



UNIVERSITI PUTRA MALAYSIA

***HEAVY METAL DISTRIBUTION, MOBILITY AND RISK ASSESSMENT IN
SURFACE SEDIMENT OF SUNGAI PULOH IN SELANGOR, MALAYSIA***

USMAN SADIQ ABUBAKAR

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MALAYSIA**

By

USMAN SADIQ ABUBAKAR

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

February 2018

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DEDICATION

This work is dedicated to Almighty Allah (SWT) and to my lovely parent, Alhaji Abubakar Sadiq Jagindi and Hajiya Hauwa'u Abubakar for their love, support, resilience, patience and understanding.



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

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USMAN SADIQ ABUBAKAR

February 2018

Chairman : Syaizwan Zahmir Zulkifli, PhD
Faculty : Science

Sungai Puloh is a mangrove swamp area plagued with industrial, agricultural and other commercial activities and has a direct small link to the straits of Malacca. It is surrounded by industries including steel and paint manufacturing companies, car repair shops etc. Heavy metals (HMs) are environmental pollutants whose sources are both natural and anthropogenic. Heavy metals bioavailability and mobility is affected by physical, chemical and biological factors among which are organic matter and sediment characteristics. Organic matter and particle size distribution play a significant role in the fate of HM in the sediment, and consequently the river. The aims and objectives therefore, are to investigate the concentration of some selected HMs (Cu, Zn, Ni, Cd and Pb) in the surface sediment of Sg. Puloh, determine organic matter content and particle size distribution as well as assess the degree of HM contamination/risk by means of pollution indices evaluation namely: risk assessment code (RAC), geoaccumulation Index (I_{geo}), contamination factor (CF) and pollution load index (PLI). Sequential extraction technique SET and Aqua regia digestion were performed using Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer 800) for heavy metal concentration. Loss on ignition and pipette method of analyses were employed for the determination of organic matter content and particle size respectively. SPSS statistical package version 22 was used to determine correlation, significance or otherwise of heavy metals concentration. Heavy metals concentrations for Cu, Zn, Ni, Cd and Pb were found between 83.05-202.34, 405.39-755.04, 114.67-226.90, 0.53-3.06 and 95.19-225.47 $\mu\text{g/g}$ respectively. Grain size analysis revealed clay in the sediment at between 52.89-60.16, silt 25.38-35.99 and sand 4.68-14.42%. Organic matter content ranged between 38.45-46.90%. Correlation between grain size and total metal concentration revealed was significant for Cd, Cu, and Ni ($r = 0.657^*$, $r = 0.705^*$ and $r = 0.682^*$) respectively. Kruskal Wallis' nonparametric test revealed significant difference in heavy metals concentrations ($P < 0.01$, $P < 0.05$). Risk

assessment code RAC showed medium (RAC= 11-30) to very high risk (RAC > 50) with Pb posing the highest risk. Geoaccumulation index, Cd highest in S5 (I_{geo}) = 3 while Cu lowest (I_{geo})= 0.2 in S2. Contamination factor (CF), Zn and Pb highest, Ni and Cu lowest. Pollution load index showed values greater than 1 (PLI > 1), indicating high level of pollution. Sediment of Sg. Puloh has high contamination of HM and the source are both from natural and anthropogenic. The presence of heavy metals in the residual fraction confirms that some of the heavy metals come from natural source. From the result obtained, it can be concluded that Sg. Puloh is highly polluted. All the stations have shown high level of heavy metal concentration from both natural and anthropogenic sources, high organic matter content from a sediment that is characteristically clay. Pollution indices have also indicated high contamination, especially in S5, S3 and S4. This can be attributed to the cited industries nearby, agriculture and other activities.



