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POLYCYCLIC AROMATIC HYDROCARBON (PAH) CONTAMINATION IN THE SEDIMENTS OF EAST COAST PENINSULAR MALAYSIA

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Abstract

The polycyclic aromatic hydrocarbons (PAHs) are pollutants of concern due to their persistent in the marine ecosystem, thus its can cause long-term adverse effect to the marine life. In this study the concentrations of PAHs in east coast Peninsular Malaysia sediments were determined. About ten stations along the east coast of the coastal area were selected to collect sediment samples using grab sampler. The PAHs from the sediment samples were soxhlet extracted using mixture of hexane and dichloromethane (DCM). Fractionation was done using the silica-alumina column. About 17 compounds of the PAHs were determined using the Gas Chromatography-Mass Spectrometer (GCMS model QP5050A). The $\sum$ PAHs was found in range between 0.26μg/g to 0.59μg/g dry weight. The data from the study signified that the main source of PAHs in the sediment of the east coast peninsular Malaysia is originated from the pyrolytic source.

Abstrak

Pencemaran polisiklik aromatik hidrokarbon (PAH) di beri perhatian disebabkan oleh sifatnya yang gigih dalam ekosistem marin, ia boleh menyebabkan kesan buruk kepada kehidupan marin dalam jangka masa panjang. Pengukuran kepekatan PAH dalam sediment di pantai timur Semenanjung Malaysia dijalankan dalam kajian ini. Sepuluh lokasi telah dipilih disepanjang kawasan pantai timur untuk diambil sampel sedimen menggunakan pensampel cangkup. PAH daripada sampel sedimen dijalankan ekstraksi soxhlet menggunakan campuran heksana dan diklorometana (DCM). Pemisahan dilakukan menggunakan turus silica/alumina. 17 sebatian PAH ditentukan dengan menggunakan Gas Kromatografi-Spektrometer Jisim (GC-MS model QP5050A). $\sum$ PAH yang diperolehi adalah diantara 0.26μg/g hingga 0.59μg/g berat kering. Data daripada kajian ini menunjukan punca utama pencemaran PAH di dalam sedimen diperairan pantai timur Semenanjung Malaysia berasal dari sumber pirolitik.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are of concern because they are widely distributed in the environment and many of them have toxic and carcinogenic properties [1-5]. PAHs are common organic contaminants and generally generated from the natural and anthropogenic processes. They can be introduced into the marine environment by various ways such as oil spill, urban runoff, domestic and industrial wastewater discharges.

Many research works on the organic geochemistry of PAHs has been done in order to understand their origins and some criteria have been developed to distinguish between different sources of PAHs from natural or anthropogenic. According to the formation mechanism, anthropogenic PAHs can be classified as pyrolytic and petrogenic. Pyrolytic PAHs are formed as a consequence of incomplete fuel combustion whereas petrogenic PAHs are mainly derived from the crude oil or unburned fuel and its refined products.

The major activities along the east coast Peninsular Malaysia area are fishery, tourism activities and petroleum production. Study on PAHs contents along the east coast off Peninsular Malaysia is still limited. In this present study, organic contamination (PAHs) were selected because they are important to the public health and also for base linedata and/or information. The goal of this work was to determined the concentration of PAH compound in the sediment and assess the possible source of these compounds whether anthropogenic or biogenic.

Method

Sampling

Ten sampling stations were selected along the east coast Peninsular Malaysia area (Figure 1 and Table 1) on August 2003. Sediment samples were collected using the Van Veen grab and sample was transfer into the glass bottle with aluminium cap using the stainless steel spatula. Samples were stored below 5°C before analysis.

Figure 1: Map showing the sampling station

Table 1: Sampling stations and coordinates of the South China Sea coastal area.

