UNIVERSITI PUTRA MALAYSIA

DETERMINING DISTRIBUTION OF ELEMENTS IN SURFACE SEDIMENT, SOFT TISSUE AND SHELL OF Cerithidea obtusa Lamarck USING NUCLEAR AND ATOMIC TECHNIQUES

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FS 2015 66

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By

KUMAR KRISHNAN

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

January 2015

DEDICATION

This thesis is dedicated to:

“My Lovely Family”

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor of Philosophy

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Chairman : Professor Elias Saion, PhD

Faculty : Science

Mangrove forests found in the coastal areas of tropical countries are the primary productive ecosystems for marine life and increasingly suffer environmental degradation due to antrophogenic sources. Therefore, it is of significant to evaluate the degree of contamination in the mangrove ecosystems to identify whether it is a health risk for consumption of marine animals found in these areas. The current study involved the determination of concentrations of heavy metals, major and trace elements, and rare earth elements in the surface sediments and the soft tissues and shell of *cerithidea obtusa* collected from ten locations of mangrove areas along the west coast of Peninsular Malaysia. The Instrumentation Neutron Activation Analysis (INAA) and Atomic Absorption Spectrometry (AAS) techniques were used for this purpose. Several methods were used to evaluate the level of pollution in the sediments. Biota-sediment accumulation factor (BSAF) used to estimate of proportion in which metal occurs in the living organism and in associated sediment and hazard Risk index (HRI) estimated to identify any unlikely adverse human health effects from consumption of contaminated seafood.

In the present investigation the order of accumulation of the heavy metal concentration in the surface sediments and the soft tissues and shell of *cerithidea obtusa* was Mn> Zn> Cr> Pb> As> Ni> Cu> Cd, Mn> Zn> Cu> Ni> Cr> As> Pb> Cd and Mn> Zn> Ni> Cu> Pb> Cr> As> Cd respectively. The highest enrichment factor was 9.18 (As) and the lowest was 0.21 (Cu) in the sediments. Contamination factors, degree of contamination (*Cd*), modified degree of contamination (*mCd*) and pollution level index (PLI) of all the heavy metal fall in the range of 0.13 - 1.90, 4.26 – 11.78, 0.70 – 1.47 and 0.42 – 1.18 respectively in the sediments. The highest geoaccumulation index was found in Zn with index 1.37 from location L5. Ecological factor and risk index varied in range 0.36 - 66.00 and 19.61 – 98.40 respectively in the sediments. The lowest health risk index was 0.010 (Cd) and the highest was 7.43 (Mn) based on the total concentration of elements in the soft

tissues of *cerithidea obtusa*. Great concern must be given to the Mn especially at L5 due to HRI value seven times greater than unity. The results of this study supporting the L5 (Juru, Penang) is one the contaminated area as mentioned previously by other studies. BSAF of heavy metal in the soft tissues and shell of *cerithidea obtusa* ranged from 0.034 to 22.30 from 0.012 to 2.35 respectively.

The total concentrations of REEs (Ce, La, Dy, Sm, Eu, Lu, Tb and Yb) in sediments samples ranged from 0.35 to 117.4 mg/kg. The geochemical behavior of REEs in surface sediments and normalized pattern (chondrite and shale) has been studied. Enrichment factor of REEs varied in the range from 0.75 to 6.75. The indicator ratios of La/Yb and Eu/Sm varied from 3.89 - 18.49 and 0.06 - 0.20 respectively. The Ce/La ratio was calculated and varied from 1.96 to 3.17. From the enrichment pattern can be concluded that LREE > HREE as the uptake sequence of the REE as in the mangrove sediment samples. No REEs was found in the soft tissues and shell of *cerithidea obtusa*.

In the present investigation the order of accumulation trace elements in the sediment, soft tissues and shell of *cerithidea obtusa* was Ba> V> Ga> Cs> Hf> Sc> Ta> Co> Sb and Co > Sc respectively. The mean concentration of Co and Sc (other elements not detected) on the soft tissues and shell of *cerithidea obtusa* ranged from 0.83 to 6.94 and 0.12 to 2.39 mg/kg respectively. The enrichment of trace elements varied in range from 0.41 to 20.76 in the sediments. Contamination factors, Degree of contamination (*Cd*) and modified degree of contamination (*mCd*) of all the trace element fall in the range of 0.10 - 3.98, 5.77-11.49 and 0.64-1.36 respectively in the sediments. The highest geoaccumulation index was found in Ta (1.41) from location L6. BSAF of in the soft tissues and shell of *cerithidea obtusa* ranged from 0.01 to 0.94 and 0.03 to 0.14 respectively.

