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Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Sediments from Sadong River Sarawak, Malaysia

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) were analysed to assess the organic chemical pollution of sediments in the Sadong River. This study was conducted on surface sediment samples from the beginning of the estuary to the upstream river. Sixteen priority polycyclic aromatic hydrocarbons (PAHs) in the surface sediments from Sadong River were quantified by gas chromatography mass spectrometry (GC-MS). The distribution and indexes of PAHs in sediments were determined to infer their sources. The ΣPAHs ranged between 18.21-184.25 µg/g. The composition, distribution pattern as well as indices of PAHs, suggested no petroleum contamination. The petrogenic PAHs were derived from crude and refined petroleum introduced to the river through municipal waste, accidental oil spills and leakages, and urban run-off from farmlands. While the pyrogenic PAHs are derived from the combustion of petroleum and biomass which are released into the river in the form of exhaust fumes and solid residues.

Keywords*:* Estuary, pollution, polycyclic aromatic hydrocarbons (PAHs), pyrogenic, Sadong River, sediment.

Introduction

Petroleum hydrocarbon are comprised of a wide variety of chemicals with different origins (Zaghden *et al*., 2005). Petroleum pollution has long been of great concern since there are components in petroleum which have mutagenic and carcinogenic impacts on organisms (Vaezzadeh *et al*., 2015). The global increasing demand for fuel besides accidental oil spills are the two main contributors to the release of petroleum into the environment (Singh *et al*., 2012). The environs of Sadong river has gone through rapid development during recent decades resulting in the release of large amounts of petroleum and its products into the environment. This has led to the increase in the intensity of discharge of domestic waste water and high amounts of urban runoff into the river. The vicinity of the Sadong River is characterized by agricultural and economic activities such as fishing, mangrove swamps, tourism spots and peat swamps. Malaysia is a tropical country characterized by continuous rainfall (Masood *et al*., 2016).

Generally, PAHs arise from two types of anthropogenic sources which are petrogenic and pyrogenic sources (Masood *et al*., 2016). Petrogenic sources include crude and refined petroleum. Whereas pyrogenic PAHs originate from the combustion of fossil fuels and biomass which are released into the environment as exhaust and soot particles. Hydrocarbon compounds may flow directly from stationary sources such as industries, motor vehicles, open burning activities and municipal waste discharges. Other sources of pollution may include urban and agricultural run-off as well as atmospheric deposition (Zakaria *et al*., 2002).

PAHs rapidly bind to particulate materials in rivers and deposited in sediments as a final sink, therefore sediments are considered the most important reservoir of PAH contaminants (Culotta *et al*., 2006). This study is focused on the identification and distribution of PAHs in the Sadong River sediment as well as their possible sources which were determined by various indices. The geology of the Sadong basin consists of the basement rocks and sedimentary rocks. There is a mosaic of volcanic rocks and sedimentary rocks together with tertiary alluvial

sediments (Hutchison, 2005). Sarawak host sedimentary deposits comprised mainly of siliciclastic rocks such as sandstone, siltstone and shale (Nagarajan *et al*., 2014). The tectonic evolution of the Borneo is believed to be formed by the collision of a Luconia microcontinental block that came from the north into the West Borneo Basement which was part of Sundaland in the south (Hutchison, 2005; Madon, 1999). The main constituents of most sediments are inorganic mineral materials, crustal rock are the main sources of these mineral components. The rate of the rock weathering is strongly dependent on the solubility and stability of the constituent minerals (Andrews *et al*., 2013).

Materials and Method

Surface sediment samples which is the top layer representing modern inputs of pollution were collected from seven stations in March 2017 and March 2018. The river is situated in the northwestern part of Borneo Island and the sampling stations were chosen based on different land uses and the contribution of upstream to downstream of the river flow. A major input of fresh water is received from upland, transport sediments at several metres then meanders along its path towards the estuary and finally discharges into the South China Sea (Omorinoye *et al*., 2019). The Sadong River basin has experienced extensive land use change from the twentieth century due to increased population, expansion of agricultural activities and industrialization. It is characterised by a shallow, gentle and bioturbated to a deep, fast and turbid river system (Bryant, 2003).

