



Validation of an analytical technique, distribution, and risk assessment of aliphatic and polycyclic aromatic hydrocarbons in surface sediments of the coastal and selected estuaries of Sarawak

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Abstract

This study explains a validation of an analytical technique, monitoring, and risk evaluation of hydrocarbons in surface sediments of the coastal and selected estuaries of Sarawak, Malaysia. The performance of an analytical methodology was validated for the evaluation of hydrocarbons in coastal and estuaries sediment samples. After the clean-up and separation process, GC-FID and GC-MS were used to quantify aliphatic and polycyclic aromatic hydrocarbon extracts, respectively. The suggested methodology is able to measure aliphatic and polycyclic aromatic hydrocarbons in samples at lower concentrations for example 10 ng/g. The precision of the technique was satisfactory as compared to 15% for most of the analytes. This method gives information concerning the distribution and characteristics of hydrocarbon contaminants in the coastal environment. In regard to monitoring and risk assessment, total n-alkane concentrations (C₁₀–C₃₃) varied from 96.63 to 367.28 ng/g dw. The lowest and highest n-alkane content is observed at Santubong estuary (CZ10) and the coastal site CZ2, respectively. Simultaneously, the contents of Σ PAHs varied from 12.54 to 21.20 ng/g dw. The highest Σ PAH content is reported in the sediments of coastal site CZ8 (21.20 ng/g dw), whereas the lowest content is recorded in the sediments of coastal site CZ3 (12.54 ng/g dw). The outcome of the risk assessment suggested that there is no risk in all the studied locations. The findings from this study will help to understand the sources and possible risks of hydrocarbons in the coastal and estuary settings, and provide information for safeguarding human health and aquatic bodies in the studied area.

Keywords Validation · Sediments · Petroleum hydrocarbons · Toxic equivalency factor · BaP equivalent

Introduction

On account of the extensive distribution of oil contamination in the environment, the determination of petroleum-related environmental samples is remarkably significant. Petroleum contaminants cause wide harm to the estuary and coastal life, natural resources, and human health. Its make-up study permits the understanding of the fate and characteristics of

contaminants and the projection of the possible long-term effect of spilled oils on the environment. Over thousands of organic compounds can be found in petroleum. The development of feasible and reasonable analytical methods for constitutional analysis by gas chromatography–flame ionization (GC-FID) and GC–mass spectrometry detection (MS) in the determination of petroleum hydrocarbons is of great concern (Ramos et al. 2000; Wang et al. 2002; Hartmann et al. 2004; Basheer et al. 2005). These analytical methods permit the assessment and their relative pattern of each petroleum hydrocarbon in compounds of a complex mixture (Damas et al. 2009). Various steps are required for organic traces in complex matrices analysis. Fundamentally, the extract was clean-up and fractionated after extraction, summing it all, chromatography procedures are employed in the separation of the analytes. According to Song et al. (2002), using Soxhlet, mechanical shaking or stirring, and ultrasonic extraction serve as the basis by which petroleum contaminants are extracted from solid samples in the environment. Numerous techniques have

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been documented in the literature for the pre-separation or fractionation of crude oil. These techniques include supercritical fluid chromatography separation (Campbell and Lee 1986; Nishioka et al. 1986; Omorinoye et al. 2020); high-performance liquid chromatography separation (Lucke et al. 1985; Guo et al. 2011); classical adsorption chromatography on different adsorbents, including alumina (Grossi et al. 2002), silica gel (Zakaria et al. 2000), and combination of silica and alumina (Hostettler et al. 1999; Grossi et al. 2002); solid-phase extraction (SPE) (Theobald 1988); and florisisil (El Nemr and Abd-Allah 2003). This study concentrates on the validation of gas chromatography–flame ionization (GC-FID) and GC–mass spectrometry (MS) for the quantitative investigation of petroleum hydrocarbons in coastal sediment. Analytes considered are aliphatic (AHs) and polycyclic aromatic hydrocarbons (PAHs). The technique validated was used on real samples to characterize the chemical constituent of petroleum remains in coastal and selected estuaries sediment samples.

The accumulation of aliphatic and polycyclic hydrocarbons in the aquatic system is inversely proportionated to the possibility and capacity of petroleum compounds to metabolize them biologically or chemically. Determining the origin of AHs and PAHs contamination is a serious interest for researchers all over the globe. In the 1970s, numerous scientists began to identify the sources of petroleum contamination in the aquatic system. In Southeast Asia, studies on particular organic compounds in the aquatic environment started by a rigorous survey in the Strait of Malacca (Zakaria et al., 1999; 2000; 2001; 2002; 2006) and also research carried out by Boonyatumanond et al. (2006, 2007) in the Gulf of Thailand. Intending to identify the origin of petroleum hydrocarbons contamination in the ecological system, there are several approaches to use, for instance, the use of isomer pair ratios (Yunker et al., 2002), biomarkers (Wang and Fingas 1995), and individual compound ratios (Zakaria et al. 2000; Aly Salem et al. 2014). Malaysia, which is found in Southeast Asia, has a distinctive tropical ecosystem. It is circumambient by the South China Sea in the west of Peninsular Malaysia and the Straits of Malacca in the west. Apart from the rapid development of Peninsular Malaysia, the eastern part of Malaysia is also undergoing some sort of development throughout the last half-century. On the contrary, the strategic area of this nation has earned Malaysia one of the busiest shipping routes in the globe because of the high demand for petroleum from the Middle East to China and Japan. While Malaysia is undergoing remarkable population and economic growth, it is as well developing rapidly in urbanization, industrialization, and motorization in the last 25 years. As a consequence of this development, the natural world of this nation is earning several threats and hazards particularly from the fundamental energy source which is petroleum. The status and sources of petroleum contamination in Malaysia differ depending on locations, for example, in the eastern part, the contamination usually comes from the urban and fewer industries due to low industrial developments. In regard to western Peninsular

Malaysia, where the existence of fast urban development and setting up of various industrial areas is taking place, hydrocarbon contamination is introduced in every part of pointed and non-point sources. Aside from that, the Malaysian Marine Department published 127 oil spill occurrences since 1976 because of heavy oil tanker traffic in the Straits of Malacca (Malaysian Marine Department 2003). It was regarded as true that the Malaysian environment is under a heightening menace of petroleum pollution (Zakaria and Takada 2003), even though it is not well-written and recorded.

For these reasons, surface sediments were collected from the coastal and selected estuaries of the Kuching Division of Sarawak to predict the source and monitor and assess the potential risk of aliphatic and polycyclic aromatic hydrocarbons.

Material and methods

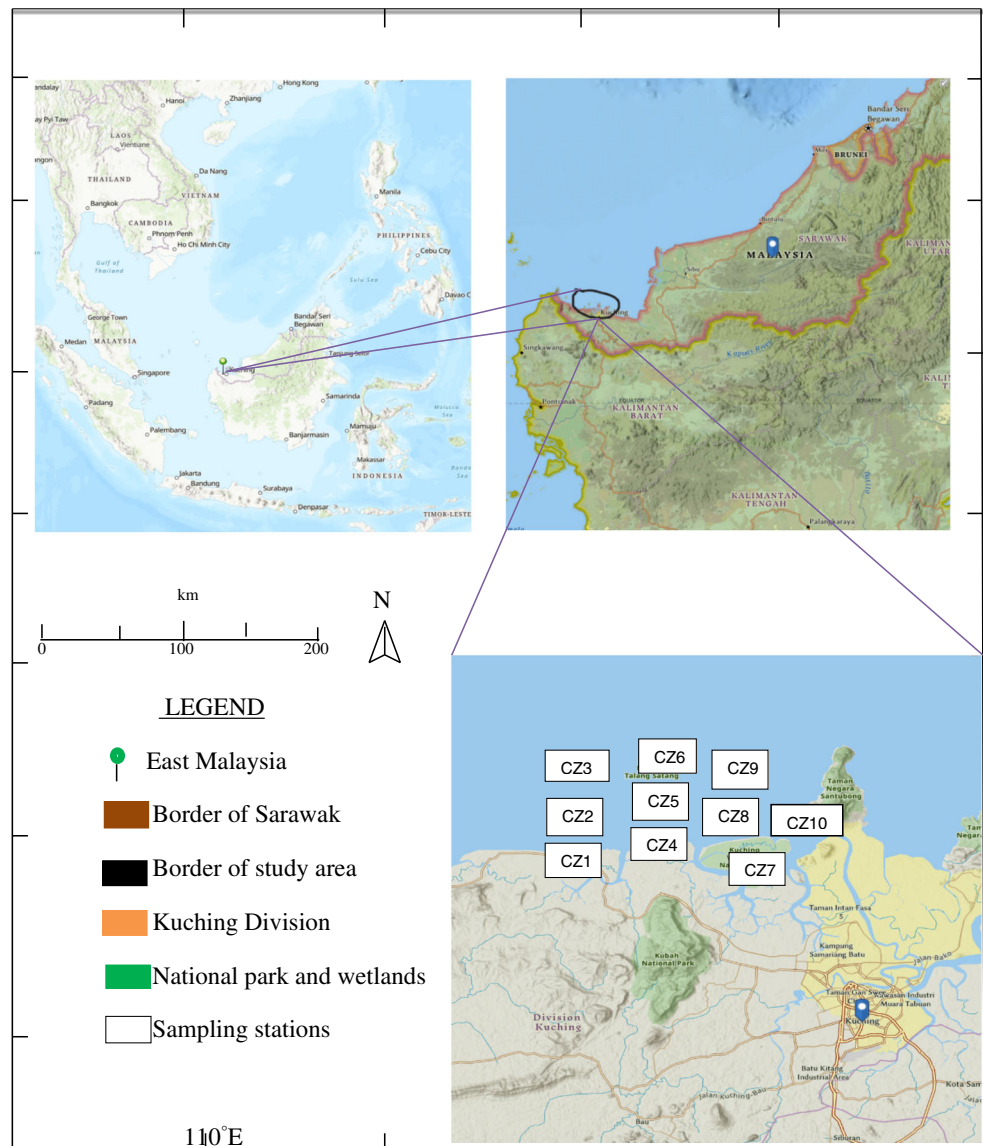
Reagents and chemicals

Germany (i.e., Merck, Darmstadt) is where toluene, n-hexane, cyclohexane, and dichloromethane (DCM) were bought and they were analytical-grade. Spain (i.e., Sharlau, Barcelona) is where anhydrous potassium sulfate was purchased. Baking of K_2SO_4 at 250 °C for 5 h was used to clean the glassware before use. Silica gel was purchased from Merck, Darmstadt, Germany. To remove the sulfur during the extraction, 10% HCl was used to activate the copper powder for 60 s; Milli-Q water and acetone were used as a cleaning agent. Switzerland (i.e., Fuka, Steinheim) is where AHs and PAHs standards were bought.