The major element concentration in the sediment was in the order of Al>Fe>Na>Mg>K>Ca>Ti>Rb. The mean concentrations of Ca, Fe, K, Mg, Na and Rb on the soft tissues of *cerithidea obtusa* ranged from 11349 to 55815, 652 to 6284, 7561 to 13327, 6010 to 11595 and 0.99 to 30.6 mg/kg respectively. On the other hand, the mean concentrations of Ca, Fe, K, Mg, and Na (Rb not detected) on the shell of *cerithidea obtusa* ranged from 138509 to 403444, 209 to 1008, 256 to 1307, 315 to 503 mg/kg respectively. The enrichment factor of major elements ranged from 0.53 to 5.92 in the sediments. Geo-accumulation index was found highest in location L5 with index 1.27 (Na). BSAF of major elements in the soft tissues and shell of *cerithidea obtusa* ranged from 0.03 to 8.05, and 0.01 to 73.58 respectively.

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

PENENTUAN TABURAN UNSUR SEDIMEN PERMUKAAN , TISU LEMBUT DAN CANGKERANG *Cerithidea Obtusa* Lamarck MENGGUNAKAN TEKNIK NUKLEAR DAN ATOM

Oleh

KUMAR KRISHNAN

Januari 2015

Pengerusi : Profesor Elias Saion , PhD

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Hutan paya bakau merupakan ekosistem yang penting bagi kehidupan marin dan biasanya ditemui di kawasan pantai negara-negara tropika. Oleh yang demikian adalah penting untuk menilai tahap pencemaran dalam ekosistem bakau dan mengkaji pasti sama ada pencemaran ini memberi sebarang kesan keatas hidupan marin. Kajian semasa memberi tumpuan kepada penentuan kepekatan unsur-unsur dalam permukaan tanah, tisu dan cangkerang *cerithidea obtusa* yang telah dikumpul daripada sepuluh lokasi paya bakau daripada Pantai Barat Semenanjung Malaysia. Instrumentasi analisis pengaktifan neutron (INAA) dan Penyerapan Atom teknik spektrometri (AAS) telah digunakan untuk menentukan kepekatan unsur-unsur. Kepekatan unsur-unsur sumber utama, peralihan, logam berat dan nadir bumi telah dikaji dalam sampel sedimen paya bakau dan kerang moluska untuk menilai tahap pencemaran. Beberapa kaedah telah digunakan untuk menilai tahap pencemaran di dalam tanah. Nisbah diantara unsur dalam organisma hidup dan dalam tanah yang berkaitan (BSAF) digunakan untuk mengenal pasti samada kerang moluska dikelasifikasikan sebagai biomonitor atau sebaliknya. Indeks bahaya (HRI) dianggarkan untuk memastikan kesihatan penguna kerang moluska *cerithidea obtusa* tidak terjejas.

Dalam penyelidikan ini didapati akumulasi kepekatan logam berat di dalam sedimen, tisu lembut dan cengkerang *cerithidea obtusa* adalah dalam turutan Mn> Zn> Cr> Pb> As> Ni> Cu> Cd, Mn> Zn> Cu> Ni> cr> As> Pb> Cd dan Mn> Zn> Ni> Cu> Pb> cr> As> Cd masing-masing. Faktor pengayaan tertinggi adalah 9.18 (unsur As) dan terendah adalah 0.21 (unsur Cu) dalam tanah. Faktor pencemaran, darjah pencemaran (Cd) dan darjah tahap pencemaran (mCd) bagi semua logam berat adalah dalam julat 0.13-1.90, 2.81-7.74 dan 0.70-1.94 masing-masing di dalam sedimen. Indeks geoakumulasi tertinggi ditemui pada unsur Zn dengan indeks 1.37 dari L5. Faktor ekologi dan indeks risiko diubah dalam julat 0.36-66.00 dan 19.61-98.40 masing-masing di dalam sedimen. Indeks risiko kesihatan, HRI

terendah adalah 0.010 (unsur Cd) dan paling tinggi ialah 7.43 (unsur Mn) berdasarkan jumlah kepekatan unsur-unsur dalam tisu lembut kerang *cerithidea obtusa* . BSAF logam berat dalam tisu lembut dan cangkerang kerang *cerithidea obtusa* antara 0.034-22.30 dan 0.012-2.35 masing-masing. Tumpuan perhatian yang tinggi perlu diberikan kepada Mn terutama di lokasi, L5 kerana nilai HRI tujuh kali lebih besar daripada tahap keselamatan.