Twenty-one representative, undisturbed surface sediment samples were taken using a Wildco stainless steel grab sampler at different stations as shown in Fig. 1. On site, each sample was kept in aluminium foils for hydrocarbon analysis, well labelled and stored in a cooler box. The hydrocarbon studies involved the identification of polycyclic aromatic hydrocarbon compounds.

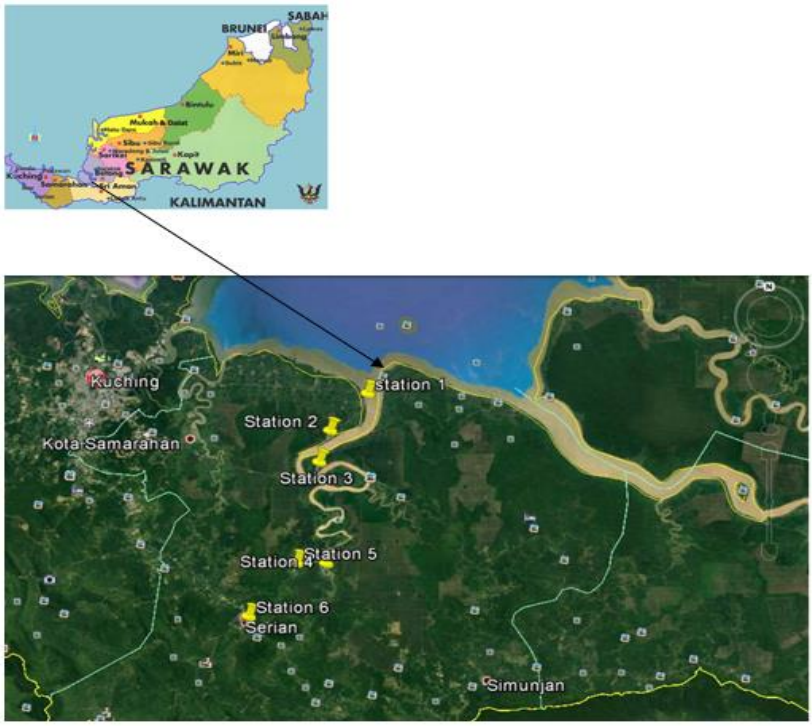


Fig.1. Map of the study area

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The sediment sample weighing 10 g in the wet state was measured in a cellulose thimble. Each of the sample was spiked with 50 µL each of the individual internal standards of anthracene d_{10} using a micro syringe. The anti-bumping weighing 0.1 g was put into the round bottom flask and 250 ml DCM was poured into it. The samples were subjected to soxhlet extraction for 8 hours (Masood *et al*., 2016) on a FAVORIT MS-EAM heating mantle. The extracted solvent was reduced by using a rotary evaporator at about 40^{O}C because DCM boils at 42^{O}C on 50 rpm.

The fractionation of geolipids was carried out on the hydrocarbon extract into fractions with (1.1 cm × 25 cm) glass column chromatography packed with silica gel with size 0.040-0.063 mm. The hydrocarbon extract was placed on the top of silica gel and eluted with appropriate solvent ratios. The chromatographic column was prepared by plugging a piece of glass wool into a long bodied burette. The solvent was dried using Heidolph Laborota 4000 efficient rotary evaporator and further dried with nitrogen gas. The geolipid was ready for GC-MS determinations.

The Gas Chromatography-Mass Spectrometer (GC-MS) Analysis was determined using Shimadzu Gas Chromatography-Mass Spectrometer (GC-MS) QP 2010. Chromatographic separation was achieved by a BPX-5 (non-polar) capillary column (30 m×0.25 mm i.d., 0.25 µm film thickness) with a splitless injector and mass spectrometer detector. Helium was used as the carrier gas (1 mL/min). Samples were injected in the splitless mode with an injector temperature of 280 °C. Oven temperature was programmed from 50°C held for 2 min and final temperature at 300°C held 10 min. The samples were analyzed in analytical sets that consist of standards, samples and quality control samples and the total PAHs were determined.

Results and Discussion

PAHs were investigated by the relative abundance of the individual compound as shown in GC-MS chromatograms in Figures 2-8. Occurrence of PAHs of sediments at Sadong River suggested a low degree of pollution in sampling sites of BS1, BS2 and BS3 whereas a medium pollution was observed in sampling sites in the midstream at BS5, BS6 and at BS7 which is the upstream.