Sample collections and preparation

The protocol for surface sediments sampling and preparation was adapted by Omorinoye et al. (2020). Surface sediments were collected from 10 stations distributed at the coastal and selected estuaries sites in the Kuching Division of Sarawak, Malaysia (Fig. 1). Sampling was carried out in September 2020. Pre-cleaned aluminum bags were used to store the samples and kept at 15 °C until further analysis. Sediment samples were defrosted, dried at room temperature overnight, and passed through a 2000- μ m sieve to remove debris and gravel. The ten sediment samples were marked as CZ1 (N01° 41' 37.7" E110° 08' 24.5"), CZ2 (N01° 44' 46.8" E110° 08' 45.4"), CZ3 (N01° 46' 22.6" E110° 08' 37.8"), CZ4 (N01° 44' 46.8" E110° 08' 45.4"), CZ5 (N01° 45' 50.4" E110° 11' 30.2"), CZ6 (N01° 47' 23.5" E110° 10' 39.7"), CZ7 (N01° 40' 41.1" E110° 16' 59.2"), CZ8 (N01° 42' 45.7" E110° 27' 63.1"), CZ9 (N01° 44' 49.6" E110° 29' 72.3"), and CZ10 (N01° 42' 32.6" E110° 19' 02.3"). CZ1 stands for the location of the estuary of river Rambungan, CZ4 represents the estuary of river Sibul, CZ7 represents the estuary of river Salak, and CZ10 is the estuary of river Santubong.

Fig. 1 Map of Sarawak depicting the sampling locations.



Spiking procedure

The protocol for the spiking of sediment samples was adapted by Damas et al. (2009) with little modification. Spiked samples were used to validate the analytical protocol. For this reason, sediments were collected from uncontaminated coastal sites. This coastal sediment contained AHs from the biogenic origin without PAH included. Before the extraction, AHs and PAHs standard mixtures were used to spike each sample, and concentration for each analyte was increased between 20 and 100 ng/g and 10 and 50 ng/g, respectively. This was then extracted and underwent a clean-up process. Comparisons were made between spiked and non-spiked samples. The recovery tests were used to assess the matrix effect.

Extraction technique, extract clean-up, and fractionation process

The Soxhlet extraction method used for extraction, clean-up, and fractionation of AHs and PAHs from sediment samples was adapted from the United States Environmental Protection Agency, EPA 3540 modified method as cited in Ugwu and Ukoha (2016). About 25.0-g dried sediment samples in a cellulose thimble were placed in a Soxhlet extractor and extracted with 200 mL of dichloromethane for 10 h. To get rid of elemental sulfur present in the sample, about 5.0 g of activated powder was added to extraction balloons. The crude extract was dried using rotary vapor to get a volume of about 2.0 mL. The solvent utilized for extraction was substituted into cyclohexane and the eluted volume was fairly reduced by a logical stream of ultra-pure nitrogen up to 1.0 mL. The extract had to undergo a clean-up process to eliminate unwanted substances that were co-extracted for instance lipids and

pigments, and biogenic macromolecules which may impede the final assessment and measurement of the compounds of concern. The clean-up process of extract helps to achieve the separations of analytes in groups into respective fractions for analysis. The effective height and internal diameter of the chromatography columns used were 55.0 cm and 1.0 cm, respectively. The columns were packed with cotton wool at the bottom and filled with 6.0 g of silica gel and 2.0 cm of potassium sulfate was added at top of the column. The column was conditioned with 10 mL of n-hexane before the addition of the extract. Approximately 400 μ L of the crude extract was transferred to the top of the column. Thirty microliters of n-hexane was added and the 1st fraction (aliphatic compounds) eluted. The 2nd fraction (polycyclic aromatic hydrocarbons) was eluted with a 30-mL mixture of DCM and hexane (50:50, v/v). Both fractions were then gently evaporated to dryness using purified nitrogen gas and kept in a dark place at 4 °C temperature until further analysis. GC-FID was used to analyze aliphatic hydrocarbon (AH) fractions, while GC-MS was used to analyze polycyclic aromatic hydrocarbon (PAH) fractions.

A procedure blank was periodically analyzed for each sample in a batch of 10. The blank was prepared by applying all the analytical techniques including the same solvents and reagents used for extracting the samples. The analytical blank aims to examine no contamination by impeding compounds, which may lead to errors during measurements.

Quantification of AHs and PAHs in the sample

The quantity of AHs and PAHs was determined by using an external standard. The external standard is a compound-like internal standard that shows similar behaviors to the analyte but is not added to the unknown sample. The quantity of the analyte could be obtained by comparing the responses of AHs and PAHs standard obtained from GC (DB-5 column) to that of the targeted analyte using a calibration curve. The peak area of the unknown compounds was compared to the peak area of AHs and PAHs standard (known compound). The presence of AH and PAH compounds in the sample was identified by the retention time. About twenty-three (23) AHs and sixteen (16) targeted PAHs were quantified using the peak area, concentration, and response factor related to the respective calibration curve based on five (5) points for each compound.

Results and discussion

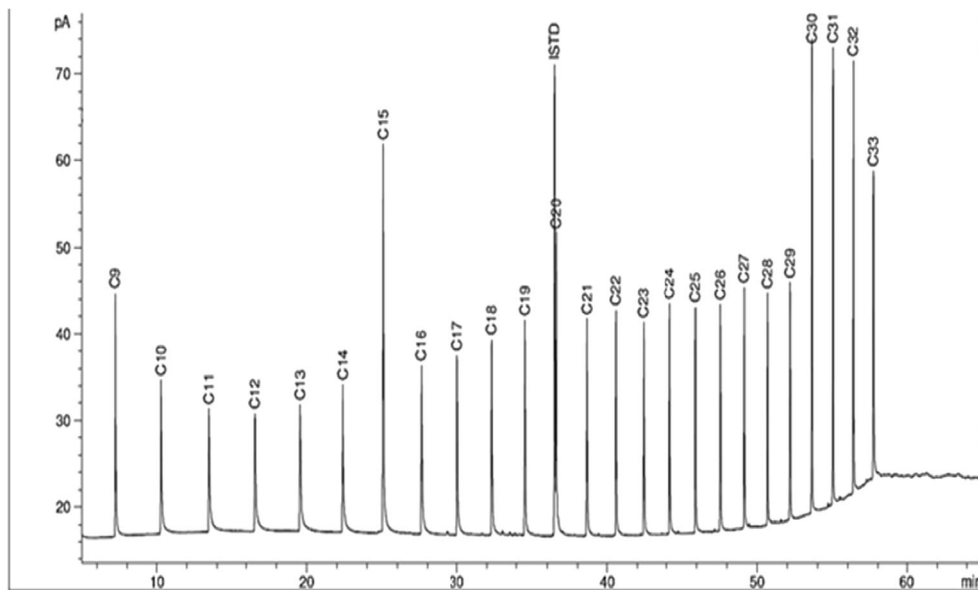
Validation of GC-FID and GC-MS for quantitative assessment of AHs and PAHs, respectively

External standard multipoint calibration was used to construct the calibration curves for each PAH and n-alkane. The linearity range of the calibration curves was achieved by the evaluation of the analyzed compounds. Unresolved PAH

compounds under chromatography conditions were assessed in pairs (see Fig. 3). The concentration ranges were relevant when compared to the levels normally observed in environmental materials. For the measurement of the total AHs and PAHs, calibration curves obeyed by certified reference mixture were ascertained. Considering this technique of quantification, all standard eluting between C_{10} and C_{33} was presumed to be a mixture of several cyclic, branched-chain, and normal-chain hydrocarbons. Regarding aromatic hydrocarbons, the eluting of all standards between naphthalene and benzo[ghi]perylene was accepted to be a combination of varied non-alkylated and alkylated aromatics, comprised of 2–6 aromatic rings, and cycloalkanes-aromatic composite patterns. In Fig. 2 and Fig. 3, the X is interpreted as the total concentrations of individual hydrocarbons, whereas Y is expressed as the total of the peak areas of individual hydrocarbons. Calibration curves based on five (5) points were established with the linearity ranges 20–100 ng/mL and 100–500 ng/mL for n-alkanes while that of PAHs were in the ranges of 10–50 ng/mL and 50–250 ng/mL from the regression analysis of the peak areas versus injected concentrations (see Supplementary Table S1). F -statistic ($P < 0.05$) was applied to examine the fitness of experimental data to a linear model. At higher concentration values is where linear ranges begin for some compounds. The regression coefficients for GC-FID and GC-MS are higher than 0.99 for all analytes. In analyzing the concentration of the analyte in standard solution, the instrumental limit of detection (LOD) in ng/mL was evaluated as a signal-noise ratio (S/N) of 3. Table S1 shows the summarized results (see Supplementary Table S1).

Recoveries were computed from the increase in the content of n-alkanes of PAHs between the spiked and non-spiked samples and assessed the accuracy of the entire method. The extraction and clean-up protocol was carried out over five (5) replicates for each spiked level. Fig. 4 shows the recoveries of the added compounds at the 100-ng/mL spiked level of n-alkanes and 50-ng/mL spiked level of PAHs. Lower recovery values correspond to the n-alkanes were observed at C_9H_{20} to $C_{33}H_{68}$ while the lower recovery values of PAHs were observed at naphthalene to acenaphthene. These compounds are incompletely lost in the course of evaporation of the solvent extract in the nitrogen stream due to their volatility behavior. For n-alkanes, recoveries that varied from 54.2 to 104.1 % were obtained from the range between C_9H_{20} and $C_{33}H_{68}$, and recoveries that varied from 52.4 to 94.0 % were obtained for PAHs ranged between naphthalene and benzo[ghi]perylene. Analytical procedure precision was represented as relative standard deviations (RSD), and for n-alkanes, it varied from 4.9 to 19.1 in the elution ranges between C_9H_{20} and $C_{33}H_{68}$. That of PAHs varied from 4.1 to 16.6 in the elution ranges between naphthalene and benzo[ghi]perylene. Higher RSD values were observed in the volatile analytes C_9H_{20} (19.1), $C_{10}H_{22}$ (14.9), naphthalene

Fig. 2 GC-FID chromatogram of aliphatic standard solutions. *X*-axis represents retention time/min, while *y*-axis denotes peak area.



