HEAVY METAL CONCENTRATIONS IN BUKIT MERAH RESERVOIR AND HUMAN HEALTH RISK DUE TO FISH CONSUMPTION

MOHD ILMAN BIN CHE ABDULLAH

UNIVERSITI SAINS MALAYSIA

2022

HEAVY METAL CONCENTRATIONS IN BUKIT MERAH RESERVOIR AND HUMAN HEALTH RISK DUE TO FISH CONSUMPTION

by

MOHD ILMAN BIN CHE ABDULLAH

Thesis submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy

July 2022

ACKNOWLEDGEMENT

Praise be to Allah S.W.T, the Most Gracious and Merciful, for allowing me to complete my study despite many challenges encountered along the way. It was being a full-time worker under the Majlis Amanah Rakyat (MARA) and a part-time student who did a PhD. It was quite challenging for me in managing the working requirements and my academic goals. Nevertheless, I could overcome the difficulty and complete this study thanks to Allah's mercy and the enormous support of my wonderful family and friends.

My first supervisor, Prof Madya Dr Amir Shah Ruddin Md Sah, and my second supervisor, Dr Hazzeman Haris, really deserved significant compliments for their guidance and patience in overseeing my study. I would like to express gratitude to University Sains Malaysia for funding this project under Research University Grant 1001/PBIOLOGI/815092 and 304/PBIOLOGI/6315070. I also would like to acknowledge the School of Biological Sciences Universiti Sains Malaysia (USM) for providing the facilities and equipment to conduct my research. My sincere thanks to Professor Dr Amirul Al-Ashraf Abdullah, Dean of School of Biological Sciences, USM, for his continuous support along my journey.

Last but not least, I would like to express my deepest gratitude to my lovely wife, Wan Salwani Wan Sidi, my father, Che Abdullah, and my mother, Fauziah, for their tremendous support, financially and emotionally motivation during my study. Not to forget my five dearest children (Fahim, Iyyad, Syifa, Aydin and Affan). May God bless you all. Thank you.

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF PLATES

Page

LIST OF SYMBOLS

As	Arsenic
$_{i}As$	Inorganic arsenic
Ca	Calcium
Cd	Cadmium
Cr	Chromium
Cu	Copper
Eh	Redox potential
F	Fishing mortality
Fe	Iron
H_2O_2	Hydrogen peroxide
HCl	Hydrochloric acid
Hg	Mercury
HNO_3	Nitric acid
K	Potassium
K	Growth coefficient
$L\infty$	Asymptotic length
Lc	Length at first capture
$m^3.s^{-1}$	Meter cubic per second
$mg.kg^{-1}$	Milligram per kilogram
$mg.L^{-1}$	Milligram per liter
$\mu S.cm^{-1}$	Micro Siemen per centimeter
$\mu g.g^{-1}$	Microgram per gram
Mn	Manganese
mV	Milivolt

Na	Natrium
Ni	Nickle
ppb	Part Per Billion
ppt	Part Per Thousand
Ø’	Growth performance index
°C	Degree Celcius
%	Percentage

LIST OF ABBREVIATIONS

AEI	AdverseEffects Index
ANZECC	Australian And New Zealand Environment And Conservation Council
BMR	Bukit Merah Reservoir
BSAF	Biota Sediment Accumulation Factor
CA	Cluster Analysis
CCME	Canadian Council Of Ministers Of The Environment
CEC	Cation Exchange Capacity
CF	Contamination Factor
CR	Carcinogenic Risk
CSF	Cancer Slope Factor
CV	Coefficient Of Variation
d.w	Dry Weight
DHA	Docosahexaenoic Acid
DID	Department Of Irrigation And Drainage
DO	Dissolved Oxygen
DOE	Department Of Environment
DOSM	Department of Statistic Malaysia
DRUP	Department of Rural and Urban Planning
E	Exploitation Level
EC	European Commission
ED	The Exposure Duration(70 Years)
EDI	Estimated Daily Intake
Eri	Ecological Risk Factor
EWI	Estimated Weekly Intake
EF	Enrichment Factor
EFA	Eicosapentaenoic Acid
Efr	The Total Exposure Frequency Which Is Equivalent To 365 Days $Year^{-1}$
ERL	Effect Range-Low
FAO	Food And Agriculture Organization
FDEP	Florida Department Of Environment Protection

HI	Hazardous Index
HCA	Hierarchical Cluster Analysis
Eri	Ecological Risk Factor
I_{geo}	Geo-accumulation Index
INWQS	Interim National Water Quality Standard For Malaysia
IRI	Index Of Relative Importance
ISQG	Interim SedimentQuality Guidelines
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ISQV	Interim Sediment Quality Value
IUCN	International Union For Conservation Of Nature
KIS	Kerian Irrigation Scheme
KMO	Kaiser-Meyer-Olkin
LEL	Lowest Effects Level
LOI	Loss On Ignition
mC_d	Modified Degree Of Contamination
MDF	Malaysian Department of Fisheries
MFA	Malaysian Food Act (1983) And Regulation (1985)
MYR	Malaysian Ringgit
m-PEL-Q	Mean Probable Effect Level Quotient
m-ERM-Q	Mean Effect Range Median Quotient
MPI	Metal Pollution Index
MMD	Malaysian Meteorological Department
MYR	Malaysian Ringgit
NOAA	National OceanicAnd Atmospheric Administration
PCA	Principal Component Analysis
PCB	Polychlorinated biphenyls
PEL	Probable Effect Level
PLI	Pollution Load Index
PMTDI	Provisional Maximum Tolerable Daily Intake
PTWI	ProvisionalTolerable Weekly Intake
RfD	The Oral Reference Dose
RI	Potential Ecological Risk Index
SEL	Severe Effect Level
SQGs	Sediment Quality Guidelines