Jumlah kepekatan unsur nadir (Ce, La, Dy, Sm, Eu, Lu, Tb dan Yb) dalam sampel permukaan tanah antara 35-117.4 mg/kg. Kelakuan geokimia daripada unsur nadir dalam sedimen dan corak normal (chondrite dan syal) telah dikaji. Faktor Pengayaan unsur nadir berubah dalam julat 0.75-6.75. Nisbah La/Yb dan Eu/Sm berubah dalam julat diantara 3.89-18.49 dan 0.06-0.20 masing-masing. Nisbah Ce/La dikira dan didapati berubah dalam julat 1.96-3.17. Dari corak pengayaan dapat disimpulkan bahawa LREE> HREE sebagai urutan pengambilan yang REE seperti dalam sampel sedimen paya bakau. Tiada unsur nadir ditemui dalam tisu lembut dan cangkerang *cerithidea obtusa*.

Dalam penyiasatan ini didapati akumulasi unsur peralihan dalam permukaan tanah, tisu lembut dan cengkerang *cerithidea obtusa* adalah dalam turutan Ba> V> Ga> Cs> Hf> Sc> Co> Ta> Sb dan Co> SC masing-masing. Purata kepekatan unsur Co dan Sc (unsur-unsur lain tidak dikesan) pada tisu-tisu lembut dan cengkerang *cerithidea obtusa* berubah dalam julat diantara 0.83-6.94 dan masing-masing 0.12-2.39 mg/kg. Pengayaan unsur peralihan berubah dalam julat 0.41-20.76 dalam sedimen. Faktor pencemaran, darjah pencemaran (Cd) dan darjah tahap pencemaran (mCd) semua unsur peralihan berubah dalam lingkungan 0.10-3.98, 5.77-11.49 dan 0.64-1.36 masing-masing didalam sedimen. Indeks geoakumulasi tertinggi ditemui dalam unsur Ta (1.41) dari L6. BSAF dalam tisu lembut dan cangkerang *cerithidea obtusa* berubah diantara 0.01-0.94 dan 0.03-0.14 masing-masing.

Kepekatan unsur utama dalam sedimen tersebut adalah dalam turutan Al> Fe> Na> Mg> K> Ca> Ti> Rb. Purata kepekatan (mg/kg, berat kering) Ca, Fe, K, Mg, Na dan Rb pada tisu-tisu lembut *cerithidea obtusa* adalah berubah dalam julat diantara 11349-55815, 652-6284, 7561-13327, 6010-11595 dan 0.99 kepada 30.6 mg/kg masing-masing. Sebaliknya, purata kepekatan Ca, Fe, K, Mg, dan Na (Rb tidak dikesan) pada cengkerang *cerithidea obtusa* antara 138509-403444, 209-1008, 256-1307, 315-503 mg/kg masing-masing. Faktor pengayaan unsur utama berubah dalam julat diantara 0.53-5.92 dalam sedimen. Indeks Geoakumulasi didapati tertinggi di L5 dengan indeks 1.27 (unsur Na). BSAF unsur utama dalam tisu lembut dan cengkerang *cerithidea obtusa* berubah dalam julat diantara 0.03-8.05 dan 0.01-73.58 masing-masing.

ACKNOWLEDGEMENTS

I am most grateful and deeply indebted to my supervisor Prof. Dr. Elias. Saion, my thesis advisor, for his advice, encouragement and valuable suggestion for completion of the writing-up of the thesis and his support during the time I spent at the Universiti of Putra Malaysia.

I would like to thank my committee members Associate Professor Dr. Halimah Mohamed Kamari, Associate Professor Dr. Yap Chee Kong and Dr. Suhaimi Hamzah for their constructive comments and criticisms. Thanks are expressed also to the Malaysia Nuclear Agency (MINT) for their continuous support and the usage of their facilities during research work. Special thanks to Mr. Lim, Mr. Kusairhi, Mrs. Irene and Mrs. Jammiliy for their help in collection of data especially during long irradiation period.

