Distribution of Polycyclic Aromatic Hydrocarbon (PAHs) in sediments in the Langat Estuary

Mohamad Pauzi ZAKARIA* and Alvin Azril MAHAT

Faculty of Evironmental Studies, 43400 UPM, Serdang, Selangor Darul Ehsan
*E-mail: drpauzi@yahoo.com

Abstract — A study has been carried out at the Langat Estuary, Selangor. The primary objective of this research is to determine the sources and concentration of polycyclic aromatic hydrocarbon (PAHs) in the sediments in the Langat Estuary. 6 stations were chosen, beginning at the Estuary and ending at the upstream river of the Langat Estuary. The determination of concentration and compound of PAHs were analyzed by using Gas Chromatography-Mass Spectrometry (GC-MS). The samples were calculated using methylphenanthrene/phenanthrene (MP/P) ratio to determine the sources. The value of less than 1 is the pyrogenic sources and more than 1, consist of petrogenic sources. Total PAHs for sediment samples of Station 1 until Station 6 ranged from 322 ng/g to 2480 ng/g (dry weight). Furthermore, MP/P ratios for sediment samples had values ranging from 0.88 to 1.27, while L/H ratios for the same samples ranged from 0.25 to 26.96. There were 17 compounds of PAHs detected in the samples. Sediment samples from Station 1 until Station 6 showed an MP/P ratio value of less than 1, with the exception of Station 4 and Station 6. This points out that this area is dominated by pyrogenic sources.

Key words: Polycyclic Aromatic Hydrocarbons (PAHs), sediment, Gas Chromatography-Mass Spectrometry, methylphenanthrene/phenanthrene (MP/P) ratio, (L/H) ratio

Introduction

Since the onset of the Industrial Revolution, which began in the late 1700 s, mankind has increased its use and dependence on fossil fuels (oil, coal and gas) primarily to power transportation and industrial processes and to generate electricity. As a result, oil product and wastes can be found in our environment. Petroleum hydrocarbon can enter river ecosystems from a variety of sources and via many routes. Major sources include emissions from wood and coal burning, automobile exhaust, heat and power generation and refuse burning. After entering the environment, polycyclic aromatic hydrocarbons (PAHs) are widely dispersed by atmospheric transport or through stream pathways, and eventually accumulate in soils and aquatic sediments. PAHs are one of the foremost widespread classes of pollutants (Vilanova et al. 2001). PAHs consist of two or more fused aromatic rings, and some of them were identified as potent human carcinogens (Baker and Herson 1994). Studies have shown that a small fraction of PAHs generated and released to the environment by human activities are known to have both carcinogenic and mutagenic effects in organisms (Guinan et al. 2001).

PAHs are mainly derived from anthropogenic inputs and are products of incomplete combustion. The PAH sources of greatest concern are anthropogenic combustion processes which are the primary sources of PAHs in the environment (Su et al. 1998). Natural sources of PAHs are insignificant compared to anthropogenic sources. Anthropogenic sources contribute significantly to the concentration of PAHs in the environment, as well as natural combustion sources of PAHs. There are two types of anthropogenic sources of PAHs: petrogenic and pyrogenic sources. Crude and refined petroleum contains PAHs, for example petrogenic PAHs (Zakaria et al. 2002). They are introduced to the aquatic environments through accidental oil spills, discharge from routine tanker operations, municipal and urban runoff and so on.

The combustion of fossil fuel (coal and petroleum) and biomass also produce PAHs (pyrogenic PAHs) which are released into the environment in the form of exhaust and solid residues.

There are also natural sources of PAHs released to the environment. For example, perylene is believed to be produced through in situ conversion of perylenequinone pigment or some other organic matter during early diagenesis. PAHs are also derived from some other natural sources such as oil seeps and ancient sediment erosion.

Polycyclic Aromatic Hydrocarbons or relatively known as PAHs, generally refer to hydrocarbons containing two or more fused benzene rings (Neff 1979). Hydrocarbons are compounds containing only carbon and hydrogen bonding.

They vary widely in boiling point, molecular size and structure. There are five major classes of hydrocarbons, which are n-alkanes, iso-alkanes, cyclo-alkanes, aromatics and alkenes.

PAHs are categorized as aromatics and its basic structure is ring compounds stabilized by electron delocalization. The total number of rings in this type of compound may be as high as six and many PAH compounds can be found in various structures in petroleum.

PAHs which contain the smallest number of rings are considered as Low Molecular Weight PAH. One example is naphthalene containing only two rings. There are also High Molecular Weight PAH such as Fluoranthene which contains four rings and Indeno(1,2,3-*cd*)pyrene which contains six rings (Tam et al. 2000).

The former class has an acute toxicity while some of the higher molecular weight PAHs shows high carcinogenic potential. Therefore, the profiles of different PAH compounds are important in determining their toxicity.

Generally, it was considered that PAHs were formed only during high temperature, about 700°C, pyrolysis of organic materials. However, the discovery of complex mixtures of PAH spanning a wide molecular weight range in fossil fuels such as coal and crude petroleum has resulted in a conclusion that given a certain amount of time, pyrolysis of organic materials at temperatures as low as 100–150°C can lead to the production of PAHs (Blumer et al. 1973). Furthermore, there are some evidence which states that PAHs can be synthesized by certain bacteria and plants such as phytoplankton and alga (Neff 1979).