(15.4), and acenaphthylene (16.6) which could be attributed to more significant losses in the course of spiking, extraction, and evaporation processes. The results obtained from precision and extraction efficiency with this protocol were similar to results that have been reported for determining PAHs in coastal sediment using Soxhlet extraction (Jaouen-Madoulet et al. 2000). The reproducibility of the extraction and pre-separation steps was acceptable, suggesting that the method is good for the assessment of aliphatic hydrocarbons and polycyclic aromatic hydrocarbons in marine coastal sediments, at a concentration interval below 500 ng/g.

The detection limit (LOD) is the minimum quantity of target analyte that generates a chromatographic peak with a signal/noise ratio (S/N) of 3. On the contrary, the quantification limit (LOQ) is considered as the lowest concentration of an analyte in a sample that can produce a chromatographic peak with a signal/noise ratio (S/N) of 10 under the stated conditions of the test. Before and after the analyte retention time, the baseline peak-to-peak noise (N) was assessed on the chromatogram of a blank sample handled by the analytical technique for a stipulated period. Detection and quantification limits were computed by gradually lessening the concentration of the analyte in the spiked sample (Omorinoye et al.

Fig. 3 GC-MS chromatogram of PAHs standard solutions. *X*-axis represents retention time/min, while *y*-axis denotes peak area.

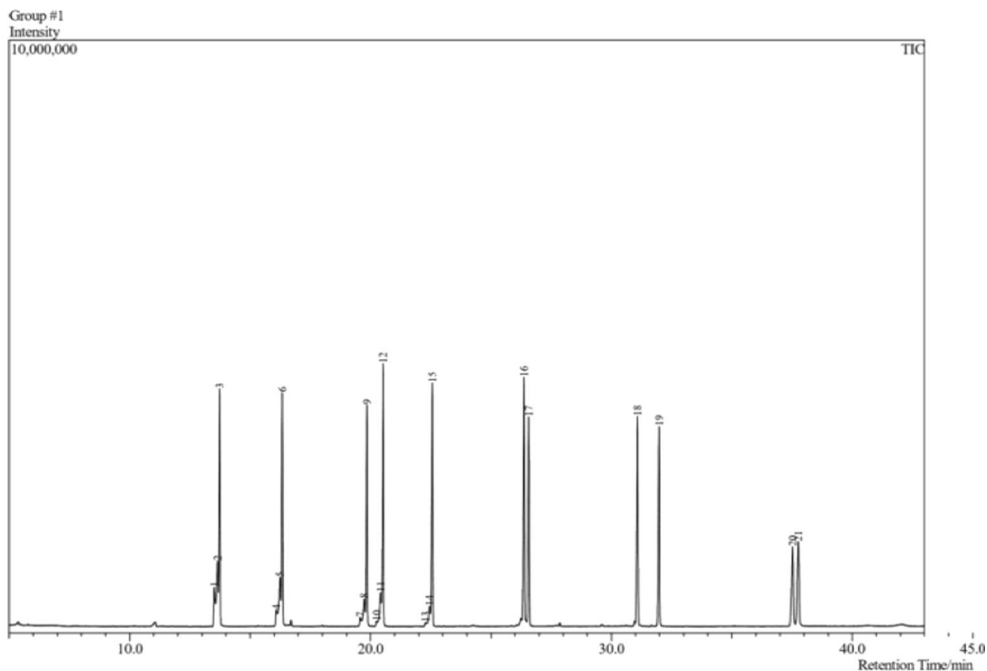
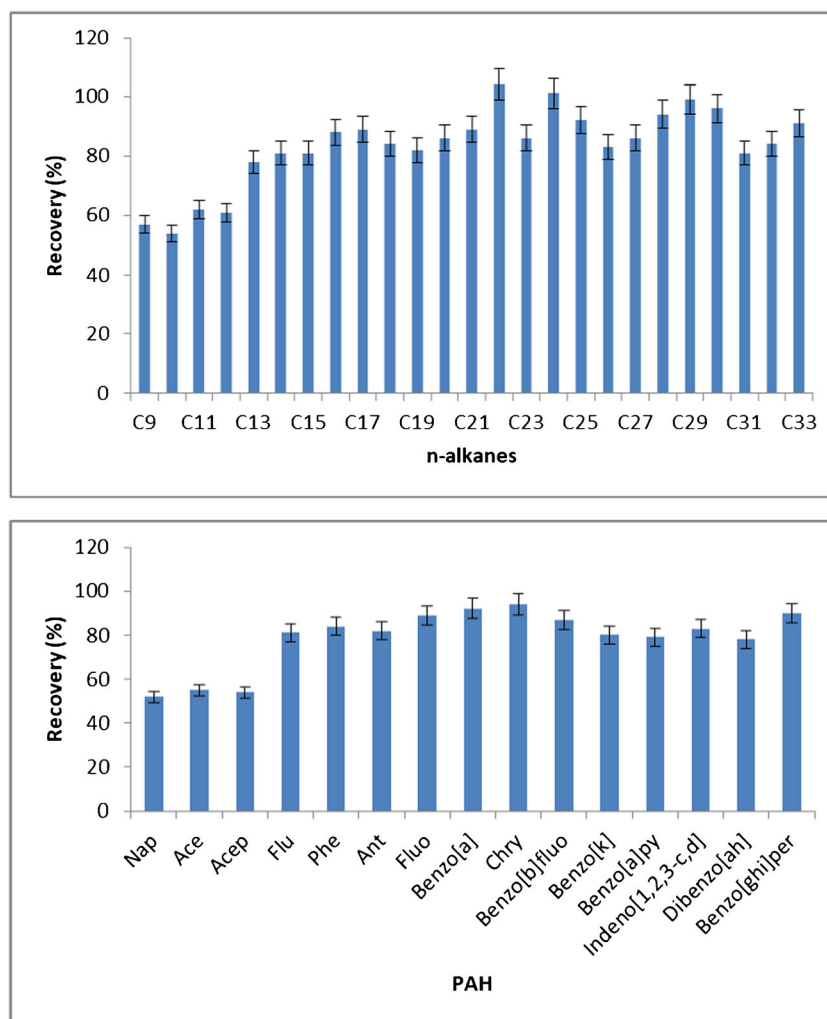


Fig. 4 n-Alkanes (GC-FID analysis) and PAHs (GC-MS analysis) recoveries from fortified coastal sediment (spiked concentration: n-alkanes (100 ng/mL) and PAH (50 ng/mL)). Vertical bars stand for the standard deviation.

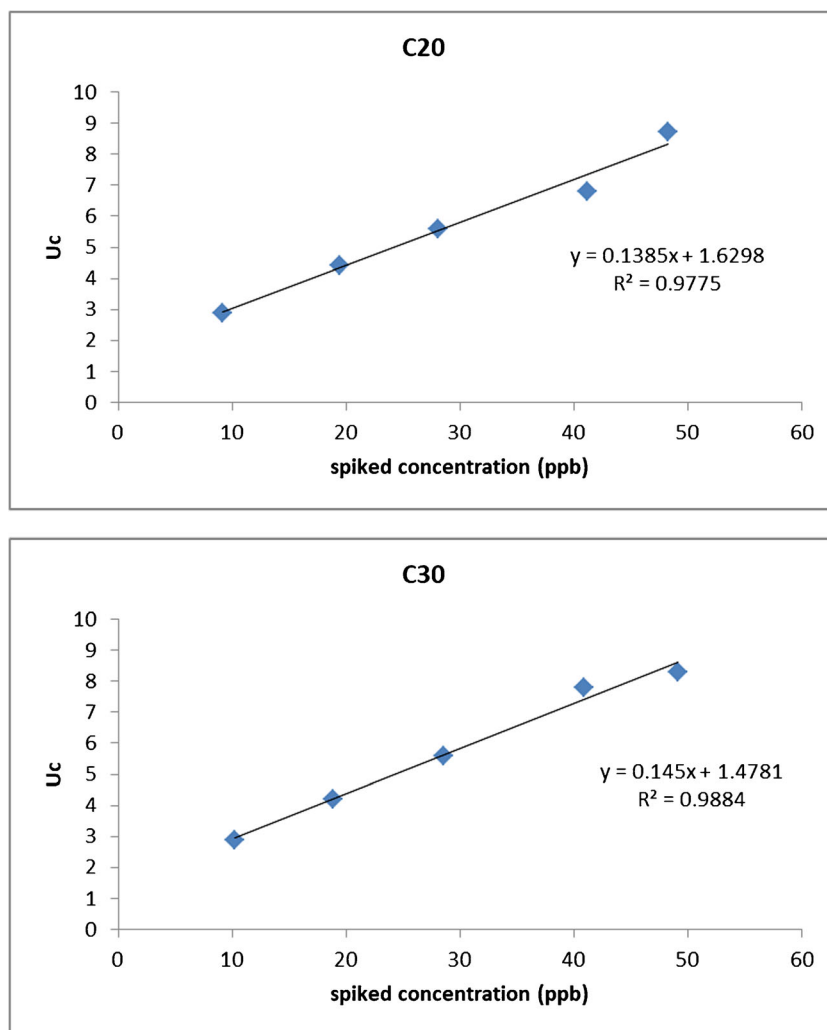


2019a), in a way that GC-FID or GC-MS signals were distinctly detected at the last lowest level of concentration with a signal/noise ratio of three and ten, respectively. Table S2 depicts the summarized results obtained (see Supplementary Table S2). The values of LOD varied from 16.2 to 26.6 ng/g for n-alkanes, and from 17.9 to 26.4 ng/g for PAHs. In regard to LOQ, the values for n-alkanes ranged from 22.9 to 38.2 ng/g, while that of PAHs varied from 26.4 to 35.8 ng/g. Evaporation losses are the main cause of higher values that correspond to analytes.