I would like to express my deepest gratitude to my parents, brothers and sister for their prayers and unending encouragement. Last but not least, to my sweetheart, my dearest in my life, my wife and kids for creating real love in my heart and encouraging me to do my study.

I certify that a Thesis Examination Committee has met on 7 January 2015 to conduct the final examination of Kumar a/l Krishnan on his thesis entitled "Determining Distribution of Elements in Surface Sediment, Soft Tissue and Shell of *Cerithidea obtusa* Lamarck using Nuclear and Atomic Techniques" 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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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

PGNAA	Prompt-Gamma, Neutron-Activation Analysis
NAA	Neutron-Activation Analysis
DGNAA	Delayed-Gamma Activation Analysis
INAA	Instrumental (or Conventional) Neutron-Activation Analysis
MINT	Malaysia Institute Nuclear Technology
UPM	Universiti Putra Malaysia
AAS	Atomic Absorption Spectroscopy
IAEA	Food and Agriculture Organization
FAO	International Atomic Energy Agency
USEPA	U.S. Environmental Protection Agency
CRM	Certified Reference Material
SRM	Standard Reference Material
EF	Enrichment Factor
BSAF	Estimation of proportion in which metal occurs in the living organism and in associated sediment
Cf	Contamination Factor
Cd	Degree of contamination
mCd	Modified degree of contamination
PLI	Pollution Level Index
LOD	Lower than Limit of Detection

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Mangrove ecosystems are coastal forests found in sheltered coastlines, estuaries, river banks or deltas in tropical countries. The mangrove forests are best developed and coldest temperature during winter above 20 °C and fairly maintained a constant temperature throughout the whole year. Mangroves are salt-tolerant evergreen trees and grow according to the climate, salinity of the water and topography. The soft substrate is predominantly made of clay and silt rather than sand. Since nutrients are often adsorbed onto muddy sediment particles, the inputs of mangrove-derived organic matter into intertidal and river estuaries are important for a variety of fish and shellfish, including many commercial species (Pauly et al., 2002). Mangrove ecosystems are important for biological diversity by providing nutrients, spawning grounds and habitats at least 80,000 – 100,000 species which are considered the second largest phylum in the animal kingdom. Mangroves are of interest not just to the biologists, but also for chemists, physicists, economics, and social scientists. Mangroves are highly primary productive ecosystems with various important economic and environmental functions (FAO, 1994). In recent years, the pressures due to increasing population in coastal areas, food production, economic activities and urban development have caused the resources of the world's mangrove to be gradually degraded. Mangrove environment is defined as the combination of external physical conditions that affect the growth, development and living organism in the coastal marine area. Environmental pollution is one of the greatest threats to marine life and society in the future. A major factor that causes environmental degradation in any area mainly is tremendous growth in population, which adversely affects the environment. Numerous of hazardous waste sites have been discovered in the whole world based on the accumulation of xenobiotic in soil and water over the years. Sediments are an important sink of a variety of pollutants (Wang et al., 2002) especially in estuarine ecosystems. Determination the concentrations of element in the sediment of mangrove are among the first steps in the quantification of the natural anthropogenic contribution to mangrove ecosystems.

In Malaysia, human activities are the main result of anthropogenic sources such as mining, agriculture, aquaculture, tourism and the widely use of metal in industries which causes contamination of living organisms in mangrove ecosystems (Sericano et al., 1995; Allen et al., 1993; Goldberg et al., 1978; Phillips, 1980). Increasing economic development and a rapid growth of population in Malaysia has taken the country from 18 million people to about 30 million people from 1980 until today was putting an adverse effect to the natural resources and the environment. Rapid industrialization further worsens the situation. The environmental pollution as we know it today, mainly originated from the industrial revolution. Consumption of immense quantities such as coal or any other fossil fuels from large scale factories and power producers gave rise to unprecedented air pollution and the large quantity of chemical discharges from the industries. It was estimated that 10,000 more chemicals are introduced worldwide annually and industrialized countries generate a total of 325-375 million tons (> 90% of the world's annual) of toxic and hazardous waste originating from chemical based industries. One particular adverse effect of this hazardous waste is the endangerment of the world's most diverse assemblage of freshwater mussel species (Williams et al., 1993; Neves 1999; Strayer et al., 2004). Therefore, in this work we would like to evaluate the degree of contamination in the mangrove ecosystems by determine the concentrations of element present in the sediment and mussel tissues in the hope to use living organisms as sensors of contamination (biomonitors) and to identify whether there is a relationship between living animals and contaminant by monitoring an organism's interaction with this contaminant.