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

**TABURAN, MOBILITI DAN PENILAIAN RISIKO LOGAM BERAT
DALAM SEDIMEN PERMUKAAN DI SUNGAI PULOH, SELANGOR,
MALAYSIA**

Oleh

USMAN SADIQ ABUBAKAR

Februari 2018

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Sungai Puloh adalah sebuah paya bakau yang telah diancam oleh pelbagai aktiviti industri, pertanian dan komersial lain serta mempunyai sebuah hubungan terus dengan Selat Melaka. Ia dikelilingi oleh kawasan industri seperti syarikat logam dan pembuatan, bengkel pembaikan kereta dsb. Logam berat (HMs) adalah bahan pencemar alam sekitar yang berasal dari sumber semulajadi dan antropogenik. Bioketersediaan dan mobility logam berat adalah dipengaruhi oleh factor-faktor fizikal, kimia dan biologi, yang merangkumi bahan organik dan ciri-ciri sedimen. Taburan bahan organik dan saiz butiran memainkan fungsi yang ketara kepada ketentuan HMs dalam sedimen dan seterusnya kepada sungai. Oleh itu, objektif kajian ini adalah untuk menyelidik kepekatan HMs terpilih (Cu, Zn, Ni, Cd dan Pb) dalam sedimen permukaan Sungai Puloh, menentukan kandungan bahan organik dan saiz butiran, serta tahap pencemaran/risiko HMs dari sudut penilaian indeks pencemaran yang termasuk: tata penilaian risiko (RAC), indeks geopengumpulan (*I_{geo}*), faktor pencemaran (CF) dan indeks beban pencemaran (PLI). Teknik pengekstrakan berjujukan SET dan pencernaan akua regia telah digunakan untuk mencerna sampel. Sebuah spektrofotometer serapan atom (AAS) (PerkinElmer AAnalyst 800) telah digunakan untuk menentukan kepekatan logam berat. Kehilangan akibat pencucuhan dan kaedah pipet telah digunakan untuk menentukan kandungan jirim organik dan saiz butiran. Pakej statistic SPSS versi 22 telah digunakan bagi menentukan kolerasi, keertian atau sebaliknya bagi logam berat dengan beberapa parameter. Kepekatan logam berat Cu, Zn, Ni, cd dan Pb telah didapati antara 83.05-202.34, 405.39-755.04, 114.67-226.90, 0.53-3.06 and 95.19-225.47 $\mu\text{g/g}$. Analisis saiz butiran menunjukkan bahawa liat dalam sedimen adalah antara 52.89-60.16, kelodak 25.38-35.99 and pasir 4.68-14.42 $\mu\text{g/g}$. Kandungan jirim organik pula berjujut antara 38.45-46.90%. Kolerasi antara saiz butiran dan jumlah kepekatan logam Cd, Cu dan Ni telah ditunjukkan signifikan ($r = 0.657^*$, $r = 0.705^*$ and $r = 0.682^*$). Ujian Kuruskal Wallis

tanpa parameter menunjukkan perbezaan beerti dalam kepekatan logam berat ($P < 0.01$, $P < 0.05$). tata penilaian risiko RAC menunjukkan sederhana ($RAC = 11 - 30$) hingga risiko sangat tinggi ($RAC > 50$) dengan Pb memberikan risiko tertinggi. Bagi indeks geopengumpulan, Cd adalah tertinggi di S5 ($I_{geo} = 3$), manakala Cu paling rendah ($I_{geo} = 0.2$) di S2. Bagi faktor pencemaran (CF), Zn dan Pb adalah tertinggi, Ni dan Cu adalah terendah. Indeks beban pencemaran pula menunjukkan nilai melebihi 1 ($PLI > 1$), yang menunjukkan pencemaran peringkat tinggi. Sedimen Sg Puloh mempunyai pencemaran HM yang tinggi dan sumber adalah dari kedua-dua semulajadi dan antropogenik. Kehadiran logam berat di peringkat baki membuktikan bahawa sebahagian logam berat berasal dari sumber semulajadi. Daripada keputusan yang dieprolehi, Sg. Puloh boleh disimpulkan mengalami pencemaran yang tinggi. Semua stesen menunjukkan kepekatan logam berat yang tinggi bagi kedua-dua sumber semulajadi dan antropogenik, kandungan jrim organik yang tinggi bagi sedimen berjenis liat. Indeks-indeks pencemaran juga menunjukkan pencemaran yang tinggi, terutamanya di S5, S3 dan S4. Ini adalah disebabkan kehadiran aktiviti-aktiviti industri, pertanian dan lain-lain berhampiran kawasan tersebut.

