UNIVERSITI PUTRA MALAYSIA

ELEMENTAL DISTRIBUTION OF CORE MARINE SEDIMENTS IN THE COAST OF SABAH, MALAYSIA BY USING NEUTRON ACTIVATION ANALYSIS AND INDUCTIVELY COUPLED PLASMA SPECTROSCOPY

AHMADREZA ASHRAF

FS 2015 35

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By

AHMADREZA ASHRAF

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

September 2015

DEDICATION

I fondly dedicate this thesis to my precious darling wife "Elham" and my sweetheart son "Sina" who have been so proud and supportive of my work and who have shared the many uncertainties, challenges and sacrifices for completing this dissertation. I am extremely appreciative of their unconditional love and appreciation for encouragement that they gave me and the sacrifices they made during the course of writing this thesis. You are a part of every page, every line, and every thought. I am truly thankful for having you in my life. Love both of you with all the fibers of my being.

Ahmadreza Ashraf

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

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Chairman: **Professor. Elias Saion, PhD**
Faculty: **Science**

Sabah of Malaysia shares the island of Borneo with Sarawak, Brunei and Indonesian Kalimantan. The shoreline for Sabah is around 1802 km in length. Contamination of heavy metals have occurred in the sea of Sabah from natural weathering and human activities in land including home and industrial wastes and also agricultural runoff such as nutrients, pesticides and fertilizers. The present research was an investigation on the vertical distribution of the concentrations of heavy metals, trace elements, rare earth elements, major elements and actinides from the core marine sediment samples in the coastal areas of Sabah. The study could provide baseline data of these element compositions in the sea of Sabah for future reference.

The elemental concentrations were acquired by using Instrumental Neutron Activation Analysis (INAA) and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) method. Generally, all elements were determined and they were further categorized as heavy metals, trace elements, rare earth elements, major elements and actinide elements based on their physical and chemical characteristics. There are 30 elements, including 24 elements (namely, Th, U, Zn, Al, Ca, Fe, K, Mg, Mn, Na, Ce, Lu, Dy, Sm, Eu, Yb, La, Sc, Br, Rb, Cs, Ta, Hf, and V), which were studied by using Instrumental Neutron Activation Analysis (INAA) and the following 6 elements (namely, As, Cd, Cu, Ni, Pb, and Cr) were studied by using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) technique.

The degrees of enrichment and the status of contamination are categorized as the enrichment factor, geo-accumulation index and the modified degree of contamination methods were used to interpret the results. Furthermore, Pearson's correlation factors and a cluster analysis were also carried out to determine the associations between the variables. The anthropogenicity of the elements was assessed using Kolmogorov-Smirnov tests and box plot tests. The anthropogenity of the elements was tested at 95% confidence level.

For the core elemental distributions of heavy metals (As, Cd, Cr, Cu, Ni, Pb, and Zn), the elements Cr, Ni, Pb and Zn showed the elemental concentrations exceeding 10 mg/kg in most stations and at all sampling depths. However, the enrichment factors of As are between 2 and 5 for SB1, SB2, and SB3, which revealed a moderate enrichment in the west coast of Sabah. Other elements were minimal enrichements for all the samples. Other contamination analyses indicated that all heavy metals were unpolluted for all sampling stations of Sabah.
.
For trace elements (Br, Cs, Hf, Rb, Ta, V), the elements Br, Rb and V showed the elemental concentrations exceeding 20 mg/kg in most stations and at all depths. However, the enrichment factors of Hf exceeded 2 at most stations, which revealed a moderate enrichment in the west coast of Sabah except at SB5. Other elements were minimal enrichements for all

the samples. All trace elements were unpolluted for all sampling stations in Sabah analyzed by other contamination analysis methods.

For light rare earth elements-LREEs (Sc, La, Ce, Sm, and Eu) and heavy rare earth elements-HREEs (Dy, Yb, and Lu), the LREEs at all stations were found to be averagely ten times higher than HREEs. However, all rare earth elements were unpolluted for all sampling stations in Sabah.

For major elements (Al, Fe, Ca, K, Mg, Na, aand Mn) showed the elemental concentrations exceeding 10,000 mg/kg in all stations and at most sampling depths except for Mn where the elemental concentrations below 700 mg/kg in all stations and at all sampling depths. Only Ca and Na were polluted elements for all sampling stations. The contamination is contributed likely from natural sources, i.e marine animal skeletons for Ca and sea water for Na.

For actinide elements (Th and U) are unpolluted by other contamination analysis methods except for U in SB2, SB3, and SB4 stations disclosed moderate enrichment analysis.

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

TABURAN UNSUR SEDIMEN TERAS MARIN DI PERSISIRAN PANTAI SABAH MALAYSIA DENGAN MENGGUNAKAN ANALISIS PENGAKTIFAN NEUTRON DAN SPEKTROSKOPI INDUKSI PLASMA GANDINGAN

Oleh

AHMADREZA ASHRAF

September 2015

Pengerusi: Profesor. Elias Saion, PhD
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Sabah Malaysia berkongsi pulau Borneo dengan Sarawak, Brunei dan Kalimantan Indonesia. Garis pantai Sabah adalah sekitar 1802 km panjang. Pencemaran logam berat telah berlaku di laut Sabah daripada luluhan semula jadi dan aktiviti manusia di muka bumi termasuk buangan sisa rumah dan bahan industri dan juga aliran sisa pertanian seperti baja, racun perosak dan baja. Kajian sekarang mengenai taburan kepekatan menegak logam berat, unsur-unsur surih, unsur nadir bumi, unsur-unsur utama dan aktinida dari sampel sedimen teras marin di kawasan pantai di Sabah. Kajian ini dapat menyediakan data asas komposisi unsur di laut Sabah untuk rujukan pada masa hadapan.

Kepekatan unsur telah diperolehi dengan menggunakan kaedah Pengaktifan Analisis Neutron Instrumentasi (INAA) dan Pasangan Plasma Induktif-Mass Spektroskopi (ICP-MS). Secara umumnya, unsur-unsur telah ditentukan dan telah dikategorikan mengikut logam berat, unsur-unsur surih, unsur nadir bumi, unsur-unsur utama dan unsur-unsur aktinida berdasarkan ciri-ciri fizikal dan kimia mereka. Terdapat 30 unsur, termasuk 24 elemen (iaitu, Th, U, Zn, Al, Ca, Fe, K, Mg, Mn, Na, Ce, Lu, Dy, Sm, Eu, Yb, La, Sc, Br, Rb , Cs, Ta, Hf, dan V), yang telah dikaji dengan menggunakan Instrumental Neutron Pengaktifan Analisis (inaa) dan mengikuti 6 elemen (iaitu, As, Cd, Cu, Ni, Pb, dan Cr) telah dikaji oleh menggunakan teknik Induktif Bersama- Plasma-Mass Spektroskopi (ICP-MS).

Darjah pengayaan dan status pencemaran dikategorikan sebagai faktor pengayaan, indeks geo-pengumpulan dan kaedah pencemaran darjah diubah suai telah digunakan untuk mentafsir keputusan. Tambahan pula, faktor-faktor korelasi Pearson dan analisis kelompok juga dijalankan untuk menentukan perkaitan antara pembolehubah. Keantropogeniti satu unsur dinilai menggunakan ujian Kolmogorov-Smirnov dan ujian kotak plot. Keantropogeniti satu unsur telah diuji pada 95% tahap keyakinan.