Therefore, it can be concluded that PAH can be formed in three ways: In high temperature pyrolysis of organic materials, low to moderate temperature diagenesis of sedimentary organic material to form fossil fuel and by direct biosynthesis of microorganisms and plants (Neff 1979).

Although PAHs are produced by natural processes (Su et al. 1998), there are a lot of human activities which increases the load of these substances. Incineration of industrial and domestic wastes, forest fires, power generation by the burning of fossil fuels, and the combustion of fuels in internal combustion engines produce emissions that are high in PAHs. These anthropogenic sources may reach the aquatic environment through industrial and domestic sewage effluents, surface run-off, from land, deposition of airborne particulates and spillage of petroleum into water bodies (Neff 1979).

In determining the source, it can be stated that each individual source is characterized by a specific molecular pattern, allowing the source of these compounds to be established (Guinan et al. 2001). Chemical properties vary with molecular weight. For example, Phenanthrene/Anthracene and Fluoranthene/Pyrene are two pairs of isomers whose difference in reactivity and solubility proves useful in providing a tracer of PAHs from origin (Guinan et al. 2001). Therefore,

PAHs in aquatic sediments may serve as tracers for identification of their sources.

Polycyclic Aromatic Hydrocarbons (PAHs) remain relatively close near their point sources, such that the PAH concentrations decrease approximately logarithmically with distance from the source. Most of the PAHs entering the aquatic environment are localized in rivers, estuaries and coastal marine water (Neff 1979). However, after being discharged into the environment, these hydrophobic pollutants are mixed and diluted by water currents. Since PAHs are less sensitive to photooxidation in water than in air, they are more persistent in the aquatic environment. PAHs entering water are quickly absorbed on particulate matter and large amounts are deposited in bottom sediments. Relative concentrations of PAHs are generally highest in the sediments, intermediate in aquatic biota and lowest in the water column (Jaffe et al. 1993).

Sediments can serve as a long-term sink for water borne petroleum hydrocarbon. Petroleum input to the aquatic environment will remain in the sediment for a period of several years in significant level. Hydrocarbon content in polluted coastal areas ranges from 100 ppb to 12000 ppb, with most level less than 1000 ppb. Where as, in unpolluted coastal areas, the hydrocarbon content in the sediment is normally below 70 ppb (Kelly et al. 2000). PAHs in the aquatic environment rapidly become associated with particles and are deposited in sediments due to its hydrophobic nature.

Many countries in the South East Asian region, such as Malaysia share similar climatic and socioeconomic conditions. One of these characteristics is heavy rain which causes surface erosion, contributing large amounts of soils to rivers and coastal zones, therefore diluting PAHs in the aquatic environments. However, frequent rainfall and fast flushing would transfer the pollutants to the aquatic environments before they undergo various removal processes in terrestrial environments such as photodegradation, the blowing away and atmospheric transport of particulate PAHs by wind, and in-stream degradation (Zakaria et al. 2002).

The purpose of this research is to determine the distribution of PAHs in river bottom sediments. Therefore, this study should be able to give some indication of the concentration or level of PAHs in the Langat River located in the state of Selangor. The Langat Estuary is chosen for the study because the river flows through the hub of commercial, industrial and residential areas (Cheras, Kajang, Bangi and Banting). Furthermore, the urban and developing areas also surround this river.

The level of PAHs detected in Langat River sediments will show the degree of hydrocarbon contamination in the river. From the analysis, the quality and quantity of hydrocarbon in the Langat River sediments can be obtained. This study is important to combat illegal discharge of contaminants into the Langat River. Data obtained from this study

can also be used as a reference in determining standards for river water quality.

Therefore, this study could reveal important information on the pollution of PAHs in the sediments of the Langat River, before the pollution gets out of control.

Methodology

Study area

The Langat River basin, located in Kuala Lumpur, is about 120 km long and the main tributary is the Semenyih River. The basin area is drained by the Langat River with it's headwaters rising from the high-hills in the north and flowing southward towards the plains before turning westward towards the sea. The headwaters of the Langat River is made up of forest foothills and rugged by mountain range.

Within the study area, there are seven towns located along the river. However, most of the industrial areas are located in Kajang and Bangi. There is also a rubber mill located south of Hulu Langat town and plam oil refineries near Banting.

Sampling location

The samples were collected from 6 stations in the Langat Estuary in the amount of sufficient quantities for the purpose of analytical procedures (Fig. 1a).

The sampling was conducted on the 8th August 2004. The Langat Estuary site was divided into six stations namely St.1, St. 2, St. 3, St. 4, St. 5 and St. 6 (Fig. 1b). Table 1 shows the GPS (Global Position) reading, time, weather and cloud condition measurement for each station. The sediments samples were collected by using Eckman Dredge Sediment Sampler. The sediment was then transferred into a stainless steel container with Teflon-lined cap to reduce any contamination. The containers were labeled and placed in icebox at 4°C prior to the transportation to the Department of Environmental Science laboratory in UPM for further analysis. Upon reaching the laboratory, the sample was stored in the Cold Room (-18°C) until futher analysis.

Freeze drying process

The collected sediment samples were in wet conditions. Therefore, before analysis, the samples were freeze dried for 3 to 4 days to get rid of any water contained in the samples. After the samples were freeze dried, they were kept in amber vials with Teflon-lined caps and labeled according to each station. They were then stored frozen before proceeding with the analysis of the PAHs.