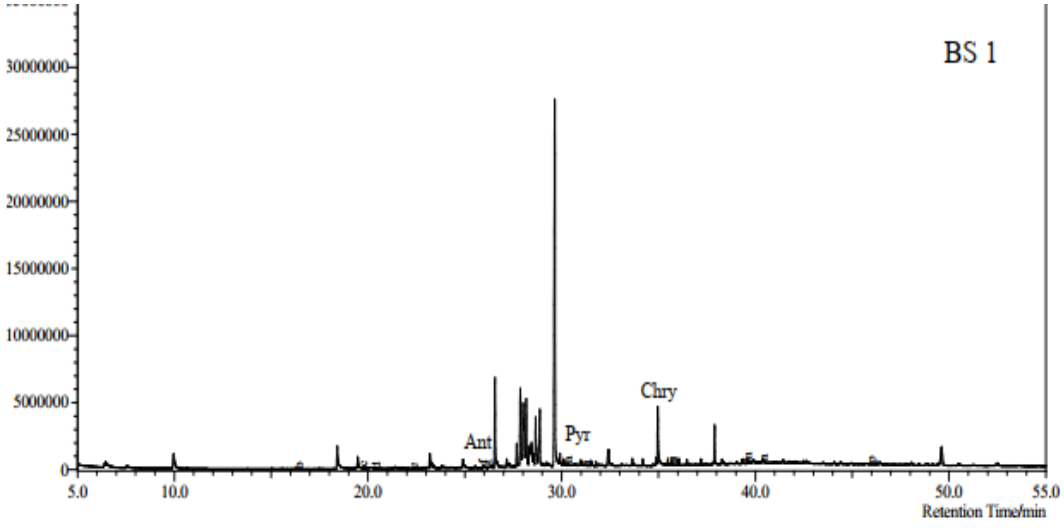


Fig.2: GC-MS chromatogram of PAHs in surface sediments from BS1

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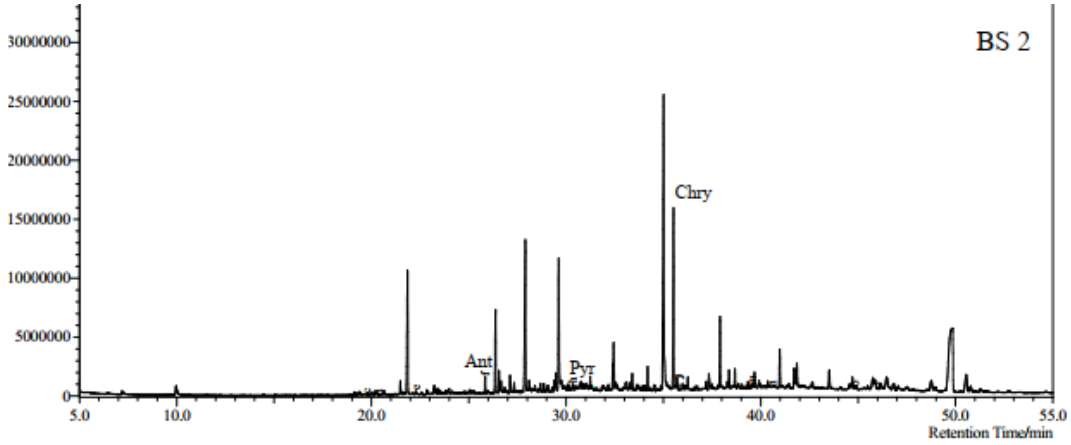


