

Use of molecular markers and compound-specific isotopic signatures to trace sources of black carbon in surface sediments of Peninsular Malaysia: Impacts of anthropogenic activities

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ABSTRACT

Black carbon (BC) acts as a reservoir of carbon in sediment due to its high persistency. Southeast Asia (SEA) is a main source region for BC emissions across the globe due to extensive biomass burning and escalating fossil fuel consumption. However, our understanding of the sources and sinks of BC in SEA is limited. Here, we have analysed BC structure using benzene polycarboxylic acid (BPCA) method in combination of stable carbon isotope ($\delta^{13}\text{C}$) signatures for B5CA and B6CA using HPLC-IRMS in sediment samples from riverine, coastal and shelf areas in Peninsular Malaysia. BPCA molecular markers indicated higher degree of aromatic condensation and lighter isotopic composition in relatively pristine environment of the East coast compared to developed environment of the West and South coast. n-Alkane biomarkers clearly demonstrated higher anthropogenic impacts on the sediments of the West and South coast compared to the East coast. Biomass burning with the predominance of C₃ plants and the large share of natural gas in the energy mix in Malaysia are possibly the main reasons for the isotopically light composition of sedimentary BC (−45.4 to −26.4‰). Atmospheric soot and petrogenic BC are the possible main sources of BC in the East coast sediments, while char residues of low temperature biomass burning likely contribute more to sedimentary BC in the West and South coast. The n-alkane indices implied that the sediments of the Kelantan adjacent shelf area receive great proportion of terrestrial organic matter and the associated BC.

1. Introduction

Black carbon (BC) is a highly refractory aromatic form of organic compound generated through incomplete combustion of fossil fuels and biomass (Goldberg, 1985). The chemical structure of BC is recalcitrant to biodegradation making sedimentary BC a stable reservoir of carbon in the aquatic environments (Elmqvist et al., 2008). BC plays important roles in various crucial processes on Earth from global carbon cycle to

climate change (Bond et al., 2013).

BC is not a singular entity but a continuum mixture of carbon-rich products with solid residues (char) from combustion of cellulose-rich plant tissues at one end-point and combustion condensates of released gas phase particles (soot) mainly from combustion of fossil fuels and biomass burning at flaming stage at the other end-point, the former is the more oxidized residues of low temperature (300–600 °C) combustion of biomass, while the latter is formed by high temperature

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(>600 °C) recondensation of combustion particles (Masiello, 2004). The benzene polycarboxylic acid (BPCA) method oxidizes the aromatic clusters to BPCAs with 3–6 carboxylic functional groups. The oxidation products of more condensed aromatic clusters are mainly B5CA and B6CA, whereas less condensed aromatic clusters produce higher percentages of B3CA and B4CA (Hindersmann and Achten, 2017). The production temperature is a decisive factor in the chemistry of BC. Even though the temperature for fossil fuel combustion is generally higher than biomass burning, the condensed aromatic domains of char increase at higher temperatures and char wood may include the entire range of BC continuum depending on the burning temperature (Schneider et al., 2010). Therefore, differentiation of BC sources based on its degree of aromatic condensation is a serious challenge (Hammes et al., 2007; Hindersmann and Achten, 2017; Masiello, 2004; Schneider et al., 2010). Moreover, other factors such as the source material and oxygen availability during pyrolysis and microbial and photochemical degradation of BC in the environment can shift the patterns of BPCAs (Coppola et al., 2014; Hammes et al., 2007; Stubbins et al., 2012). BPCA-specific stable carbon isotope ($\delta^{13}\text{C}$) signatures of BC can provide complementary data for tracing the BC sources in the environment (Wagner et al., 2017).

Southeast Asia (SEA) is a major emission source of BC worldwide due to massive forest, peatland and agricultural fires (both natural and man-made) and escalating fossil fuel consumption causing occasional haze episodes in the region (Latif et al., 2018; Zakaria et al., 2018). SEA faces a 6% annual increase in electricity demand, one of the fastest across the globe. Despite the great potential for solid biomass fuel, its use is mainly limited to traditional cooking in SEA (Hosseini et al., 2013). Malaysia has experienced rapid developments during recent decades. The energy demand has recorded a rise of 80% since 2000 which resulted in doubling the use of fossil fuels mainly consumed by cement, steel and iron industries (International Energy Agency, 2019). Natural gas is the major fossil fuel used in Malaysia, while coal has been replacing natural gas to supply the increasing number of coal-fired power stations since 2010. Oil holds the smallest share of energy supply in Malaysia reducing to as low as 0.6% in 2017. BC and other pyrolysis released hydrocarbons are transported to the aquatic environment either vertically by aerosol deposition or laterally via runoff (Flores-Cervantes et al., 2009; Vaezzadeh et al., 2015).

BPCA method has been broadly used for BC analysis in dissolved organic matter (DOM) (e.g., Ziolkowski and Druffel, 2010) and the distribution of BPCAs in DOM showed a loss of condensability along river-to-sea. The sorption of more condensed BC to particulate organic carbon (POC) was suggested to be responsible for the loss of BC condensability in the oceanic DOM (Coppola et al., 2014; Ziolkowski and Druffel, 2010; Flores-Cervantes et al., 2009). Therefore, river-to-sea condensability of sedimentary BC is the missing link in the investigation of biogeochemical cycle of BC and carbon cycling in the aquatic environment and this study aims to patch this gap of data. Additionally, this study presents the first data on BPCA-specific $\delta^{13}\text{C}$ signatures of BC in riverine, coastal and shelf sediments. Isotopic composition of BC will help probe the sources of BC in the sediments. We hypothesized that biomass burning predominates the sources of sedimentary BC in the East coast of Peninsular Malaysia which is relatively pristine, whereas fossil fuel combustion contributes more to BC in the more developed West and South coast and the degree of aromatic condensation of BC in combination of BPCA-specific $\delta^{13}\text{C}$ signatures assist us to further investigate this hypothesis. Finally, molecular signatures of n-alkanes and polycyclic aromatic hydrocarbons (PAHs) were investigated to help us evaluate the intensity of anthropogenic impacts and sources of hydrocarbons in the aquatic environments of Peninsular Malaysia.

2. Materials and methods

2.1. Sampling stations

The sampling stations (Fig. 1) in this study covered the most

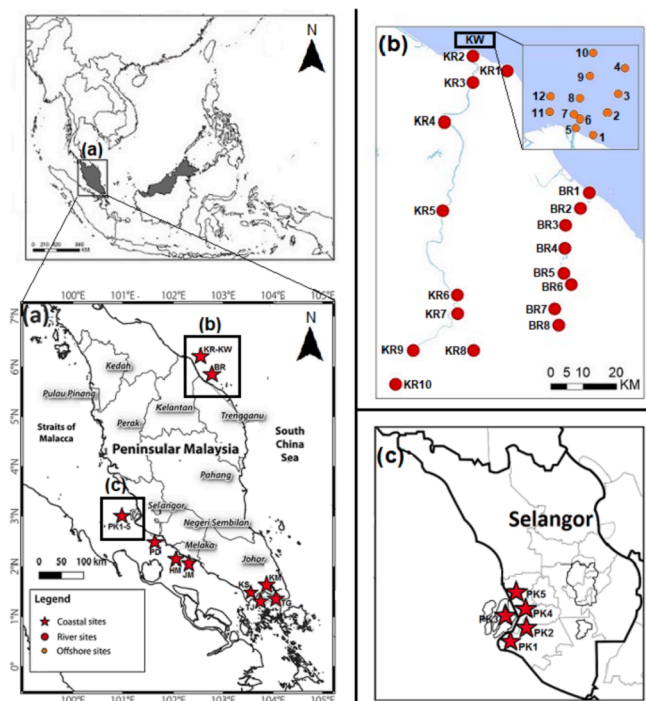


Fig. 1. Map of the study area location and sampling stations.

