Investigation of Aliphatic and Polycyclic Aromatic Hydrocarbons in Surface Sediments of Brunei Bay, East Malaysia

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The surface distributions of aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) were investigated from coastal sediments of Brunei Bay, southern South China Sea. The concentrations of total *n*-alkane (TNA) and 16 USEPA priority PAHs ranged from 0.67 to 9.88 µg/g and 4.72 to 102 ng/g, respectively. Principal component analysis (PCA) clustered the hydrocarbons in surface sediments according to their relationship and geographical locations, anticipated to the inputs and activities in proximity. Biomarker diagnostic ratios revealed that biogenic *n*-alkane inputs in the coastal sediments are exported from the fluviomarine and mangrove swamp environment, while the PAHs inputs are derived from mixed petrogenic and petroleum combustion residues. Overall, the level of PAHs in the study area is between low to moderate, based on the comparison with other areas worldwide.

Keywords: Diagnostic ratios, Fluviomarine, Petrogenic, Petroleum combustion, Brunei Bay.

INTRODUCTION

Hydrocarbons are organic compounds, which are the dominant components of petroleum related products (*i.e.* lubricating oil, gasoline, coal tar, *etc.*) in everyday life. Polycyclic aromatic hydrocarbons (PAHs) are among the group of hydrocarbon compounds that consist of merged aromatic rings. Polycyclic aromatic hydrocarbons can be formed during incomplete combustion processes of organic matter, produced naturally by microorganisms or plants or through natural phenomena (*i.e.* low-temperature diagenesis process, forest fires, volcanic activities and petroleum seepage) [1-3]. Once emitted to the atmosphere, PAHs tend to adsorb on particulate matter, persist for long periods of time in the environment and accumulate in food chains and biota. Due to their known toxic effects, mutagenic and carcinogenic properties, 16 PAHs have been listed as priority pollutants by the U.S. Environmental Protection Agency (EPA) [4].

Brunei Bay lies in the north-western coast of Borneo Island, bordering Brunei Darussalam and Sabah, Sarawak and the Federal Territory of Labuan in East Malaysia. The bay features many interconnecting river channels and important ecosystems including rainforests, reefs, mangrove swamps, wetlands and mudflats, for fishing and recreational activities. Due to its strategic geographical location, the bay also functions as a hub for active crude oil *trans*-shipments and maritime transportation. Although having a relatively small population (between 19,426 to 66,406) at the coastal districts around the Brunei Bay [5,6], the inputs of human induced anthropogenic contamination can still be observed, which is generally anticipated to the inputs and activities in proximity [7,8].

To the best of our knowledge, limited studies have been carried out in Brunei Bay. Mohamed *et al.* [9] assessed the impact of pulp and paper mill operations near the Sipitang coast of the bay; Saleh *et al.* [7] performed a baseline study of physicochemical parameters for sustainable development; Ghazali *et al.* [10] worked on tracing the sources of rare earth elements; Suratman *et al.* [11] studied the distribution of Si compounds; Pang *et al.* [8] investigated the distribution and level of contamination in terms of total petroleum hydrocarbons, oil and grease in Brunei Bay. Overall, these studies highlight the need for monitoring pollutants and the extent of pollution

in East Malaysia. Thus, the current study aims to investigate the level of aliphatic hydrocarbons and PAHs in the coastal sediments of Brunei Bay, identify their sources using biomarker ratios and characterize the hydrocarbons using multivariate statistics approach.

EXPERIMENTAL

Sampling procedures: Thirteen coastal sediments (stations B1-B13) were sampled at a distance of approximately 2 km from the coast of Brunei Bay in May 2018 using Ponar grab (Fig. 1). Samples were packed into aluminium foil bags and kept refrigerated (-4 ℃) before being transported back to the laboratory.

Extraction procedures: All the solvents and reagents used in the analysis were analytical and chromatographic grade. Details about the extraction have already been described [12]. In short, freeze-dried and sieved sediments (< 2.0 mm) were extracted three times using ultrasonic agitation in a 50 mL mixture of dichloromethane/methanol (3:1 v/v) for 30 min. Internal standards of ($^2H_{50}$) tetracosane and ($^2H_{10}$) phenanthrene

were spiked into samples before extraction for recovery assessment. Sulphur in the extract was removed using mercury treatment. One drop of mercury was added into the extract in a caped test tube and was shaken thoroughly for 2 h and 30 min. The extract was pipetted out into a centrifuge tube, centrifuged and then the clear supernatant was pipetted into a new test tube. The process was repeated until no formation of black precipitate was observed. The supernatants were then combined for the derivatization process. An aliquot of the final extract (~ 100 μL) was evaporated to almost dryness under a gentle stream of nitrogen and about 50-100 μL of N,O-*bis*-(trimethyl-silyl)trifluoroacetamide (BSTFA) plus 1% of trimethylchloro-silane (TMCS) was added and heated at 70 ℃ for 60 min. Once cooled to room temperature, the excess BSTFA was evaporated with a stream of nitrogen to dryness and reconstituted with a known volume of isooctane, prior to GC-MS analysis.

