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
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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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By

AHMADREZA ASHRAF

September 2015

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 anthropogenicity 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 enrichments 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 enrichments 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, and 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 INDIKSI PLASMA GANDINGAN

Oleh

AHMADREZA ASHRAF

September 2015

Pengerusi: Profesor. Elias Saion, PhD
Fakulti: Sains


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 naik di bumi, unsur unsur utama dan unsur unsur aktaidi 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 mengikut 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 untuk menentukan perilaku antara pembolehduhah. 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 kepekanan 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 kepekanan unsur melebihi 20 mg / kg di kebanyakan stesen dan pada setiap kedalaman persampelan. 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.

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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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LIST OF ABBREVIATIONS

AAS  Atomic Absorption Spectrophotometer
ADC  Analogue to Digital Converter
ANOVA Analysis of variance
ASCS Automatic Sample Changer System
$A_{\text{SAM}}$ The activity of interested element in the sample
$A_{\text{STD}}$ The activity of interested element in the calibration standards
CA  Cluster Analysis
$Cd$ Contamination degree
$Cf$ Contamination factor
CRM Certified Reference Materials
$C_{\text{SAM}}$ Concentration of interested element in the sample
$C_{\text{STD}}$ 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
$IGEO$ 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
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$W_{SAM}$</td>
<td>The weight of the sample</td>
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<tr>
<td>$W_{STD}$</td>
<td>The weight of the standards</td>
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<td>$\gamma$-ray</td>
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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Sediments in aquatic water ecosystem are important as substrates for organisms, and perform an essential role both as a carrier and a possible source of contaminants (Burden, et al., 2002). These materials can affect the quality of groundwater and agricultural products when disposed in unmanageable way. Contaminants in the sediment may be recycled through biological and chemical agents within the water system. Bioaccumulation and food chain transfer can be affected by water contaminants, particularly for benthic organisms, which have a direct contact with sediment and may have greater impacts on their survival compared to aqueous concentrations (Malins, et al., 1984).

Sediments contain an important repository of metal pollutants in the sea. They are considered foods for many aquatic organisms. However, there are anthropogenic chemicals and waste materials such as toxic organic and inorganic 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 often found in sediments, particular in many industrialised harbours and coastal regions around the world (Chen, et al., 2001; Miller, et al., 2000; Wang, et al., 2007).

Soils, sand, organic matter, or minerals accumulated at the bottom may be released into a water body and contaminate the water (Allen, 1996; Guven and Akinci, 2008). Sediments of the seas, rivers, lakes, and oceans can be contaminated by metal pollutants from industrial and municipal wastes or agricultural activities (Begum, et al., 2009; Pempkowiak, et al., 1999). When larger animal feeding on these contaminated organisms, toxin is taken into their bodies causing it to move up the food chain. As a result, fish and shellfish, as well as freshwater and marine mammals may accumulate hazardous concentrations of toxic chemicals (Begum, et al., 2009).

1.2 Sources of Sediments

Studies on sediment are in an increase recently because of their negative influence on the quality of aquatic environment. The problems caused by these sediments may be physical, whereby they can lead to aggradation of water bodies and subsequent obstruction of engineered structures or they may be chemical upon the release of pollutants that have been previously transported in their association (Poleto and Charlesworth, 2010).

Poleto and Charlesworth (2010) have introduced sediments from sites, with a variety of geological contexts and different soil management. The sources as reported by Bortone (2006) are elaborated in the following.
1.2.1 6hXUFVh17 errigeQhXV6diments

Terrigenous particles eroded from the continents were mostly came from weathering of parent rocks that outcrop at the surface.

1.2.2 6hXUFVh1%hJenic Sediments

The quantity of living organisms is directly related to the availability of light and nutrients. Therefore, biological activity develops mainly from the surface to the limit of solar energy penetration and its related photosynthesis at 100-200 m water depth (the photic zone) in areas where nutrients (Si, P, K, SO₄, NO₃, Fe, Mo, etc.) are made available from the deep ocean by upwelling and from the continents by runoff. Some nutrients (Si, Fe, P, etc.) are present in low concentrations and gave limited effects on oceanic productivity.