developed areas in the West and South coast of Peninsular Malaysia as well as relatively pristine environment of the East coast which has remained highly rural with an agricultural-based economy (Vaezzadeh et al., 2021). Kelantan and Besut Rivers (KR1–10, BR1–8) and Kelantan coast and adjacent shelf (KW1–12) were selected in the East coast of Peninsular Malaysia. The East coast faces the South China Sea which is the route for numerous vessels and oil tankers and Malay Basin, the largest oil and gas reservoir of the country, is located mainly at the Kelantan offshore (Bishop, 2002). The study of riverine, coastal and shelf sediments assists us to investigate transportation, biogeochemical cycles and fate of BC in the tropical aquatics. The Kelantan River is a tropical mountainous river, highly turbid due to the increasing sand mining activities and deforestation in the watershed and influenced by tropical monsoon (Ahmad et al., 2009; Yen and Hashim, 2013; Wang et al., 2020). The aforementioned factors favour export of disproportionate loads of particles to the coastal and marine shelf making this river an ideal candidate for the river-to-sea investigation of carbon biogeochemical cycles. The Kelantan River has a drainage basin of 11,900 km², ~95% of the basin is mountainous peaking at 2135 m and the length of the river is 248 km (Wang et al., 2017). The watershed experiences northeast monsoon in the winter (Oct-Jan) causing heavy rainfall and strong monsoon waves in the estuary and southerly or southwesterly winds in the other periods which bring about a less rainy season (Daryabor et al., 2016). The average annual rainfall at Kota Bharu, the capital city of Kelantan, was estimated at 2417 mm between 1950 and 2014. The Pergau dam, a hydroelectric power station located about 100 km west of Kota Bharu, can reduce water and sediment yields of the Kelantan River. The average annual water yield of the Kelantan River was estimated at 1.8×10^{10} m³ and the mean sediment load into the sea was estimated at 2.5×10^6 t (Milliman and Farnsworth, 2011). A barrier spit is grown at the estuary's seaward margin which continues with a sandy beach of up to 150 m (Satyanarayana et al., 2011; Wang et al., 2017). The sampling locations at the Kelantan adjacent shelf had a depth of 5–25 m and a gentle slope at the sea floor with the 10-fathom line, up to 15 km offshore (Radzir et al., 2016; Wang et al., 2020). The whole area is characterized by frequent tropical rainfall, elevated temperature and humidity. Surface sediments (0–3 cm) were collected using

a stainless steel grab sampler during 2016. The description of the sampling sites is presented in Table S1. Sediments were placed in pre-cleaned aluminum foils and transported inside ziplock bags and on ice to the laboratory. Sediments were freeze-dried and stored at $-18\text{ }^{\circ}\text{C}$ for further analysis.

2.2. Analysis of BPCAs

BPCA method as described by Wiedemeier et al. (2016) was used for the separation and quantification of BPCAs. The freeze-dried sediment samples (50 mg) were placed in 10 mL glass ampoules. After adding 2 mL of 65% nitric acid, the ampoules were sealed and put into 100 mL Teflon-lined stainless-steel reaction vessels. The reaction vessels were tightly closed and then heated in an oven at $180\text{ }^{\circ}\text{C}$ for 8 h. Approximately 100 μL water was added to the reaction vessels to maintain a steady vapor pressure inside and outside the ampoules and prevent explosion of the ampoules. The reaction vessels were cooled in room temperature and the solution in the ampoules was transferred into 4 mL vials and dried under a stream of high pressure nitrogen gas at $50\text{ }^{\circ}\text{C}$. The samples were redissolved in 1 mL ultrapure water, filtered with a syringe filter (13 mm \times 0.22 μm , PTFE, ANPEL Laboratory Technologies) and measured for BPCAs with a Shimadzu LC-20AT high performance liquid chromatography (HPLC) equipped with a Shimadzu SPD-M20A photodiode array detector (PAD). Tri- to hexasubstituted acid BPCAs including 1,2,3-benzenetricarboxylic acid and 1,2,4-benzenetricarboxylic acid (B3CAs), 1,2,4,5-benzenetetracarboxylic acid, 1,2,3,5-benzenetetracarboxylic acid, 1,2,3,4-benzenetetracarboxylic acid (B4CAs), 1,2,3,4,5-benzenepentacarboxylic acid (B5CA) and 1,2,3,4,5,6-benzenhexacarboxylic acid (B6CA) were measured. Quantification of BPCAs was carried out by using external calibration curves (linear regression $r^2 \geq 0.999$) of standard solutions of BPCAs except for 1,2,3,5-B4CA and 1,2,3,4-B4CA which were commercially unavailable and their quantifications were performed based on the calibration curve of their isomer (i.e., 1,2,4,5-benzenetetracarboxylic acid) as was done in previous studies (Dittmar, 2008; Wiedemeier et al., 2016). All BPCA standards were purchased from Sigma Aldrich. The concentration levels of the calibration curves were 3.2, 4.8, 6.4, 8, 16, 32, 48, 64 and 80 ng/ μL . We tested the accuracy of the BPCA method developed in our laboratory by a marine sediment reference material (NIST SRM 1941b) and the result was 9.88 ± 0.26 g BC/kg sediment (or 55.37 ± 1.46 g BPCA-C/kg total organic carbon (TOC), three replicates) which was similar to those reported by Ziolkowski et al. (2011) (10.7 g BC/kg sediment) and Wiedemeier et al. (2016) (~ 50 g BPCA-C/kg TOC), and a little higher than that of Hindersmann and Achten (2017) (~ 43 g BPCA-C/kg TOC). The coefficient of variation were $< 5\%$ for duplicate analysis. The average number of carboxylic acid functional groups generated during the oxidation of BC (Ave BPCA) had an uncertainty of ± 0.02 . A procedural blank was run with every batch of samples for quality control.

2.3. HPLC-PAD method

The HPLC-PAD method was similar to that of Wiedemeier et al. (2016). Briefly, HPLC grade acetonitrile (Sigma Aldrich) was used as mobile phase A. Mobile phase B was prepared by mixing 20 mL of 85% phosphoric acid (Sigma Aldrich) with 980 mL ultrapure water and filtering through a mixed cellulose ester filter (0.22 μm pore size, ANPEL Laboratory Technologies). BPCAs were separated on an Agilent InfinityLab Prooshell 120 SB-C18 (4.6 \times 100 mm, 2.7 μm) column under a mixing gradient of the two mobile phases, as described elsewhere (Wiedemeier et al., 2016). The injection volume of the samples and standards was 10 μL . The flow rate was set as 0.4 mL min^{-1} . The column temperature was maintained at $30\text{ }^{\circ}\text{C}$ and the scanning wavelength range was set at 190–400 nm. BPCAs were identified by their retention time and absorbance spectrum and were quantified by their absorption signal at 240 nm. Satisfying chromatographic separation of BPCAs was obtained for the samples (Fig. 2).

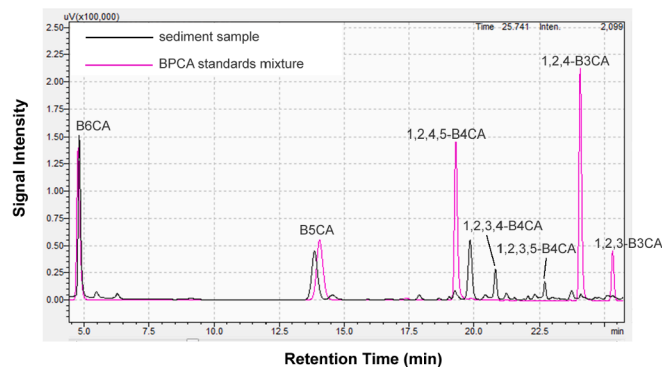


Fig. 2. HPLC-PAD chromatogram for BPCA separation of standard mixtures and a sediment sample.

2.4. Stable carbon isotope ($\delta^{13}\text{C}$) analysis of BPCAs

Selected sediment samples were analysed for $\delta^{13}\text{C}$ signatures of the two most abundant BPCAs, i.e., B5CA and B6CA. A larger sample size of sediment (450 mg) was used for $\delta^{13}\text{C}$ analysis of BPCAs. Similar to BPCA procedure, the sediment samples were oxidized in 10 mL ampoules using 2 mL of 65% nitric acid at $180\text{ }^{\circ}\text{C}$ for 8 h, followed by filtration with a pre-cleaned glass fibre filter (2 cm diameter, Whatman). Nitric acid was then removed under a stream of high pressure nitrogen gas at $50\text{ }^{\circ}\text{C}$ and the samples were redissolved in 1 mL ultrapure water and subjected to cation removal using a glass column packed with cation exchange resin (Dowex 50 WX8 400, Sigma Aldrich) as described by Wiedemeier et al. (2016). About 50 mL aqueous solutions were obtained from cation exchange column which were frozen at $-20\text{ }^{\circ}\text{C}$ and freeze-dried subsequently. Then the samples were redissolved in an aqueous solution (pH: ~ 1.3) prepared by mixing 3.8 mL HPLC grade trifluoroacetic acid (TFA) with 1000 mL ultrapure water and subjected to isolation of B5CA and B6CA with preparative liquid chromatography (pre-LC). Aliquots of the collected B5CA and B6CA fractions were re-injected and no detectable contaminants were found (Fig. 3). The isolated B5CA and B6CA were measured for $\delta^{13}\text{C}$ with a Surveyor HPLC system connected to a Delta V IRMS via an Isolink interface (Thermo Scientific). $\delta^{13}\text{C}$ values were expressed as per mil (‰) relative to Vienna Pee Dee Belemnite (VPDB). Recoveries of B5CA and B6CA were tested with standards and a maize char sample ranging between $81.2 \pm 2.6\%$ and $88.0 \pm 2.8\%$ for B5CA and B6CA (five replicates), respectively. $\delta^{13}\text{C}$ signatures of isolated B5CA and B6CA were measured for a maize char sample and marine sediment reference material (NIST SRM 1941b). The difference between the $\delta^{13}\text{C}$ values of B5CA (or B6CA, two replicates) for the bulk material for the maize char sample was less than 1‰ (Table 1). $\delta^{13}\text{C}$ values of B5CA and B6CA for the marine sediment reference material were $-23.10 \pm 0.35\text{‰}$ and $-23.45 \pm 0.15\text{‰}$ (two replicates), respectively. The accuracy of $\delta^{13}\text{C}$ values of B5CA and B6CA based on duplicate analysis of the sediments was similar to that of marine sediment reference material.