Laboratory analysis

Solvents including HPLC grade methanol, DCM (dichloromethane), n-hexane, and deionized water were distilled in glass before use. Glassware was washed with detergents and tap water, and rinsed successively with methanol, acetone, and distilled hexane and muffled at 60°C for 24 hours to get rid of organic contaminants.

The sediment samples were precisely weighed between 15–20 g. The samples were extracted with a soxhlet extractor using 150 ml dichloromethane (DCM) for more than 8 hours. Whatman cellulose thimbles were used for this purpose. The condensers were circulated with cold water (<10°C). Then, the solvents were collected in a 250 ml round bottom flasks at the end of the extraction process.
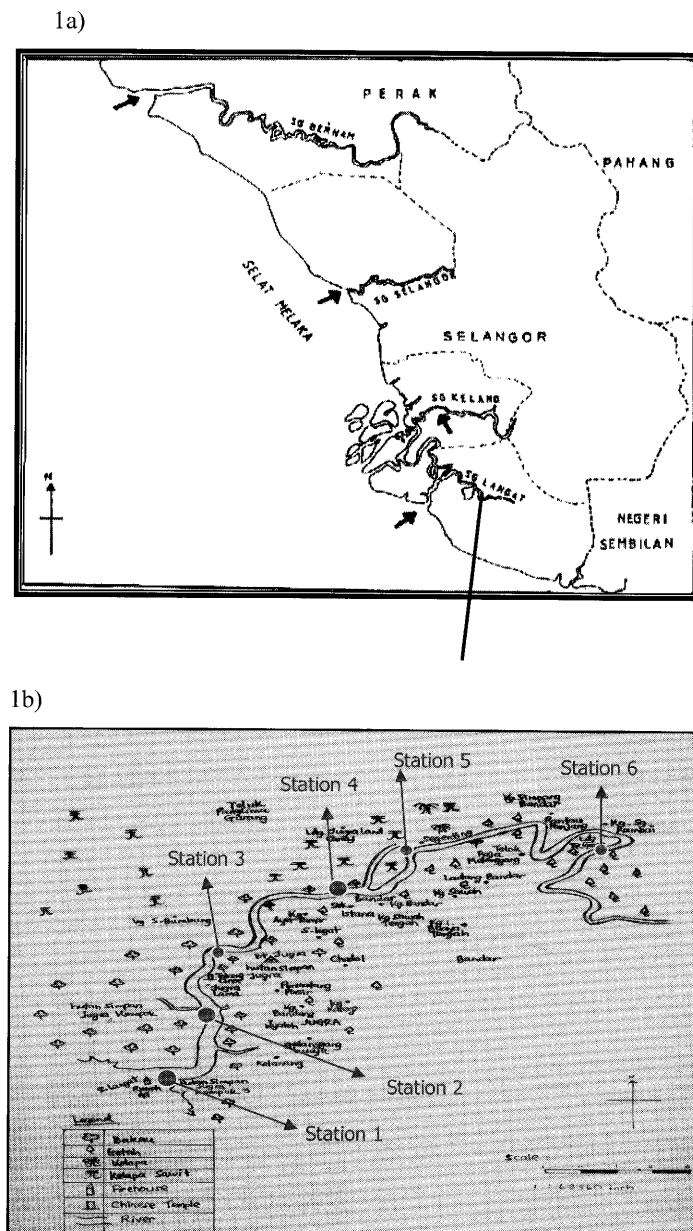
After Soxhlet Extraction, immediately 150 μl of deuterated PAH surrogate internal standard mixture (1,4-dichlorobenzene-D4, naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12 and perylene-D12) was added to the sample extracts. Volume of the solvents was reduced using Rotary-evaporator. The temperature of the water bath kept at 30°C to avoid loss of samples by volatilization. The vacuum flask was rotated slowly with a vacuum of 40 cmHg for DCM and 76 cmHg for Hexane. The samples were concentrated to near dryness and then transferred into 25 ml pear shape flasks with a Pasteur pipette and rinsed several times with DCM.

A few of copper chips were added into the sample, the flask covered with foil and Teflon sealed, and then left overnight. The purpose of copper treatment is to eliminate any sulfur in the samples that were produced by microorganism that may cause the interference in chromatogram reading. The samples were then apportioned into two parts, approximately 1 : 1, one part to be stored for further analysis and one part to be analyzed.

Clean up step is an open column chromatography and in this step most of the organic pollutants including n-alkanes, linear alkyl benzenes (LABs), PCBs, pesticides and PAHs were separated from other unwanted polar compounds. 5% H_2O deactivated silica gel was used to pack the glass column (0.9 mm internal diameter). First of all, the column was rinsed with High Grade Hexane. Quartz wool was put into the bottom of the column. Then the hexane was poured into the column. The 5% H_2O deactivated silica gel was added using Pasteur pipette until 9 cm heights. The column was vibrated gently to make it packed. It was ensured that there was no air bubbles trapped in the column. The level of hexane was reduced to 1/2 cm height above the activated silica gel by letting the hexane flow out from the column. The flask with reduced sample was rinsed with 2 ml Hexane: DCM (3 : 1 v/v) in sequence of 0.4 ml, 0.3 ml, 0.3 ml, 0.5 ml and 0.5 ml respectively. The extract was transferred to the column each time. The 18 ml remaining Hex/DCM (3 : 1 v/v) was transferred into the column directly. Hydrocarbon ranging from n-alkanes to PAHs was eluted with 20 ml Hex/DCM (3 : 1, v/v). The stopper was opened to allow all the samples with Hex/DCM (3 : 1 v/v) passed through the column into 25 ml

Table 1. Physical measurements of sampling sites.

