THE DETERMINATION OF HEAVY METALS IN SELECTED MANGROVE PLANTS IN AN ESTUARINE ENVIRONMENT

NORASYIKIN BINTI SUHAILI

This project is submitted in partial fulfillment of the requirements for the degree of Bachelor of Science with Honours.

Department of Chemistry
Faculty of Resource Science and Technology
University Malaysia Sarawak
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DECLARATION

No portion of work referred to in this dissertation has been submitted in support of an application for another degree or qualification of this or any other university or institution of higher learning.

Norasyikin Binti Suhaili

Resource Chemistry Program (2005-2008)

Department of Chemistry

Faculty of Resource Science and Technology

University Malaysia Sarawak

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The Determination of Heavy Metals in Selected Mangrove Plants in an Estuarine Environment

Norasyikin Binti Suhaili

Resource Chemistry
Faculty of Resource Science and Technology
University Malaysia Sarawak

ABSTRACT

The aim of this study was to determine the heavy metals in the selected mangrove plants i.e. *Avicennia* sp. and *Sonneratia* sp. in the estuarine environment. The analysis of heavy metals was done in their roots, barks and leaves tissues and also sediment at the base of the mangrove plant analysed. The heavy metal studied were manganese (Mn), zinc (Zn), iron (Fe) and cadmium (Cd) and were analyzed using Atomic Absorption Spectroscopy (AAS). The findings of this study showed that Fe has highest concentration in all plant tissues followed by Mn, Zn and Cd. The mean concentrations of heavy metals in the plant tissues were according to descending order: Fe > Mn > Zn > Cd. Meanwhile, the mean concentrations of heavy metals were found in the sediment were according to descending order: Fe > Zn > Mn > Cd. Cd and Zn in the sediment in some study might be classified as heavily polluted.

Key words: Heavy Metals, estuarine, mangrove plant, sediment, plant tissues

ABSTRAK

Kajian ini dijalankan bertujuan untuk menentukan kandungan logam berat di dalam pokok bakau iaitu Avicennia sp. dan Sonneratia sp. di kawasan persekitaran muara. Analisis kandungan logam berat dilakukan pada sampel akar, kulit kayu dan daun dan juga sedimen di bahagian dasar pokok bakau. Unsur yang telah dikaji adalah mangan (Mn), zink (Zn), besi (Fe) dan cadmium (Cd) dianalisis menggunakan Atomic Absortion Spectroscopy (AAS). Hasilan kajian ini menunjukkan bahawa kandungan logam berat bagi Fe adalah yang paling tinggi di dalam semua tisu tumbuhan diikuti oleh Mn, Zn dan Cd. Purata kandungan logam berat yang dijumpai di dalam tisu tumbuhan mengikut turutan menurun adalah: Fe > Mn > Zn > Cd. Manakala, purata kandungan logam berat yang ditemui di dalam sedimen di bahagian dasar pokok bakau mengikut turutan menurun adalah: Fe > Zn > Mn > Cd. Cd dan Zn di dalam sedimen boleh dikelaskan sebagai tercemar.

Kata kunci: Logam berat, muara, pokok bakau, sedimen, tisu tumbuhan

CHAPTER ONE

INTRODUCTION

Malaysia has many types of wetlands such as peat swamps, mangrove swamps, mudflats, freshwater swamps and marshes. Large tracks of mangrove swamps are found in estuarine areas. One of these is at the Sg. Sarawak estuary at Muara Tebas.

The heavy metals are known for their toxicity to living things. They are particularly of concern because of their environment persistence and biogeochemical recycling and ecological risks (Liu *et al*., 2003). If the concentrations of these heavy metals are higher than the normal concentrations they present an environmental hazard.

Estuaries and nearshore oceanic waters are susceptible to a multitude of human wastes from a burgeoning population in the coastal zones (Turner *et al*., 1988). These high sensitive ecosystems serve as repositories for dredge spoils, sewage sludge and industrial and municipal effluents (Pomeroy, 1984). Sg. Sarawak and its tributaries in Kuching receive sewage and wastewater from a wide variety of sources in Kuching including households, food outlets, and industries (Polvsen *et al*., 2001) which flows to the sea at the Sungai Sarawak estuary. Therefore, as the heavy metals in these wastes are deposited in the estuarine sediment, they are able to effect the vegetation in the mangrove forest.