2.5. Detailed pre-LC separation of B5CA and B6CA and $\delta^{13}\text{C}$ analysis of BPCAs with LC-IRMS

The mobile phase A of preparative liquid chromatography (pre-LC) was HPLC grade acetonitrile and the mobile phases B was an aqueous solution (pH: ~ 1.3) prepared by mixing 3.8 mL HPLC grade TFA with 1000 mL ultrapure water. The pre-LC included the HPLC-PAD used for BPCAs' quantification and a fraction collector (FRC-10A, Shimadzu). The column, oven temperature, detector, flow rate and mixing gradient of mobile phases used for pre-LC were also the same as those of the HPLC-PAD method used for quantification of BPCAs. Up to 3.5–4.0 μg carbon of B5CA or B6CA was injected by setting an injection volume of 15 μL . The isolated B5CA and B6CA fractions were obtained from one

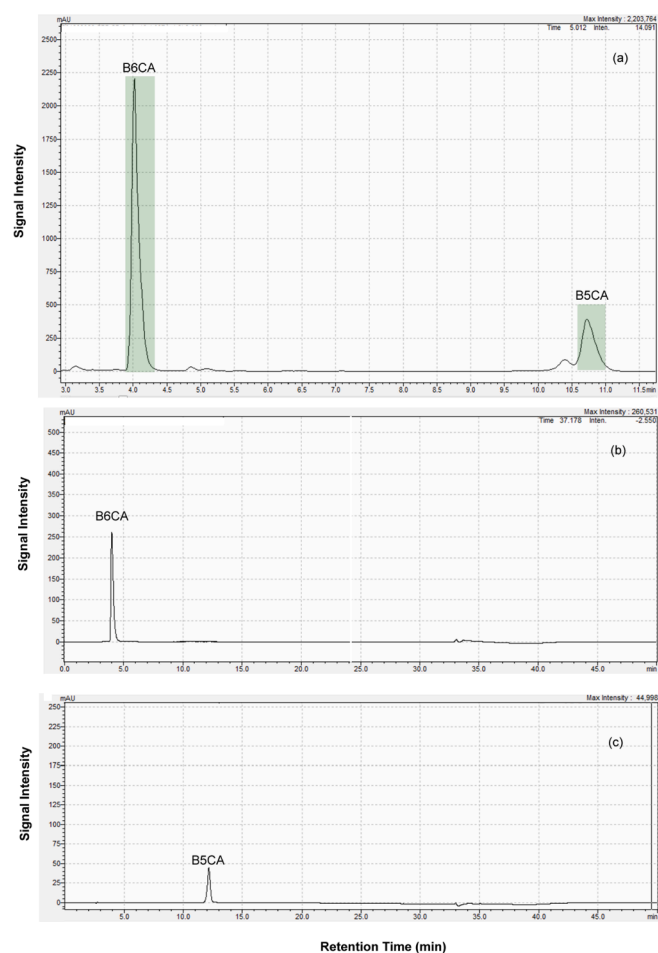


Fig. 3. A sample Pre-LC chromatogram for BPCA separation in sediment.

Table 1

$\delta^{13}\text{C}$ of isolated B5CA and B6CA for a maize char and the marine sediment reference material (NIST SRM 1941b).

	Average $\delta^{13}\text{C}$ (‰) ^a
B5CA of maize char	-13.68 ± 0.23^b
B6CA of maize char	-12.57 ± 0.24
B5CA of marine sediment reference material (NIST SRM 1941b)	-23.10 ± 0.35
B6CA of marine sediment reference material (NIST SRM 1941b)	-23.45 ± 0.15

^a Results for two replicates.

^b $\delta^{13}\text{C}$ of bulk material of the maize char is $-13.04 \pm 0.19\%$.

injection. Aliquots of the collected fractions were re-injected and no detectable contaminants were found (Fig. 3).

The isolated B5CA and B6CA fractions were transferred into a 1.5 mL vial, dried under a stream of high pressure nitrogen gas at 70 °C and then redissolved in 0.5 mL of ultrapure water. This process was repeated one more time to effectively remove TFA and acetonitrile and avoid possible artifacts of BPCA- $\delta^{13}\text{C}$ measurement. Afterwards, the isolated B5CA and B6CA fractions were kept under a stream of high pressure nitrogen gas at 70 °C for 1 h and finally redissolved in 600 μL ultrapure water.

The LC-IRMS was run without a LC column, since B5CA and B6CA were isolated with pre-LC. The injected samples (25 μL) were introduced into the Isolink interface by ultrapure water (200 $\mu\text{L}/\text{min}$). BPCAs were oxidized into CO_2 in the Isolink reaction chamber by acid (H_3PO_4 , 0.41 M) and oxidant ($\text{Na}_2\text{S}_2\text{O}_8$, 0.17 M). High purity H_3PO_4 and $\text{Na}_2\text{S}_2\text{O}_8$ were purchased from Sigma Aldrich. Flow rates of acid and oxidant were

optimized to yield an O_2 signal of 8–12 V (ion m/z 32). The peak area of CO_2 derived from oxidation of BPCA standards was positively linearly correlated with the amount of BPCAs injected (up to 1600 ng, $r^2 > 0.999$), which indicated BPCAs were efficiently oxidized. Since the injected amounts of the isolated B5CA and B6CA were lower than 1600 ng, they should be efficiently oxidized too. The BPCA-derived CO_2 was transferred from aqueous phase to helium carrier gas (2 mL min^{-1}) through an in-line membrane. Following water removal using a Nafion dryer membrane, the CO_2 was transferred to the IRMS. During analysis, two pulses of CO_2 (99.995%) of known $\delta^{13}\text{C}$ value were introduced into the IRMS and used to calculate the $\delta^{13}\text{C}$ values of the sample peaks.

2.6. Analysis of n-alkanes and PAHs

The analytical method for n-alkanes and PAHs is described elsewhere (Mao et al., 2019). Briefly, 10 g of the freeze-dried sediments were weighed and placed in pre-cleaned cellulose thimble inside a glass chamber. For extraction, a Soxhlet apparatus was run for 24 h with 150 mL dichloromethane (DCM) as solvent. Prior to the extraction, surrogates including n-tetracosane- d_{50} for n-alkanes and naphthalene- d_8 , acenaphthylene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} , and perylene- d_{12} for PAHs were spiked to the samples and copper granules were added for removal of elemental sulfur. The extracts were concentrated to 1 mL and solvent exchanged to hexane using a rotary evaporator. The concentrated extracts were loaded onto a glass column (0.8 cm i.d.) packed with 3% deactivated silica gel and aluminum oxide and eluted with DCM/hexane (1:1, v/v) to separate the hydrocarbon fraction. The eluates were concentrated to 0.5 mL under a stream of high pressure nitrogen gas and further purified with a gel permeation chromatography (GPC, 2 cm i.d.) column packed with 14 g Bio-Beads® S-X3 using DCM/hexane (1:1, v/v) as the mobile phase to separate n-alkanes and PAHs fractions, successively. The collected eluates were concentrated to 0.5 mL using rotary evaporator and a stream of high pressure nitrogen gas, successively. Hexamethylbenzene (1000 ng) was injected into the eluates as an internal standard. n-Alkanes from C_{10} to C_{39} and PAHs including acenaphthene (Ace), acenaphthylene (Acy), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthracene (DahA) and benzo[ghi]perylene (BghiP) were quantified by a gas chromatograph mass spectrometer (SHIMADZU, GCMS-QP2010) equipped with a DB-5MS column (Agilent, 30 m \times 0.25 mm \times 0.25 μm). The mass spectrometer was operated under electron ion source (-70 eV) in selective ion monitoring (SIM) mode. The details of the instrumental settings can be found in Mao et al. (2019). The mean recoveries of the surrogates of PAHs and n-alkanes were $86 \pm 26\%$ and $118 \pm 19\%$, respectively. The concentrations of PAHs and n-alkanes were corrected for recoveries. A procedural blank was conducted with every batch of samples and the concentrations of the target compounds were negligible in blanks. Reproducibility of the analysis was tested by conducting duplicate samples and the coefficient of variation were $< 15\%$ for PAHs and n-alkanes.

