selangor River

Compound	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	Mean	STD
T_m	14	6	6	33	43	7	6	14	38	21	7	5	12	16.2	13.4
T_s	17	3	8	46	21	8	10	17	31	23	9	3	23	16.9	12.2
$C_{29}17\alpha$	12	105	11	31	25	12	13	6	59	20	13	15	15	25.9	27.3
$C_{29}17\beta$	9	22	6	9	19	26	19	15	274	69	55	7	14	41.9	72.1
$C_{30}17\alpha$	9	97	13	15	23	8	6	6	143	24	10	28	6	29.8	41.8
$C_{30}17\beta$	75	95	90	108	126	141	97	143	96	117	190	47	95	109.1	35.5
C31-S	7	37	9	18	20	26	10	14	16	13	18	22	12	17.1	8.2
C31-R	10	56	9	17	17	10	9	17	53	38	20	9	12	21.3	16.6
C32-S	8	21	14	30	26	19	10	14	45	40	30	14	15	22.1	11.6
C32-R	8	10	10	29	19	21	11	25	31	31	35	12	37	21.5	10.5
C33-S	9	14	9	10	44	10	9	10	35	32	18	19	25	18.9	11.6
C33-R	8	16	15	12	17	14	14	13	67	57	29	20	15	22.9	18.2
C34-S	9	24	6	9	22	35	15	15	45	38	26	13	16	20.9	12.3
C34-R	16	28	8	9	22	21	20	26	18	8	16	14	9	16.6	6.9
C35-S	12	21	11	12	17	18	43	30	59	19	25	11	9	22.1	14.6
C35-R	14	34	11	7	21	18	15	12	33	10	50	10	12	19.0	12.5
[a]$\sum$Hopanes	238	590	235	396	481	396	305	377	1044	560	550	249	326	442.1	218.8
[b]T_m/T_s	0.96	1.76	0.94	1.16	1.98	1.06	0.83	0.71	1.21	1.50	0.93	1.45	1.53	1.23	0.38
[c]C_{29}/C_{30}	1.71	1.43	1.47	2.01	1.30	1.63	2.23	1.40	0.68	1.43	1.44	1.40	2.33	1.57	0.43
[d]ΣC_{31} -C_{35}/C_{30}	1.50	1.55	1.19	1.47	1.57	1.41	1.54	1.27	1.82	2.11	1.44	1.91	1.64	1.57	0.25

[a] *$\sum$Hopanes* Sum of the concentration of T_S, T_m, $C_{29}17\alpha$, $C_{29}17\beta$, $C_{30}17\alpha$, $C_{30}17\beta$, C_{31} S, C_{31} R, C_{32} S, C_{32} R, C_{33} S, C_{33} R, C_{34} S, C_{34} R, C_{35} S, and C_{35} R

[b] *T_m/T_s* Ratio of 17α-22,29,30-trisnorhopane over 18α-22,29,30-trisnorhopane

[c] *C_{29}/C_{30}* Ratio of 17α, 21β (H)-30-norhopane to17α, 21β (H)-hopane

[d] *ΣC_{31}–C_{35}/C_{30}* Ratio of sum of 17α, 21β (H)-C31 homohopane to 17α, 21β (H)-C35 homohopane relative to 17α, 21β (H)-hopane

the ratio of ΣC_{31}–C_{35}/C_{30} ranges from 1.80 to 2.30 and 0.41 to 0.89 in MECO and SEACO, respectively (Table S3). Such differences reflect the effects of the different geological processes on the formation of crude oils. The ratios of C_{29}/C_{30} and ΣC_{31}–C_{35}/C_{30} in the Selangor River ranged from 0.68 to 2.33 and 1.19 to 2.11, respectively. The range of C_{29}/C_{30} ratios for SEACO was lower than those found in the sediments of the Selangor River (Fig. 6), therefore excluding SEACO as a contributor to the sedimentary petroleum. On the other hand, the hopanes in the sediments of the Selangor River had C_{29}/C_{30} ratios similar to those of MECO. This suggests signature of the MECO in the sediments of the Selangor River, which is consistent with results reported by Zakaria et al. (2002) for urban sediments in Malaysia. For the most part, the ratios of ΣC_{31}–C_{35}/C_{30} do not match either of MECO and SEACO range of values.

