UNIVERSITI PUTRA MALAYSIA

ASSESSMENT OF HEAVY METAL POLLUTION IN SEAWATER, SUSPENDED PARTICULATE MATTER, ALGAL MAT, SEDIMENT AND GASTROPOD (*Nerita lineata*) IN DUMAI COASTAL WATERS, SUMATRA, INDONESIA

BINTAL AMIN

FS 2009 25

ASSESSMENT OF HEAVY METAL POLLUTION IN SEAWATER, SUSPENDED PARTICULATE MATTER, ALGAL MAT, SEDIMENT AND GASTROPOD (*Nerita lineata*) IN DUMAI COASTAL WATERS, SUMATRA, INDONESIA

By

BINTAL AMIN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

May 2009

DEDICATION

to my beloved late parents Redjo Moestomo and Soemini

and

to the most patient and understanding persons that I love more than ever

Irvina Nurrachmi, Fadilla Rizki Putri, Andina Dwi Kurnia and Inayah Tria Putri

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

ASSESSMENT OF HEAVY METAL POLLUTION IN SEAWATER, SUSPENDED PARTICULATE MATTER, ALGAL MAT, SEDIMENT AND GASTROPOD (*Nerita lineata*) IN DUMAI COASTAL WATERS, SUMATRA, INDONESIA

By

BINTAL AMIN

May 2009

Chairman: Prof. Dr. Ahmad Ismail

Faculty: Science

Concentrations of Cd, Cu, Pb, Zn, Ni and Fe in the surface seawater, suspended particulate matter, algal mat, sediments and gastropod *Nerita lineata* were determined to assess the status of heavy metal pollution in Dumai coastal waters. Concentrations of heavy metal in sediments varied from 0.88, 6.08, 32.34, 53.89, 11.48 µg/g dry weight and 3.01 % for Cd, Cu, Pb, Zn, Ni and Fe, respectively. These concentrations were comparable to metal concentrations in non polluted coastal waters and even lower than concentrations found in the sediments from the west coast of Peninsular Malaysia which is located just at the opposite side of the study area by the Malacca Straits. Generally, higher metal concentrations in the surface seawater, suspended particulate matter, algal mat, sediment and gastropod *Nerita lineata* were found at the stations with more industrial and anthropogenic activities near Dumai city center (eastern and central regions). Metal pollution index (MPI) of *N. lineata* further confirm higher level of heavy metal contaminations at

the eastern region of Dumai coastal waters. Cd in sediments from the eastern region was the only metal that slightly higher than effective range low (ERL) but still below effective range medium (ERM) values. The enrichment factor (EF) and pollution load index (PLI) values for Cd and Pb in the eastern region were also higher than other regions. Index of geoaccumulation (I_{geo}) indicated that most of the stations were categorized as class 1 (unpolluted to moderately polluted environment) and only Cd in Cargo Port was in class 2 (moderately polluted).

More than 50 % of Cd, Cu, Pb, Zn, Ni and Fe in sediments were accumulated in the 'resistant' fraction which indicated that the mobility of these metals in Dumai coastal waters were quite low. The eastern and center regions of Dumai coastal waters accumulated higher percentages of 'nonresistant' fraction of metals, especially Pb. However, only Pb in the eastern region was dominated by 'nonresistant' fraction (> 60 %). For overall stations, Pb also showed the highest percentage (45.32 %) of 'non-resistant' fraction, suggesting more anthropogenic inputs of Pb in Dumai coastal waters in comparison with other metals (43.22, 40.85, 37.34, 25.93 and 18.03 % for Cd, Zn, Ni, Cu and Fe, respectively).

All biomonitor organisms analyzed in the present study showed their ability to accumulate metals from their environment. *T. telescopium* accumulated the highest concentrations of Cd, Cu and Pb, whilst *N. lineata* accumulated the highest concentration for Zn. However, the difference between concentrations of Cd, Cu and Pb in both species was not significant and *T. telescopium* was not widely distributed in Dumai coastal waters as for *N. lineata*. Furthermore, among the studied biomonitors, *N. lineata* has wider range of distribution in the study area and

it also fulfilled some of the prerequisites for being indicator organisms for heavy metal pollution.