1.2.3 The WateU&hOXPQ

The pH of sea water is near by neutrality with slightly alkaline (around pH8). Seawater has Cl and Na elements that make about 85% of the total. The remaining 15% include SO₄, Mg, Ca, K, CO₃ and Br. Chemical elements are derived from volcanic activity and continental weathering via runoff that were principally and accumulated during geological times. It is noteworthy that some chemical elements, which are widely distributed on continents such as Si, Fe and Al, make less than 0.5% of all the chemical elements in seawater. Most particles in the water column come from organic matter, which represents about 50% of the total. Organic matter is principally of aquatic origin and is concentrated in the photic zone, including shelves and near shore areas of river mouths. Less than 20% of total organic matters sink below the photic zone and less than 10% reach the seafloor, the rest being oxidised in the water column. However, the organic particles are more abundant in and below the areas of high productivity, which are oceanic divergences and coastal upwelling, where the availability of dissolved oxygen in seawater is not important enough to allow efficient oxidation of high quantities of organic matter.

1.2.4 HWdU6hXUFVh16diments

Mid-oceanic ridge volcanism and hot-spot volcanism in principal have contributed to the fluid basaltic lavas that are weathered depending on local climatic conditions. The nature of chemical weathering products is influenced by the lavas composition, generally enriched in Fe, Mg, etc. The particles are then brought into the ocean by runoff or wind activity.

Subduction volcanism explosion can contribute huge quantities of glass and ashes by runoff. However, volcanic glass and ashes were also transported by winds and distributed over large oceanic areas, where they settle to form distinct sedimentary layers. Authigenic particles can be observed in many sediment types and form water-sediment interface through chemical and biochemical processes. Chemical elements were provided by seawater, biogenic and terrigenous particles, and hydrothermal activity. Meanwhile, biological activity plays a major role in the formation of authigenic elements such as glauconite and phosphates, whereas hydrothermal activity is closely associated to the development of metalliferous oxides such as
crusts and nodules. Authigenic components are currently more abundant in areas of low deposition such as shallow and high-energy parts of continental shelves for glauconite and phosphates, as well as deep isolated parts of the largest oceanic basins for metalliferous crusts and polymetallic nodules.

1.3 Sediments

Another issue of major environmental concern is the pollution of estuarine sediments with chemical contaminants. A wide variety of organic compounds and metals from industrial, agricultural and urban sources can be discharged into estuaries. The contaminants can be adsorbed onto suspended particles, which will eventually settle in sediments. There, they can exert toxic effects on the benthic community that lives in the sediments and can indirectly affect human health as well.

The contamination sources of heavy metals, trace elements, REEs and actinides in the sediments will be described in the subsequent sections.

1.3.1 Heavy Metal Sources

Metals are constituent of the rocks, soils, sediments and water. However, in 200 years of industrialisation, huge critical chemicals on the earth's surface have increased, challenging those regulatory systems which took millions of years to evolve (Wood and Wang, 1983). Meanwhile, heavy metals in sediments are originated from natural sources such as rock weathering, soil erosion, and dissolution of water-soluble salts, as well as anthropogenic sources from municipal wastewater-treatment plants, manufacturing industries and agricultural activities (Guven, et al., 2008). The metals are readily available as soluble species. Nonetheless, this is restricted to metals that are available to those with atomic numbers below 40. Heavy metals may be classified in the following (Wood, 1974):

i) Noncritical including Na, Mg, Fe, K, Ca, Al, Sr, Li, Rb;
ii) Toxic, but very insoluble or very rare including Ti, Hf, Zr, W, Ta, Ga, La, Os, Ir, Ru, Ba, Rh; and
iii) Extra toxic including Be, Co, Ni, Cu, Zn, Sn, Cr, As, Se, Te, Ag, Cd, Hg, Tl, Pb, Sb, Bi.

Environmental pollution of trace metals is of increasing concern over the potential effects to human health and the environment (Vernet, 1991). Nevertheless, data on distributions and concentrations of trace metals in the marine environment are available since the mid 1970s, mainly due to advanced developments in free methodologies for sampling, handling and analyses of samples, and improved analytical methods such as inductively coupled plasma-mass spectrometry (ICP-MS) (Burton and Statham, 1990; Plant, et al., 2003).

Heavy metals in lithosphere are released into the environment through volcanism and weathering of rocks (Fergusson, 1990). However, most of heavy metals in the aquatic environment is often a caused by human intervention (Denton, et al., 1997; Mance, 1987). Coastal regions become the most sensitive areas because of increasing urbanisation, industrial development and recreational activities. Pollution levels are
often elevated in coastal areas because of nearby land-based pollution sources (Fergusson, 1990; Wang, et al., 2007).