Moreover, the composition of hopanes in some samples discloses a crankcase oil signature. Similarly, the range of the values of the Tm/Ts ratio in used crankcase oil (0.62–0.92) to some extent agrees with the range of the values of the Tm/Ts ratio in the sediments (0.71–1.98). As Fig. 6 shows, the ranges of values for the ratios of C_{29}/C_{30} and ΣC_{31}–C_{35}/C_{30} in used crankcase oil are 1.56–2.66 and 1.20–2.08, respectively. These values are consistent with the values calculated for sediments at all the sampling locations in the Kuala Selangor River which ranged from 0.68 to 2.33 and 1.19 to 2.11 for C_{29}/C_{30} and ΣC_{31}–C_{35}/C_{30}, respectively. These results indicate that the sediments of the Kuala Selangor River carry

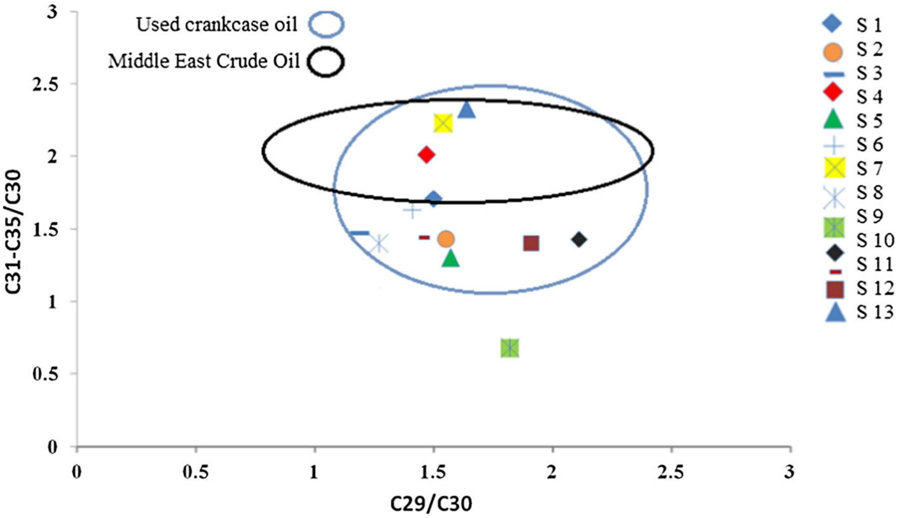


Fig. 6 Plot of C_{29}/C_{30} versus $\sum C_{31}$–C_{35}/C_{30} for the sediments of Selangor River

signature of used crankcase oil which can be transferred to the river via urban runoffs.

Conclusion

PAHs found in the sediments of the Selangor River are categorized at moderate to moderately high level of contamination. In this study, the highest levels of PAHs were detected during wet season and in the estuarine stations which indicates the influence of heavy tropical rainfall in transportation and fate of PAHs. Diagnostic indices of PAHs and hopanes were used for source identification of petroleum pollution in the sediments of the Kuala Selangor River. As mentioned earlier, PAHs are toxic to the aquatic organisms and have harmful health impacts on humans. Source identification of PAHs provides the necessary data for controlling their release into the environment. Identification of sources of PAHs in aquatic environment is specifically important in Malaysia where the majority of population are concentrated along the rivers or near the coastal areas due to the economic benefits. Thus, local community is exposed to PAHs from the river and seawater, sediment and consumption of aquatic animals. Composition of the PAHs showed that sediments were dominated by the 4–6 ring compounds at all sampling stations, implying various incomplete combustion-derived PAHs as the main sources of PAHs. Similarly, diagnostic ratios of PAHs and clustering analysis pointed out the significance of combustion sources such as biomass burning and vehicular emission in sediments of the Kuala Selangor River. The concentrations of LMW PAHs, HMW PAHs and total PAHs were far lower than the ERL, SCL, ERM, PEL, and TEL indicating low probability of adverse effects to the benthic organisms in the Kuala Selangor River, however, health risks of PAHs to humans need to be addressed in the future studies. Due to the toxic effects of PAHs for humans and other organisms, their bioavailability in the ecosystem of the Kuala Selangor River also needs to be investigated. The bioavailable fraction of PAHs can bioaccumulate in aquatic organism tissues, cause toxic effects on the aquatic organisms and pose health risks to humans at the top of the food chain. Thus, future research needs to also clarify the potential health risks of PAHs from the consumption of aquatic animals inhabiting the Kuala Selangor River. The values of the C_{29}/C_{30} ratio for the sediments of the Selangor River were found to be higher than those reported for the SEACO, excluding SEACO as a contributor to hydrocarbons in the sediments of the Kuala Selangor River. However, the values of the C_{29}/C_{30} ratio were found to be similar to those of MECO, hence evidencing contribution of MECO to the hydrocarbons in the sediments of the Selangor River, which is consistent with findings of some previous studies in other areas of Malaysia. The composition of hopanes was homogeneous in the sediments of the Kuala Selangor River and the use of multi-modal approach to source identification in this study showed signature of used crankcase oil in some of the sediment samples as suggested by the previous studies.

Acknowledgements This study was a part of Japan Society for the Promotion of Science (JSPS) Asian Core Project on Straits of Malacca funded by the Ministry of Higher Education of Malaysia, through Universiti Putra Malaysia (Project No. 6379005) and HICoE-MOHE Grant IOES-2014. We would like to thank them for supporting this research financially.

References

Abas, M., Rahman, N. A., Omar, N. Y. M., Maah, M. J., Abu Samah, A., Oros, D. R., et al. (2004). Organic composition of aerosol particulate matter during a haze episode in Kuala Lumpur, Malaysia. *Atmospheric Environment, 38,* 4223–4241.

