# DETERMINATION OF HEAVY METALS IN SELECTED ESTUARY VEGETATION IN THE MUARA TEBAS ESTUARY

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This project is submitted in partial fulfilment of the requirements for a
Bachelor of Science with Honours
(Resource Chemistry)

Faculty of Resource Science and Technology
UNIVERSITI MALAYSIA SARAWAK
2008

## DECLARATION

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

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## ACKNOWLEDGEMENT

First of all, I would like to thank The Almighty Allah SWT for His blessing and the courage that has been given for me to pull through this Final Year Project, that I was finally able to finish.

I would like to express my gratitude to my supervisor, Dr. Harwant Singh for his guidance and advice. Thank you for his supervision of this project.

Appreciation is extended to my beloved parents, Encik Mhd Nasir and Puan Huzaimah, for their support and constant encouragement that motivated me to complete this project and to do my best in my studies.Thank you.

I am also indebted to Mr. Sent Takuk, En. Jahina and En. Rajuna, laboratory staff of the Department of Chemistry who have been helped me in the lab. Thanks also to the entire laboratory staff not mention here who helped me to complete this Final Year Project (FYP).

Not forgetting my friends and coursemates, who along the way have given me the strength and ideas to complete this project, as well as for sharing their knowledge. Last but not least, thanks to all the lecturers of the Faculty of Resource Science and Technology (FRST), faculty administrative staff and others who have directly and indirectly aided in this project. Thank you very much.

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**Determination of Heavy Metals in Selected Estuary Vegetation in Muara Tebas Estuary**

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## ABSTRACT

Heavy metals are toxic substances that can cause harmful effects in organisms. Heavy metals are also one of the sources of toxicity in an environment. Most of the pollution at an estuary occurs because of the high concentrations of heavy metals at the estuary. Selected heavy metals i.e. iron (Fe), zinc (Zn), manganese (Mn) and cadmium (Cd) in selected estuary vegetation i.e. *Sonneratia sp*. and *Avicennia sp.* were studied. The concentrations of metals were determined by using the Atomic Absorption Spectrometry (AAS). Iron (Fe) was the most abundant metal found present in the estuary vegetation and in the sediments. Heavy metals investigated are a source of contamination for the estuary ecosystem.

Key words: Heavy metals, estuary, estuary vegetation, sediment

## ABSTRAK

*Logam berat adalah bahan toksik yang memberi kesan terhadap organisma hidup. Logam berat juga merupakan salah satu punca yang menyumbang kepada kesan toksik kepada alam sekitar. Kebanyakan pencemaran yang berlaku di paya bakau adalah disebakan kandungan logam berat yang tinggi dalam paya bakau itu sendiri atau dari kawasan sekitar. Kajian terhadap kehadiran logam-logam berat ini seperti Ferum (Fe), Zink( Zn), Manganese ( Mn) dan Cadmium (Cd) dijalankan dengan mengambil tumbuhan paya bakau( Sonneratia sp dan Avicennia sp.) sebagai sampel. Kuantiti logam berat yang terkandung dalam sampel diperolehi dengan menjalankan ujikaji dan analisis menggunakan Spektoskopi Serapan Atom (AAS). Ferum merupakan logam berat yang paling dominant wujud dalam tumbuhan paya bakau terutamanya dalam kelodak. Kesimpulannya, kehadiran logam berat dalam tumbuhan paya bakau menunjukkan punca berlakunya pencemaran di paya bakau.*

*Kata kunci: logam berat, paya bakau, tumbuhan paya bakau, sedimen*

# 1. Introduction

Heavy metals are toxic substances that can cause harmful effects in organisms either animals, plants or the other living organisms when they are consumed. Therefore, high concentrations of heavy metals in the environment may cause toxicity and have hazardous effects on the ecosystem. Due to the increasing the heavy metals release into the environment, as a result of human activities such as industry activities, mining activities and the diffuse sources like petrol from the automotive industry, the biogeochemical cycle fluxes and the balance of some heavy metals in the environment have drastically changed.