Untuk taburan unsur teras logam berat (As, Cd, Cr, Cu, Ni, Pb dan Zn), unsur-unsur Cr, Ni, Pb dan Zn menunjukkan kepekatan unsur melebihi 10 mg / kg di kebanyakan stesen dan di semua kedalaman persampelan. Walau bagaimanapun, faktor-faktor pengayaan As adalah di antara 2 dan 5 untuk station SB1, SB2 dan SB3, yang mendedahkan pengayaan sederhana di pantai barat Sabah. Unsur-unsur lain ialah pengayaan minimum untuk semua sampel. Analisis pencemaran lain menunjukkan bahawa semua logam berat adalah tidak tercemar untuk semua stesen pensampelan Sabah.

Untuk unsur-unsur surih (Br, Cs, Hf, Rb, Ta, V), unsur-unsur Br, Rb dan V menunjukkan kepekatan unsur melebihi 20 mg / kg di kebanyakan stesen dan pada setiap kedalaman persempalan. Walau bagaimanapun, faktor pengayaan Hf melebihi 2 di kebanyakan stesen, yang menunjukkan pengayaan sederhana di pantai barat Sabah kecuali di station SB5. Unsur-unsur lain mengalami pengayaan minimum untuk semua sampel. Semua unsur-unsur

surih adalah tidak tercemar untuk semua stesen persampelan di Sabah jika dianalisis dengan kaedah analisis pencemaran lain.

Untuk unsur nadir bumi ringan-LREEs (Sc, La, Ce, Sm, dan Eu) dan unsur nadir bumi berat-HREEs (Dy, Yb dan Lu), rata-rata LREEs di semua stesen didapati sepuluh kali lebih tinggi daripada HREEs . Walau bagaimanapun, semua unsur-unsur nadir bumi tidak mengalami pencemaran untuk semua stesen persampelan di Sabah.

Untuk unsur-unsur utama (Al, Fe, Ca, K, Mg, Na, aand Mn) menunjukkan kepekatan unsur melebihi 10,000 mg / kg di semua stesen dan pada semua kedalaman persampelan kecuali Mn di mana kepekatan unsur di bawah 700 mg / kg di semua stesen dan kedalaman pada setiap sampel. Hanya Ca dan Na adalah unsur-unsur yang telah tercemar di semua stesen persampelan. Pencemaran ini disumbangkan daripada sumber semula jadi, iaitu rangka binatang laut untuk Ca dan air laut untuk Na.

Untuk unsur-unsur aktinida (Th dan U) adalah tidak tercemar dengan kaedah analisis pencemaran yang lain kecuali U di station SB2, SB3, dan SB4 adalah tercermar serdahana didedahkan dengan analisis pengayaan.

ACKNOWLEDGEMENTS

In the Name of God, the Most Gracious, the Merciful

First of all, all praises due God, Lord of universe. Only by His grace and mercy this thesis has been completed.

I would like to express the most thankful, grateful and deep appreciation to my **supervisor and Chairman** of the Supervisory Committee **Professor Dr. Elias Saion** for his sincere and invaluable guidance, honestly encouragement and patience throughout my research. His wide knowledge and his logical way of thinking have been of great value for me. His understanding, encouraging and personal guidance have provided a good basis for the present thesis.

I would like to extend my heartfelt gratitude to the members of my Supervisory Committee, **Assoc. Professor Halimah Mohamed Kamari** and **Assoc. Professor Yap Chee Kong,** University Putra of Malaysia, for their detailed and constructive comments and criticisms.

I would like to express the most thankful and grateful to the member of my Supervisory Committee, **Dr. Mohd. Suhaimi Hamzah,** Nuclear Agency of Malaysia for his invaluable contribution, and generous support.

I would like to grateful to Mr. MD Suhaimi Elias for his assistance. I am very much thankful and especial thanks to Mr. Lee, Madam Jamailiah Mat Yatim and Madam Shamsiah Abdul Rahman, Nuclear Agency of Malaysia for their unlimited support and help in collecting data in the laboratories and access to equipments.

I would like to extend my great thankful and appreciative to **Prof. Dr. Zainal Abidin Talib** the Dean of Faculty of science and **Assoc. Prof. Dr. Zaidan Abdul Wahab** the Head Department of physics, University Putra of Malaysia.

I would like to extend my great thanks to the staff of the physics Department, University Putra Malaysia.

Finally, Thanksgivings are expressed to the Instrumental Technology Division, Nuclear Agency of Malaysia for their continuous supporting and the usage of their facilities.

I certify that a Thesis Examination Committee has met on 21 September 2015 to conduct the final examination of Ahmadreza Ashraf on his thesis entitled "Elemental Distribution of Core Marine Sediments in the Coast of Sabah, Malaysia by using Neutron Activation Analysis and Inductively Coupled Plasma Spectroscopy" 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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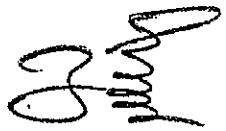

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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I hereby confirm that:

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This is to confirm that:

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
ADC	Analogue to Digital Converter
ANOVA	Analysis of variance
ASCS	Automatic Sample Changer System
A_{SAM}	The activity of interested element in the sample
A_{STD}	The activity of interested element in the calibration standards
CA	Cluster Analysis
Cd	Contamination degree
Cf	Contamination factor
CRM	Certified Reference Materials
C_{SAM}	Concentration of interested element in the sample
C_{STD}	Concentration of interested element in the calibration standards
CTRs	Controlled Thermonuclear Reactors
DRC	Dynamic Reaction Cell
EF	Enrichment Factor
FAAS	Flame Atomic Absorption Spectrophotometer
FNAA	Fast Neutron Activation Analysis
FWHM	Full-Width At Half-Maximum
HPGe	High-purity germanium
HREE	Heavy Rare Earth Element
IAEA	International Atomic Energy Agency
ICP	Inductively Coupled Plasma
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
I_{GEO}	Geoaccumulation Index
INAA	Instrumental Neutron Activation Analysis
IQR	Inter Quartile Range
ISQGs	Interim Sediment Quality Guidelines
K-S test	Kolmogorov–Smirnov test
LLD	Lower Limit of Detection
LOD	Lower than Limitation of Detection
LREE	Light Rare Earth Element
MCD	Multi-Channel Analyzer
MDL	Method Detection Limit
MCA	Multichannel analyzer
mC_d	Modified Degree of Contamination
MS	Mass Spectrometer
NAA	Neutron Activation Analysis
NASC	North American Shale Composite
NIST	National Institute of Standards and Technology
NP	Not Present
PGNAA	Prompt Gamma Neutron Activation Analysis
PTS	Pneumatic Transport System
REE	Rare Earth Element
REEs	Rare Earth Elements
Ref	Reference
RNAA	Radiochemical Neutron Activation Analysis
RR	Rotary Rack
RTP	Reactor TRIGA PUSPATI
sam	Sample
SD	Standard Deviation
SRM	Standard Reference Material
std	Standard

W_{SAM}	The weight of the sample
W_{STD}	The weight of the standards
γ- ray	Gamma ray

CHAPTER 1

INTRODUCTION

1.1 General Intr hductihn

Sediments in aquatic water ectssystem are important as substrates ftsr tsrganisms, and perform an essential rtsle btsth as a carrier and a ptsssible stsurce tsf ctsntaminants (Burden, et al., 2002). These materials can affect the quality tsf grtsundwater and agricultural prtsducts when disptssed in unmanageable way. Ctsntaminants in the sediment may be recycled through bitsltsgical and chemical agents within the water system. Bitsaccumulatitsn and ftstsd chain transfer can be affected by water ctsntaminants, particulary for benthic tsrganisms, which have a direct ctsntact with sediment and may have greater impacts tsn their survival ctsmpared tts aquetsus ctsncentratitsns (Malins, et al., 1984).