Station	Weather	Time	GPS Location	Clouds
1st Station	Partly Sunny	8.53 am	2°47.988 N 101°24.249 E	Hazy
2nd Station	Partly Sunny	9.38 am	2°50.674 N 101°24.873 E	Hazy
3rd Station	Partly Sunny	10.11 am	2°51.980 N 101°26.253 E	Hazy
4th Station	Partly Sunny	11.00 am	2°53.387 N 101°28.411 E	Hazy
5th Station	Partly Cloudy	11.44 am	2°52.222 N 101°28.607 E	Hazy
6th Station	Partly Cloudy	12.15 pm	2°51.056 N 101°30.844 E	Hazy

1a)

1b)

Fig. 1. (a) Langat River Estuary, the study area. (b) Sampling location. Sediment samples were taken from 6 stations.

pear shape flask. The eluted sample was reduced in volume to near dryness for the use in second step column chromatography.

In the 2nd step column chromatography, 100% fully activated silica gel was used to pack the column with an internal diameter of 4.5 mm and the height of activated silica gel was 18 cm. There would be three fractions resulting from these steps: the first fraction consists of alkanes; the second LABs and PCBs; and the third, the PAHs. The concentrated sample from first column was added to the column and charged through with 4 ml of hexane to get alkane fraction. After this, 4 ml hexane was charged through to get the LABs and PCBs fraction. Finally, 14 ml of Hex/DCM (3 : 1 v/v) was charged through to get PAHs fraction. PAHs fraction was evaporated to approximately 1 ml, rinsed with iso-octane and transferred to glass ampoule, evaporated to dryness under gentle stream of nitrogen and re-dissolved into 150 μl iso-octane containing p-terphenly-D14 as an IIS (Internal Injection Standard) for PAHs.

Gas chromatography-mass spectrometry (GC-MS) analysis

PAHs was analyzed by Gas Chromatography-Mass Spectrometry (GC/MS) using a Hewlett-Packard 5972A quadruple mass spectrometer integrated with a gas chromatograph (HP5890), equipped with 30 m fused silica capillary column (HP-5MS), 0.25 mm i.d. and 0.25 μm film thickness, using helium as carrier gas on a constant pressure at 60 kg/cm^2. Detailed instrumental conditions and quantification of individual PAHs were described in Zakaria et al. (2002). A selected ion monitoring method was employed after a delay of 4 min. PAHs were monitored at $m/z=128$ (naphthalene), $m/z=154$ (acenaphthene), $m/z=178$ (phenanthere, anthracene), $m/z=184$ (dibenzothiophene), $m/z=192$ (2-methylphenanthrenes, 2-methylanthracene), $m/z=202$ (fluoranthene, pyrene), $m/z=216$ (1-methylpyrene), $m/z=228$ (benzo[a]anthracene, chrysene), $m/z=252$ (benzo[k]fluoranthene, benzo[e]acephenanthene, benzo[e]pyrene, benzo[a]pyrene, perylene), $m/z=278$ (dibenzo[a, h]anthracene).

In order to get the concentration of PAHs, the following calculation has been done. The calculation of recovery loses of the compound was also done according to the compound nature which is easy to volatile. The following formula (formula (1), (2) and (3)) was used to determine the concentration of each individual pesticides target compound in the final sample solution.

$$CS' = \frac{AS' \times AD \times CD' \times CS}{AS \times AD' \times CD} \quad (1)$$

Where, AS is area of peak compound X in the standard mixture solution,

AS' is area of peak of compound X in the sample solution,

AD is area of peak deuterated compound (IIS) X in the standard mixture solution,

AD' is area of peak compound (IIS) in sample solution,

CS is concentration of compound X in the standard mixture solution,

CS' is concentration of compound X in the sample solution,

CD is concentration of deuterated compound (IIS) in standard mixture solution,

CD' is concentration of deuterated compound (IIS) in sample solution

$$\text{Recovery} - \text{corrected } CS' = CS' \times (C1\text{-SIS} / C2\text{-SIS}) \quad (2)$$

Where C1-SIS is the original concentration surrogate internal standard compound,

C2-SIS is the concentration surrogate internal standard compound in sample.

$$\text{Concentration in sediment} = \frac{\text{Recovery-corrected,} CS' \times \text{Volume of final sample solution (ml)}}{\text{Weight of analyzed sediment (g)} \times \text{Apportion ratio}} \quad (3)$$

Results and Discussions

Table 1 lists the composition of PAHs compound and total PAHs concentration of river sediment samples in the Langat River Estuary that has been analyzed in this study. There were six samples collected, beginning from Station 1 located at the center of the Estuary and slowly going upstream to Station 2, Station 3, Station 4, Station 5 and finally Station 6.

According to Table 1, total PAHs for sediment samples of Station 1 until Station 6 ranged from 322 ng/g to 2480 ng/g (dry weight). Furthermore, MP/P ratios for sediment samples had values ranging from 0.88 to 1.27, while L/H ratios for the same samples ranged from 0.25 to 26.96.