2.7. Statistical analysis

Statistics was conducted using a SPSS software version 19 for windows (IBM-SPSS). The data was tested for homogeneity and equity of variance and non-parametric Mann-Whitney U test was performed to evaluate the significant differences between the datasets in the sediments. Non-parametric spearman correlation coefficient was tested to evaluate the correlations between the datasets in the sediments. Where p -value was less than 0.05, the differences between the datasets were considered as statistically significant.

2.8. Specific diagnostic indices

The diagnostic indices of BC and n-alkanes were calculated to trace the sources of hydrocarbons in the sediments. The relative distribution and number of substituted carboxylic acid groups (2–6) on the aromatic rings of BPCAs produced from oxidized BC can be an indicator of the degree of condensation of the aromatic structure of BC, its generation temperature and origin (Ziolkowski, 2009). The ratio of B5CA/B6CA inversely represents the degree of BC condensation and can be an indicator of the condensity of the aromatic structure of BC (Wolf et al., 2013).

As for n-alkanes, the terrigenous/aquatic (TAR) ratio was calculated as $C_{27} + C_{29} + C_{31} / C_{15} + C_{17} + C_{19}$. This ratio is based on the principle that C_{27} , C_{29} and C_{31} abound in terrestrial plants, whereas C_{15} , C_{17} and C_{19} are characteristics of aquatic algae (Silliman et al., 1996).

The overall carbon preference index (CPI) for C_{14} to C_{34} n-alkanes evaluates the predominance of odd to even carbon atom n-alkanes:

$$CPI_{14-34} = 0.5 * [\text{odd}(C_{15} - C_{33}) / \text{even}(C_{14} - C_{32}) + \text{odd}(C_{15} - C_{33}) / \text{even}(C_{16} - C_{34})]$$

Petroleum lacks any predominance of odd or even carbon atom number n-alkanes and the CPI is near unity (Kennicutt et al., 1987; Petersen et al., 2007), whereas CPI values >3 show predominance of biogenic n-alkanes (Rieley et al., 1991).

The CPI for C_{24} to C_{34} specifically investigates the predominance of biogenic n-alkanes with higher plants' epicuticular wax origin since aquatic algae generate little or no long chain n-alkane homologous series (Kennicutt et al., 1987):

$$CPI_{24-34} = 0.5 * [\text{odd}(C_{25} - C_{33}) / \text{even}(C_{24} - C_{32}) + \text{odd}(C_{25} - C_{33}) / \text{even}(C_{26} - C_{34})]$$

Average chain length (ACL) is defined as the average chain length of n-alkanes with terrestrial higher plant origins:

$$ACL = (25 * (C_{25}) + 27 * (C_{27}) + 29 * (C_{29}) + 31 * (C_{31}) + 33 * (C_{33})) / (C_{25} + C_{27} + C_{29} + C_{31} + C_{33})$$

The values of ACL are specific for every geographical location, while occurrence of petroleum pollution can reduce the values and increase the variability in data (Jeng, 2006).

Since the distribution of n-alkanes with petrogenic origins is dominated by short chain (LMW; C_{10} - C_{23}) homologues, the ratio of LMW over long chain (HMW; C_{24} - C_{39}) n-alkanes is usually higher in more developed areas with petrogenic inputs and is a sign of anthropogenic activities (Vaezzadeh et al., 2015).

3. Results and discussion

3.1. Anthropogenic impacts on sediments of peninsular Malaysia

The West and South coast of Peninsular Malaysia has experienced fast urbanization and industrialization during recent decades, whereas the East coast is mainly rural with an agricultural based economy (Vaezzadeh et al., 2021). We used n-alkanes as biomarkers of anthropogenic impacts to evident the intense human activities in the West and South coast compared to the East coast. The concentrations of C_{10} to C_{39} n-alkanes varied broadly (Table S2) and the average concentrations of n-alkanes in developed environment of the West and South coast ($398 \pm 355 \mu\text{g g}^{-1} \text{dw}$) were significantly higher than relatively pristine environment of the East coast ($55.1 \pm 47.3 \mu\text{g g}^{-1} \text{dw}$) ($p < 0.05$; Mann-Whitney U test) (Fig. 4a) indicating excessive anthropogenic impacts on the sediments of the West and South coast. Different molecular indices of n-alkanes are shown in Table S2. The average values for the

ratio of LMW/HMW n-alkanes in the West and South coast (0.27 ± 0.25) were higher than the East coast (0.18 ± 0.11) as expected for more developed areas (Vaezzadeh et al., 2015). The overall CPI for C_{14} to C_{34} n-alkanes, a sign of the predominance of odd to even carbon atom n-alkanes, ranged from 1.41 to 7.33 (mean: 3.13 ± 1.53) and were significantly lower in sediments of the West and South coast than the East coast (Fig. 4b) which is indicative of higher anthropogenic impacts ($p < 0.05$; Mann-Whitney U test) (Kennicutt et al., 1987). The CPI for C_{24} to C_{34} showed higher values ranging from 1.40 to 10.5 (mean: 3.99 ± 2.21) indicating that the biogenic n-alkanes are mainly terrigenous. The

major hydrocarbon (MH) which is defined as the most predominant carbon atom number n-alkane was C_{31} , an n-alkane homologue which is abundant in higher plants' epicuticular wax (Silliman et al., 1996). The values of TAR ratio were more than unity (mostly >5) indicating the

predominance of terrigenous over marine biogenic sources of n-alkanes (Silliman et al., 1996) (Table S2). The values of ACL were lower in the West and South coast stations (28.9–29.9; mean: 29.5 ± 0.38) than the East coast stations (29.1–30.7; mean: 30.2 ± 0.47), however, the narrow range of ACL values as detected in this study is an indication of intense vascular plant sources of n-alkanes (Jeng, 2006). Taken together, n-alkane indices revealed the significance of terrigenous OM in the sediments of Peninsular Malaysia, while the remarkably elevated n-alkane concentrations and decreased CPIs are indicative of more intense anthropogenic impacts on the sediments of the West and South coast than the East coast (Laskov et al., 2002; Petersen et al., 2007).

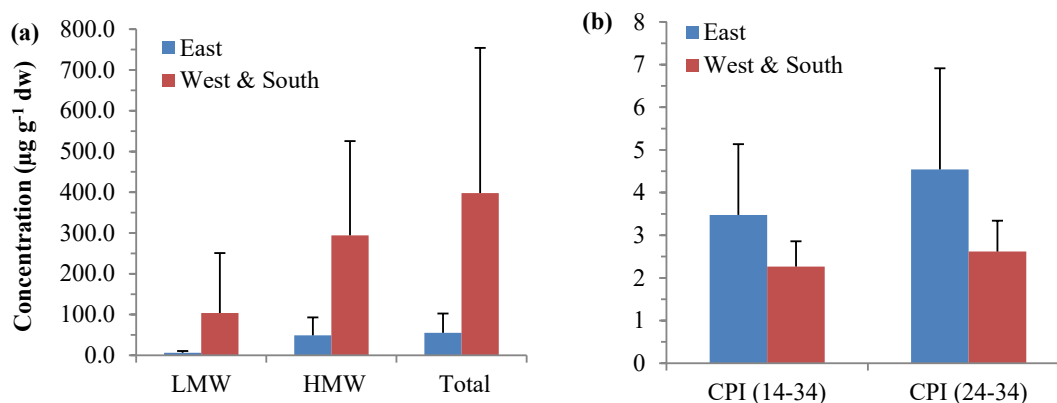


Fig. 4. Distribution of short chain (LMW; $\text{C}_{10}\text{-C}_{23}$), long chain (HMW; $\text{C}_{24}\text{-C}_{39}$) and total n-alkanes (a) and CPI_{14-34} and CPI_{24-34} (b) in sediments of the East coast ($n = 30$) versus sediments of the West and South coast ($n = 12$) of Peninsular Malaysia (av. + SD).