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I certify that a Thesis Examination Committee has met on 9 February 2018 to conduct the final examination of Usman Sadiq Abubakar on his thesis entitled "Heavy Metal Distribution, Mobility and Risk Assessment in Surface Sediment of Sungai Puloh in Selangor, Malaysia" 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 Master of Science.

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LIST OF ABBREVIATIONS

AMD	Acid Mines Drainage
ANOVA	Analysis Of Variance
ATSDR	Agency for Toxic Substances and Disease Registry
B _n	Background value of metals
CF	Contamination Factor
C _n	Concentration of a metal
Co	Company
CNS	Central Nervous System
DDW	Double Distilled Water
DNA	Deoxyribonucleic Acid
dw	Dry Weight
EFLE	Easily and freely leachable or exchangeable
EPA	Environmental Protection Agency
FEDRIP	Federal Research in Progress
F	Fraction
g/cm ³	Gram Per Centimeters Cube
GPS	Global Positioning System
<i>I_{geo}</i>	Geoaccumulation Index
IZA	International Zinc Association
Km ²	Kilometer Square
LOI	Loss on Ignition
Ltd	Limited
M _A	Mass of burnt sample (Ash)
M _D	Mass of Dry sample

Mo	Mass of organic matter
M _{PDS}	Mass of Porcelain and Dry Sample
Mg/Kg	Miligram per Kilogram
n	Number
NB	Note Before
NEM	Northeast Monsoon
OM	Organic Matter
PCA	Principal Component Analysis
PC	Principal Component
PLI	Pollution Load Index
PNS	Peripheral Nervous System
RAC	Risk Assessment Code
S	Sites
SE	Standard Error
SET	Sequential Extraction Technique
Sg	Sungai
SPSS	Statistical Package for Social Sciences
SWM	Southwest Monsoon
UPM	Universiti Putra Malaysia
USDI	United State Department of Interior
°C	Degree Celsius
μ	Micro
%	Percentage

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Malaysia is a tropical rainforest region and traditionally, agricultural-based country but transformed gradually into a multi-sector economy, especially in the direction of electrical and electronic appliances industries. It is rich in natural resources, given its significant land mass of mangroves which are highly complex, diverse and productive. It geographically lies above the equator between 2° and 8° N and it is divided into West and East by South China Sea with total land area of 329,350 km². West Malaysia has a land mass of 131,573 km² with characteristically extensive coastal plains topographically. Generally, the temperature of west Malaysia ranges from 23-31 °C and rainfall throughout the year with high humidity. The heaviest rain being experienced around October to December. The coastal nature of the region has made it prone to environmental pollution.

Coastal environments have been identified as reservoirs of waste materials especially in sediment, coming from both anthropogenic and natural source (Song, Choi, Lee, & Jang, 2014). It is also very rich in natural resources and diverse economic activities (Looi, Aris, Wan Johari, Yusoff, & Hashim, 2013). The coastal marine sediment is composed of a mixture of complex organic compounds whose origins are terrestrial and marine sources. Coastal zones are known for its capacity to trap reasonable amount of organic matter from both anthropogenic as well as natural sources through the activities of physical, chemical and biological phenomena (Gao, Chen, & Bay, 2012). A considerable portion of the coastal area is made up of mangrove, with a sediment generally consisting of sandy and muddy deposit and also plays a major role in the overall fluxes of heavy metals in coastal systems as source of metals and/or sink (Sakellari, Plavšić, Karavoltos, Dassenakis, & Scoullas, 2011; Song et al., 2014). Mangroves are specific intertidal ecosystems covering between 160,000 and 200,000 km² along more than 70 percent of tropical and subtropical coastline (Marchand, Allenbach, & Lallier-Vergès, 2011). It comprises of close to 80 percent species worldwide from around 20 families of vascular plants. It is one of the most productive ecosystems with high level of biodiversity (Marchand et al., 2011).