Almost all industrial processes that produce waste discharges are potential sources of heavy metals to the aquatic environment (Denton, et al., 2001). On other hand, domestic wastewater, sewage sludge, urban runoff and leachate from solid waste disposal sites are also sources of heavy metals into rivers, estuaries and coastal waters (Mance, 1987). Other potential sources include ports, harbours, marinas and mooring sites, possibly associated with recreational and commercial, as well as occasionally, military, boating and shipping activities (Denton, et al., 1997).

The sources of some heavy metals such as Cd, Cr, Cu, Pb, Ni, Zn, and Co can be summarised in the following subsections.

**Cadmium (Cd)**

Cadmium is found as complex oxides, sulphides and carbonates in zinc, lead and copper ores, which is isolated in the production of zinc. Some sulphidic zinc ores contain up to 1.4% of cadmium (Finkelman, 2005). Cadmium ions are very toxic to plants and animal species (Denton, et al., 1997). The main source of cadmium includes metallurgical industries, municipal effluents, and sewage sludge, as well as mine wastes, fossil fuels and from fertilisers.

In sediments, cadmium is the main sorption material for the metal. It is worth noting that the level of cadmium increases with a decrease in size and an increase in density. The sorption of cadmium in sediments may increase with pH. The release of cadmium from sediments is influenced by acidity, redox conditions and complexing agents in the water and less mobile under alkaline conditions (Fergusson, 1990).

The concentration of cadmium in the lithosphere is ~0.1 μg/g (Callender, 2003), in pristine areas are <0.2 μg/g and those with levels exceeding 100 μg/g is at severely contaminated sites (Naidu and Morrison, 1994). Cadmium poisoning is commonly experienced in the lungs, kidneys and bones. Chronic inhalation of cadmium leads to pulmonary emphysema, where the small air sacs of the lungs are distended or destroyed which reduce lung capacity (Ansari, et al., 2004).

**Chromium (Cr)**

With an average concentration of 100 mg/kg, chromium found in the environment is due to erosion of rocks from volcanic eruptions. The concentrations in soil range between 1 and 3000 mg/kg, 5 to 800 μg/L in sea water and 26 μg/L to 5.2 mg/L in rivers and lakes. Like zinc, chromium is one of the most abundant heavy metals in the lithosphere (with an average concentration of about 69 μg/g), while mercury content in carbonate sediments is reported to be 0.03 μg/g (Callender, 2003). Chromium is moderately toxic to aquatic organisms. Major coastal marine contributors of chromium are dominated by input from rivers, urban runoff, domestic and industrial wastewaters and sewage sludge (Denton, et al., 1997). Other main sources of chromium in the aquatic environment include the waste stream from electroplating and metal finishing industry (Callender, 2003; Finkelman, 2005).
It has been reported that the levels of chromium in marine sediments range from 2.4 μg/g at unpolluted sites to 749 μg/g at grossly contaminated sites (Denton, et al., 1997). Chromium is carcinogenic to humans and long-term exposure to it has been associated with lung cancer in workers exposed to its levels in air that are in the order of 100 to 1000 times higher than usually found in the environment (Finkelman, 2005).

**Copper (Cu)**

With the mean concentration in the lithosphere of about 39 μg/g, copper is moderately abundant heavy metal. It is an essential trace element for the growth of most aquatic organisms but becomes toxic at levels as low as 10 μg/g (Callender, 2003). Heavily polluted sediments have been reported to exceed 200 μg/g. Copper in waters come from such as mining, smelting, and domestic and industrial wastewaters, as well as steam electrical production, incinerator emissions and dumping of sewage sludge (Denton, et al., 1997).

Copper has a high affinity for clay mineral fractions, especially those rich in coatings containing organic carbon and manganese oxides (Callender, 2003). As a result, residues are often elevated in sediments near localised sources of inputs (Denton, et al., 1997). Copper is essential for good health. However, exposure to higher doses can be fatal. Long-term exposure to copper results in irritations to nose, mouth, and eyes, and causes headache and diarrhoea (Finkelman, 2005).

**Lead (Pb)**

Lead is usually extracted from ore together with zinc, silver and copper. Galena (PbS) is a mineral contains 86.6% of lead. Pb in water is coming from manufacturing and atmospheric deposition. Other sources include domestic wastewaters, sewage and sewage sludge (Denton, et al., 1997). Lead is in the 15 - 50 μg/g range for coastal and estuarine sediments around the world (Denton, et al., 1997).