The mean concentrations of Cd, Cu, Pb, Zn, Ni and Fe in *N. lineata* were 4.14, 5.90, 44.43, 3.74, 20.73, 24.91 µg/g in shell; 4.16, 7.31, 51.78, 17.63, 23.52, 30.60 µg/g in operculum and 0.71, 15.16, 9.34, 94.69, 5.08, 397.96 µg/g d.w in the total soft tissue, respectively. Concentrations of Cd, Pb and Ni decreased in the order: operculum > shell > soft tissue whilst Cu, Zn and Fe in the order of soft tissue > operculum > shell. Metal concentrations, especially Cd in the shells and Pb in the soft tissues of *N. lineata* were significantly correlated with some of the respective geochemical fractions of metal concentrations in sediment as well as with metal concentrations in algal mat, suspended particulate matter and seawater which suggest that *N. lineata* could be used as biomonitoring agent for heavy metals pollution in Dumai coastal waters.

Geochemical fractionation analysis and calculated pollution indices using surface sediments and gastropod *N. lineata* revealed that Dumai coastal waters can be classified as unpolluted to moderately-polluted coastal environment. Therefore, although Dumai coastal waters is still not seriously polluted, a continuous environment monitoring program should be implemented as the ever increasing human activities and rapid developments in many infrastructures and industry sectors are continuously expanding.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENILAIAN PENCEMARAN LOGAM BERAT DI DALAM AIR LAUT, PEPEJAL TERAMPAI, HAMPARAN ALGA, SEDIMEN DAN GASTROPOD (*Nerita lineata*) DI PERAIRAN PANTAI DUMAI, SUMATRA, INDONESIA

Oleh

BINTAL AMIN

May 2009

Pengerusi: Prof. Dr. Ahmad Ismail

Fakulti: Sains

Kepekatan logam berat Cd, Cu, Pb, Zn, Ni dan Fe di dalam air laut permukaan, pepejal terampai, hamparan alga, sedimen dan gastropoda *Nerita lineata* telah diukur untuk menilai tahap pencemaran logam berat di perairan pantai Dumai. Kepekatan logam berat dalam sedimen berkisar daripada 0.88, 6.08, 32.34, 53.89, 11.48 µg/g dan 3.01 % masing-masing untuk Cd, Cu, Pb, Zn, Ni dan Fe. Kepekatan ini adalah setara dengan kepekatan logam di kawasan perairan tidak tercemar, malahan lebih rendah daripada kepekatan yang dijumpai di dalam sedimen daripada kawasan barat Semenanjung Malaysia yang berada hanya bertentangan dengan kawasan kajian ini di Selat Melaka. Secara amnya, kepekatan logam berat dalam air laut, pepejal terampai, hamparan alga, sedimen dan gastropoda *Nerita lineata* yang lebih tinggi didapati di stesen-stesen yang berhampiran dengan kawasan perindustrian dan aktiviti antropogenik di sekitar pusat bandar Dumai (kawasan timur dan tengah). Lebih tingginya tahap pencemaran logam berat di kawasan ini

disokong oleh pengiraan nilai indeks pencemaran logam (MPI) pada *N. lineata*. Cd dalam sedimen di kawasan timur adalah satu-satunya logam yang agak tinggi daripada nilai julat efektif rendah (ERL) namun masih kurang daripada nilai julat efektif menengah (ERM). Nilai faktor pengkayaan (EF) dan indeks beban pencemaran Tomlinson (PLI) untuk logam Cd dan Pb di kawasan timur juga lebih tinggi berbanding kawasan lain. Berdasarkan nilai indeks geoakumulasi (I_{geo}) pula, kebanyakan stesen dikategorikan sebagai Kelas 1 (tidak tercemar sehingga sederhana tercemar) dan hanya Cd di stesen Pelabuhan Kargo tergolong dalam Kelas 2 (sederhana tercemar).

