UNIVERSITI PUTRA MALAYSIA

DISTRIBUTION AND CONCENTRATION OF HEAVY METALS AND POLYAROMATIC HYDROCARBONS IN SURFACE SEDIMENTS OF KUALA SEPETANG, PERAK, MALAYSIA

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DISTRIBUTION AND CONCENTRATION OF HEAVY METALS AND POLYAROMATIC HYDROCARBONS IN SURFACE SEDIMENTS OF KUALA SEPETANG, PERAK, MALAYSIA.

By

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ubmitted to the Faculty of Agriculture, University Putra Malaysia in fulfillment of the requirement of SPS 5999 (Project) for the award of the master of Master of Science in Environmental Soil Science

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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APRIL 2007

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Faculty : Agriculture

A study was conducted to determine the concentration and levels of six heavy metals (Ni, Zn, Pb, Cu, Cr and Cd: total 65 samples) and polyaromatic hydrocarbons (PAHs) (16 USEPA listed PAHs: total 45 samples) in the sediment surface layer (0-10 cm) of Kuala Sepetang estuary. Sediment samples were freeze dried (-30^{0}C for 12-16 hour) to preserve the sample prior to analysis. From the analysis, the sediment pH (range: pH 3.48-7.48), the total carbon (organic and inorganic sources) ranges 1.8-8.3%, higher than the organic carbon (sedimentation and decomposition of leaf litter) content that ranges from 1.3% to 4.2%. The highest CEC was found at Sg. Reba (51.04 $cmol_c/kg$) while other rivers averaged at 20 $cmol_c/kg$. X-ray diffractometry analysis showed dominant presence of kaolinite (7.26Å, 3.57 Å) and quartz (4.26 Å, 3.33 Å) in the sediment. On the other hand, sequential extraction showed that Ni, Zn, Pb, Cu, Cr and Cd were primarily present in the residual fraction (non-mobile); especially Ni, Pb and Cd up to 80%. Meanwhile, the heavy

metals concentration at S1, S2, S3, S4, S5 and S6 in Kuala Sepetang showed Ni (5.2-36 mg/kg), Zn (52.4-312.80 mg/kg), Pb (1.8-159.60 mg/kg), Cu (7.6-31.20 mg/kg), Cr (3.2-77.2 mg/kg) and Cd (0.32-5.04 mg/kg) in dry weight basis are comparable with other Malaysian studies. The enrichment factor (EF) value showed very high enrichment of Pb and Cd compared to the other heavy metals. Despite that, Ni, Zn, Cu and Cr concentrations showed deficiency to minimal enrichment, indicating lithigenous material origin rather than anthropogenic input. Meanwhile, total PAHs range from 72ng/g to 2606 ng/g dry weight of sediment. PAHs concentration decreases in the order of: Sg. Reba (S1) (8548 ng/g) > Sg. Selinsing (S4) (5462 ng/g) > Sg. Sepetang (S3) (4249 ng/g) > Sg. Sangga Besar (S5)(3216 ng/g) > Sg. Sepetang (S2) (2961 ng/g) > Sg. Sangga Kecil (S6) (1184 ng/g). The concentrations of PAHs reported in Kuala Sepetang were comparable to those reported by Malaysia (Zakaria et al., 2002) and other regional studies. Generally, Kuala Sepetang showed much lower concentration of total PAHs with mixed pattern of strong pyrolitic and low petrogenic sources compared to Pearl River Estaury, China (408-10811 ng/g) with high petrogenic origin contamination level. Sediment in Sg. Reba (close to town area) has the most significant correlation (at $p<0.01$) with physico-chemical properties. This study can be used by environmental agencies and private sector as a baseline data for mangrove sediments.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

TABURAN DAN KANDUNGAN LOGAM BERAT DAN POLIAROMATIK HIDROKARBON DI PERMUKAAN SAMPEL ENAPAN DI KUALA SEPETANG, PERAK, MALAYSIA.

Oleh

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Kajian untuk menentukan taburan dan kandungan logam berat (Ni, Zn, Pb, Cu, Cr dan Cd) sebanyak 65 sampel dan poliaromatik hidrokarbon (PAH) sebanyak 45 sampel pada permukaaan (0-10 cm) dalam enapan telah dijalankan disekitar kawasan paya laut, Kuala Sepetang. Sampel enapan disejuk bekukan (-30^{0}C selama 12-16 jam) untuk memelihara sample sebelum analisa. Dari analisa pH, julat pH enapan sekitar 3.48 hingga 7.48. Julat bagi karbon organik berbanding jumlah karbon keseluruhan adalah sekitar 1.8% hingga 8.3%. Ini mungkin disebabkan oleh pereputan tumbuhan dan fauna yang termendak di dalam enapan. Kadar tukarganti kation didapati paling tinggi di kawasan Sg. Reba (51.04 $cmol_c$/kg), manakala sungai yang lain mempunyai julat sekitar 20 $cmol_c$/kg. Data analisa diffraktometri X-ray menunjukkan kehadiran mineral kaolinit (7.26Å, 3.57 Å) dan kuarza (4.26 Å, 3.33 Å) adalah paling banyak dalam enapan. Manakala, pengekstrakan berperingkat menunjukkan kehadiran logam berat dalam bahagian sisa-baki adalah paling tinggi, terutamanya unsur Ni, Pb dan Cd. Julat logam berat dalam sample enapan di