The uncertainty of a measurement is the doubt that exists about the results of any measurement, which defines the distribution of the values that could fairly be ascribed to the quantity intended to be measured (measurand) (Quantifying the Uncertainty in Analytical Measurement, EURACHEM/CITAC Guide 2000; Asare et al. 2019a; Asare et al. 2019b). The measurement of uncertainty was made as stated by the protocol recommended in the literature (Barwick and Ellinson 1999, 2000). The accuracy and recovery investigations initiated for the validation were organized and accomplished in

such a manner that supplies the data needed to generate a value of the uncertainty of a measurement. The recovery study concentration range obtained was used. Equations S1–S5 are the fundamental equations used for uncertainty evaluation (see Supplementary Equation S1–S5). In connection with spiked compounds which were native congeners in the sediments, Equation S1 is used to determine the uncertainty in the recovery $u(\bar{R})^2$. Contrarily, Equation S2 is used if the standard was added to blank sediments. The uncertainty in the concentration of the spike added to the samples [$u(C_{\text{spike}(i)})$] is evaluated by taking into consideration all the spotted effects operating on these concentration values. The uncertainty obtained from the concentration of the native analyte $u(C_{\text{native}})$ is calculated as s.d (standard deviation) of these compounds' concentration. The combined uncertainty for each spiked level is computed from the s.d of the concentration of the analyte (S_{Cobs}) and $u(\bar{R})^2$ using Equations S3 and S4. Hence, constructed graphs for (U_c) considered in the concentrations in sediments investigated by the analytical technique are

Fig. 5 The link between combined uncertainty (U_c) and concentration for C_{20} and C_{30}



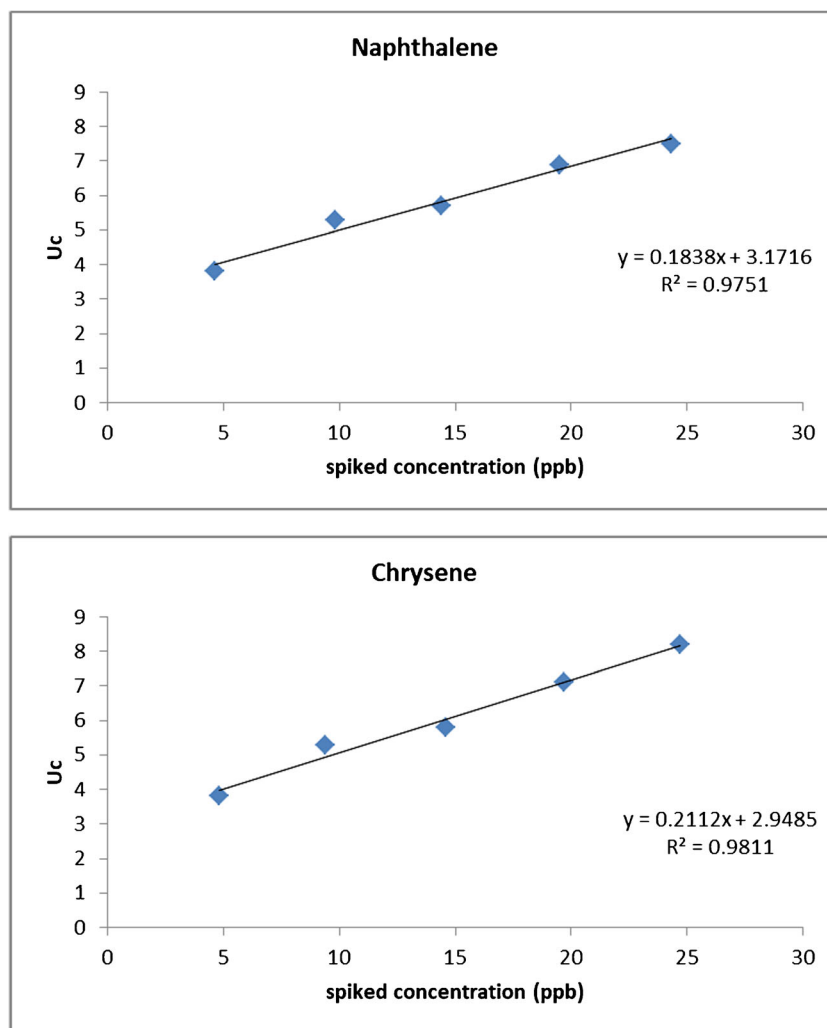
depicted in Fig. 5 and Fig. 6. Besides, the expanded uncertainty (U), was quantified impacting the U_c by a coverage factor (k) as stated in Equation S5 (see supplementary material). This limiting factor defines an interval that is anticipated to include a large fraction of the distribution of values fairly accountable to the measurand (ISO/TS 21748: 2004).

Nature of GC chromatograms detected from selected real sediment samples

Analysis of coastal and estuaries sediments proceeded once the analytical technique was defined and validated. Fig. 7 and Fig. 8 are typical chromatograms of the aliphatic hydrocarbon analyzed by GC-FID and GC-MS chromatogram of polycyclic aromatic hydrocarbon compounds extracted from the coastal sediment sample at stations CZ5 and CZ8, respectively. The most important resolved constituents were characterized by the homologous series of n-alkanes varying in the number of carbon from nC_{14} to nC_{33} for station CZ5 and nC_{10} to nC_{33} for station CZ8 and correlate with only a small

quantity of the total aliphatic hydrocarbons. The polycyclic aromatic hydrocarbon compounds detected from station CZ5 are Naph, Acthy, Ace, Fl, Phe, and BaP benzo[a], whereas PAH compounds detected from sample station CZ8 include Naph, Acthy, Ace, Fl, Phe, Ant, BaA, Chry, and BaP. The preponderance of the compounds available in this portion is molecules that cannot be resolved by GC capillary columns and are named unresolved complex mixture (UCM) (Damas et al. 2009). Fig. 7 and Fig. 8 explain the appearance of the unresolved complex mixture in the gas chromatography trace as a hump region between the solvent baseline and the curve characterizing the base of resolvable peaks. It is made up of a composite mixture of branched alicyclic hydrocarbons concerning GC-FID chromatogram (Fig. 7) and other aromatic compounds in regard to GC-MS chromatogram (Fig. 8) (Peters et al. 2005) and has a widely known linkage to biodegraded petroleum remains (Grossi et al. 2002; Wang and Fingas 1995; Wang et al. 1998). An 85-m/z fragmentogram was used to come up with upstanding and comprehensive compositional information concerning n-

Fig. 6 The link between combined uncertainty (U_c) and concentration for naphthalene, and chrysene.



alkanes constituents with minimal intrusion from other aliphatic hydrocarbons. The n-alkanes with lower molecular weight were absent in some of the sample stations. The representative sediment sample's quantitative results analyzed are shown in Table 1. The possible motive is that organic compounds with LMW are more willingly volatilized to the atmosphere, while on the contrary, the HMW constituents can be anticipated to partition onto the phase of the particulate and undergo sedimentation. However, due to further losses in the course of the evaporation process, volatile analytes can lessen their concentration to non-detected levels. The concentration of each n-alkane was taken into consideration when quantifying the total n-alkane concentration in samples. Fig. 8 (CZ5PAH and CZ8PAH) depicts the profiles of chromatograms of polycyclic aromatic fractions that emerge as an envelope with limited resolved peaks which is representative of aromatic fractions attributed to highly weathered sources (Charrie-Duhaut et al. 2000; Damas et al. 2009). The 2–3 aromatic ring compounds were under these highly weathered conditions and the remaining composition was at a level that

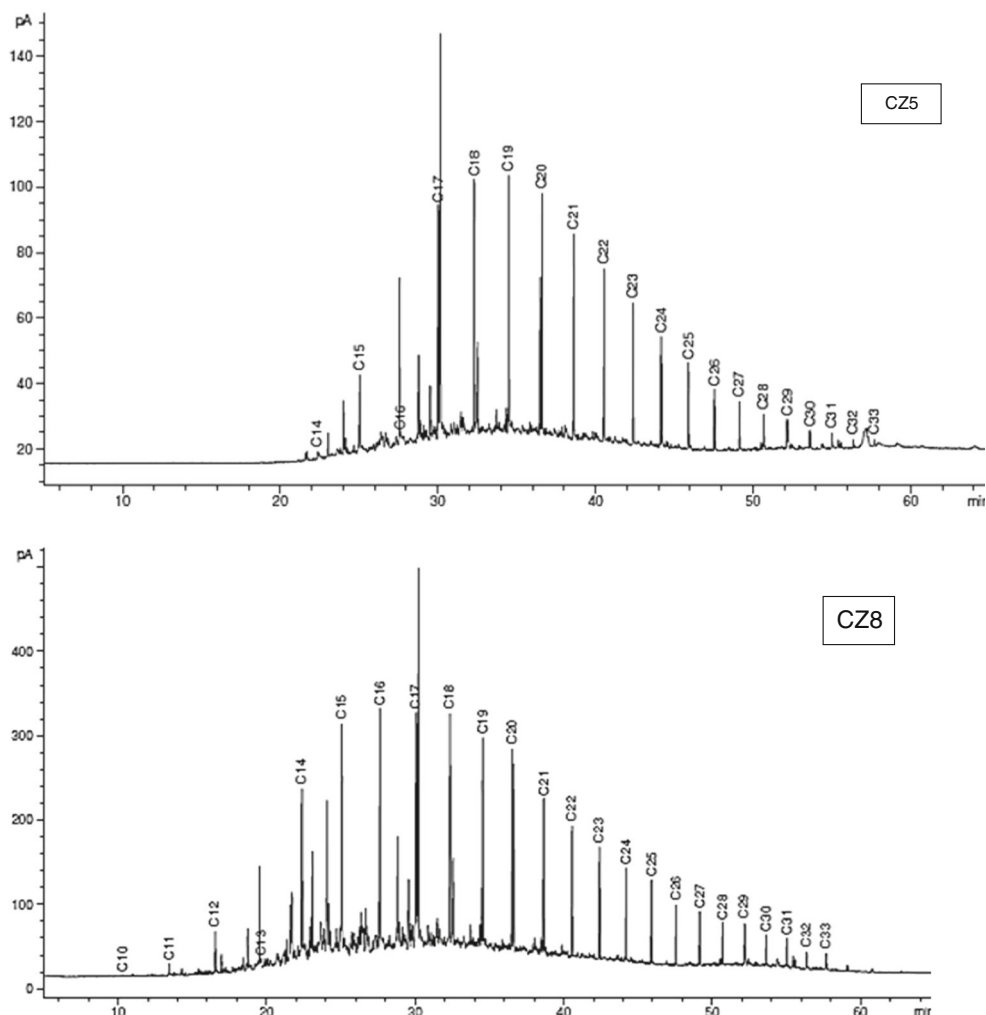
the GC-MS and the full scan analyses were insufficient for a comprehensive assessment. Because of that, few individual polycyclic aromatic compounds were able to evaluate.