3.2. The degree of BC condensation in the sediments

The distributions of BPCAs showed the highest B6CA% in the majority of the East coast stations (27.1 to 48.7% of BPCAs [mean: $40.7 \pm 5.0\%$]; Fig. 5 and Table S3), whereas the highest B4CA% in the West and South coast stations (26.1 to 39.7% of BPCAs [mean: $34.9 \pm 3.4\%$]; Fig. 5 and Table S3). The B4CA, B5CA and B6CA% showed statistically significant differences between the sediments of the East coast and the West and South coast ($p < 0.05$; Mann-Whitney U test). This implies that the starting material and formation temperature of BC might have been different in these two environments (Hammes et al., 2007; Roth et al., 2012; Schneider et al., 2010). Higher B6CA% in the East coast sediments illustrates elevated degree of aromatic condensation of BC which was also reflected by higher average number of acids on BPCAs generated from oxidized BC in the East coast sediments (5.1 ± 0.1) compared to the West and South coast (4.9 ± 0.1) (Wiedemeier et al., 2016; Ziolkowski and Druffel, 2010) (Table S2 and Fig. 5). B6CA is predominant in soot formed at high temperature through condensation of combustion gases during fossil fuel combustion and biomass burning at flaming stage, whereas B4CA is more dominantly found in low temperature char residues and diagenetic coal (Hammes et al., 2007; Roth et al., 2012; Schneider et al., 2010).

The BPCA content and condensation increase from slightly charred biomass to soot along the BC continuum (Hindersmann and Achten, 2017). Generally, fossil fuels burn at higher temperatures than biomass and biomass burning at temperatures above $600\text{ }^\circ\text{C}$ mainly produces soot and leaves limited char residues behind (Elmqvist et al., 2008; Wolf

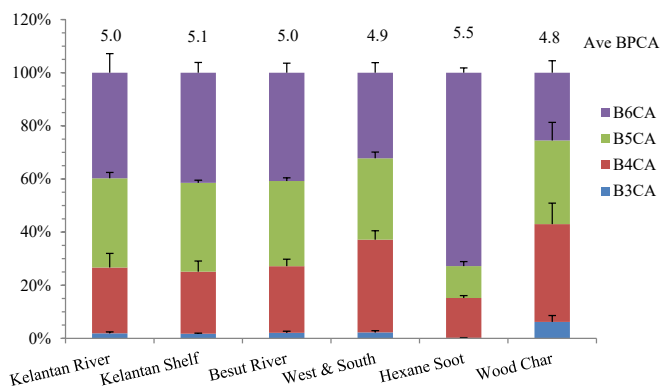


Fig. 5. Percentage of BPCAs (av. + SD) in the sediments from the East coast (Besut River [$n = 8$], Kelantan River [$n = 10$] and Kelantan Shelf [$n = 12$]) and the West and South coast ($n = 12$); Hexane Soot ($n = 3$) and Wood Char ($n = 3$). The Ave BPCA of reference materials has an uncertainty of ± 0.2 (Ziolkowski and Druffel, 2010).

et al., 2013). Therefore, char residues mainly have lower condensity and volatility than soot (Fernandes et al., 2003). Overall, due to the abundant sources of fossil fuel-derived soot BC in developed areas, higher content and condensity of BC are expected (Chow et al., 2004; Hammes et al., 2007; Brodowski et al., 2007; Roth et al., 2012). On the other hand, the contribution of char from anthropogenic sources of biomass burning is also expected to be higher in developed environments where more than 90% of the generated BC deposits proximate to the source and only limited dispersal of char might happen via erosion (Czimeczik and Masiello, 2007). A possible hypothesis for higher condensation of polycyclic aromatic carbon in relatively pristine environment of the East coast with lower BC concentrations (Table S2) could be atmospheric transportation of soot particles. Soot particles have submicron sizes and a lifetime of up to a month, thus can be transported long distances from their emission sources (Masiello and Druffel, 1998; Muri et al., 2003). Due to limited local anthropogenic activities in pristine environments, the background signal from airborne soot particles can become predominant (Ding et al., 2015). The predominance of airborne BC and PAHs was previously documented in pristine sediments of Tibetan Plateau and East Mediterranean Sea basin, respectively (Cong et al., 2013; Tsapakis et al., 2003). The study area in the East coast is influenced by the southwest (summer) and northeast (winter) monsoon winds which can potentially transport different types of pollutants to its environment (Daryabor et al., 2016).

Soot from combustion of fossil fuels contains fully substituted BPCAs (number of acids = 5.5) dominating by B6CA ($\sim 70\%$ of BPCAs; Ziolkowski and Druffel, 2010) (Fig. 5), while the aromatic condensation degree of biomass burning emissions is directly related to the formation temperature (Schneider et al., 2010). Therefore, unless BC in the East coast sediments (average number of acids = 5.1; B6CA = $\sim 40\%$ of BPCAs) has lost its aromatic condensation due to photodegradation during airborne transportation (Stubbins et al., 2012) and/or atmospheric oxidation of soot in the process of solubilisation (Decesari et al., 2002), fossil fuel-derived soot BC could not be the only source of BC in the East coast sediments. However, when discussing the source of BC on the basis of the values achieved under lab conditions, great care should be taken as there might be large variations with actual values from combustion in the real environment.

The East coast of Peninsular Malaysia has an agricultural based economy and the contribution of char residues from agricultural biomass burning to the East coast sediments is probable. Soil is an intermediate reservoir of pyrogenic carbon which is partially mobilized by the first rainfall and acts as a continuous source of BC in the aquatic environment (Cotrufo et al., 2016). Liu et al. (2020) estimated the annual average contribution of biomass burning (f_{bb}) to the Kelantan aerosol BC at $\sim 50\%$ and assuming the predominance atmospheric BC in the sediments, equal proportions of fossil fuel and biomass emissions are expected in the Kelantan sedimentary environment. Reduced aromatic

condensation of BC was observed in some of the riverine stations indicating possible contributions of low temperature char residues from river basin. The distribution of BPCAs at KR4–5 showed the highest B4CA%, the lowest B6CA% and the lowest number of acids (4.8) among KR stations (Tables S2 and S3). In addition, BR2 showed BPCA patterns similar to KR4–5 and the lowest number of acid (4.9) among BR stations (Tables S2 and S3). The abundance of char in watershed was previously reported and ascribed to the fact that a large proportion of the eroded soil remains within the watershed (Hockaday et al., 2007).

Carbon sources might be partially petrogenic in the East coast sediments for the following reasons: 1. intense dredging and mining activities along the Kelantan River basin; 2. offshore oil and gas production in the East coast; 3. predominance of small PAHs particularly Phe as an indicator of petrogenic PAHs in the East coast sediments (Hindersmann and Achten, 2017; Wang et al., 2017; Zakaria et al., 2002) (Table S3). Petrogenic carbon species were shown to produce BPCAs upon hot nitric acid oxidation (Hindersmann and Achten, 2017). Similar to pyrogenic carbon, the BPCA content and degree of condensation of petrogenic carbon increase with the degree of coalification causing overlapping BPCA patterns with pyrogenic sources, thus difficulty in constraining the BC origins on the basis of BPCA distributions (Hindersmann and Achten, 2017).

Unexpectedly, BC structure showed an overall lower degree of aromatic condensation in the sediments of the developed West and South coast. The highest proportions of BPCAs were mainly those of B4CA (mean: $34.9 \pm 3.4\%$) abundantly produced from low temperature char residues and different types of coal (Roth et al., 2012) (Fig. 5). Thus, we hypothesized that the West and South coast sediments received higher contributions from biomass burning-derived BC. Depending on the production temperature, the BPCA patterns of char might differ and Schneider et al. (2010) showed that the B6CA% of char increases constantly as combustion temperature rises. The B6CA% of char produced under laboratory conditions at $450\text{ }^{\circ}\text{C}$ ($\sim 30\%$) was close to the mean B6CA% ($32.2 \pm 3.8\%$) (Fig. 5) in the West and South coast sediments, despite various factors such as the type of vegetation and climatic conditions can affect aromatic condensation of char in the real environment (Schneider et al., 2010). The typical combustion temperatures for forest fires are $275\text{--}500\text{ }^{\circ}\text{C}$ at the soil surface, while might rise up to $800\text{ }^{\circ}\text{C}$ in the vegetation (Alexis et al., 2007). The BPCA percentages shift towards the predominance of B6CA% at temperatures above $600\text{ }^{\circ}\text{C}$ (Schneider et al., 2010). The ratio of B5CA/B6CA in the West and South coast sediments (0.72 to 1.31; Table S2) were mainly within the range of vegetation fires (0.8 to 1.9; Wolf et al., 2013). The predominance of Flu, Pyr and Phe in the sediments of the West and South coast (Table S3) supports our hypothesis indicating biomass burning is the main source of pyrogenic carbon (Bzdusek et al., 2004; Fang et al., 2016). Agricultural waste burning, massive charcoal production from mangrove trunks in kilns and man-made forest and peatland fires at local and regional scales are among possible anthropogenic sources of char in the West and South coast (Latif et al., 2018; Wolswijk et al., 2020). In addition, smouldering fires at low temperature occurring in vast peatland areas in SEA mainly produce char (Chen et al., 2007; Latif et al., 2018). The West coast of Peninsular Malaysia is downwind to biomass burning hotspots in Indonesia which contribute more than 50% to fine particulate matter ($\text{PM}_{2.5}$) concentrations of the West coast during the southwest monsoon (Fujiia et al., 2017). Effective washout by tropical rainfall facilitates transportation of these particles to the coastal environment (Zakaria et al., 2002).