SQO	Sediment Quality Objective
TDS	Total Dissolved Solids
TEL	Threshold Effect Level
THQ	Target Hazard Quotient
USEPA	United States Environmental Protection Agency
USFDA	United StatesFood And Drug Administration
w.w	Wet Weight
WHO	World Health Organization
WQI	Water Quality Index

LIST OF APPENDICES

KEPEKATAN LOGAM BERAT DI EMPANGAN BUKIT MERAH DAN RISIKO KESIHATAN MANUSIA KESAN PENGAMBILAN IKAN

ABSTRAK

Ekosistem air tawar seperti empangan Bukit Merah (BMR) memainkan peranan penting secara ekologi dan ekonomi kepada penduduk setempat. Pencemaran logam berat pada enapan permukaan BMR boleh menyebabkan kesan buruk kepada biota di dalam empangan tersebut dan seterusnya menjejaskan kesihatan manusia. Objektif kajian ini adalah untuk menentukan taburan logam berat di enapan permukaan BMR dan menilai indeks ekologi. Kajian ini juga menerangkan biotumpukan logam berat di dalam beberapa bahagian dari lapan spesis ikan di BMR dan penilaian risiko kesihatan terhadap manusia. Sebanyak 30 sampel enapan permukaan diambil dan parameter psiko-kimia air dan sedimen juga turut diukur. Dapatan kajian ini menunjukkan purata kepekatan logam berat dalam enapan permukaan mengikut susunan menurun adalah Fe > Mn > Pb > Zn > Cr > As > Cu > Ni. Pengumpulan logam berat yang tinggi telah direkodkan di bahagian selatan BMR di mana aktiviti antropogenik adalah ketara. Kesimpulannya pengumpulan dan pengayaan logam berat adalah disebabkan aktiviti antropogenik seperti perladangan, pembalakan, perlombongan pasir dan sisa buangan dari jeti dan bot nelayan. Walau bagaimanapun, kesemua purata kepekatan logam berat adalah di dalam julat yang dibenarkan oleh garis panduan kualiti enapan (SQG). Berdasarkan penilaian indeks - indeks ekologi seperti Indeks Pengumpulan Geo (I_{geo}), Faktor Pengayaan (EF) dan Indeks Beban Pencemaran (PLI), enapan permukaan BMR boleh dikelaskan sebagai menghadapi pengayaaan sederhana dengan pencemaran yang minimun. Biotumpukan logam berat di dalam ikan adalah di bawah julat yang dibenarkan mengikut Akta Makanan

Malaysia (1983) dan Peraturan Makanan (1985) kecuali bagi Fe. Secara umumnya biotumpukan logam berat di dalam lapan spesis ikan secara susunan menurun adalah Fe > Zn > Mn > Cu > As > Pb > Cr. Berdasarkan kadar pengambilan ikan di negara ini sebanyak 168 $g.hari^{-1}$, Anggaran Pengambilan Harian (EDI) bagi setiap spesis ikan menunjukkan EDI bagi kesemua logam berat adalah di bawah Pengambilan Harian Maksimun Yang Boleh Diterima Sementera (PMTDI) di mana Zn mencatatkan kadar pengambilan harian yang paling tinggi manakala $_{i}As$ mencatatkan nilai yang terendah. Penilaian risiko bukan karsinogenik seperti yang ditunjukkan oleh Darjah Bahaya Sasaran (THQ) dan Indeks Bahaya (HI) menunjukkan nilai di bawah 1 bagi kedua-dua indeks tersebut. Ini menunjukkan paras logam berat di dalam ikan yang dikaji, tidak akan menyebabkan sebarang risiko bukan karsinogenik kepada populasi setempat. Risiko karsinogenik bagi logam berat Pb dan $_{i}As$ terhadap populasi setempat dinilai menggunakan indeks Risiko Karsinogenik (CR). Dapatan menunjukkan bahawa paras Pb dan $_{i}As$ adalah di dalam julat yang boleh diterima iaitu $\leq 10^{-6}$, ini bermakna tiada kemungkinan berlakunya barah kepada populasi setempat berdasarkan kadar semasa pengambilan ikan. Dapatan yang diperolehi daripada kajian ini boleh digunakan sebagai makluman asas bagi kajian yang lebih menyeluruh di BMR pada masa hadapan dan membolehkan pihak berkuasa tempatan menjalankan program pemantauan bagi menjamin sumber semulajadi ini dan juga kesihatan manusia pada masa yang sama.

