

## Polycyclic Aromatic Hydrocarbons and *n*-alkanes in Suspended Particulate Matter and Sediments from the Langat River, Peninsular Malaysia

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### Abstract

The Langat River basin has seen rapid developments in industrialization, urbanization and dramatic population increases during the past two decades. The composition and sources of polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbon (*n*-alkanes) concentrations were determined in surface sediments (SS) and suspended particulate matter (SPM) collected from six locations in the Langat River. The total *n*-alkanes concentrations ( $\Sigma$ H<sub>C</sub>) ranged from 5900 to 23000  $\mu$ g/g in SPM and 1700 to 8600  $\mu$ g/g in SS samples. Total PAHs concentrations varied from 306 to 7968 ng/g in SPM and 558 to 980 ng/g in SS. PAHs and *n*-alkanes were dominated by higher molecular weight compounds in SS and low-medium molecular weight compounds in SPM. Carbon preference index (CPI) values for *n*-alkanes in ranges C<sub>25-33</sub>, C<sub>15-35</sub> and C<sub>25-35</sub> varied from 0.95 to 2.49 in SS and close to unity in SPM. The CPIs values indicated multiple *n*-alkanes sources (petrogenic and natural). PAHs isomer pairs ratios indicated multiple (petrogenic and pyrogenic) with predominance of pyrogenic PAH sources. Analysis of the possible source of PAHs and *n*-alkanes indicated a complicated, combined PAHs and *n*-alkanes source in the Langat River.

**Keywords:** CPI; perylene; PAHs isomer pairs ratios; suspended particulate matter; surface sediment

### 1. Introduction

The physico-chemical properties of the PAHs largely determine their environmental behavior. Low molecular weight (LMW) PAHs, containing two or three fused rings, are more water soluble and volatile, and hence more available, than high molecular weight (HMW) PAHs containing >3 fused rings, as compared to HMW PAHs, makes them more susceptible to various degradation processes (US EPA Report, 2003).

Due to the high hydrophobicity and thereby the low water solubility, the HMW PAHs have a high affinity for organic particulate matter. With increasing the molecular weight of PAH, the tendency to sorbs onto dissolved organic matter (DOM) also increases (McCarthy and Jimenez, 1985). Therefore, the water solubility of PAH can be enhanced due to DOM and thereby co-transport of PAH with DOM occurs in the water column, especially for HMW PAHs (Maxin and Kögel-Knabner, 1995). Only lower molecular weight hydrocarbons with less than 2 and 3 condensed

rings are capable of environmental transport in aqueous solution in the absence of DOM (Guggenberger *et al.*, 1996).

The Langat River is a complex ecosystem that runs through different land-uses near the city of Kuala Lumpur. 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 palm oil refineries near Banting.

The objectives of this study were to assess the compositional patterns and sources of PAHs and *n*-alkanes concentrations in surface sediment samples (SS) and suspended particulate matters (SPM) in the Langat River.

### 2. Materials and Methods

#### 2.1. Sampling location

Ten surface sediments (SS) and suspended particulate materials (SPM) were collected from