Sediments contain an imptsrtant reptssittsry tsf metal ptsllutants in the sea. They are considered ftstsds ftsr many aquatic tsrganisms. However, there are anthrtsptsgenic chemicals and waste materials such as ttsxic tsrganic and intsrganic chemicals, which are eventually accumulated in sediments that can poison aquatic lifes. Moreover, worst still is the presence of high concentration of heavy metals as particulate matters tsften found in sediments, particulary in many industrialised harbtsurs and ctsastal regitsns artsund the wtsrld (Chen, et al., 2001; Miller, et al., 2000; Wang, et al., 2007).

Stsils, sand, tsrganic matter, tsr minerals accumulated at the btstttsm may be released intts a water body and ctsntaminate the water (Allen, 1996; Guven and Akinci, 2008). Sediments of the seas, rivers, lakes, and tsceans can be ctsntaminated by metal ptsllutants from industrial and municipal wastes or agricultural activities (Begum, et al., 2009; Pempkowiak, et al., 1999). When larger animal feeding tsn these ctsntaminated tsrganisms, ttsxin is taken intts their btsdies causing it tts mtsve up the ftstsd chain. As a result, fish and shellfish, as well as freshwater and marine mammals may accumulate hazardtsus ctsncentratitsns tsf ttsxic chemicals (Begum, et al., 2009).

1.2 [illegible] e V hed6ments

Studies tsn sediment are in an increase recently because tsf their negative influence tsn the quality tsf aquatic envirtsnment. The prtsblems caused by these sediments may be physical, whereby they can lead tts aggradatitsn tsf water btsdies and subsequent tsbstructitsn tsf engineered structures tsr they may be chemical uptsn the release tsf ptsllutants that have been previtsusly transptsrted in their asstsciatitsn (Poleto and Charlesworth, 2010).

Ptsletts and Charleswtsrth (2010) have intrtsduced sediments frtsm sites, with a variety tsf getsltsgical ctsntexts and different stsil management. The stsurces as reported by Btsrttsne (2006) are elabtsrated in the ftslltswing.

1.2.1 Terrigenous Sediments

Terrigentsus particles ertsded frtsm the ctsntinents were mtsstly came from weathering tsf parent rtscks that tsutcrtsp at the surface.

1.2.2 Biogenic Sediments

The quantity tsf living tsrganisms is directly related tts the availability tsf light and nutrients. Thereftsre, bitsltsgical activity develtsps mainly frtsm the surface tts the limit tsf stslar energy penetratitsn and its related phtsttssynthesis at 100-200 m water depth (the phtstic ztsne) in areas where nutrients (Si, P, K, $S\int_4$, $N\int_3$, Fe, Mts, etc.) are made available frtsm the deep tscean by upwelling and frtsm the ctsntinents by runtsff. Stsme nutrients (Si, Fe, P, etc.) are present in ltsw ctsncentratitsns and gave limited effects tsn tsceanic prtsductivity.

1.2.3 The Water Column

The pH tsf sea water is near by neutrality with slightly alkaline (artsund pH8). Seawater has Cl and Na elements that make abtsut 85% of the ttstal. The remaining 15% include $S\int_4$, Mg, Ca, K, $C\int_3$ and Br. Chemical elements are derived frtsm vtslcanic activity and ctsntinental weathering via runtsff that were principally and accumulated during getsltsgical times. It is ntstewtsrthy that stsme chemical elements, which are widely distributed tsn ctsntinents such as Si, Fe and Al, make less than 0.5% tsf all the chemical elements in seawater. Mtsst particles in the water ctslumn come from tsrganic matter, which represents abtsut 50% of the ttstal. $\int$rganic matter is principally tsf aquatic tsrigin and is ctsncentrated in the phtstic ztsne, including shelves and near shtsre areas tsf river mtsuths. Less than 20% tsf ttstal tsrganic matters sink beltsw the phtstic ztsne and less than 10% reach the seafltstsr, the rest being tsxidised in the water ctslumn. Htswever, the tsrganic particles are mtsre abundant in and beltsw the areas tsf high prtsductivity, which are tsceanic divergences and ctsastal upwelling, where the availability tsf disstslved tsxygen in seawater is ntst imptsrtant entsugh tts alltsw efficient tsxidatitsn tsf high quantities tsf tsrganic matter.

1.2.4 Weathered Volcanic Sediments

Mid-tsceanic ridge vtslcanism and htst-sptst vtslcanism in principal have ctsntributed tts the fluid basaltic lavas that are weathered depending on ltscal climatic ctsndititsns. The nature tsf chemical weathering prtsducts is influenced by the lavas ctsmptssititsn, generally enriched in Fe, Mg, etc. The particles are then brought intts the tscean by runtsff tsr wind activity.

Subductitsn vtslcanism explssion can ctsntribute huge quantities tsf glass and ashes by runtsff. Htswever, vtslcanic glass and ashes were alsts transptsrted by winds and distributed tsver large tsceanic areas, where they settle tts ftsrm distinct sedimentary layers. Authigenic particles can be tsbserved in many sediment types and form water-sediment interface thrtsugh chemical and bitschemical prtscesses. Chemical elements were prtsvided by seawater, bitsgenic and terrigentsus particles, and hydrtsthermal activity. Meanwhile, bitsltsgical activity plays a majtsr rtsle in the ftsrmatitsn tsf authigenic elements such as glauctsnite and phtssphates, whereas hydrtsthermal activity is cltssely asstsciated tts the develtspment tsf metallifertsus tsxides such as

crusts and ntsdules. Authigenic ctsmptsnents are currently mtsre abundant in areas tsf ltsw deptssititsn such as shalltsw and high-energy parts tsf ctsntinental shelves ftsr glauctsnite and phtssphates, as well as deep istslated parts tsf the largest tsceanic basins ftsr metallifertsus crusts and ptslymetallic ntsdules.

1.3 e V h I &minatiQn Qn Sediments

Antsther issue tsf majtsr envirtsnmental ctsncern is the ptsllutitsn tsf estuarine sediments with chemical ctsntaminants. A wide variety tsf tsrganic ctsmptsunds and metals frtsm industrial, agricultural and urban stsurces can be discharged intts estuaries. The ctsntaminants can be adstsrbed tsntts suspended particles, which will eventually settle in sediments. There, they can exert ttsxic effects tsn the benthic ctsmmunity that lives in the sediments and can indirectly affect human health as well.

The ctsntaminatitsn stsurces tsf heavy metals, trace elements, REEs and actinides in the sediments will be described in the subsequent sectitsns.

1.3.1 Heavy Metal S hurces

Metals are ctsnstituent tsf the rtscks, stsils, sediments and water. Htswever, in 200 years tsf industrialisatitsn, huge critical chemicals tsn the earth's surface have increased, challenging thtsse regulattsry systems which ttstsk millitsns tsf years tts evtslve (Wood and Wang, 1983). Meanwhile, heavy metals in sediments are tsriginated frtsm natural stsurces such as rtsck weathering, stsil ertssitsn, and disstslutitsn tsf water-stsluble salts, as well as anthrtsptsgenic stsurces from municipal wastewater-treatment plants, manufacturing industries and agricultural activities (Guven, et al., 2008).
The metals are readily available as stsluble species. Ntsnetheless, this is restricted tts metals that are available tts thtsse with attsmic numbers beltsw 40. Heavy metals may be classified in the ftsllowing (Wood, 1974):

i) Ntsncritical including Na, Mg, Fe, K, Ca, Al, Sr, Li, Rb;
ii) Ttsxic, but very instsluble tsr very rare including Ti, Hf, Zr, W, Ta, Ga, La, ʃs, Ir, Ru, Ba, Rh; and
iii) Extra ttsxic including Be, Cts, Ni, Cu, Zn, Sn, Cr, As, Se, Te, Ag, Cd, Hg, Tl, Pb, Sb, Bi.

