DETERMINATION OF HEAVY METAL CONCENTRATIONS AND ORGANOCHLORINE PESTICIDE RESIDUES FROM RIVER WATER SAMPLES OF KINABATANGAN RIVER, SABAH

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ABSTRACT

This dissertation was aimed to evaluate the concentration of heavy metals and organochlorine pesticide residues in the river water of Kinabatangan River, Sukau, Sabah. *In situ* tests were conducted on the spot during sampling collection and all samples were preserved for transportation. Heavy metal tests were conducted using Atomic Absorption Spectrophotometer (AAS) to evaluate the concentration of cadmium, chromium, copper, iron, lead and zinc. Gas Chromatography – Mass Spectrometer (GC-MS) was selected for the determination of organochlorine pesticides. Pesticides tested were aldrin, 2,4-DDD, 4,4-DDD, 2,4-DDE, 4,4-DDE, DDT, heptachlor, hexachlorobenzene, isodrin, α-lindane, β-lindane, and γ-lindane. Samples tested during the *in situ* tests showed that the water quality was low in terms of dissolved oxygen while the pH level was acidic. Most of the heavy metals tested were either too low to be detected or its concentration was too low. Only lead was tested to be present at high concentrations that might pose a threat towards the environment. None of the organochlorine pesticides tested were detected. Steps have to be taken to ensure the lead levels do not exceed the permissible limit. Further monitoring has to be conducted from time to time to ensure the water quality of Kinabatangan River.

ABSTRAK

KAJIAN KEPEKATAN LOGAM-LOGAM BERAT DAN PESTISID ORGANOKLORIN DI DALAM SAMPEL-SAMPEL AIR SUNGAI DARI SUNGAI KINABATANGAN, SABAH

Disertasi ini bertujuan untuk mengkaji kepekatan logam-logam serta mengesan kehadiran residu pestisid organoklorin di dalam sampel air Sungai Kinabatangan, Sabah. Ujian *in situ* telah dijalankan ketika persampelan sedang dijalankan dan semua sampel telah diawet untuk tujuan pengangkutan. Ujian logam-logam berat telah dijalankan menggunakan *Atomic Absorption Spectrophotometer* (AAS) untuk mengkaji kepekatan logam kadmium, kromium, kuprum, ferum, plumbum dan zink. *Gas Chromatography – Mass Spectrometer* (GC-MS) pula digunakan untuk kajian pestisid organoklorin. Pestisid organoklorin yang diuji di dalam kajian ini merupakan aldrin, 2,4-DDD, 4,4-DDD, 2,4-DDE, 4,4-DDE, DDT, heptaklor, heksaklorobenzena,isodrin, α-lindan, β-lindan, dan γ-lindan. Sampel-sampel yang diuji ketika ujian *in situ* menunjukkan kualiti air di Sungai Kinabatangan adalah rendah kerana kepekatan oksigen terlarut adalah rendah dan pH adalah berasid. Kebanyakan logam-logam berat yang diuji adalah sama ada terlalu rendah untuk dikesan atau kepekatannya adalah terlalu rendah. Hanya logam plumbum merupakan logam yang dikesan mengandungi kepekatan yang mungkin boleh memberi kesan negatif kepada alam sekitar. Tiada pesitisid organoklorin yang dapat dikesan di dalam kajian ini. Langkah-langkah perlu diambil untuk memastikan kandungan logam plumbum di dalam Sungai Kinabatangan dalam dikurangkan ke paras yang lebih selamat.Pantauan dari semasa ke semasa juga perlu dibuat memantau kualiti air di Sungai Kinabatangan.

LIST OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

%	Percent
°C	Degree of Celcius
°C min^{-1}	Degree of Celsius per minute
µg/L	Microgram per liter
µL	Micro liter
µm	Micrometer
AAS	Atomic Absorption Spectrometer
AOAC	Association of Analytical Chemists
ATSDR	Agency for Toxic Substances and Disease Registry
Cd	Cadmium
CDC	Center for Disease Control
Cr	Chromium
Cu	Copper
DDD	Dichloro-diphenyl-dichloroethane
DDE	Dichloro-diphenyl-dichloroethylene
DDT	Dichloro-diphenyl-trichloroethane
Fe	Iron
g	Gram
GC-MS	Gas Chromatography – Mass Spectrometer
K	Degree of Kelvin
km	Kilometer
L	Liter
M	Molar (Mole per liter)
m	Meter
min	Minute
mL	Milliliter
mm	Millimeter
Pb	Lead
ppb	Parts per billion
ppm	Parts per million
PTFE	Polytetrafluoroethylene
R^2	Correlation coefficient
SIM	Selected Ion Monitoring
v/v	Volume per volume
WHO	World Health Organization
WWF	World Wildlife Foundation
Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1. Background of Study

The Kinabatangan River is the longest river in Sabah. It is the second longest river in Malaysia, with a length of 560 kilometers from its headwater in the mountains of southwest of Sabah, to its outlet at the Sulu Sea, east of Sandakan. As the massive river reaches the lowlands, it meanders through the lower Kinabatangan, a great floodplain laden with oxbow lakes, open swamps and distinctive vegetation (WWF, 1997).

