

UNIVERSITI PUTRA MALAYSIA

CONCENTRATION AND DISTRIBUTION OF LINEAR ALKYLBENZENE IN SEDIMENTS OF SELECTED MALAYSIAN RIVERS AS MOLECULAR MARKERS OF SEWAGE TREATMENT EFFICIENCY

SAMI MUHSEN SLEMAN MAGAM

FPAS 2012 11

CONCENTRATION AND DISTRIBUTION OF LINEAR ALKYLBENZENE IN SEDIMENTS OF SELECTED MALAYSIAN RIVERS AS MOLECULAR MARKERS OF SEWAGE TREATMENT EFFICIENCY

By MAGAM SAMI MUHSEN S Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirement for the Degree of Master of Science in the Faculty of Environmental Studies

March 2012

DEDICATION

To my dear wife, close friends, my family, and my supervisor who have been the most important reasons of hopefulness during my study.

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

CONCENTRATION AND DISTRIBUTION OF LINEAR ALKYLBENZENE IN SEDIMENTS OF SELECTED MALAYSIAN RIVERS AS MOLECULAR MARKERS OF SEWAGE TREATMENT EFFICIENCY

By

SAMI MUHSEN SLEMAN MAGAM

March 2012

Chairman : Associate Professor Mohamad Pauzi Zakaria, hD

Faculty : Environmental Studies

The present study investigates the distribution inea. alkylbenzenes (LABs) in tion, in Sarawak, Sembulan, and sediment samples collected from sele ed lo Kuantan rivers in Peninsular Malays adies were conducted to assess the current status of domestic y stes nd synthetic detergent pollution in sediments in these three rivers. Twenty three empling stations have been selected for sediment collection. Ana and quantification of LABs was carried out using gas s spectrometry (GC-MS). Concentrations of total LABs in ng/g chromatography weight pasis (dw) in the sediment samples of Sarawak River, Sembulan on a di ver, and Kuantan River ranged from 156.5 to 7386.2; 643.2 to 5567.1; and 772.8 to g dw, respectively. The *I/E* ratio (ratio of internal to external isomers of LABs) is employed to estimate the degree of degradation of LABs in aquatic environments, making it a powerful, though simple, tool for monitoring biodegradation of LABs in the environment. The I/E ratios for Sarawak, Sembulan, and Kuantan rivers fell in the ranges 0.52 to 1.24; 0.81 to 1.79; and 0.50 to 1.28, respectively. The *I/E* ratio at station two in Kuantan River was much lower than those at the other stations, indicating that the sewage discharged into Kuantan River was poorly treated.

Anthropogenic activities may contribute to high levels of LABs in sediment samples. In addition to anthropogenic activities, natural features of the sampling location may contribute significant amounts of LAB discharges to the aquatic systems. In sum, the study results demonstrate that the LABs are useful as indicators of poluta ts originating from domestic wastes and synthetic detergents. Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

KEPEKATAN DAN PENGAGIHAN LINEAR ALKYLBENZENE DALAM ENAPAN SUNGAI TERPILIH MALAYSIA SEBAGAI PENANDA MOLEKUL KECEKAPAN PENGOLAHAN KUMBAHAN

Oleh

SAMI MUHSEN SLEMAN MAGAM

Mac 2012

Pengerusi : Profesor Madya Mohamad Pauzi Zakaria, NJ

Fakulti : Pengajian Alam Sekitar

Kajian ini dijalankan bagi menyiasa tat hear alkil benzen (LAB) di dalam i beberapa lokasi terpilih di sungai Sarawak, sampel sedimen yang diam al da Sembulan dan Kuantan di Semen njung Malaysia. Kajian sacara berkelompok telah dijalankan untuk ilai status terkini bagi pencemaran detergen sintetik dan sisa edimen dari tiga sungai tersebut. Dua puluh tiga stesen telah domestic di dala dipilih ntuk per ampelan sedimen. Analisis dan kuantifikasi LAB telah dijalankan menggunakan Kromatografi gas-spektometri jisim (GC-MS). Kepekatan ngan B dalam unit ng/g berasaskan berat kering (dw) di dalam sampel sedimen sungai Sarawak, sungai Sembulan dan sungai Kuantan berjulat dari 156.5 hingga 7386.2; 643.2 hingga 5567.1; dan 772.8 hingga 7517.6 ng/g dw. Nisbah I/E (nisbah isomer LAB dalaman kepada luaran) diaplikasikan untuk menganggarkan darjah degradasi LAB di persekitaran akuatik, menjadikan ia suatu alat yang mudah lagi berkesan dalam pengawasan biodegradasi LAB di dalam alam sekitar. Nisbah I/E bagi sungai Sarawak, Sembulan dan Kuantan berjulat dari 0.52 hingga 1.24; 0.81 hingga 1.79; dan 0.50 hingga1.28. Nisbah I/E di stesen dua di sungai Kuantan adalah sangat rendah dari stesen lain, menunjukkan bahawa pembuangan sisa kumbahan ke dalam sungai Kuantan adalah tidak dirawat dengan sempurna. Aktiviti antropogenik mungkin menyumbang kepada tahap kepekatan LAB yang tinggi di dalam sampel sedimen. Merujuk kepada aktiviti antropogenik, ciri-ciri semulajadi yang enupandi stesen penyampelan mungkin telah menyumbang amaun LAB yang shunikan di dalam sistem akuatik. Kesimpulannya, hasil kajian menunjukkan ahawa nAB adalah berkesan sebagai penunjuk aras bagi bahan pencemar yang berasal dan sisa domestik dan detergen sintetik.