Instrumental analysis: Identification and quantification of compounds was carried out using a Shimadzu-QP2010 ultra gas chromatograph-mass spectrometer (GC-MS) fitted with a DB-5 fused silica capillary column (30 m length × 0.32 mm i.d., 0.25 μm film thickness). The MS was operated at full-
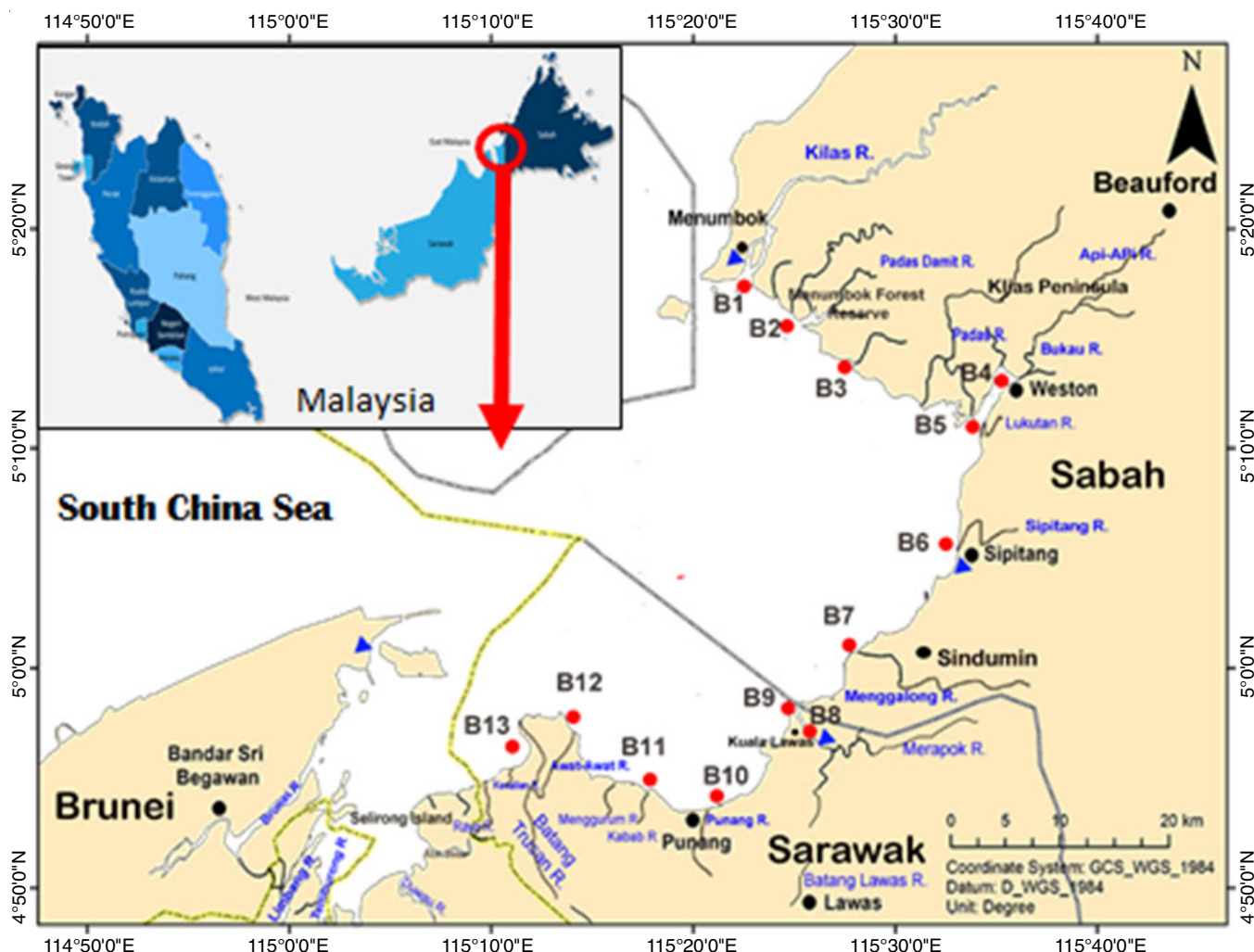

Fig. 1. Sampling area located in East Malaysia (on top left); sampling stations are labeled as B1-B13 (red dots), black dots indicate towns or villages, blue triangles indicate ferry terminals and the blue text indicates river names. The grey line delineates state and federal territories of Malaysia and the yellow line indicates the international border with Brunei

scan in the electron impact mode (70 eV) using the mass range from 45 to 800 da, at a scan speed of 1.25 s. Helium (99.9% purity) was used as the carrier gas with an initial flow of 1.2 mL/min, pressure at 68.3 kPa and average velocity of 39.7 cm/s. The extract was injected in splitless mode with injector temperature at 300 ℃. The GC column oven temperature program was set as follows: hold at 50 ℃ for 1 min, ramp from 50 to 140 ℃ at 5 ℃/min, 140 to 300 ℃ at 4 ℃/min and finally isothermal at 300 ℃ for 15 min.

Identification and quantification: Identification of aliphatic hydrocarbons and PAHs was carried out based on their molecular weight ions and MS library search. Identified aliphatic hydrocarbons include resolved n-alkanes (nC_{15}–nC_{37}), isoprenoid hydrocarbons and unresolved complex mixtures (UCM). A total of 19 parent PAHs were identified, which included naphthalene (Nap), acenaphthylene (Acp), acenaphthene (Ace), fluorene (Flo), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Py), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (Ind), dibenz[a,h]anthracene (DBA), benzo[ghi]perylene (BghiP), benzo[e]pyrene (BeP), perylene (Pery) and dibenzothophene (DBT). Six groups of alkyl PAHs were identified, which included napthalenes (C_0–C_4 Nap), fluorenes (C_0–C_3), dibenzothiophenes (C_0–C_3 DBT), phenanthrenes/anthracenes (C_0–C_4 P/A), fluoranthenes/pyrenes (C_0–C_3 F/P) and benzo[a]anthracenes/chrysenes (C_0–C_2 B/C). Quantification was carried out based on external standard calibration. The concentrations of identified compounds were reported in dry weight (dw). The mean recoveries and standard deviations (±SD) for $^2H_{50}$ and $^2H_{10}$ in the samples were 76.8% ± 10.7 and 86.5% ± 7.94, respectively.

Data analysis and interpretation: Principal component analysis (PCA) was performed using the IBM SPSS 15.0 program (Chicago, USA). Prior to PCA analysis, the concentrations of individual aliphatic hydrocarbons and PAHs were normalized to their total concentrations in order to minimize the differences between samples [13]. Values below the detection limit were replaced with half of the detection limit for the statistical calculations. Bartlett's sphericity and the Kaiser-Mayer-Olkin (KMO) test were performed to verify the sampling data adequacy for each variable in the PCA model, with a minimum acceptable KMO value of 0.50. Communality was also checked with an acceptable value of > 0.50 for each variable. The data set was then normalized with Kaiser normalization, followed by the application of Varimax rotation, to give a PCA projection. The result of principal component factors was illustrated by biplots using XLstat.

RESULTS AND DISCUSSION

Aliphatic hydrocarbons: In present study, concentrations of total n-alkane (TNA; nC_{15}–nC_{37}) in the surface sediments ranged between 0.67 and 9.88 µg/g (Fig. 2), while the concentrations of total aliphatic hydrocarbons (TAH; sum of nC_{15}–nC_{37} n-alkanes, pristane, phytane and UCM) ranged from 2.74 to 25.2 µg/g (Table-1). The highest levels of TNA and TAH were observed near the Kuala Lawas area, whereas the lowest TNA and TAH concentrations were measured at station B6 (near Sipitang coast) and station B4 (near Padas estuary), respectively. UCM is an unresolved alkane envelope, that occurred between nC_{17} and nC_{35} n-alkanes in GC chromatogram of the studied samples and the concentrations ranged between 2.04 and 14.9 µg/g.