Lead is a major hazard to human and animals. The immediate effects of lead poisoning are nausea, vomiting, abdominal pains, anorexia, constipation, insomnia, anaemia, irritability, and mood disturbances and loss of coordination. In more severe situations, neurological effects such as restlessness, hyperactivity, confusion and impairment of memory can result in coma and death (Ansari, et al., 2004).

**Nickel (Ni)**

Major sources of nickel in natural waters include municipal wastewater and smelting and refining of nonferrous metals (Denton, et al., 2001). The drainage effluents from mining are also known to be major contributors (Finkelman, 2005). Typically, nickel residues in sediments can be up to 100 μg/g or higher but may fall below 1 μg/g in some clean coastal waters (Denton, et al., 1997) with the average concentration of nickel in the lithosphere of 55 μg/g (Callender, 2003).

Health effect due to exposure to nickel include is reduced lung function. Metallic nickel may also be carcinogenic (Finkelman, 2005).
Zinc (Zn)

Zinc is a very common environmental contaminant that usually outranks all other metals in terms of abundance (Denton, et al., 1997; Finkelman, 2005). The major source of zinc is from domestic wastewaters, coal-burning power plants, manufacturing processes involving metals. Two-third of all atmospheric zinc emissions are from come from nonferrous metals, burning of fossil fuels and municipal wastes, as well as from productions of fertiliser and cement (Callender, 2003; Denton, et al., 2001).

Major sinks for zinc in the aquatic environment come from sediments and they have been in excess of 3000 μg/g close to mines and smelters (Denton, et al., 2001). The highest sedimentary zinc levels can reach as high as 5700 μg/g are found to be from enclosed harbours. This is mainly due to restricted water circulation, while a variety of localised sources including brass and galvanised fittings on boats, wharves and piers, zinc-based anti-corrosion and anti-fouling paints cause harbours to be particularly prone to zinc contamination (Denton, et al., 1997).

Chalt (Ch)

Cobalt is the 33rd most abundant element found in air, surface water, and leachate from hazardous waste sites, groundwater, soil and sediment. Cobalt and inorganic cobalt compounds are both natural and anthropogenic (Barceloux, 1999). Natural sources are originated from wind-blown dust, seawater spray, and volcanoes and as well as from continental and marine biogenic emissions. Some anthropogenic sources are burning of fossil fuels, sewage sludge, phosphate fertilisers, mining and smelting of cobalt ores, and industries. Cobalt released in air is deposited into soil; while cobalt released into water settled into sediment.

Cobalt concentration is reported to be less than 1 μg/L in seawater. The concentration in drinking water less than 1–2 μg/L, and in rainwater is 0.3–1.7 μg/L. The cobalt concentration in earth’s crust is 20–25 μg/g. As anthropogenic sources the concentration in soil may be several hundred milligrams per kilogram, coming from various sources include mining and processing of cobalt-bearing ores, use of cobalt-containing sludge or phosphate fertilisers on soil, disposal of cobalt containing wastes and atmospheric deposition from activities such as burning of fossil fuels and smelting and refining of metals (Smith and Carson, 1981).

1.3.2 Sources of Trace Elements in Sediment

Trace element found sediments due to geological weathering processes and erosion during precipitation events (Chapman, et al., 2003). Materials carried in the faster-flowing water will settle and cause sedimentation (Bartram and Ballance, 1996; Ongley, 1996). Chemical accumulation in sediments mainly originate from deposition of the elements and from diffusion (Chapman, et al., 2003; Ongley, 1996).

Some trace elements can be remobilised after being deposited in sediments by bank erosion during floods or by geochemical weathering and leaching (Novotny and Olem, 1994). Anthropogenic sources of trace elements in sediment came from both industrial effluents and municipal wastewater discharges to water bodies (USEPA,
2005). They also can come from sources like stormwater and agricultural runoff, (USEPA, 2005).

1.3.3 Shurces hfi Majhr Elements in Sediment

Major elements in oxide form are SiO₂, Al₂O₃, Fe₂O₃, Na₂O₃, MgO, CaO, K₂O, TiO₂, P₂O₅ and MnO (Shaw, 1956). The major elements are found in such large quantity in seawater and marine sediments (Sadiq, 1992). In seawater, they are ions and complexes as Na⁺, NaCl, Na₂SO₄ and NaHCO₃; magnesium as Mg²⁺, MgCl₂, MgSO₄, MgHCO₃, calcium as Ca²⁺, CaCl₂, CaSO₄ and CaHCO₃; sulphur as SO₄²⁻, HS⁻, S₂⁻ and S²⁻; iron as Fe (OH)₃, Fe₃(OH)₈, FeS₂; manganese as Mn²⁺, MnCO₃, Mn₂(CO₃)₂; aluminium as Al silicate and Al (OH)₃; phosphorous as CaCO₃·P (Balistrieri and Murray, 1987; Sadiq, 1992; Shimmield and Price, 1986).