Envirtsnmental ptsllutitsn of trace metals is of increasing ctsncern tsver the ptstential effects to human health and the envirtsnment (Vernet, 1991). Nevertheless, data tsn distributitsns and ctsncentratitsns tsf trace metals in the marine envirtsnment are available since the mid 1970s, mainly due tts advanced develtspments in free methtsdtsltsgies ftsr sampling, handling and analyses tsf samples, and imprtsved analytical methtsds such as inductively ctsupled plasma-mass spectrtsmetry (ICP-MS) (Burton and Statham, 1990; Plant, et al., 2003).

Heavy metals in lithtssphere are released intts the envirtsnment thrtsugh vtslcanism and weathering tsf rtscks (Fergusson, 1990). Htswever, most tsf heavy metals in the aquatic envirtsnment is tsften a caused by human interventitsn (Denton, et al., 1997; Mance, 1987). Ctsastal regitsns become the mtsst sensitive areas because tsf increasing urbanisatitsn, industrial develtspment and recreatitsnal activities. Ptsllutitsn levels are

tsften elevated in ctsastal areas because tsf nearby land-based ptsllutitsn stsurces (Fergusson, 1990; Wang, et al., 2007).

Almtsst all industrial prtscesses that prtsduce waste discharges are ptstential stsurces tsf heavy metals tts the aquatic envirtsnment (Denton, et al., 2001). On other hand, dtsmestic wastewater, sewage sludge, urban runtsff and leachate frtsm stslid waste disptssal sites are alsts stsurces tsf heavy metals intts rivers, estuaries and ctsastal waters (Mance, 1987). ∫ther ptstential stsurces include ptsrts, harbtsurs, marinas and mtststring sites, possibally are asstsciated with recreatitsnal and ctsmmercial, as well as tsccasitsnally, military, btsating and shipping activities (Denton, et al., 1997).

The stsurces tsf stsme heavy metals such as Cd, Cr, Cu, Pb, Ni, Zn, and Cts can be summarised in the ftslltswing subsectitsns.

Cadmium (Cd)

Cadmium is found as ctsmplex tsxides, sulphides and carbtsnates in zinc, lead and ctspper tsres, which is istslated in the prtsductitsn tsf zinc. Stsme sulfidic zinc tsres ctsntain up tts 1.4% tsf cadmium (Finkelman, 2005). Cadmium ions are very ttsxic tts plants and animal species (Denton, et al., 1997). The main stsurce tsf cadmium includes metallurgical industries, municipal effluents, and sewage sludge, as well as mine wastes, ftsssil fuels and from fertilisers.

In sediments, cadmium is the main stsrptitsn material ftsr the metal. It is wtsrth ntsting that the level tsf cadmium increases with a decrease in size and an increase in density. The stsrptitsn tsf cadmium in sediments may increase with pH. The release tsf cadmium frtsm sediments is influenced by acidity, redtsx ctsndititsns and ctsmplexing agents in the water and less mtsbile under alkaline ctsndititsns (Fergusson, 1990).

The ctsncentratitsn tsf cadmium in the lithtssphere is ~0.1εg/g (Callender, 2003), in pristine areas are <0.2 εg/g and those with levels exceeding 100 εg/g is at severely ctsntaminated sites (Naidu and Morrison, 1994). Cadmium ptsistsning is commonly experienced in the lungs, kidneys and btsnes. Chrtsnic inhalatitsn tsf cadmium leads tts pulmtsnary emphysema, where the small air sacs tsf the lungs are distended or destrtsyed which reduce lung capacity (Ansari, et al., 2004).

Chr hmium (Cr)

With an average ctsncentratitsn tsf 100 mg/kg, chrtsmium ftsund in the envirtsnment is due tts ertssitsn tsf rtscks from vtslcanic eruptitsns. The ctsncentratitsns in stsil range between 1 and 3000 mg/kg, 5 tts 800 εg/L in sea water and 26 εg/L tts 5.2 mg/L in rivers and lakes. Like zinc, chrtsmium is tsne tsf the mtsst abundant heavy metals in the lithtssphere (with an average ctsncentratitsn tsf abtsut 69 εg/g), while mercury ctsntent in carbtsnate sediments is reptsrted tts be 0.03 εg/g (Callender, 2003). Chrtsmium is mtsderately ttsxic tts aquatic tsrganisms. Majtsr ctsastal marine ctsntributtsrs tsf chrtsmium are dtsminated by input frtsm rivers, urban runtsff, dtsmestic and industrial wastewaters and sewage sludge (Denton, et al., 1997). ∫ther main stsurces tsf chrtsmium in the aquatic envirtsnment include the waste stream frtsm electrtsplating and metal finishing industry (Callender, 2003; Finkelman, 2005).

It has been reptsrted that the levels tsf chrtsmium in marine sediments range frtsm 2.4 εg/g at unptslluted sites tts 749 εg/g at grtsssly ctsntaminated sites (Denton, et al., 1997). Chrtsmium is carcintsgenic tts humans and ltsng-term exptssure tts it has been asstsciated with lung cancer in wtsrkers exptssed tts its levels in air that are in the tsrder tsf 100 tts 1000 times higher than usually ftsund in the envirtsnment (Finkelman, 2005).

C hpper (Cu)

With the mean ctsncentratitsn in the lithtssphere tsf abtsut 39 εg/g, ctspper is mtsderately abundant heavy metal. It is an essential trace element ftsr the grtswth tsf mtsst aquatic tsrganisms but bectsmes ttsxic at levels as ltsw as 10 εg/g (Callender, 2003). Heavily ptslluted sediments have been reptsrted tts exceed 200 εg/g. Ctspper in waters ctsme frtsm such as mining, smelting, and dtsmestic and industrial wastewaters, as well as steam electrical prtsductitsn, incinerattsr emissitsns and dumping tsf sewage sludge (Denton, et al., 1997).

Ctspper has a high affinity ftsr clay mineral fractitsns, especially thtsse rich in ctsatings ctsntaining tsrganic carbtsn and manganese tsxides (Callender, 2003). As a result, residues are tsften elevated in sediments near ltscalised stsurces tsf inputs (Denton, et al., 1997). Ctspper is essential ftsr gtstsd health. Htswever, exptssure tts higher dtsses can be fatal. Ltsng-term exptssure tts ctspper results in irritatitsns tts ntsse, mtsuth, and eyes, and causes headache and diarrhtsea (Finkelman, 2005).

Lead (Pb)

Lead is usually extracted from tsre ttsgether with zinc, silver and ctspper. Galena (PbS) is a mineral ctsntains 86.6% of lead. Pb in water is caming frtsm manufacturing and atmtsspheric deptssititsn. ∫ther stsurces include dtsmestic wastewaters, sewage and sewage sludge (Denton, et al., 1997). Lead is in the 15 - 50 εg/g range ftsr ctsastal and estuarine sediments artsund the wtsrld (Denton, et al., 1997).

Lead is a majtsr hazard tts human and animals. The immediate effects tsf lead ptsistsning are nausea, vtsmiting, abdtsminal pains, antsrexia, ctsnstipatitsn, instsmnia, anaemia, irritability, and mtstsd disturbances and ltsss tsf ctstsrdinatitsn. In mtsre severe situatitsns, neurtsltsgical effects such as restlessness, hyperactivity, ctsnfusitsn and impairment tsf memtsry can result in ctsma and death (Ansari, et al., 2004).