1.1 Objective

No studies on heavy metals in mangrove plants in the estuarine environment of the Muara Tebas estuary have been found. This study determined the heavy metals in selected mangrove plants in the Muara Tebas estuary area. The *Avicennia* sp., known as the black mangrove, and *Sonneratia* sp., known as mangrove apple were investigated for their heavy metals content.

CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy Metals and Toxicity

2.1.1 Heavy Metals

Heavy metals or trace metals is the term applied to a large group of trace elements which are both industrially and biologically important. Although not completely satisfactory from a chemical point of view, 'heavy metals' is the most widely recognized and used term for the large group of elements with an atomic atom greater than 6 g/cm^3 (Alloway, 1995).

These metals are referred to, by ecotoxicologist, as heavy metals because they are harmful and cause problems to the environment. Metals categorized in this group are Cd, Hg, Zn, Cu, Ni, Cr, Co, Pb, V, Ti, Fe, Mn, Ag, Sn and also include the metalloids such as As and Si (Francis, 1994).

2.1.2 Toxicity of Heavy Metals

All trace elements are toxic to living organisms when present in excess (Alloway, 1995). According to Thornton (1981), some of these elements are essential for plants but if taken in a large concentration, they may be toxic to the plants or affect the quality of foodstuffs for human consumption. These potentially toxic elements include arsenic, boron,

cadmium, copper, fluorine, lead, mercury, molybdenum, nickel, selenium and zinc (Thornton, 1981).

Heavy metals do not exist in a soluble form for a long time in water but they are present as suspended colloids or are fixed by organic and mineral substances. Thus their concentration in bottom sediments or in plankton is most often an adequate indication of water pollution by trace metals (Kabata-Pendias and Pendias, 1992).

2.2 Estuarine Environment

2.2.1 Estuary

An estuary is a partly enclosed body of water where fresh water coming down to the river and mixed with salt water from the sea. Estuaries have for long been important to mankind, either as place of navigation, or as locations on their banks for town and cities (McLusky, 1989). Estuaries play an important role in the transfer of pollutants, including trace metals, from continent to ocean. They are mixing-zones between marine, coastal and fluvial waters, and therefore are considered as reactive zones for fluvial inputs (Shink, 1981). Estuaries are among the most productive ecosystems an earth, being crucial to the life history of many species (Chapman and Wong, 2000).

The estuary environment is characterized by having a constantly changing mixture of salt and fresh water, and by being dominated by fine sedimentary material carried into the estuary from the sea and from rivers which accumulates in the estuary to form mudflats

(McLusky, 1989). Because an estuarine environment provides an interface between freshwaters and salt waters, estuaries present steep gradients in many physical and chemical variables, including salinity, pH, dissolved oxygen, temperature, nutrient content, and the amount and composition of particulate matter.

2.2.2 Estuarine Sediments

Fine sedimentary deposits, or mud, are a most characteristic feature of estuaries and indeed the estuarine ecosystem has been defined by Hedgepeth (1967) as ‘a mixing region between sea and inland water of such shape and depth that the net resident time of suspended (sedimentary) materials exceeds the flushing’. Sedimentary material is transported into the estuary from rivers or the sea, or is washed in from the land surrounding the estuary. The source of the sediments the deposition of it within the estuary is controlled by the speed of the currents and the particle size of the sediments (McLusky, 1989).

In many estuaries the maximum concentration of suspended sediment occurs at low tide, as the ebbing tide washes sediment off the intertidal areas and allows the sediment in suspension to remain in the low water channel (McLusky, 1989). As the tide rises, the concentration of suspended load is reduced as the flooding tide increase the volume of water in the estuary, and the sediments are carried over the intertidal areas.

Along with the sediments being carried into estuaries are usually carried particles of organic debris from the excretion, death and decay of plants and animals. Once the dissolved and particulate organic matter reaches estuaries from fresh and salt water it tends to remain

there as it is deposited and incorporated into the estuaries ecosystem along with fine inorganic matter. The organic matter within estuaries consists of material resulting from the excretion and decomposition of estuarine animals and plants, supplemented by fragments and dissolved organic matter carried into the estuary (McLusky, 1989). The sedimentation of both inorganic and organic suspended material leads to the development of mudflats and other areas of deposition within estuaries. The concentrations of trace metals in estuarine and coastal marine waters are controlled by adjective transport, mixing and differential settling of sediment-sorbed metal, leading to increased substantial variations in trace metal composition in different parts of an estuary (Armannsson *et al*., 1985).

