UNIVERSITI PUTRA MALAYSIA

SOURCES AND DISTRIBUTION OF *n*-ALKANE AND POLYCYCLIC AROMATIC HYDROCARBONS IN SELECTED LOCATIONS IN PENINSULAR MALAYSIA

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By

ALIREZA RIYAHI BAKHTIARI

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DEDICATION

To my father, mother, my wife and my daughters who have been the nucleus of constant inspiration, love, encouragement and moral support during the study period.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia
In fulifilment of the requirement for the degree of Ph.D.

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Chairman: Associate Professor Mohamad Pauzi B Zakaria, PhD

Faculty: Environmental Studies

Distribution and sources of perylene have not been thoroughly investigated and are therefore not well understood in the tropical environment. This study focusses on the distribution pattern and source identification of aliphatic hydrocarbons and polycyclic aromatic hydrocarbons particularly perylene. Surface sediments, suspended particulate matter, sediment core samples, different compartments of termite nests (*Macrotermes gilvus*) and the surrounding soils and plants were collected from the Klang River, Langat River, Chini Lake and in the campus of Universiti Putra Malaysia, respectively. Alkanes and perylene concentrations were significantly different in new and old fungus combs particularly in large termite nests. There are also significant differences between alkyl-C, neutral carbohydrate, aromatic rings of lignin and chitin concentrations in new and old fungus combs. The levels of $n\mathrm{C}_{31}$/ ($n\mathrm{C}_{27}$+$n\mathrm{C}_{29}$+$n\mathrm{C}_{31}$) ratios revealed that new and old fungus combs may receive more contribution from grass waxes relative to tree and shrub waxes. Termites *M. gilvus* and woody plants are sources of perylene in the tropical environment. The distribution patterns of *n*-alkanes and PAHs suggest that the upstream stretch of the Langat River receives greater inputs of these compounds when compared to

the downstream stretches. This may be due to the fact that industrial areas are concentrated in Kajang and Bangi towns. Lower and medium molecular weight PAHs and *n*-alkanes were dominant in suspended particulate matter, whereas higher molecular weight PAHs and *n*-alkanes were dominant in surface sediments. Results of diagnostic ratios indicate mixed petrogenic and pyrogenic sources with predominance of pyrogenic inputs for 18 PAHs and perylene in Langat River sediments. The data collected from Klang River sediments show that petrogenic inputs were predominant at all of the stations investigated.

In Lake Chini sediment core samples, perylene concentrations were high in the top layers (0-12cm) and increased with increasing depths. Analysis of variance (ANOVA) and least significant difference (LSD) tests revealed that there were significant differences ($p<0.05$ at the 95% confidence level) in TOC-normalized perylene concentrations between the top layers and the bottom layers of the sediment core samples. This can be attributed to different sources of perylene. The results of analysis of critical ratios of perylene, such as perylene/total PAHs, perylene/panta-aromatic isomers of perylene and pyrene/perylene indicate biological sources in the top layers and *in situ* formation of perylene in the bottom layers. These results are consistent with the results for *n*-alkane concentrations and suggest that Lake Chini sediments are highly affected by terrestrial vascular plants.

Source identification of metals exhibits the predominance of natural inputs for Cu and Zn in the top layers and anthropogenic inputs for Cu, Zn, Pb, and Cd in the bottom layers of the Lake Chini sediment profiles. Results of correlation analysis among the metals and between each metal and ∑19PAHs, perylene and perylene/TOC indicate significant positive correlations between PAHs and Cu concentrations ($r = 0.79$, $p = 0.002$), Zn concentrations

(r = 0.73; p = 0.007) and Pb concentrations (r = 0.68; p = 0.016), respectively. There was no significant correlation found between PAHs and Ni and Cd (r = 0.53; p = 0.077), (r = 0.57; p = 0.051). Furthermore, perylene and perylene/TOC were significantly correlated with Cu, Zn and Pb. A possible explanation for these results may be ascribed to enzymatic activities of microorganisms. Cu and Zn are essential elements in many metallo-enzyme processes for microorganisms. In addition, Pb can be used by anaerobic bacteria during the methylation process using methylase enzymes.