Analisis pecahan geokimia mendapati lebih daripada 50 % Cd, Cu, Pb, Zn, Ni and Fe dalam sedimen terkumpul di dalam pecahan 'resistant', di mana ia menunjukkan mobiliti logam-logam berat itu di perairan Dumai adalah rendah. Kawasan timur dan tengah perairan Dumai mencatatkan peratusan pecahan 'non-resistant' yang tinggi terutama sekali untuk Pb. Walaubagaimanapun, hanya Pb yang mendominasi pecahan 'non-resistant' (> 60 %) untuk kawasan timur perairan itu. Secara keseluruhan, pecahan 'non-resistant' Pb yang tinggi (45.32 %) menunjukkan lebih input antropogenik Pb di perairan pantai Dumai jika dibandingkan dengan logam-logam lain (masing-masing 43.22, 40.85, 37.34, 25.93 dan 18.03 % untuk Cd, Zn, Ni, Cu dan Fe).

Kesemua biomonitor yang dianalisis dalam kajian ini menunjukkan kebolehan mereka untuk mengumpul logam-logam berat daripada kawasan persekitaran mereka. *T. Telescopium* mengumpul kepekatan logam Cd, Cu dan Pb yang paling tinggi sedangkan *N. lineata* merupakan pengumpul tertinggi untuk logam Zn.

Walaubagaimanapun, perbezaan diantara kepekatan logam Cd, Cu dan Pb pada kedua-dua spesies tersebut tidak signifikan dan *T. telescopium* tersebut di perairan pantai Dumai tidaklah dijumpai sebanyak *N. lineata*. Terlebih lagi, daripada kesemua biomonitor yang dikaji, hanya *N. Lineata* yang mempunyai julat taburan lebih luas dan dengan itu memenuhi salah satu dari persyaratan organisma indikator untuk pencemaran logam berat.

Purata kepekatan bagi logam Cd, Cu, Pb, Zn, Ni dan Fe pada *N. lineata* masing-masing adalah 4.14, 5.90, 44.43, 3.74, 20.73, 24.91 μg/g dalam cengkerang; 4.16, 7.31, 51.78, 17.63, 23.52, 30.60 μg/g dalam operkulum dan 0.71, 15.16, 9.34, 94.69, 5.08; 397.96 μg/g berat kering dalam keseluruhan tisu lembut. Kepekatan Cd, Pb dan Ni menyusut mengikut urutan: operkulum > cengkerang > tisu lembut; manakala bagi Cu, Zn dan Pb pula mengikut urutan: tisu lembut > operkulum > cengkerang. Hubungan yang signifikan telah dijumpai di antara kepekatan logam-logam berat terutamanya Cd di dalam cengkerang dan Pb di dalam tisu lembut *N. lineata* dengan sebahagian besar pecahan geokimia logam dalam sedimen dan juga dengan logam berat dalam hamparan alga, pepejal terampai dan air laut. Oleh sebab yang demikian maka dicadangkan bahawa cengkerang *N. lineata* boleh dijadikan sebagai agen biomonitor bagi pencemaran logam berat di perairan pantai Dumai.

Berdasarkan kajian pecahan geokimia dan pengiraan indeks pencemaran menggunakan sedimen dan gastropoda *N. lineata*, perairan pantai Dumai dikelaskan sebagai kawasan tidak tercemar sehingga sederhana tercemar. Namun demikian, meskipun perairan pantai Dumai pada masa ini tidak tercemar secara serius, program pengawasan persekitaran berterusan seharusnya dijalankan memandangkan

peningkatan aktiviti manusia dan pembangunan yang pesat dalam pelbagai sektor infrastruktur dan industri terus berkembang.

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my principle supervisor Prof. Dr. Ahmad Ismail for his expertise and consistent constructive advice, ideas and guidance for the successful completion of my study. My sincere thanks also go to my co-supervisors Assoc. Prof. Dr. Aziz Arshad and Assoc. Prof. Dr. Mohd. Salleh Kamarudin for their professional advice and comments.

I am indebted and grateful to Dr. Yap Chee Kong for his valuable feedback and helped to clarify the discussion, the Dean of the Faculty of Fisheries and Marine Science and the Rector of the University of Riau Pekanbaru for the given opportunity to pursue my study and also to the Local Government of Riau Province for providing me with a partial financial support.