HEAVY METAL CONCENTRATIONS IN BUKIT MERAH RESERVOIR AND HUMAN HEALTH RISK DUE TO FISH CONSUMPTION

ABSTRACT

The freshwater ecosystem, such as Bukit Merah Reservoir (BMR), plays an important role ecologically and economically to the local population. The contamination of heavy metals in the surface sediment of BMR may cause adverse effects on the living biota in the reservoir and ultimately affect humans' health. This study's objectives were to evaluate the spatial distribution of heavy metals in the surface sediment of BMR and assess the ecological index assessment. This study also investigated the bioaccumulation of heavy metals in different parts of eight fish species found in the BMR and the health risk assessment for humans. A total of 30 surface sediment samples were collected and the physicochemical parameters of both water and surface sediments were also measured. The results showed that, the descending order of mean concentrations of heavy metals in the surface sediments of BMR was Fe > Mn > Pb > Zn > Cr > As > Cu > Ni. High accumulation of heavy metals was found in the southern part of the lake, where anthropogenic activities were predominant. In summary, the accumulation and enrichment of heavy metals in the surface sediment of BMR were due to anthropogenic factors such as plantations, logging, sand mining and discharges from fisherman piers. Nevertheless, heavy metals concentrations in BMR surface sediments were within the permissible limit of sediment quality guidelines. Based on the evaluation of several ecological indices such as the Geoaccumulation Index (I_{geo}), Enrichment Factor (EF) and Pollution Load Index (PLI), the BMR surface sediments can be classified as moderately enrichment and minimally contamination. The bioaccumulation of all heavy metals in all fish species was below the permissible limit set by the Malaysian Food Act (1983) and Food Regulation (1985), except for Fe. In general, the descending mean bioaccumulation of heavy metals for eight fish species was Fe > Zn > Mn > Cu > As > Pb > Cr. Based on the 168 g.day^{-1} rate of fish consumption in this country, the Estimation Daily Intake (EDI) for each fish species showed that all EDIs for heavy metals were below the Provisional Maximum Tolerable Daily Intake (PMTDI) with Zn recorded the highest daily intake whereas $_{i}$As recorded the lowest. The evaluation of noncarcinogenic, represented by the Total Hazard Quotient (THQ) and Hazardous Index (HI), showed a value of less than 1 for both indices. This result revealed that the heavy metal in the fish species examined will not cause any noncarcinogenic risk to the local population. The carcinogenic risk to the local population from the heavy metals Pb and $_{i}$As was examined using the Carcinogenic Risk Index (CR). The result showed that the Pb and $_{i}$As levels were within the acceptable range of $\leq 10^{-6}$, which means that there is no probability of cancer in the local population with the current fish consumption. The results obtained in this study could serve as preliminary information for future extensive research and in the reservoir and enable monitoring program by local authorities to simultaneously protect natural resources and human health at the same time.

CHAPTER 1

INTRODUCTION

1.1 General introduction

Fish is considered a highly nutritious food rich in macronutrient such as omega-3 polyunsaturated fatty acids, high-quality proteins, and countless vitamins and minerals which play an essential role in the prevention of cardiovascular disease and promote healthy growth of the brain, nervous system, and vision in children (Annette et al., 2018; Arulkumar et al., 2017; Milenkovic et al., 2019; Storelli et al., 2020). The high nutritional value of fish has led to a 2.1 % increasement in global production of fish for human consumption, reaching 178.8 million tons in 2018 due to easy accesibility and affordability for local populations (FAO, 2020).

However, the possibility of human health risk from fish is alarming worldwide, as aquatic ecosystems are highly polluted due to anthropogenic activities, especially in developing countries (Storelli et al., 2020; Xu et al., 2020). Consumption of fish is considered the main route of heavy metals exposure for humans. The heavy metals from anthropogenic activities enter the aquatic ecosystem and due to the immobility of heavy metals in the water column some of the heavy metals are precipitated and deposited in the surface sediment of lakes and reservoirs. The heavy metals in the sediment can be released back into the water column under the influence of various physicochemical parameters of water and sediment and then taken up by fish (Maurya & Malik, 2018; Titilawo et al., 2018; Yu et al., 2020). Fish can bioaccumulate the heavy metals in variety of ways, including ingestion of particles suspended in the water column, adsorption to tissue and skin surfaces, and also ion-exchange into lipophilic tissues such as gills (Ahmed et al., 2019). Heavy metal levels in fish can increase to toxic levels over time due to effects of biomagnification. Many cases of heavy metal contamination in fish have been reported worldwide, the adverse effects of which on humans may include kidney failure, impairment of nervous system and cardiovascular diseases (Arisekar et al., 2020; Matouke & Abdullahi, 2020; Palash et al., 2020; Yu et al., 2020).

Thus, heavy metal contamination in the aquatic environment is one of the main problems. It has caused concern among scientists due to its extensive sources, persistence, non-biodegradable nature, bioavailability, and toxicity to living organisms when the permissible concentration limit is exceeded (Liang et al., 2015; Nowrouzi & Pourkhabbaz, 2014; Rieuwerts, 2015; Shafie et al., 2013; Ying et al., 2015). The situation is exacerbated by the increasing input of heavy metals into aquatic environments, such as reservoirs and lakes in recent decades. A report on the total concentration of heavy metal pollution in rivers and lakes worldwide from the 1970s to 2017 shows a rapid increase in heavy metal concentrations due to anthropogenic activities from the 1990s to the 2010s (Zhou et al., 2020). The typical heavy metals associated with health risks due to the fish consumption are arsenic (As), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), and Zinc (Zn). Some of the heavy metals listed above are essential heavy metals (Cu, Fe, Mn, and Zn). Nevertheless, these heavy metals can pose a severe threat to humans if they exceed the permissible limit. Therefore, this kind of heavy metal still need to be evaluated for continuous monitoring to protect the vital food source for local population.

1.2 Problem statement

Potentially toxic elements such as heavy metals are among the pollutants that can severely affect aquatic biota and cause various health problems in humans. Malaysia has been addressing this problem since the 1990s. According to Fathi Alhashmi et al. (2012), the amount of heavy metals in the aquatic ecosystem has been of significant concern since then. Sources of heavy metal contamination in this country are metal finishing and electroplating, agriculture, deforestation, animal husbandry and sand mining. This situation is exacerbated by the non-compliance with heavy metals regulation issued by the Malaysian Department of Environment (Ahmad & Shuhaimi-Othman, 2010; Rohasliney et al., 2014; Taweel et al., 2013a).

Indiscriminate discharge of waste water containing heavy metals from households and industries into the lakes and reservoirs can cause severe toxicity to organisms through bioaccumulation and biomagnification processes along the food chain (Razak et al., 2021). Organisms at the top of the food chain, such as fish, birds, mammals and humans are ultimately the most affected. Some of the heavy metals such as As, Cd, Pb and Hg are carcinogenic, immunotoxic, cytotoxic, nephrotoxic and genotoxic to living organism even at low concentration (Puneet & Anu, 2010; Sfakianakis et al., 2015).