Assessment and characterization of aliphatic hydrocarbons (AHs)

Table 1 shows the concentration of n-alkanes evaluated in representative coastal and selected estuaries sediment samples of Sarawak while Table 2 depicts the other related parameters.

Total aliphatic hydrocarbon concentrations (C_9 – C_{33}) ranged from 96.63 to 367.28 ng/g dw (see Table 1). The station with the highest total n-alkane concentration was recorded at the coastal location CZ2, whereas the lowest total n-alkanes content was observed at the coastal station CZ10. In regard to the estuaries, an estuary station CZ1 recorded higher total aliphatic hydrocarbon concentrations as compared to estuary stations CZ4, CZ7, and CZ10. LMW and HMW n-alkane which are used as a source identifier and other related parameters are shown in Table 2. LMW and HMW ranged

Fig. 7 Characteristic gas chromatogram of aliphatic hydrocarbon (n-alkanes) fractions extracted from coastal sediments in locations CZ5 and CZ8. X-axis represents retention time/min, while y-axis denotes peak area.

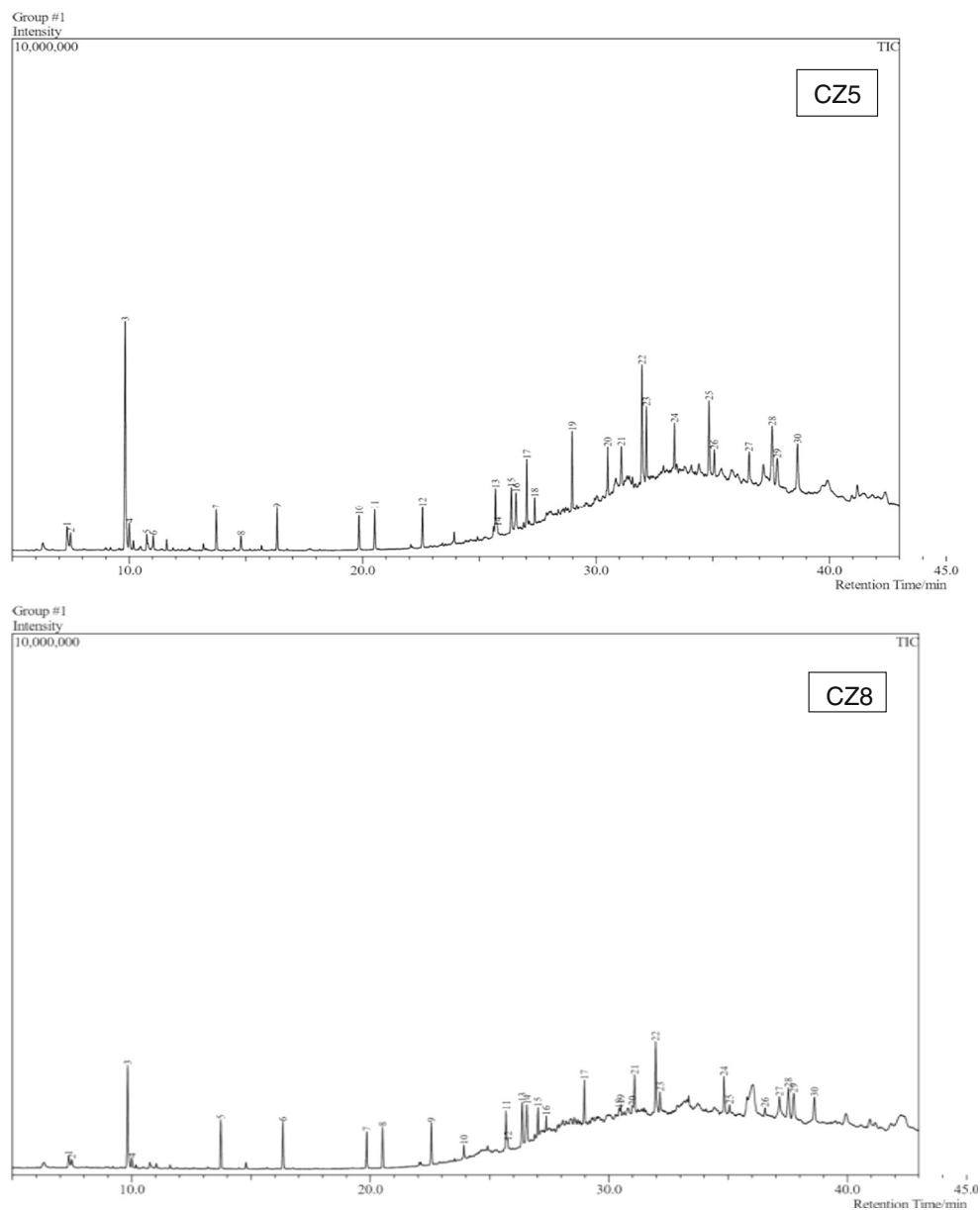


from 29.90 to 87.69 ng/g dw and 45.10 to 291.80 ng/g dw, respectively. Sample station CZ1 recorded the highest value of LMW (i.e., 87.69 ng/g dw), while the lowest value of LMW was reported at station CZ5 (i.e., 29.90 ng/g dw). Besides, the highest value of HMW was observed at station CZ2 (i.e., 291.80 ng/g dw) whereas station CZ10 recorded the lowest value of HMW (i.e., 45.10 ng/g dw). The low molecular weight to high molecular weight ratios (LMW/HMW) varied from 0.26 to 1.14 at stations CZ2 and CZ10, respectively. Slightly higher LMW/HMW ratio at station CZ10 (1.14), CZ6 (0.94), CZ7 (0.85), CZ8 (0.81), CZ9 (0.72), CZ1 (0.67), and CZ1 (0.67) could be as a result of fresh oil inputs, whereas low LMW/HMW ratio at CZ2 (0.26), CZ4 (0.38), and CZ5 (0.31) could be influenced by sedimentary bacteria, higher plants, and marine animals inputs (Sakari et al. 2008). Thus, the differences in normal alkane concentration may relate to the natural inputs for example emergent terrestrial plants, submerged/floating macrophytes, and microbial activity; and anthropogenic sources such as shipping activities, industrial discharges, and sewage (El Nemr et al. 2013). In the GC-FID chromatograms, a representative example of

which is exhibited in Fig. 7, there is a vivid resolution of all aliphatic hydrocarbons and enrichment of longer chain normal alkanes (LHC, C₂₅ to C₃₃) than the shorter chain normal alkanes (SHC, C₁₀–C₂₄).

Figure 9 shows the sum of hydrocarbons of the two ranges (Σ LHC and Σ SHC). In regard to Σ SHC, station CZ2 recorded the highest value (179.18 ng/g dw), whereas the lowest Σ SHC value was observed at station CZ9 (64.9 ng/g dw). The order of increasing Σ SHC value is as follows: CZ9 < CZ5 < CZ10 < CZ8 < CZ7 < CZ6 < CZ4 < CZ3 < CZ1 < CZ2. Considering Σ LHC, the highest value was recorded at station CZ2 (188.1 ng/g dw), while station CZ10 recorded the lowest value of 21.05 ng/g. The order of increasing Σ LHC value is as follows: CZ10 < CZ8 < CZ9 < CZ7 < CZ5 < CZ6 < CZ3 < CZ1 < CZ4 < CZ2. To evaluate the dominant higher plant and/or phytoplankton-derived macrophyte-derived organic matter in the sediments, the LHC/SHC ratios were computed and had values varying from 0.28 to 1.08 (see Table 2) (El Nemr et al. 2013). The ratios obtained suggested that the stations are dominated by higher plants and/or macrophyte waxes (Commendatore et al. 2000). Petroleum may be the

Fig. 8 Characteristic gas chromatogram of polycyclic aromatic hydrocarbon fractions extracted from coastal sediments in locations CZ5 and CZ8. X-axis represents retention time/min, while y-axis denotes peak area.



anthropogenic source, also recycled organic matter of several sources for example discharges from treatment plants, erosion of soil organic matter by rains, and sewage may be a contributing factor. Bacteria, algae, plankton, marine animals, and terrestrial vascular plants which are an example of biogenic sources may also be the reason (Commendatore et al. 2000). The source identification of pollution caused by aliphatic hydrocarbon was determined using the ratio of odd to even carbon which is mostly referred to as the Carbon Preference Index (CPI). Odd number carbon is usually associated with natural origins, while even number carbon is accredited to anthropogenic origins. Jeng (2006) opined that CPI values of 5–10 are attributed to terrestrial higher plant waxes. According to Hedges and Prahl (1993), higher values of CPI found in soil or sediment indicate a greater influence on

vascular plants. Inputs from recycled organic matter, petroleum, and/or microorganisms give CPI values close to unity (Kennicutt et al. 1987; Aly Salem et al. 2014). In this present study, there were no significant differences between stations in terms of CPI values for all stations. The CPI values ranged from 0.80 to 1.54 which throwbacks that all sediment samples are likely polluted with petrogenic hydrocarbons dependent on CPI values less than 3 suggesting oiled sediments (Aly Salem et al. 2014). When the ratio of natural n-alkanes (NAR) is close to zero then the source of the hydrocarbon is obtained from petroleum and crude oils and close to unity means the source is from marine plants or higher terrestrial plants. The values of natural n-alkanes ratios of the current study varied from -0.35 to 0.23. The ratio of terrigenous to aquatic (TAR) values ranged from 0.25 to 1.96. The highest