Heavy metals are deposited into the Muara Tebas Estuary after being brought down by the Sarawak River. The heavy metals are very likely to have been absorbed by the mangrove plants found in the Muara Tebas Estuary.

Therefore, the purpose of doing this study was to determine the some common heavy metals i.e. iron ( Fe ), zinc ( Zn ), cadmium ( Cd ) and manganese ( Mn ) in the selected estuary vegetation and sediment found at the Muara Tebas Estuary, Sarawak.

Previous research done in Muara Tebas Estuary had determined heavy metals in the sediments (Junaidah Gaine, 2005). Elevated concentrations of heavy metals content was reported in the sediments. This research will study the level of heavy metals in the selected estuary vegetation by investigating two species of mangrove i.e. *Avicennia* sp. and *Sonneratia* sp. for the heavy metal content.

# 2. Literature Review

## 2.1 Heavy Metals and Its Toxicity

### 2.1.1 Heavy metals

Heavy metals which are also known as trace metals is a specific term applied to a large group of trace elements. All these trace elements are essential in biologically and industrially as well (Alloway, 1990). Viarengo (1989) defined heavy metals as elements that have an atomic weight in the range of 63.546 to 200.596. Elements which are consider as heavy metals when they have density which is below than 5 or 6 g/cm.

All these heavy metals are classified according to their electron distribution in their outer shell. These classifications exclude alkaline earth metals, alkali metals, lanthanides and actinides.

Heavy metals are classified into three major groups which are noncritical; very rare and toxic but very insoluble; and very toxic and relatively accessible (Kennish, 1992). Heavy metals have a large or high atomic number and most of them can be relatively toxic to organism in small concentrations. In fact due to their toxicity, according to Alloway (1990), trace elements or heavy metals are also called 'toxic elements' and heavy metals can be a toxicant in excess amounts. The examples of heavy metals are chromium ( Cr ), arsenic ( Ar ), cadmium ( Cd ), lead ( Pb ), copper ( Cu ), zinc ( Zn ), mercury ( Hg ) and manganese ( Mn ).

Heavy metals are persistent in all part of the environment and they cannot be degraded or destroyed either by physically or chemically by the decomposer organisms. According to Alloway and Ayres (1993), heavy metals are naturally occurring in the rocks and in ore

minerals. There are various concentrations of trace elements in soils, sediments, water and living organisms. Heavy metals are necessary in certain amounts to stabilize the functions and regulate of the body of living organisms. Most living organisms need a certain concentration of this 'essential trace element' or 'micronutrient' for normal and healthy growth. Difference trace elements are beneficial for different life organisms (Alloway and Ayres, 1993).

### 2.1.2 The Effect of Heavy Metals

Even thought, heavy metals are essential for living organisms for a healthy growth in specific concentrations, exceeds of heavy metals will cause toxicity to the environment and the organisms itself. According to Alloway (1990), the reference to the harmful properties of these trace elements is called "potentially toxic element" (PTE) which it is newer term and seems to be accepted. This toxicity problem may affect even not the whole ecosystem but affect a part of living organisms in term of healthy, agriculture and ecotoxicology.

Toxicity effect occurs can also be defined by Holdgate (1998). He stated that, pollution is "the introduction by man into environment of substances or energy liable to cause hazards to human health, harm to living resources and ecological systems, damage to structure or legitimate uses of the environment". By the excess of the concentration of these trace metals, the toxic effects caused at the biochemical level include competition for site with essential metabolites, the replacement of the essential ions, reaction with –SH groups, damage the cell membranes and reaction with the phosphate group of ADH and ATP ( Alloway and Ayres, 1993 ). Upon long time expose to excess trace elements, the capacity of the homeostatic system to cope with it is overcome. When this occurs, the enzyme of living

organisms will degrade or be destroyed. Thus, it will lead to the metabolic disfunction. It may be able to cause death of the organisms (Garbarino *et al*, 1995).