Other essential heavy metals such as Fe and Zn are also known to cause various health risks such as cancer and cellular respiration disorders in humans when bioaccumulated at higher concentrations (Razak et al., 2021).

In Malaysia, most of the research on heavy metal contamination focuses on coastal sediment, with about 141 studies published in the last two decades (Yunus et al., 2020). However, studies on heavy metal contamination in freshwater ecosystems, particularly in lakes and reservoirs, have been limited with less than 100 published studies. Despite the hazardous effects of heavy metal pollution, there is limited information in the literature on the status of heavy metals in surface sediment and fish in Bukit Merah Reservoir (BMR).

Currently, studies on the presence of heavy metals in BMR are limited to the detection of heavy metals in the water column, as reported by Shuhaimi-Othman et al. (2010) and Akinbile et al. (2013). These studies mainly focused on the southern part of the reservoir. To date, there has been no work on the northern part of the reservoir. This reflects a gap in knowledge about the level of heavy metals in surface sediments and biota in the BMR, especially fish. In addition, As level in surface sediments and biota in BMR was not reported in either of the previous studies. Heavy metals such as Arsenic (As) are known for their toxicity and potential long term effects on aquatic biota and human health (Varol, 2020; Zhong et al., 2018). Thus, the status of As concentration in both sediment and biota is highlighted in this study.

The assessment of heavy metals in BMR surface sediment is of paramount importance because sediment is known to serve as a sink and source for heavy metals in the aquatic ecosystem. The release of heavy metals in BMR surface sediment to the water column can occur under a variety of physicochemical conditions such as pH, salinity, and dissolved oxygen (Atkinson et al., 2007). These heavy metals in the water column can be taken up by the fish and bioaccumulate in different parts of the fish.

The level of heavy metals in fish can then increase to the toxic levels through the process of biomagnification. Therefore, the assessment of heavy metals in surface sediments and fish in BMR is crucial for the continuous monitoring of BMR, which is a significant source of inland fisheries for the local population (Hidzrami, 2010).

This study examined the concentrations of heavy metals in sediments in both the northern and southern parts of the BMR, as well as several species of fish found in the BMR. This provides a comprehensive preliminary status of heavy metal distribution in sediment and the health risk effects of consuming fish in the BMR.

1.3 Scopes of study

Concisely, this study elucidate the following scopes :

i. This study provides information on the distributions of heavy metals such as As, Cr, Cu, Fe, Pb, Mn, Ni and Zn in the surface sediment of BMR. Physicochemical parameters of the water and sediment such as pH, conductivity, redox potential, TDS, DO and temperature are also recorded.

ii. This study also addresses the bioavailability of heavy metals in common fish species found in BMRsuch as *Barbonymus gonionotus* (lampam jawa), *Barbonymus schwanefeldii* (lampam sungai), *Cyclocheilichthys apogon* (temperas), *Hampala macrolepidota* (sebarau), *Labiobarbus leptocheilus* (kawan), *Notopterus notopterus* (selat), *Osteochilus vittatus* (terbol) and *Oreochromis niloticus* (tilapia). Comparison of bioaccumulation of heavy metals is measured in different parts of fish (gills and muscle) for *B. gonionotus*, *B. schwanefeldii*, *C. apogon*, *H. macrolepidota*, *L. leptocheilus*, *N. notopterus*, *O. vittatus*. In *O. niloticus*, however, the comparison is made in three different parts of the fish, namely, gills, muscle and liver.

iii. Indices related to the heavy metals in the surface sediment, such as, Geo-accumulation Index (I_{geo}), Enrichment Factor (EF), Contamination Factor (CF), Pollution Load Index (PLI), Modified Degree of Contamination (mC_d), Ecological Risk Factor (Eri), Potential Risk Index (RI), mean Probable Effect Level Quotient (m-PEL-Q), mean Effect Range Median Quotient (m-ERM-Q) and Adverse Effect Index (AEI) are calculated. Meanwhile, indices such as Metal Pollution Index (MPI), Estimated Daily Intake (EDI), Target Hazard Quotient (THQ), Hazardous Index (HI) and Carcinogenic Risk (CR) are calculated for the heavy metals concentration in fish.

iv. These indices provide a comprehensive interpretation of the status of metal(loids) in the BMR and their impact on aquatic biota and human consumption. Details of these indices are explained in Chapter 3 of this thesis.

1.4 Justification of study

Based on the literature search on Scopus and Science Direct, there is almost no information on the presence of heavy metals in fish species in BMR. Only one study of heavy metals in tropical eel *Anguilla bicolor bicolor* in Kurau River was conducted by Arai et al. (2012). Kurau River is the primary source of water supply for the BMR reservoir. However, using the eel as a biomonitoring agent of heavy metals is quite difficult. This species is rare, as reported in the current fish checklist in BMR by Mohd

Shafiq et al. (2014). They found no *A. bicolor bicolor* in BMR or any tributaries of the catchment area. The rarity of this species could affect the effectiveness of its use as a bioindicator.

Besides, Arai et al. (2012) only found seven specimens in the Kurau River. The choice of biomonitor is crucial. Several factors must be considered for an effective biomonitor, such as the species is abundant and easy to sample, long-lived, easy to identify, and of sufficient size for adequate laboratory analysis (Li et al., 2010; Naigaga et al., 2011; Prabhakaran et al., 2017).

According to Mohd Shafiq et al. (2014), the BMR and its tributaries consist of 47 fish species from 19 families, with 25 species recorded in the BMR. This shows the BMR is relatively rich in species, given the BMR is a shallow lake with a maximum depth of 5 m. In this sense, biomonitoring in BMR should focus on fish species. The most abundant species in the BMR and its tributaries are *B. schwanefeldii*, *B. gonionotus*, *C. apogon*, *H. macrolepidota*, *L. leptocheilus*, *N. notopterus*, *O. vittatus* and *O. niloticus*. These fish species might be the best choice for biomonitoring program. In addition, fish should be considered the best candidate for heavy metal bioindicators since they occupy different trophic levels at different sizes and ages.