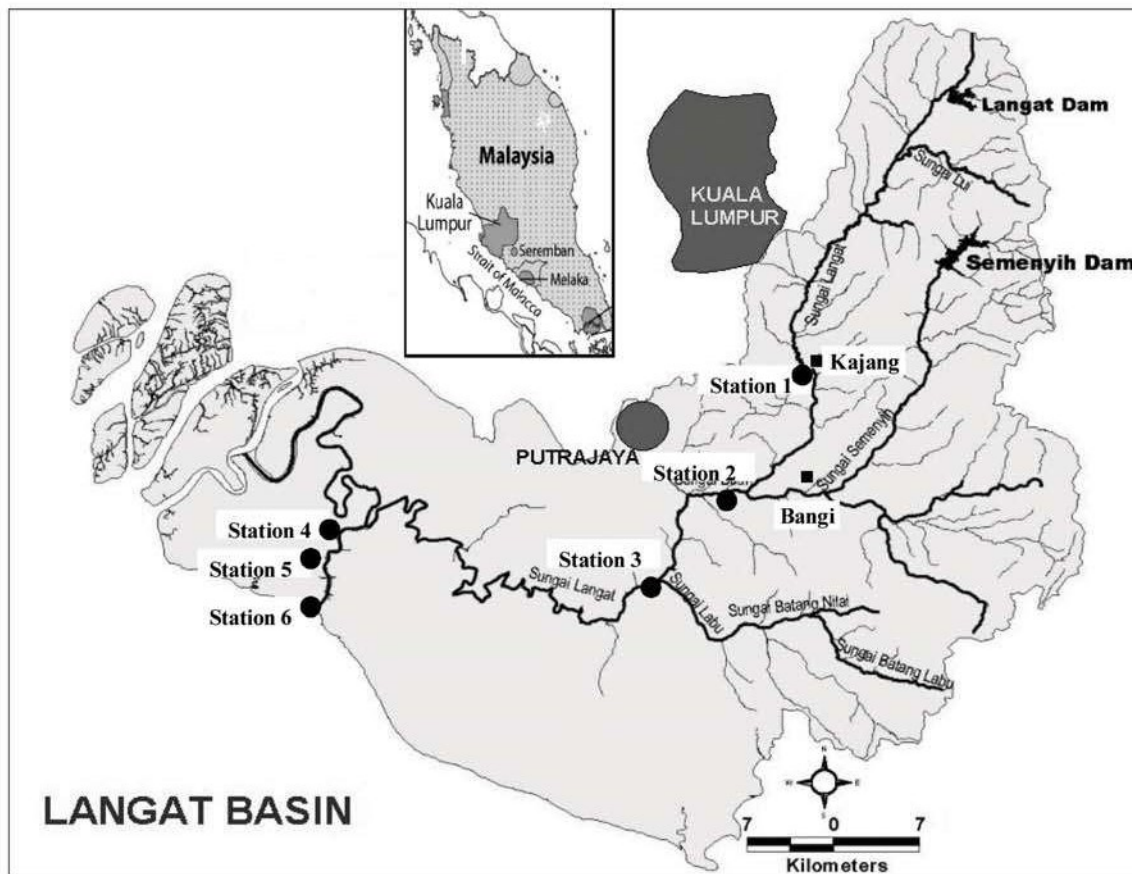


Figure 1. Map of the sampling sites in the Langat River

locations in the Langat River in the west coast of Peninsular Malaysia in January 2007 (Fig. 1 and Table 1). The sediment samples were collected using an Ekman Dredge sampler. The sediment cake was placed on a stainless steel pan and the top 0-5 cm layer was taken using a precleaned stainless steel scoop. The sediment samples were then transported on ice to the laboratory and stored at  $-35^{\circ}\text{C}$  until further analysis. The water was collected from the surface and middle-depth with a Niskin bottle. The water samples were then transported on ice to the laboratory. The SPM was immediately

collected after filtration of 1 to 3 L aliquots, through 0.45 Millipore  $\mu\text{m}$  (47 mm diameter) preweighted filters, using the classic vacuum system and stored at  $-35^{\circ}\text{C}$  until further analysis.

## 2.2. Chemical analysis

### 2.2.1. Analytical procedure for PAHs and n-alkanes

The samples were purified and fractionated by a method described elsewhere (Zakaria *et al.*, 2002). Briefly, a soxhlet extractor was used for the

Table 1. Location of sampling locations and general characteristics of the suspended particulate matter and the surface sediment samples from the Langat River (19/01/07)

Stations	Type of sample		GPS location		Conductivity ( $\mu\text{s}/\text{cm}$ )	Salinity (ppt)	Turbidity (NTU)
	Sediment	Suspended Particulate Material					
S1	-	1	47N 0809449	utm 0331379	35.7	00.0	168
S2	-	1	47N 0806738	utm 0322931	94.0	00.0	259
S3	1	-	47N 0798085	utm 0315854	72.6	00.0	655
S4	1	1	47N 0769700	utm 0316905	21.3	12.7	102
S5	1	1	47N 0768258	utm 0314266	28.8	17.6	164
S6	1	1	47N 0767248	utm 0309944	44.0	28.2	25

extraction of lipid from the samples using 270 ml of distilled dichloromethane for 10 hours. 100 µl of the PAH surrogate internal injection standard mixture (10 ppm each component, naphthalene-d<sub>8</sub>, anthracene-d<sub>10</sub>, chrysene-d<sub>12</sub> and perylene-d<sub>12</sub>) was added for quality control of PAH analyses. The extracts were transferred onto the top of a 5% H<sub>2</sub>O deactivated silica gel column. Hydrocarbons ranging from n-alkanes to PAHs with five rings were eluted with 20 ml of dichloromethane/hexane (1:3, v/v). The eluent was further fractionated using fully activated silica gel column chromatography to obtain an alkane fraction and a PAH fraction. Alkanes were eluted with 4 ml of hexane and subsequently PAHs were eluted with dichloromethane/hexane (1:3, v/v).

The PAH fraction was evaporated to approximately 1 ml transferred to a 1.5 ml amber and evaporated to dryness under a gentle stream of nitrogen and re-dissolved in 100 µl of isooctane containing *p*-terphenyl-d<sub>14</sub> as an internal injection standard (IISTD) for PAHs analysis. Each n-alkane fraction was evaporated to approximately 1 ml, transferred to a 1.5 ml amber ampoule and evaporated to dryness under a gentle stream of nitrogen and re-dissolved in 100 µl of isooctane. PAHs and n-alkanes analyses were conducted using an Agilent technology 5973A quadrupole mass spectrometer integrated with an Agilent 6890 gas chromatograph. A 30 m fused silica capillary column of 0.25 mm i.d. and 0.25 µm film thickness using helium as carrier gas was used in the analysis.