Abas, M. R. B., Simoneit, B. R. T., Elias, V., Cabral, J. A., & Cardoso, J. N. (1995). Composition of higher molecular weight organic matter in smoke aerosol from biomass combustion in Amazonia. *Chemosphere, 30,* 995–1015.

Bahry, P. S., Zakaria, M. P., Bin Abdullah, A. M., Abdullah, D. K., Sakari, M., Chandru, K., et al. (2009). Forensic Characterization of Polycyclic Aromatic Hydrocarbons and Hopanes in Aerosols from Peninsular Malaysia. *Environmental Forensics, 10,* 240–252.

Bakhtiari, A. R., Zakaria, M. P., Yaziz, M. I., Lajis, M. N. H., & Bi, X. (2009). Polycyclic aromatic hydrocarbons and n-alkanes in suspended particulate matter and sediments from the Langat River, Peninsular Malaysia. *Environment Asia, 2,* 1–10.

Bakhtiari, A. R., Zakaria, M. P., Yaziz, M. I., Lajis, H., Nordin, M., Bi, X., et al. (2010). Distribution of PAHs and n-alkancs in Klang River surface Sediments, Malaysia. *Pertanika Journal of Science & Technology, 18,* 167–179.

Barrick, R. C., & Prahl, F. G. (1987). Hydrocarbon geochemistry of the Puget Sound region—III. Polycyclic aromatic hydrocarbons in sediments. *Estuarine, Coastal and Shelf Science, 25,* 175–191.

Baumard, P., Budzinski, H., & Garrigues, P. (1998). Polycyclic aromatic hydrocarbons in sediments and mussels of the western Mediterranean sea. *Environmental Toxicology and Chemistry, 17,* 765–776.

Boonyatumanond, R., Wattayakorn, G., Togo, A., & Takada, H. (2006). Distribution and origins of polycyclic aromatic hydrocarbons (PAHs) in riverine, estuarine, and marine sediments in Thailand. *Marine Pollution Bulletin, 52,* 942–956.

Bouloubassi, I., Roussiez, V., Azzoug, M., & Lorre, A. (2012). Sources, dispersal pathways and mass budget of sedimentary polycyclic aromatic hydrocarbons (PAH) in the NW Mediterranean margin, Gulf of Lions. *Marine Chemistry, 142,* 18–28.

Budzinski, H., Jones, I., Bellocq, J., Pierard, C., & Garriques, P. (1997). Evaluation of sediment contaminant by polycyclic aromatic hydrocarbons in the Gironde estuary. *Marine Chemistry, 58,* 85–97.

Burton, G. A., Jr. (2002). Sediment quality criteria in use around the world. *Limnology, 3,* 65–76.

Cailleaud, K., Forget-Leray, J., Peluhet, L., LeMenach, K., Souissi, S., & Budzinski, H. (2009). Tidal influence on the distribution of hydrophobic organic contaminants in the Seine Estuary and biomarker responses on the copepod *Eurytemora affinis*. *Environmental Pollution, 157,* 64–71.

Cao, B., Nagarajan, K., & Loh, K. C. (2009). Biodegradation of aromatic compounds: Current status and opportunities for biomolecular approaches. *Applied Microbiology and Biotechnology, 85,* 207–228.

Chalov, S. R., Jarsjö, J., Kasimov, N. S., Romanchenko, A. O., Pietroń, J., Thorslund, J., et al. (2015). Spatio-temporal variation of sediment transport in the Selenga River Basin, Mongolia and Russia. *Environmental Earth Sciences, 73,* 663–680.

Chandru, K., Zakaria, M. P., Anita, S., Shahbazi, A., Sakari, M., Bahry, P. S., et al. (2008). Characterization of alkanes, hopanes, and polycyclic aromatic hydrocarbons (PAHs) in tar-balls collected from the East Coast of Peninsular Malaysia. *Marine Pollution Bulletin, 56,* 950–962.

Chen, C. W., & Chen, C. F. (2011). Distribution, origin, and potential toxicological significance of polycyclic aromatic hydrocarbons (PAHs) in sediments of Kaohsiung Harbor, Taiwan. *Marine Pollution Bulletin, 63,* 417–423.

Commendatore, M. G., Esteves, J. L., & Colombo, J. C. (2000). Hydrocarbons in coastal sediments of Patagonia, Argentina: Levels and probable sources. *Marine Pollution Bulletin, 40,* 989–998.

Daka, E. R., & Ugbomeh, A. P. (2013). Polycyclic aromatic hydrocarbons in sediment and tissues of the Crab *Callinectes pallidus* from the Azuabie Creek of the Upper Bonny Estuary in the Niger Delta. *Research Journal of Applied Sciences, Engineering and Technology, 6,* 2594–2600.

Dobbins, R. A., Fletcher, R. A., Benner, B. A., & Hoeft, S. (2006). Polycyclic aromatic hydrocarbons in flames, in diesel fuels, and in diesel emissions. *Combustion and Flame, 144,* 773–781.