1.1.1 Biomonitors

Bio-monitoring is the measurement of concentration of elements in biological tissues (Becker et al., 2003). Biomonitor organisms can be used to assess the bioavailability of pollutants in aquatic environments (Rainbow, 1995). Biomonitor organisms accumulate pollutants from the water or sediment they inhabit, as well as their food (Phillips and Segar, 1986). Biomonitoring allows bioaccumulation of pollutants in organisms and biomagnification in food chains to be monitored directly rather than using surrogate measurements of the surrounding environment (Phillips and Segar, 1986). The use of biomonitors of measuring geographical and temporal 12 variations in contaminant concentrations is a well established process (Phillips and Rainbow, 1993). The selection of biomonitor species is based on the species ability to take up a contaminant in a manner that will be representative of the degree of contamination to the environment over a wide concentration range and period. Factors such as metabolic regulation of contaminants and the contaminant interactions within the organism must be recognized (Phillips and Segar, 1986). The organism must be tolerant to contaminants, acidity, salinity and other physico-chemical variables (Gay and Maher, 2003; Hare et al., 2008). In addition to this, a good biomonitor must be representative of the study area, abundant in the study area and have a simple correlation between the contaminant concentration in their tissue and the contaminant concentration found in the environment (Phillips and Rainbow, 1993).

1.1.2 Heavy metals

Heavy metals such as Pb, As, Cu, Mn, Cd, Ni, Cr and Zn are a major concern because of their persistent and bio-accumulative nature. The level of contamination may extend its hazardous effect to aquatic life, system and human health, especially to human consumers of seafood, by bioaccumulation in the food chain. As examples, Cu is an essential element which exists in several enzymes in human to maintain metabolic functions and needed in small amount. Higher uptake of Cu can cause serious effects such as irritation of the eyes, mouth and nose and abdominal pain that is associated with nausea, stomach cramping, vomiting, diarrhea, and even death. Carcinogen such as an arsenic and can cause cancer of the internal organs. Pb can affect every organ and system in the body, especially for adults can result in decreased performance in the nervous system, blood pressure and anemia. Even though Zn and Mn also essential for the human body, but high levels of Zn and Mn can interrupt metabolism of protein and can cause respiratory disorders.

1.1.3 Rare earth elements (REEs)

The rare earth elements (REEs) (known as lanthanides) with their atomic number varied from 57-71. REEs can be divided into two subgroups: light REEs (LREEs) and heavy REEs (HREEs). The light REEs (LREEs: 57-62) are La, Pr, Nd, Ce, Eu, Sm, and Pm, and heavy REEs (HREEs: 63-71) are Gd, Dy, Ho, Tb, Er, Yb, Tm and Lu (Hu et al., 2006). Lanthanides as a group separate from the rest of the other elements in periodic table due to their properties of 4*f* electron orbitals with electronic configuration [Xe] $4f^n$ $5d^n$ $6s^n$, (Sabbatini et al., 1996). The REE's normally grouped together as they show chemical similarity. Referable to the ability act as a donor and an acceptor of electrons, making them essential usage in many subjects such as electronic, optical, magnetic, glass fibers, and catalytic applications (Svetlana and Jean-Claude, 2011). Besides the usage of REE's, the disadvantages of REEs eco-toxicological point of view of these elements and their risk into the environment are less known. REEs mainly enters the environment much more soluble (water solubility) and more reactive ionic forms due to anthropogenic rather than naturally occurring, making them more bioavailable. The eco-toxicological effect of REEs is almost similar to the essential metals, which has less effect at low concentrations. At the same time it's become toxic at higher concentrations (Kulaksız and Bau, 2013). REEs are mainly toxic because they affect biological processes of living organisms by disruption of calcium ion due to their similar size or by their high affinity for phosphate groups of biological macromolecules. So far in that respect is no important role of REEs to humans, plants or creatures.