I would also like to thank all the members of Ecotoxicology Laboratory at the Department of Biology Universiti Putra Malaysia for their warm friendship and to the crews of the University of Riau 'Senangin' Research Vessel for all the help especially during the fieldwork.

And finally I would like to thank all my family members, especially my wife Irvina, my daughters Oki, Dina and Yaya and my father in-law for their love, understanding, and motivation which gave me strength throughout the whole period of my study. I can not even begin to express how much their love and continuous support mean to me. All of you are my rock in the turbulent seas of life and you all played an important role in my achievements and success in life.

I certify that a Thesis Examination Committee has met on 30 March 2009 to conduct the final examination of Bintal Amin on his thesis entitled "Assessment of Heavy Metal Pollution in Seawater, Suspended Particulate Matter, Algal mat, Sediment and Gastropod (*Nerita lineata*) in Dumai Coastal Waters, Sumatra, Indonesia" 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.

Members of the Thesis Examination Committee were as follows:

Hishamuddin Omar, PhD
Lecturer
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Nor Azwady Abd. Aziz, PhD
Lecturer
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Abdul Rahim Ismail, PhD
Lecturer
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Noor Azhar Mohamed Shazili, PhD
Professor
Faculty of Science and Technology
Universiti Malaysia Terengganu
(External Examiner)

_____

BUJANG KIM HUAT, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 21 May 2009

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The Members of the Supervisory Committee were as follows:

AHMAD ISMAIL, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

AZIZ ARSHAD, PhD
Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Member)

MOHD. SALLEH KAMARUDIN, PhD
Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Member)

_____

HASANAH MOHD. GHAZALI, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date :

DECLARATION

I hereby 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 institutions.

_____

BINTAL AMIN

Date:

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Abbreviation/symbols	Definition
%	percentage
ºC	degree Celsius
µg/g	microgram per gram
µm	micrometer
AAS	atomic absorption spectrophotometer
Anova	analysis of variance
BDL	below detection limit
cm	centimeter
CRM	certified reference material
DDW	double distilled water
d.w	dry weight
EF	enrichment factor
EFLE	easily or freely, leachable and exchangeable
ERL	effective range low
ERM	effective range medium
g	gram
H_2O_2	hydrogen peroxide
HCl	hydrochloric acid
$HClO_4$	perchloric acid
HNO_3	nitric acid
I_{geo}	index of geoaccumulation
mg/L	milligram per liter
ml	milliliter
mm	millimeter
MΩ	Mega Ohms
M	Molar volume
MPI	Metal Pollution Index
$NH_2OH.HCl$	Hydroxyl ammonium chloride
NH_4CH_3COO	Ammonium acetate
No.	number
PLI	pollution load index
ppm	part per million
SET	sequential extraction technique
Sg.	Sungai
SPM	suspended particulate matter
SQG	standard quality guidelines
Tj.	Tanjung

CHAPTER 1

INTRODUCTION

1.1 General

Heavy metal contamination of the coastal environment continues to attract the attention of environmental researchers due to its increasing input to the coastal waters, especially in the developing countries. As for other contaminants, heavy metals could be introduced into the coastal environments by several pathways including disposal of liquid effluents, runoff carrying chemicals originating from a variety of urban, industrial and agricultural activities as well as atmospheric deposition.

Due to their toxicity, persistence and bioaccumulation problems, heavy metals become one of the more serious pollutants in our natural environment (Phillips, 1980; Martin and Coughtrey, 1982; Luoma, 1983; Salomons and Forstner, 1984; Rainbows, 1995; Tam and Wong, 2000; Cravo and Bebianno, 2005; Upadhyay *et al*., 2006). Heavy metals in natural waters and their corresponding sediments have become a significant topic of concern for scientists in various fields associated with water quality, as well as a concern of the general public (Timothy, 2000; Chen *et al*., 2004). The focus of this concern is direct toxicity to man and aquatic life as well as indirect toxicity through accumulations of metals in the aquatic food chain (Tam and Wong, 1997; Chen *et al*., 2000; Cravo and Bebianno, 2005).