From Station 1 until Station 6, 18 compounds of PAHs were analyzed, however only 17 compounds were detected in the samples. The total PAHs for the sediment samples in each Station are shown in Fig. 3.

The results show that the total PAHs concentration in river sediments of this area is considered high in certain Stations. The Langat River Estuary received a mixture of municipal, commercial, agriculture, recreational, residential and mixed industrial wastes and anthropogenic wastes originating from households and industrial chemicals.

Total PAHs concentration of sample in Station 4 and Station 5 are higher, with the exception of Station 2, compared to the other stations. Stations 4 and 5 are located near the downstream of the Langat Estuary (Fig. 1b) and are pathways for industrial shipping boats and situated near a few docks and factories. This finding suggests that the waste discharged in this area carries a higher percentage of PAH com-
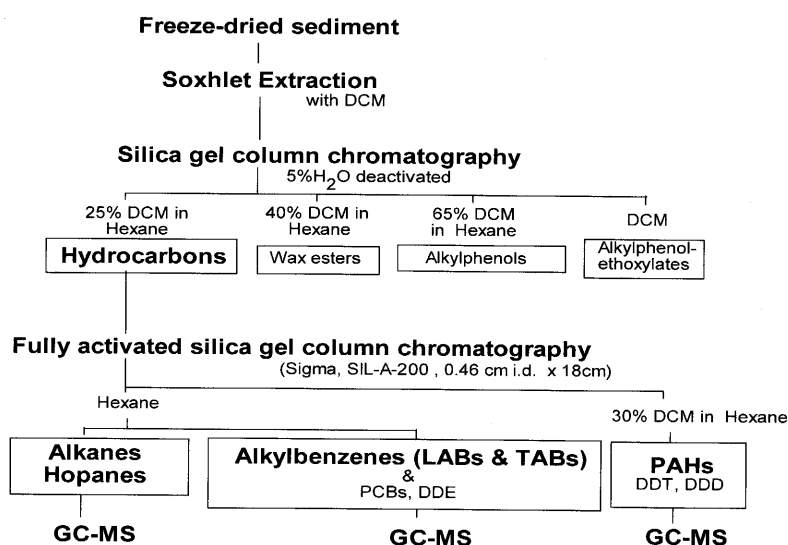
Freeze-dried sediment

|

Soxhlet Extraction
with DCM

|

Silica gel column chromatography
5%H$_2$O deactivated

25% DCM in Hexane	40% DCM in Hexane	65% DCM in Hexane	DCM
Hydrocarbons	Wax esters	Alkylphenols	Alkylphenol-ethoxylates

Fully activated silica gel column chromatography
(Sigma, SIL-A-200 , 0.46 cm i.d. x 18cm)

Hexane

30% DCM in Hexane

Alkanes Hopanes	**Alkylbenzenes (LABs & TABs)** & PCBs, DDE	**PAHs** DDT, DDD
GC-MS	**GC-MS**	**GC-MS**

Fig. 2. Analytical procedure for PAHs in sediments.

Table 2. Concentrations (ng/g) of PAHs in sediment samples in the Langat Estuary.

	Station 1	Station 2	Station 3	Station 4	Station 5	Station 6
DBT	3.88	0.78	0.15	0.44	0.42	0.3
Phe	8	1	0.3	1	1	nd
Ant	2.99	0.13	0.04	0.08	0.7	0.11
3MPhe	2	nd	0.06	nd	nd	nd
2MPhe	2.65	0.21	0.08	0.2	0.26	0.1
2MAnt	22	9	3.69	18	17	8
9MPhe	2	0.19	0.07	0.17	0.22	0.08
1MPhe	0.46	0.19	0.08	0.28	0.28	0.18
Fluo	7.18	628.27	232.5	523.9	707.66	221.54
Pyr	14.33	797.13	335.78	828.12	1663.21	422.45
1Mpyr	59	1	0.4	1	1	nd
BaAnt	115	1	0.29	1	1	nd
Chry	78	67	59.91	115	82	49
BkFluo	0.65	0.47	0.35	0.89	0.64	0.2
BeAcep	0.45	0.58	0.56	1.26	1.12	0.32
BePyr	2	1	1	3	2	1
BaPyr	1.4	0.92	0.67	1.87	1.1	0.32
DBahAnt	nd	nd	nd	nd	nd	nd
Total PAHs (ng/g)	322	1508	635.93	1495.64	2480	704
MP/P Ratio[b]	0.94	0.88	0.97	1.27	0.90	1.07
L/H Ratio[c]	0.25	20.09	9.07	11.09	26.96	12.93

[a]Total PAHs=sum concentrations of dibenzothiophene (DBT), phenanthrene (Phe), anthracene (Ant), 2-methylphenanthrene (2MPhe), 2-methylanthracene (2MAnt), fluoranthene (Fluo), pyrene (Pyr), 1-methylpyrene (1MPyr), benzo(a)anthracene (BaAnt), chrycene (Chry), benzo(k)fluoranthrene (BkFluo), benzo(e)acephenanthrelene (BeAcep), benzo(e)pyrene (BePyr), benzo(a)pyrene (BePyr) and dibenzo(a,h)anthracene (DBahAnt).
[b]MP/P Ratio=a ratio of the sum of 3, 2, 9, 1-methylphenanthrene (MPhe) to phenanthrene (Phe).
[c]L/H Ratio=a ratio of the sum of dibenzothiophene (DBT) to pyrene (Pyr) relative to sum of 1-methylpyrene to dibenzo(a,h)anthracene (DBahAnt).

