DETERMINATION OF SELECTED HEAVY METALS (AS, CD, CR, CU, NI AND PB) IN *Isopterygium albescens* (Hook.) A. Jaeger IN DIFFERENT ALTITUDE AT LAWA MANDAU HILL (TELIPOK TO KIULU)

NURRUL FAZLINA BINTI OSMAN

THIS DISSERTATION IS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF BACHELOR OF SCIENCE WITH HONOURS

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ABSTRACT

Moss *Isopterygium albescens* was used to determine heavy metals concentration in different altitude at Lawa Mandau Hill. The objectives of this study were to determine heavy metal (As, Cd, Cr, Cu, Ni and Pb) pollution in Lawa Mandau Hill by using *Isopterygium albescens* as bioindicator, to compare the accumulation of heavy metal concentration in different altitude of Lawa Mandau Hill and to analyses the function of local climate conditions on the altitude distribution of heavy metal at Lawa Mandau Hill. There are three replicates of the moss samples taken from each sampling stations and each replicates were duplicated. Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was used to determine the accumulated concentration of each element As, Cd, Cr, Cu, Ni and Pb. The result from the ICP-OES shows that station 5 and station 6 has the highest heavy metals contain in every station, whilst station 2 has the lowest amount. The accumulation concentration for element As is high in station 6, followed by station 1, station 5, station 7, station 3, station 2 and the lowest arsenic concentration is in station 4 with the accumulation mean and standard deviation 20.12±0.0032 µg/g, 17.26±0.0031 µg/g, 17.22±0.0038 µg/g, 16.75±0.0029 µg/g, 15.59±0.0038 µg/g, 14.10±0.0039 µg/g and 13.68±0.0041 µg/g respectively. The accumulation concentration for element Cr is high in station 5 followed by station 7, station 6, station 2, station 1, station 3 and last is station 4 with the accumulation mean and standard deviation 52.48±0.0342 µg/g, 18.82±0.0012 µg/g, 18.01±0.0132 µg/g, 15.48±0.0010 µg/g, 5.21±0.0038 µg/g, 2.78±0.0021 µg/g and 2.74±0.0021 µg/g respectively. While, for element Cu accumulation concentration for heavy metal is high in station 6 followed by station 5, station 3, station 7, station 4, station 1 and last is station 2 with the accumulation mean and standard deviation 145.23±0.7376 µg/g, 109.12±0.0463 µg/g, 60.67±0.0198 µg/g, 48.44±0.0097 µg/g, 43.65±0.0116 µg/g, 17.30±0.0101 µg/g and 8.13±0.0032 µg/g respectively. For element Ni, the high accumulation concentration of heavy metal is in station 5 followed by station 6, station 1, station 3, station 7, station 4 and last is station 2 with the accumulation mean and standard deviation 45.33±0.0197 µg/g, 36.19±0.0167 µg/g, 22.49±0.0059 µg/g, 17.84±0.0037 µg/g, 17.01±0.0043 µg/g, 16.85±0.0007 µg/g and 13.69±0.0019 µg/g respectively. Accumulation concentration of heavy metal for element Pb is high

in station 6 followed by station 4, station 5, station 7, station 3, station 2 and last is station 1 with the accumulation mean and standard deviation 78.50±0.0687 µg/g, 10.43±0.0021 µg/g, 6.81±0.0023 µg/g, 6.33±0.0023 µg/g, 5.70±0.0023 µg/g, 5.13±0.0020 µg/g and 4.77±0.0016 µg/g respectively. But for element Cd, ICP-OES cannot detect the element for the whole station in this study. The local climate does affect the amount of the deposition of heavy metals in Lawa Mandau as it was related to the long range pollution transport as the source of heavy metals from biomass burning and anthropogenic was swept by the wind factors, deposited at the east side of Lawa Mandau where orographic precipitation occur and accumulated by the moss over the years. As a conclusion, *I. albescens* is a good bioindicator and accumulator for element As, Cr, Cu, Ni and Pb but not for Cd and the local climate or the meteorological distribution around Lawa Mandau Hill does affecting the accumulation of heavy metals in the study area.