Polycyclic aromatic hydrocarbons: Total concentrations of 16 priority PAHs listed by the USEPA ranged from 4.72 to 102 ng/g, whilst their alkyl-PAHs ranged from 32.8 to 563 ng/g (Table-1, Fig. 3). Total concentrations of 19 parent PAHs (PAH$_{16}$, Bep, DBT, Pery) and their alkyl-PAHs ranged between 8.45-147 ng/g and 32.8-640 ng/g, respectively. Similar to TNA, highest concentration of both parent and alkyl-PAHs was observed at station B8 and the lowest levels were measured at station B6. Among the identified PAH compounds, low molecular weight PAHs of 2-3 rings (*i.e.* Nap, Acp, Ace, Flo, Phe, Ant, DBT and their alkyl-substituted) were the most predominated PAHs group in the studied samples, accounted a mean of 67.6%; 4-ring PAHs (*i.e.* Fla, Py, BaA, Chr and their alkyl substituted) formed the second major group with a mean of 18.3%, while PAHs prevalence in 5-6 rings (*i.e.* BbF, BkF, Bep, Bap, Pery, Ind, BghiP and DBA) accounted for a mean of 14.3% of the total PAHs.
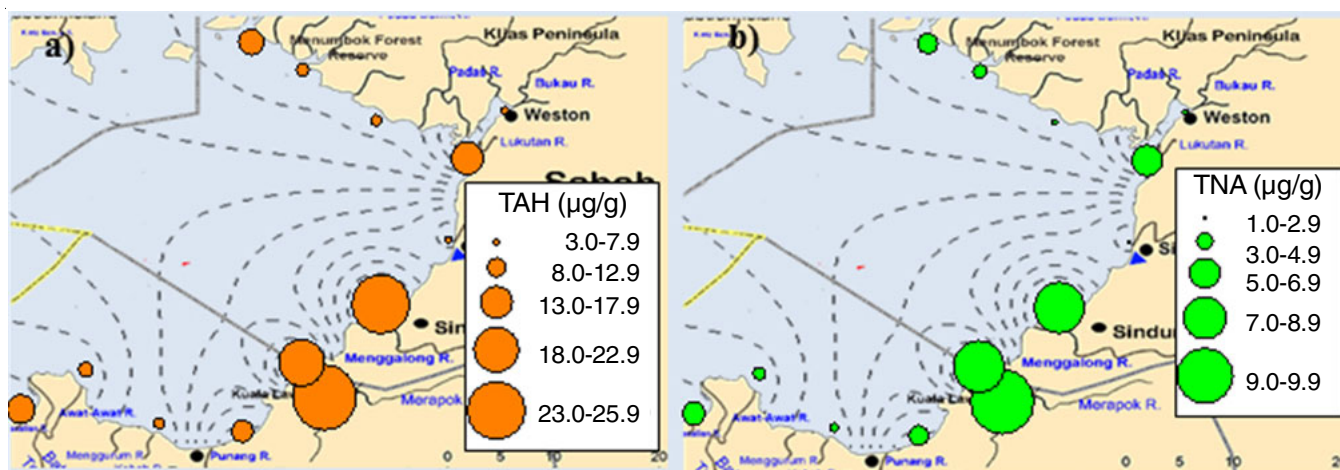

Fig. 2. Distribution contours of (a) total aliphatic hydrocarbons (TAH) and (b) total n-alkanes (TNA) (µg/g dw)

TABLE-1
MEAN CONCENTRATION OF ALIPHATIC HYDROCARBONS AND PAHs AND THEIR SELECTED DIEAGNOSTIC RATIOS

Parameter	Mean (range)	Parameter	Mean (range)	Parameter	Mean (range)
TNA (µg/g)	3.75 (0.67-9.88)	$OEPI_{17-21}$	1.06 (0.79-1.63)	Fla/(Fla + Py)	0.41 (0.30-0.50)
TAH (µg/g)	10.4 (2.74-25.2)	$OEPI_{21-25}$	1.29 (1.02-1.72)	BaA/(BaA + Chr)	0.24 (0.16-0.46)
UCM (µg/g)	6.49 (2.04-14.9)	$OEPI_{27-31}$	2.90 (1.60-5.90)	Ind/(Ind + BghiP)	0.24 (n.a.-0.62)
Pris/Phy	3.19 (1.97-4.08)	Wax alk terr (%)	26.1 (15.7-38.6)	1,7/(1,7 + 2,6)-DMP	0.54 (0.45-0.59)
CPI_{15-37}	2.14 (1.51-2.86)	ΣPAH_{16} (ng/g)	40.0 (4.72-110)	$C_0/(C_0 + C_1)$ P/A	0.32 (0.19-0.45)
$HCPI_{25-37}$	2.81 (1.88-4.17)	$\Sigma AlkPAH_{16}$ (ng/g)	187 (32.8-563)	THC (µg/g)	10.6 (2.79-26.0)

n.a. = not available; CPI_{13-37} = 0.5[(odd ΣnC_{13}-nC_{37}/even ΣnC_{14}-nC_{38}) + (odd ΣnC_{13}-nC_{37}/even ΣnC_{12}-nC_{36})]; $HCPI_{25-37}$ = 0.5[(odd ΣnC_{25}-nC_{37}/even ΣnC_{26}-C_{38}) + (odd ΣnC_{25}-nC_{37}/even ΣnC_{24}-nC_{36})]; $OEPI_{17-21}$ = (nC_{17} + (6*nC_{19}) + nC_{21})/((4*nC_{18}) + (4*nC_{20})); $OEPI_{21-25}$= (nC_{21} + (6*nC_{23}) + nC_{25})/((4*nC_{22}) + (4*nC_{24})); $OEPI_{27-31}$= (nC_{27} + (6*nC_{29}) + $nC31$)/((4*nC_{28}) + (4*nC_{30})); Wax Alk Terr (%) = percentage of terrestrial wax *n*-alkanes (sum of *wax *n*-alkane nC_{27}, nC_{29}, nC_{31} and nC_{33} over total *n*-alkanes, where wax *n*-alkane C_n = C_n - 0.5[C_{n-1} + C_{n+1}] and negative value was taken as zero; ΣPAH_{16} = sum of Nap, Ace, Acp, Flo, Phe, Ant, Fla, Py, BaA, Chr, BbF, BkF, BaP, Ind, DBA and BghiP; $\Sigma AlkPAH_{16}$ = sum of alkyl Nap, Flo, Phe/Ant, Fla/Py, BaA/Chr; THC = sum of TAH, PAHs and alky-PAHs.
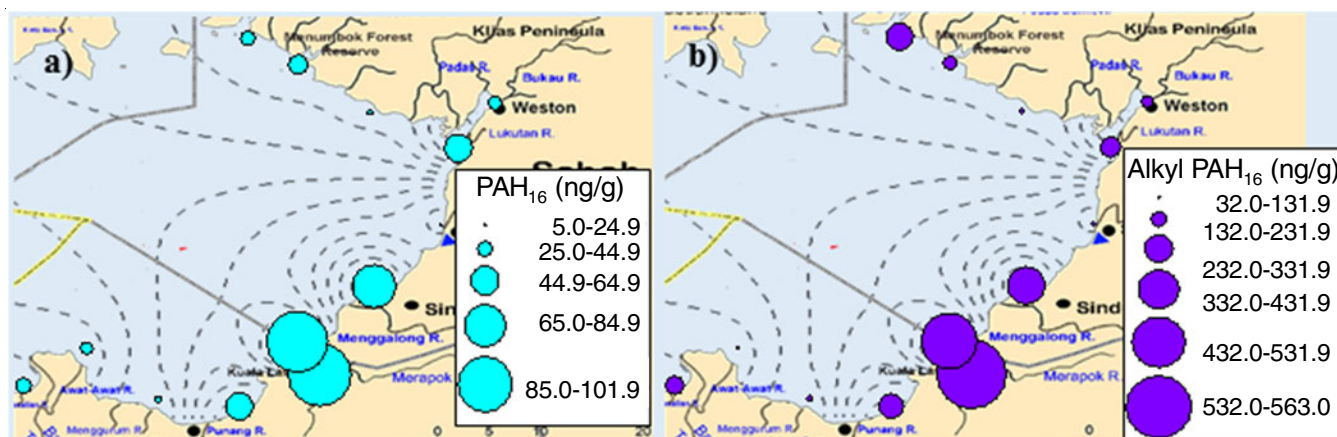

