A STUDY ON HEAVY METALS DISTRIBUTION IN MANGROVE SEDIMENT OF MENGKABONG, SABAH

SARVA MANGALA PRAVEENA

THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE DEGREE OF MASTER OF SCIENCE

**SCHOOL OF SCIENCE AND TECHNOLOGY
UNIVERSITI MALAYSIA SABAH**
2008

UNIVERSITI MALAYSIA SABAH

BORANG PENGESAHAN STATUS TESIS[@]

JUDUL: A STUDY ON HEAVY METALS DISTRIBUTION IN MANGROVE SEDIMENT OF MENGKABONG, SABAH

IJAZAH: SARJANA SAINS

SESI PENGAJIAN: 2005-2007

Saya, SARVA MANGALA PRAVEENA mengaku membenarkan tesis sarjana ini disimpan di perpustakaan Universiti Malaysia Sabah dengan syarat-syarat kegunaan seperti berikut:

1. Tesis adalah hak milik Universiti Malaysia Sabah.
2. Perpustakaan Universiti Malaysia Sabah dibenarkan membuat salinan untuk pengajian saya.
3. Perpustakaan dibenarkan membuat salinan tesis ini sebagai bahan pertukaran antara institusi pengajian tinggi.
4. TIDAK TERHAD

Disahkan oleh

ANITA BINTI ARSAD
PUSTAKAWAN KANAN
UNIVERSITI MALAYSIA SABAH

Penulis: SARVA MANGALA PRAVEENA

TANDATANGAN PUSTAKAWAN

Penyelia: Prof Dr Mohd Harun Abdullah
9 Julai 2008

Penyelia: Prof Madya Dr Miroslav Radojevic
9 Julai 2008

Tarikh: 2007

CATATAN: [@] Tesis dimaksudkan sebagai tesis Ijazah Doktor Falsafah dan Sarjana secara penyelidikan atau ddisertasi bagi pengajian secara kerja kursus dan penyelidikan, atau laporan Projek Sarjana Muda (LPSM)

DECLARATION

I hereby declare that the material in this thesis is my own except for quotations, excerpts, summaries and references, which have been duly acknowledged.

30 March 2008

SARVA MANGALA PRAVEENA
PS05-001-021

ACKNOWLEDGEMENT

It is a pleasure for me to thank many people who made this thesis possible. First and foremost, I would like to thank God who is the essence of everything for giving me strength, wisdom and guidance during this study. I am deeply indebted to my supervisors Associate Professor Dr Miroslav Radojevic and Professor Dr Mohd Harun Abdullah whose comments, stimulating suggestions and encouragements helped me in all the time of research. Their overly enthusiasm and integral view on research and their mission for providing 'only high-quality work and not less', has made a deep impression on me. Special thanks to Professor Dr Amran Ahmed for his kind assistance in statistics and helping me with various applications of statictics to this study. I gratefully thank Mr Asram Ramun and Mr Neldin Jeoffrey for their help in field samplings. Warmest thanks to "Skim Zamalah Yeoh Tiong Lay", Universiti Malaysia Sabah as a financial support for this postgraduate study. My respects and thanks to all the rest of the Mengkabong residents, Environmental Science lecturers, Environmental Science, Geology and Industrial Chemistry lab assisstants (Mr Jalaludin Majalip, Mr Yusri Jasli and Mr Recyheidy Mohd Rashid, Mr Sufie) and friends especially to Mr Coneliues Robert (EPD, Sabah), Miss Kamsia Budin, Mr Ahmad Zaharin Aris, Miss Baizurah and Mrs Dayang. To others who helped me direcly and indirectly in this study, thank you very much for the kind help and kindness. Your help will always be appreciated. I cannot end without thanking my family, on whose constant encouragement and love I have relied throughout my time. Their unflinching courage and conviction will always inspire me, and I hope to continue, in my own small way to achieve my ambition. It is to them that I dedicate this work.