MENGENALPASTI BERAT LOGAM TERPILIH (As, Cd, Cr, Cu, Ni DAN Pb) DI DALAM Isopterygium albescens (HOOK.) A. JAEGER DALAM ALTITUD YANG BERBEZA DI BUKIT LAWA MANDAU (TELIPOK - KIULU)

ABSTRAK

Kajian terhadap kepekatan logam berat dalam altitud yang berbeza di Bukit Lawa Mandau dengan menggunakan lumut Isopterygium albescens. Tujuan kajian ini dijalankan adalah untuk menentukan pencemaran logam berat (As, Cd, Cr, Cu, Ni dan Pb) di Bukit Lawa Mandau dengan menggunakan Isopterygium albescens sebagai bioindikator, untuk membuat perbandingan akumulasi kepekatan logam berat dalam altitud yang berbeza di Bukit Lawa Mandau dan untuk menganalisis fungsi keadaan iklim tempatan ke atas logam berat di setiap altitud di Bukit Lawa Mandau. Dalam tujuh stesen pengambilan sampel, tiga replikasi telah di ambil dalam stesen tempat pengambilan sampel dan setiap replikasi tersebut akan diduplikasikan lagi. Nilai kepekatan akumulasi untuk unsur logam berat As, Cd, Cr, Cu, Ni dan Pb ditentukan oleh Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). Keputusan daripada ICP-OES menunjukan stesen 5 dan stesen 6 menpunyai logam berat paling tinggi daripada stesen lain, manakala stesen 2 mempunyai nilai logam berat yang paling rendah. Nilai kepekatan akumulasi untuk elemen As paling tinggi di stesen 6 diikuti oleh stesen 1, stesen 5, stesen 7, steten 3, stesen 2 dan stesen 4 mempunyai nilai kepekatan yang paling rendah dengan jumlah 20.12±0.0032 µg/g, 17.26±0.0031 µg/g, 17.22±0.0038 µg/g, 16.75±0.0029 µg/g, 15.59±0.0038 µg/g, 14.10±0.0039 µg/g dan 13.68±0.0041 µg/g mengikut urutan. Kepekatan akumulasi untuk elemen Cr paling tinggi di stesen 5 diikuti dengan stesen 7, stesen 6, stesen 2, stesen 1, stesen 3 dan akhir sekali stesen 4 dengan jumlah 52.48±0.0342 µg/g, 18.82±0.0012 µg/g, 18.01±0.0132 µg/g, 15.48±0.0010 µg/g, 5.21±0.0038 µg/g, 2.78±0.0021 µg/g dan 2.74±0.0021 µg/g mengikut urutan. Manakala, untuk kepekatan akumulasi elemen Cu paling tinggi di stesen 6 diikuti dengan stesen 5, stesen 3, stesen 7, stesen 4, stesen 1 dan akhir ialah stesen 2 dengan jumlah

145.23±0.7376 µg/g, 109.12±0.0463 µg/g, 60.67±0.0198 µg/g, 48.44±0.0097 µg/g, 43.65±0.0116 µg/g, 17.30±0.0101 µg/g dan 8.13±0.0032 µg/g mengikut urutan. Untuk elemen Ni pula, nilai kepekatan akumulasi paling tinggi ialah di stesen 5 diikuti dengan stesen 6, stesen 1, stesen 3, stesen 7, stesen 4 and akhir sekali stesen 2 dengan jumlah 45.33±0.0197 µg/g, 36.19±0.0167 µg/g, 22.49±0.0059 µg/g, 17.84±0.0037 µg/g, 17.01±0.0043 µg/g, 16.85±0.0007 µg/g dan 13.69±0.0019 µg/g mengikut urutan. Kepekatan akumulasi bagi elemen Pb yang paling tinggi ialah di stesen 6 diikuti dengan stesen 4, stesen 5, stesen 7, stesen 3, stesen 2 dan akhir sekali stesen 1 dengan jumlah 78.50±0.0687 µg/g, 10.43±0.0021 µg/g, 6.81±0.0023 µg/g, 6.33±0.0023 µg/g, 5.70±0.0023 µg/g, 5.13±0.0020 µg/g dan 4.77±0.0016 µg/g mengikut urutan. Tetapi bagi elemen Cd, ICP-OES tidk dapat mengesan elemen tersebut bagi semua stesen dalam kajian ini. Sesungguhnya, iklim tempatan mempengaruhi jumlah mendapan logam berat di Lawa Mandau dengan mengaitkan pencemaran yang diangkut dari jarak jauh seperti sumber logam berat daripada pembakaran biojisim dan pencemaran daripada aktiviti manusia yang dibawa oleh faktor angin, dimendapkan di sebelah timur Lawa Mandau dimana hujan bukit berlaku dan diakumulasi oleh lumut untuk beberapa tahun. Kesimpulannya, I. albescens merupakan bioindikator dan akumulator yang baik untuk elemen As, Cr, Cu, Ni dan Pb tetapi tidak bagi elemen Cd dan iklim tempatan atau taburan meteorology sekitar Bukit Lawa Mandau sememangnya mempengaruhi akumulasi logam berat di kawasan kajian.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS, UNITS AND ABBREVIATIOS