It is concluded that perylene is formed in termite (*M. gilvus*) nests. It accumulates in new fungus comb. High concentrations of aromatic rings of lignin as a precursor of perylene are found in new fungus combs. It is postulated that perylene is supplied to the river as a result of the heavy and frequent rains in the tropical climate. The fact that perylene was found in abundance in the top layers of the sediment core samples from Lake Chini under aerobic conditions is in contrast with the results of other studies elsewhere. A minor concentration of perylene is believed to be degraded into derivative isomers which are found in old fungus combs and also in Lake Chini sediments.

Abstrak tesis yang dikemukakan kepada Senta Universiti Putra Malaysia
Sebagai memenuhi keperluan untuk ijazah Ph.D

SUMBER DAN TABURAN *n*-ALKANA DAN POLISIKLIK AROMATIK HIDROKARBON DI LOKASI TERPILIH DI SEMENANJUNG MALAYSIA

Oleh

ALIREZA RIYAHI BAKHTIARI

July 2009

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Taburan dan sumber perylene tidak sepenuhnya di kaji dan di fahami di alam tropika ini. Kajian terkini lebih mengkhusus kepada corak taburan dan pengecaman sumber hidrokarbon linear and hidrokarbon polisiklik beraromatik (HPB) terutamanya perylene. Sedimen permukaan, bahan terampai, sampel sediment teras, bahagian sarang anai-anai yang berbeza, sampel tanah dan tumbuhan sekitar di ambil daripada Sungai Klang, Sungai Langat, Tasik Chini dan kampus Universiti Putra Malaysia. Kepekatan N-alkana dan perylene sangat berbeza antara *fungus comb* yang lama dan yang baru terutamanya dalam sarang anai-anai yang besar. Keadaan ini dapat dikaitkan dengan perbezaan yang ketara antara alkyl-C, karbohidrat neutral, gelang aromatic lignin dan kepekatan chitin dalam *fungus comb* yang lama dan yang baru. Di semua stesyen, tahap nisbah $nC_{31}/(nC_{27}+nC_{29}+nC_{31})$ menunjukkan *fungus comb* yang lama dan yang baru mungkin terhasil daripada lalang berlilin seperti pokok dan tumbuhan renek yang berlilin. Anai-anai *M. gilvus* dan tumbuhan berkayu merupakan sumber perylene di alam tropika ini. Corak taburan n-alkana dan PAHs menunjukkan bahawa kawasan hulu Sungai Langat menerima lebih banyak komponen ini berbanding di kawasan hilir Sungai Langat. Ini adalah kerana

kawasan industri lebih tertumpu di Bandar Kajang dan Bangi. Tambahan itu, berat molekul PAHs dan n-alkana yang rendah dan sederhana lebih dominan dalam bahan pepejal terampai. Walaubagaimanapun, berat molekul PAHs dan n-alkana yang tinggi lebih dominan dalam sedimen permukaan. Keputusan nisbah diagnostik menunjukkan campuran petrogenik dan pirogenik dengan pendominasian daripada input petrogenik 18 PAHs dan perylene serta input semulajadi dari naftalena dalam sedimen di Sungai Langat. Data yang di perolehi daripada sedimen Sungai Klang menunjukkan bahawa sumber petrogenik dan input semulajadi lebih dominan di semua stesyen yang di kaji.

Di sampel sedimen teras Tasik Chini, kepekatan perylene didapati bertambah selari dengan pertambahan kedalaman iaitu kebanyakannya di bahagian sedimen paling atas (0-12cm). Keputusan analisa varian (ANOVA) dan LSD menunjukkan bahawa terdapat perbezaan ketara (p<0.05 pada tahap keyakinan 95%) dalam TOC-normal kepekatan perylene antara lapisan yang paling atas sampel sedimen teras dengan lapisan yang 12 cm dibawah sedimen. Keputusan ini adalah konsisten dengan keputusan yang diperolehi daripada kepekatan n-alkana dengan mencadangkan bahawa sedimen Tasik Chini sangat dipengaruhi oleh tumbuhan vascular yang tumbuh di atas tanah.