ABSTRACT

A STUDY ON HEAVY METALS DISTRIBUTION IN MANGROVE SEDIMENT OF MENGKABONG, SABAH

The distribution of selected heavy metals (Fe, Cu, Zn, Pb and Al), pH, salinity, electrical conductivity, organic matter, particle size and base cations (Na, K, Ca and Mg) in surface sediment of a mangrove forest situated on the northwest of Sabah were examined from March 2006 to November 2006 at high and low tides. The heavy metal levels, expressed as mg/kg in the studies area were scattered in the ranges: 1434-18360 for iron, 2-49 for copper, 12-93 for zinc, 13-69 for lead and 2410-35393 for aluminium. The Two-Way ANOVA results indicated that the underlying significant variations exist between stations at high and low tides. Results of Spearman correlation coefficient showed a large variety and complexity in these relationships at high and low tides. Multivariate statistics approach (factor analysis) was used to discover and interpret relationships between variables. At high tide, six factors were obtained, which accounted for nearly 70% of the total variance. The results of factor analysis groups at high tide contain salinity, electrical conductivity and clay in factor one, sand in factor two, Cu and K in factor three, Fe, Ca and Al in factor four, pH and Na in factor five as well as Pb in factor six. Whereas at low tide, seven factors were extracted and demonstrated the 77% of the total variance. The results of factor analysis groups at low tide contain silt, Al and Zn in factor one, Mg, Ca and Pb in factor two, Cu and clay in factor three, salinity and K in factor four, pH in factor five, Fe in factor six and Na in factor seven. Different types of indexes (enrichment factors (EF), Geoaccumulation Index (I_{geo}), pollution load index (PLI) and metal sediment pollution index, MSPI) were tested and compared to assess the contamination level. Based on these indexes, MSPI was chosen as having an advantage over the earlier indexes. MSPI uses PCA to interpret and calculated the pollution scores derived from the PCA results. The MSPI value indicates that the Mengkabong mangrove sediment is in excellent condition and confirms that it is in low contamination condition. Moreover, the mean of heavy metals were compared to several sediment quality guidelines (Washington Department of Environment, Australian and New Zealand Environment and Conservation Council (ANZECC), Swedish Environmental Sediment Quality, Screening Quick Reference Table (SQUIRT), Portuguese Legislation on the Classification of Dredged Materials in Coastal Zones and Interim Sediment Quality Guideline for Hong Kong) in order to evaluate the degree to which the sediment-associated chemical status might adversely affect the aquatic organisms. The interim sediment quality values for Hong Kong were chosen and being the most appropriate guideline that meet the prioritization criteria consistent with international regulations and initiatives. However, site-specific, biological testing and ecological analysis of existing benthic community structure (crabs, mollusks, mudskippers) related to sediment contamination are needed for final decision making in the case of Mengkabong mangrove forest management.

KEYWORDS: Mangrove surface sediment, Statistical results, Indexes, Sediment quality guidelines