Heavy metals pollution in Malaysia has been on the increase in recent times as a result of activities of many kinds, arising from urban development, agricultural activities, intense industrial as well as water transportation (Khodami, Surif, W.O., & Daryanabard, 2017). Heavy metals are characteristically toxic in high concentration, persistent and non-biodegradable with the tendencies of bioaccumulation and biomagnification in the environment (Lim, Choi, Shin, Jeong, & Jung, 2013). Most of these activities are far more intense in the west coast of Peninsular Malaysia with over 60% of the total Malaysian population living in this area, coupled with the fact that

most developmental projects as well as industrialization are being carried out. It is therefore imperative to investigate the distribution and the degree of heavy metal pollution as this will help in providing desired information for bioavailability, transportation and accumulation of pollutants which in turn will help with information required for coast utilization and supervision (Armynot du Châtelet, Bout-Roumazeilles, Riboulleau, & Trentesaux, 2009; Hu et al., 2013). Several activities have prompted interest and needs to embark on intense environment assessment along the west coast of Peninsula Malaysia. This may include but not limited to the following characteristics: (1) dense population more than any other region in Malaysia, (2) It is the most industrialized area, (3) It has many flowing rivers within, and (4) The straits of Malacca, which is said to be one of the most important shipping lane in the world, is also part of the west coast of Malaysia (Yap, Ismail, Tan, & Omar, 2002a).

Industrial/manufacturing activities have no doubt large implications toward natural environment. It enhances development, creating wealth and generally improving on the life of people. However, it usually comes with serious ramifications, resulting to environmental degradation. Interactions between manufacturing activities and natural environment create enormous unfavourable environmental condition due to inevitable release of pollutants (Nagajyoti, Lee, & Sreekanth, 2010).

Sungai Puloh is a small town located not far from Klang. Like Klang, Sungai Puloh also has a few industries cited and numerous human activities, ranging from car and motorcycle workshops, agriculture and several other small and medium scale businesses. There is also the problem of land clearing for municipal development. Sungai Puloh is in mangrove area and the river runs from communities and meanders through the mangrove, down to the strait of Malacca. This river receives wastes due to the human activities and most likely natural given that it is a mangrove area. It is therefore imperative that its pollution status is known and closely monitored.

1.2 Problem Statement

Human and industrial activities are very common in and around Sungai Puloh area with attendant wastes generation that may, in high level, pose a great risk to biota. Heavy metal pollution occurs via waste generation through industrial, agricultural as well as other human activities, like municipal wastes deposition. Mangrove environments are known to be characteristically rich in biodiversity and therefore prone to human and natural activities. These activities usually result in waste generation and potentially pollute the environment. Organic matter is one of the wastes components that associates highly with heavy metals. Other sediment characteristics, example grain size equally influence the distribution and transport of heavy metals within the water system. This river is important because of its strategic location, providing an avenue for fishing and other farming activities. However, possible contamination from the surrounding industries, workshop also, excessive fertilizer and pesticides application could contaminate the fish and other aquatic organisms carried

and deposited into the river. This could ultimately affect human since human consumes the fish that are likely contaminated from the river.

1.3 Aim and Objectives

1. To investigate heavy metal concentration in Sungai Puloh, Selangor
2. To determine the impact of anthropogenic activities and potential mobility of heavy metals in the sediment of Sungai Puloh by estimating the level of organic matter and particle size on the distribution and mobility
3. To assess the risks pose by heavy metals to the biota in the area through risk assessment code (RAC), contamination factor (CF), Geoaccumulation Index and Pollution load index (PLI)



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