1.1.4 Major and trace elements

Major and trace elements (Na, Mg, Ca, Fe, Al, K and Ba, Co, Cs, Ga, Sc, Sb, Ta, V) are sets of elements which are required or exist in only a small amount in ordinary soil, water, air, plant and animals. Major and trace metals are present in the environment from both natural and anthropogenic (man's activities) process (Fergusson, 1990). The accumulation of these metals in both agricultural product and sea food causes various forms of pollution (Jankiewicz et al., 2002). The term trace metals have been variously referred to as common pollutants, which are widely distributed in the environment with source mainly from the weathering of minerals and soil. However, trace metals are defined as those metallic elements, low in the periodic table with high atomic number (weight) > 100, or a relative density greater than five (Malhi et al., 2004). Some trace metals may be important in the nutrition of plant and animals or humans while others are known to possess virtually negative nutritional effect. All these trace metals over large territories and long time periods may cause gradual damage of organisms which now necessitate a careful assessment of their input. Thus, this work seeks to analyze these groups of trace heavy metals relative to our health (Teng et al., 2002, Ewa et al., 2002).

1.2 Significance of the study

There are many ways to evaluate the environmental contamination. The most common one, many researchers used bivalve species to evaluate the level of contamination from environmental (Goldberg, 1983, Phillips, 1990). In marine systems, bivalve species as a biomonitor accumulate contaminants from the water or sediment they inhabit, as well as their food, hence fulfilling the criteria as good bio-indicators (Phillips, 1986, Huang et al; 2004). Based on the information from Department of Fisheries, Malaysia Fisheries Directory published in 2005, there are 27 bivalves species in the coastal area of Malaysia (Department of Fisheries Malaysia, 2005). Many researchers used bivalves such as a *Pernaviridis, Anadaragranosa, Donaxfaba, Polymesodaerosa, Scpharcabroughtonii* and *Trisidoskiyonoi* to monitor contamination levels in the coastal areas of Malaysia (Yap, 2004a, 2006c, 2006a, 2003; Ismail 2008; Awang-Hazmi, 2007; Bharathi, 1994; Ibrahim and Mat, 1995; Ong and Din, 2001). Due to lacking application of bivalves other than mentioned above as a bio-indicators, therefore, very important for studies to be conducted on the levels of these metals in the tissues of *cerithidea obtusa* and in sediments of the mangrove estuary of the west coast of Malaysia. This ascertains whether or not the concentrations in the mollusc are within the permissible limits for human consumption in comparison to the safety reference standards for consumption of bivalve molluscs.

1.3 Problem statement

Malaysia lies entirely in the equatorial zone with average temperatures about, 26 °C, and mean annual rainfall is 2,875 mm throughout the year. On the other hand the variations of temperature and rainfall between regionally depending on the altitude. It was estimated about 29 % lived in rural areas along the west coast of peninsular Malaysia with an average population density of 84 inhabitants/km^2. In Malaysia, mangrove vegetation covers a total area of about 577,500 ha, with Sabah has the most extensive coverage of mangroves, accounting for 341,000 ha (59%) of the country’s total, whereas, Sarawak has 132,000 ha (23%) and Peninsular Malaysia 104,200 ha (18%). Sabah’s mangrove forests occur largely along the east coast, facing the Sulu and Sulawesi seas.

The primary sources of organic water pollution in Malaysia are domestic and industrial sewage, effluent from palm oil mills, rubber factories and animal husbandry. On the other hand a major factor that causes a high concentration of suspended sediments in the rivers are pollutants from and mining operations, undervaluation of the economic and environmental values of natural resources and the ecosystems they generate, clearing of coastal forests and poorly planned development. In several urban and industrial areas, organic pollution of water has resulted in environmental problems and has adversely affected aquatic life. Besides organic waste, rivers remain a convenient means of solid waste disposal. A major portion of household refuse, which is not collected, burned or buried, finds its way into drains and rivers.