ACKNOWLEDGEMENTS

First of all, all Praise be to Allah, the Cherisher and the Sustainer of the world. This thesis would not have come into existence without the valuable help and support of great people. I am extremely grateful to Professor Dr. Mohamad Pauzi Zakaria, my supervisor for his keen supervision, continuous support and encourage throughout my research study. His discussions and suggestions 1gnifi antly improved the outcomes of this research. His sharp critical reading and m'n. nts on the manuscript did enhance the quality of my study. Special thank and espect are also due to Dr.Normala Halimoon, the Co-supervisor, constructive comments, valuable pieces of advice and the continuous support.

I would like also to express my deep aratitude to Mr. Mohd Reza, Ms. Norliza Ismail, Mr. Abdalah Bakhet, M. Shazhan bin Jamhari and Ms. Norazida Manan who helped and encouraged motion the initial stages of my study. Truly speaking I have been so much lack, where such supportive research group at our laboratory. I would like also to think Dr. Najat Al-odini, Dr.Anwar Al-shamiry, Dr. khaled Alkodimi, Mr. Morad Al-salahi, Mr. Mohammed Gazaz and Mr. Esam for their kind assistant.

I would like to express my appreciation to Dr. Ahmad Homadi, Assistant President of Hodeidah University and Hodeidah University in general for granting me the scholarship to pursue my studies in UPM.

I wish to express my unlimited and eternal appreciation to my father, deceased mother, brothers and sisters for their endless support and encouragement. A special thank goes to my dear wife Najat Masood and my kids for their relentless support throughout my study .They have been the source of strength and inspiration in times of hardships throughout the period of my study.

Finally, I would like to thank everyone who helped me in one way or another.

APROVAL

I certify that a Thesis Examination Committee has met on 1st April 2012 to conduct the final examination of Sami Muhsen Sleman Magam on his thesis entitled Concentration And Distribution Of Linear Alkylbenzene In Sediments Of Selected Malaysian Rivers as Molecular Markers of Sewage Treatment Efficiency ´ L Q 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 Master of Science.

Members of the Thesis Examination Committee were as follows:

Ahmad Makmom Abdullah, Ph.D.

Associate Professor Department of Environmental Science Faculty of Environmental Studies Universiti Putra Malaysia (Chairman)

Karen Anne Crouse, Ph.D.

Y. Bhg. Professor Department of Chemistry Faculty of Science Universiti Putra Malaysia (Internal Examiner 1)

Mansor b Hj Ahmad, Ph

Associate Professor Department of Chemises Faculty of Science Universiti Putre Mala sia (Internal Examiners)

Mohd ⁷ alib Lat¹, Ph.D. Associate Profes or

Invironmental and Natural Resource Sciences faculty of Science and Technology University Kebangsaan Malaysia (UKM) (External Examiner)



Zulkarnain Zainal, PhD

Professor and Deputy Dean School of Graduate Studies Universiti Putra Malaysia

Date: 24 April 2012

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Mohamed Pauzi Zakaria, PhD

Associate Professor Faculty of Environmental Studies Universiti Putra Malaysia (Chairman)

Normala Halimoon, PhD

Lecturer Faculty of Environmental Studies Universiti Putra Malaysia (Member)

> **PojANG BIN KIM HUAT, PhD** Professor and Dean School of Graduate Studies Universiti Putra Malaysia

Date:

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.