Fig.3: GC-MS chromatogram of PAHs in surface sediments from BS2

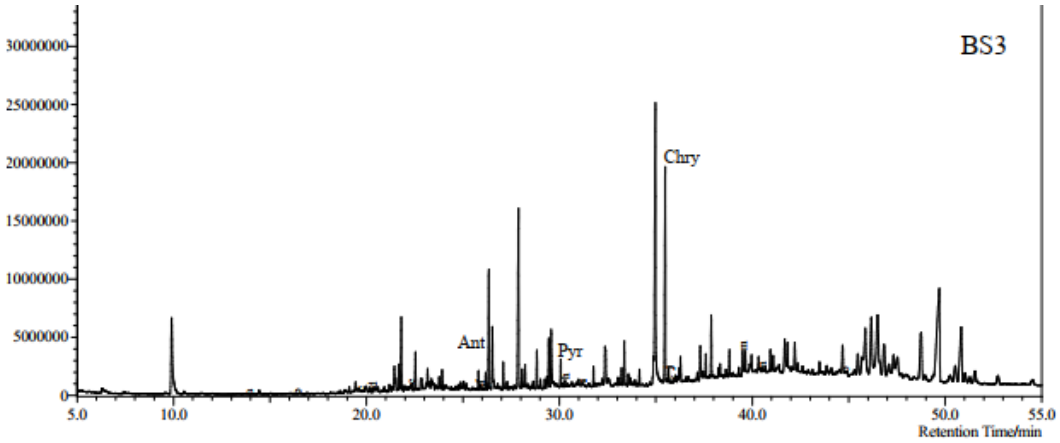


Fig.4: GC-MS chromatogram of PAHs in surface sediments from BS3

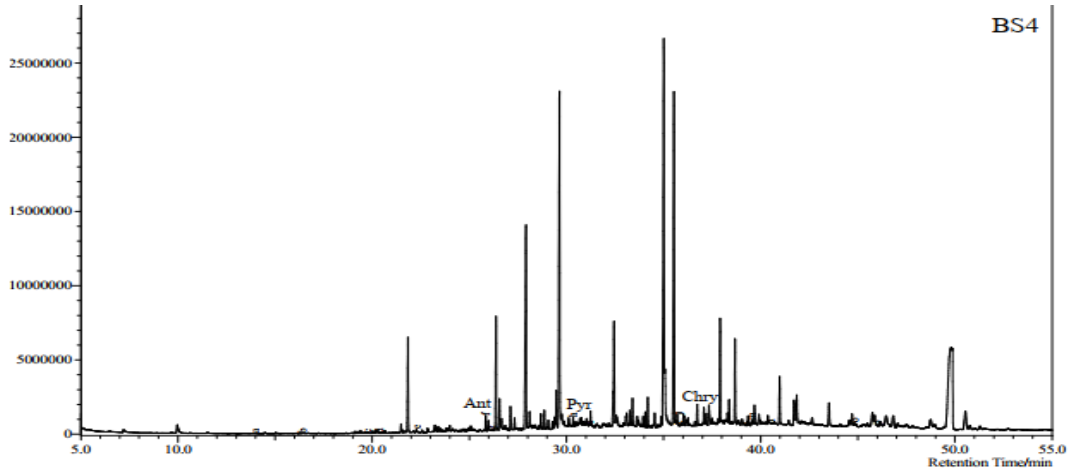


Fig.5: GC-MS chromatogram of PAHs in surface sediments from BS4

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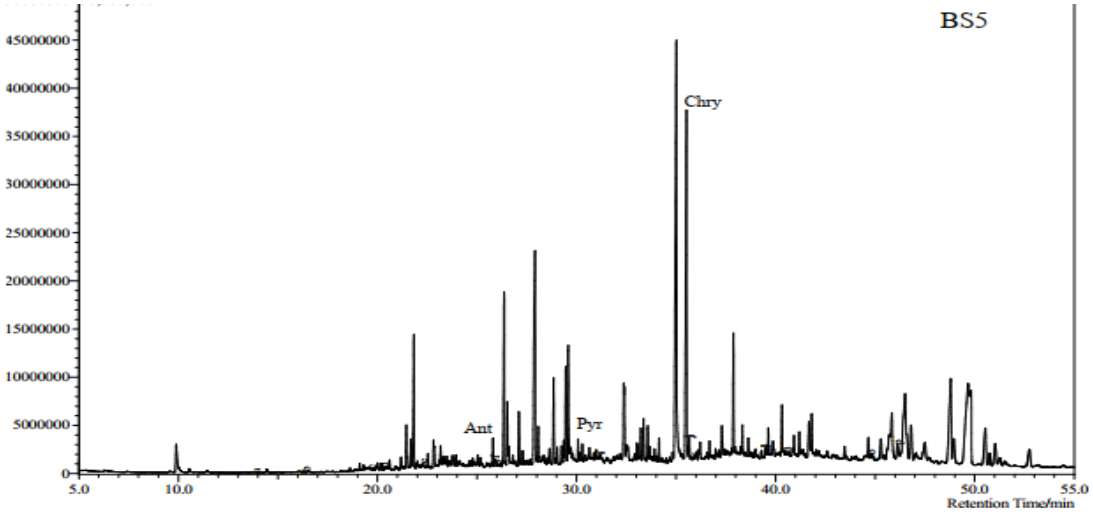