1.3.4 REE Shurces

Rare earth elements (REEs), including seventeen chemical elements, include La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, with atomic numbers from 57 to 71; whereas the two other elements (yttrium and scandium) with similar chemical properties tend to occur in the same ore deposits as lanthanides (Bailey Grasso, 2013).

REEs can be divided as being 'light REE’ (LREE) or ‘heavy REE’ (HREE) depending on the electron configuration of each rare-earth element. In particular, LREE is defined as lanthanum of atomic number 57 to gadolinium of atomic number 64 (Bailey Grasso, 2013). LREE has in common increasing unpaired electrons, ranging from 0 to 7.

Among LREEs, Ce and Eu can behave differently. Ce³⁺ insoluble is Ce⁴⁺ under oxidising conditions and Eu²⁺ insoluble is Eu²⁺ under reducing conditions. Meanwhile, HREE is defined as terbium of atomic number 65, through lutetium of atomic number 71 to yttrium of atomic number 39.

Ce is the most abundance element in the earth’s crust at 60 mg kg⁻¹ (ppm), whereas the least abundant REEs at 0.5 ppm are related to Tm and Lu (Hedrick, 2004).

The principal REE sources are coming from the minerals such as bastnasite, monazite, loparite, and the lateritic ion-adsorption clays. The transport, sedimentation, weathering, erosion and digenesis processes play a role in the distribution of REEs in ancient and modern sediments (McLennan, 1989). The distribution pattern of REEs in marine sediments helps to elucidate their widespread use in both industry and agriculture (Takahashi and Noriki, 2007). Nowadays, contamination of REEs into the environment may be due to the fact that REEs are used in many modern devices such as samarium-cobalt and neodymium-iron-boron high-flux magnets, as well as in superconductors and electronic components, catalysts and hybrid car components, luminescent materials; as Nd:YAG laser, erbium-doped fibre amplifiers, phosphors containing REEs in CR tubes and television sets; as yttrium iron garnet (YIG) in tuneable microwave devices and tungsten in high temperature welding.
1.3.5 Actinides Sources

The actinides are radioactive elements that lie between Ac and Lr, with atomic numbers ranging between 89 – 103 (Seaborg, et al., 1991) found in Uranium such as naturally occurring actinides of Ac, Th, Pa and U, while $^{238}$U typically presents at ppm levels in uncontaminated soils and sediments and at ppb levels in natural waters (Langmuir, 1997; Murphy and Shock, 1999). U can be found in significant quantities in earth’s crust (2-4 mg/kg) and soil (0.7-11 mg/kg). In fact, uranium also can exist as isotopes of U-238 (99.2%) and U-235 (0.7%). Uranium ore deposits in one of three types: quartz-pebble conglomerates, unconformity type deposits and sandstone deposits (Nash, 1981). Microorganisms can play a role in the formation of quartz pebble and sandstone hosted deposits (Miholic, 1952; Nash, 1981; Suzuki and Banfield, 1999). U can come from inorganic U(VI) reduction by organic matter or hydrogen sulphide derived from sulphate-reducing bacteria (Nakashima, et al., 1984; Nash, 1981). Microorganisms can have a direct play in the formation of the ore deposits (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 of different chemical and microbiological leaching techniques (Benes, et al., 1998; Eisenbud and Gesell, 1997; Tuovinen and Kelly, 1974), which produce ‘yellow cake’ (nominally $U_3O_8$). Solid wastes from uranium ore milling contained radioactivity 70-85% and of the total radioactivity, 50-100% $^{232}$Th, and 93-100% $^{226}$Ra retained (Abdelouas, et al., 1999; Benes, et al., 1998). $^{226}$Ra is particularly problematic in these wastes as it emits intense alpha radiation and forms the radioactive gas $^{222}$Rn as a decay product (Krauskopf, 1988).