Table 1 Content of n-alkanes determined in representative coastal and selected estuaries sediment samples.

n-Alkane compounds	Sample									
	CZ1	CZ2	CZ3	CZ4	CZ5	CZ6	CZ7	CZ8	CZ9	CZ10
	ng/g dw									
C ₁₀ H ₂₂	n.d ^x	n.d	n.d	n.d	n.d	n.d	n.d	0.15	0.47	n.d
C ₁₁ H ₂₄	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.58	0.14	n.d
C ₁₂ H ₂₆	n.d	n.d	n.d	n.d	n.d	n.d	n.d	1.03	0.62	n.d
C ₁₃ H ₂₈	3.12	n.d	7.21	1.36	n.d	5.01	n.d	2.75	1.51	n.d
C ₁₄ H ₃₀	2.49	4.22	0.87	2.33	0.15	4.90	n.d	2.05	2.08	1.52
C ₁₅ H ₃₂	5.32	3.96	10.2	3.71	1.32	7.36	6.20	4.24	2.32	1.96
C ₁₆ H ₃₄	12.12	9.07	6.41	8.01	1.02	2.91	7.74	6.02	3.06	3.61
C ₁₇ H ₃₆	17.03	13.2	9.71	7.87	4.11	9.36	20.4	8.08	4.08	2.81
C ₁₈ H ₃₈	19.88	17.7	9.98	11.3	9.05	16.5	10.2	19.2	13.1	16.2
C ₁₉ H ₄₀	24.02	23.9	17.6	14.8	13.1	15.2	13.7	11.5	16.4	16.4
C ₂₀ H ₄₂	3.71	3.43	5.14	4.05	1.15	14.9	5.19	2.06	2.04	9.03
C ₂₁ H ₄₄	18.15	36.1	21.2	10.9	4.01	8.13	16.2	5.33	1.17	13.0
C ₂₂ H ₄₆	14.62	27.9	13.1	7.11	7.81	3.06	1.04	14.9	6.76	2.34
C ₂₃ H ₄₈	9.43	16.6	3.51	12.4	16.9	0.54	2.81	3.22	2.11	7.18
C ₂₄ H ₅₀	7.19	23.1	8.98	9.03	7.94	1.89	5.53	6.03	9.04	1.53
C ₂₅ H ₅₂	8.06	17.9	2.05	5.21	3.07	6.23	6.01	4.51	11.0	6.41
C ₂₆ H ₅₄	11.23	10.1	7.36	7.83	16.9	9.04	3.63	3.48	3.06	3.03
C ₂₇ H ₅₆	24.62	37.2	12.0	18.4	6.03	4.59	6.24	6.11	6.14	1.03
C ₂₈ H ₅₈	12.20	13.0	16.4	6.27	2.11	10.2	10.4	4.90	5.10	0.81
C ₂₉ H ₆₀	6.61	15.7	22.6	19.6	5.51	2.78	6.02	7.03	3.24	0.23
C ₃₀ H ₆₂	14.01	31.0	6.31	11.7	7.32	8.31	7.21	4.51	4.08	2.71
C ₃₁ H ₆₄	5.66	27.4	4.21	9.26	8.03	10.4	3.17	2.11	4.25	4.02
C ₃₂ H ₆₆	n.d	25.7	7.81	13.1	5.23	9.11	5.05	6.04	5.01	1.34
C ₃₃ H ₆₈	n.d	10.1	2.75	9.01	4.71	7.03	1.35	3.10	3.16	1.47
ySum of C ₉ to C ₃₃	219.47	367.28	195.40	193.25	125.47	157.45	138.09	128.93	109.94	96.63

^x n.d, non-detected^y Sum of concentration of n-alkanes from C₉ to C₃₃

TAR value (1.96) was recorded at station CZ2 and according to Jeng and Huh (2006), this could be influenced by n-alkanes with short-chain which are more susceptible to degradation as compared to longer-chain types. Another parameter to estimate the sources of aliphatic hydrocarbons is an n-alkane proxy (*Paq*). From Table 4, the *Paq* varied from 0.21 to 0.73 and on the report of Ficken et al. (2000), *Paq* values between 0.01 and 0.23 are ascribed to waxes from the terrestrial plant, while *Paq* values between 0.48 and 0.94 are attributed to submerged/floating species of macrophytes. Overall, the outcomes obtained from the current study indicated the contribution of both phytoplankton-derived organic carbon and higher plant/macrophyte waxes derived (EL Nemr and Abd-Allah 2003; El Nemr et al. 2013). The important parameter for the identification of environmental variations for a particulate ecosystem is the average carbon chain length (ACL). A continual value for average carbon chain length suggests that little ecological variations are happening in the

system (Aly Salem et al. 2014). Colombo et al. (1989) opined that biogenic samples contain higher (> 50) values of n-alkanes/nC₁₆ ratio, whereas petrogenic samples contain lower (< 15) n-alkanes/nC₁₆ ratio. From Table 2, the values of the n-alkanes/nC₁₆ ratio suggested a mixture of origins comprising petrogenic and biogenic.

Assessment and characterization of polycyclic aromatic hydrocarbons (PAHs)

The contents of polycyclic aromatic hydrocarbon and other associated parameters are headlined in Table 3. There were no significant differences among the studied locations of the concentrations of Σ PAHs in surface sediments. The contents of total PAHs were in the range of 12.34–21.20 ng/g dw, with an average value of 16.10 ± 2.06 ng/g dw. Samples from station CZ8 reported the highest concentration of Σ PAHs (21.20 ng/g dw), whereas the lowest concentration of

Table 2 Concentrations of n-alkanes (ng/g) and computed distribution indexes in surface sediments of coastal and selected estuaries of Sarawak.

Station	LMW ^a	HMW ^b	%LMW	%HMW	LMW/HMW ^c	CPI _d	NAR	TAR	Paq	CPI _{SHC}	CPI _{LHC}	LHC/SHC	ACL _{LHC}	n-Alkanes/C ₁₆
CZ1	87.69	131.78	39.96	60.04	0.67	1.11	0.21	0.80	0.59	1.29	1.20	0.63	27.44	18.12
CZ2	75.48	291.80	20.55	79.45	0.26	1.21	0.13	1.96	0.45	1.16	1.36	1.05	28.53	40.49
CZ3	67.12	128.28	34.35	65.65	0.52	1.04	0.12	1.04	0.21	1.43	1.15	0.72	29.11	30.48
CZ4	53.43	139.82	27.65	72.35	0.38	1.43	0.21	1.79	0.38	1.26	1.58	1.08	28.95	24.13
CZ5	29.90	95.57	23.83	76.17	0.31	0.78	0.08	1.06	0.60	1.46	0.87	0.86	29.39	123.01
CZ6	76.14	81.31	48.36	51.64	0.94	0.83	-0.35	0.56	0.34	1.03	0.85	0.75	29.48	54.11
CZ7	63.43	74.66	45.93	54.07	0.85	0.80	0.18	0.38	0.49	2.00	0.87	0.55	27.91	17.84
CZ8	57.66	71.27	44.72	54.90	0.81	1.07	0.09	0.64	0.49	0.67	1.21	0.48	28.40	21.42
CZ9	45.82	64.12	41.68	53.32	0.72	1.34	0.12	0.60	0.56	0.77	1.61	0.69	27.74	35.93
CZ10	51.53	45.10	53.33	46.67	1.14	1.54	0.23	0.25	0.73	1.26	1.67	0.28	27.95	26.77

^a Sum of low molecular weight hydrocarbon from C₁₀ to C₂₀

^b Sum of high molecular weight from aliphatic hydrocarbons C₂₁ to C₃₃

^c Ratio of LMW alkanes to HMW alkanes

^d Carbon Preference Index (CPI) = $\frac{1}{2} \left(\frac{nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33}}{nC_{24} + nC_{26} + nC_{28} + nC_{30} + nC_{32}} + \frac{nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33}}{nC_{24} + nC_{26} + nC_{28} + nC_{30} + nC_{32}} \right)$

^e Average Carbon Length of LHC (ACL_{LHC}) = $\frac{25(nC_{25}) + 27(nC_{27}) + 29(nC_{29}) + 31(nC_{31}) + 33(nC_{33})}{nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33}}$

^f Natural n-alkanes ratio (NAR) = $\frac{[\sum n\text{-alkanes}(C_{19}-C_{32}) - 2\sum \text{even } n\text{-alkanes}(C_{20}-C_{32})]}{\sum n\text{-alkanes}(C_{19}-C_{32})}$

^g Terrigenous / Aquatic ratio (TAR) = $\frac{nC_{27} + nC_{29} + nC_{31}}{nC_{15} + nC_{17} + nC_{19}}$

^h Ficken et al. (2002) formulated n-alkane proxy (Paq): Paq = $\frac{(C_{23} + C_{25})}{(C_{23} + C_{25} + C_{29} + C_{31})}$

∑PAHs was observed in sediments collected from station CZ3 (12.34 ng/g dw). The order of increasing ∑PAH contents among researched stations is as follows: CZ3 < CZ2 < CZ6 < CZ1 < CZ7 < CZ4 < CZ9 < CZ10 < CZ5 < CZ8. The discrepancy in PAH status along the experimented sediments could be attributed to the different origins of discharged waters, fuel combustion emissions, and closeness to human activities. Furthermore, Table 4 depicts some published studies reporting PAHs in sediments collected from other seas or

ivers. The total PAH concentrations of the coastal and selected estuaries detected in this study were comparatively smaller than the selected areas of the world. For instance, in a study of PAH contents in sediments collected from the Red Sea, Egypt, by Aly Salem et al. (2014), the total contents of PAH range from 0.74 to 436.91 ng/g with a mean value of 93.49 ng/g. Also, research conducted by Omorinoye et al. (2019b) to determine PAH concentrations in surface sediments from Sadong River, Sarawak, Malaysia, indicated higher PAH