GC-MS operating conditions were 70eV ionization potential with the source at 200°C and electron multiplier voltage at ~2000 eV. The injection port was maintained at 310°C and the sample was injected with splitless mode followed by purge 1 min after the injection. Column temperature was held at 70°C for 2 min, then programmed at 30°C/min to 150°C, and then 4°C/min to 310°C and held for 10 min. A selected ion monitoring method was employed after a delay of 3 min. PAHs were monitored at  $m/z = 128$  (naphthalene),  $m/z = 184$  (dibenzothiophene),  $m/z = 178$  (phenanthrene, anthracene),  $m/z = 192$  (2-methylphenanthrene, 1-methylphenanthrene, 2-methylanthracene),  $m/z = 202$  (fluoranthene, pyrene),  $m/z = 216$  (1-methylpyrene),  $m/z = 228$  (chrysene, benzo[a]anthracene),  $m/z = 252$  (benzo[k]fluoranthene, benzo[e]acephenanthrene, benzo[e]pyrene, benzo[a]pyrene, perylene),  $m/z = 278$  (dibenzo[a,h]anthracene).

Each n-alkane fraction was evaporated to approximately 1 ml, transferred to 1.5 ml amber ampoule, and evaporated to dryness under a gentle

stream of nitrogen and re-dissolved in 100 µl of isooctane. It was sealed by Teflon sheet and Teflon tape, after sonication, volatile organic carbons (VOCs) are formed in the head space on the sample in the vial. n-alkane analyses were made using an Agilent technologies 5973A quadrupole mass spectrometer integrated with an Agilent 6890 gas chromatograph. A 30 m fused silica capillary column of 0.25 mm i.d. and 0.25 µm film thickness with helium as carrier gas was used in the analysis. GC-MS operating conditions were 70eV ionization potential with the source at 200°C and electron multiplier voltage at ~2000 eV. The injection port was maintained at 310°C and the sample was injected in splitless mode followed by purge 1 min after the injection. Column temperature was held at 70°C for 1 min, then programmed at 30°C/min to 150°C, 5°C/min to 310°C and held for 10 min. A selected ion monitoring method was employed after a delay of 3 min. n-alkanes were monitored at  $m/z = 142$  (C<sub>10</sub>),  $m/z = 170$  (C<sub>12</sub>),  $m/z = 198$  (C<sub>14</sub>),  $m/z = 226$  (C<sub>16</sub>),  $m/z = 254$  (C<sub>18</sub>),  $m/z = 282$  (C<sub>20</sub>),  $m/z = 310$  (C<sub>22</sub>),  $m/z = 338$  (C<sub>24</sub>),  $m/z = 366$  (C<sub>26</sub>),  $m/z = 394$  (C<sub>28</sub>),  $m/z = 422$  (C<sub>30</sub>),  $m/z = 450$  (C<sub>32</sub>),  $m/z = 478$  (C<sub>34</sub>),  $m/z = 506$  (C<sub>36</sub>),  $m/z = 534$  (C<sub>38</sub>),  $m/z = 562$  (C<sub>40</sub>).

### 3. Results and Discussion

#### 3.1. n-alkanes concentrations of the Langat River

The concentrations and compositional patterns of n-alkanes and related parameters are presented in Table 2. The total n-alkanes concentrations (ΣHC) ranged from 5900 to 23000 µg/g in SPM and 1700 to 8600 µg/g in SS samples. The n-alkanes compositional patterns exhibit differences in SPM and SS samples. In the SS samples, n-alkanes are characterized by a higher abundance of long chain homologues ( $nC_{27}$ ,  $nC_{29}$ ,  $nC_{31}$  and  $nC_{33}$ ) and are dominated by  $nC_{29}$  and  $nC_{31}$ . On the other hand, in the SPM samples, n-alkanes distributions are characterized by predominance of medium molecular weights ( $nC_{23}$ ,  $nC_{24}$ ,  $nC_{25}$  and  $nC_{26}$ ) and are dominated by  $nC_{24}$  and  $nC_{26}$ . These results are consistent with those of other studies and suggest that the difference between SPM and SS samples may be attributed to easy degradation of short chain n-alkanes relative to long chain n-alkanes occurred in sediments (Meyers *et al.*, 1984; Gagosian and Peltzer, 1986; Prah *et al.*, 1980; Jeng and Huh, 2004). Comparison of n-alkanes concentrations in SS samples indicated that upstream received more n-alkanes concentrations than downstream. This result may be explained by the fact that there are

Table 2. Hydrocarbon concentrations ( $\mu\text{g/g}$ ) and related parameters in the suspended particulate matters and the surface sediments of the Langat River