El Nemr, A., El-Sadaawy, M. M., Khaled, A., & El-Sikaily, A. (2013). Distribution patterns and risks posed of polycyclic aromatic hydrocarbons contaminated in the surface sediment of the Red Sea coast (Egypt). *Desalination and Water Treatment, 52,* 7964–7982.

Fang, M., Zheng, M., Wang, F., To, K. L., Jaafar, A. B., & Tong, S. L. (1999). The solventextractable organic compounds in the Indonesia biomass burning aerosols–characterization studies. *Atmospheric Environment, 33,* 783–795.

Feng, C., Xia, X., Shen, Z., & Zhou, Z. (2007). Distribution and sources of polycyclic aromatic hydrocarbons in Wuhan section of the Yangtze River, China. *Environmental Monitoring and Assessment, 133,* 447–458.

Gallon, C., Tessier, A., Gobeil, C., & Beaudin, L. (2005). Sources and chronology of atmospheric lead deposition to a Canadian Shield lake: Inferences from Pb isotopes and PAH profiles. *Geochimica et Cosmochimica Acta, 69,* 3199–3210. https://doi.org/10.1016/j.gca.2005.02.028.

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. *Polycyclic Aromatic Compounds, 7,* 275–284.

González, J., Viñas, L., Franco, M., Fumega, J., Soriano, J., Grueiro, G., et al. (2006). Spatial and temporal distribution of dissolved/dispersed aromatic hydrocarbons in seawater in the area affected by the *Prestige* oil spill. *Marine Pollution Bulletin, 53,* 250–259.

Guo, Z., Lin, T., Zhang, G., Yang, Z., & Fang, M. (2006). High-resolution depositional records of polycyclic aromatic hydrocarbons in the central continental shelf mud of the East China Sea. *Environmental Science and Technology, 40,* 5304–5311.

Harji, R. R., Yvenat, A., & Bhosle, N. B. (2008). Sources of hydrocarbons in sediments of the Mandovi estuary and the Marmugoa harbour, west coast of India. *Environment International, 34,* 959–965.

Hartmann, P. C., Quinn, J., King, J. W., Tsutsumi, S., & Takada, H. (2000). Intercalibration of LABs in marine sediment SRM1941a and their application as a molecular marker in Narragansett Bay sediments. *Environmental Science and Technology, 34,* 900–906.

He, J., Zielinska, B., & Balasubramanian, R. (2010). Composition of semi-volatile organic compounds in the urban atmosphere of Singapore: influence of biomass burning. *Atmospheric Chemistry and Physics, 10,* 11401–11413.

Hu, L., Guo, Z., Feng, J., Yang, Z., & Fang, M. (2009). Distributions and sources of bulk OM and aliphatic hydrocarbons in the surface sediments of the Bohai Sea, China. *Marine Chemistry, 113,* 197–211.

Iqbal, J., Overton, E. B., & Gisclair, D. (2008). Polycyclic aromatic hydrocarbons in Louisiana Rivers and coastal environments: source fingerprinting and forensic analysis. *Environmental Forensics, 9,* 63–74.

Irwin, R. (1997). *National Park Service. Environmental Contaminants Encyclopedia, PAHs Entry*. Colorado: National Park Service.

Jiang, J. J., Lee, C. L., Fang, M. D., & Liu, J. T. (2009). Polycyclic aromatic hydrocarbons in coastal sediments of Southwest Taiwan: An appraisal of diagnostic ratios in source recognition. *Marine Pollution Bulletin, 58,* 752–760.

Karacik, B., Okay, O., Henkelmann, B., Bernhöft, S., & Schramm, K. W. (2009). Polycyclic aromatic hydrocarbons and effects on marine organisms in the Istanbul Strait. *Environment International, 35,* 599–606.

Karami, A., Christianus, A., Ishak, Z., Shamsuddin, Z. H., Masoumian, M., & Courtenay, S. C. (2012). Use of intestinal *Pseudomonas aeruginosa* in fish to detect the environmental pollutant benzo [a] pyrene. *Journal of Hazardous Materials, 215–216,* 108–114. https://doi.org/10.1016/j.jhazmat.2012.02.038.

Karyab, H., Nasseri, S., Ahmadkhaniha, R., Rastkari, N., Mahvi, A. H., Nabizadeh, R., et al. (2014). Determination and source identification of polycyclic aromatics hydrocarbons in Karaj River, Iran. *Bulletin of Environmental Contamination and Toxicology, 92,* 50–56.

Katsoyiannis, A., Terzi, E., & Cai, Q. Y. (2007). On the use of PAH molecular diagnostic ratios in sewage sludge for the understanding of the PAH sources. *Chemosphere, 69,* 1337–1339.

Keshavarzifard, M., Zakaria, M. P., & Hwai, T. S. (2017). Bioavailability of polycyclic aromatic hydrocarbons (PAHs) to short-neck clam (Paphia undulata) from sediment matrices in mudflat areas of West coast of Peninsular Malaysia. *Environmental Geochemistry and Health*. https://doi.org/10.1007/s10653-016-9835-z.