Fig. 3. Distribution contours of (a) 16 priority PAHs listed by USEPA (ΣPAH_{16} and; (b) Alkyl PAH_{16} ($\Sigma AlkPAH_{16}$) (ng/g dw)

Sources of sedimentary inputs as indicated by aliphatic hydrocarbons: All stations exhibited *n*-alkanes distributions with nC_{31} or nC_{29} as maxima (C_{max}). Such distributions are commonly associated with wax inputs from higher plant lipids [14,15], or airborne plant wax particles or smoke from biomass combustion [13,16]. Some stations (B4, B6-B9 and B13) were also observed with a bimodal distribution C_{max} at 31 in higher molecular homologues and also at nC_{16}, nC_{17} or nC_{18} in lower molecular homologues. C_{max} of nC_{16}, nC_{17} or nC_{18} are likely to be attributed to algae, bacteria or diatoms depending on the species [17] or petrogenic residues [18]. In general, long-chain homologues (nC_{25}-nC_{35}) showed an overall prevalence than the short-chain range of nC_{15}-nC_{20}, suggesting a predominance of high plant inputs.

The coastal area of Brunei Bay is enriched in vegetation such as mangrove forest, mudflat and brackish riverine. Commonly observed mangrove plant species include *Rhizopora apiculate*, *Rhizophora mucronata, Nypa fruticans*, *Avicennia* sp, *Nypa fruticans* and others. These plants were characterized by *n*-alkane maximized at C_{31} for *Hibiscus tiliaceus,* C_{25} for *Nypa fruticans,* C_{29} or C_{31} for *Rhizopora apiculate* and *Rhizophora mucronata* [15,19,20]. Apart from the litter fall of the mangrove plants, soil washout from inland forests (such as marshy grassland, peat swamp, freshwater swamp forest) could also contribute to the sedimentary organic matter *via* riverine transport.

The UCM consists of mixed cyclic and branched hydrocarbons, which are associated with weathered oils [16] or microbial degradation (algal detritus) at lower *n*-alkane homologs [21]. The concentrations of UCM detected in the samples were typically low (< 10 µg/g) except for Kuala Menggalong (B7) and Kuala Lawas (B8). Despite the UCM concentrations > 10 µg/g in these two stations, the ratio of U:R and UCM:TNA measured were < 4 and < 10, respectively, suggesting an insignificant contamination by petroleum [22,23].

Pristane (Pris) and phytane (Phy) are isoprenoid hydrocarbons used to determine hydrocarbon source rocks and also act as indicators for terrestrial and marine organic origins [24, 25]. Pris/Phy ratio < 0.8 indicates oil source rocks or depositional environment condition (anoxic condition) [26], 0.8-3.0 could also indicate crude oil inputs and > 3 indicates terrigenous inputs [25]. Lijmbach [27] also used the Pris/Phy ratio to ascribe aquatic environments from fresh and brackish water (< 2), fluviomarine and/or coastal swamps (2–4), or peat swamp (up to 10). In this study, the Pris/Phy ratios ranged from 1.97 to 4.08 (mean = 3.19) (Fig. 4a), suggesting that most of the samples were derived from fluviomarine and a coastal swamp depositional environment, which is quite related to the study environment.

Carbon preference index (CPI) is used as a source indicator to examine the contribution of biogenic and anthropogenic inputs from different origins [28,29], while an odd-to-
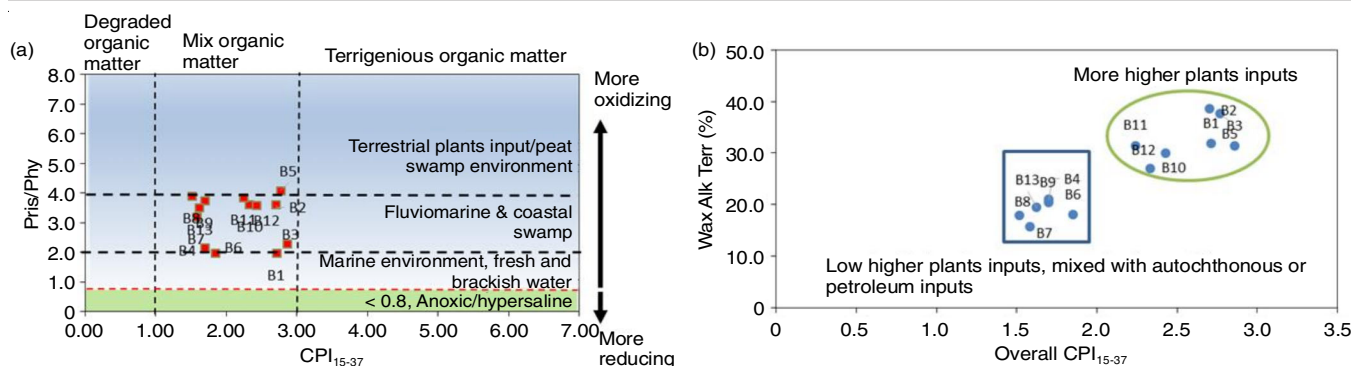
Fig. 4. Cross plot of (a) CPI_{15-37} against terrestrial plant wax n-alkanes (%Alk Terr) and (b) CPI_{15-37} against Pris/Phy ratio. In Fig. 4b the stations from the southern part and the northern part of the bay were grouped in a green circle, whereas the stations from the eastern and south-eastern part were grouped under the blue rectangle