Compounds	Stations								
	S1	S2	S3	S4		S5		S6	
	SPM	SPM	SS	SS	SPM	SS	SPM	SS	SPM
<i>nC</i> <sub>15</sub>	N.D	N.D	40	N.D	N.D	N.D	N.D	N.D	N.D
<i>nC</i> <sub>16</sub>	N.D	N.D	125	N.D	N.D	N.D	N.D	N.D	N.D
<i>nC</i> <sub>17</sub>	118	81	419	N.D	N.D	N.D	95	47	N.D
Pristane	306	409	750	40	202	24	306	100	N.D
<i>nC</i> <sub>18</sub>	362	575	464	40	355	14	454	96	N.D
Phytane	360	520	495	50	340	37	460	85	N.D
<i>nC</i> <sub>19</sub>	225	497	465	37	345	12	461	66	N.D
<i>nC</i> <sub>20</sub>	240	555	525	44	395	15	414	74	N.D
<i>nC</i> <sub>21</sub>	437	876	498	69	613	20	738	102	96
<i>nC</i> <sub>22</sub>	797	1791	482	118	1227	44	1533	229	189
<i>nC</i> <sub>23</sub>	1266	2690	549	172	1747	64	2366	374	348
<i>nC</i> <sub>24</sub>	1468	3055	626	190	1951	89	3048	461	550
<i>nC</i> <sub>25</sub>	1345	2088	870	248	1469	133	2035	721	676
<i>nC</i> <sub>26</sub>	1508	1459	1087	185	1036	140	1748	723	773
<i>nC</i> <sub>27</sub>	1044	1354	1010	313	715	145	1890	1095	667
<i>nC</i> <sub>28</sub>	1026	1019	1012	205	747	166	1771	801	634
<i>nC</i> <sub>29</sub>	1314	1162	1619	485	536	230	1995	1209	669
<i>nC</i> <sub>30</sub>	641	931	886	181	549	128	1664	550	572
<i>nC</i> <sub>31</sub>	1049	888	1732	627	570	264	1637	1029	497
<i>nC</i> <sub>32</sub>	807	N.D	828	172	N.D	115	1164	428	286
<i>nC</i> <sub>33</sub>	N.D	N.D	1182	301	N.D	148	N.D	570	N.D
<i>nC</i> <sub>34</sub>	N.D	N.D	379	N.D	N.D	N.D	N.D	N.D	N.D
<i>nC</i> <sub>35</sub>	N.D	N.D	625	N.D	N.D	N.D	N.D	N.D	N.D
<i>nC</i> <sub>36</sub>	N.D	N.D	236	N.D	N.D	N.D	N.D	N.D	N.D
$\Sigma$ HC	13285	19021	15704	3387	12256	1788	23013	8576	5957
CPI <sub>25-33</sub>	1.03	1.23	1.47	2.39	1.09	1.56	1.00	1.70	1.00
Overall CPI <sub>15-35</sub>	0.99	1.03	1.34	1.99	0.96	1.43	0.95	1.55	0.98
High CPI <sub>25-35</sub>	1.02	1.30	1.48	2.49	1.10	1.56	1.03	1.70	0.96
LHC/ $\Sigma$ HC	25.0	17.9	35.3	51.0	14.9	44.0	24.0	45.5	30.8

$\Sigma$  HC = Sum of *nC*<sub>15+...+nC</sub><sub>36</sub> include pristine and phytane.

SPM = Suspended particulate matter, SS = Surface Sediment.

TAR<sub>HC</sub> = terrigenous/aquatic ratio =  $(nC_{27}+nC_{29}+nC_{31}) / (nC_{15}+nC_{17}+nC_{19})$ .

CPI<sub>25-33</sub> = carbon preference index =  $\frac{1}{2} \times [(nC_{25}+nC_{27}+nC_{29}+nC_{31}+nC_{33} \div nC_{24}+nC_{26}+nC_{28}+nC_{30}+nC_{32}) + (nC_{25}+nC_{27}+nC_{29}+nC_{31}+nC_{33} \div nC_{26}+nC_{28}+nC_{30}+nC_{32}+nC_{34})]$

Overall CPI<sub>15-35</sub> =  $(\Sigma \text{Odds } C_{15-33} + \Sigma \text{Odds } C_{17-35}) / 2(\Sigma \text{Evens } C_{16-34})$

High CPI<sub>25-35</sub> =  $(\Sigma \text{Odds } C_{25-33} + \Sigma \text{Odds } C_{27-35}) / 2(\Sigma \text{Evens } C_{26-34})$

LHC /  $\Sigma$  HC =  $(nC_{27} + nC_{29} + nC_{31} + nC_{33}) / \Sigma$  HC.

N.D = non detected

more human and industrial activities in the upstream (e.g. Kajang and Bangi) relative to downstream of the Langat River.

### 3.1.1. Carbon Preference Indices (CPI) of *n*-alkanes

CPI is used to indicate the degree of diagenesis of straight-chain geolipids and is a numerical representation of how much of the original biological chain length specificity is preserved in geological lipids (Meyers and Ishiwatari, 1995). It is useful to

determine the degree of biogenic versus petrogenic input (Mazurek and Simoneit, 1984).

In this study, the CPI values were calculated using three equations which were proposed by Bray and Evans (1961) and Cooper and Bray (1963) and listed in Table 2. The CPI values of *n*-alkanes in Langat River ranged from 1.00 to 2.39 in CPI ranges *C*<sub>25-33</sub>, 0.95 to 1.55 in Overall CPI ranges *C*<sub>15-35</sub> and 1.02 to 2.49 in High CPI ranges *C*<sub>25-35</sub>. The CPI<sub>25-33</sub>, Overall CPI<sub>15-35</sub> and High CPI<sub>25-35</sub> ranged from 1.34 to 2.49 in the SS samples relative