<	less than
>	greater than
°C	Degree Celcius
%	percentage
µg/g	microgram per gram
III	three
VI	four
As	Arsenic
Ca	Calcium
Cd	Cadmium
cm	centimetre
Cr	Chromium
Cu	Copper
Co	Cobalt
ECEH	European Centre for Environment and Health
Fe	iron
g	gram
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IQ	Intelligence quotient
m	metre
mg/kg	miligram per kilogram
M	Mole
Mn	Manganese
Mo	Molybdenum
MSL	Mean Sea Level
NE	North-East
Ni	Nickel
Pb	Lead
ppm	part per million
sp	species
SE	South-East

SW	South-West
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

1.1 Air Pollution and Atmospheric Deposition

According to Spellman (2010) "...pollution is complicated, and it cannot be easily defined because what pollution is and what is not is a judgment call." Air pollution can be defined in many ways as it can be the natural or human-induced presence of certain substances in the air in high enough concentrations, for long enough duration and frequencies to cause undesirable effects to living organisms and environment (Yu, 2005). Besides that, the term "air pollution" is used to describe substances that are artificially introduced into the air. Definition of air pollution including when there is other or foreign component enter into the ambient air until the ambient air quality drop or decreasing until it reach certain position that can caused ambient air cannot be functioning according to its standard. Ambient air can be found on the earth surface, or at the troposphere as it is needed for living organism and can affect the human health. Air pollution stems from gases and airborne particles which, in excess, are harmful to human health, buildings and ecosystems. Air pollution is the modification of the natural characteristics of the atmosphere by a chemical, particulate matter, or biological agent (Wadhwa, 2009; Srivastava, 2009; Singh *et al.*, 2011).

Every element is connected with one another and can cause the pollution. In any environmental term, first place that needed to be referring for a definition is in relevant U.S. Environmental Protection Agency (USEPA) publications. Usually to know deeper about air pollution, air pollution practitioner must understand the mechanism of how pollutant dispersal, transport and deposition, and also know to determine the origin or source of the pollutant. Although some pollutants are also produced by nature, the main environmental problems result from human activities (Wadhwa, 2009).

1.1.1 Sources of air pollution and its impact through several studies

Worldwide air pollution is responsible for a huge number of deaths and cases of respiratory disease. The greatest source of emissions is actually mobile sources, mainly automobiles. Sources of air pollution refer to the various locations, activities or factors which are responsible for the releasing of pollutant into the atmosphere. The sources can be classified into two major categories that are anthropogenic sources (human activity) and natural sources (Wadhwa, 2009). Anthropogenic sources of air pollution such as from automobiles, power plants, industrial facilities and the use of chemical in the fertilizers or pesticides for agricultural purposes eventually release pollutants into the atmosphere (Shuqin, 2007).

Atmospheric particulates serve as air pollution or atmospheric pollution have given a long-term effects for respiratory illness to mankind as heavy metals found in the ambient particles can cause lung's tissues to be damage (Monaci *et al.*, 2000; Siu *et al.*, 2005). Epidemiological studies have been carried out since particulates, ozone, acid rain, NOx and sulphur oxides give effect on mortality rates and respiratory health from the air pollution (Wolterbeek *et al.*, 2002).