In addition, fish from the BMR is used to make a local delicacy known as *ikan pekasam,* or fermented fish with roasted rice. This delicacy can be sold at MYR 20 per kg, reflecting the importance of inland fishery in the BMR to the local economy. Most of the *ikan pekasam* in BMR is produced from the cyprinid species or known as *ikan putih* or white fish, due to their generally white coloration.

In short, the assessment of heavy metals contamination in fish will provide important information in two aspects. From the aspect of public health, this assessment will prevent unnecessary health risk to the human due to the consumption of the fish. The second aspect is that it will provide crucial information for a better understanding of the biological status of aquatic ecosystems and the cause and effect of the anthropogenic activities in the aquatic ecosystem (Ahmad & Sarah, 2015). The present study will provide the basic information about the status of heavy metals pollution in the common fish species in the BMR, thus providing a more holistic approach to the conservation and management of natural resources in the BMR.

1.5 Objectives

The present research comprises of three foremost objectives :

i. To determine the distribution and concentration of heavy metals in surface sediment of BMR.

ii. To determine the level of heavy metalloids in the different body parts (gill, liver, and muscle) of different fish species from BMR.

iii. To perform the ecological index assessment and health risk assessment of heavy metals in human.

1.6 The significance of the study

This study is expected to elucidate several key factors, such as :

i. Provide a basic assessment of heavy metal levels in fish and surface BMR sediments.

ii. Provide the preliminary human health assessment from consumption of fish from the BMR.

iii. Provide a general overview of the potential use of fish species in BMR as a bioindicator of metalloids that will provide crucial information for reservoir conservation and management.

1.7 Limitation of study

This study is conducted in BMR. Therefore, the result of this study reflects the local impact of anthropogenic activities around this area and cannot be generalized to the other freshwater ecosystems in this country. The levels of heavy metals in both fish and sediment are highly influenced by a complex interaction between the abiotic and biotic factors of the reservoir and the fish species in the reservoir. It is well known that biological parameters such as length, weight, condition factor, and feeding play a significant factor in the accumulation of heavy metals. However, these factors are not considered as part of the study objectives, and the information provided is based on the general differences between species. The presence of heavy metals in the BMR water column was not evaluated in this study based on the detailed information provided by Shuhaimi-Othman et al. (2010) and Akinbile et al. (2013).

CHAPTER 2

LITERATURE REVIEW

2.1 Condition and status of lakes and reservoirs in Malaysia

Since 1980, Malaysia has experienced rapid urbanization and development shifting from an agricultural nation to become a high-income industrial nation by 2020. Highly developed heavy industries such as automotive, electronics and small-scale industries have boomed. However, this economic success has been bought by serious environmental problems such as deforestation, unsustainable natural resources and pollution. One of the vital natural resources for development is a continuous supply of water. Although the primary source of Malaysia's water supply has been the river, lakes and reservoirs still play an important role in water supply. Since 1930, 90 large lakes across the country have been used for various purposes such as drinking water, flood management, hydropower and irrigation (Sharip et al., 2016). However, more than 60 % of these lakes have been reported as eutrophic due to various anthropogenic activities (Sharip et al., 2014). Siltation and sedimentation of reservoirs is also a major threat as this process reduces the storage capacity of the reservoirs.

One of the oldest man-made reservoirs in this country is the Bukit Merah Reservoir (BMR). The 41 km^2 reservoir was built in 1906 and is considered the oldest man-made reservoir in Peninsular Malaysia. This reservoir is also a natural sanctuary for valuable and endangered fish species such as the Golden Arowana (*Scleropages formosus*).

According to the Department of Urban and Rural Planning (DURP) (2017), cited by Fadhullah et al. (2020), the total catchment of BMR is 494.2 km^2. Forest is the most dominant land use in this catchment (53.5 %), which includes Kerian, Larut, Matang and Selama districts (264.4 km^2). Oil palm plantations occupy 23.77 % of the area (117.28 km^2), while rubber plantations account for 7.7 %. (37.92 km^2). Other land uses (5.83 %), including fruit orchards (1.63 km^2), rice fields (15.55 km^2), various agricultural crops (1.55 km^2) and chicken and goat farming (10.21 km^2). According to land use data, there are also small and medium downstream industries, such as oil palm mills and wood or rubber processes (0.51 km^2). The majority of the residential areas, totaling 45.49 km^2, consist of traditional Malay houses (9.2 %).

As the oldest reservoir in the country, BMR has faced many problems such as eutrophication, deforestation, sedimentation, and pollution from agricultural activities that affect the water quality in BMR. According to Hidzrami (2010), it is estimated that 40 % of the watershed in the northern and eastern part of BMR is covered by floating aquatic plants, especially near the mouth of Merah and Kurau Rivers. Between 2006 and 2009, DID spent more than MYR 12.8 million to remove this floating vegetation known as 'Bakong' (*Hanguana malayana*), which covers 700,000 m^2. One of the main reasons for this problem is the constant influx of nutrients from the runoff water of the plantations in the lake. Sedimentation is also a major problem in this reservoir. Extensive land development near the lake basin poses a significant threat to BMR water quality. To date, there are no legal or environmental regulationsto control these activities.

This lake has long been of interest to local researchers, especially in the study of water quality (Akinbile et al., 2013; Fadhullah et al., 2020; Mohd Shafiq, 2016; Mohd Shafiq et al., 2016; Mokhtar et al., 2020; Nur Syahirah et al., 2017; Shuhaimi-Othman, Ahmad, et al., 2010) sedimentation (Ismail & Najib, 2011; Mohd Najib et al., 2017); fish diversity (Mohd Shafiq et al. 2014; Yap 1988).