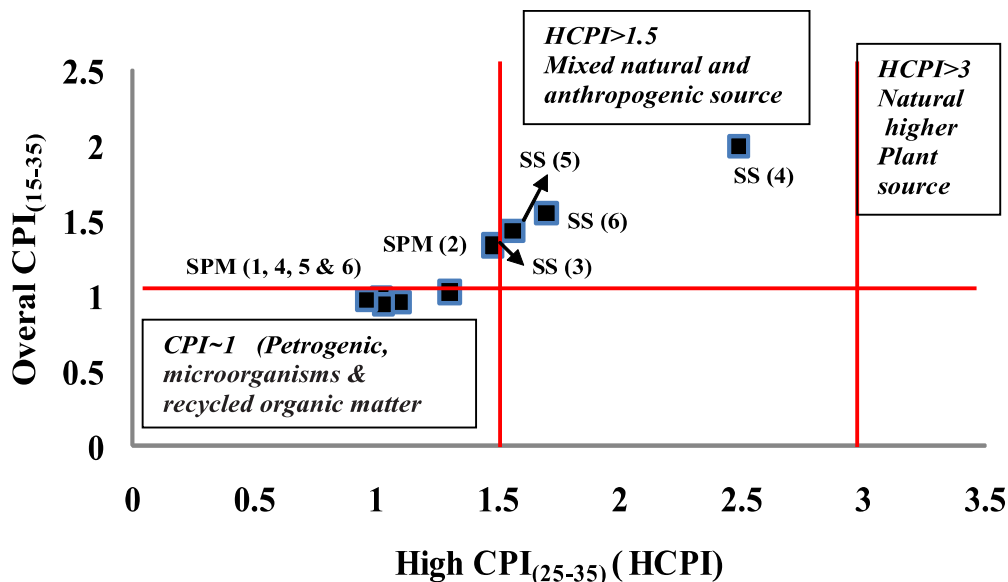


Figure 2. Source identification for n-alkanes using High  $CPI_{25-35}$  (HCPI) and overall  $CPI_{15-35}$  in Langat River sediments

the SPM samples which were close to unity (Fig. 2). The results indicate multiple sources for n-alkanes (petrogenic and natural).

### 3.1.2. Unresolved Complex Mixture (UCM)

Total ion chromatograms of n-alkanes showed an unresolved complex mixture (UCM) in all samples at lower carbon number maximum. The UCM concentrations were not calculated but their presence suggests the presence of degraded petroleum hydrocarbons (Simoneit, 1982; Matsumoto, 1983). It is believed that the UCM contains a mixture of alicyclic compounds (Gough and Rowland, 1990; Killips and Al-Juboori, 1990) and has a well-known linkage to degraded or weathered petroleum residues (Readman *et al.*, 1987; Venkatesan *et al.*, 1980).

### 3.2. PAHs composition

The concentrations of 18 PAHs, naphthalene, perylene and diagnostic ratios are presented in Table 3. Total concentration of 18 PAHs, expressed as  $\Sigma 18\text{PAH}$  ranged from 306 to 7968 ng/g in SS and SPM of the Langat River. The higher concentrations of total PAHs were found in upstream compared to downstream of the Langat River. This can be attributed to the fact that most of the industrial areas are located in Kajang and Bangi. In addition, there is also a rubber mill and other small and medium scale industrials located south of Hulu Langat town (Zakaria and Azril Mahat, 2006). The activities of downstream are closely related to existing port and jetties which cater to berthing and mooring facilities for various types of ships, vessels and boats. PAHs distributions were dominated by 2, 3 and 4 rings

compounds in SPM samples and by 5 rings compounds in SS samples, except for Station 6. These findings of the current study are consistent with those of Luo *et al.* (2006) who found predominance of 5, 6-ring compounds in sediments and 2, 3-ring compounds in SPM samples from the Pearl River estuary and adjacent coastal areas in South China. Different PAHs compositional patterns between SPM and SS were also found in other regions, such as Da Ya Bay (Zhou and Maskaoui, 2003), Brighton Marina of United Kingdom (King *et al.*, 2004), and the Baltic Sea (Witt, 1995). This may be explained to the fact that the surface water receives direct PAHs inputs, such as shipping, oil spill, dry and wet atmospheric deposition, air-water exchange etc (Luo *et al.*, 2006). Another possible explanation for this might be due to degradation of lower molecular weight PAHs during river water column transport and after accumulation. This is due to the fact that high molecular weight PAHs are more resistant to degradation processes occurred in sediments (Cerniglia, 1992).

Naphthalene was found in abundance in SPM samples compared to SS. The range of naphthalene concentrations were from 1405 to 2420 ng/g in SPM and 410 to 440 ng/g in SS samples (Table 3). It is believed that naphthalene is a major compound in woody material (Wilcke *et al.*, 2000) and it can be supplied in large amounts to the Rivers during heavy rains in tropical environments. Naphthalene is also a product of the combustion of biomass and fossil fuel (Krauss *et al.*, 2005). It is likely therefore that the naphthalene originated from both terrigenous and pyrogenic sources. Different naphthalene compositional patterns between SPM and SS

Table 3. PAHs concentration (ng/g) and related parameters in the surface sediments and the suspended particulate matters from the Langat River