Nowadays, increasing release of heavy metals due to rapid growth of the industrialization mining, agriculture, metallurgical industries, electronic and chemical industries, food industries, affect the health of the living organisms and much more. For example, atmospheric aerosol particle which is release by industries contain heavy metals such as Pb, Cd, Zn, As and Se. These heavy metals particles are suspended in the air maybe inhaled by the humans and the animals and subsequently absorbed by into the bloodstream through the alveoli and lungs. It also can enter the plant tissues by the absorption through the cuticles of the plant. Phytotoxicity or simply describe as toxicity in plant occur depending on the soil factors, such as pH of the soils, plant genotype and the condition under which the plant is growing.

## 2.2 The Estuaries

### 2.2.1 Pollution in the estuarine environment

Day *et al.,* (1989) defined an estuary as an "inlet of the sea reaching to a river valley as far as the upper limit of tidal rise." The estuary can be divided into three areas which are a) the lower estuary, which is free connection to the sea, b) the middle estuary, which has high salt content and fresh water mixing, c) upper estuary, this part is characterized by the fresh water but focus on the action of daily tidal.

Kennish, 1992 stated that pollution enters the estuarine and marine ecosystem via several pathways, specifically direct pipeline discharges from the coastal communities,

discharges and dumping from ships, atmospheric deposition and also non-point source which is run off from the land. The mostly common anthropogenic wastes which are disposed to the coastal area are the industrial and community wastes, sewage sludge, and also from the other materials. The most common pollutant that the estuaries are expose to include heavy metals, synthetic organic compound ( xenobiotics), organic carbon, nutrient element and also pathogens. 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 estuarine environment. According to Armannsson et al., (1985), the concentration 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 part of an estuary.

To decrease the degree of pollution which causes the contamination to the living organisms in the estuarine water, bioaccumulation is applied. Kennish, (1992), he said that toxicologist normally describe the bioaccumulation into two terms which are ‘bioconcentration’ and ‘biomagnifications ‘. These two terms are describing different things. Bioconcentration is the term that refers to the organism that has an ability to accumulate the excess contamination in the water. Biomagnifications is a term that refers to the ratio or fraction of the concentration of pollutants in the food chain. When the quantity and the concentration of the pollutant are getting higher, the possibility of the contaminating estuarine ecosystem and all the organisms getting worse is increase. Thus it can be very harmful and can cause death. Capuzzo and Kester (1987) stated that bioaccumulation or bioavailability in the estuarine depends upon biological, physical and chemical processes that control the concentration of the pollutants. The processes are such as microbial degradation, dissolution,

redox reaction, and also sorption-desorption of compounds can change the structure of the pollutants.

Capuzzo and Kester (1987) stated that release of all the contaminations are done by the estuarine organisms via eliminating the contamination in either soluble or in the particulate form. Toxicity is also the major problem occurring at the estuarine ecosystem and thus impacts the marine ecosystem as well. Rand and Petrocelli (1985) define toxicity as chemicals substance that gave a harmful effect to the living microorganisms. The effect of toxicity can be detected based on its concentration and its duration of exposure. Other than toxicity, estuaries have high probability to be polluted by the loading of organic matter. This will lead to cause enrichment of the water by the presence of nutrient elements. This process is called eutrophication. Major causes that contribute to this phenomena are sewage from the industry and residential mean; domestic wastes; industrial discards such as from food industry, textile industry and also paper manufacturing (Kennish, 1992). Such a contamination has high probability of happening along the Sarawak River such as at place where mangrove plants that are located along its cause as there are difference types of activities are doing. For example, one part of this river has industrial activities so the probability factories to release domestic wastes are higher. Releasing the contaminants into the river will cause their deposited further at the other place along the river such as at the estuary.