Keshavarzifard, M., Zakaria, M. P., Hwai, T. S., Mustafa, S., Vaezzadeh, V., Magam, S. 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. *Marine Pollution Bulletin, 88,* 366–372.

Keshavarzifard, M., Zakaria, M. P., Hwai, T. S., Yusuff, F. M., & Mustafa, S. (2015). Distributions and source apportionment of sediment-associated polycyclic aromatic hydrocarbons (PAHs) and hopanes in rivers and estuaries of Peninsular Malaysia. *Environmental Science and Pollution Research*. https://doi.org/10.1007/s11356-015-4093-7.

Keshavarzifard, M., Zakaria, M. P., & Keshavarzifard, S. (2016). Evaluation of polycyclic aromatic hydrocarbons contamination in the sediments of the Johor Strait, Peninsular Malaysia. *Polycyclic Aromatic Compounds*. https://doi.org/10.1080/10406638.2016.1257997.

Khalili, N. R., Scheff, P. A., & Holsen, T. M. (1995). PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions. *Atmospheric Environment, 29,* 533–542.

Larsen, R. K., III, & Baker, J. E. (2003). Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: A comparison of three methods. *Environmental Science and Technology, 37,* 1873–1881.

Liang, Y., Tse, M., Young, L., & Wong, M. (2007). Distribution patterns of polycyclic aromatic hydrocarbons (PAHs) in the sediments and fish at Mai Po Marshes Nature Reserve, Hong Kong. *Water Research, 41,* 1303–1311.

Liu, Y., Chen, L., Jianfu, Z., Qinghui, H., Zhiliang, Z., & Hongwen, G. (2008). Distribution and sources of polycyclic aromatic hydrocarbons in surface sediments of rivers and an estuary in Shanghai, China. *Environmental Pollution, 154,* 298–305.

Liu, A., Egodawatta, P., Guan, Y., & Goonetilleke, A. (2013). Influence of rainfall and catchment characteristics on urban stormwater quality. *Science of the Total Environment, 444,* 255–262.

Long, E., Macdonald, D., Smith, S., & Calder, F. (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management, 19,* 81–97.

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

Luo, X. J., Chen, S. J., Ni, H. G., Yu, M., & Mai, B. X. (2008). Tracing sewage pollution in the Pearl River Delta and its adjacent coastal area of South China Sea using linear alkylbenzenes (LABs). *Marine Pollution Bulletin, 56,* 158–162.

Ma, X., Ran, Y., Gong, J., & Zou, M. (2007). Concentrations and inventories of polycyclic aromatic hydrocarbons and organochlorine pesticides in watershed soil in the Pearl

River Delta, China. *Environmental Monitoring and Assessment, 145,* 453–464.

Macdonald, D. D., Carr, R. S., Calder, F. D., Long, E. R., & Ingersoll, C. G. (1996). Development and evaluation of Sediment quality guidelines for Florida coastal waters. *Ecotoxicology, 5,* 253–278.

Magi, E., Bianco, R., Ianni, C., & Di Carro, M. (2002). Distribution of polycyclic aromatic hydrocarbons in the sediments of the Adriatic Sea. *Environmental Pollution, 119,* 91–98.

Mai, B. X., Fu, J. M., Sheng, G. Y., Kang, Y. H., Lin, Z., Zhang, G., et al. (2002). Chlorinated and polycyclic aromatic hydrocarbons in riverine and esturine sediments from Pearl River Delta China. *Environmental Pollution, 117,* 457–474.

Maioli, O. L. G., Rodrigues, K. C., Knoppers, B. A., & Azevedo, D. A. (2010). Polycyclic aromatic and aliphatic hydrocarbons in Mytella charruana, a bivalve mollusk from Mundaú Lagoon, Brazil. *Microchemical Journal, 96,* 172–179.

Mandalakis, M., Gustafsson, O., Reddy, C. M., & Xu, L. (2004). Radiocarbon apportionment of fossil versus biofuel combustion sources of polycyclic aromatic hydrocarbons in the Stockholm metropolitan area. *Environmental Science and Technology, 38,* 5344–5349.

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. *Atmospheric Environment, 60,* 375–382.

Masood, N., Zakaria, M. P., Ali, M. M., Magam, S. M., Alkhadher, S. A., Keshavarzifard, M., 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). Singapore: Springer. https://doi.org/10.1007/978-981-4560-70-2_64.

Masood, N., Zakaria, M. P., Halimoon, N., Aris, A. Z., Magam, S. M., Kannan, N., et al. (2016). Anthropogenic waste indicators (AWI) particularly PAHs and LABs in Malaysian sediments: Application of aquatic environment for identifying anthropogenic pollution. *Marine Pollution Bulletin, 102,* 160–175.

Mirsadeghi, S. A., Zakaria, M. P., Yap, C. K., & Gobas, F. (2013). Evaluation of the potential bioaccumulation ability of the blood cockle (*Anadara granosa*) for assessment of environmental matrices of mudflats. *Science of the Total Environment, 454,* 584–597.