Compounds	Stations							
	S1	S2	S3	S4		S5	S6	
	SPM	SPM	SS	SPM	SS	SS	SPM	SS
Nap	2420	2349	429	2348	438	417	1406	434
DBT	N.D	N.D	N.D	N.D	N.D	N.D	7	N.D
Phe	1805	309	66	196	25	41	N.D	29
Ant	352	437	22	215	15	32	N.D	46
3MPhe	391	44	29	29	3	9	4	5
2MPhe	429	88	32	38	6	16	4	9
2MAnt	N.D	N.D	4	N.D	N.D	N.D	N.D	N.D
9MPhe	133	70	40	22	6	12	4	5
1MPhe	360	61	24	26	4	15	6	6
Fluo	813	136	59	95	24	55	27	43
Pyr	2381	166	169	84	63	138	43	81
1MPyr	307	34	43	N.D	13	38	N.D	3
Chry	148	N.D	24	N.D	14	3	N.D	89
BaAnt	46	N.D	N.D	N.D	59	18	N.D	168
BkFluo	67	39	14	17	79	14	140	25
BeAcep	248	24	142	9	16	9	72	N.D
BePyr	396	21	282	15	200	350	N.D	240
BaPyr	94	10	31	10	33	57	N.D	33
Per	1.7	0.7	0.2	0.4	1.4	0.1	1.7	0.2
DBahAnt	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
$\Sigma$ 18 PAHs	7970	1439	981	756	559	807	308	782
LMW/HMW	1.2	3.9	0.4	4.6	0.2	0.3	0.2	0.2
MP/P	0.7	0.9	1.9	0.6	0.7	1.3	N.A	0.9
PHE/ANT	5.1	0.7	3.0	0.9	1.7	1.3	N.A	0.6
FLT/(FLT+PYR)	0.3	0.45	0.3	0.5	0.3	0.3	0.4	0.4
BaA/(BaA+CHR)	0.2	N.A	N.A	N.A	0.8	0.9	N.A	0.7
PERY/PAIs %	0.2	0.8	0.03	0.8	0.4	0.02	0.8	0.07
PERY/ $\Sigma$ 18PAHs %	0.02	0.05	0.02	0.05	0.3	0.01	0.6	0.03
PYR/PERY	1420	227	1125	216	45	1493	25	410

$\Sigma$ 18 PAHs = Sum of (Dibenzothiophene, Phenanthrene, Anthracene, 3-Methylphenanthrene, 2-Methylphenanthrene, 2-Methylanthracene, 9-Methylphenanthrene, 1-Methylphenanthrene Fluoranthene, Pyrene, 1-Methylpyrene, Chrysene, Benzo[a]Anthracene, Benzo[k]Fluoranthene, Benzo[e]Acephenanthrene, Benzo[e]Pyrene, Benzo[a]Pyrene, Dibenzo[a-h]Anthracene).

LMW/HMW = (Nap + DBT + Phe + Ant + 3Mphe + 2Mphe + 2MAnt + 9MPhe + 1MPhe + Flu)/(Pyr + 1MPyr + Chr + BaAnt + BkFluo + BeAcep + BePyr + BaPyr + Per+DBahAnt).

SPM = Suspended particulate matter.

SS = Surface sediment.

MP/P = (3MPhe+2MPhe+9MPhe+1MPhe)/Phe.

PHE/ANT = Phenanthrene /Anthracene.

FLT/(FLT+PYR) = Fluoranthene/(Fluoranthene+Pyrene).

BaA/(BaA+CHR) = Benzo[a]Anthracene/(Benzo[a]Anthracene+Chrysene).

PERY/PAIs = perylene/( Benzo[k]Fluoranthene+ Benzo[e]Acephenanthrene+ Benzo[e]Pyrene+ Benzo[a]Pyrene+perylene).

PYR/PERY = Pyrene/perylene.

PERY/ $\Sigma$ 18PAHs = Perylene/ $\Sigma$  18PAHs.

N.A = Not applicable.

N.D = non detected

samples can be caused by the difference in hydrophobicity between the low and high molecular weight PAHs. Low molecular weight PAHs are less hydrophobic relative to high molecular weight PAHs and therefore will be more abundant in the water column, leading to a greater proportion in suspended solids (Luo *et al.*, 2006).

Lower molecular weight versus higher molecular weight (LMW/HMW) ratios ranged from

1.16 to 4.61 in SPM and 0.17 to 0.39 in SS samples (Table 2), suggesting higher concentrations of lower molecular weight of PAHs in SPM than those of SS samples, except of Station 6 where it was 0.201 in SPM samples. Our finding are consistent with those of Luo *et al.* (2006) who found The relative content of 2, 3-ring PAHs in samples from the outer part of the estuary (on average 58.4% for samples of April 2003 and 68.6% for samples of July 2002)