Higher proportions of BaA, Chr and BbF in the sediments of the West and South coast than the East coast evidenced higher inputs from coal combustion (Fang et al., 2016) (Table S3). The coal-fired power plants are concentrated in the West and South coast and bituminous coal which is dominantly burnt in these power plants produces high char/soot ratio of BC (Han et al., 2010; Mokhtar et al., 2014). Moreover, the major coal mining activities take place in the West coast of Peninsular Malaysia. The BPCA patterns of coal and char are quite similar, while combustion

of coal increases B6CA% compared to its source material (Hindersmann and Achten, 2017).

The sources of fossil fuel derived-soot BC are widespread in developed environments such as the West and South coast. In addition to the coal combustion emissions, gas power plant emissions and vehicular exhausts are the main sources of soot in the West and South coast. Higher proportions of IcdP and BghiP in sediments of the West and South coast than the East coast revealed higher gasoline and diesel combustion emissions from the transport sector (Table S3) (e.g., Wang et al., 2015). Despite slightly lower proportions than B4CA, B6CA% was also relatively high in the West and South coast sediments (mean: $34.9\% \pm 3.4$ and $32.2\% \pm 3.8$ for B4CA and B6CA%, respectively) (Fig. 5). However, the abundance of char possibly overwhelmed the soot content of the sediments reducing the degree of aromatic condensation of BC. Char is a sign of local pyrolysis, whereas emitted soot from anthropogenic sources can affect pristine environments as well through long-range atmospheric transportation (Ding et al., 2015). Despite almost constant distribution of BPCAs in the West and South coast sediments, PD station was an exception showing higher aromatic condensation of BC identical to the East coast stations (Table S3).

Finally, higher B4CA% in the West and South coast sediments could partially be ascribed to higher ratio values of PAH/BC (mg g^{-1}) (Table S2). A significant correlation was found between PAH/BC and B4CA% in the sediments ($p < 0.05$; $r = 0.58$). Our data suggests that the small molecules with fused benzene rings including PAHs could possibly contribute to generation of B4CA during hot nitric acid oxidation. Due to insolubility of BC in organic solvents, we suggest sediments with high PAH concentrations to be first solvent extracted for removal of the small molecules with fused benzene rings to achieve more precise BPCA contents and patterns.

The formation temperature, transportation and fate of BC in the environment can influence the BPCA distributions, therefore the applicability of BPCA patterns as the only source identifier of BC is highly conjectural. For example, the preferential photodegradation of the most condensed forms of BC can shift the BPCA patterns towards less aromatic condensation (Stubbins et al., 2012). The inevitable variabilities in BPCA patterns of the same starting material and the overlapping BPCA patterns of petrogenic and pyrogenic origins were also documented previously (Hindersmann and Achten, 2017). BPCA-specific $\delta^{13}\text{C}$ signatures can provide complementary data on BC origins.

3.3. $\delta^{13}\text{C}$ signatures of BC

$\delta^{13}\text{C}$ signatures of BC were analysed for some of the sediment samples to further trace BC sources. $\delta^{13}\text{C}$ values for B5CA and B6CA were more depleted in the East coast sediments ranging from -32.9 to -41.2‰ (mean: $-38.5 \pm 2.0\text{‰}$) and -31.1 to -45.4‰ (mean: $-34.7 \pm 3.0\text{‰}$), whereas ranged from -35.9 to -37.8‰ (mean: $-36.6 \pm 0.8\text{‰}$) and -26.4 to -32.5‰ (mean: $-30.5 \pm 2.6\text{‰}$) in the West and South coast sediments, respectively (Fig. 6 and Table S2). The isotopic depletion of B5CA and B6CA in the East coast compared to the West and South coast was statistically significant ($p < 0.05$; Mann-Whitney U test). The values of $\delta^{13}\text{C}$ -B6CA showed a moderate but significant positive correlation with the B4CA% ($p < 0.05$; $r = 0.52$), whereas a negative correlation with B6CA% ($p < 0.05$; $r = -0.42$). Excluding KR4, the $\delta^{13}\text{C}$ -B5CA values showed similar correlation trends with B4CA% ($p < 0.05$; $r = 0.46$) and B6CA% ($p < 0.05$; $r = -0.42$). In other words, sediments with increased B4CA% generally exhibited $\delta^{13}\text{C}$ enrichment, while sediments with increased B6CA% showed $\delta^{13}\text{C}$ depletion (Fig. 6). This implies that the most condensed forms of BC in the sediments generated through hotter burning conditions such as fossil fuel combustion are isotopically light, thus combustion of isotopically light components of fossil fuel are probable in the study area. A significant, though moderate correlation was found between $\delta^{13}\text{C}$ signatures of B5CA and B6CA in sediments ($p < 0.05$; $r = 0.49$). The isotopic offsets between B5CA and B6CA were inconsistent and wide in some of the sediments ranging from 1.5 to 9.5‰

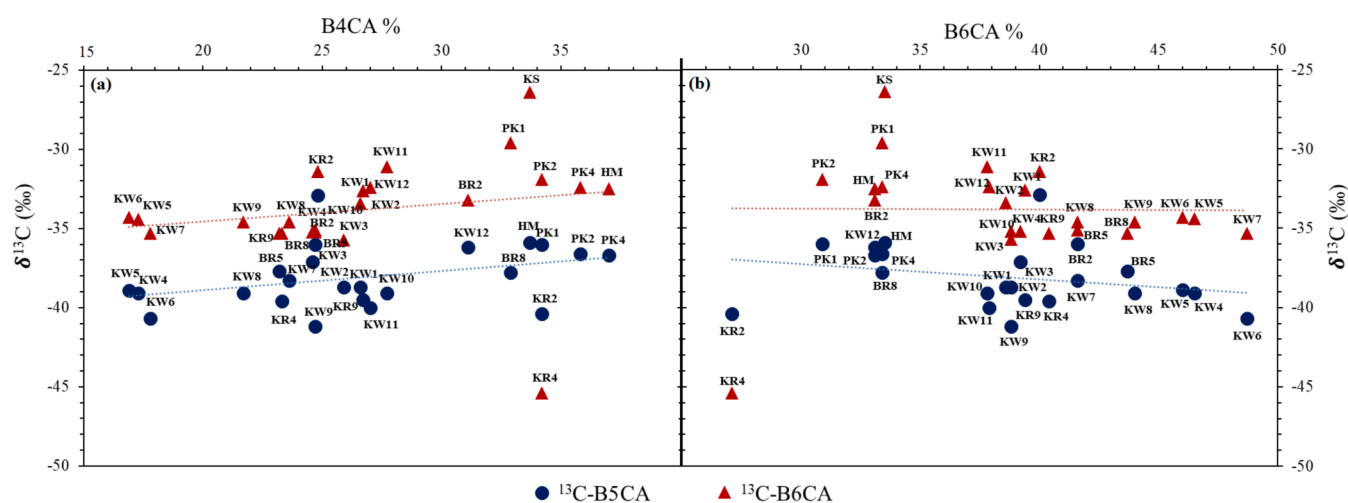


Fig. 6. Relationships between stable carbon isotope signatures ($\delta^{13}\text{C}$) for B5CA and B6CA and B4CA% (a) and B6CA% (b) in the sediments from the East coast (Kelantan River [KR; $n = 3$], Kelantan Shelf [KW; $n = 12$] and Besut River [BR; $n = 3$]) and the West and South coast ($n = 5$).

with enrichment of $\delta^{13}\text{C}$ -B6CA compared to $\delta^{13}\text{C}$ -B5CA (except KR4) (Fig. 6). The biogeochemical procedures responsible for the isotopic offsets between B5CA and B6CA in the sediments need further investigations.