Natural habitats here include freshwater swamp forest and lowland dipterocarp forest – home to some of the largest and most diverse concentrations of wildlife species in Borneo today. Many rare and endangered species of animals can be found here, such as the fascinating proboscis monkey, herds of wild Asian elephant, the estuarine crocodile and a spectacular assembly of birdlife (WWF, 1997).

It is the main water source for many villagers surrounding the river for daily activities. With an abundance of marine life forms present in the river, the Kinabatangan is also a major source of food and nutrition especially protein to these people (WWF, 1997).

Much has turned, however since the turn of the century when forests covered most of the state of Sabah. Over the recent years, the Kinabatangan has witnessed tremendous development surrounding the area. Activities such as agriculture were blooming due to the water supply provided by the river for irrigation purposes. And with the rapid pace of development in Sabah, the growth of the timber industry and the expansion of agriculture have dramatically transformed the landscape. However, the ecology of the upper reaches of the river has been severely disrupted by excessive logging and clearing of land for plantation purposes. Forested areas are shrinking and many have declined in quality (WWF, 1997).

High quantities of pesticides were used for agricultural purposes to kill bugs and pests from destroying the crops. Pesticides were introduced after the World War II for their various benefits but general worldwide intensive usage today poses potential hazards to the environment and human health (Chambers *et al.*, 2001). Organochlorine pesticide represents an important group of persistent organic pollutants (POPs), which are believed to be possible carcinogens or mutagens as well as endocrine disruptors (Thomas *et al.*, 1998; Peter *et al.*, 2002). Despite the fact that the use of certain organochlorine insecticides in agriculture is prohibited in many countries, these compounds have been detected in the environment worldwide due to their persistency (Rajendran and Subramaniam, 1997).

This study focused on the concentration of heavy metals as well as organochlorine pesticide residues found in water samples collected from the Kinabatangan River. The samples will then be analyzed to determine the residue levels.

1.2. Objectives

The objectives for this study were:

1. To determine the concentration of heavy metals from the water samples using Atomic Absoprtion Spectrophotometer (AAS)
2. To extract organochlorine pesticides from water samples
3. To analyze and determine the organochlorine pesticides extracted using Gas Chromatography—Mass Spectrometry (GC-MS)

1.3. Scope of Study

This study focused on heavy metal concentrations and organochloride pesticide residues found in different water samples collected in various sampling points in the Kinabatangan River. The locations of the sampling points were about 5 km away from the small town of Sukau, Sabah. The water samples collected were filtered before being analysed by Atomic Absorption Spectrophotometer (AAS). Organochlorine pesticides were then extracted from the water samples using solvent-solvent extraction with ethyl acetate together with dichloromethane against the river water sample. The extracts were further analyzed by Gas Chromatography–Mass Spectrometry (GC-MS) and the components of the pesticides were compared to internal standards of organochloride pesticides.

CHAPTER 2

LITERATURE REVIEW

2.1. Heavy Metals

2.1.1. Definition of Heavy Metals

Heavy metal, according to Oxford Dictionary of Chemistry, is defined as a metal with a high relative atomic mass. The term is usually applied to common transition metals, such as copper, lead and zinc. These metals are a cause of environmental pollution from a number of sources, including lead in petrol, industrial effluents, and leaching of metal ions from the soil into lakes and rivers by acid rain.

2.1.2. General Information

a. Cadmium

Cadmium is a chemical element with the symbol Cd and atomic number 48. It is categorized under the transition metal series in the 12^{th} group, 5^{th} period and d block. Cadmium is a soft, malleable, ductile, toxic, bluish-white bivalent metal and available in a relatively abundant amount. Cadmium is silvery gray metallic in color with a standard atomic weight of 112.411 $g{\cdot}mol^{-1}$. It has an electron configuration of [Kr] $5s^2$ $4d^{10}$ and 2, 8, 8, 18, 18, 2 electrons in each shell (CDC, 2005b; Oxford, 2004).

At room temperature, it exists in solid form with a density of 8.65 g·cm^{-3}. At its melting point of 594.22 K, its density drops to 7.996 g·cm^{-3}. Boiling point is recorded to be at 1040 K. Both its heat of fusion and vaporization are recorded to be at 6.21 and 99.87 kJ·mol^{-1} respectively (CDC, 2005b; Oxford, 2004).