According to Shuhaimi-Othman et al. (2010), BMR's water can be considered as Class I according to NWQS (National Water Quality Standard). The levels of 11 investigated heavy metals (Al, Ba, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, and Zn) in BMR's water are lower than permissible concentrations allowed by Malaysian and international standard, except for Al and Fe. However, Akinbile et al. (2013) indicated that the water in BMR has been classified as Class III, indicating slightly polluted water. They reported Cd, Cr, Cu, Fe, Mg, Mn, Ni, and Zn and also pointed out the high level of Fe in BMR water. A study by Mohd Shafiq et al. (2016) reported improved water quality in BMR, where they classified BMR as Class II based on the Water Quality Index (WQI). However, they did not report the presence of heavy metals.

Based on the reports by Shuhaimi-Othman et al. (2010) and Akinbile et al. (2013), the presence of heavy metals in the BMR's water was below the permissible limit except Fe. The reason could be the laterite soil, which is common in Peninsular Malaysia. This type of soil contains high percentage of Fe, which can reach up to 35.5 % in the form of Fe oxide (Fe_2O_3) (Latifi et al.,2013). Overall, heavy metals in BMR water are not of health concern to human or aquatic biota. However, there are no reports of heavy metals in surface sediment and aquatic biota in the BMR. Although, Arai et al. (2012) reported the levels of heavy metals (Cd, Cu, Fe, Ni, Pb, and Zn) in freshwater eel (*Anguilla bicolor bicolor*) caught in the Kurau River, which is the main water supply to the BMR. The study showed that heavy metals in eel tissue are still within the acceptable limits of heavy metal in aquatic biota. However, there is little information on the level of heavy metals in other aquatic biota in the BMR, especially in fish. Thus, it is important to determine the potential level of heavy metals in fish in the reservoir.

2.2 Definition of heavy metals

The term heavy metal is an ill-defined term that refers to a group of metal and semi-metal (metalloids) that has been used extensively in many environmental journals. According to Ali and Khan (2017), the term " heavy metal" was first coined in academic publications by Bjerrum (1936). This term is routinely associated with environmental pollution, bioaccumulation and toxicity to living organisms, including humans (Adebola et al., 2018; Bosch et al., 2016; Roy, 2010; Siong et al., 2016). There are other terms, such as trace metals, toxic metals, transition metals and micronutrients. However, the term heavy metal is widely used compared to the other terms. The term heavy metal has been defined in many ways, such as density, atomic weight, atomic number, chemical properties, and toxicity (Duffus, 2002).

Nevertheless, the ambiguity of the term heavy metal had caused a great division in the scientific community; some considered the term meaningless and obsolete and had to change it, while others insisted on keeping the term (Ali & Khan, 2017; Batley, 2012; Chapmen, 2012; Duffus, 2002; Pourret & Bollinger, 2017). One of the earliest publications calling for the elimination of the term heavy metal was presented by Nieboer and Richardson (1980). They proposed replacing the term heavy metal based on class A (O-seeking), class B (N/S seeking), and intermediate class.

However, the scientific community has ignored the proposal of Nieboer and Richardson (1980), and the term heavy metals is still used. However, the debate on the inappropriate use of heavy metal was resurfaced by Duffus (2002) in the International Union of Pure and Applied Chemistry, a highly cited journal. According to Duffus (2002), the term heavy metal should be omitted and replaced with the classification based on chemical properties. This classification would allow researchers to interpret the biochemical basis for the metal toxicity. It would thus provide a rational basis for evaluating the most likely toxic types of metal. However, this proposal had led to a major split among researchers. Some authors agreed with Duffus (2002), such as Chapmen (2012) and Hubrer et al.(2010).

On the other hand, a well-known researcher in the field of environmental chemistry and ecotoxicology defends the use of the term "heavy" metal (Batley, 2012). He further stated that the term heavy metal is sufficient to distinguish the metals of environmental concern such as Pb, Hg, and Cd from other "light" metals that are least harmful to the environmental (Na, K, and Ca). Furthermore, since there is no better definition of the term to cover the group of metals, which considered to be environmental concern, the term should be retained. However, Pourret and Bollinger (2017), insisted in the Science of the Total Environment Journal, that the term heavy metal should be replaced by a more acceptable term such as potentially toxic metal(s)/element(s) or trace metal(s) /element(s).

Considering all the arguments of previous authors, Ali and Khan (2017) decided to keep the term heavy metal. The decision was made based on several considerations. None of the newly proposed terms can provide a reasonable alternative. The term heavy metal is used ubiquitously in the environmental literature, and it is impossible to change it in the current situation. Therefore, a broader definition of heavy metal was proposed : "naturally occurring metals with an atomic number (Z) greater than 20 and an elemental density greater than 5 g cm^{-3}". They also emphasized that for an element to be classified as a heavy metal, it must be primarily metallic and heavy. Regardless of whether it is essential or non-essential to living organisms, whether it is toxic or not, and whether it has the reputation of being an environmental pollutant. From this point of view, As should never be considered as heavy metal. Their proposal was submitted to the editors of several highly cited journals, including Pure and Applied Chemistry. These editors agreed on their proposal and will ask the future author to abandon the term heavy metals when referring to metalloids such as As (arsenic) and light metals such as Al.

However, according to Briffa et al. (2020), the debate among researchers on the term heavy metals is still ongoing, and no decision can be made whether the term should refer to their high atomic weight or to their high density. Currently, the term heavy metal is commonly associated in the scientific community with metallic chemical elements and metalloids that present potential for toxicity to the environment and humans, regardless of their weight, such as As (arsenic) and Se. Therefore, this study will retain the term heavy metals when referring As, Cr, Cu, Fe, Pb, Mn, Ni, and Zn since they have long been considered heavy metal in many environmental journals.