Fig. 9 sum of n-alkanes of the two ranges (∑LHC and ∑SHC) at all sample stations

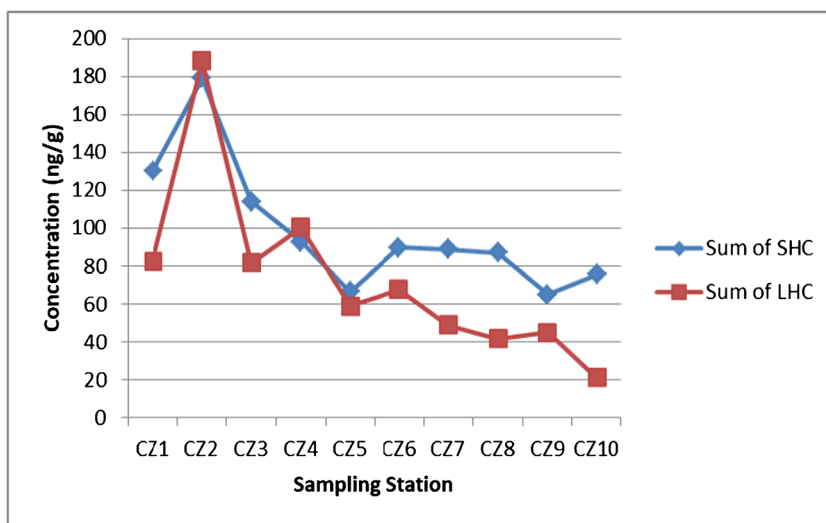


Table 3 Concentration of polycyclic aromatic hydrocarbons (ng/g dw) assessed in representative coastal and selected estuaries sediment samples of Sarawak

PAHs	Station									
	CZ1	CZ2	CZ3	CZ4	CZ5	CZ6	CZ7	CZ8	CZ9	CZ10
Naph	2.79	0.77	1.43	0.94	3.44	1.06	2.06	1.04	3.03	1.19
Acthy	1.43	2.91	0.73	n.d	n.d	1.93	3.49	3.91	2.16	0.84
Ace	2.21	n.d	1.21	4.01	1.06	3.41	n.d	1.28	1.48	2.04
Fl	n.d	n.d	2.17	0.11	3.21	0.64	4.33	3.96	n.d	1.31
Phe	2.05	1.57	1.04	3.42	1.26	2.82	n.d	2.71	n.d	0.51
Ant	n.d	1.04	1.22	n.d	3.37	n.d	n.d	1.06	1.04	n.d
Flu	n.d	3.21	n.d	n.d	n.d	n.d	2.51	n.d	n.d	n.d
Pyr	2.61	n.d	n.d	1.28	n.d	n.d	n.d	n.d	2.09	n.d
BaA	n.d	1.66	1.02	1.15	4.01	1.22	2.68	3.03	1.41	1.52
Chry	3.31	n.d	2.51	2.09	0.63	0.88	0.42	2.46	n.d	2.21
BbF	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
BkF	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	3.31	3.26
BaP	1.03	2.07	1.21	3.96	1.22	1.56	n.d	1.72	n.d	4.66
InP	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
DBA	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	2.35	n.d
BghiP	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Σ PAHs	15.43	13.23	12.54	16.96	18.20	13.52	15.49	21.20	16.87	17.54
Σ PAH _{CARC}	4.24	3.73	4.74	7.20	5.86	3.66	3.10	7.21	4.72	11.65
% CARC	27.45	28.19	37.80	42.45	32.20	27.07	20.01	34.01	27.98	66.42
TEQ _{CARC}	1.03331	2.2360	1.3145	4.0771	1.6216	1.6829	0.2684	2.0255	2.8220	5.1402
BaPE	1.03	2.17	1.27	4.03	1.46	1.63	0.16	1.90	0.46	4.98

concentrations (i.e., 18.21–184.25 ug/g) as compared to this current study (see Table 4 for more details). Nevertheless, the relative contamination level of PAHs has been classified into four groups by Baumard et al. (1998a): (i) low, 0–100 ng/g; (ii) moderate, 100–1000 ng/g; (iii) high, 1000–5000 ng/g; and (iv) very high, more than 5000 ng/g. Based on the above classification, all the levels of PAHs in all stations studied were low.

Table 5 shows the total of individual PAH compounds analyzed in all locations and their number of aromatic rings, while Table S3 (see Supplementary Table S3) and Fig. 10 depict the percentage distribution of PAHs in all stations depending on the number of aromatic rings.

Stout et al. (2004) opined that PAH primary sources in the aquatic environment originate primarily from the sources of pyrolytic or petrogenic. Baumard et al. (1998a) and Aly Salem et al. (2014) reported that pyrolytic PAHs obtained from combustion have four or more rings, whereas petrogenic PAHs obtained from petroleum have less than four aromatic rings. To differentiate between pyrolytic and petrogenic PAH sources, the estimated ratio of 2–3 rings to 4–6 rings is used in this study (De Luca et al. 2005). Regarding studied settings, stations CZ2, CZ9, and CZ10 Σ LPAH/ Σ HPAH ratios were <

1, which suggest that they are from pyrogenic origins, while stations CZ2, CZ3, CZ4, CZ5, CZ6, CZ7, and CZ8 Σ LPAH/ Σ HPAH ratios were > 1, which indicate that they were obtained from petrogenic origins (see Supplementary Table S3, Fig. 10 and Table 6).

The main ratios to investigate the pyrogenic or petrogenic sources of polycyclic aromatic hydrocarbons in sediments are (i) Phe/Ant ratio by Aly Salem et al. (2014) or according to Baumard et al. (1998a, b), Soclo et al. (2000), Magi et al. (2002), Qiao et al. (2006), and Aly Salem et al. (2014), Ant/(Phe + Ant), ratios disclose whether the sediment is primarily polluted by inputs of petrogenic or pyrogenic. The thermodynamically more stable behavior of Phe and its preponderance over Ant suggests that the PAHs in sediment samples were primarily attributable to the activities of petrogenesis. The value of the Phe/Ant ratio is normally high for petroleum products. Baumard et al. (1998a) and Qiao et al. (2006) reported that if the ratio of Phe and Ant is greater than 10 or Ant/(Phe + Ant) is higher than 0.1, it generally shows that the source of the PAH is from pyrolytic inputs. It can be observed from Table 6 that the Phe/Ant and Ant/(Phe + Ant) ratios in all investigated stations were less than 10 and greater than 0.1, respectively. Based on the study by Chen and Chen (2011),

Table 4 Comparison of PAH contents in sediments from the coastal and selected estuaries of Sarawak with those from different coastal and estuaries of the world.

Location	Range	Mean	References
Coastal (CZ2, 3, 5, 6, 8, and 9), Rambungan estuary (CZ1), Sibul estuary (CZ4), Salak estuary (CZ7), Santubong estuary (CZ10), Sarawak, Malaysia	12.34–21.20 ng/g	16.10 ± 2.06 ng/g	This study
<i>Africa</i>			
Red sea, Egypt	0.74–436.91 ng/g	93.49 ng/g	Aly Salem et al. 2014
Suef Gulf, Egypt	18.99–97.19 ng/g	45.51 ng/g	
Aqaba Gulf, Egypt	6.86–100.05 ng/g	40.998 ng/g	
Buffalo river estuary, South Africa	1107–22,310 µg/L		Adeniji et al. 2019b
Algoa Bay, South Africa	1.17–10.47 mg/kg		Adeniji et al. 2019a
Lake Victoria, Uganda	44.2–80.2 ng/g		Kerebba et al. 2017
River Sasa, Nigeria	777.68–2431.39 ng/g		Adekunle et al. 2020
<i>Asia</i>			
Sadong River, Sarawak, Malaysia	18.21–184.25 ug/g		Omorinoye et al. 2019b
Langkawi Island, Malaysia	869–1637 ng/g	1167 ng/g	Nasher et al. 2013
Zhanjiang Bay, China	41.96–933.90 ng/g	315.98 ng/g	Huang et al. 2012
Zhanjiang Bay, China	22.65–79.76 ng/g		Zhu 2007
Deep Bay, China	184.1–581 ng/g	353.8 ng/g	Qiu et al. 2007
Kyeonggi Bay, Korea	9.1–1400 ng/g	120 ng/g	Kim et al. 1999
Hsin-ta Harbour, Taiwan	1156–3382 ng/g		Fang et al. 2003
<i>Europe</i>			
Santander Bay, Spain	20–344,600 ng/g	49079.40 ng/g	Viguri et al. 2002
Aquitaine Bay, France	3.5–853 ng/g	256 ng/g	Soclo et al. 2000
Coast of Porto Region, Portugal	51.98–54.79 µg/kg dw		Rocha et al. 2011
Douro River estuary, Portugal	58.98–156.45 µg/kg dw		Rocha et al. 2011
<i>America</i>			
Narragansett Bay, USA	569–216,000 ng/g	21100 ng/g	Hartmann et al. 2004
Todos Santos Bay, Mexico	7.6–813 ng/g	96 ng/g	Macias-Zamora et al. 2002
Boston Harbour, USA	7266–358,092 ng/g		Wang et al. 2001

Table 5 Sum of individual PAH compounds analyzed in all stations with its abbreviation and number of aromatic rings

Compounds	Abbreviations	Number of cycles	∑	%
Naphthalene	Naph	C2	17.75	11.00
Acenaphthylene	Acthy	C2	17.40	10.80
Acenaphthene	Ace	C2	16.70	10.40
Fluorene	Fl	C2	15.73	9.77
Phenanthrene	Phe	C3	15.38	9.55
Anthracene	Ant	C3	7.73	4.80
Fluorathene	Flu	C3	5.72	3.55
Pyrene	Pyr	C4	5.98	3.70
Benzo(a)anthracene	BaA	C4	17.70	11.00
Chrysene	Chr	C4	14.51	9.01
Benzo(b)fluoranthene	BbF	C4	0	0
Benzo(k)fluoranthene	BkF	C4	6.57	4.08
Benzo(a)pyrene	BaP	C5	17.43	10.80
Indeno[1,2,3-cd]pyrene	InP	C5	0	0
Dibenzo[a,h]anthracene	DBA	C5	2.35	1.46
Benzo(ghi)perylene	BghiP	C6	0	0