ABSTRAK

Taburan logam berat terpilih (Fe, Cu, Zn, Pb and Al), pH, saliniti, kekonduksian elektrik, bahan organik, saiz partikel and kation (Na, K, Ca and Mg) di dalam tanah permukaan sedimen hutan paya bakau yang terletak di Barat Laut, Sabah telah dikaji dari Mac 2006 hingga November 2006 pada keadaan air pasang dan air surut. Tahap logam berat ditunjukkan di dalam unit mg/kg di kawasan kajian berjulat: 1434-18360 bagi ferum, 2-49 bagi kuprum, 12-93 bagi zink, 13-69 bagi plumbum and 2410-35393 bagi aluminium. Keputusan "Two-Way" ANOVA menunjukkan bahawa perbezaan bererti wujud di antara semua stesen yang dikaji pada keadaan air pasang dan air surut. Keputusan pekali korelasi "Spearman" menunjukkan kepelbagaian yang besar dan kompleks wujud dalam perhubungan pada keadaan air pasang dan air surut. Kaedah statistik "multivariate" ("factor analysis") telah digunakan untuk mengenalpasti dan menerangkan hubungan yang wujud di antara semua parameter yang dikaji. Keputusan "factor analysis" pada keadaan air pasang, ia mengandungi saliniti, kekonduksian elektrik dan tanah liat di dalam faktor satu, tanah pasir di dalam faktor dua, Cu dan K di dalam faktor tiga, Fe, Ca dan Al di dalam faktor empat, pH dan Na di dalam faktor lima serta Pb di dalam faktor enam. Manakala, bagi keputusan "factor analysis" pada keadaan air surut, ia mengandungi tanah lempung, Al dan Zn di dalam faktor satu, Mg, Ca dan Pb di dalam faktor dua, Cu dan tanah liat di dalam faktor tiga, saliniti dan K di dalam faktor empat, pH di dalam faktor lima, Fe di dalam faktor enam dan Na di dalam faktor tujuh. Pelbagai jenis indeks ("Enrichment Factor" (EF), "Geoaccumulation Index" (I_{geo}), "Pollution Load Index" (PLI) and "Metal Sediment Pollution Index" (MSPI) telah diuji dan dibandingkan untuk mengetahui tahap pencemaran di tanah permukaan sedimen yang dikaji. Berdasarkan semua indeks yang telah dikira, MSPI telah dipilih sebagai indeks yang terbaik dari semua indeks yang telah digunakan. MSPI menggunakan keputusan PCA dalam menilai dan menghitung skor pencemaran. Nilai MSPI mengambarkan sedimen pemukaan tanah paya bakau berada dalam keadaan yang sangat baik dan ia mengesahkan bahawa tahap pencemaran yang rendah di kawasan tersebut. Tambahan lagi, nilai min logam berat dibandingkan dengan beberapa garis panduan kualiti sedimen ("Washington Department of Environment", "Australian and New Zealand Environment and Conservation Council" (ANZECC), "Swedish Environmental Sediment Quality", "Screening Quick Reference Table" (SQUIRT), "Portuguese Legislation on the Classification of Dredged Materials in Coastal Zones" dan "Interim Sediment Quality Guideline for Hong Kong") dalam menilai darjah berkait rapat dengan tahap kimia sediment tersebut yang boleh membawa kesan kepada organisma akuatik. "Interim Sediment Quality Guideline for Hong Kong" telah dipilih sebagai garis panduan yang paling sesuai yang memenuhi kriteria-kriteria utama sejajar dengan peraturan dan inisiatif antarabangasa. Walaubagaimanapun, lokasi spesifik, pemeriksaan biologi dan analisis ekologi terhadap komuniti bentik (ketam, moluska, ikan belacak) yang berkait rapat dengan pencemaran sedimen diperlukan dalam menentukan keputusan muktamad mengenai pengurusan hutan paya bakau Mengkabong.

Kata Kunci: *Sedimen permukaan tanah paya bakau, Keputusan statistik, Indeks, Garis panduan kualiti sedimen*

CONTENTS

LIST OF TABLES

LIST OF FIGURES/ PHOTOS

LIST OF ABBREVIATIONS

EC	Electrical Conductivity
OM	Organic Matter
Sa	Salinity
HNO_3	Nitric Acid
SPSS	Statistical Package for Social Science
PCA	Principal Component Analysis
EF	Enrichment Factor
I_{geo}	Geo-accumulation Index
PLI	Pollution Load Index
MSPI	Marine Sediment Pollution Index
CF	Concentration Factors
ANZECC	Australian and New Zealand Environment And Conservation Council
SQG	Sediment Quality Guidelines
ISQGs	Interim Sediment Quality Guidelines
SQUIRT	Screening Quick Reference Table
CEC	Cation Exchange Capasity
ICP	Inductively Coupled Plasma
USEPA	United States Environmental Protection Agency
AAS	Atomic Absorption Spectroscopy
FAAS	Flame Atomic Absorption Spectroscopy
APHA	American Public Health Association
EIA	Environmental Impact Assessment
KKIP	Kota Kinabalu Industrial Park
DOM	Dissolved Organic Matter
DO	Dissolved Oxygen

LIST OF SYMBOLS

O	Oxygen
Si	Silicon
Al	Aluminium
Fe	Iron
C	Carbon
La	Lanthanum
Li	Litium
Pb	Lead
P	Phosphorus
Ca	Calcium
K	Potassium
As	Arsenic
B	Boron
Be	Beryllium
Br	Bromine
Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cs	Cesium
Cu	Copper
Ca	Calcium
K	Potassium
Mn	Manganese
Na	Sodium
Rb	Rubidium
S	Sulfur
Sc	Scandium
Sn	Tin
Sr	Strontium
Th	Thorium
Ti	Titanium