Fig.6: GC-MS chromatogram of PAHs in surface sediments from BS5

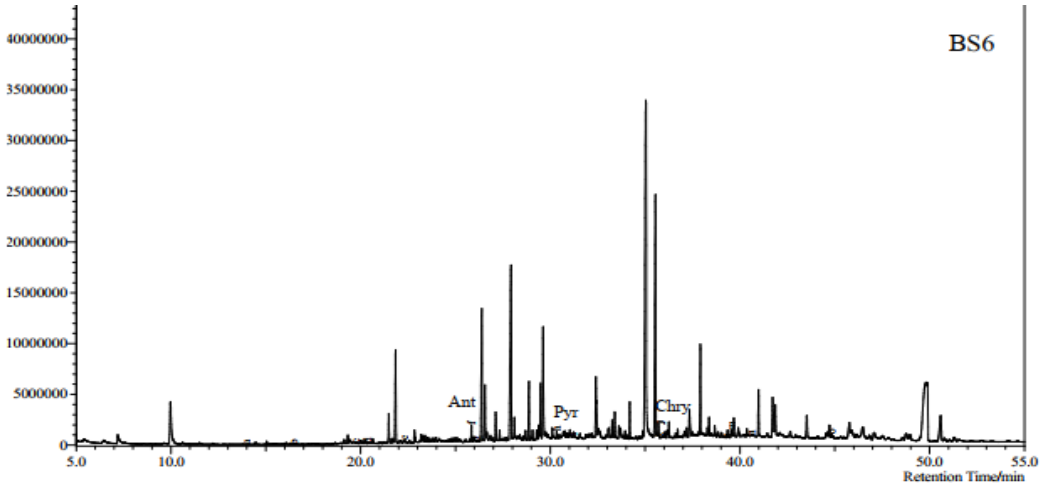


Fig.7: GC-MS chromatogram of PAHs in surface sediments from BS6

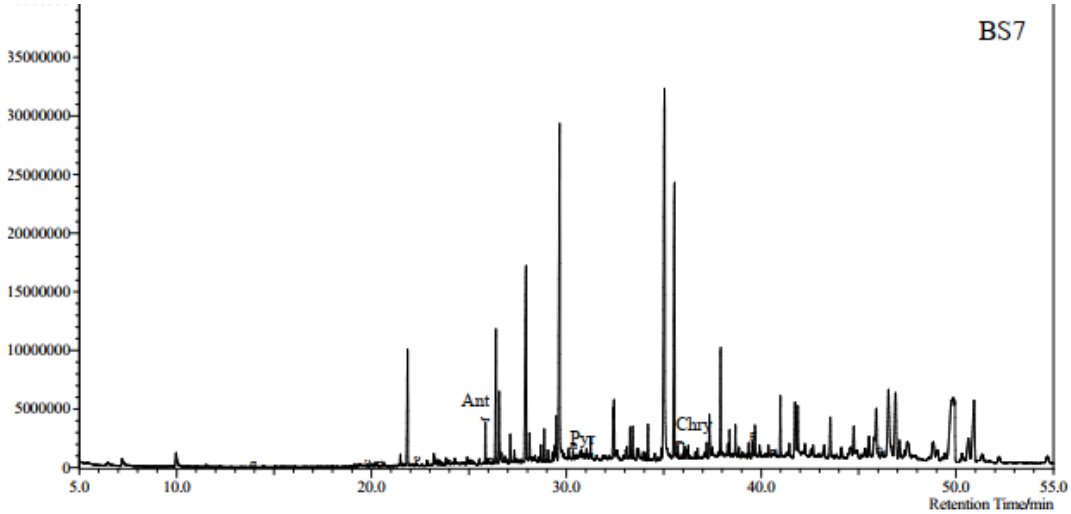


Fig.8: GC-MS chromatogram of PAHs in surface sediments from BS7

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Several studies in some parts in Malaysia showed the PAHs concentrations decreased towards the sea, with the conclusion that river discharge and urban runoff were the principal sources of sedimentary PAHs (Masood *et al*., 2016; Keshavarzifard *et al*., 2014; Sakari *et al*., 2008; Zakari *et al*., 2001). Concentrations of total HMW PAHs in surface sediments ranged between 7.48-100 μg/g with BS7 with the highest concentration of HMW PAHs (100.05 μg/g) followed by BS5 (86.99 μg/g), BS6 (66.49 μg/g), BS2 (32.69 μg/g), BS4 (28.67 μg/g), BS3 (22.00 μg/g) and BS1 (7.48 μg/g). The low molecular weight PAH (LPAH) compounds are naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe) and anthracene (Ant) while the high molecular weight PAH (HPAH) compounds are fluoranthene (Flt), Pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]Fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (InP), dibenzo[a,h]anthracene (DBA) and benzo[ghi]perylene (BgP). The concentration of individual