Station	Latitude	Longitude	Water depth	Temperature
EC6C	06° 16.580' N	102° 08.712' E	9.2	30.3
EC7C	05° 51.793' N	102° 33.902' E	7.9	30.2
EC8C	05° 21.967' N	103° 09.120' E	8.2	30.0
EC9C	04° 47.234' N	103° 26.737' E	17.3	29.3
EC10C	04° 13.450' N	103° 27.600' E	9.5	29.7
EC11C	03° 47.630' N	103° 24.130' E	11.9	29.9
EC12C	03° 32.092' N	103° 29.735' E	9.4	30.2
EC13C	02° 50.790' N	103° 30.780' E	8.8	29.3
EC14C	01° 53.117' N	104° 12.313' E	12.8	29.4
EC15C	01° 25.716' N	104° 18.553' E	17.0	29.5

Extraction and Fractionation
Approximately 20 g wet weight of sediment was weighted in a glass beaker where about 30 g of Na_2SO_4 was added to the sediment sample, mix together for a homogenous. Sample was added into the soxhlet apparatus and spike with two internal standard (n-octadecene for aliphatic fraction and orto-terphenyl for PAHs fraction) for recovery assessment. The sample was extracted using 250 ml (50:50 v/v) mixture of dichloromethane (DCM) and hexane. After 18 hours extraction, the extracted samples were dry up until 1ml using rotary evaporator. About 1ml of extracted sample was fractioned into subfraction using silica-alumina column with 8 g of silica gel and 8 g of alumina. The silica gel and alumina should be deactivated with 0.16 ml and 0.4 ml deionzed water respectively. Then 30 ml of hexane was eluted pass through into the silica-alumina column to elute aliphatic (C_{12} – C_{34}) fraction and followed by the 40 ml mixture of DCM and hexane (50:50 v/v) to eluted the PAHs fraction.

Gas Chromatography-Mass Spectroscopy (GC-MS) Analysis
The PAHs fraction were analysed using GC-MS model Shimadzu QP5050A with selective ion monitoring mode. PAHs fraction were injected into the GC-MS by using DB-5 silica capillary column (30m x 0.25 mm i.d.; 0.25μm filmed thickness). The initial injection and interface temperature of GC-MS was setup at 70^oC and 270^oC respectively. The column oven temperature will rise up 5^oC/minute up to 300^oC and will be maintained at 300^oC for 12 minutes. Helium gas was used as a carrier gas with flow rate at 1.5 ml min^{-1}. The PAHs identification and quantification base on ion fragmentation and retention time compared to of that the external PAHs standard.

Results and Discussion

About 17 species of PAHs were measured as shown in Table 2. The ∑ PAHs concentration varies from 0.26 – 0.59 μg/g dry weight with a mean concentration is 0.34 ug/g. The highest concentration of ∑ PAHs was detected at station EC13 and the lowest at station EC11. Two stations (EC 7 and EC 13) are detected for all species of PAHs. The recovery of the internal standard orto-terphenyl of the PAH separation procedure were ranged from 70% to 123%.

It is generally accepted that the sources of PAHs are categorized into two origins: pyrolytic (incomplete combustion of organic matters – combustion fossil fuel, vehicular engine combustion, smelting, waste incinerators, forest fire and coal combustion) and petrogenic (unburned petroleum and its product – gasoline, kerosene, diesel, lubricating oil and asphalt). Several molecular ratios such as Phenanthrene/Anthracene (Phen/Anth), Fluoranthene/Fluoranthene + Pyrene (Fl/Fl + Py) and MethyPhenanthrene/Phenanthrene (MePhen/Phen) have been commonly used as a way of determining origin of PAHs sources.

Table 2 shows that the Phen/Anth ratio in this study are in the range of 1.2 – 1.9. The value is much lower then 10 which is generally considered indicative of a predominance of petrogenic sources, whereas ratio values lower than 10 are characteristic of pyrolytic sources [6]. The Phen/Anth concentration ratios indicate that the PAHs in this study area were derived from pyrolytic rather then petrogenic sources.

PAH isomer pairs ratios Fluoranthene/Fluoranthene + Pyrene (Fl/Fl + Py) has also been used as distinct chemical tracers to infer possible source of PAHs in environmental sample [7]. Yunker et.al (2002) promulgated that the PAH isomer ratio measurements Fl/ Fl + Py of less than 0.4 implies petrogenic, 0.4 – 0.5 implies pyrolytic sources and more than 0.5 implies combustion of coal, grass and wood. The result in Table 2 shown that the Fl/Fl + Py ratios was found to be in the range of 0.4 – 0.5 in all station except station EC6C (0.6), it again implies that the source of PAHs is most likely originated from pyrolytic.