### 2.2.2 Heavy Metals Affect in the Estuarine Ecosystem

Directly expose to the industrialization and development contributes to the estuarine ecosystem increase in heavy metal and, thus will increase in the rate of contamination. Abel (1989), has listed the heavy metals according to their decreasing toxicity : Hg, Cd, Cu, Zn, Ni,

Pb, Cr, Al and Co. Viarengo et al. ( 1985 ) stated that heavy metals can be separated from the aquatic organisms through metallothioneins and lysosomes and thus enhance the cell detoxification by the organisms. Metallothionein has low molecular weight, containing sulfur and metal-binding protein to control the releasing of heavy metals to the living organisms. Wood (1974) defined common heavy metal in the estuaries such as Cu, Zn, Pb and Ni which are highly toxic and have the potentially to become harmful pollutants.

Most of the pollution occurring at the estuary cause by heavy metals is derived from the industrialization at or the 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, Wittman and Förstner, (1975) mentioned that heavy metals are also released to the environment especially estuarine via production of cement, and discharges of metals from waste materials. Living organisms at the estuarine response to the toxic effect of heavy metal in a varies way such as by change in their physiology in term of their respiratory system, feeding behavior and digestive ability; reproduction processes and also its development processes. Lastly, heavy metals enter the estuarine ecosystem via three pathways which are freshwater input; the anthropogenic activity; and from the atmosphere.

## 2.3 Mangrove Plants

Duke (1992) defined mangrove as a group coastal plant with high about half meter and grow in an intertidal area with the similar adaptation that allows them to continue their life successfully. The mangrove plants always grow in the conditions which are normally salty water, ‘nasty’ habitat and lack of soils. Because of the salty the environment of the mangrove

plant, they need to compete to continue their life. They have a lot of adaptation they do to ensure they can survive in their life. Bortone (2005) stated that the excessive salt content inside the mangrove plants are remove through by excreting the salt which is in or near their leaves; and secondly by excluding the salt which is at their roots. Around the world, they are about 65 species of mangrove plant had been discovered (Tomlinson, 1986; Field, 1995). The examples of mangrove plants are red mangrove (*Rhizophora mangle* L.), black mangroves (Avicennia *germinans* L.) and also *Sonneratia sp*. The physical appearance of the black mangroves are the rough and dark bark, its also have one part that can be identified easily with naked eyes which is fingerlike roots or we called pneumatophores, they have whitish underside of their leaves that are capable to remove the excess salt content (Bortones, 2005).

Odum and McIver, 1990 stated that mangrove is very important to the estuarine environment as a land stabilizer which prevent the erosion and provide the habitat for the living ecosystem. The roots of mangrove which are above and below the water provide a safe place for organisms. Based on condition of the mangrove, we can predict whether the estuary is healthy or not, in decline or not, or under recovery. The growth of the mangroves is controlled by the nutrient limitation, and the salinity of soil, nutrient chemistry and the geological aspect also (Davis, 1940). Black mangroves are easily to detect when the condition of the estuary is at a normal condition. Bortones (2005), explained that when the level of water at the estuary is rising and exceeds the limitation level and does not drain or evaporate quickly, the pneumatophores of the mangroves are submerged for a quite long time, then the black mangroves drown and this results in mass mortality. To prevent this occur the ecosystem surrounding the mangroves must be managed properly. The time of floodwater must be decrease to prevent the “drowning” of the plants.

## 2.4 Heavy Metals and Mangrove Relationships

### 2.4.1 Heavy Metals in Plants

When certain plants are detected to have excess heavy metals, the plant itself shows symptoms. The symptoms shown by plants growing under the enrichment of heavy metals are stated by Martin and Coughtrey, (1982) maybe gigantism or dwarfism; chlorosis at the leaves of the plants; fruits produce are abnormal; the flower's color and pattern are change dramatically; the rhythm of growth and flowering periods are totally disturbed. Chlorosis of leaves is the most common symptom that happens to the plants when they are highly exposed to the heavy metals like iron (Fe) and nitrogen (N). The degrees of uptake of heavy metals by different species of plants are different even though they grow in the same soils.