pounds and this could be coming from the nearby docks, ships or factories. The waste generated might be discharged to the river through surface runoff or through groundwater transport. This could lead to hazardous chemicals like PAHs to be distributed to the Langat River and deposited in the

sediments. According to Cerniglia and Heitkamp (1989), PAHs may be absorbed onto fine particles, dissolved organic matter or suspended particles. As more PAHs get absorbed on to particles, they start to grow bigger and become heavier which will eventually lead to the settlement of these particles
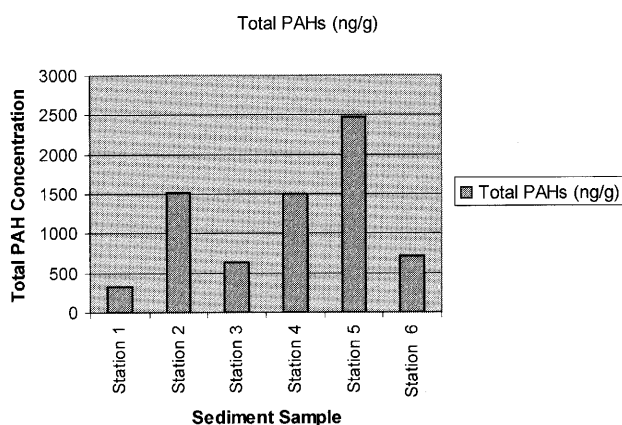
Total PAHs (ng/g)

Fig. 3. Concentration of PAHs in all samples.

carrying the PAHs into the sediments due to gravity. Total concentration for PAH compounds at Station 6 decreased rapidly as it is located upstream of the Langat Estuary.

The samples were calculated using methylphenan-threne/phenanthrene (MP/P) ratio to determine the sources of the PAHs. The value of less than 1 is the pyrogenic sources and more than 1 consists of petrogenic sources.

According to a previous study done by Zakaria et al., 2002, MP/P ratio of greater than unity was achieved for 26 sediment samples analyzed in urban rivers of Peninsular Malaysia. The MP/P ratio in Malaysian sediment is strongly correlated with the total PAHs concentration with r^2 value of 0.74, indicating that Malaysian urban sediments are highly impacted with petrogenic PAHs. These include crude oil and refined products (gasoline, diesel fuel and fuel oil). PAHs. The results for that study are shown in Table 3.

For this study, as shown in Fig. 4, sediment samples from Station 1 until Station 6 show an MP/P ratio value of less than 1, with the exception of Station 4 and Station 6. This points out that this area is dominated by pyrogenic sources which means that most of the PAH compounds are coming from the atmosphere such as street dust. PAHs are transported over long and short distances by atmosphere movement (Smith et al. 2000 and Chetwittayachan et al. 2002).

Station 4 and Station 6 show an MP/P ratio value of 1.27 and 1.07 respectively. This shows that the PAH compounds in this area originate from petrogenic sources. Therefore, PAHs in these areas are likely distributed through industrial activities as it is located near to shipping docks and factories. Petrogenic source includes the crude oil and refined product (Zakaria et al. 2002).

However, due to the fact that most of the sediment samples analyzed in this area show an MP/P ratio value of less than 1, therefore this respectively indicates that sources of PAHs in the Langat Estuary are from pyrogenic origin.

Previous analysis of PAHs in leachates by Khor (2004) indicated that leachate received petrogenic PAHs from illegal

dumping of used crankcase oil and petroleum product. Normally, according to Zakaria et al. 2002, petrogenic source of PAHs contain lower molecular weight PAHs (dibenzothiophene to pyrene) with severe depletion of higher molecular weight PAHs (1-methyl-pyrene to dibenzo(a,h)anthracene), while pyrogenic source are abundant in high molecular weight PAHs.

These PAHs profile are useful to estimate sources and fates of PAHs pollutants (Zakaria and Takada 2003). To quantitively express the abundance of alkyl homologues, an MP/P ratio, a relative abundance of total methyl phenanthrenes (3, 2, 9, 1 MPhe) to phenanthrenes had been proposed.

As shown in Fig. 5, the MP/P ratio for this study is relatively low compared to previous studies by Zakaria et al. (2002) and Zulrahman (2002).

Analysis also proposed the L/H ratio, as shown in figure 6, which is a ratio of sum of dibenzothiophene (DBT) to pyrene (Pyr) relative to the sum of 1-methylpyrene (1MPyr) to dibenzo(a,h)anthracene (DBahAnt). All samples showed a lower value in higher molecular weight (HMW) compared to the value of lower molecular weight (LMW).

The highest concentration from HMW was chrysene (Chry), which is suspected to give carcinogenic effect if accumulated in the body in a certain amount.