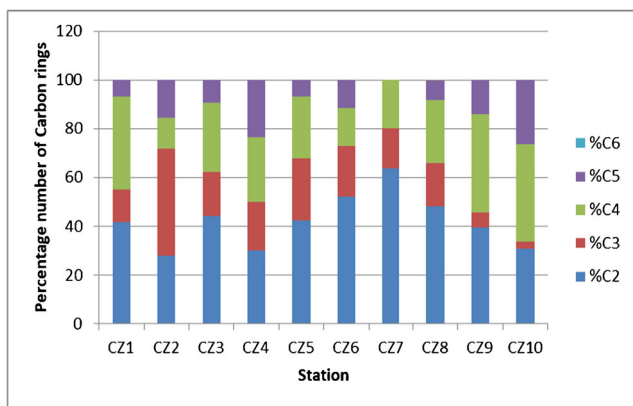


Fig. 10 Polycyclic aromatic hydrocarbons source characterization in sediment

this indicates that the PAH source could be attributed to the activities of combustion and the sediment is primarily polluted by petrogenic inputs. In regard to the studies conducted by Guinan et al. (2001) and Li et al. (2006), other important indicators for assessing the source of PAH contamination in sediments are the Flu/Pyr and Flu/(Flu + Pyr) ratios. Surprisingly, all the studied stations showed no detection of either Flu or Pyr or both; therefore, the evaluation of Flu/Pyr and Flu/(Flu + Pyr) ratios was not successful. Besides, BaA/(BaA +Phe) ratio was performed and it was found that the values of all the studied stations were < 1 indicating that the source is from petroleum. The sum of major combustion-specific compounds (Σ COMB) varied from 3.66 to 11.65 ng/g dw, and ratios of Σ COMB to the sum of PAHs varied from 0.27 to 0.66. El Nemr et al. (2013) reported that an extensive combustion activity affected the content of PAHs in the studied settings when the Σ COMB/ Σ PAH values are higher. As headlined in Table 6, Σ COMB/ Σ PAH values were higher indicating extensive combustion activities.

To examine the biological impacts of PAHs of coastal and selected estuaries of Sarawak, the effect range-medium (ERM) and effect range-low (ERL) were compared to the mean concentration of PAH (Li et al. 2012; Aly Salem et al. 2014). These two values describe three concentration ranges for a specific chemical. When the PAH content < ERL, it suggests that biological effects are unusual, when the PAH concentration \geq ERL but < ERM, it suggests that adverse biological impacts would happen sometimes, while PAH concentration \geq ERM indicates that adverse biological effects would occur frequently. In regard to Fig. S1 (see Supplementary Fig. S1), the green-colored graph represents the mean concentration of PAH detected in this current study, the blue-colored graph denotes effect range-low (ERL), and the red-colored graph signifies the effect range-medium (ERM). From Table 7 and Fig. S1, the three ranges of chemical concentrations, unfavorable biological impacts were anticipated rarely in all stations because the levels of PAH chemicals detected were below effect range-low.

Qiao et al. (2006) reported that some PAHs possessed carcinogenicity characteristic and their availability in the environment are of high concern. In regard to the study by Wang et al. (2009), to quantitatively evaluate the potential health risk of PAH, the BaP equivalent (BaPE) is used. Thus, the BaPE was derived using equation 1 (Liu et al. 2009a):

$$BaPE = 0.06(BaA) + 0.07(BbF) + 0.07(BkF) + BaP + 0.06(DBA) + 0.08(InP) \tag{1}$$

From Table 3, the calculated values of BaPE for all sediment samples ranged from 0.16 to 4.98 ng/g dw. The maximum value of BaPE was reported at Santubong estuary (CZ10),

Table 6 PAHs isomeric ratio in sediment from the coastal and selected estuaries of Sarawak

Station	TH	Σ COMBa	Σ COMB/ Σ PAH	Σ LPAHb	Σ HPAHc	Σ LPAH/ Σ HPAH	Phe/Ant	Ant/(Phe+Ant)	Flu/Pyr	Flu/(Flu+Pyr)	BaA/(BaA +Phe)	Flu/(Flu+Phe)
CZ1	234.90	6.95	0.45	8.48	6.95	1.22	-	-	-	-	-	-
CZ2	380.51	6.94	0.53	6.29	6.94	0.90	1.51	0.40	-	-	0.51	0.67
CZ3	207.94	4.74	0.38	7.80	4.74	1.65	0.85	0.54	-	-	0.50	-
CZ4	210.21	8.48	0.50	8.48	8.48	1.00	-	-	-	-	0.25	-
CZ5	143.67	5.88	0.32	12.32	5.88	2.10	0.37	0.73	-	-	0.76	-
CZ6	170.97	3.66	0.27	9.86	3.66	2.69	-	-	-	-	0.30	-
CZ7	153.58	5.61	0.36	9.88	5.61	1.76	-	-	-	-	-	-
CZ8	150.13	7.21	0.34	13.99	7.21	1.94	2.56	0.28	-	-	0.53	-
CZ9	126.81	6.81	0.40	7.71	9.16	0.84	-	-	-	-	-	-
CZ10	114.17	11.65	0.66	5.89	11.65	0.51	-	-	-	-	0.75	-

^a Σ COMB = Flu + Chry + Pyr + BaA + BbF + BaP + BkF + InP + BghiP

^b Σ LPAH^b = Naph + Achthy + Ace + Fl + Phe + Ant

^c Σ HPAH = Flu + Pyr + BaA + Chry + BbF + BkF + BaP + InP + DBA + BghiP

Table 7 Guidelines values (i.e., ERL and ERM) of PAHs in surface sediments (ng/g dw) (Long et al. 1995; Liu et al., 2009a, b, c; Aly Salem et al. 2014).

	Effect range-low	Effect range-medium	Present study				
			Mean	Minimum	Maximum	>ERL	<ERM
Naph	160.00	2100.00	1.78	0.77	3.03	-	-
Acthy	16.00	500.00	2.18	0	3.91	-	-
Ace	44.00	640.00	2.09	0	4.01	-	-
Fl	19.00	540.00	2.25	0	3.96	-	-
Phe	240.00	1500.00	1.71	0	3.42	-	-
Ant	853.00	1100.00	1.55	0	3.37	-	-
Flu	600.00	5100.00	2.86	0	3.21	-	-
Pyr	665.00	2600.00	1.99	0	2.61	-	-
BaA	261.00	1600.00	1.97	0	3.03	-	-
Chry	384.00	2800.00	1.81	0	3.31	-	-
BbF	320.00	1880.00	-	0	-	-	-
BkF	280.00	1620.00	3.29	0	-	-	-
BaP	430.00	1600.00	2.18	0	4.66	-	-
InP	-	-	-	0	-	-	-
DBA	63.40	260.00	2.35	0	2.35	-	-
BghiP	230.00	1600.00	-	0	0	-	-

suggesting that PAHs in this station exhibited relatively high toxicity as compared to other studied stations (Zhang et al. 2012). Out of \sum PAH (i.e., 160.98 ng/g dw), 36.80% represents \sum PAH_{CARC} and the highest percentage of \sum PAH_{CARC} was reported at Santubong estuary (66.42%) (Table 3).

To quantitatively evaluate the possible toxicological impacts of PAHs on human health, toxic equivalency factors of seven carcinogenic PAHs (PAHs_{CARC}) were used (Table 3). Out of the seven PAHs_{CARC}, the one having adequate toxicological data for the derivation of a carcinogenic factor is BaP (Aly Salem et al. 2014). On the report of the UNEP (1995), the toxic equivalent factor for BkF, BaA, BaP, BbF, DBA, Chry, and InP are 0.1, 0.1, 1.0, 0.1, 1.0, 0.001, and 0.1, respectively. The toxic equivalents (TEQs) or total toxicity of seven PAHs_{CARC} was established by equation 2 (Gesine and Erika 1999; Guo et al. 2011):

$$\text{TEQs} = \text{TEF}_i \times \sum \text{Conc.}_i \quad (2)$$

where TEF_i stands for a toxic equivalent factor of individual PAH compound and Conc._i stands for the concentration of each PAH compound. From Table 3, the values of total TEQ_{CARC} in sediments samples ranged from 0.2684 to 5.1402 ngTEQ/g. The estuary of Santubong River (CZ10) recorded the higher total value of TEQ_{CARC} (i.e., 5.1402 ngTEQ/g).

Conclusion

The present study describes the validation of an analytical technique, monitoring, and risk evaluation of

petroleum hydrocarbons in surface sediments of the coastal and selected estuaries of Sarawak, Malaysia. The suggested technique is able to quantify the available n-alkanes and polycyclic aromatic hydrocarbons (PAHs) in sediment samples at lower concentrations for instance as small as 10 ng/g, with better precision as compared to 15% for most of the analytes. The analytical technique was used to assess petroleum hydrocarbons from sediments collected from the coastal and selected estuaries of Sarawak. The total n-alkane concentrations (C_{10} – C_{33}) varied from 96.63 to 367.28 ng/g dw. The lowest and highest n-alkane content was observed at Santubong estuary (CZ10) and the coastal site labeled CZ2, respectively. Thus, the difference in concentration of n-alkanes could be attributed to the anthropogenic sources and inputs from natural processes. At the same time, the contents of \sum PAHs varied from 12.54 to 21.20 ng/g dw. The highest total PAH content was reported in the sediment of coastal site CZ8 (21.20 ng/g dw), whereas the lowest content was reported in the sediment of coastal site CZ3 (12.54 ng/g dw). In regard to the studied sites, the ratios of most stations were > 1, suggesting their petrogenic inputs except stations CZ2, CZ9, and CZ10 which ratios were < 1, which could be ascribed to pyrogenic sources. The average PAH concentrations were compared to ERL and ERM values and found that the result of all the studied sites suggested no adverse biological effect. Risk assessment of PAHs was assessed using BaP equivalent values technique, and the outcomes indicated no risks

in all studied locations. The information obtained from this study can lead to understanding the distribution, sources, and potential risk of aliphatic and polycyclic aromatic hydrocarbons in coastal and river bodies.

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Author contribution EAA, ZBA, and RW conceived of the study and carried out the design of the experiment. EAA carried out the sample preparation and analysis, EAA assessed the data, and EAA, ZBA, and RW helped to draft and edited the manuscript. The author(s) read and approved the final manuscript.

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Declarations

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