even predominance index (OEPI) is used to evaluate the preference pattern of n-alkanes coupled with CPI [25,30]. Here, the CPI ratios for nC_{15}-nC_{37} (CPI_{15-37}) and nC_{25}-nC_{37} ($HCPI_{25-37}$) were 1.51–2.86 (mean = 2.15) and 1.88-4.17 (mean = 2.82), respectively. The OEPI for nC_{17}-nC_{21}, nC_{25}-nC_{29} and nC_{27}-nC_{31} for most stations were found to be more than 1, suggesting lower n-alkane inputs from marine biogenic bacterial, while upper n-alkanes were ascribed biogenic higher plant sources. Only OEPI (nC_{17}-nC_{21}) and CPI_{15-37} at stations B4, B7, B8 and B9 were < 1 and < 2, respectively, suggesting lower n-alkanes at these stations were ascribed to be the contribution of petroleum sources. Residual plant wax n-alkanes (Alk Terr%) calculated from wax C_n equation [31], are used to infer the delivery of land plant input to aquatic environment and also to differentiate the terrigenous organic matter from aquatic organic matter [25,32]. Based on a low range of wax Alk Terr (15.7–38.6% of TNA) obtained in this study, together with OEPI and CPI_{15-37} ratios in the range of 1.0–3.0, the stations in Brunei Bay which have coastal area can be grouped into the northern part (Menumbok, Weston, Padas Bay) and southern part (Trusan-Sundar area) with a predominance of higher plant inputs; while areas in the east and southeastern part (Sipitang to Kuala Lawas estuary) reflected a lower contribution of higher plants, possibly mixed with bacterial, degraded organic matter and also petrogenic inputs in surface sediments (Fig. 4b).

Sources of sedimentary inputs as indicated by PAHs: The alkyl-substituted homologues of naphthalenes (C_0-C_4 Nap), phenanthrenes/anthracenes (C_0-C_4 P/A), dibenzothiophenes (C_0-C_3 DBT), fluoranthenes/pyrenes (C_0-C_3 F/P) and benzo[a]anthracenes/chrysenes (C_0-C_2 B/C) were also measured in this study. The alkyl-PAHs maxima at C_1 or higher alkyl indicates coal deposits or unburned petroleum products, whereas the loss of the alkyl group during high temperature organic material combustion will generate a PAH profile that favours the unsubstituted or parent compounds [33,34]. Herein, alkyl substituted homologues contributed an average of 72.0% of the total identified PAHs. Phenanthrene and its alkylated homologues were the most abundant in the study area, followed by the naphthalene series and the fluoranthene series. Most of the alkyl substituted groups exhibited a maxima at C_1 or C_2 ($C_3 > C_2 > C_1 > C_4 > C_0$), creating a "bell" shaped like profile, with a decreasing degree of alkylation from C_1 to C_3, which is

in agreement with the characteristic of petroleum or PAHs that underwent weathering or degradation [33-35].

Several PAH diagnostic ratios were plotted in cross plot to provide the confident origin of the input [13,34,36] (Fig. 5). With an exception of station B12, most surface samples in the study area exhibited Fla/(Fla + Py) ratio < 0.5, BaA/(BaA + Chr) ratio < 0.35 and Ind/(Ind + BghiP) ratio < 0.50, fingerprinting a mixed petrogenic and combustion sources. The ratio
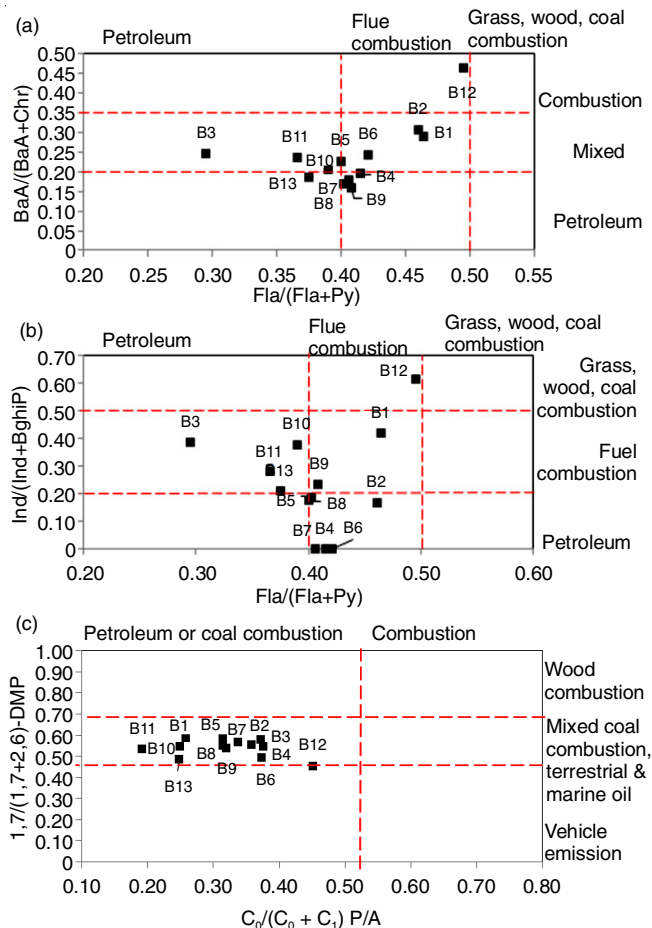

Fig. 5. PAH ratio cross plot for (a) BaA/(BaA + Py) against Fla/(Fla + Py); (b) Ind/(Ind + BghiP) against Fla/(Fla + Py) and; (c) 1,7/(1,7 + 2,6)-DMP against $C_0/(C_0 + C_1)$ P/A in the surface sediments of Brunei Bay. The dashed lines represent the thresholds for different sources

of BaA/(BaA + Chr) > 0.35, Fla/(Fla + Py) > 0.40, Ind/(Ind + BghiP) > 0.50 at station B12, indicated combustion derived PAHs predominance. The ratio of dimethylphenanthrene 1,7/(1,7+2,6)-DMP and alkyl-parent phenanthrene/anthracene C_0/(C_0 + C_1) P/A < 0.50 further pinpointed to a mixture of combustion and petroleum in the studied samples.