The leaves of plant can be used to detect the quantity of heavy metals in a plant. Martin and Coughtrey (1982) explained that, heavy metal concentration in most plants is expressed in per unit weight which is µg/g dry or fresh weight.

The bark of a tree is the external covering part of woody trees which function as part of trees protection either to protect the bark area itself and also to protect the tree itself. The outermost part of the bark is the older bark and directly exposed to the surface. And the other tissue is called the cork tissue which is nonliving. The type of bark in terms of its surface is the difference between different species of tree. It is much depended on the age of tree and degree to which the bark dries and cracks when the tree-trunk expands during its growth (Martin and Coughtrey, 1982). Martin and Coughtrey (1982) also stated that the trace elements like heavy metals reach inside the bark through two steps. First, indirectly; this is through the uptake from the soils. Secondly, directly; this is through the deposition and

impaction of airborne particulate. The concentration of heavy metal, normally lead, in the bark is high from the roadside trees than the other areas and the higher concentration in at the outermost layer of the bark (Ward, et al., 1974; Hampp and Holl, 1974).

### 2.4.2 Soil-plant relationship of the Heavy Metals

Chaney (1973) has listed; there are several factors which effect the metal distribution of the plant by its roots. These factors are 1) the quantity of heavy metal in the soil, 2) types of metal present, 3) the organic matter contain in the soil, 4) the pH of the soil, 5) the species of the plants, 6) the phosphate content in the soil, 7) the metals distribution and the depth of the plant's root, and 8) transportation of metal from the roots surface into the roots. Alloways (1990) said that, the absorption of heavy metal affects most chemical processes that will change the behavior and the bioavailability of the metals in the soils. All the chemical processes are done to control the concentration of metals exist in the soil and thus will give an effect of the uptake by plant roots. Soil and plant are closely related in living the ecosystem. Every contamination to the plants mostly comes from their soils. Alloways (1990) explained that the soil-plant system is an open system that focuses on contaminants, fertilizers and pesticides.

The absorption of metals by plant roots are going through either by a passive process or an active process (Alloways, 1990). This metabolism process needs metabolic energy as at take place against a concentration gradient and the toxins content will inhibited the soil-plant uptake. Beside root-up take, Alloways (1990) also mentions that the quantity of the some elements can be measured through foliar absorption. This kind of absorption depends on the species of the plant, the nutritional status, the age of its leaf, the thickness of the cuticles,

humidity at the leaf surface and nature of the solute itself. After up- take either by plant-root up- take or foliar absorption, then its will enter the plant system via the translocation process. This process occurs to transport the elements to the xylem vessel and probability to the entire plant system. This is the distribution mechanism of all these metals in part of the plants; a) element that are readily translocated are Mn, Zn, Cd, B. and Se. b) Ni, Co and Cu are at the intermediate part of the plant and c) Cr, Pb and Hg are translocated to the least extent area.

## 2.5 Sediments and metals in sediments

Sediments are refers to the loose particles of clay, silt and sand that are suspended in the body of water and eventually settle to the bottom of the sea. Sediments are deposited either at the side or bottom of the sea or water bodies. Sediments are very important in the formation of beaches, spits, sand bars and also the estuary ecosystem. It provides the substrate for aquatic plant and also animals. It will supply the nutrients vital to the health of downstream ecosystem.

Sediments play a major role as one of the parts of the ecosystem. Processes occurring in sediments also have an impact of the organism is surrounding. Land use or industrialization beside the sea or beaches will cause excessive amount of sediment to enter the aquatic ecosystem. Sediments will move to the ecosystem and sometimes it will be stored in the wetlands, streams and parts of estuaries also.