kawasan Kuala Sepetang bagi Ni (5.2-36 mg/kg), Zn (52.4-312.80 mg/kg), Pb (1.8-159.60 mg/kg), Cu (7.6-31.20 mg/kg), Cr (3.2-77.2 mg/kg) dan Cd (0.32-5.04 mg/kg) berjaya dibandingkan dengan kajian berkaitan yang terdahulu di Malaysia. Kadar kandungan logam Pb dan Cd didapati paling tinggi berbanding logam berat lain, dikawasan kajian. Jumlah kandungan keseluruhan PAH dalam enapan adalah dari 72 ng/g hingga 2606 ng/g berdasarkan berat kering. Kandungan PAH di kawasan kajian adalah seperti berikut: Sg. Reba (S1) (8548 ng/g) > Sg. Selinsing (S4) (5462 ng/g) > Sg. Sepetang (S3) (4249 ng/g) > Sg. Sangga Besar (S5)(3216 ng/g) > Sg. Sepetang (S2) (2961 ng/g) > Sg. Sangga Kecil (S6) (1184 ng/g). Kandungan PAH setara dibandingkan dengan kajian terdahulu dari Malaysia. Didapati , kandungan PAH di kawasan paya laut di sekitar Kuala Sepetang dipengaruhi oleh gabungan pencemaran dari sumber pirolitik dan petrogenik. Secara umum, dilihat kandungan PAH dalam enapan kawasan paya laut lebih rendah berbanding enapan kawasan marin yang tercemar seperti Pearl River Estaury, China (408-10811 ng/g). Ini sejajar dengan hasil kajian yang mendapati kandungan PAH dalam enapan dikawasan kajian masih rendah dengan kesan sumber pirolitik yang tinggi dan sumber petrogenik yang rendah. Enapan di Sg. Reba mempunyai korelasi yang amat singnifikan dengan sifat kimia tanah pada $p<0.01$. Hasil dan data dari kajian ini, sesuai digunakan oleh pelbagai agensi kerajaan dan swasta yang terlibat dengan aktiviti paya bakau sebagai sumber rujukan untuk kajian-kajian di masa hadapan.

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DECLARATION

I hereby declare that the thesis is based on 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.

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LIST OF ABBREVIATIONS

PAHs	polyaromatic hydrocarbons
HM	heavy metals
HMW	High Molecular Weight
LMW	Low Molecular Weight
EDTA	Ethylenediaminetetraaceticacid
DTPA	Diaminetetraphenylaceticacid
mg/kg	concentration in part per million (ppm)
ng/g	concentration in part per billion (ppb)
S1	Sg.Reba
S2	Sg.Sepetang (northern part)
S3	Sg.Sepetang (southern part)
S4	Sg.Selinsing
S5	Sg.Sangga Besar
S6	Sg.Sangga Kecil
Naph	Naphthalene
Acy	Acenapthylene
Ace	Acenapthene
Fl	Fluorene
Ant	Anthracene
Phe	Phenanthrene
Fluo	Fluoranthene
Pyr	Pyrene
BaA	Benzo(a)anthracene

Chry	Chrysene
BbF	Benzo(b)fluoranthene
BkF	Benzo(k)fluoranthene
BaP	Benzo(a)pyrene
BghiP	Benzo(g,h,i)perylene
IP	Indeno(1,2,3-cd)perylene
dBahA	Dibenz(a,h)anthracene
CEC	Cation exchange capacity
OM	Organic matter
EC	Electrical conductivity
**	highly significant at $p<0.05$
*	significant at $p<0.05$

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CHAPTER ONE

INTRODUCTION

1.0 Introduction to Mangrove Forest

At present, Malaysia (Figure 1) still has 566,856 hectare (ha) of mangroves that 99,767 ha in the Peninsular Malaysia, and nearly 44,000 ha are situated in Perak under the Matang Mangrove Forest Reserve area (Figure 1.1a); 340,689 ha in Sabah, and the rest, 126,400 ha in Sarawak. From year 1980 to 1990, Malaysia has lost nearly 12% of its mangrove forest, with more than 1% rates of loss per year. In respond to rate of the loss, ecological restoration is being carried out throughout South East Asia, by simple management plan based on clear felling small patches and replanting with seedlings (Figure 1.2). Generally, mangrove soils are found along intertidal shores and estuarine such as Brazil, Australia, Malaysia, China and many other tropical countries. Mangroves forest help to protect the coastline from erosion, storm damage, and wave action by acting as buffers zone. It catches alluvial materials and deposits them in sediment, thus stabilizing land elevation. In recent years, many concerns have been raised regarding the threat of contamination on the mangrove forest ecosystem around the world. Human activities, such as industrialization and urbanization have led to various source of effluent being channeled into the mangrove ecosystem. The effluents may contain contaminants such as heavy metals and PAHs. The heavy metals and PAHs can precipitate and settle into sediments as studied elsewhere (Budzinski et al., 1997; Kucklik et al., 1997; Hartmann et al., 2000).

Figure 1: Peninsular Malaysia shows Perak state
Source: taken online from www.ipoh-online.com.my

Figure 1.1a: Matang mangrove forest located in Larut Matang and Selama

Note: The red circle in the map shows the study area

Source: taken online from www.ipoh-online.com.my