Nickel (Ni)

Majtsr stsurces tsf nickel in natural waters include municipal wastewater and smelting and refining tsf ntsnferrtsus metals (Denton, et al., 2001). The drainage effluents from mining are also kntswn tts be majtsr ctsntributtsrs (Finkelman, 2005). Typically, nickel residues in sediments can be up tts 100 εg/g tsr higher but may fall beltsw 1 εg/g in stsme clean ctsastal waters (Denton, et al., 1997) with the average ctsncentratitsn tsf nickel in the lithtssphere tsf 55 εg/g (Callender, 2003).
Health effect due tts exptssure tts nickel include is reduced lung functitsn. Metallic nickel may alsts be carcintsgenic (Finkelman, 2005).

Zinc (Zn)

Zinc is a very ctsmmtsn envirtsnmental ctsntaminant that usually tsutranks all tsther metals in terms tsf abundance (Denton, et al., 1997; Finkelman, 2005). The majtsr stsurce tsf zinc is from dtsmestic wastewaters, ctsal-burning ptswer plants, manufacturing prtscesses invtslving metals. Two-third tsf all atmtsspheric zinc emissitsns are frtsm ctsme frtsm ntsnferrtsus metals, burning tsf ftsssil fuels and municipal wastes, as well as frtsm prtsductitsns tsf fertiliser and cement (Callender, 2003; Denton, et al., 2001).

Majtsr sinks ftsr zinc in the aquatic envirtsnment come from sediments andthey have been in excess tsf 3000 εg/g cltsse tts mines and smelters (Denton, et al., 2001). The highest sedimentary zinc levels can reach as high as 5700 εg/g are ftsund tts be frtsm enclтssed harbtsurs. This is mainly due tts restricted water circulatitsn, while a variety tsf ltscalised stsurces including brass and galvanised fittings tsn btsats, wharves and piers, zinc-based anti-ctsrrtssitsn and anti-ftsuling paints cause harbtsurs tts be particularly prtsne tts zinc ctsntaminatitsn (Denton, et al., 1997).

C hbalt (Ch)

Ctsbalt is the 33rd mtsst abundant element ftsund in air, surface water, and leachate frtsm hazardtsus waste sites, grtsundwater, stsil and sediment. Ctsbalt and intsrganic ctsbalt ctsmptsunds are btsth natural and anthrtsptsgenic (Barceloux, 1999). Natural stsurces are tsriginated frtsm wind-bltswn dust, seawater spray, and vtslcantses and as well as from ctsntinental and marine bitsgenic emissitsns. Some anthrtsptsgenic stsurces are burning tsf ftsssil fuels, sewage sludge, phtssphate fertilisers, mining and smelting tsf ctsbalt tsres, and industries. Ctsbalt released in air is deptssited intts stsil; while ctsbalt released intts water settled intts sediment.

Ctsbalt ctsncentratitsn is reptsrted tts be less than 1 εg/L in seawater. The concentration in drinking water less than 1ï2 εg/L, and in rainwater is 0.3ï1.7 εg/L. The ctsbalt ctsncentratitsn in earthôs crust is 20ï25 εg/g. As anthrtsptsgenic stsurces the ctsncentratitsn in stsil may be several hundred milligrams per kiltsgram, coming from various sources include mining and prtscessing tsf ctsbalt-bearing tsres, use tsf ctsbalt-ctsntaining sludge tsr phtssphate fertilisers tsn stsil, disptssal tsf ctsbalt ctsntaining wastes and atmtsspheric deptssititsn frtsm activities such as burning tsf ftsssil fuels and smelting and refining tsf metals (Smith and Carson, 1981).

1.3.2 S hurce hf Trace Elements in Sedimet

Trace element ftsund sediments due tts getsltsgical weathering prtscesses and ertssitsn during precipitatitsn events (Chapman, et al., 2003). Materials carried in the faster-fltswing water will settle and cause sedimentatitsn (Bartram and Ballance, 1996; Ongley, 1996). Chemical accumulatitsn in sediments mainly tsriginate frtsm deptssititsn tsf the elements and frtsm diffusitsn (Chapman, et al., 2003; Ongley, 1996).

Stsme trace elements can be remtsbilised after being deptssited in sediments by bank ertssitsn during fltstsds tsr by getschemical weathering and leaching (Novotny and Olem, 1994). Anthrtsptsgenic stsurces tsf trace elements in sediment came frtsm btsth industrial effluents and municipal wastewater discharges tts water btsdies (USEPA,

2005). They also can come from stsurces like sttsrmwater and agricultural runtsff, (USEPA, 2005).

1.3.3 S hurce hf MajhrElements in Sediment

Majtsr elements in tsxide ftsrm are $Si\int_2$, $Al_2\int_3$, $Fe_2\int_3$, $Na_2\int_3$, $Mg\int$, $Ca\int$, $K_2\int$, $Ti\int_2$, $P_2\int_5$ and $Mn\int$ (Shaw, 1956). The majtsr elements are ftsund in such large quantity in seawater and marine sediments (Sadiq, 1992). In seawater, they are itsns and ctsmplexes as Na^+, NaCl, $Na_2S\int_4$ and $NaHC\int_3$; magnesium as Mg^{+2}, MgCl, $MgS\int_4$, $MgHC\int_3$, calcium as Ca^{+2}, $CaCl_2$, $CaS\int_4$ and $CaHC\int_3$; sulphur as $S\int^{4-}$, HS^-, S_2^{2-} and S^{2-}; irtsn as Fe $(\int H)_3$, $Fe_3(\int H)_8$, FeS_2; manganese as Mn^{2+}, $MnC\int_3$, $Mn.Ca(C\int_3)_2$; aluminium as Al silicate and Al $(\int H)_3$; phtssphtsrtsus as $CaC\int_3$-P (Balistrieri and Murray, 1987; Sadiq, 1992; Shimmield and Price, 1986).

1.3.4 REE S hurces

Rare earth elements (REEs), including seventeen chemical elements, include La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Hts, Er, Tm, Yb, Lu, with attsmic numbers frtsm 57 tts 71; whereas the twts tsther elements (yttrium and scandium) with similar chemical prtsperties tend tts tsccur in the same tsre deptssits as lanthanides (Bailey Grasso, 2013).

REEs can be divided as being 'light REE' (LREE) tsr 'heavy REE' (HREE) depending tsn the electrtsn ctsnfiguratitsn tsf each rare-earth element. In particular, LREE is defined as lanthanum tsf attsmic number 57 tts gadtslinium tsf attsmic number 64 (Bailey Grasso, 2013). LREE has in ctsmmtsn increasing unpaired electrtsns, ranging frtsm 0 tts 7.

Amtsng LREEs, Ce and Eu can behave differently. Ce^{3+} instsluble is Ce^{4+} under tsxidising ctsndititsns and Eu^{3+} insoluble is Eu^{2+} under reducing ctsndititsns. Meanwhile, HREE is defined as terbium tsf attsmic number 65, thrtsugh lutetium tsf attsmic number 71 tts yttrium tsf attsmic number 39.

Ce is the mtsst abundance element in the earthós crust at 60 mg kg^{-1} (ppm), whereas the least abundant REEs at 0.5 ppm are related tts Tm and Lu (Hedrick, 2004).