Keputusan yang diperolehi daripada pengecaman sumber besi menunjukkan pendominasian oleh input semulajadi kuprum dan zink di lapisan atas dan input antropogenik oleh kuprum, zink, plumbum dan cadmium di lapisan bawah tanah. Keputusan analisis hubungan antara kepekatan besi dan antara setiap elemen serta ∑19PAHs, perylene dan perylene/TOC menunjukkan hubungan positif yang ketara di antara PAHs dan kepekatan kuprum (r = 0.79, p = 0.002), kepekatan zink (r = 0.73, p = 0.007) dan kepekatan plumbum (r = 0.68, p =

0.016). Sementara itu, tiada hubungan yang ketara antara PAHs dengan nikel dan cadmium (r = 0.53, p = 0.077), (r = 0.57, p = 0.051). Di samping itu, perylene dan perylene/TOC adalah sangat berkait dengan kuprum, zink dan plumbum berbanding dengan nikel dan cadmium.

Adalah dipercayai bahawa hubungan yang ketara antara kuprum, zink dan plumbum dengan ∑19PAHs terutamanya perylene tidak dapat di terangkan dengan sumber yang umum. Ini mungkin disebabkan oleh aktiviti-aktiviti enzim mokroorganisma. Adalah dipercayai bahawa kuprum dan zink adalah elemen yang penting dalam kebanyakan proses metallo-enzim untuk mikroorganisma. Di samping itu, plumbum juga dapat di gunakan oleh bakteria anerobik semasa proses metilasi menggunakan enzim metilase.

Secara kesimpulannya, perylene memang terbentuk dalam sarang anai-anai, *M. gilvus*. Ianya terkumpul di *fungus comb* yang baru. Ini mungkin menyumbang kepada kepekatan gelang lignin beraromatik yang tinggi sebagai penunjuk perylene dalam *fungus comb* yang baru. Berdasarkan keputusan yang diperolehi, dapat di jangkakan bahawa perylene turut menyisip masuk ke sungai dan laut disebabkan cuaca tropika yang mempunyai kadar hujan yang kerap dan tinggi. Disebabkan kepekatan perylene paling tinggi di bahagian sedimen teras Tasik Chini yang paling atas dalam keadaan erobik, corak ini merupakan corak yang berbeza dengan kajian yang dijalankan di kawasan lain. Sementara itu, kepekatan perylene yang rendah dipercayai telah terurai kepada isomer terbitan seperti yang telah dijumpai di *fungus comb* yang lama dan pada sedimen Tasik Chini.

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I certify that a Thesis Examination Committee has met on 21 July 2009 to conduct the final examination of Alireza Riyahi Bakhtiari on his thesis entitled "Sources and Distribution of *n*-Alkane and Polycyclic Aromatic Hydrocarbons in Selected Locations in Peninsular Malaysia" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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Date: 11 Sep 2009

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously and is not concurrently submitted for any other degree at Universiti Putra Malaysia or at any other institution.

Alireza Riyahi Bakhtiari

Date: 14/10/2008

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LIST OF ABBREVIATIONS

1MPhe	Mehylphenanthrene
1MPyr	1-methylpyrene
2MAnt	2-methylanthracene
2MPhe	2-methylphenanthrene
3MPhe	3-methylphenanthrene
9MPhe	9-methylphenanthrene
ACL	Average Chain Length
Ant	Anthracene
BaAnt	Benzo(a)antracene
BaPyr	Benzo(a)pyrene
BeAcep	Benzo(e)acephenanthrylene
BePyr	Benzo(e)pyrene
BkFluo	Benzo(k)fluoranthrene
C/N	Organic carbon/ Total nitrogen
Cd	Cadmium
Chry	Chrycene
CombPAH	Combustion Polycyclic Aromatic Hydrocarbon
CPI	Carbon Pereference Index
Cu	Copper
DB	Decomposed Bark
DBahAnt	Dibenzo(a,h)anthracene