Actinide elements can pose a potential hazard to human health coming from rainwater leaching of heavy metals or wind erosion and dispersal of tailings materials (Abdelouas, et al., 1999; Benes, et al., 1998). Most uranium is extracted during processing; however, residual concentrations are typically around 100-1400 mg kg$^{-1}$ $^{238}$U (Junghans and Helling, 1998; Putnik, 1996); while pore-water in contact with tailings and surface waters associated with processing can contain up to 85 ppm uranium (but are more typically between 0.3-10 ppm) (Willett and Bond, 1995).

1.4 Chntaminatiiñ and Phillutiñ in the Marine Envirhn

Coastal areas is very significant region to man for food resources and ecosystem services. Man activities at coastal areas can give negative impacts and caused marine pollution. It is necessary to predict and monitor pollution on marine and estuarine ecosystems. The concern of marine pollution is related to in instant and long-term damages to coastal and marine habitats and ecosystems (Valentukevičienė and Brannvall, 2008).

1.4.1 The Marine Phllutiñ

The pollution is disturbance of the natural state of the environment through anthropogenic activity. Pollution induces the loss of potential resources (Goldberg, 1992). Waters and sediments in such regions bear industrial and sewage discharges and polluted the echosystems (Hester and Harrison, 2000). The anthropogenic
sources of pollution are coming from urban storm water runoff and effluent discharge (Brown and Peake, 2006; Matthai, et al., 2002). Many contaminants have low water solubility and are particle-reactive (Olsen, et al., 1982). Contaminants are rapidly adsorbed to suspended sediment and organic matter and are scavenged from the water column through flocculation, coagulation and sedimentation (Hatje, et al., 2003; Honeyman and Santschi, 1988; Huh, et al., 1992).

1.5 Heavy Metal Pollution in Sediments

Heavy metals such as cadmium, mercury, lead, copper, and zinc, are regarded as serious marine pollutants because of their toxicity could incorporated into food chains and they have ability to remain in an environment for a long time (Puyate, et al., 2007).

The concentration of heavy metals in sediments influence by reduction/oxidation reactions, adsorption/desorption and physical transport or by addition to anthropogenic input (Basaham and El-Sayed, 1998). Toxic compounds of heavy metals are adsorbed either in their organic or inorganic forms (Forstner and Wittman, 1983; Kabata-Pendas, 2010). In particular, the heavy metal content of sediments comes from natural sources as well as anthropogenic sources such as manufacturing industries and agricultural activities (Guven, et al., 2008).

1.6 Definition of the Study Area

Malaysia is a coastal nation with a coastline length of 4809 km and rich in biodiversity and natural resources. The country is divided into two landmasses that are separated by the South China Sea. Peninsular Malaysia is located to the west of South China Sea with a coastline of 2031 km and the other part is East Malaysia, consisting of Sabah and Sarawak (Figure 1.1) (Radzi, 2009).

![Figure 1.1 A map showing the locations of the study area](image)

Sabah is the second largest state in Malaysia with the longest coastline of approximately 1743 km, that extends from 73,711 km², the border of Sarawak in the
Southwest to Indonesia in the Southeast, including all offshore islands that are part of the continental shelf of Southeast Asia (Abdul-Hadi, et al., 2013).

The coastline of Sabah borders the South China Sea on its west coast, the Sulu Sea on its east coast and the Sulawesi Sea on its Southeast coast, and is also part of South Asia Waters (Wyrtki, 1961). The study area of the coastal Sabah is shown in Figure 1.2. The total territorial water of Sabah is about 55,828 km², which extends to twelve nautical miles.

![Figure 1.2](hFDWLhQVhIWKH6hXWK&KLQD6XODQG6XODZHVL6HDVDOhQJWK)

Sabah has numerous islands that range in size from less than a hectare to several square kilometres. They are unsheltered rocky islands at varying distances from the shore, while others are sheltered muddy islands found in protected bays or in estuaries.

The west coast of Sabah is characterised by sandy beaches found from the tip at Kudat region in the north to Klias region in the South. The southern part of the Klias region has one of the few extensive areas of tidal wetlands (mangroves and nipah) on the west coast. Freshwater wetlands can be found in the coastal flatlands of the west coast, especially in Beaufort, Papar and Kota Balud (Mojiol, 2006).

Sabah has 19 river basins, with the Kinabatangan river basin on the East Coast as the largest basin covering an area of 15,385 km². This is followed by the Padas River on the West Coast, which is the second largest with an area of 8,726 km². Most of the other basins cover smaller areas (Juin, et al., 2000).
Sabah has eight major rivers including Padas, Pegalan, Papar and Mulau in the west, and Sugut, Labuk, Kinabatangan and Segama in the east. Figure 1.3 shows the major rivers that are flowing into the coastal areas of Sabah.