U	Uranium
V	Vanadium
Zn	Zinc
µm	Micrometer
Ni	Nickel
Mg	Magnesium
Mm	Millimeter
Ha	Hectare
%	Percentage
km^2	Square kilometer
USA	United States Of America
^oC	Celsius
SOM	Soil Organic Matter
HCO_3^-	Bicarbonate
T_2O_5	Tetrahedral Cation
H^+	Hydrogen Ion
CO_3^{2-}	Carbonate Ion
EC	Electrical Conductivity
g/cm^3	Gram per Cubic Centimetre
Fe_3O_4	Magnetite
Fe_2O_3	Hematite
mg/dl	Milligrams per deciliter
mg/kg	Milligram/kilogram
µS/cm	Microsiemen /centimeter
Ppm	Part per million
G	Gram
=	Equals to
ms^{-1}	Meters per second
mL	Milliliter
Mg	Milligram
A-A	Air–Acetylene
N_2O-A	Nitrous Oxide – Acetylene

LIST OF APPENDIX

CHAPTER 1

INTRODUCTION

1.1 SOIL CHEMISTRY

Soil chemistry is the branch of soil science that deals with the chemical composition, chemical properties and chemical reactions of soils. Soils are heterogeneous mixtures of air, water, inorganic and organic solids, microorganisms (both plant and animal in nature) and water capable of supporting plant life on the earth's surface (Sparks, 1995; Manahan, 2000). Soil chemistry has traditionally focused on the chemical reactions in soils that affect plant growth and plant nutrition. On the other hand, beginning in the 1970s to now, there are increasing concerns about inorganic and organic contaminants in water and soil as well as the impacts on plant, animal and human health. Soil chemistry is concerned with chemical reactions involving these phases (solid, solution and gas). For an example, carbon dioxide in air combined with water acts to weather the inorganic solid phase. Chemical reactions between the soil solids and the soil solution influence both plant growth and water quality (Sparks, 1995).

Environmental soil chemistry is the study of chemical reactions between soils and environmentally important plant nutrients, radionuclides, metals and organic metals. Knowledge of environmental soil chemistry is fundamental in predicting the fate of contaminants in the surface and subsurface environments. An understanding of the chemistry and mineralogy of organic and inorganic soil components is vital to comprehend the array of chemical reactions that contaminants may undergo in the soil environment. These reactions, which may include equilibrium and kinetic process such as dissolution, precipitation, polymerization, adsorption/ desorption and oxidation-reduction, affect the solubility, mobility, form and the toxicity of contaminants in soils and in surface waters and groundwaters. Knowledge of environmental soil chemistry is also useful in making sound decision and also cost effective decision about remediation of contaminated soils (Sparks, 1995).

1.2 SOIL CONTENT

Soil is the final product of the weathering of parent rock and the decomposition of organic matter; the action of physical, chemical, and biological processes on rocks that produce mainly clay minerals. The organic portion of soil consists of plant biomass in various stages of decay. High populations of bacteria, fungi, and animals such as earthworms may be found in soil. Soil contains air spaces and generally has a loose texture. The solid fraction of typical productive soil is approximately 5% organic matter and 95% inorganic matter. Some soils, such as peat soils, may contain as much as 95% organic material. Other soils contain as little as 1% organic matter (Manahan, 2000).

The median and range of elemental content of soils from around the world are given in Table 1.1. The elements that are found in the highest quantities are oxygen (O), silicon (Si), aluminium (Al), iron (Fe), carbon (C), calcium (Ca), potassium (K), nickel (Ni) and magnesium (Mg). These are also major elements found in earth crust and in sediments. Oxygen is the most prevalent element in the earth crust and in soils. It comprises about 47% of the earth's crust by weight and greater than 90% by volume (Sparks, 1995). The inorganic components of soils represent more than 90% of the solid components. Properties such as size, surface area and charge behavior greatly affect many important equilibrium and kinetic reactions and processes in soils (Manahan, 2000).