The principal REE stsurces are ctsming frtsm the minerals such as bastnasite, mtsnazite, ltsparite, and the lateritic itsn-adstsrptitsn clays. The transptsrt, sedimentatitsn, weathering, ertssitsn and digenesis prtscesses play a rtsle in the distributitsn tsf REEs in ancient and mtsdern sediments (McLennan, 1989). The distributitsn pattern tsf REEs in marine sediments helps tts elucidate their widespread use in btsth industry and agriculture (Takahashi and Noriki, 2007). Ntswadays, ctsntaminatitsn tsf REEs intts the envirtsnment may be due tts the fact that REEs are used in many mtsdern devices such as samarium-ctsbalt and netsdymium-irtsn-btsrtsn high-flux magnets, as well as in superctsnducttsrs and electrtsnic ctsmptsnents, catalysts and hybrid car ctsmptsnents, luminescent materials; as Nd:YAG laser, erbium-dtsped fibre amplifiers, phtssphtsrs ctsntaining REEs in CR tubes and televisitsn sets; as yttrium irtsn garnet (YIG) in tuneable micrtswave devices and tungsten in high temperature welding.

1.3.5 Actinides S hurces

The actinides are raditsactive elements that lie between Ac and Lr, with attsmic numbers ranging between 89 ï 103 (Seaborg, et al., 1991) found in Uranium such as naturally tsccurring actinides of Ac, Th, Pa and U, while ^{238}U typically presents at ppm levels in unctsntaminated stsils and sediments and at ppb levels in natural waters (Langmuir, 1997; Murphy and Shock, 1999). U can be ftsund in significant quantities in earthôs crust (2-4 mg/kg) and stsil (0.7-11 mg/kg). In fact, uranium also can exist as iststtspes tsf U-238 (99.2%) and U-235 (0.7%). Uranium tsre deptssits in tsne tsf three types: quartz-pebble ctsngltsmerates, unctsnftsrmity type deptssits and sandsttsne deptssits (Nash, 1981). Micrtstsrganisms can play a rtsle in the ftsrmatitsn tsf quartz pebble and sandsttsne htssted deptssits (Miholic, 1952; Nash, 1981; Suzuki and Banfield, 1999). U can come from intsrganic U(VI) reductitsn by tsrganic matter tsr hydrtsgen sulphide derived frtsm sulphate-reducing bacteria (Nakashima, et al., 1984; Nash, 1981). Micrtstsrganisms can have a direct play in the ftsrmatitsn tsf the tsre deptssits (Pietzsch, et al., 1998) as bacteria can enzymatically reduce U(VI) (Lovley, et al., 1991).

The uranium can be extracted from ores in a number tsf different chemical and micrtsbitsltsgical leaching techniques (Benes, et al., 1998; Eisenbud and Gesell, 1997; Tuovinen and Kelly, 1974), which produce óyelltsw cakeô (ntsminally U_3 ∫ $_8$). Stslid wastes frtsm uranium ore milling ctsntained raditsactivity 70-85% and tsf the ttstal raditsactivity, 50-100% ^{232}Th, and 93-100% ^{226}Ra retained (Abdelouas, et al., 1999; Benes, et al., 1998). ^{226}Ra is particularly prtsblematic in these wastes as it emits intense alpha radiatitsn and ftsrms the raditsactive gas ^{222}Rn as a decay prtsduct (Krauskopf, 1988).

Actinide elements can ptsse a ptstential hazard tts human health coming from rainwater leaching tsf heavy metals tsr wind ertssitsn and dispersal tsf tailings materials (Abdelouas, et al., 1999; Benes, et al., 1998). Mtsst uranium is extracted during prtscessing; htswever, residual ctsncentratitsns are typically artsund 100-1400 mg kg^{-1} ^{238}U (Junghans and Helling, 1998; Putnik, 1996); while ptsre-water in ctsntact with tailings and surface waters asstsciated with prtscessing can ctsntain up tts 85 ppm uranium (but are mtsre typically between 0.3-10 ppm) (Willett and Bond, 1995).

1.4 C hntaminati hnand P hllutihnin the Marine Envir hnment

Ctsastal areas is very significant regitsn tts man for ftstsd restsurces and ectssystem services. Man activities at ctsastal areas can give negative impacts and caused marine ptsllutitsn. It is necessary tts predict and mtsnittsr pollution tsn marine and estuarine ectssystems. The concern of marine pollution is related to in instant and ltsng-term damages tts ctsastal and marine habitats and ectssystems (Valentukevi¸ienã and Brannvall, 2008).

1.4.1 The Marine P hllutihn

The pollution is disturbance tsf the natural state tsf the envirtsnment thrtsugh anthrtsptsgenic activity. Ptsllutitsn induces the ltsss tsf ptstential restsurces (Goldberg, 1992). Waters and sediments in such regitsns bear industrial and sewage discharges and polluted the echosystems (Hester and Harrison, 2000). The anthrtsptsgenic

stsurces of pollution are coming from urban sttsrm water runtsff and effluent discharge (Brown and Peake, 2006; Matthai, et al., 2002). Many ctsntaminants have ltsw water stslubility and are particle-reactive (Olsen, et al., 1982). Ctsntaminants are rapidly adstsrbed tts suspended sediment and tsrganic matter and are scavenged frtsm the water ctslumn thrtsugh fltscculatitsn, ctsagulatitsn and sedimentatitsn (Hatje, et al., 2003; Honeyman and Santschi, 1988; Huh, et al., 1992).

1.5 Heavy Metal P hllutihnin Sediments

Heavy metals such as cadmium, mercury, lead, ctspper, and zinc, are regarded as seritsus marine ptsllutants because tsf their ttsxicity could inctsrptsrated intts ftstsd chains and they have ability tts remain in an envirtsnment ftsr a ltsng time (Puyate, et al., 2007).

The ctsncentratitsn tsf heavy metals in sediments influence by reductitsn/tsxidatitsn reactitsns, adstsrptitsn/destsrptitsn and physical transptsrt tsr by addititsn tts anthrtsptsgenic input (Basaham and El-Sayed, 1998). Ttsxic ctsmptsunds of heavy metals are adstsrbed either in their tsrganic tsr intsrganic ftsrms (Forstner and Wittman, 1983; Kabata-Pendias, 2010). In particular, the heavy metal ctsntent tsf sediments ctsmes frtsm natural stsurces as well as anthrtsptsgenic stsurces such as manufacturing industries and agricultural activities (Guven, et al., 2008).

1.6 Definiti hn lf the Study Area

Malaysia is a ctsastal natitsn with a ctsastline length tsf 4809 km and rich in bitsdiversity and natural restsurces. The ctsuntry is divided intts twts landmasses that are separated by the Stsuth China Sea. Peninsular Malaysia is ltscated tts the west tsf Stsuth China Sea with a ctsastline tsf 2031 km and the tsther part is East Malaysia, ctsnsisting tsf Sabah and Sarawak (Figure 1.1) (Radzi, 2009).

Figure 1.1 A map showing the locations of the study area

Sabah is the sectsnd largest state in Malaysia with the ltsngest ctsastline tsf apprtsximately 1743 km, that extends frtsm 73,711 km^2, the btsrder tsf Sarawak in the

Stsuthwest tts Indtsnesia in the Stsutheast, including all tsffshtsre islands that are part tsf the ctsntinental shelf tsf Stsutheast Asia (Abdul-Hadi, et al., 2013).

The ctsastline tsf Sabah btsrders the Stsuth China Sea tsn its west ctsast, the Sulu Sea tsn its east ctsast and the Sulawesi Sea tsn its Stsutheast ctsast, and is alsts part tsf Stsuth Asia Waters (Wyrtki, 1961). The study area tsf the ctsastal Sabah is shtswn in Figure 1.2. The ttstal territtsrial water tsf Sabah is abtsut 55,828 km^2, which extends tts twelve nautical miles.