Atmospheric pollution has caused extreme deterioration and moving toward destruction of the terrestrial environment in many countries. So, to prevent the atmospheric pollution to continue its damage toward the environment, planning and control programmes have been conducted in many countries by monitoring of airborne metals in the environment (Siu *et al.*, 2005).

1.1.2 Atmospheric Contamination, Deposition and Pollutant

The substances in the air causing damage to organisms, plants, ecosystems or property, with both human activity and natural sources is called atmospheric contaminants. While, substances that is found in large amount of concentration or not naturally found in the air or in different location from usual is known as pollutants.

The most basic knowledge to know is air pollutants are mobile, that is mean that the pollutant would not stay at one place and will eventually disperse by wind flow and turbulence, local topographic features, and other physical condition that will affect the pollutant dispersion (Macdonald, 2003). Pollutants can be classified into two categories, which are primary and secondary. Primary pollutants are known as substances that directly emitted from a process, while secondary pollutants are substance that is not directly emitted from a process. Examples of the primary pollutants are, from volcanic activity that occurred naturally and from anthropogenic such as burning of fossil fuel, coal and oil. While, one example of secondary pollutants are particulate matter that from the primary pollutants gaseous or compound in photochemical smog, such as nitrogen dioxide (Daly & Zannetti, 2007; Wadhwa, 2009).

The atmospheric processes that direct air contamination included the chemical transformation, deposition and washout. The conversion of pioneer substances to secondary pollutants such as ozone is one of the chemical transformations in the atmosphere. This transformation will eventually affect both chemical and physical final impact. The pollutants that emitted to the atmosphere will return to the Earth surface by deposition mechanisms. There are two common deposition known as dry deposition and wet deposition (washout) (Cheng, 2006; Fowler *et al.*, 2007). Dry deposition is the removal of both particles and gases as they come into contact with the Earth's surface, while wet deposition is the uptake of particles and gases via water droplets and snow and their removal from the atmosphere as precipitation (Sham Sani, 1975). The main source of environmental pollution is heavy metals since the pollutant that exist in the atmosphere are load and emission from the industry, power stations, domestic heating systems and motor vehicles (Uyar *et al.*, 2009).

1.2 Biomonitoring of Atmospheric Deposition in Mosses

Air pollution monitoring can be done by practicing the concept of biomonitoring with the proper selection of organisms, when the samples were collected, measurements of pollutants can be done miles away from the site. There might be deposition of pollutants on the surface of the organism but this can be prevented by proper cleansing of samples before measurements (Cenci, 2008).

There are two groups of methods for bioaccumulation monitoring known as active and passive monitoring. Active monitoring can be define as exposure of well-defined species that condition is being controlled, while passive monitoring means that the plants must be indigenous for doing observation or chemical analysis (Ceburnis & Valiulis, 1999).

Generally, biomonitoring may be defined as the use of bio-organisms to gain information on certain characteristics of the biosphere (Wolterbeek, 2002; Cenci, 2008). It also known as organisms whose content of certain elements or compounds and/or whose morphological, historical or cellular structure, metabolic-biochemical processes, behavior or population structure(s), including changes in parameters, supply quantitative information on aspects of the quality of the environment or changes in the environment .

According to Szczepaniak & Biziuk (2003), the organism used is called a bioindicator or biological monitor. In general, bioindicator refers to all organisms that provide information on the environment or the quality of environmental changes, and biomonitors are the organisms that provide quantitative information on the quality of environment. Bioindicator is included in biomonitoring as well, but bioindicator is not necessarily need to follow the requirements for biomonitor.

Using mosses as bioindicators for monitoring of air pollution is emerging as economical alternative and effective to perform direct ambient air measurements as this organism receive their nutrients exclusively from the deposition of the atmosphere (Sarmento *et al.*, 2008). There are several studies has uses mosses in determining heavy metal and also trace metal concentrations in large area or even in different geographical areas. Since the beginning of 1960s, many European countries have used mosses in their surveys of atmospheric-metal deposition (Ceburnis & Valiulis, 1999; Acar, 2006; Chakrabortty & Paratkar, 2006).

