

VERTICAL DISTRIBUTIONS OF ZINC, CADMIUM, LEAD AND COPPER IN SEDIMENTS OF SELECTED COASTAL AREAS IN THE WEST COAST OF PENINSULAR MALAYSIA



NAZERITA LASUMIN

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

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DEDICATION

My beloved parents and family, supervisor and fellow friends who endlessly provide their mental, spiritual, and financial support until the completion of this thesis.



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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

VERTICAL DISTRIBUTIONS OF ZINC, CADMIUM, LEAD AND COPPER IN SEDIMENTS OF SELECTED COASTAL AREAS IN THE WEST COAST OF PENINSULAR MALAYSIA

By

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July 2020

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A comprehensive study on sediment profile is important in comprehending the historical condition of sediment degradation by heavy metal content elevation caused by anthropogenic activities such as agricultural practices, urbanization, and industries such as tourism. The extraction of heavy metals in sediment particularly in getting measurement with good accuracy and precision is challenging, hence, this study includes the optimization of heavy metals extraction in sediment through acid digestion, assessing sediment quality from Sungai Buloh, Bagan Pasir estuary, and Kampung Baharu coastline through the determination of heavy metal profiles, and analyzing data using pollution indices. The optimization of metals namely zinc (Zn), cadmium (Cd), lead (Pb), and copper (Cu) extractions from Certified Reference Material, BCR®-667 of Estuarine Sediment was carried out to get good metals recoveries with Differential Pulse Stripping Voltammetry (DPSV) and Inductive Coupled Plasma-Mass Spectrometry (ICP-MS) determination. The recovery values determined by DPSV and ICP-MS ranged from 18.85-154.38% and 75.28-90.13%, respectively, where Zn, Cd, Pb, and Cu were simultaneously measured in BCR®-667. The mixture of hydrochloric acid, nitric acid, and hydrofluoric acid coupled with ICP-MS determination was selected as the best method and employed to assess the status of Zn, Cd, Pb, Cu distribution in core sediments of Bagan Pasir estuary, Sungai Buloh, and the coastline of Kampung Baharu, Port Dickson. Based on the vertical profiles of heavy metals concentrations, the order of metals in decreasing manner was Zn>Pb>Cu>Cd in Bagan Pasir estuary and Sungai Buloh stations, while Zn>Cu>Pb>Cd in Kampung Baharu, Port Dickson. Most of the means of the analyzed metals were below Interim Sediment Quality Guidelines and the effect range-low (ERL) in all sampling locations except for Cu in Kampung Baharu coastline and Zn in Sungai Buloh where their concentrations ranges were between the ERL and effect range-median (ERM). The results of geo-accumulation index,

contamination factor and pollution load index classified the sediment quality as not polluted with studied metals with the exception of the element Pb at certain depths of the sediment cores as well as historical pollution at bottom sediment of SB2 sediment core. Therefore, heavy metal concentration in the sediments of these three areas were not at an alarming stage, however, requires regular monitoring from the authorities to maintain sustainable management of these areas.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

TABURAN MENEGAK ZINK, KADMIUM, PLUMBUM, DAN KUPRUM DI DALAM SEDIMEN TERPILIH PANTAI BARAT SEMENANJUNG MALAYSIA

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Penyelidikan menyeluruh terhadap profil sedimen adalah penting untuk mengetahui sejarah degradasi sedimen disebabkan oleh penambahan terutamanya disebabkan kepekatan logam yang oleh aktiviti-aktiviti antropogenik sepertiaktiviti pertanian, perbandaran, dan industri seperti pelancongan. Pengekstrakan logam berat terutamanya dalam mendapatkan ukuran yang tepat adalah mencabar, oleh itu, penyelidikan ini merangkumi pengoptimuman pengekstrakan logam berat daripada sedimen melalui pencernaan asid, menilai kualiti sedimen dari Sungai Buloh, kuala Bagan Pasir, and persisiran pantai Kampung Baharu melalui profil logam berat, dan menganalisis data menggunakan indeks-indeks pencemaran. Pengoptimuman pengekstrakan logam berat zink (Zn), cadmium (Cd), plumbum (Pb), kuprum (Cu) daripada Bahan Rujukan Bersijil, BCR®-667 Estuarine Sediment telah dijalankan untuk mendapatkan perolehan logam berat yang baik dengan menggunakan penentuan Differential Pulse Stripping Voltammetry (DPSV) dan Inductive Coupled Plasma-Mass Spectrometry (ICP-MS). Nilai perolehan yang ditentukan oleh DPSV dan ICP-MS masing-masing adalah dalam julat dari 18.85-154.38% dan75.28-90.13% di mana Zn, Cd, Pb, dan Cu telah diukur secara serentak di dalam BCR®-667. Campuran asid hidroklorik, asid nitrik, dan asid hidrofluorik bersama penggunaan ICP-MS telah dipilih sebagai kaedah vang terbaik serta digunakan untuk menilai status taburan Zn, Cd, Pb, Cu di dalam sediment core kuala Bagan Pasir, Sungai Buloh dan pantai Kampung Baharu, Port Dickson. Berdasarkan profil menegak kepekatan logam berat, sususan kepekatan logam berat secara menurun adalah Zn>Pb>Cu>Cd di kuala Bagan Pasir dan Sungai Buloh, manakala Zn>Cu>Pb>Cd di Kampung Baharu, Port Dickson. Kebanyakan purata kepekatan logam yang dianalisis adalah di bawah nilai Interim Sediment Quality Guidelines dan effect range-low (ERL)di semua lokasi persampelan kecuali Cu di pantai Kampung Baharu dan Zn di Sungai Buloh yang mana nilai kepekatannya terletak di antara (ERL) dan effect range-median (ERM)Keputusan dari indeks geoakumulasi, faktor pencemaran dan indeks beban pencemaran mengkelaskan kualiti sedimen sebagai tidak tercemar dengan logam berat yang dikaji kecuali elemen Pb pada beberapa kedalaman di dalam *sediment core* serta pencemaran terdahulu pada bahagian dasar *sediment core* SB2. Oleh itu, kepekatan logam berat di dalam sedimen di kawasan-kawasan ini adalah tidak membimbangkan tetapi perlu pemantauan teratur daripada pihak-pihak berkuasa untuk tujuan pengekalan pengurusan lestari kawasan-kawasan tersebut.