PAHs in sediments are illustrated in Table 1, it showed the highest concentration of PAHs was detected in surface sediments of BS7 (184.25 μg/g) followed by BS6 (123.45 μg/g), BS5 (108.43 μg/g), BS2 (79.22 μg/g) and BS4 (65.62 μg/g). Low concentration of PAHs was detected in surface sediments of BS1 (18.21 μg/g) and BS3 (43.87 μg/g) as shown in Figure 9.

Table 1: PAHs (μg/g) in surface sediments from Sadong River

PAH	BS1	BS2	BS3	BS4	BS5	BS6	BS7
Napthalene	0.02	0.03	0.03	0.17	0.02	0.24	0.51
Acenapthylene	0.19	0.87	0.25	0.29	0.21	1.62	0.03
Acenapthene	1.02	1.76	0.54	1.29	2.07	2.12	1.98
Fluorene	0.12	0.54	0.98	0.41	1.50	2.18	0.49
Phenanthrene	1.18	7.98	3.61	5.93	4.00	7.53	7.92
Anthracene	4.25	24.85	9.54	18.33	7.72	29.48	59.05
Fluoranthene	1.24	0.54	0.32	0.53	0.84	2.69	2.33
Pyrene	2.71	9.96	1.11	10.01	5.08	11.12	11.88
Benzo[a]anthracene	0.78	0.71	5.54	1.22	13.71	2.67	1.74
Chrysene	3.87	12.20	0.59	9.40	53.67	17.99	14.77
Benzo[b]fluoranthene	0.19	0.41	0.75	0.50	0.97	0.68	0.49
Benzo[k]fluoranthene	0.13	0.63	2.97	0.79	4.00	0.89	0.92
Benzo[a]pyrene	0.67	8.91	0.53	8.25	1.29	15.13	27.66
Indeno[1,2,3-c,d]Pyrene	1.78	2.05	0.67	1.08	1.18	2.88	3.90
Dibenzo[ah]anthracene	0.04	4.83	0.53	4.61	1.10	21.57	45.07

Benzo[ghi]perylene	0.03	2.95	15.91	2.82	11.08	4.68	5.49
ΣPAH (µg/g)	18.21	79.22	43.87	65.62	108.43	123.45	184.25