Mirsadeghi, S. A., Zakaria, M. P., Yap, C. K., & Shahbazi, A. (2011). Risk assessment for the daily intake of polycyclic aromatic hydrocarbons from the ingestion of cockle *(Anadara granosa)* and exposure to contaminated water and sediments along the west coast of Peninsular Malaysia. *Journal of Environmental Sciences, 23,* 336–345.

Mitchell, P. K. K., Mills, G., Fisher-Niwa, G., Eason-Landcare, C., (1998). Technical paper No. 37 Toxic.

Nozar, S. L. M., Ismail, W. R., & Zakaria, M. P. (2014). Distribution, sources identification, and ecological risk of PAHs and PCBs in coastal surface sediments from the Northern Persian Gulf. *Human and Ecological Risk Assessment: An International Journal, 20,* 1507–1520.

Okuda, T., Kumata, H., Zakaria, M. P., Naraoka, H., Ishiwatari, R., & Takada, H. (2002). Source identification of Malaysian atmospheric polycyclic aromatic hydrocarbons nearby forest fires using molecular and isotopic compositions. *Atmospheric Environment, 36,* 611–618.

Omar, N.-Y.-M.-J., Abas, M.-R.-B., Ketuly, K.-A., & Tahir, N-Md. (2002). Concentrations of PAHs in atmospheric particles (PM-10) and road side soil particles collected in Kuala Lumpur, Malaysia. *Atmospheric Environment, 36,* 247–254.

Omar, N.-Y.-M.-J., Mon, T.-C., Rahman, N.-A., & Abas, M.-R.-B. (2006). Distributions and health risks of polycyclic aromatic hydrocarbons (PAHs) in atmospheric aerosols of Kuala Lumpur, Malaysia. *Science of the Total Environment, 369,* 76–81.

Ouyang, Y., Zhang, J. E., & Ou, L. T. (2006). Temporal and spatial distributions of sediment total organic carbon in an estuary river. *Journal of Environmental Quality, 35,* 93–100.

Pereira, W. E., Hostettler, F. D., Luoma, S. N., Van Geen, A., Fuller, C. C., & Anima, R. J. (1999). Sedimentary record of anthropogenic and biogenic polycyclic aromatic hydrocarbons in San Francisco Bay, California. *Marine Chemistry, 64,* 99–113.

Peters, K. E., & Moldowan, J. M. (1993). *The Biomarker Guide: Interpreting molecular fossils in petroleum and ancient sediments*. Englewood Cliffs, New Jersey: Prentice Hall.

Phelps, H. L. (2000). DC AES contaminated Anacostia Estuary sediments: A biomonitoring approach. Report, DC Water Resources Research Center, Washington, DC.

Prahl, F. G., Crecelius, E., & Carpenter, R. (1984). Polycyclic aromatic hydrocarbons in Washington coastal sediments: An evaluation of atmospheric and riverine routes of introduction. *Environmental Science and Technology, 18,* 687–693.

Prince, R. C., Elmendorf, D. L., Lute, J. R., Hsu, C. S., Halth, C. E., Senlus, J. D., et al. (1994). 17a(H),21a(H)-Hopane as a conservative internal marker for estimating the biodegradation of crude oil. *Environmental Science and Technology, 28,* 142–145.

Qiao, M., Wang, C., Huang, S., Wang, D., & Wang, Z. (2006). Composition, sources, and potential toxicological significance of PAHs in the surface sediments of the Meiliang Bay, Taihu Lake, China. *Environment International, 32,* 28–33.

Ramdahl, T. (1983). Retene—A molecular marker of wood combustion in ambient air. *Nature, 306,* 580–582.

Raza, M., Zakaria, M. P., Hashim, N. R., Yim, U. H., Kannan, N., & Ha, S. Y. (2013). Composition and source identification of polycyclic aromatic hydrocarbons in mangrove sediments of Peninsular Malaysia: Indication of anthropogenic input. *Environmental Earth Sciences, 70,* 2425–2436.

Retnam, A., Zakaria, M. P., Juahir, H., Aris, A. Z., Zali, M. A., & Kasim, M. F. (2013). Chemometric techniques in distribution, characterisation and source apportionment of polycyclic aromatic hydrocarbons (PAHS) in aquaculture sediments in Malaysia. *Marine Pollution Bulletin, 69,* 55–66.

Saha, M., Togo, A., Mizukawa, K., Murakami, M., Takada, H., Zakaria, M. P., et al. (2009). Sources of sedimentary PAHs in tropical Asian waters: Differentiation between pyrogenic and petrogenic sources by alkyl homolog abundance. *Marine Pollution Bulletin, 58,* 189–200.

Sakari, M., & Zakaria, M. P. (2013). Distribution, characterization and origins of polycyclic aromatic hydrocarbons (PAHs) in surficial sediment of Penang, Malaysia: The presence of fresh and toxic substances. *World Applied Sciences Journal, 23,* 1481–1488.