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LIST OF ABBREVIATIONS

Zn	Zinc
AI	Aluminium
Cd	Cadmium
Pb	Lead
Cu	Copper
Ni	Nickel
Cr	Chromium
Hg	Mercury
Fe	Iron
V	Vanadium
Со	Cobalt
Ag	Silver
Bi	Bismuth
Sn	Tin
ТІ	Thallium
g.cm ⁻³	Gram per Cubic Centimetre
mg.kg ⁻¹	Milligram per Kilogram
ug.g ⁻¹	Microgram per Gram
mg/L	Milligram per Litre
PTFE-Bombs	Polytetrafluoroethylene
SRM	Standard Reference Material
CRM	Certified Reference Material
BCR	Community Bureau of Reference
GIS	Geographical Information System

- USEPA United State Environmental Protection Agency
- FAO Food and Agriculture Organization
- HCI Hydrochloric acid
- HNO₃ Nitric acid
- HF Hydrofluoric acid
- HClO₄ Perchloric acid
- H₂SO₄ Sulphuric acid
- H₂O₂ Hydrogen peroxide
- KCI Potassium Chloride
- I(A) Current
- U(V) Voltage
- SET Sequential Extraction Technique
- FIZ Free Industrial Zone
- EEZ Exclusive Economic Zone
- EF Enrichment Factor
- Igeo Geoaccumulation Index
- CF Contamination Factor
- Cd Degree of Contamination
- Er Potential Risk for Individual Metal
- PERI Potential Ecological Risk Index
- PLI Pollution Load Index
- CPI Combined Pollution Index
- SQGs Sediment Quality Guidelines
- CCME Le Conseil Canadien des Ministres de L'environnement
- ICP-MS Coupled Plasma Mass Spectrometry

- AAS Atomic Absorption Spectroscopy
- ICP-OES Inductively Coupled Plasma Optical Emission Spectrometry
- PM₁₀ Particulate Matter
- DPSV Differential Pulse Stripping Voltammetry
- IRMM Institute for Reference Materials and Measurements
- HMDE Hanging Mercury Drop Electrode
- WE Working Electrode
- AE Auxiliary Electrode
- SD Standard Deviation
- ERL Effective Range Low
- ERM Effective range Median
- ISQG Interim Sediment Quality Guidelines
- ANOVA Analysis of Variance

CHAPTER 1

INTRODUCTION

1.1 Background

For the past centuries, elevation of heavy metals concentration has been threatening us due to its tenacity in the environment and their potential toxicity and bioavailability (Idriss & Ahmad, 2013; Xu et al., 2017). In response to population growth and anthropogenic activities, heavy metal pollution has become a great worldwide concern as their input to the coastal areas particularly in developing countries are exponentially increasing (Hamzan et al., 2015). Urbanizations, industrialization, shipping activities, and domestic wastes are the major sources for the contamination to occur (Elias et al., 2018). Metals are usually bound to particulate matter when discharged into the aquatic system eventually settled and incorporated into the sediment (Khodami et al., 2017) through the processes of precipitation, diffusion, chemical reactions or biological activity and adsorption (Idriss & Ahmad, 2013; Tavakoly Sany et al., 2013).

The settling of heavy metals in sediment could become secondary or point source of metals from the remobilization of heavy metals resulted from the sediment mixing at the sediment-seawater interface level (Turki, 2007). Eventually, the re-suspended heavy metals will be taken up by aquatic organisms that have direct contact with contaminated sediment (Pejman et al., 2015) and subsequently, human health is to be affected (Yap et al., 2002). As in many developing countries, the Malaysian coastal zone has experienced severe deterioration as a result of pollution (Buhari & Ismail, 2016). As the final destination of considerable pollutant input from the land, coastal areas became an active targets for the study of heavy metals changes in the marine environment (Al-Mur et al., 2017; Nawrot et al., 2019). Furthermore, studying the metals distribution in sediments next to industrial and residential zones could provide researchers with indications of the anthropogenic effects on ecosystems, while assisting in assessing the potential risks with the disposal of human waste (Tiwari et al., 2013).