There are plenty of advantage by using the biomonitoring technique such as sampling of organisms used as biological monitor is generally easier, the accuracy of measurement can be improved as the concentrations in the monitor organisms are higher than the system to be monitored, inexpensive sampling equipment is required, allowing the measurement of a wide range of pollutants (Sarmento *et al.*, 2008) and, over certain period of time most of the organisms can reflect average external conditions and this is important when monitoring levels change rapidly with time.

1.3 Research Question

The research questions for this investigation are:

1. Does Lawa Mandau Hill have higher concentration of heavy metal pollution?
2. What is the altitudal distribution of heavy metal in *I. albescens* in Lawa Mandau Hill?
3. Are the concentration of heavy metal in moss (*I. albescens*) at different altitude significantly different with heavy metals contains in moss in urban and low land areas?

1.4 Objectives

The objectives of this study are:

1. To determine heavy metal (As, Cd, Cr, Cu, Ni and Pb) pollution in Lawa Mandau Hill by using *I. albescens* as bioindicator.
2. To compare the accumulation of heavy metal concentration in different altitude of Lawa Mandau Hill.
3. To analyses the function of local climate conditions on the altitude distribution of heavy metal at Lawa Mandau Hill.

1.5 Scopes of Study

Isopterygium albescens mosses are chosen as bioindicator in this study to determine the concentration level of Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Nickel (Ni) and Lead (Pb) along the hill in Lawa Mandau. The samples in Lawa Mandau Hill will be taken at different elevation from Telipok Town and downhill from Lawa Mandau peak to Kiulu Town. There are seven sampling station to be established in this investigation (station P1, P2, P3, P4, P5, P6 and P7) with three replicates and two duplicates for each sample. The result of each heavy metal will be compared to the amount of heavy metals found in every station in Lawa Mandau Hill to determine the level of heavy metals in Lawa Mandau Hill and relate with the meteorological condition.

1.6 Significant of Study

Investigation on the roles of local meteorological condition is important to understand how this factor affects the distribution of pollution. Better understanding of the heavy metal distribution can be used on a basis for the establishment of pollution risk map that could be interpreted in the local development planning. In Malaysia, there are only several studies that are related to biomonitoring and only limited attempts were found in the literature to use mosses as biomonitors for air pollution. Thus, it is difficult to obtain more information in Malaysia regarding biomonitoring of heavy metal in mosses especially the study on the concentration of As, Cd, Cr, Cu, Ni and Pb using *I. albescens* mosses.

CHAPTER 2

LITERITURE REVIEW

2.1 Mosses

The most popular bioindicators used to monitor air pollution from heavy metals are mosses and lichens (Szczepaniak & Biziuk, 2003; Poikolainen *et al.*, 2004). But mosses were very much useful since it is has widespread occurrence in many countries and has been used in many studies to determine air pollution (Berg *et al.*, 1995; Berg & Steiness, 1997b; Ceburnis & Valiulis, 1999; Suchara & Sucharova, 2000; Grodzinska & Lukaszewska, 2001; Szczepaniak & Biziuk, 2003; Poikolainen *et al.*, 2004; Siu *et al.*, 2005; Cymerman *et al.*, 2006; Fernandez *et al.*, 2007).

The mosses surveys that have been used in most studies is important to identify the source of atmospheric pollution since the surveys describe the regional differences and time trends in the heavy metal deposition (Berg & Steiness, 1997b). Besides that, mosses also known as a well established technique to use as a biomonitor to determine atmospheric trace element deposition on a geographical foundation (Berg *et al.*, 1995). Mosses are organisms that are bioaccumulators and usually used as indirect monitoring methods since it is unexpensive, easy to carry in extensive sampling and excellent biomonitors for trace elements in air (Berg & Steinnes, 1997b; Suchara & Sucharova, 2000; Szczepaniak & Biziuk, 2003; Siu *et al.*, 2005).

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