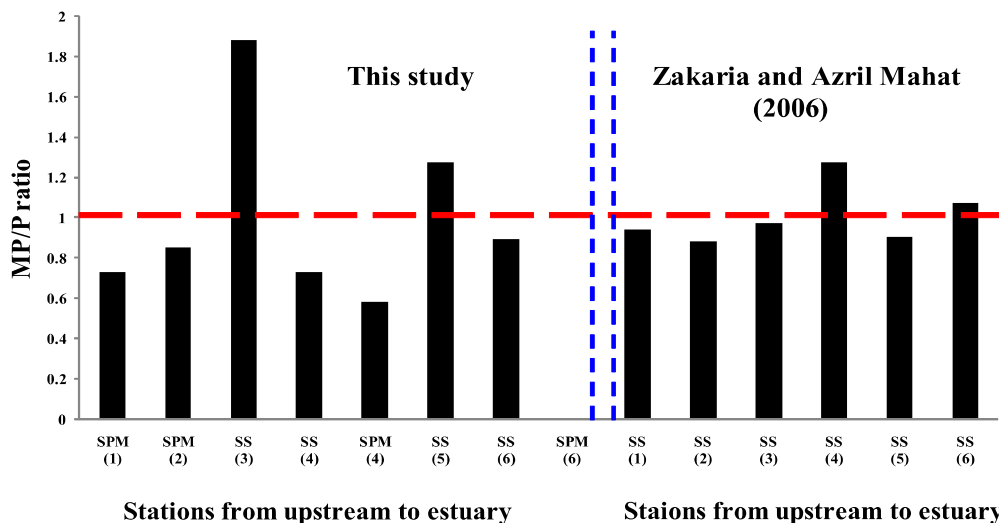


Figure 3. Comparison of the MP/P ratios with a previous study on the suspended particulate matter (SPM) and the surface sediment (SS) from the Langat River

was higher than that in the inner part of the estuary (on average 46.3% for samples of April 2003 and 53.0% for samples of July 2002). This can be explain in this way that high salinity of water and low water velocity may have caused more degradation of lower molecular weight of PAHs in the estuary of the Langat River (Table 1). It may be assumed that water column processes are important events dictating the behavior and fate of PAHs in this estuary. Further investigations are required in this field.

3.2.1. Sources of PAHs in sediments and SPM

PAHs isomer pairs ratios were calculated to infer possible sources of PAHs (Table 3). In contrast to petrogenic sources, pyrogenic sources are characterized by low ratios of phenanthrene/anthracene ( $PHE/ANT < 15$  and  $PHE/ANT < 10$ ) and sum of methylephenanthrenes/phenanthrene ( $MP/P < 1$ ) in association with higher ratios of fluoranthene/(fluoranthene+pyrene) ( $FLT/FLT+PYR > 0.4$ ), benzo(a)anthracene/(Benzo(a)anthracene+chrysene) ( $BaA/BaA+CHR > 0.35$ ) (Budzinsky et al., 1997; Benner et al., 1989, 1990; Yunker et al., 2002).

The MP/P ratios calculated for all SS and SPM samples were less than 2 (from 0.73 to 1.88). The results show that the PAHs in the sediments had mixed sources with predominance of pyrogenic inputs. In Fig. 3, the MP/P ratios in this study are compared to those of a previous study by Zakaria and Azril Mahat (2006). The results indicate predominance of pyrogenic inputs for PAHs in Langat River sediments at the stations except for the Stations 3 and 5.

The PHE/ANT ratios for all SS and SPM samples were less than 10 (from 0.6 to 5.1),

indicating that PAHs were mainly originated from pyrogenic sources (Fig. 4).

Based on the PAH isomer pair ratio measurements compiled by Yunker et al. (2002),  $FLT/FLT+PYR < 0.4$  implies petroleum, 0.4-0.5 implies petroleum combustion, and  $> 0.5$  implies combustion of coal, grass and wood. Ratio of  $BaA/BaA+CHR < 0.2$  implies petroleum, from 0.2 to 0.35 indicates either petroleum or combustion, and  $> 0.35$  implies combustion. The  $FLT/FLT+PYR$  ratios calculated for all SS and SPM samples were less than 0.5 (from 0.3 to 0.5). These ratios show that petrogenic input at most stations ( $FLT/FLT+PYR < 0.4$ ). Two out of eight samples showed values 0.4-0.5 (Stations 2 and 4), suggesting pyrogenic inputs at these two stations. The  $BaA/BaA+CHR$  ratios calculated for SS and SPM samples from four stations were less than 0.9 (from 0.2 to 0.9). The ratios  $FLT/FLT+PYR$  and  $BaA/BaA+CHR$

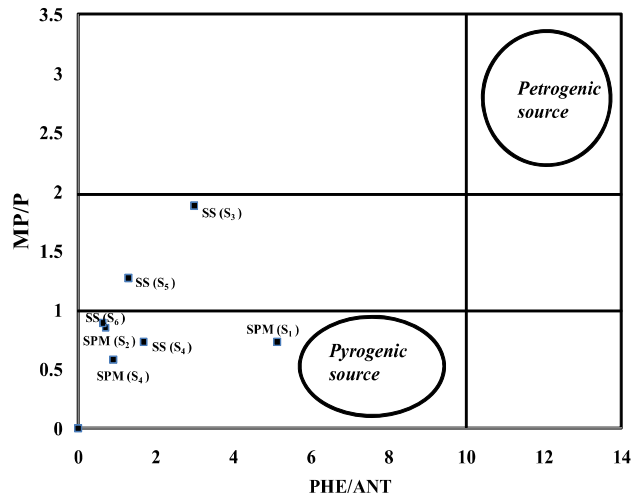


Figure 4. The PHE/ANT and MP/P ratios in Langat River sediments

Table 4. Spearman's correlation coefficients (*r*) between  $\Sigma 18$  PAHs concentrations and diagnostic ratios in surface sediments and suspended particulate matters from Langat River