The sources of PAHs pollution may also be distinguished by comparing the PAH isomer of ∑ MethyPhenanthrene/Phenanthrene (∑MePhen/Phen) ratio. However the ∑ MePhen/Phen ratio has been widely used and proves to be more successful to distinguish petrogenic and pyrolytic sources of PAHs [7-14]. The ∑MePhen/Phen ratio in this study is defined as the ratio of the sum of concentrations of three isomers of methylphenanthrenes (2 Methyl Phenanthrene, 1 Methyl Phenanthrene, 3,6 Dimethyl Phenanthrene) to that of phenanthrene. The ∑MePhen/Phen ratio value of less than 1 indicates that the sources of PAHs are of pyrolytic origin, while a ratio value of between 2 to 6 suggests unburned petroleum sources or petrogenic [15]. Table 2 shows that the ∑MePhen/Phen ratio in this study for all the sediment samples were less than 1 (0.28 – 0.93). This further indicates that the source of PAHs in the sediment samples mainly originated from the pyrolytic.

Table 2. Concentration level of species, total, ratios of some species of PAHs and % of phenanthrene and its derivatives

PAH Species	Stations									
	EC6C	EC7C	EC8C	EC9C	EC10C	EC11C	EC12C	EC13C	EC14C	EC15C
Naphthalene	0.011	0.046	0.023	0.026	0.028	0.024	0.032	0.047	0.031	0.036
1 Methyl Naphthalene	0.012	0.012	0.013	0.015	0.014	0.014	N.D	0.025	0.016	0.020
1 Ethyl Naphthalene	0.018	0.011	0.012	0.013	0.013	0.013	0.016	0.022	0.014	0.016
Acenaphthylene	0.034	0.021	N.D	0.026	N.D	N.D	0.032	0.042	N.D	0.032
Acenaphthene	0.025	0.015	0.017	0.019	N.D	N.D	0.024	0.031	N.D	N.D
2,3,6 Trimethyl Naphthalene	0.015	0.012	0.014	0.015	0.014	0.014	0.018	0.026	0.016	0.019
Fluorene	0.015	0.024	0.026	0.029	0.028	0.028	0.035	0.049	0.030	0.037
Phenanthrene	0.052	0.036	0.038	0.041	0.037	0.030	0.036	0.079	0.044	0.052
Anthracene	0.034	0.021	0.023	0.025	0.024	0.025	0.031	0.042	0.026	0.032
2 Methyl Phenanthrene	0.012	0.011	0.013	0.012	0.012	0.011	0.017	0.024	0.013	0.017
1 Methyl Phenanthrene	0.003	0.006	0.004	0.003	0.002	0.002	0.003	0.006	0.003	0.004
3,6 Dimethyl Phenanthrene	N.D	0.013	0.014	0.015	0.014	0.015	N.D	0.025	0.016	0.019
Fluoranthene	0.007	0.017	0.018	0.018	0.019	0.017	0.022	0.035	0.020	0.023
Pyrene	0.005	0.020	0.023	0.024	0.024	0.024	0.031	0.042	0.025	0.033
1 Methyl Pyrene	N.D	0.010	0.011	0.012	0.020	N.D	0.015	0.021	0.013	0.016
Chrysene	0.048	0.024	0.026	N.D	0.027	0.028	0.036	0.048	0.030	0.037
Perylene	0.034	0.011	N.D	N.D	0.013	0.012	0.016	0.023	N.D	0.017
∑ PAHs (µg/g)	0.32	0.31	0.27	0.29	0.29	0.26	0.36	0.59	0.30	0.41
Percent, total phenanthrene and its derivatives										
% Phen	78.4	54.5	55.2	57.2	56.1	51.8	63.8	58.9	58.5	56.8
% C1-MPhen	21.6	26.1	24.6	21.8	21.8	22.7	36.2	22.4	20.3	22.5
% C2-DMPhen	0.0	19.3	20.2	21.1	22.1	25.5	0.0	18.8	21.2	20.7
Σ (Phen + C1-MPhen + C2-DMPhen) (µg/g)	0.067	0.065	0.069	0.071	0.065	0.058	0.057	0.135	0.075	0.092
PAH species ratio										
Phen/Anth ratio	1.6	1.7	1.7	1.6	1.5	1.2	1.2	1.9	1.7	1.6
Fl/(Fl+ Py) ratio	0.6	0.5	0.4	0.4	0.4	0.4	0.4	0.5	0.4	0.4
∑ MePhen/Phen ratio	0.28	0.83	0.81	0.75	0.78	0.93	0.57	0.70	0.71	0.76

N.D = not detected; Phen = Phenanthrene; Anth = Anthracene; Fl = Fluoranthene; Py =Pyrene; C1-MPhen = 2 Methyl Phenanthrene +1 Methyl Phenanthrene; C2-DMPhen = 3,6 Dimethyl Phenanthrene; ∑MePhen= 2 Methyl Phenanthrene +1 Methyl Phenanthrene + 3,6 Dimethyl Phenanthrene.