The name cadmium was derived from the Latin word *cadmia* and Greek word *καδμεία* which means "calamine", a Cadmium-bearing mixture of minerals, which was named after the Greek mythological character, Κάδμος or Cadmus. It was discovered by Friedrich Strohmeyer in Germany in 1817. He found the element within an impurity of calamine or zinc carbonate. For 100 years, Germany remained to be the only important producer of this metal. Cadmium was named after the Latin word for calamine since it was found in this zinc compound. Strohmeyer also noted that while pure calamine did not change color while being heated, impure samples of calamine was reported to change colors (CDC, 2005b; Oxford, 2004).

b. Chromium

Chromium has the symbol Cr and atomic number 24. Like Cadmium, it is also categorized under the transition metal series in the 6th group, 4th period and d block. Steel-gray in color, chromium is a lustrous, hard metal that takes a high polish and has a high melting point. Besides that, it is also odorless, tasteless and malleable. It has a standard atomic weight of 51.9961 g·mol^{-1}. Electrons are arranged as 2, 8, 13, 1 in each shell with an electron configuration of [Ar] 3d^5 4s^1 (CDC, 2005c; Oxford, 2004).

Cadmium exist in the solid phase at room temperature with a density of 7.19 $g{\cdot}cm^{-3}$. The density drops to 6.3 $g{\cdot}cm^{-3}$ once it reaches the melting point at 2180 K. Cadmium then boils at 2944 K. The heat of fusion and heat of vaporization are reported to be at 21.0 and 339.5 $kJ{\cdot}mol^{-1}$ respectively (CDC, 2005c; Oxford, 2004).

The name chromium was derived from the Greek word "Chrôma", which brings the meaning color due to many colorful compounds that were made from it. It was discovered back in 1761 by Johann Gottlob Lehmann in the form of lead chromate, today more widely known as crocoite. However, it was only on 1797 that Louis Nicolas Vacquelin was able to isolate the elemental chromium successfully (CDC, 2005c; Oxford, 2004).

c. Copper

Copper, with its symbol Cu, has an atomic number 29. It is also categorized under the transition metal series in the 11^{th} group, 4^{th} period and d block. It is ductile with excellent electrical conductivity. Copper is also rather soft in its pure state and has a pinkish luster that is unusual for a metal which is usually silvery white in color. Standard atomic weight is measured to be 63.546 $g{\cdot}mol^{-1}$. Electron configuration is recorded to be of [Ar] $3d^{10}\ 4s^{1}$ and arranged as 2, 8, 18, 1 in each shell (CDC, 2005d; Oxford, 2004).

Solid at room temperature, copper has a density of 8.96 $g{\cdot}cm^{-3}$ at room temperature. Once it reaches its melting point at 1357.77 K, it has a density of 8.02

$g \cdot cm^{-3}$. Boiling point is reported to be at 2835 K. The heat of fusion and vaporization of copper are measured to be at 13.26 and 300.4 $kJ \cdot mol^{-1}$ (CDC, 2005d; Oxford, 2004).

Copper played a significant role throughout the history of mankind. In fact, it was known to exist since 10,000 years ago as the uncompounded metal can be accessed easily. The name cuprum was derived from the name Cyprium, "metal of Cyprus", as it was mined primarily on Cyprus during the Roman Empire (CDC, 2005d; Oxford, 2004).

d. Iron

Iron, also under the transition metal series, has an atomic number 26 and symbol Fe. This metal is situation in the 8^{th} group, 4^{th} period and d block. A lustrous and silvery soft metal, it is also one of the few ferromagnetic elements. Iron has a standard atomic weight of 55.845 $g \cdot mol^{-1}$. Electrons are arranged as 2, 8, 14, 2 in each shell with an electron configuration of [Ar] $3d^6\ 4s^2$ (CDC, 2005a; Oxford, 2004).

At room temperature, iron is found to be in solid form. Once it starts to melt at 1811 K, the density for iron is at 6.98 $g \cdot cm^{-3}$. It has to be further heated until 3134 K for it to reach its boiling temperature. It has the heat of fusion and vaporization of 13.81 and 340 $kJ \cdot mol^{-1}$ (CDC, 2005a; Oxford, 2004).

The first iron used by mankind during prehistory came from meteors. The smelting of iron in bloomeries probably began in Anatolia or the Caucasus in the second millennium BC or the latter part of the preceding one. Cast iron was first produced in China about 550 BC, but not in Europe until the medieval period. During the medieval period, means were found in Europe of producing wrought iron from cast iron (in this context known as pig iron) using finery forges. For all these processes, charcoal was required as fuel (CDC, 2005a; Oxford, 2004).