Sakari, M., Zakaria, M. P., Junos, M. B. M., Annuar, N. A., Yun, H. Y., Heng, Y. S., et al. (2008a). Spatial distribution of petroleum hydrocarbon in sediments of major rivers from east coast of peninsular Malaysia. *Estuarine and Coastal Marine Science, 31,* 9–18.

Sakari, M., Zakaria, M. P., Lajis, N. H., Mohamed, C. A. R., Bahry, P. S., & Anita, S. (2008b). Characterization, distribution, sources and origins of aliphatic hydrocarbons from surface sediment of Prai Strait, Penang, Malaysia: A widespread anthropogenic input. *Environment Asia, 2,* 1–14.

Sakari, M., Zakaria, M. P., Mohamed, C. A. R., Lajis, N. H., Chandru, K., Bahry, P. S., et al. (2010). Urban vs. Marine based oil pollution in the strait of Johor, Malaysia: A century record. *Soil and Sediment Contamination, 19,* 644–666.

Sanger, D. M., Holland, A. F., & Scott, G. I. (1999). Tidal creek and salt marsh sediments in South Carolina coastal estuaries: II. Distribution of organic contaminants. *Archives of Environmental Contamination and Toxicology, 37,* 458–471.

Schumacher, B. A. (2002). *Methods for the determination of total organic carbon (TOC). Soils and Sediments*. Washington DC: U.S. Environmental Protection Agency.

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. *Atmospheric Environment, 21,* 2247–2259.

Simoneit, B. R. T. (2002). Biomass burning—A review of organic tracers for smoke from incomplete combustion. *Applied Geochemistry, 17,* 129–162.

Soclo, H. H., Garrigues, P., & Ewald, M. (2000). Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: Case Studies in Cotonou (Benin) and Aquitaine (France) areas. *Marine Pollution Bulletin, 40,* 387–396.

Stout, S. A., Uhler, A. D., & Emsbo-Mattingly, S. D. (2004). Comparative evaluation of background anthropogenic hydrocarbons in surficial sediments from nine urban waterway. *Environmental Science and Technology, 38,* 2987–2994.

Suneel, V., Vethamony, P., Naik, B. G., Vinod Kumar, K., Sreenu, L., Samiksha, S. V., et al. (2014). Source investigation of the Tar Balls deposited along the Gujarat Coast, India, using chemical fingerprinting and transport modeling techniques. *Environmental Science and Technology, 48,* 11343–11351.

Tahir, N. M., Fadzil, M. F., Ariffin, J., Maarop, H., & Wood, A. K. H. J. (2011). Sources of polycyclic aromatic hydrocarbons in mangrove sediments of pulau cik wan dagang, kemaman. *Journal of Sustainability and Science Management, 6,* 98–106.

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. *Science of the Total Environment, 107,* 45–69.

Tee, L. T., & Mohamed, C. A. R. (2005). Activities of 210Po and 210Pb in the water column at Kuala Selangor, Malaysia. *Journal of Environmental Radioactivity, 80,* 273–286.

Tsymbalyuk, K. K., Den'ga, Y. M., Berlinsky, N. A., & Antonovich, V. P. (2011). Determination of 16 priority polycyclic aromatic hydrocarbons in bottom sediments of the Danube estuarine coast by GC/MS. *Geo-Eco-Marina, 17,* 67–72.

Vaezzadeh, V., Zakaria, M. P., & Bong, C. W. (2017a). Aliphatic hydrocarbons and triterpane biomarkers in mangrove oyster *(Crassostrea belcheri)* from the west coast of Peninsular Malaysia. *Marine Pollution Bulletin*. https://doi.org/10.1016/j.marpolbul.2017.07.008.

Vaezzadeh, V., Zakaria, M. P., Bong, C. W., Masood, N., Mohsen Magam, S., & Alkhadher, S. (2017b). Mangrove oyster *(Crassostrea belcheri)* as a biomonitor species for bioavailability of polycyclic aromatic hydrocarbons (PAHs) from sediment of the West Coast of Peninsular Malaysia. *Polycyclic Aromatic Compounds*. https://doi.org/10.1080/10406638.2017.1348366.

Vaezzadeh, V., Zakaria, M. P., Mustafa, S., Ibrahim, Z. Z., Shau-Hwai, A. T., Keshavarzifard, M., et al. (2015a). Source type evaluation of polycyclic aromatic hydrocarbons (PAHs) in surface sediments from the Muar River and Pulau Merambong, Peninsular Malaysia. *Environmental Forensic, 16,* 135–142.

Vaezzadeh, V., Zakaria, M. P., Mustafa, S., Ibrahim, Z. Z., Shau-Hwai, A. T., Keshavarzifard, M., 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). Singapore: Springer.

Vaezzadeh, V., Zakaria, M. P., Shau-Hwai, A. T., Ibrahim, Z. Z., Mustafa, S., Jahromi, F. A., et al. (2015b). Forensic investigation of aliphatic hydrocarbons in the sediments from selected mangrove ecosystems in the west coast of Peninsular Malaysia. *Marine Pollution Bulletin, 100,* 311–320.