The concentration distribution of Phenanthrene and methylated phenanthrene (C1-Mphen and C2-DMPhen) also can be used to distinguished between pyrolytic and petrogenic sources [16,17]. The highest concentration distribution (%) of methylated phenanthrene can be taken as a sign of petrogenic (unburned petroleum), while highest concentration distribution of phenanthrene usually indicate a pyrolytic (petroleum combustion), as a source of PAHs (Sicre et al. 1987; Gogou et al., 1996). Figure 2 show the concentration distribution (%) of Phenanthrene and methylated Phenanthrene in each station. These results (Figure 2) show those phenanthrenes are higher than methylated phenanthrene. This finding also indicates that the sources of PAHs are pyrolytic.

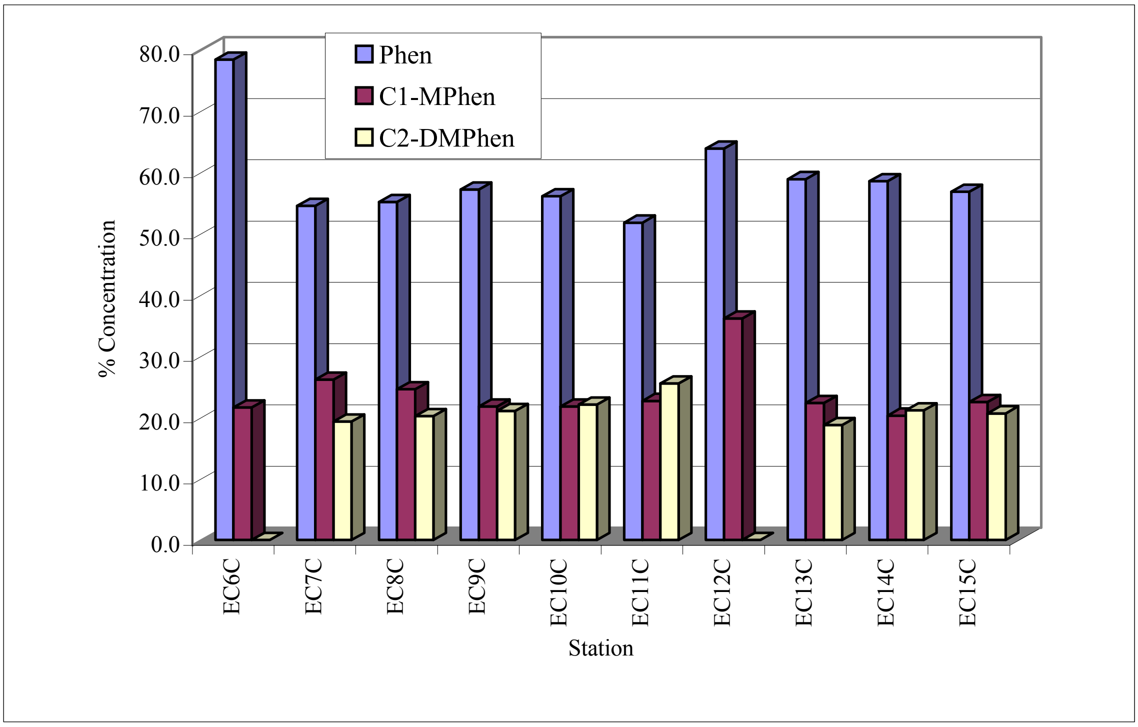

Figure 2: Concentration distribution (%) of Phenanthrene and methylated Phenanthrene in sediment

Conclusion

Total concentration of PAHs in the sediment of east coast of Peninsular Malaysia were in the range of between 0.26 to 0.59 µg/g dry weight, which is considered by Ulun et. al. as slightly polluted [18]. Several ratio of PAHs species concentration such as Phen/Anth, Fl/FL+Py and ∑MePhen/Phen were applied to identify sources of the anthropogenic pollutants, which indicate that the source is pyrolytic (petroleum combustion).

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