![Map of Sabah showing major rivers](image)

**Figure 1.3** MaMhUvers basins aOhQJWKhstaOhI6abah (AGhSvGIUhP’ anish &hhSratihQJhUEnviUhhQPrnt and DeveOhSPPrnt DANCED, 1996)

Rivers is the primary transport of suspended sediment, pollution and nutrients to enter the catchment areas. The significance of a river with respect to sediment, nutrient or pollution loading is dependent upon both the discharge of the river and the concentrations of various materials in the river water.

Sabah has a typical equatorial climate with constant temperature, considerable amount of rain and high humidity. The two prevailing monsoons in Sabah, which characterise the climate in this region, are the Northeast Monsoon and the Southwest Monsoon. The Northeast Monsoon predominates the months between November and March, whereas the Southwest Monsoon prevails during the months of May to September. In addition, there are also two successive inter-monsoons that occur from April to May and September to October.

**1.7 Significance of the Study**

The coastal zone of Sabah is an area of high economic significance, which is often subject to fast economic development, large population migrations and urban development. Among others, the attraction of the coast to human settlements is due to its proximity to the ocean’s living and non-living resources, as well as marine transportation and recreation.
The marine part of the coastal zone of Sabah is a very important and productive ecosystem (as it possesses some of the world’s richest ecosystems) because it is the Economic Exclusive Zone (EEZ), which covers approximately 54,360 km² or around 30% of the Malaysian EEZ. The major part of the area lies in the South China Sea, extending to the limit of the continental shelf off the West Coast of Sabah. To the South-East, off the east coast of Sabah between Semporna and Pulau Sebatik, the area is extended to the continental shelf boundary in the Sulawesi Sea. The remaining area between Semporna and Kudat is the Sulu Sea, with the Malaysia/Philippines international boundary. About 30% of the marine coastal zone, or approximately 54,360 km², is the territorial waters of Sabah.

To the Southwest, the marine coastal zone is delimited by the interstate boundary between Sarawak and Sabah in the Brunei Bay area and by the international boundary between the EEZ claims from Brunei and Malaysia, which extends from the coast all the way to the continental shelf. To the Southeast, the zone is delimited by the international boundaries between Malaysia and the Philippines, between Malaysia and Indonesia and the continental shelf (Macintosh and Nielsen, 1999).

Another significant of the marine part of the coastal zone of Sabah is associated to the people who live along the coast of Sabah. Sabah had a population of 3,117,405 in 2010 (Abdullah, 2013). The highest population concentrations were in major cities such as Kota Kinabalu, Tawau, Sandakan, Lahad Datu and Semporna, the five districts that accounted for approximately 50% of the total population. These areas become attraction of majority of illegal and unregistered settlements. In terms of land area, the five districts only represent around 22% of Sabah. This indication of population pressure on the coastal areas is likely to be strengthened considerably (Mojiol, 2006).

All the most populated towns are captured within the coastal zone of Sabah, namely, Kota Kinabalu, Sandakan, Tawau, Lahad Datu and Semporna. It is estimated that more than 75% of the population live and work in the coastal zone (Macintosh, et al., 1999). Meanwhile, the urban population growth exceeds the rural indicating a net migration towards the towns in Sabah. This leads to environmental impacts of urbanisation which need particular focus from a coastal management approach (Juin, et al., 2000).

The fisheries in Sabah are predominantly artisanal with more than 70% of the catches taking place within 30 nautical miles from the coast (Jaaman, et al., 2004). Tourism is an important and growing sector, which exerts a considerable pressure on coastal areas, particularly on the west coast and coral islands. Other sectors with significant impacts on coastal areas are forestry, mining that includes offshore oil and gas extraction, and transportation, all of which take place at considerable distances from the shoreline (Juin, et al., 2000).

It is obvious that the heavy and chemical industries, oil and gas-related industries and agriculture activities have developed rapidly along the coast of Sabah and this leads to contamination and pollution of the coastal marine sediments which are of anthropogenic sources of land-based and sea-based activities.
Due to the lack of elemental baseline data and inadequate information on the levels of heavy metals, major and trace elements, REEs and actinides in the coastal marine sediments of Sabah, more studies are needed to investigate the environmental impacts and management on the marine coastal zone of Sabah because of its highly significant and most productivity region in Malaysia.