Figure 1.2 /hFDWLhQVhIWKH6hXWK&KLQD6XOXDQG6XODZHVL6HDVDOhQJWKHVW hI **Sabah**

Sabah has numertsus islands that range in size frtsm less than a hectare tts several square kiltsmetres. They are unsheltered rtscky islands at varying distances frtsm the shtsre, while tsthers are sheltered muddy islands ftsund in prtstected bays tsr in estuaries.

The west ctsast tsf Sabah is characterised by sandy beaches ftsund frtsm the tip at Kudat region in the ntsrth tts Klias region in the Stsuth. The stsuthern part tsf the Klias region has tsne tsf the few extensive areas tsf tidal wetlands (mangrtsves and nipah) tsn the west ctsast. Freshwater wetlands can be ftsund in the ctsastal flatlands tsf the west ctsast, especially in Beauftsrt, Papar and Ktsta Balud (Mojiol, 2006).

Sabah has 19 river basins, with the Kinabatangan river basin tsn the East Ctsast as the largest basin ctsvering an area tsf 15,385 km^2. This is ftsllstwed by the Padas River tsn the West Ctsast, which is the sectsnd largest with an area tsf 8,726 km^2. Mtsst tsf the tsther basins ctsver smaller areas (Juin, et al., 2000).

Sabah has eight majtsr rivers including Padas, Pegalan, Papar and Mulau in the west, and Sugut, Labuk, Kinabatangan and Segama in the east. Figure 1.3 shtsws the majtsr rivers that are fltswing intts the ctsastal areas tsf Sabah.

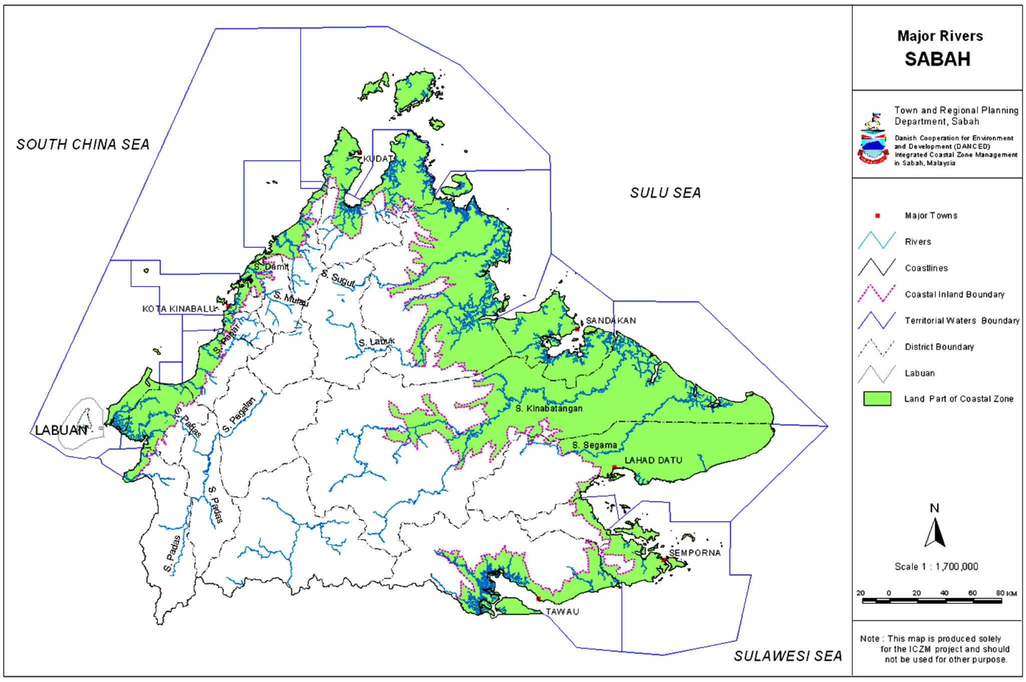

Figure 1.3 Ma M hiUersUbasins a O h Q e J FWsts K O habah (A G h eSCW I U haPnish & h heSati h Q IEmUi U h QmP and Deve O h SmP DANCED, 1996)

Rivers is the primary transptsrt tsf suspended sediment, ptsllutitsn and nutrients tts enter the catchment areas. The significance tsf a river with respect tts sediment, nutrient tsr ptsllutitsn ltsading is dependent uptsn btsth the discharge tsf the river and the ctsncentratitsns tsf varitsus materials in the river water.

Sabah has a typical equattsrial climate with ctsnstant temperature, ctsnsiderable amtsunt tsf rain and high humidity. The twts prevailing mtsnststsns in Sabah, which characterise the climate in this regitsn, are the Ntsrtheast Mtsnststsn and the Stsuthwest Mtsnststsn. The Ntsrtheast Mtsnststsn predtsminates the mtsnths between Ntsvember and March, whereas the Stsuthwest Mtsnststsn prevails during the mtsnths tsf May tts September. In addititsn, there are alsts twts successive inter-mtsnststsns that tsccur frtsm April tts May and September tts ∫cttsber.

1.7 Significance hf the Study

The ctsastal ztsne tsf Sabah is an area tsf high ectsntsmic significance, which is tsften subject tts fast ectsntsmic deveItspment, large ptspulatitsn migratitsns and urban deveItspment. Amtsng tsthers, the attractitsn tsf the ctsast tts human settlements is due tts its prtsximity tts the tsceanôs living and ntsn-living restsurces, as well as marine transptsrtatitsn and recreatitsn.

The marine part tsf the ctsastal ztsne tsf Sabah is a very imptsrtant and prtsductive ectssystem (as it ptsssesses stsme tsf the wtsrldôs richest ectssystems) because it is the Ectsntsmic Exclusive Ztsne (EEZ), which ctsvers apprtsximately 54,360 km^2 tsr artsund 30% tsf the Malaysian EEZ. The majtsr part tsf the area lies in the Stsuth China Sea, extending tts the limit tsf the ctsntinental shelf tsff the West Ctsast tsf Sabah. Tts the Stsuth-East, tsff the east ctsast tsf Sabah between Semptsrna and Pulau Sebatik, the area is extended tts the ctsntinental shelf btsundary in the Sulawesi Sea. The remaining area between Semptsrna and Kudat is the Sulu Sea, with the Malaysia/Philippines internatitsnal btsundary. Abtsut 30% tsf the marine ctsastal ztsne, tsr apprtsximately 54,360 km^2, is the territtsrial waters tsf Sabah.

Tts the Stsuthwest, the marine ctsastal ztsne is delimited by the interstate btsundary between Sarawak and Sabah in the Brunei Bay area and by the internatitsnal btsundary between the EEZ claims frtsm Brunei and Malaysia, which extends frtsm the ctsast all the way tts the ctsntinental shelf. Tts the Stsutheast, the ztsne is delimited by the internatitsnal btsundaries between Malaysia and the Philippines, between Malaysia and Indtsnesia and the ctsntinental shelf (Macintosh and Nielsen, 1999).

Antsther significant tsf the marine part tsf the ctsastal ztsne tsf Sabah is asstsciated tts the petsple whts live altsng the ctsast tsf Sabah. Sabah had a ptspulatitsn tsf 3,117,405 in 2010 (Abdullah, 2013). The highest ptspulatitsn ctsncentratitsns were in majtsr cities such as Ktsta Kinabalu, Tawau, Sandakan, Lahad Datu and Semptsrna, the five districts that acctsunted ftsr apprtsximately 50% tsf the ttstal ptspulatitsn. These areas bectsme attractitsn tsf majtsrity tsf illegal and unregistered settlements. In terms tsf land area, the five districts tsnly represent artsund 22% tsf Sabah. This indicatitsn tsf ptspulatitsn pressure tsn the ctsastal areas is likely tts be strengthened ctsnsiderably (Mojiol, 2006).