Heavy metals exist in the environment through the natural leaching process, but the levels of these metals and metalloids may increase above the permissible limit due to human activities, especially in recent decades. These heavy metals are non-biodegradable, bioaccumulative, and biomagnifying and contribute to the significant water pollution (Giri & Singh, 2013; Liang et al., 2015). These heavy metals can accumulate in organs and tissues of organisms through strong binding to metallothioneins. Metallothioneins consist of metalloproteins molecules with the additional amino acid cysteine and are potent substances for binding metalloid. This substance is heat resistant and has a low molecular weight. Metallothioneins play an important role in metals homeostasis, protecting the organism from the negative effect of heavy metals and scavenging free radicals (Chasapis et al., 2020; Samuel et al., 2021).

Anthropogenic activities are the most important factor contributing to heavy metals such as As (arsenic), Cd, Fe, Pb, Zn, and other metals in the aquatic ecosystem. These include agriculture, deforestation, and sand mining in the upstream (Ahmad & Shuhaimi-Othman, 2010; Beckers & Rinklebe, 2017; Canli & Atli, 2003; Islam et al., 2015; Younis et al., 2015). In addition, many pesticide preparations used in the agriculture contain heavy metals such as Pb, Cd, and Ni due to their toxicity properties (Radojevic & Bashkin, 2006).

At large, heavy metals can be divided into biologically essential and non-essential groups. The essential heavy metals (e.g., Cu, Zn, Cr, Ni, Co, Mo, Mn, and Fe) are essential for functioning of physiological processes in living organisms. Therefore, a deficiency of these heavy metals can impair physiological function. Non-essential heavy metals, on the other hand, are elements that have no specific function in living organisms. Non-essential heavy metals can be further subdivided into non-toxic and toxic. Non-toxic non-essential heavy metals are those that have no toxicity below the permissible limit, such as Ni and chromium, Cr. Toxic non-essential heavy metals, on the other hand, are elements that are toxic even at low levels, such as Cd, Hg, and Pb, which are very toxic and can cause severe health problem including death (Ali & Khan, 2017; Roy, 2010; Sauliutė & Svecevičius, 2015; Sfakianakis et al., 2015).

Metalloid, such as As (arsenic), are of great concern because As is very toxic to humans. As is regarded the king of poison and has been used throughout human history to eliminate enemies. One of the most famous incidents is the As poisoning of the French Emperor, Napoleon Bonaparte (Mudhoo et al., 2011). Detailed information about the types of heavy metals, their sources and their health effects were explained in more detail in subchapter 2.2.2.

2.2.1 Heavy metals in surface sediment

Sediments are particulate materials that accumulate at the bottom of water bodies such as ponds, lakes, reservoirs, streams, and rivers in varying proportions of clay, sand, silt sediment or organic material (MacDonald et al., 2003). Sediments act as fundamental components of an abiotic factor in the freshwater ecosystem and provide the much-needed nutrient to benthic organisms (Köse et al., 2020; Suresh et al., 2012). Heavy metals (i.e., As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, and Zn) from the anthropogenic activities (agriculture, sand mining, smelting, electroplating and agricultural activities) and rock weathering enter the river and transported in soluble form into the lake ecosystem.

These potentially toxic elements gradually bind to particulate in the water column (i.e., suspended sediment, organic and inorganic colloidal particles). Nearly 85 % of the particles eventually settle and accumulate in the surface sediment of the water body (Adel Mashaan et al., 2011; Khodami et al., 2017; Shafie et al., 2013). In general, the accumulation of heavy metals in the surface sediment of freshwater bodies could be attributed to the adsorption, precipitation, organic flocculation, complexation, and also gradually integration of heavy metals over a long period of time (Xia et al., 2020). Since heavy metals are not biodegradable, they will remain in the sediment for an extended period until they are transformed into other elements in the sediment orcan also react with other elements present in the sediment to become more toxic or less toxic.

Therefore, sediment is a major reservoir or sink of these heavy metals. Contamination of sediment by these anthropogenic activities is a crucial environmental concern for several reasons. First, contaminated sediment is known to be toxic to sediment organisms and fish, thus threatening their survival, growth, and reproduction. Second, aquatic organisms can take contaminants such as heavy metals through bioaccumulation. When passed down the food chain, the concentration of the contaminants will be higher and become more toxic through the biomagnification process. Many studies have reported that the concentration of potentially toxic elements such as heavy metals is much higher in sediments than in the water column (Jia et al., 2018; Mir Mohammad et al., 2016; Rajeshkumar et al., 2018). This is well understandable since heavy metals have low solubility in water. Most of the metalloids accumulate in biota and sediments.

Even though sediment acts as a reservoir or sinks for heavy metals, they also can act as a source that gradually releases these heavy metals into the water, through the resuspension of sediments naturally, e.g., water currents and also by human activities such as sand mining, trawling and large vessels (Liang et al., 2015; Naji & Ismail, 2012). The complex interaction of several physico-parameters and other variables, i.e., salinity, pH, redox potential, dissolved oxygen, organic and inorganic carbon, the presence of cation, soil texture, precipitation, iron, and manganese oxides, is also known to influence the transfer of the heavy metals from sediment to water (Khan et al., 2016; Maurya & Kumari, 2021; Rieuwerts et al., 1998). Hence, the sediment assessment is important for a better understanding of the presence and behavior of heavy metals in the aquatic environment. Aquatic organisms can only take up the mobile portion of heavy metals that enter the water column from the sediment and later bioaccumulate and biomagnify through the food chain in the aquatic ecosystem (Qianet al., 2020).