Distribution of hydrocarbons in coastal sediments of Brunei Bay: Overall, high concentrations of total hydrocarbons (THC) (*i.e.* the sum of TAH, PAHs and alkylated homologues) were found in the surface sediments located near the estuary of the Kuala Lawas area. Intermediate concentrations were observed in the northern part (Menumbok-Weston-Padas Bay) and also in the southern part (Trusan-Sundar coastal) of the Brunei Bay. Surface sediments near the Sipitang River estuary, eastern part of the Bay, exhibited the lowest THC concentration, which could be due to the dilution by fluvial and tidal effect near coastal water. PCA also clustered the hydrocarbons in surface sediments according to their relationship and geographical locations (Fig. 6). The first two components (PC1 and PC2) explained 31.29 and 29.90% of the total variance, respectively. It is interesting to see that the biogenic higher plants *n*-alkanes and 5-6 rings PAHs were clustered in the positive loading of PC1, while *n*-alkanes of marine origin and 2-4 rings PAHs were clustered in the negative loading of PC1.

Biogenic *n*-alkanes of terrestrial higher plants were highly loaded in the stations from the northern (B2 and B5) and southwest part (B11 and B12), where fluvial transport (from Padas river, Trusan river and Limbang river) could play an important role in transporting mangrove organic matter (*e.g.* leaf, tree branches, debris and soil organic matter erosion) into the coastal sediments. These stations were also loaded with 5-6 ring PAHs, suggesting possible indirect atmospheric deposition, *i.e.*, urban deposition into watershed transported to the coastal sediments *via* fluvial transport. Meanwhile, stations (B7-B10) near Kuala Lawas area were loaded with 4-ring PAHs of combustion origin, indicating that the hydrocarbon inputs at these stations were likely to be contributed from human activities, particularly vehicular exhausts from shipping vessels near terminal and active maritime activities (*i.e.* fishing and boating).
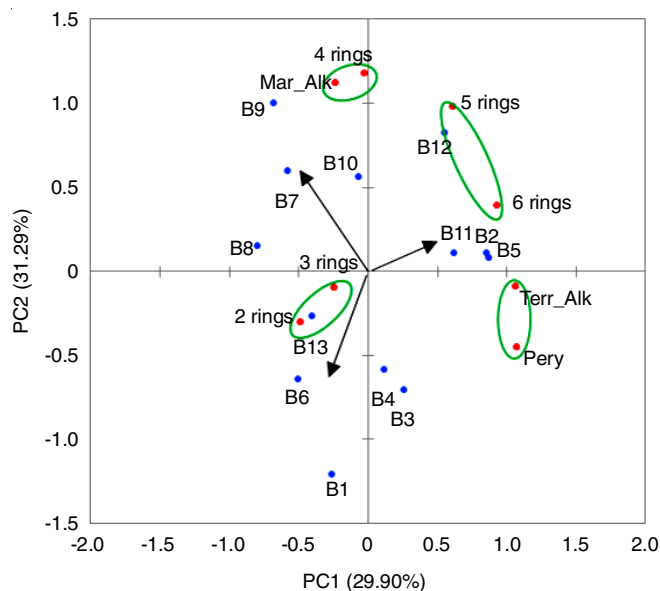

Fig. 6. Biplot of the PCA result for hydrocarbons in surface sediments from Brunei Bay. The aliphatic hydrocarbons and PAHs (as total concentration-normalized) were grouped into the following: Terr_Alk = nC_{27}, nC_{29}, nC_{31}; Mar_Alk = nC_{15}, nC_{17}, nC_{19}; 2-rings = C_0–C_4 Nap; 3-rings = Ace, Acp, C_0–C_3 Flo, C_0–C_3 DBT, C_0–C_4 P/A; 4-rings = C_0–C_3 F/P, C_0–C_2 B/C; 5-rings = BbF, BkF, BaP, BeP, DBA; 6-rings = Ind, BghiP (Terr alk = terrestrial *n*-alkanes, Mar_Alk = marine *n*-alkanes)

Concentration comparison to previous studies: A comparison between TNA and PAH concentrations in the current study and several previous works worldwide is summarized in Table-2. Here, the TNA result in this study was comparable to those reported in the Southern part of Terengganu [19] and Batang Sadong estuary [37] in Malaysia; Jiaozhou Bay (China) [38], Cienfuegos Bay (Cuba) [39], Todos os Santos (Brazil) [40], Jakarta Bay (Indonesia) [41] and Northern Cyprus (Eastern Mediterranean) [42]. The TNA result also shows lower than those values reported in Kuching Bay in Malaysia [43]; Ushuaia Bay (Argentina) [15] and El-Mex Bay (Alexandria, Egypt) [44]. On the other hand, the PAH concentrations in this study were found comparable to those reported in SCS off Terengganu, Malaysia [45]; Weihai coast (Yellow Sea) [46], Khao Lak

TABLE-2
CONCENTRATIONS OF TNA AND PAHs IN SURFACE SEDIMENTS SAMPLED FROM DIFFERENT LOCATIONS

Area	TNA (µg/g)	Ref.	Area	ΣPAH_{16} (ng/g)	Ref.
Brunei Bay, Malaysia	0.67-9.88	This study	Brunei Bay, Malaysia	4.72-102	This study
Southern part of Terengganu, Malaysia	0.15-6.91	[19]	SCS off Terengganu coast, Malaysia	16.1-334	[45]
Batang Sadong estuary, Sarawak	1.47-20.8	[37]	Weihai coast, Yellow Sea	2.69-167	[46]
Jiaozhou Bay, China	0.50-8.12	[38]	Khao Lak coastal, Thailand	12.6-272	[47]
Cienfuegos Bay, Cuba	2.25-7.25	[39]	Laizhou Bay, China	23.3-293	[48]
Todos os Santos, Brazil	0.33-11.4	[40]	Malacca Strait, Malaysia	25.0-2183	[49]
Jakarta Bay, Indonesia	0.48-1.94	[41]	Klang Strait, Malaysia	100-3447	[50]
Northern Cyprus, Eastern Mediterranean	1.07-6.34	[42]	Johore Strait, Malaysia	651-1441	[51]
Kuching Bay of Sarawak, Malaysia	35.6-2466	[43]	Jiaozhou Bay, Malaysia	16.0-2164	[38]
Ushuaia Bay, Argentina	5.5-1185	[14]	Todos os Santos, Brazil	39.4-882	[40]
El-Mex Bay, Alexandria	50-300	[44]	Abu Qir Bay and El-Max Bay, Egypt	3.51-2010	[52]
			Southeast China Northern Bohai and Yellow Sea	52.3-1871	[53]
			Northern Gulf of Mexico	200-856	[54]

coastal (Thailand) [47] and Laizhou Bay (China) [48]; but lower than those reported in Malacca Strait [49], Klang Strait [50] and Johore Strait [51] in Malaysia; Jiaozhou Bay (China) [38], Todos os Santos (Brazil) [40], Abu Qir Bay and El-Max Bay (Egypt) [52], Northern Bohai and Yellow Sea (Southeast China) [53] and Northern Gulf of Mexico [54].