Table 1.1: Contents of elements in soils, the Earth's crust and sediment

Element	Soils (mg/kg) Range [a, b]	Earth Crust (mean)[c]	Sediments (mean)[c]
Al	700 – 300, 000	82, 000	72, 000
As	< 0.1 - 97	1.5	7.7
B	< 20 – 300	10	100
Ba	10 – 5, 000	500	460
Be	< 1 – 40	2.6	2
Br	< 0.5 – 110	0.37	19
C, Total	600 – 500, 000	480	29, 400
Ca	100 – 500, 000	41, 000	66, 000
Cd	< 0 - 2	0.11	0.17
Cl	< 0 – 1800	130	190
Co	< 3 – 70	20	14
Cr	1 – 2000	100	72
Cs	< 0 - 20	3	4.2
Cu	< 1 - 700	50	33
F	< 10 – 3, 700	950	640
Fe	100 - > 550,000	41, 000	41, 000
Ga	< 5 – 100	18	18
Ge	< 0.1 – 50	1.8	1.7
I	< 0.10 – 25	0.14	16
K	50 – 63, 000	21, 000	20, 000
La	< 30 – 200	32	41
Li	< 3 - 350	20	56
Mg	50 - > 100, 000	23, 000	14, 000
Mn	< 2 – 10, 000	950	770
Mo	< 3 – 40	1.5	2
N	< 0 – 5, 000	25	470
Na	< 150 – 100, 000	23, 000	5, 700
Nb	< 6 – 300	20	13
Nd	< 4 - 300	38	32
Ni	< 2 - 750	80	52
O	-	474, 000	486, 000
P	< 20 – 6, 800	1, 000	670
Pb	< 10 - 700	14	19
Rb	< 20 – 1, 000	90	135
S, Total	< 30 – 48,000	260	2, 200
Sb	< 0.20 – 10	0.2	1.2
Sc	< 0.5 -55	16	10
Se	< 0.011 – 4.3	0.05	0.42
Sn	< 1- 200	2.2	4.6
Sr	< 4 – 3, 000	370	320
Th	1 - 35	12	9.6
Ti	70 – 25, 000	5, 600	3, 800
U	0.29 - 11	2.4	3.1
V	< 7 - 500	160	105
Y	< 10 - 250	30	40
Yb	< 0.04 – 50	3.3	3.6
Zn	< 1 – 2, 900	75	95
Zr	< 20 – 2, 000	190	150

[a] Shacklette & Boerngen (1984). Represent analyses from soils and other surficial materials from throughout the continental United States. [b,c] Bowen (1979)

The inorganic components of soils include both primary and secondary minerals which range in size (particle diameter) from clay-sized colloids (< 2 μm or 0.002 mm) to gravel (> 2mm) and rocks. A mineral can be defined as a natural inorganic compound with definite physical, chemical and crystalline properties ionically bonded and their structures based on Pauling's Rules. The primary mineral is the one that has not been altered chemically since deposition and crystallization from molten lava. Examples are quartz and feldspar while in smaller quantities minerals such as micas, olivines and many more. A secondary mineral results from weathering of primary mineral, either by alteration in the structure or from reprecipitation of product weathering (dissolution) of primary mineral.

Common secondary minerals are aluminosilicate minerals. The nature of the parent material is the main factor determining the present soil type and soil chemical properties. The bedrock at the presented sites are either acid metamorphic rock (gneiss), or the more basic petrified sedimentary deposits (sandstone or shales). Ionic bonds are formed when an ion interacts with another ion of opposite charge in the mineral structure to form a chemical bond. Covalent bonds are those which share electrons. Most chemical bonds have a combination of ionic and covalent Character. For an example, the Al-O bond is approximately 40% covalent and 60% (Sparks, 1995).

1.3 OBJECTIVES OF THE STUDY

The present research objectives are stated as follows:.

i. To determine selected heavy metals (Fe, Cu, Zn, Pb and Al), pH, salinity, electrical conductivity, organic matter, particle size and base cations (Na, K, Ca and Mg) in mangrove sediments at low and high tide.

ii. To examine the relationship between heavy metals and base cations with soil chemical and physical parameters during high and low tides.