However, higher molecular weight (HMW) is the one to be concern as it has hazardous effects (i.e., mutagenic and carcinogenic). For this study, HMW contains 8 PAHs from 1-methylpyrene (1 MPyr) to dibenzo(a,h)anthracene (DBahAnt). It consist in a larger amount in soil and street dust than LMW because HMW are less water soluble, less volatile, and had higher persistent than LMW as done by a previous study by Nurhafizah (2002). Furthermore, they remain longer in sediments subjected to slower removal from the top soil by either vaporization, washing out or degradation than LMW. In this study, LMW was more dominant than HMW, however, the results achieved from this study show that the PAH compounds in the Langat Estuary came from mixed sources which contained both of LMW and HMW PAHs.
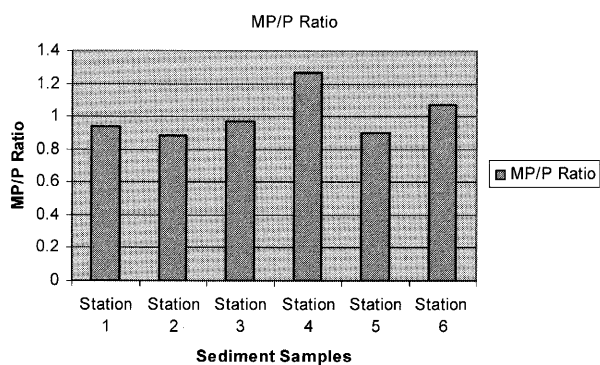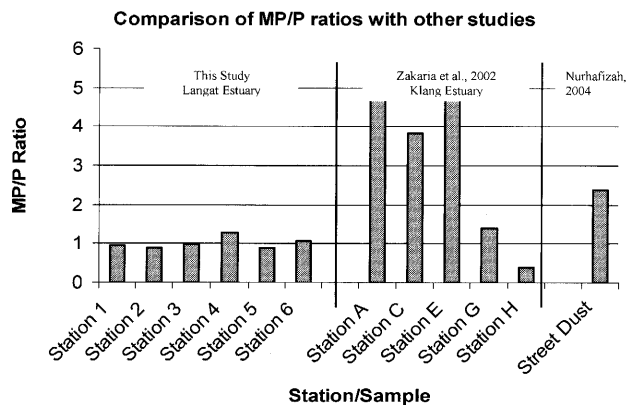
Conclusions

Malaysian estuary and coastal environment is an important ecosystem as it acts as receptors for land-derived pollutants. The coasts of Peninsular Malaysia are important for fisheries, recreational and marine activities, tourism and maintaining the bio-diversity in the tropical area (Zakaria et al. 2001). However, the coasts are under constant threat of various pollutions. The Langat estuary which contains many species of fishes is also one of the estuaries which are polluted, other than Klang Estuary, by PAHs.

Table 3. PAHs in Malaysian and Tokyo sediment.

Sample	Organic carbon (mg/g)	Total PAHs (ng/g)	Perylene (ng/g)	PAHs/OC (ng/g)	H/L ratio	MP/P ratio
						Malaysia
Rivers						
Prai River	15.7	81	38	5	1.46	1.52
Pinang River	24.5	924	43	38	1.47	6.65
Nibong Tebal	16.8	62	40	4	1.09	2.21
Teluk Intan	32.5	20	884	1	1.1	2.59
Kuala Selangor	23.4	42	88	2	1.27	2.04
Port Klang	11.5	387	87	34	0.48	5.19
Malacca River (1998)	15.4	494	31	32	1.24	3.76
Malacca River (1999)	15.8	262	47	17	0.94	3.01
Muar River	16.4	69	33	4	1.85	1.33
Johor Bahru (1998)	23.7	239	20	10	1.42	1.56
Kim Kim river	6.6	41	1	6	0.82	2.47
Kim Kim estuary	23.7	37	8	2	1.63	1.34
Klang estuary						
Station A	10.9	378	124	35	0.47	5.38
Station C	22.1	431	130	19	0.91	3.82
Station E	22.4	257	109	11	0.66	5.1
Station G	10.0	82	45	8	1.41	1.41
Station H	15.2	19	6	1	0.64	0.39
Klang Coast (inshore)						
Station 2K	14.2	27	17	2	1.09	1.44
Station 15	11.7	21	19	2	1.6	1.2
Station 11	2.7	9	11	3	1.8	1.09
Station 9	13.0	39	36	3	1.79	1.08
Straits of Malacca (offshore)						
Station 2	8.3	4	1	0	0.87	0.56
Station 8	6.1	6	3	1	1.47	1.35
Station 14	1.2	11	4	9	1.5	1.12
Station 17	6.9	7	2	1	1.61	0.59
Station 18	4.7	10	17	2	1.6	1.42
Station 21	5.8	73	12	13	1.89	1.2
Station 22	5.7	4	1	1	1.55	1.73
Station 23	2.5	11	3	5	1.76	1.36
						Tokyo
n=64 m						
Average	25.3	9546	424	420	1.39	0.85
SD	18.7	38770	1177	1490	0.37	0.24
Minimum	5.1	534	2	35	0.55	0.43
Maximum	99.8	292370	9310	10118	2.24	1.55

Source: Zakaria et al. 2002.

Fig. 4. MP/P ratio in sediment samples.

Fig. 5. Comparison of MP/P ratios with other studies.
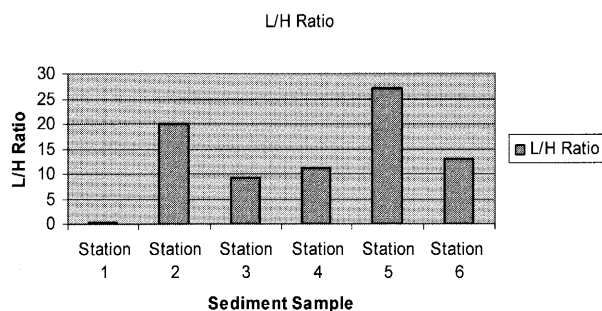
L/H Ratio

Fig. 6. L/H ratio in sediment samples.