Such light $\delta^{13}\text{C}$ values have seldom been detected in sedimentary environment (Laskov et al., 2002). Light $\delta^{13}\text{C}$ values (-45% and -48%) were detected for BC isolated from POC through chemothermal oxidation method at $375\text{ }^\circ\text{C}$ (CTO-375) in the Gulf of Maine despite the source remained unknown (Flores-Cervantes et al., 2009). Isotopically depleted PAHs (-36 to -62%) detected in lagoon sediments near the Adriatic Sea originated from pyrolysis of natural methane (Fabbri et al., 2003). In this study, the $\delta^{13}\text{C}$ -B5CA signatures exhibited consistently light values ($<-35.0\%$) except for KR2 (-32.9%) resembling those of light $\delta^{13}\text{C}$ fossil fuel components such as methane and the majority of other thermogenic gases generated through oil-prone organic matter (Tang et al., 2000) (Fig. 6 and Table S2). Natural gas is a major energy supply in Malaysia used for domestic applications and electricity generation (Mokhtar et al., 2014). Flaring of sub-quality natural gas at oil flow stations such as in Malay Basin in the East coast can be a source of light $\delta^{13}\text{C}$ BC. Despite gas flaring contributes to 3% of the emitted BC worldwide, this contribution might be higher in pristine environments such as the East coast, for example 42% of annual average aerosol BC in Arctic was ascribed to gas flaring (Stohl et al., 2013).

We hypothesized that aerosol soot BC contributes to the East coast sediments on the basis of BPCA distributions. The isotopic composition of atmospheric BC is not well constrained and could vary remarkably as the f_{bb} and combustion source materials are dramatically different in various geographical regions and different seasons. The isotopic composition of Malaysian aerosols is expected to be depleted due to raised f_{bb} (C_3 plants) and large share of natural gas in electricity generation (Liu et al., 2020). However, heavier range of $\delta^{13}\text{C}$ values was previously reported for aerosol PAHs in the West coast of Peninsular Malaysia (-17.7 to -27.9%) (Okuda et al., 2002).

As mentioned earlier, petrogenic BC could abound in the East coast sediments. The variabilities in the isotopic composition of condensates and petroleum components were previously documented (-17.6 to -38.4%) (Huang et al., 2017). The source material and formation condition can tremendously affect the isotopic range of values for petrogenic compounds. However, the characteristics of Southeast Asian crude oil (SEACO) and other petrogenic components in the environment of the East coast of Peninsular Malaysia are poorly understood and this area is open for further investigations.

Biomass burning in SEA is dominated by forest fires (C_3 plants) having light $\delta^{13}\text{C}$ values (-25 to -35%) which shift towards more $\delta^{13}\text{C}$

depletion in tropical climate with raised precipitation (Liu et al., 2005). Thus, biomass burning could be a source of isotopically depleted sedimentary BC in the study area resembling $\delta^{13}\text{C}$ -B6CA values in several stations (Fig. 6 and Table S2). PAH and BPCA molecular markers support the significance of biomass burning in the West and South coast. The $\delta^{13}\text{C}$ values of PAHs emitted from the combustion of Malaysian wood were within the range of -26.8 to -31.6% (Okuda et al., 2002) which almost match those of $\delta^{13}\text{C}$ -B6CA in the West and South coast sediments (-26.4 to -32.5%). Burning of agricultural wastes such as palm oil biomass residues and rice husk is commonly practiced in the West and South coast. Moreover, massive charcoal production from mangrove trunks in kilns is common in the West and South coast (Wolswijk et al., 2020). These vegetations follow C_3 plant photosynthesis pathway for carbon fixation and show light range of $\delta^{13}\text{C}$ values (-25 to -30%) in Peninsular Malaysia (Miyajima et al., 2009; Muhammad et al., 2017).

Coal combustion and vehicular emissions are widespread in the West and South coast and PAH and BPCA molecular markers pointed to their significance. The $\delta^{13}\text{C}$ value of -27.4% was previously reported from Indonesian coal which is the main imported coal to Malaysia (Suto and Kawashima, 2016). However, the interpretation of $\delta^{13}\text{C}$ values of BC from coal combustion is difficult since more negative $\delta^{13}\text{C}$ signature corresponds to higher combustion temperatures (Petrisic et al., 2013). Okuda et al. (2002) reported heavier $\delta^{13}\text{C}$ values for PAHs emitted from gasoline and diesel exhaust in Malaysia (-12.9 to -26.6%) than those of BC in the West and South coast sediments. The range of $\delta^{13}\text{C}$ values for global dominant crude oils is -26 to -32% , however, oil accounts for a very small share of energy supply in Malaysia (Yeh and Epstein, 1981). Finally, it is worth mentioning that plastic waste burning is widespread in SEA including Malaysia and can be a potential source of the sedimentary BC. Petrochemical $\delta^{13}\text{C}$ range of values (-24 to -36%) are within the range detected for several sediments in this study (Rogers et al., 2021).

The reduced BC condensity and predominance of B4CA% in KR4 had us hypothesize the possibility of low temperature char residue contribution. The unanticipatedly $\delta^{13}\text{C}$ -depleted values in KR4 (-40.4% and -45.4% for B5CA and B6CA, respectively), however, were inconsistent with the BPCA distributions, causing an obscurity in justification of BC sources in this station. The precision of $\delta^{13}\text{C}$ values of B5CA and B6CA was tested by analysing a maize char, marine sediment reference material and duplicate sediments, thus this discrepancy cannot be due to inaccurate measurement. The discrepancy between BPCA distribution and $\delta^{13}\text{C}$ values could be ascribed to some yet to be discovered aromatic materials resembling BC in the sediments. Some materials with broad range of $\delta^{13}\text{C}$ values were known to resemble BC in the environment

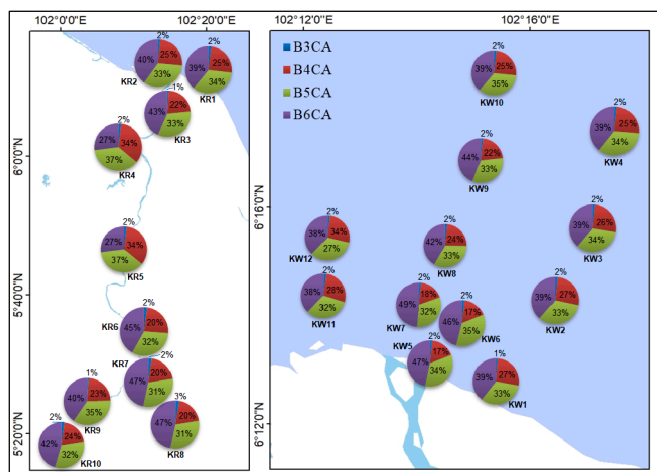


Fig. 7. Distributions of BPCAs in Kelantan River (KR1–10; left side) and Kelantan adjacent shelf (KW1–12; right side).

(Ziolkowski and Druffel, 2009). For example, single-walled carbon nanotubes (SWCNs) which have gained popularity in different industries, particularly electrical appliances due to unique electrical conductivity were shown to produce large proportions of B6CA and had a broad range of $\delta^{13}\text{C}$ values (-23.5 to -53.2‰) (Plata et al., 2008; Ziolkowski and Druffel, 2009). On the other hand, despite similar BPCA patterns of KR2 with the majority of other East coast stations, heavier isotopic signatures were detected (Fig. 6 and Table S2). One explanation for the variations observed in the isotopic composition among KR stations could be biodegradation of BC in the sediments. Despite BC is the refractory fraction of OC, part of BC can undergo biodegradation in soil and sediment (Middelburg et al., 1999). Biodegradation of combustion-derived polycondensed aromatic moieties takes place at different levels under various oxic/anoxic conditions resulting in isotopic enrichment (Fabbri et al., 2003). Fluctuations in oxic/anoxic conditions are highly

probable among KR stations due to intense dredging and mining activities at the river basin. Assuming that the smaller polycyclic clusters are more prone to biodegradation, biodegradation of BC can lead to increased aromatic condensity, decreased concentration and enriched isotopic composition as were observed in KR2 compared to KR4 (Fig. 6 and Table S2). However, the biolability of BC is poorly understood and this hypothesis needs further investigation. Moreover, the isotopic enrichment ascribed to biodegradation is at lower scales than the isotopic offsets observed between KR2 and KR4, especially for B6CA (14%; Fig. 6) (Mazeas et al., 2002). Thus, different feedstocks are highly probable at KR4 which also showed different BPCA patterns from the majority of other East coast stations.