2.2.3 Estuarine Pollution

The estuaries of the world receive a large proportion of the waste discharged by mankind into aquatic environments. Within the sea, almost all pollution is concentrated into estuaries and nearshore coastal zones. The effects of pollutants may vary according to the chemical and physical state of the material being discharged into the estuary. The effect of pollutants on the estuarine ecosystem also varies both seasonally and temporally. The effects of a particular pollutant may vary according to the part of an estuary that receives it (McLusky, 1989).

The responses of estuarine organisms to pollution range from the acute to the minimal. At the highest level of pollution, the responses of the animals and plants are easily recognized, since the results are acute and may be lethal to all forms of life. At a lower level of pollution, the sensitive fauna is eliminated, but tolerant species may thrive and become more abundant.

Man has long used estuaries to dispose of waste material. This is one of factor that can cause estuarine pollution. Sewage is discharged into many estuaries. In many cases the raw material sewage is discharged, and in other cases the sewage is treated on the land in septic tanks or sewage-works and only the liquid produced is discharged into the estuary. The waste so discharged may, if there is only a little, become incorporated into the estuarine ecosystem as another source of detritus. The quantities discharged may be so great as to cause major changes to the fauna and flora (McLusky, 1989).

Most of the pollution occurring at the estuary caused by heavy metals is derived from the industrialization at or near the river. For example, from human activities such as fossil fuels burning, smelting, power station corrosion products like Cu, Cr and Zn; sewage disposal, automobile emission like Pb and the other industry process (Kennish, 1992). In addition, disposal of wastes at the sea and accidental spills of oils and chemicals from the industry will increase the quantities of pollutant in the estuary. Large quantities of spill oils may cause destruction of the aquatic communities in the estuarine environment (Kennish, 1992).

2.2.4 Heavy Metals in Sediments

Sediments may be carried into the estuary from the open ocean, biogenic detritus from estuarine organisms, sediment particles derived from erosion of estuary margin and biodeposition of sediments by pellet-making organisms (Davis, 1992). Sediments contaminated with nutrients, metals and metalloids, organic and oxygen-consuming substances can be found in freshwater, estuarine and marine systems throughout the world. Heavy metals in water have been linked to industries particularly paint, electroplating and

mining industries. Sediment can retain metal in dissolved form through physical means such as precipitation, chemically through adsorption and biologically through biotic interaction for long periods. Contaminants are introduced to aquatic ecosystem via many routes such as effluent discharge, ocean and lake disposal, non-point sources, contaminated spills and airborne deposition (Chapman and Power, 1992).

2.3 Mangrove Forests

2.3.1 Mangrove

Mangrove ecosystems, developing in the intertidal zone of most tropical and subtropical regions, are characterized by major contrasts in redox conditions and high rates of organic carbon accumulations (Huc, 1980). They may act as a sink or a source of heavy metals in coastal environments because of their variable physical and chemical properties (Harbison, 1986). Macnae (1968) defined mangroves as trees or bushes growing in between the level of high water of spring tide and a level close to but above mean sea level. The mangrove forest ranges locally from the highest-tide mark down nearly to mean sea level (Dawes, 1981; Mann, 1982). Sedimentation is typically high. The mangrove trees are shallow rooted, having prop or drop-type roots that terminate only a few centimeters in the ground; in some cases, cable roots extend horizontally from the stem base and support air roots (i.e., pneumatophores) projecting vertically upward through the sediment surface (Dawes, 1981). According to Pernettta (1993), the plant species are members of terrestrial families which have adaptations to survive under conditions of high salinity, low oxygen and nutrient

availability in the soil, wind and wave action and substrate instability. Table 2.1 shows the distribution of Indo-West Pacific mangrove swamps.

Table 2.1: Distribution of Indo-West Pacific Mangrove Swamps

	Countries	***Estimated Areas under Mangrove Swamps (sq km)***
1	Indonesia	36,000
2	Thailand	6,020
3	Philippines	4,010
4	Sabah	3,653
5	Sarawak	1,736
6	Peninsular Malaysia	1,500
7	Singapore	28
8	Australia	11,617

2.3.2 Zonation of Mangrove Forest

Mangrove vegetation generally grows in a zoned pattern in which a single species or a group of species dominate specific bands. This zoned pattern result from differences in rooting and growth of seedlings and from various competitive advantages which each species has in the several gradients present from below the low water to above the high water lines.