Baumard *et al*. [55] proposed a classification for PAH contamination in sediments, in which ΣPAH concentrations of 0-100, 100-1000, 1000-5000 and > 5000 ng/g are classified as being at low, moderate, high and very high levels, respectively. This classification system is limited to parental PAH and is not taking into account the alkyl PAH homologues (petrogenic inputs). Nonetheless, using this classification, the PAH contaminations (ΣPAH_{16} = 4.72-102 ng/g) in the study area were considered to be at low to moderate level. Petroleum related contamination in the study area could be related to active crude oil trans-shipments and maritime traffic in Labuan, Menumbok, Lawas and Brunei Darussalam area, as well as inputs from tourism, fishing and boating activities; effluents from industrial processing, agriculture, aquacultures, quarry, chemical industry, paper mill construction and palm oil plantation.

Conclusion

This paper presents the spatial distribution of aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) in surficial sediments collected from the coastal areas of Brunei Bay, Malaysia. Results showed that the concentrations of total hydrocarbons were found to be the highest near the estuary of Kuala Lawas, while low concentrations were measured at areas near to the Sipitang river estuary. The biogenic *n*-alkanes of terrestrial higher plants exported from fluviomarine or mangrove swamp environments were characterized by a unimodal distribution and C_{max} at 31 or 29 and the isoprenoid ratios. The PAH contamination levels in the studied area were considered to be at low to moderate level, with PAHs diagnostic ratios indicating a mixed input of petrogenic and petroleum combustion residues. PCA clustered the PAHs and *n*-alkanes according to their likely contribution origins and abundance of samples. The present study provides an assessment of aliphatic hydrocarbons and PAHs distribution in the coastal sediment of Brunei Bay.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. O.E. Kawka and B.R.T. Simoneit, *Appl. Geochem.*, **5**, 17 (1990); https://doi.org/10.1016/0883-2927(90)90032-Z

2. B.R.T. Simoneit, Biomarker PAHs in the Environment. A.H. Neilson, Berlin: Springer-Verlag, p. 175 (1998).

3. D. He, B.R.T. Simoneit, J.B. Cloutier and R. Jaffé, *Org. Geochem.*, **125**, 196 (2018); https://doi.org/10.1016/j.orggeochem.2018.09.005

4. A. Nikolaou, M. Kostopoulou, G. Lofrano and S. Meric, *Glob. NEST J.*, **11**, 391 (2009).

5. Department of Statistics Malaysia (DOSM) Sabah, 2014 Sabah Statistics year book, Kota Kinabalu, Malaysia (2015); http://www.malaysiaeconomy.net/download/18072016_1.pdf (Accessed on 25 May 2019).

6. Department of Statistics Malaysia (DOSM) Sarawak, 2014 Sarawak Statistics year book. Kuching, Malaysia (2015); http://www.malaysiaeconomy.net/download/18072016_2.pdf (Accessed on 25 May 2019).

7. E. Saleh, S. Saad, M.A. Hoque, A.M.H. Ladoni and M.H. Abdullah, eds.: S. Mustafa and E. Saleh, Physical and Chemical Features, Kota Kinabalu: Universiti Malaysia Sabah, p. 25 (2007).

8. S.Y. Pang, H.S. Tan, S. Suratman and N.M. Tahir, ed.: S. Suratman, Study of Oil and Grease and Total Petroleum Hydrocarbons in Brunei Bay, Borneo Island, Malaysia, Kuala Terengganu: Universiti Malaysia Terengganu, p. 67 (2016).

9. M. Mohamed, L.L. Chin and T.S. Lim, *Pertanika*, **13**, 123 (1990).

10. N.A. Ghazali, M. Shazili and J. Bidai, ed.: S. Suratman, The Geochemistry of Rare Earth Element in Brunei Borneo, Kuala Terengganu: Universiti Malaysia Terengganu, p. 133 (2016).

11. S. Suratman, Y.Y. Hee and N. Mohd Tahir, *Int. J. Chem. Environ. Biol. Sci.*, **3**, 471 (2015).

12. S.Y. Pang, J.H. Tay, S. Suratman, B.R.T. Simoneit and N. Mohd Tahir, *Mar. Pollut. Bull.*, **156**, 111269 (2020); https://doi.org/10.1016/j.marpolbul.2020.111269

13. M.B. Yunker, R.W. Macdonald, P.S. Ross, S.C. Johannessen and N. Dangerfield, *Org. Geochem.*, **89-90**, 80 (2015); https://doi.org/10.1016/j.orggeochem.2015.10.002

14. M.G. Commendatore, M.L. Nievas, O. Amin and J. Esteves, *Mar. Environ. Res.*, **74**, 20 (2012); https://doi.org/10.1016/j.marenvres.2011.11.010

15. R. Wöstmann and G. Liebezeit, *Mires and Peat*, **10**, 1 (2012).

16. B.R.T. Simoneit and M.A. Mazurek, *Atmos. Environ.*, **16**, 2139 (1982); https://doi.org/10.1016/0004-6981(82)90284-0

17. J. Grimalt and J. Albaigés, *Mar. Geol.*, **95**, 207 (1990); https://doi.org/10.1016/0025-3227(90)90117-3

18. X. Gao, S. Chen, X. Xie, A. Long and F. Ma, *Environ. Pollut.*, **148**, 40 (2007); https://doi.org/10.1016/j.envpol.2006.11.001

19. N.M. Tahir, S.Y. Pang and B.R.T. Simoneit, *Environ. Sci. Pollut. Res. Int.*, **22**, 7557 (2015); https://doi.org/10.1007/s11356-015-4184-5

20. H.S. Tan, M.R. Abas and N. Mohd Tahir, *Sains Malays.*, **45**, 365 (2016).

21. M.I. Venkatesan and I.R. Kaplan, *Geochim. Cosmochim. Acta*, **46**, 2135 (1982); https://doi.org/10.1016/0016-7037(82)90190-9

22. M.A. Mazurek and B.R.T. Simoneit, ed.: L.H. Keith, Characterization of Biogenic and Petroleum-Derived Organic Matter in Aerosols Over Remote, Rural and Urban Areas, ACS Symposium Ann Arbor Science/ Butterworth: Woburn, MA. p. 353 (1984).

23. I. Tolosa, S. de Mora, M.R. Sheikholeslami, J.P. Villeneuve, J. Bartocci and C. Cattini, *Mar. Pollut. Bull.*, **48**, 44 (2004); https://doi.org/10.1016/S0025-326X(03)00255-8

24. B.P. Tissot and D.H. Welte, Petroleum Formation and Occurrence. A New Approach to Oil and Gas Exploration, Springer-Verlag: Berlin (1978).