Pollution may also occur from the industrialization occur at the mangrove itself or by the industrialization occur at the nearest site. Greaney, (2005) stated that the level of heavy metals existing in the most of the sediment is about due to the natural soil erosion and mineral weathering. The input of heavy metals in the environment and specifically in sediment is

dangerous to the living organisms. Even though the concentration of heavy metals in sediments is low, it is not means that the sediment is still natural. The polluted substances will present as a mixture of small quantity of the pollutants which is dilute by a large amount of natural sediment (Herut *et al*., 1993). The risks associated with the presence of heavy metals are depends on primarily on their speciation. The speciation taken in its broadest sense includes metal characteristics such as electronic structure (oxidation state, nature of chemical bonds) and its chemical state, nature of the functional groups to which the metals are bonded, fixation by minerals either clays or oxides and the formation of crystal chemical mechanism of this fixation (adsorption vs. lattice substitution) or simply said the precipitation of the pollutant as salt (sulfate, carbonate, oxides etc.) (Manceau *et al.*, 1996).

There are three mechanisms by which the trace metals can be taken up by the sediments. There are:

a) Physicochemical adsorption from the water column.
b) Biological uptake by the organic matter or the organisms.
c) Physical accumulation of metal enriched particulate matter by sedimentation or entrainment (Greaney, 2005).

# 3. Materials and Methods

## 3.1 Field Method

### 3.1.1 Sampling Area

The study was carried out in a part of the Muara Tebas Estuary, Sarawak. The study area is shown in the map of the Muara Tebas Estuary give in Figure 1 below.


**Figure 1: The study area location at the estuary at Muara Tebas. (Source adapted from http: // maps.google.com/maps/Malaysia/Sarawak/muara-tebas/muara-tebas-google-earth.hotmail)**

### 3.1.2 Sample Selection & Collection

#### 3.1.2 (a) Samples Investigated

The mangroves plants studied were the *Sonneratia* sp. and *Avicennia sp.* These two species are shown in Figures 2 and 3.

**Figure 2: *Sonneratia sp***

**Figure 3 : *Avicennia sp.***

#### 3.1.2 (b) Sample Collection

Ten plants of each species were collected for analyses. The leaves, barks and roots were collected from each tree. Each sample was collected in triplicate. All the samples were placed in polythene bags according to their type and brought to the laboratory for analyses.

Sediment samples were collected from each sampling station separated by the site of trees sampled mentioned above by using the bottom grab sampler (Lau et al., 1998).

## 3.2 Laboratory Analysis of Plant Samples

### 3.2.1 Sample Treatment

#### i. Washing

The freshly harvested leaves, barks and roots were washed with tap water followed by distilled water at the laboratory. This process was done to ensure that all the unwanted materials were removed from the samples. The sediment samples were kept in the polyethylene bottles and later air dried in the laboratory.

**ii. Oven drying**

Water from the plant tissues and sediments was removed by air drying and these were then placed in a paper container. They were then dried in the forced-air oven at a temperature of 80°C for 12-24 hours (Kalra, 1998).

**iii. Particles size reduction**

The tissues were ground to reduce the particle size to 0.5- 1.0 mm. After that, the sample was thoroughly mixed with an aliquot of 5-10g was withdrawn for analysis. The dried sediment samples were again grounded to a size of 60 mesh. (Lau *et al.*, 1998).

### 3.2.2 Storage

The sample was stored in an air-tight plastic storage container which was placed in a cool, dark place (refrigerator). It was ensured that the sample was dried, sealed properly and put under refrigeration (4°C) until the analyses could be done. The samples were stored for the minimum time after the treatment process to minimize the decline in sample quality (Kalra, 1998).

### 3.2.2 Sample Analysis

**i. Dry- Ashing**

0.5-1.0g of dried sample that had been ground was taken for dry ashing. It was put into the porcelain crucible and was again dried at 80°C for about 12-24 hours. Then, the sample was put in the cool muffle furnace and dried again at 500-550°C for 4-5 hours. After that the sample was cooled. A few drops of concentrated nitric acid were added as an ashing aid. The