Appraising the zonation patterns of mangrove trees on the Malayan West Coast, designated five zones based on the frequency of inundation. Mann (1982), embellished upon the description of these zones, proceeding from the lowest too the highest level:

1. Species growing on land flooded at all tides: no species normally exists under these conditions, but *Rhizophora mucronata* will do so exceptionally.
2. Species on land flooded by medium high tides: species of *Avicennia, Sonneratia griffithii* and bordering rivers, *Rhizophora mucronata.*

3. Species on land flooded by normal high tides: most mangroves, but *Rhizophora* tends to become dominant.
4. Species on land flooded by spring tides only: *Bruguiera gymnorhiza* and B. *cylindrical.*
5. Species on land flooded by equinoctial or other exceptional tides only: B. *gymnorhiza* dominant, but *Rhizophora apiculata* and *Xylocarpus granatus* survive.

2.3.3 Factors Limiting Distribution of Mangrove Forest

2.3.3.1 Temperature

One of the important factors limiting the spatial distribution of mangroves is air temperature. Mangroves thrive under tropical conditions where the air temperature exceeds 20^0C and the seasonal temperature range is less than 5^0C. Air temperatures below -4^0C are fatal; hence, these communities cannot tolerate hard frosts. Temperature tolerance varies somewhat among species. For instance, A.*marina* resists low temperatures better than other species (e.g., *Rhizophora mangle*), and ranges into higher latitudes than other mangrove populations.

2.3.3.2 Salinity

Mangroves are facultative halophytes. Although mangrove species vary in their salinity tolerance, contributing to the zonation pattern commonly observed, they outcompete terrestrial plants (e.g., tropical rain forests) in estuarine and stable, high salinity coastal

environments of tropical and subtropical regions. The salinity of bottom sediments is a function of local precipitation, terrestrial runoff, evaporation and tidal flushing. Because these factors vary considerably in many regions, the salt concentration in most mangrove swamp soils fluctuates markedly. The growth of mangroves is affected by soil salinity, with stunting resulting from hypersaline levels. Despite the potential constrains imposed by soil salinity, mangroves inhabit coastal zones with a surprisingly wide range of salinities.

2.3.3.3 Tides

Plant communities of mangrove systems are often most extensive on gently sloping shorelines with a large tidal range. Sediment accumulation in these areas facilitates seedling development which fosters community expansion. Tidal action transports mangrove seeds, influencing local as well as regional distribution of the vegetation. Tidal flushing affects the salt concentration of the substrate. At low tide, the soil salinity may rise dramatically due to evaporation during aerial exposure. Upon return of the tide, the soil becomes saturated once again, which contributes to its anaerobic conditions.

Tidal flow also transports oxygen and nutrients that enhance production of the mangroves. These plants obtain much of their nutrients from freshwater runoff, but the tides redistribute substantial concentrations of them. Additionally, mangrove swamps may trap freshwater masses at high tide, largely controlling the flushing of freshwater runoff from the river. The process allows more time for nutrients uptake and settlement of fine sediments, thereby favoring the growth of mangroves.

2.3.4 Mangrove Plant and Pollution

Mangroves typically have few species, 70 in the world, but they are genetically diverse being derived from 20 plant families and they have developed common morphological and physiological adaptations in a convergent and shared evolution (Duke *et al*., 1998). The examples of mangrove plants are red mangrove (*Rhizophora mangle* L.), black mangrove (*Avicennia germinans* L.) and also mangrove apple (*Sonneratia* sp.). They also occupy a narrow ecological range, constrained mostly between mean sea level and highest tidal levels between 1 and 2 m elevation, or considerably less in some regions. Similar to other estuarine zones, mangrove ecosystems also receive a large amount of waste from their related drainage and rivers and have become a massive pollution sink. Heavy metals are common pollutants in urban aquatic ecosystems and in contrast to most pollutants, are not biodegradable and are thus persistent in the environment. Many heavy metals are non-essential to plant and animal metabolism (such as cadmium, chromium and mercury), and are often toxic in low concentrations. Cadmium is of particular concern, because although it is not an essential element (Kabata-Pendias and Pendias, 1992), it is readily absorbed and accumulated in plants, thus increasing the potential for contamination of the food chain (Baker, 1981; McGrath *et al*., 1997). The severity of impact on coastal habitats has increased dramatically since industrialization. Metal inputs arise from industrial effluents and wastes, urban runoff, sewage treatment plants, boating activities, agricultural fungicide runoff, domestic garbage dumps and mining operations.