3.4. BC characteristics in riverine and shelf sediments

The percentages of different BPCAs in the Kelantan River and its adjacent shelf sediments showed no statistically significant differences and neither did the number of carboxylic acids on BPCAs ($p > 0.05$; Mann-Whitney U test). Therefore, the aromatic condensation of BC mainly remained unchanged in the Kelantan River and its adjacent shelf sediments (Fig. 7) unlike the previous observations on dissolved BC (DBC) which suggested a seaward decrease in condensity (e.g., Ziolkowski and Druffel, 2010). Coppola et al. (2014) found higher degree of aromatic condensation of BC in abyssal sediments than DBC suggesting that aggregation and sedimentation removal of the most condensed forms of BC in DOC result in higher condensity of sedimentary BC. Our results are consistent with those of Coppola et al. (2014) showing higher condensed BC structures in the sediments. An almost constant distribution of $\delta^{13}\text{C}$ -BPCA signatures were detected in the East coast and no statistically significant differences were found between the riverine and shelf sediments in agreement with the fairly homogenous distribution of BPCAs ($p > 0.05$; Mann-Whitney U test) (Fig. 8a). The overall homogeneous BC characteristics in the Kelantan River and adjacent shelf sediments suggest that the most prevalent source of BC in the riverine and shelf sediments could be similar.

The major transportation pathway of modern BC from biomass combustion to the sea is runoffs and rivers. The effective transportation of terrestrial OM to the Kelantan adjacent shelf area by the river plume was previously documented, especially during wet season (Wang et al., 2020). Different molecular indices of n-alkanes such as the CPI_{14-34} (range: 1.43–5.28), the CPI_{24-34} (range: 1.46–6.78), the TAR ratios (range: 4.7–54.2); the ratio of LMW over HMW n-alkanes (range: 0.04–0.49) and the MH (C_{31}) showed the significance of terrestrial OM in the sediments of the Kelantan shelf (Table S2 and Fig. 8). The maximum CPI values in the Kelantan adjacent shelf sediments were found at the most distal stations (KW4 and KW10; Fig. 8) similar to what was observed on other offshore sediments affected by terrestrial plant wax n-alkanes (Drenzek et al., 2007). The abundance of n-alkanes showed an overall increasing trend seaward despite dropped at the most distal stations (range: 9.1–117 $\mu\text{g g}^{-1}$ dw) (Fig. 8). The indices of n-alkane biomarkers indicate that the Kelantan adjacent shelf area receives a great proportion of terrestrial OM and the associated BC. On the other hand, except for KW5–8 in the vicinity of the river mouth, the BC concentrations increased seaward implying that the Kelantan River is possibly not the only BC source inputs to the Kelantan shelf sediments and atmospheric and/or marine sources possibly contribute to the shelf sediments' BC pool (Fig. 8; Table S2). Previous studies showed marine sources of DBC are possibly a contributor to oceanic DBC (e.g., Wagner et al., 2019). As mentioned earlier, occurrence of petrogenic materials in the East coast sediments is highly probable and isotopically depleted petrogenic compounds might be a marine source of BC. However, this hypothesis needs further investigations due to limited available data on characteristics of petrogenic components in the region. Wagner et al. (2019) found that oceanic DBC is isotopically enriched compared to riverine DBC hypothesizing that the carbon in oceanic DBC might have been fixed by phytoplanktons. However, the isotopically depleted BC in

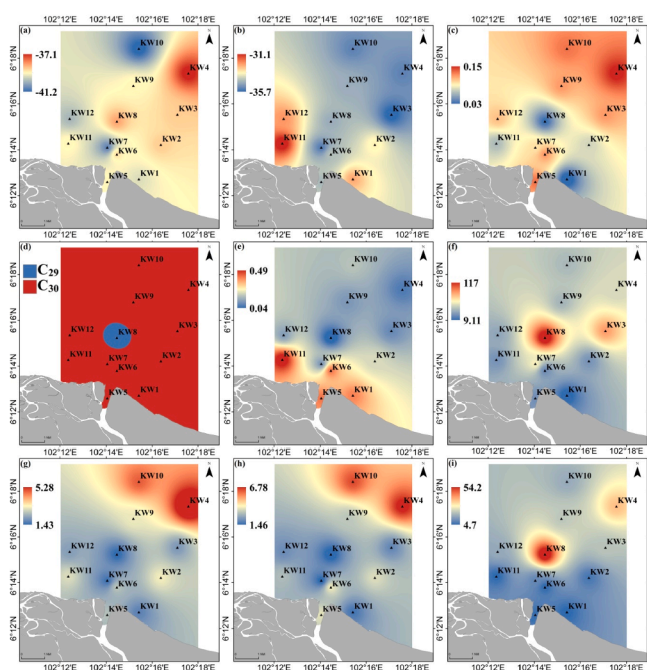


Fig. 8. Spatial distribution of stable carbon isotope ($\delta^{13}\text{C}$)-B5CA (‰) (a); $\delta^{13}\text{C}$ -B6CA (‰) (b); BC (% dw) (c); major hydrocarbon (MH) (d); ratio of short chain ($\text{C}_{10}\text{-C}_{23}$) / long chain ($\text{C}_{24}\text{-C}_{35}$) homologues (LMW/HMW) (e); n-alkanes ($\mu\text{g g}^{-1}$ dw) (f); carbon preference index (CPI_{14-34}) (g); CPI_{24-43} (h); terrigenous/aquatic ratio (TAR) (i) in Kelantan shelf sediments.

the Kelantan shelf sediments is not consistent with the enriched isotopic composition of phytoplanktonic sources (-21% or lower). Moreover, n-alkane indices indicated predominance of terrestrial versus aquatic OM in the shelf sediments (Fig. 8). Excluding marine sources of BC from the equation, atmospheric deposition can be a contributor to terrestrial OM and the associated BC in the shelf sediments. This is consistent with our hypothesis on the basis of the BPCA distributions implying that airborne BC contributes to the East coast sediments. Despite fluvial system is the major transportation pathway for marine sedimentary BC, the great contribution of aeolian pathway was shown previously (Flores-Cervantes et al., 2009), which is expected to be higher in remote areas where the local pyrolysis sources are limited. Therefore, we conclude that both river fluxes and atmospheric depositions contribute to the BC loads of the Kelantan shelf sediments.

4. Conclusion

In this study, we used distributions of molecular markers including n-alkanes, PAHs and BPCAs in combination of $\delta^{13}\text{C}$ values for B5CA and B6CA to trace sources of BC in riverine, coastal and shelf sediments of Peninsular Malaysia. The B4CA, B5CA and B6CA% and $\delta^{13}\text{C}$ values for B5CA and B6CA were significantly different in the sediments of the relatively pristine East coast and the developed West and South coast ($p < 0.05$; Mann-Whitney U test) indicating different prevalent sources of BC. The higher condensity of BC structure in the sediments of the East coast indicated that the sediments possibly received higher contributions from atmospheric soot, while the occurrence of petrogenic BC is also probable due to petrogenic background of the sampling sites. Despite the sources of fossil fuel-derived soot are omnipresent in the West and South coast, abundance of less condensed char residues from local pyrolysis of biomass seems to overwhelm the soot content of the sediments in this area. The wide range of $\delta^{13}\text{C}$ values for B5CA and B6CA (-45.4 to -26.4%) in combination of the variabilities in molecular marker signatures showed a variety of possible sources for BC in the sedimentary environment of Peninsular Malaysia. Some of these sources could be combustion of light $\delta^{13}\text{C}$ components of fossil fuels, biomass burning dominated by the widespread C_3 plants and/or some undiscovered materials in the environment which produce BPCAs upon hot nitric acid oxidation. The condensed aromatic structure of BC mainly remained unchanged in the Kelantan River and its adjacent shelf sediments indicating the predominance of terrestrial BC in the shelf sediments. These results were backed up by almost uniform $\delta^{13}\text{C}$ depleted values for B5CA and B6CA and molecular indices of n-alkanes. This is in contract with the variabilities in condensity and $\delta^{13}\text{C}$ values between riverine and oceanic DBC reported by previous workers. Future simultaneous investigations of the characteristics of DBC, PBC and sedimentary BC in different aquatic ecosystems are recommended for a better understanding of the biogeochemical cycling of BC.

Declaration of Competing Interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marchem.2021.104032>.

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