Volkman, J. K. (1986). A review of sterol markers for marine and terrigenous OM. *Organic Geochemistry, 9,* 83–99.

Volkman, J. K., Revill, A. T., & Murray, A. P. (1997). *Applications of biomarkers for identifying sources of natural and pollutant hydrocarbons in aquatic environments. ACS Symposium Series* (pp. 110–132). Washington DC: American Chemical Society.

Wang, Z., Fingas, M., & Sergy, G. (1994). Study of 22-year-old Arrow oil samples using biomarker compounds by GC/MS. *Environmental Science and Technology, 28,* 1733–1746.

Wang, H. S., Liang, P., Kang, Y., Shao, D. D., Zheng, G. J., Wu, S. C., et al. (2010). Enrichment of polycyclic aromatic hydrocarbons (PAHs) in mariculture sediments of Hong Kong. *Environmental Pollution, 158,* 3298–3308.

Wang, Z., Stout, S. A., & Fingas, M. (2006). Forensic fingerprinting of biomarkers for oil spill characterization and source identification. *Environmental Forensics, 7,* 105–146.

Wang, Z., Yang, C., Fingas, M., Hollebone, B., Yim, U. H., & Oh, J. R. (2007). Petroleum biomarker fingerprinting for oil spill characterization and source identification. In Z. Wang & S. A. Stout (Eds.), *Oil spill environmental forensics: Fingerprinting and source identification* (p. 73). London: Academic Press.

Witt, G., & Trost, E. (1999). Polycyclic aromatic hydrocarbons (PAHs) in sediments of the Baltic Sea and of the German coastal waters. *Chemosphere, 38,* 1603–1614.

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, H. H., Chien, S. M., Lo, M. Y., Lan, J. C. W., Lu, W. C., & Ku, Y. Y. (2007). Effects of biodiesel on emissions of regulated air pollutants and polycyclic aromatic hydrocarbons under engine durability testing. *Atmospheric Environment, 41,* 7232–7240.

Yang, Y., & Hofmann, T. (2009). Aqueous accelerated solvent extraction of native polycyclic aromatic hydrocarbons (PAHs) from carbonaceous river floodplain soils. *Environmental Pollution, 157,* 2604–2609.

Yang, H.-H., Jung, R.-C., Wang, Y.-F., & Hsieh, L.-T. (2005). Polycyclic aromatic hydrocarbons emission from joss paper furnaces. *Atmospheric Environment, 39,* 3305–3312.

Ye, B., Zhang, Z., & Mao, T. (2006). Pollution sources identification of polycyclic aromatic hydrocarbons of soils in Tianjin area, China. *Chemosphere, 64,* 525–534.

Youngblood, W. W., & Blumer, M. (1975). Polycyclic aromatic hydrocarbons in the environment: Homologous series in soils and recent marine sediments. *Geochimica et Cosmochimica Acta, 39,* 1303–1314.

Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., & Sylvestre, S. (2002). PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry, 33,* 489–515.

Zaghden, H., Kallel, M., Louati, A., Elleuch, B., Oudot, J., & Saliot, A. (2005). Hydrocarbons in surface sediments from the Sfax coastal zone (Tunisia), Mediterranean Sea. *Marine Pollution Bulletin, 50,* 1287–1294.

Zakaria, M. P., Horinouchi, A. I., Tsutsumi, S., Takada, H., Tanabe, S., & Ismail, A. (2000). Oil pollution in the Straits of Malacca, Malaysia: Application of molecular markers for source identification. *Environmental Science and Technology, 34,* 1189–1196.

Zakaria, M. P., & Mahat, A. A. (2006). Distribution of polycyclic aromatic hydrocarbon (PAHs) in sediments in the Langat Estuary. *Coastal Marine Science, 30,* 387–395.

Zakaria, M. P., Okuda, T., & Takada, H. (2001). Polycyclic aromatic hydrocarbon (PAHs) and hopanes in stranded tarballs on the coasts of Peninsular Malaysia: Applications of biomarkers for identifying sources of oil pollution. *Marine Pollution Bulletin, 42,* 1357–1366.

Zakaria, M. P., Takada, H., Tsutsumi, S., Ohno, K., Yamada, J., Kouno, E., et al. (2002). Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in Malaysia: A widespread input of petrogenic PAHs. *Environmental Science and Technology, 36,* 1907–1918.

Zemo, D. A. (2009). Use of parent polycyclic aromatic hydrocarbon (PAH) proportions to attribute PAH sources in sediments: A case study from the Pacific Northwest. *Environment Forensics, 10,* 229–239.

Zhao, X., Ding, J., & You, H. (2014). Spatial distribution and temporal trends of polycyclic aromatic hydrocarbons (PAHs) in water and sediment from Songhua River, China. *Environmental Geochemistry and Health, 36,* 131–143.