SAMI MUTSEN SLEMAN MAGAM

TABLE OF CONTENTS

		Page
DEI	DICATION	i
ABS	STRACT	ii
	TRAK	iv
	KNOWLEDGEMENTS	vi
	PROVAL	viii
	CLARATION	
	T OF TABLES	
	T OF FIGURES	XVI V
LIS	T OF ABBREVIATIONS	xix
CHA	APTER	
1	INTRODUCTION	1
	1.1 Background of Study	1
	1.2 Problem Statement	6
	1.3 Significance of Study	7
	1.4 The Objectives of the Study	7
2	LITERATURE REVIEW	8
	2.1 The Concept of Molecular Markers Analysis	8
	2.1.1 Biogenic Marker	8
	2.1.2 Fossil biomarke	9
	2.1.3 Anthropogenic Nolecula Markers	10
	2.2 Linear Alkylbenzer, (LAbs)	14
	2.3 Nomenclature	17
	2.4 Production CLABs	17
	2.5 Physicochemical Properties of LABs	18
	2.5.1 Phylical and Chemical Properties	19
	2.5.2 Aqueous Solubility and Log Octanol-Water	19
	Actitioning Coefficient 2.5.3 Forms and Persistence	20
	2.5.4 Biodegradability of Detergent Products	20 21
	2.6 Sources of LABs	23
	2.6.1 Incomplete Sulfonation of LABs	23 24
	2.6.2 Fluid Drilling	24
	2.7 Transport and Distribution of LABs	25
()	2.7.1 Distribution of LABs in Sediments	25
	2.7.2 Distribution of LABs in Sewage	27
	2.7.3 Distribution of LABs in Water	27
	2.8 Toxic of LABs	28
	2.9 Biodegradation of LABs	28
	2.10 Ratios of Internal to External LAB Isomers (I/E Ratio)	30
	2.11 Effectiveness of Sewage Treatment Plants	33
	2.12 Gas Chromatography-Mass Spectrometry (GC-MS)	34

3	METHODOLOGY	36
	3.1 Sampling Locations and Sample Collection	36
	3.2 Sediment Sample Collection	40
	3.3 Chemicals and Materials	41
	3.3.1 Surrogate Internal Standard (SIS), Internal Injection	
	Standard (IIS) and Native Standard Mixture of LABs	41
	3.3.2 Organic Solvents	44
	3.3.3 Preparation of 5% Deactivated Silica Gel	44
	3.3.4 Anhydrous Sodium Sulphate (Na ₂ SO ₄)	45
	3.4 Cleaning of Glassware and Apparatus	
	3.5 Analytical Procedure	
	3.5.1 Extraction and Fractionation	46
	3.5.1.1 Activated Copper Treatment	46
	3.5.1.2 Vacuum Rotary Evaporation	47
	3.5.2 Purification - First Step Silica Gel Column	
	Chromatography	47
	3.5.3 Fractionation - Second Step Silica Gel Column	10
	Chromatography	48
	3.5.4 Nitrogen Blow-down	49
	3.5.5 Preparation for GC-MS	49
	3.5.6 Gas Chromatography-Mass Sp. ctr metry (GC-MS)	
	Analysis	51
	3.6 Identification of Sample Perks	55
	3.7 Calibration Curves and Linearity of the Response Factor	56
	3.8 Quality Control and Quality Accurate	57
	3.9 LAB Concentration in the samples	59
	3.10 Analysis of Variance (ANOVA) for the LAB	
	Concentrations in the Three Rivers	60
4	RESULTS AND SCUSSION	63
	4.1 Level CLABs is the Sediments of the Studied Rivers	63
	4.14 The Concentrations of LABs in Sediments of	C A
	arawak River	64
	4.12 The Concentrations of LABs in Sediments of	69
	Sembulan River	68
	4.1.7 The Concentrations of LABs in Sediments of	71
	Kuantan River	71
	4 Biodegradation of LABs and the Internal to External	74
	LAB Congener Ratios (<i>I/E</i>) in the Three Rivers	74
	4.2.1 Biodegradation of LABs and the <i>I/E</i> Ratios for	75
(c)	Sarawak River	75
\bigcirc	4.2.2 Biodegradation of LABs and the <i>I/E</i> Ratios for	70
	Sembulan River	78
	4.2.3 Biodegradation of LABs and the <i>I/E</i> Ratios for	00
	Kuantan River	80
	4.2.4 Comparison of Total LABs Concentrations in	
	Sediments from Different Countries	83
	4.2.5 Comparison of I/E Ratios in Sediments from Different	83
	Countries	

	 4.3 Spatial Distribution of LABs in the Three Rivers 4.4 Statistical Analysis 4.4.1 Analysis of Variance (ANOVA) for the LAB Concentrations in the Three Rivers 4.4.2 Cluster Analysis 	84 87 88 91
5	CONCLUSION AND RECOMMENDATIONS FOR FUTURE RESEARCH	95
A F	REFERENCES APPENDICES BIODATA OF STUDENT LIST OF PUBLICATIONS	N 125 126
\bigcirc		