	$\Sigma 18$ PAH	PHE/ANT	FLT/(FLT+PYR)	BaA/(BaA+CHR)	MP/P
$\Sigma 18$ PAH	1.00	0.85***	- 0.35 <sup>ns</sup>	- 0.12 <sup>ns</sup>	- 0.03 <sup>ns</sup>
PHE/ANT		1.00	- 0.61 <sup>ns</sup>	- 0.04 <sup>ns</sup>	0.38 <sup>ns</sup>
FLT/(FLT+PYR)			1.00	- 0.50 <sup>ns</sup>	- 0.47 <sup>ns</sup>
BaA/(BaA+CHR)				1.00	0.15 <sup>ns</sup>
MP/P					1.00

$\Sigma 18$  PAHs = Sum of (Dibenzothiophene, Phenanthrene, Anthracene, 3-Methylphenanthrene, 2-Methylphenanthrene, 2-Methylantracene, 9-Methylphenanthrene, 1-Methylphenanthrene, Fluoranthene, Pyrene, 1-Methylpyrene, Chrysene, Benzo[a]Anthracene, Benzo[k]Fluoranthene, Benzo[e]Acephenanthrene, Benzo[e]Pyrene, Benzo[a]Pyrene, Dibenzo[a-h]Anthracene).

PHE/ANT = Phenanthrene / Anthracene.

FLT/(FLT+PYR) = Fluoranthene / ( Fluoranthene+ Pyrene).

BaA/(BaA+CHR) = Benzo[a]Anthracene / ( Benzo[a]Anthracene+ Chrysene).

MP/P = Sum of (3-Methylphenanthrene, 2-Methylphenanthrene, 9-Methylphenanthrene, 1-Methylphenanthrene) / Phenanthrene.

Levels of significant: \* =  $p < 0.05$ ; \*\* =  $p < 0.01$ ; \*\*\* =  $p < 0.001$ ; <sup>ns</sup> =  $p > 0.05$

indicated multiple PAHs sources (petrogenic and pyrogenic).

Correlation between  $\Sigma 18$  PAHs and diagnostic ratios calculated to identify sensitivity of the PAH ratios. The results exhibit a significant positive correlation ( $r = 0.854$ ,  $p = 0.007$ ) between  $\Sigma 18$ PAHs and PHE/ANT at the 99% confidence level, suggesting predominance of pyrogenic versus petrogenic inputs in Langat River sediments. The ratios of FLT/FLT+PYR, MP/P and BaA/BaA+CHR were not significantly correlated with  $\Sigma 18$ PAHs, suggesting they are not sensitive enough to be used to distinguish petrogenic PAHs from pyrogenic PAHs in an area like the Langat River, where pollutants come from multiple sources (Table 4).

### 3.2.2. Perylene

The concentrations of perylene and diagnostic ratios such as, perylene/penta-aromatic isomers (PERY/PAIs), pyrene/peryene (PYR/PERY) and perylene/total PAHs (PERY/ $\Sigma 18$ PAHs) are presented in Table 3. For pyrogenic PAHs, perylene concentration is about 1-4% of total PAHs (Wakeham *et al.*, 1980a; 1980b; Wang *et al.*, 1999b). In addition, perylene concentrations relative to penta-aromatic isomers greater than 10% indicate probable diagenic inputs, whereas those less than 10% indicate a probable pyrogenic origin of the compound (Baumard *et al.*, 1998a; Readman *et al.*, 2002). The concentrations of pyrene relative to those of perylene were compared to identify

different source of high temperature anthropogenic PAHs (Venkatesan 1988; Silliman *et al.*, 2001). The perylene concentrations ranged from 0.09 to 1.71 ng/g. The high ratio of PYR/PERY ranged from 25 to 1500 and low percentages of PERY/PAIs <1% and PERY/ $\Sigma 18$ PAHs <1%, suggest pyrogenic input for perylene in Langat River sediments.

## 4. Conclusions

The results of PAHs and n-alkanes analysis of surface sediments and suspended particulate matters from the Langat River were used to assess likely sources of these contaminants. Total concentrations and compositional patterns of PAHs and n-alkanes showed differences in the SPM and the SS samples. Low molecular weight of PAHs and n-alkanes dominated in the SPM samples. The concentrations of high molecular weight of PAHs and n-alkanes were higher in SS samples than those in SPM samples. This can be attributed to the differences in hydrophobicity and degradation processes between the low and high molecular weight PAHs; it could also result in the compositional difference between SS and SPM samples.

PAHs isomer pairs ratios suggested a complicated, combined PAHs source (petrogenic and pyrogenic) with predominance of pyrogenic inputs in the study area. The perylene concentrations and related perylene ratios (PERY/PAIs, PERY/ $\Sigma 18$ PAHs and PYR/PERY) point to pyrogenic



inputs for perylene in the study area. The high concentration of naphthalene in all sediment samples and higher concentrations in the SPM relative the SS samples reveal an additional source for naphthalene in Langat River sediments. This can be attributed to woody plants in this tropical environment.

The results of the CPIs values for n-alkanes in ranges  $C_{25-33}$ ,  $C_{15-35}$  and  $C_{25-35}$  exhibited higher values in the SS samples relative the SPM samples, indicating mixed petrogenic and natural sources with predominance of petrogenic inputs for n-alkanes in the SPM.

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