However, slow and continuous changes by human activities over the decade caused the major changes in their natural state with respect to their dissolved and suspended particulate matter of the ecosystems (Jobling, 1995). In Malaysia, human activities are the main result of anthropogenic sources such as mining, agriculture, aquaculture, tourism and the use of metal in industries resulting in increased heavy metal concentrations which causes contamination of living organisms in mangrove zones (Jefferies and Freestone, 1984; Phillips et al., 1980; Sericano et al., 1995; Goldberg et al., 1978; Cicin-Sain and Knecth, 1998; Rainbow et al., 1997). Marine living organism such as deposit feeds on the detritus could absorb the metals from the polluted sediment and water, which then form the significant route of entry of contaminants into their predators (including human being as a consumer). It was noted that a number of the studies on multi-element have been focused on the west coast of Peninsular Malaysia due to huge economic growth and activities, human population and agriculture are concentrated in this coastal area (Abdullah et al., 1999). Surface sediment is the last destination to settle down for all kinds of pollution that comes from human activities and ultimately causes a variety of problems in the ecosystem. On the other hand, surface sediment often exchanges with suspended materials, thereby affecting the release of metals to the overlying water (Zvinowanda et al., 2009). The top few centimeters of the sediments reflect the continuously changing present day degree of contamination. Therefore, it needs to investigate the elemental pollution level in the east coast of peninsular Malaysia using sediment samples due to the ability of sediment to provide useful information regarding the marine pollution. There is a need to monitor and understand the effect of these contaminants, level of pollution and bioaccumulation in the coastal area of Malaysia. Therefore, for the current study data of Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Eu, Fe, Ga, Hf, K, La, Li, Mg, Mn, Na, Ni, Pb, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Th, Ti, V, Yb and Zn concentrations were measured in sediment samples, soft tissues and shell of *cerithidea obtusa* collected from the west coast of peninsular Malaysia, to assess the level of contamination of mangrove ecosystems for which limited study is available in the literature.

1.4 The Scope of the Present Study

The current study focused on determination of elements concentration in the surface sediment, soft tissues and shell of *cerithidea obtusa* samples collected from a mangrove area of west coast of Peninsular Malaysia. Before this can be done systematically suitable analytical method must be available. Two techniques, Instrumentations Neutron Activation Analysis (INAA) and Atomic Absorption

Spectrometry (AAS) can give the necessary sensitivity. The sensitivity (10–30 ng/sample), accuracy and precision are of the same order for both techniques and the choice can only be made on grounds of urgency or convenience.

The INAA is the most used method for determining various types of elements due to its small sample size, chemical free procedure, high sensitivity of low detection limit (LOD), simultaneous multi-element detection (30-40 elements), negligible matrix interference, samples changed to radioactive materials (David Tin Win, 2004) and high sensitivity of measurement of REEs compared with other methods. The reliability and accuracy of the methods used were checked by analyzing the recoveries between the measured and certified elemental concentration of the standard reference materials of IAEA-Soil-7, SL-1, SRM 1566b, SRM 2976, MIX PTS-1 and 2 and MIX RR-1 and 2. Accuracy and precision of the applied analytical procedures were also evaluated by Z-test. The accuracy of the analytical method is obtained by the determination of the standardized difference *Z* by consideration of the uncertainties of the measured results of CRM and the uncertainty in the certified value.

The elements that are less sensitive by INAA method can be determined by the AAS is a commonly used and reliable analytical technique for the detection of certain elements, which is easy to use, but can only measure one element at a time. The reliability and accuracy of analytical methods used were checked by analyzing the recoveries between the measured and certified concentrations of standard reference materials similar to the INAA method.

1.5 The Objectives of Study

The aim of this present study is to determine the concentrations of REE's, major, trace and heavy metal in the surface sediment, soft tissues and shell of *cerithidea obtusa* collected from west coast of Peninsular Malaysia by using two methods, INAA and AAS. The main objectives of this study are summarized as below:

1- To determine the concentrations and distribution of heavy metals, major and trace elements, and rare earth elements in surface sediments, soft tissues and shell of *cerithidea obtusa* by INAA and AAS methods.
2- To determine the pollution levels by evaluating the enrichment factor, geo-accumulation index, pollution level index, degree of contamination and modified degree of contamination.
3- To determine biota-sediment accumulation factor (BSAF) factor by using bivalve mollusk, *cerithidea obtusa*.
4- To evaluate the safety level of mollusk's consumption as food based on metals distribution in edible tissues of mollusks by evaluating the daily intake of these metals and the health risk index.

1.6 Outlines of thesis

The report of this study is divided into six chapters. Chapter One consists of a brief introduction to the field of the study, which includes the significance and objectives of the study. Chapter two briefs on the a literature review of the field of study and the related work that have previously been published. Chapter three mainly discussed theoretical parts which cover principal, derivation of formulas for AAS technique and interactions neutrons and gamma rays with matter of INAA technique. Chapter four discussed detail description of experimental procedures and techniques used for each of sampling, preparation and measurement processes by INAA and AAS of the analysis performed in this study. Chapter five is the major parts of the thesis which contains results, analysis of results and critical discussion on the results. The thesis also includes the results and their comparison with the data obtained from the literature. Chapter Six draws the conclusions and include the recommendation for the future work.

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