Steel (with smaller carbon content than pig iron but more than wrought iron) was first produced in antiquity. New methods of producing it by carburizing bars of iron in the cementation process were devised in the 17th century AD. In the Industrial Revolution, new methods of producing bar iron without charcoal were devised and these were later applied to produce steel. In the late 1850s, Henry Bessemer invented a new steelmaking process, involving blowing air through molten pig iron, to produce mild steel. This and other 19th century and later processes have led to wrought iron no longer being produced (CDC, 2005a; Oxford, 2004).

e. Lead

Lead is a transitional metal with the symbol Pb and has an atomic number of 82. It is situated in the 14th group, 6th period and d block. Bluish white in color when freshly cut, lead tarnishes to dull grayish color when it is exposed to air. The standard atomic weight for lead is 207.2 $g \cdot mol^{-1}$. The electrons are arranged as 2, 8, 18, 32, 18, 4 in each shell and has an electron configuration of [Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^2$ (CDC, 2005e; Oxford, 2004).

Like almost all metals, lead stays in solid form at room temperature. At its melting point of 600.61 K, it has a density of 10.66 $g \cdot cm^{-3}$. When heated further, lead boils at 2022 K. it has heat of fusion and vaporization of 4.77 and 179.5 kJ·mol^{-1} respectively (CDC, 2005e; Oxford, 2004).

Lead has been commonly used for thousands of years because it is widespread, easy to extract and easy to work with. It is highly malleable and ductile as well as easy to smelt. In the early Bronze Age, lead was used with antimony and arsenic. Lead also refers collectively to the organic and inorganic compounds of lead, which are toxic. Lead poisoning was documented in ancient Rome, Greece, and China (CDC, 2005e; Oxford, 2004).

In the 20th century, the use of lead in paint pigments was sharply reduced because of the danger of lead poisoning, especially to children. By the mid-1980s, a significant shift in lead end-use patterns had taken place. Much of this shift was a result of the U.S. lead consumers' compliance with environmental regulations that significantly reduced or eliminated the use of lead in non-battery products, including gasoline, paints, solders, and water systems. Lead use is being further curtailed by the European Union's RoHS directive. Lead may still be found in harmful quantities in stoneware, vinyl (such as that used for tubing and the insulation of electrical cords), and brass manufactured in China. Around 2006-2007, many children's toys made in China had been recalled due to lead in paint used to color the product (CDC, 2005e; Oxford, 2004).

f. Zinc

Zinc, with an atomic number of 30, is a metallic chemical element with the symbol Zn. It is situated at the 12^{th} group, 4^{th} period and d block. It is bluish grey in color and moderately reactive. It tarnishes in moist air and burns in air to emit a bright bluish-green flame, exhuming fumes of zinc oxide. It has a standard atomic weight of 65.409 $g{\cdot}cm^{-3}$. Zinc also has an electron configuration of [Ar] $3d^{10}$ $4s^2$ and are arranged as 2, 8, 18, 2 (CDC, 2005f; Oxford, 2004).

At room temperature, zinc is a solid with a density value of 7.14 $g{\cdot}mol^{-1}$. Once it starts to melt at 692.68 K, the density drops to 6.57 $g{\cdot}mol^{-1}$. When further heating it to 1180 K, it will start to boil. Heat of fusion and vaporization are reported to be at 7.32 and 123.6 $kJ{\cdot}mol^{-1}$ respectively (CDC, 2005f; Oxford, 2004).

The name of the metal zinc is unusual and, while vague in origin, was probably first used by Paracelsus, a Swiss-born German chemist, who referred to the metal as "Zincum", in the 16th century. These words in German apparently mean "tooth-like, pointed or jagged part" and, as zinc metallic crystals are needle-like, the derivation appears plausible (CDC, 2005f; Oxford, 2004).

2.1.3. Heavy Metal Profiles

a. Cadmium

Cadmium is a natural element in the Earth's crust. Cadmium is not usually present by itself in the environment but as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulfur (cadmium sulfate, cadmium sulfide). Soil and rocks, including coal and mineral fertilizers, contain some cadmium. Most cadmium used in the United States is extracted during the production of other metals like zinc, lead, and copper (CDC, 2005b). Cadmium is used in many products especially in the steel industry and in plastics, including batteries, pigments, and metal coatings and is found in cigarette smoke (WHO, 2006).

Cadmium is released to the environment in wastewater, and diffuse pollution is caused by contamination from fertilizers and local air pollution (WHO, 2006). The weathering and mining of rocks and minerals that contain cadmium also allow the element to get into the environment. Forest fires and volcanoes also release some cadmium to the air. Cadmium does not corrode easily and has many uses, including batteries, pigments, metal coatings, and plastics (CDC, 2005b).

Contamination in drinking-water may also be caused by impurities in the zinc of galvanized pipes and solders and some metal fittings. Food is the main source of daily exposure to cadmium. The daily oral intake is 10–35µg. Smoking is a significant additional source of cadmium exposure (WHO, 2006).

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