The total PAHs concentration in river sediments of this area is considered high especially in Station 2, Station 4 and Station 5.

Sediment samples from Station 1 until Station 6 show an MP/P ratio value of less than 1, except for Station 4 and Station 6. This points out that the Langat Estuary is dominated by pyrogenic sources which means that most of the PAH compounds are coming from the atmosphere such as street dust.

All samples showed a lower value in higher molecular weight (HMW) compared to the value of lower molecular weight (LMW). This suggests that the pyrogenic sources came from mixed sources of HMW and LMW of PAHs.

Acknowledgement

References

Baker, K. H. and Herson, D. S.,1994. Bioremediation. McGraw-Hill, Inc, New York.

Blumer, M. 1976. Polycyclic aromatic compounds in nature. Scientific American 234(3): pp. 34–45.

Cerniglia, C. E. and M. A. Heitkamp. 1989. Microbial Degradation of Polycyclic Aromatic Hydrocarbon (PAHs) in the Aquatic Environments. *In* U. Varanasi [Ed]. Metabolism of Poycyclic Aromatic Hydrocarbon in the Aquatic Environment. CRC Press Florida. 329.

Chetwittayachan, T., Shimazaki, D. and Yamamoto. K. 2002. A comparison of temporal variation of particle-bound PAHs concentration in different urban environments: Tokyo, Japan and Bangkok, Thailand. Atmospher. Environ. 36: 2027–2037.

Smith, D. J. T., Edelhauser. E. C. and Harrison, R. M. 1995. Polynu-

clear aromatic hydrocarbon concentrations in road dust and soil samples collected in the United Kingdom and Pakistan. Environ. Technol. 16: 45–53.

Guinan, J., Charlesworth, M., Service, M. and Oliver, T. 2001. Sources and Geochemical Constraints of Polycyclic Aromatic Hydrocarbons (PAHs) *In* Sediments and Mussels of two Northern Irish Sea Loughs. Mar. Pollut. Bull. Vol. 42, No 11, pp. 1073–1081.

Jaffe, R., Cabrera, A., Carrero, H. and Alvarado, J, 1993. Oraganic Compounds and Heavy Metals in the City of Caracas, Venezuela-II. Atmospheric Deposition. Water, Air and Soil Pollution. Vol. 71. pp. 315–329.

Kelly, C. A., Law, R. J. and Emerson, H. S. 2000. Methods of Analyzing Hydrocarbons and Polycyclic Aromatic Hydrocarbons (PAH) in Marine Samples. The Centre for Environment, Fisheries and Aquaculture Science (CEFAS) Science Series, Aquat. Environment Protection. Analytical Methods, No.12

Khor, H. G. 2004. Composition and Sources of PAHs in Landfill Leachate in Selected Location in Peninsular Malaysia. Master of Sciences Thesis, Department of Environmental Science, Faculty of Environmental Studies, UPM.

Ming-chien, Su., Christensen, Erik, R., Karl, S. and Jay, F. 1998. Determination of PAH sources in dated sediments from Green Bay, Wisconsin, by a chemical mass balance model. Environ. Pollut. 98, pp. 411–419.

Neff, J. M. 1979. Polycyclic aromatic hydrocarbons in the aquatic environment: sources, fates, and biological effects. Applied Science Publishers, London.

Tam, N. F. Y., Ke, L., Wang, X. H. and Wong, Y. S. 2001. Contamination of Polycyclic Aromatic Hydrocarbons in Surface Sediments of Mangrove Swamps. Environmental Pollution 114, pp. 255–263.

Vilanova, R. M., Fernandez, P., Martinaz, C. and Grimalt, J. O. 2001. Polycyclic Aromatic Hydrocarbons in Remote Mountain Lake Waters. Wat. Res. Vol. 35, No. 16, pp. 3916–3926.

Zakaria, M. P., Okuda, T. and Takada, H. 2001. Polycyclic Aromatic Hydrocarbons (PAHs) and Hopanes in Stranded Tar-balls on the Coast of Peninsular Malaysia: Applications of Biomarkers for Identifying Sources of Oil Pollution. pp. 1357–1366.

Zakaria, M. P. and Takada, H. 2003. Biogeochemistry of (PAH) Polycyclic Aromatic Hydrocarbons and (LAB) Linear Alkylbenzenes in Klang River and Estuary: Understanding the Transport of PAHs from Rivers to the Straits of Malacca. pp. 275–289.

Zakaria, M. P., Takada, H., Tsutsumi, S., Ohno, K., Yamada, J., Kuono, E. and Kumata, H. 2002. Distribution of Polycyclic Aromatic Hydrocarbon (PAHs) in Rivers and Estuaries in Malaysia: A Widespread Input of Petrogenic PAHs. Environ. Sci. Technol. 36: 1907–1918.

Zulrahman, N. 2002. Composition and Distribution of PAHs in Soil from Vegetable Farm and Street Dust from a Nearby Busy Highway. Undergraduate Thesis, Department of Environmental Science, Faculty of Environmental Studies, UPM.