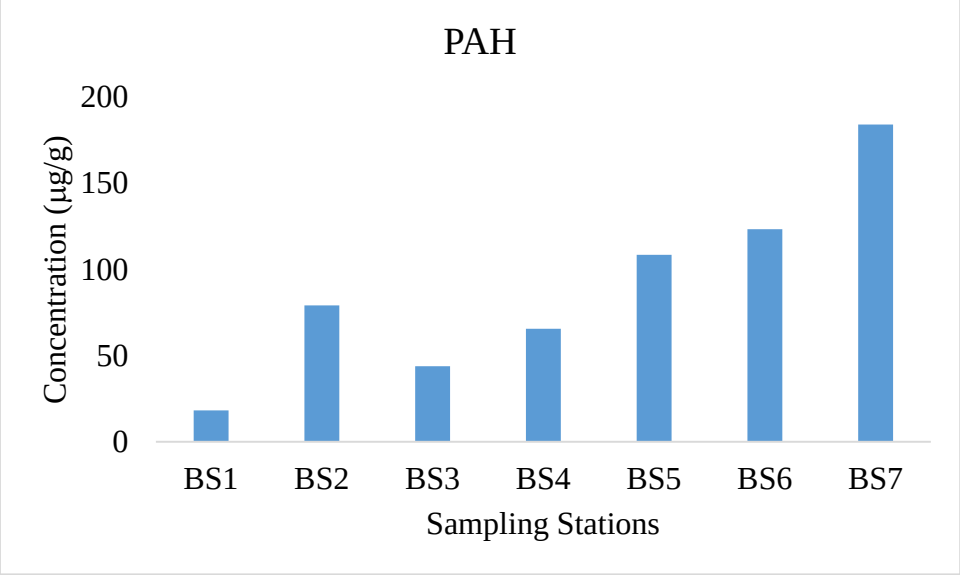


Figure 9: The concentration of PAHs in the surface sediment from Sadong River

Table 2 shows the sources of PAHs in the surface sediments. The petrogenic PAHs were derived from crude and refined petroleum introduced to the river through accidental oil spills, municipal and urban run-off (Monza *et al*., 2013; Commendatore *et al*., 2012; Shaw *et al*., 2004). While the pyrogenic PAHs are derived from the combustion of petroleum and biomass which are released into the river in the form of exhaust fumes and solid residues (Sakari *et al*., 2008; Zakaria *et al*., 2002). PAHs with LMW/HMW > 1 had petrogenic input has observed in BS1, BS2 and BS4, while LMW/HMW <1 have pyrogenic sources as observed in BS3, BS5, BS6 and BS7 (Soclo *et al*., 2000). The Phe/Ant was < 1 in all sampling stations indicated petrogenic origin. The Fluo/Pyr was <1 in all sampling stations which indicated petrogenic origin. The Chr/BaA was > 1 which is petrogenic origin in all sampling stations except BS3 which indicated pyrogenic origin. Fluo/ (Fluo+Pyr) was < 1 in all sampling stations which indicated petrogenic origin (Tahir *et al*., 2011; Simoneit *et al*., 2002; Commendatore *et al*., 2000). The BaA/ (BaA+Chr) was < 1 in all sampling stations which indicated petrogenic origin, the BaA/(BaA+Chr) ratio of PAHs was > 0.35 in BS3 which clearly indicated pyrogenic origin. Hence, the sources of PAHs in river sediments were petrogenic and pyrogenic.

Table 2: Sources of PAHs in surface sediments from Sadong River

PAH Ratios	BS1	BS2	BS3	BS4	BS5	BS6	BS7
Phe/Ant	0.28	0.32	0.38	0.32	0.52	0.26	0.13
Fluo/Pyr	0.46	0.05	0.29	0.05	0.17	0.24	0.20
Chr/BaA	4.96	17.18	0.11	7.74	3.91	6.73	8.47

Fluo/(Fluo+Pyr)	0.31	0.05	0.22	0.05	0.14	0.19	0.16
BaA/ (BaA+Chr)	0.17	0.06	0.90	0.11	0.20	0.13	0.11

Note: *Phe/Ant: Phenanthrene/Anthracene, Fluo/Pyr: Fluoranthene/Pyrene: Chr/BaA: Chrysene/Benzo[a]anthracene, Fluo/Fluo+Pyr: Fluoranthene/Fluoranthene+Pyrene, BaA/(BaA+Chr): Benzo[a]anthracene/Benzo[a]anthracene+Chrysene*

Conclusion

The use pesticides, herbicides and toxic chemicals as well as microbial pathogens contributed to the presence of PAHs in river sediments. The increase of PAH concentration in surface sediments at the upstream of Sadong River could be attributed to dilution of PAH compounds related to river flushing. Based on composition and distribution of individual PAH in surface sediments, seven sampling sites were characterized by different compounds that varied from more volatile LMW PAHs like acenaphthylene and acenaphthene to the less volatile HMW PAHs like fluoranthene and benzo[k]fluoranthene. It was clear that the 4-ring PAH which include flouranthene, pyrene, benzo[a]anthracene and chrysene as well as 5 and 6-ring PAH like benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene were detected in abundance in most of the sediment samples. In addition, 2-ring PAHS like naphthalene, acenaphthylene, acenaphthene and fluorene had low concentration in the sediments.

Conflict of Interest

The authors declare no conflict of interest in this study.

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