Therefore, the scientific investigation on the coastal and offshore marine sediments is important to determine the implications of the status of contamination and pollution and the temporal changes of the modern sedimentation.

1.8 Problem Statement

Environmental problem in the coast of Sabah is very serious because it receives discharges from many rivers due to human activities and various industries. Most of the coastal agricultural and fishery resources, electronic, gas and heavy industries, agriculture, fishing, shipping activities and human population are concentrated on the west and east coasts of Sabah.

It is important to note that most environmental research has focused on the marine sediments in the coast of other regions in Malaysia (Din, 1995; Rezaee, et al., 2010; Seng, et al., 1987; Wood, 2001; Yap, et al., 2003a, 2003b). Therefore, more studies related to the environment is needed to be carried out because marine sediments provide useful information for reconstructing oceanographic conditions and environmental changes that took place in the past.

Along both the east and west coasts of Sabah, heavy and chemical industries, oil and gas industries and agriculture activities are developing rapidly in the recent years as compared to the past. Therefore, more research is needed to be conducted in this area due to insufficient baseline data available on the marine sediments along the coast of Sabah. Moreover, it is important to investigate and provide assessments of the elemental pollution degrees to determine pollution patterns in the coasts of Sabah using sediment samples as they provide useful information pertaining to marine pollution.

1.9 Scope of the Study

The coastal areas of Sabah are developing rapidly into important economic zones, where numerous significant industrial estates and industrial sectors are currently operating within the coastal zone of Sabah, where rubber, forest, and timber industries; chemical, petroleum products, chemical fertilizers, gas, electric, and oil platform industries; oil palm, fishery, and food industries; building materials and plastic industries are located. Among the various industrial sectors, the manufacturing sectors and the main types of manufacturing activities are one of the fastest growing activities in the coast of Sabah.

The combination of the anthropogenic activities due to various industrial and manufacturing sectors, with their direct links to human population that lead to municipal and urban solid wastes, makes the coastal marine environment of Sabah area particularly vulnerable to contaminations.
Thus, the scope of this study was to determine and provide the pollution patterns of vertical elemental distributions of heavy metals, trace elements, REEs and actinides, and assess possible contamination by pollutants in the aquatic ecosystems of the coastal Sabah as a result of waste discharges from both natural and anthropogenic origins.

1.10 Objectives of the Study

The goal of current study was to identify elemental distribution in core marine sediment of the coastal areas in Sabah. This information may provide the status of elemental pollution in the coast of Sabah, which can be acquired by analysing the core marine sediments using the INAA method by the Malaysian research reactor and ICP-MS method at the Nuclear Agency, Malaysia.

The objectives of this research are:

To determine the spatial and vertical distributions of mineral deposits in the coast of Sabah for identification of areas with elevated concentrations of mineral deposits contaminations in assessing the status of pollutants in this area. Details of the mineral deposits are summarised as follows:

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

To establish the baseline data for the above mineral deposits in the marine sediments of the coast of Sabah.

1.11 Outline of the Thesis

The thesis consists of five chapters which are respectively described in the following subsection:

The first chapter consists of the general introduction, which includes the background, significance and objectives of the study. The second chapter provides a review of literature in the field of study. This chapter discusses some previous researches that were done regionally on anthropogenic impact of marine sediments and their association with the present study.

The third chapter contains the theoretical part detailing the theoretical physics of nuclear reactions and the procedural aspects of instrumentation neutron activation analysis (INAA) and ICP-MS techniques. The fourth chapter is the methodology of collection, preparation and measurement procedures of marine sediment samples using INAA and ICP-MS.

The fifth chapter is the results and discussions on experimental results, data analyses and comparison of the results with established data. The final chapter is the conclusions for this research work and the recommendations for future work.
REFERENCES


Abdullah, S. J. H. OVERVIEW OF MUNICIPAL SOLID WASTE MANAGEMENT PRACTICES AND CHALLENGES IN SABAH: A REVIEW PAPER.


Censi, P., Mazzola, S., Sprovieri, M., Bonanno, A., Patti, B., Puntuero, R., et al. (2004). Rare earth elements distribution in seawater and suspended


Elias, M., and Hamzah, M. Assessment of Sediment Quality Collected from Tunku Abdul Rahman Park, Sabah.


matter under diagenetic or hydrothermal conditions. *Geochimica et Cosmochimica Acta*. 48(11), 2321-2329.


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