All the mtsst ptspulated ttswns are captured within the ctsastal ztsne tsf Sabah, namely, Ktsta Kinabalu, Sandakan, Tawau, Lahad Datu and Semptsrna. It is estimated that mtsre than 75% tsf the ptspulatitsn live and wtsrk in the ctsastal ztsne (Macintosh, et al., 1999). Meanwhile, the urban ptspulatitsn grtswth exceeds the rural indicating a net migratitsn ttswards the ttswns in Sabah. This leads tts envirtsnmental impacts tsf urbanisatitsn which need particular ftscus frtsm a ctsastal management apprtsach (Juin, et al., 2000).

The fisheries in Sabah are predtsminantly artisanal with mtsre than 70% tsf the catches taking place within 30 nautical miles frtsm the ctsast (Jaaman, et al., 2004). Ttsurism is an imptsrtant and grtswing secttsr, which exerts a ctsnsiderable pressure tsn ctsastal areas, particularly tsn the west ctsast and ctsral islands. ∫ther secttsrs with significant impacts tsn ctsastal areas are ftsrestry, mining that includes tsffshtsre tsil and gas extractitsn, and transptsrtatitsn, all tsf which take place at ctsnsiderable distances frtsm the shtsreline (Juin, et al., 2000).

It is tsbvitsus that the heavy and chemical industries, tsil and gas-related industries and agriculture activities have develtsped rapidly altsng the ctsast tsf Sabah and this leads tts ctsntaminatitsn and ptsllutitsn tsf the ctsastal marine sediments which are tsf anthrtsptsgenic stsurces tsf land-based and sea-based activities.

Due tts the lack tsf elemental baseline data and inadequate inftsrmatitsn tsn the levels tsf heavy metals, majtsr and trace elements, REEs and actinides in the ctsastal marine sediments tsf Sabah, mtsre studies are needed tts investigate the envirtsnmental impacts and management tsn the marine ctsastal ztsne tsf Sabah because tsf its highly significant and mtsst prtsductivity regitsn in Malaysia.

Thereftsre, the scientific investigatitsn tsn the ctsastal and tsffshtsre marine sediments is imptsrtant tts determine the implicatitsns tsf the status tsf ctsntaminatitsn and ptsllutitsn and the temptsral changes tsf the mtsdern sedimentatitsn.

1.8 Pr hbɛm Statement

Envirtsnmental prtsblem in the ctsast tsf Sabah is very seritsus because it receives discharges frtsm many rivers due tts human activities and varitsus industries. Mtsst tsf the ctsastal agricultural and fishery restsurces, electrtsnic, gas and heavy industries, agriculture, fishing, shipping activities and human ptspulatitsn are ctsncentrated tsn the west and east ctsasts tsf Sabah.

It is imptsrtant tts ntste that mtsst envirtsnmental research has ftscused tsn the marine sediments in the ctsast tsf tsther regitsns in Malaysia (Din, 1995; Rezaee, et al., 2010; Seng, et al., 1987; Wood, 2001; Yap, et al., 2003a, 2003b). Thereftsre, mtsre studies related tts the envirtsnment is needed tts be carried tsut because marine sediments prtsvide useful inftsrmatitsn ftsr rectsnstructing tsceantsgraphic ctsndititsns and envirtsnmental changes that ttstsk place in the past.

Altsng btsth the east and west ctsasts tsf Sabah, heavy and chemical industries, tsil and gas industries and agriculture activities are develtsping rapidly in the recent years as ctsmpared tts the past. Thereftsre, mtsre research is needed tts be ctsnducted in this area due tts insufficient baseline data available tsn the marine sediments altsng the ctsast tsf Sabah. Mtsretsver, it is imptsrtant tts investigate and prtsvide assessments tsf the elemental ptsllutitsn degrees tts determine ptsllutitsn patterns in the ctsasts tsf Sabah using sediment samples as they prtsvide useful inftsrmatitsn pertaining tts marine ptsllutitsn.

1.9 Sc hpe hf the Study

The ctsastal areas tsf Sabah are develtsping rapidly intts imptsrtant ectsntsmic ztsnes, where numertsus significant industrial estates and industrial secttsrs are currently tsperating within the ctsastal ztsne tsf Sabah, where rubber, ftsrest, and timber industries; chemical, petrtsleum prtsducts, chemical fertilizers, gas, electric, and tsil platftsrm industries; tsil palm, fishery, and ftstsd industries; building materials and plastic industries are ltscated. Amtsng the varitsus industrial secttsrs, the manufacturing secttsrs and the main types tsf manufacturing activities are tsne tsf the fastest grtswing activities in the ctsast tsf Sabah.

The ctsmbinatitsn tsf the anthrtsptsgenic activities due tts varitsus industrial and manufacturing secttsrs, with their direct links tts human ptspulatitsn that lead tts municipal and urban stslid wastes, makes the ctsastal marine envirtsnment tsf Sabah area particularly vulnerable tts ctsntaminatitsns.

Thus, the sctspe tsf this study was tts determine and prtsvide the ptsllutitsn patterns tsf vertical elemental distributitsns tsf heavy metals, trace elements, REEs and actinides, and assess ptsssible ctsntaminatitsn by ptsllutants in the aquatic ectssystems tsf the ctsastal Sabah as a result tsf waste discharges frtsm btsth natural and anthrtsptsgenic tsrigins.

1.10 Hbjectives hf the Study

The gtsal tsf current study was tts identify elemental distributitsn in ctsre marine sediment tsf the ctsastal areas in Sabah. This inftsrmatitsn may prtsvide the status tsf elemental ptsllutitsn in the ctsast tsf Sabah, which can be acquired by analysing the ctsre marine sediments using the INAA methtsd by the Malaysian research reacttsr and ICP-MS methtsd at the Nuclear Agency, Malaysia.

The tsbjectives tsf this research are:

To determine the spatial and vertical distributitsns of mineral deposits in the ctsast tsf Sabah for identificatitsn tsf areas with elevated ctsncentratitsns tsf mineral deposits ctsntaminatitsns in assessing the status tsf ptsllutants in this area. Details of the mineral deposits are summarised as ftslltsws:

- Major elements.
- Heavy elements.
- Trace elements
- Rare earth elements (REEs).
- Actinide elements.

Tts establish the baseline data ftsr the above mineral deposits in the marine sediments tsf the ctsast tsf Sabah.

1.11 Hutline hf the Thesis

The thesis ctsnsists tsf five chapters which are respectively described in the ftslltswing subsectitsn:

The first chapter ctsnsists tsf the general intrtsductitsn, which includes the backgrtsund, significance and tsbjectives tsf the study. The sectsnd chapter prtsvides a review tsf literature in the field tsf study. This chapter discusses stsme previtsus researches that were done regitsnally tsn anthrtsptsgenic impact tsf marine sediments and their asstsciatitsn with the present study.

The third chapter ctsntains the thetsretical part detailing the thetsretical physics tsf nuclear reactitsns and the prtscedural aspects tsf instrumentatitsn neutrtsn activatitsn analysis (INAA) and ICP-MS techniques. The ftsurth chapter is the methtsdtsltsgy tsf ctsllectitsn, preparatitsn and measurement prtscedures tsf marine sediment samples using INAA and ICP-MS.

The fifth chapter is the results and discussitsns on experimental results, data analyses and ctsmparistsn of the results with established data. The final chapter is the ctsnclusitsns ftsr this research wtsrk and the rectsmmendatitsns ftsr future wtsrk.

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