25. K.E. Peters, C.C. Walters and J.M. Moldowan, The Biomarker Guide, Cambridge University Press: United Kingdom (2005).

26. B.M. Didyk, B.R.T. Simoneit, S.C. Brassell and G. Eglinton, *Nature*, **272**, 216 (1978); https://doi.org/10.1038/272216a0

27. G.W.M. Lijmbach, On the Origin of Petroleum, Proceedings Ninth World Petroleum Congress, Applied Sciences Publisher: London, vol. 2, p. 357 (1975).

28. E.E. Bray and E.D. Evans, *Geochim. Cosmochim. Acta*, **22**, 2 (1961); https://doi.org/10.1016/0016-7037(61)90069-2

29. R.C. Clark Jr. and M. Blumer, *Limnol. Oceanogr.*, **12**, 79 (1967); https://doi.org/10.4319/lo.1967.12.1.0079

30. E.S. Scalan and J.E. Smith, *Geochim. Cosmochim. Acta*, **34**, 611 (1970); https://doi.org/10.1016/0016-7037(70)90019-0

31. B.R.T. Simoneit, J.N. Cardoso and N. Robinson, *Chemosphere*, **21**, 1285 (1990); https://doi.org/10.1016/0045-6535(90)90145-J

32. J. He, S. Zhang, X. Zhang, Y. Qian, H. He and H. Wu, *J. Chem.*, **2016**, 4741939 (2016); https://doi.org/10.1155/2016/4741939

33. Z. Wang, M. Fingas, Y. Shu, L. Sigouin, M. Landriault, P. Lambert, R. Turpin, P. Campagna and J. Mullin, *Environ. Sci. Technol.*, **33**, 3100 (1999); https://doi.org/10.1021/es990031y

34. M.B. Yunker, R.W. Macdonald, R. Vingarzan, R.H. Mitchell, D. Goyette and S. Sylvestre, *Org. Geochem.*, **33**, 489 (2002); https://doi.org/10.1016/S0146-6380(02)00002-5

35. G. Grimmer, J. Jacob, K.-W. Naujack and G. Dettbarn, *Anal. Chem.*, **55**, 892 (1983); https://doi.org/10.1021/ac00257a018

36. M.A. Sicre, J.C. Marty, A. Saliot, X. Aparicio, J. Grimalt and J. Albaiges, *Atmos. Environ.*, **21**, 2247 (1987); https://doi.org/10.1016/0004-6981(87)90356-8

37. M.K. Said, Z.A. Assim, R. Carpenter and M. Mohamed, In proceeding of the International Conference on Natural Resources and Environment Management Kuching, Sarawak: UNIMAS, p. 310 (2005).

38. X. Wang, S. Sun, H.-Q. Ma and Y. Liu, *Mar. Pollut. Bull.*, **52**, 129 (2006); https://doi.org/10.1016/j.marpolbul.2005.08.010

39. I. Tolosa, M. Mesa-Albernas and C.M. Alonso–Hernandez, *Mar. Pollut. Bull.*, **58**, 1624 (2009); https://doi.org/10.1016/j.marpolbul.2009.07.006

40. A. Wagener, C. Hamacher, C. Farias, J.M. Godoy and A. Scofield, *Mar. Chem.*, **121**, 67 (2010); https://doi.org/10.1016/j.marchem.2010.03.005

41. M. Yazis, L. Asia, A. Piram, P. Doumenq and A.D. Syakti, *IOP Conf. Ser.: Mater. Sci. Eng.* **107**, 012007 (2016); https://doi.org/10.1088/1757-899X/107/1/012007

42. E. Darilmaz, *Environ. Earth Sci.*, **76**, 220 (2017); https://doi.org/10.1007/s12665-017-6537-5

43. H. Yusoff, Z.A. Assim and S. Mohammaed, *Malays. J. Anal. Sci.*, **16**, 1 (2012).

44. L.A. Mohamed, G.M. El Zokm, K.Z. El Deeb and M.A. Okbah, *Egypt. J. Aquat. Res.*, **42**, 375 (2016); https://doi.org/10.1016/j.ejar.2016.10.001

45. M.M. Mohd Sanip, M.F. Fadzil, S. Suratman, S. Rozmi and N. Mohd Tahir, *Malays. J. Anal. Sci.*, **23**, 1120 (2019).

46. D. Zhang, J. Liu, P. Yin, X. Lin, N. Liu and X. Meng, *Mar. Pollut. Bull.*, **109**, 643 (2016); https://doi.org/10.1016/j.marpolbul.2016.05.018

47. D. Tipmanee, W. Deelaman, S. Pongpiachan, K. Schwarzer and P. Sompongchaiyakul, *Nat. Hazards Earth Syst. Sci.*, **12**, 1441 (2012); https://doi.org/10.5194/nhess-12-1441-2012

48. A. Liu, Y. Lang, L. Xue and J. Liu, *Environ. Monit. Assess.*, **159**, 429 (2009); https://doi.org/10.1007/s10661-008-0640-8

49. M. Sakari, M.P. Zakaria, C.A.R. Mohamed, N.H. Lajis and K. Chandru, *Environ. Asia*, **3**, 131 (2010).

50. S.B. Tavakoly Sany, R. Hashim, A. Salleh, M. Rezayi, A. Mehdinia and O. Safari, *PLoS One*, **9**, e94907 (2014); https://doi.org/10.1371/journal.pone.0094907

51. M. Keshavarzifard, M.P. Zakaria and S. Keshavarzifard, *Polycycl. Aromat. Compd.*, **39**, 44 (2019); https://doi.org/10.1080/10406638.2016.1257997

52. A.O. Barakat, A. Mostafa, T.L. Wade, S.T. Sweet and N.B. El Sayed, *Mar. Pollut. Bull.*, **62**, 1969 (2011); https://doi.org/10.1016/j.marpolbul.2011.06.024

53. W. Jiao, T. Wang, J.S. Khim, W. Luo, W. Hu, J.E. Naile, J.P. Giesy and Y. Lu, *Environ. Geochem. Health*, **34**, 445 (2012); https://doi.org/10.1007/s10653-011-9445-8

54. Z. Wang, Z. Liu, K. Xu, L.M. Mayer, Z. Zhang, A.S. Kolker and W. Wu, *Geochem. Trans.*, **15**, 2 (2014); https://doi.org/10.1186/1467-4866-15-2

55. P. Baumard, H. Budzinski, Q. Michon, P. Garrigues, T. Burgeot and J. Bellocq, *Estuar. Coast. Shelf Sci.*, **47**, 77 (1998); https://doi.org/10.1006/ecss.1998.0337