Therefore, continuous researches of metals content in the marine environment are crucial for the following reasons; to assess the risks of environmental health, to understand the heavy metals distribution, to identify the problem, causes and solution relating to the contamination of heavy metals, to monitor and mitigate industrial development, to manage river developments, to control the sustainable future usage of the river water, to provide scientific references for protecting the relative local aquatic environment, and ultimately to protect human from the deleterious effect of heavy metals (Khodami et al., 2017; Wang et al., 2017; Wong et al., 2017; Xu et al., 2017). The inclusive study of the ecotoxicology of the deadly heavy metals and metalloids and the environmental chemistry confirms that we should act to minimize the implication of heavy metals to the environment and humans (Ali et al., 2019).

1.2 Problem statements

The surrounding anthropogenic activities of Bagan Pasir, Sungai Buloh, and Port Dickson varied from agriculture, urban, and tourism industry as well as port activities (Abdullah et al., 2012; Kadhum at el., 2016; Ramli et al., 2013). Sediment in these areas are expected to have the risk of degradation if the nearby lands are not regularly monitored and sustainably managed (Redzwan et al., 2014). The degradation of sediment quality poses an unfavourable effect to the aquatic organisms such as blood cockles. The production rate of blood cockles declined from 40,000 tons in 2010 to 25,000 in 2011 (Yurimoto et al.. 2014). High amount of ammonia in water, low food availability as well as freshwater flooding associated in changing environments (Yurimoto et al., 2014) were reported to be the potential factors that had affected the production of blood cockles (Ramli et al., 2013). Nonetheless, information on heavy metals pollution level of these sites are scarce and still requires studies to be executed because the main factor has yet to be confirmed due to the constantly changing environment in cockles breeding grounds (Harith et al., 2016). In addition, it is crucial to have good condition of cockles breeding ground because heavy metals tend to be accumulated in blood cockles whole body tissue and this poses a threat to human beings (Yurimoto et al., 2014) and this makes it is unarguably important to study heavy metal levels in the sediment. Despite some heavy metals are essential to humans such as zinc and copper, excess of these metals pose threat to human health (Nriagu, 2011). Whereas, non-essential heavy metals such as cadmium and lead provide harmful effects even in trace amount (Wani et al., 2015). Which is why study on these four metals is important to emphasize.

Coastal degradation is inevitable as the activities in its surrounding continue to increase. For example, the ruined of the beaches of Port Dickson's natural surrounding from the effects of the tourism industry (Nair et al., 2016). The building of beach resorts, and related services to meet the needs of the tourism industry in Port Dickson had given the authorities hard times to restore the beaches to its natural beauty and still is (Abdullah et al., 2012; Nair et al, 2016). Coastal area contamination in Malaysia is yet to be controlled nor completely reported, despite the constant monitoring by the authority (Redzwan et al., 2014). Hence, there should be ongoing studies on the status of pollution in these areas so the data could be utilized as scientific references in the future for a sustainable management to be maintained.

Sediment cores was chosen instead of surface sediment in the present study because studies on sediments at depths greater than 5cm are still very limited in Malaysia despite the valuable information that can be extracted from core sediment. The recent and historic contamination can be extracted from sediment core (Nartey et al., 2019) and when coupled with dating analysis, it

provided us to historical evidence of anthropogenic effect in the aquatic environment (Al-Mur et al., 2017; Natesan & Ranga, 2011; Yusoff et al., 2015).

1.3 Objectives

The general objective of this study is to identify the status of heavy metals distribution at a few selected sites along the west coast of Peninsular Malaysia. To achieve the main goal, the scope of study includes specific objectives as follow;

i) Determination of Zinc, Cadmium, Lead, and Copper distributions in sediment profiles from Bagan Pasir Estuary, Sungai Buloh, Selangor, and Kampung Baharu coastline, Port Dickson.

ii) Assessment of Zinc, Cadmium, Lead, and Copper pollution status with pollution indices in selected study sites.

1.4 Research Questions

Based on the objectives of study, the research questions were as follows;

- a) What is the level of Zn, Cd, Pb, and Cu in sediment cores of Bagan Pasir estuary, Sungai Buloh, and Kampung Baharu coastline?
- b) What is the status of studied heavy metals pollution in these areas?

1.5 Significance of study

The study managed to determine all metals of interest throughout the sediment cores and assessed their pollution status. The established vertical profiles of Zn, Cd, Pb, and Cu in sediment of Bagan Pasir estuary, Sungai Buloh, Selangor, and coastline of Kampung Baharu, Port Dickson could serve as scientific references for further sustainable management of the studied areas. The heavy metals vertical profiles successfully determined, however due to financial constraint, the study did not manage to perform sediment dating.

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