Studies on the heavy metals in marine, and river sediments had gained much interest among local researchers in Malaysia (Anandkumar et al., 2019; ELTurk et al., 2019; Haris et al., 2020; Razak et al., 2021; Salam et al., 2019; Sukri et al., 2018; Zaini et al., 2020). However, studies on lakes and reservoirs in this country are limited (Ebrahimpour & Mushrifah, 2008; Gharibreza et al., 2013; Shuhaimi-Othman et al., 2010).

2.2.2 Types of heavy metals, its sources, uses and health effects

This study focused on potentially toxic elements represented by several types of heavy metals . The heavy metals are further classified as essential heavy metals such as Fe, Cu, Zn, Mn, and Ni and non-essential heavy metals such as Cr, Cd, and Pb. While As represent metalloid. These potentially toxic elements are the most common pollutants found in lakes and reservoirs due to the various anthropogenic activities and Earth's crust Nevertheless, it is crucial to note that all heavy metals both essential and non-essential, can cause toxicity in the human body when they accumulate at high concentrations (Storelli et al., 2020). Heavy metal can be found in minerals and rocks in the earth's crust in varying concentrations.

A mineral is naturally occurring homogenous solid with different chemical composition that determines it crystalline shape and form. Rocks, on the other hand, are composed of several minerals and are generally classified according to the process of their formation. Rocks consist of aggregates of one or more minerals that form naturally, and these aggregates form the basic unit of the solid earth. Rocks can be classified into three (3) main classes based on their formation such as i) Igneous rock that forms from the solidified magma during volcanic eruption, ii) sedimentary rock, formed from the precipitated solution or fragment of pre-existing rocks and lastly iii) metamorphic rocks formed from either igneous or sedimentary rock which has changed its texture, structure and mineralogical composition due to various geological conditions (Rafferty, 2012).

2.2.2(a) Arsenic (As)

Arsenic is the 65th most abundant metalloid with a density of 10.5 $g.cm^{-3}$ and exists in minerals such as argentite, acanthite, and chlorargyrite (Briffa et al., 2020). Arsenic is a highly toxic and carcinogenic metalloid naturally distributed in the earth's crust (Bosch et al., 2016; Shtangeeva, 2005). This metalloid has been responsible for numerous accidental, occupational, and therapeutic poisonings since its first discovery in 1250 (Mudhoo et al., 2011). Arsenic is ubiquitous in soil, sediment, and groundwater. In unpolluted soil, the average As concentration ranges from 1 – 40 $mg.kg^{-1}$ and can reach up to 14000 – 27000 $mg.kg^{-1}$ in the heavily polluted soil. The average concentration of As in surface sediment is usually below 10 $mg.kg^{-1}$ (Huang et al., 2016; Loska et al., 2003; Sakan et al., 2012).

In the 20th century, the most devastating As poisoning was reported in Bangladesh, where 70 - 80 million people are affected by groundwater contaminated with As. The level of As in water tube well of West Bengal district was between 150 ppb-200 ppb, almost four times higher than the permissible limit (Alam et al., 2002; Hassan et al., 2011; Riaz Uddin & Naz Hasan, 2011). As is the first metalloid known to be carcinogenic to humans. As can cause acute and chronic effect in humans such as neurotoxicity, skin problems, cardiovascular disease, hematological, respiratory symptoms, developmental effects and various types of cancer (Bosch et al., 2016; Kapaj et al., 2006; Rasheed et al., 2016; Sanyal et al., 2017; Yang et al., 2016).

Due to its toxicity, the USEPA has developed a reference dose known as RfD. In general, the RfD is a calculation of a daily exposure to the human population that is unlikely to cause adverse effects over a lifetime. The oral RfD for As is 0.0003 mg. kg $^{-1}$.day $^{-1}$ and a higher level will cause dermatitis, the formation of liver carcinoma and reduced neuron transmission (Korkmaz et al., 2017).

The source of As might came from natural factors such as geological weathering, biological, and anthropogenic. Geological weathering is the primary factor of groundwater contamination by As. High level of As in groundwater can enter the food chain through the accumulation of arsenic in aquatic plants and phytoplankton, and then move to the next trophic level. Consumption of arsenic-contaminated aquatic organisms, such as fish, is considered to be one of the leading factors contributing to As toxicity. In a eutrophic lake, arsenic contamination could be higher due to the possible release of As from the sediment (Qin et al., 2016).

Nevertheless, the source of As from anthropogenic activities is the primary issue of arsenic pollution. As was used in gold mining, smelting of non-ferrous metals activities, production of semiconductor (gallium arsenide), manufacturing of arsenic-based pesticides and the wood preservative (Bosch et al., 2016; Rasheed et al., 2016; Roy, 2010). In the agriculture industry, As in the form of calcium arsenite and copper acetoarsenite is commonly used as a pesticide. At the same time, methylarsenic acid and dimethylarsenic acid are used as an herbicide (Osuna-Martínez et al., 2021).

It is known that fish and seafood contribute for about 90 % of the As exposure in humans. However, some authors suggested that health risk assessment of As should be conducted based on inorganic As since this type of As is the most toxic and responsible for the adverse effects on humans. Besides, most of the As in fish is in organic form, such as arsenobetaine, arsenosugars and arsenolipids, which are less toxic or not toxic at all (Avigliano, 2019; Fakhri & Sarafraz, 2021; Mol et al., 2018; Varol & Sünbül, 2018). Several authors in this country had reported the accumulation of As in fish. For example, Fathi Alhashmi et al. (2012) reported the level of As in gills, liver, and muscle tissue of two commercial species, namely *Arius thalassinus* (duri) and *Pennahia anea* (gelama) in Kapar and Mersing coastal water. They found that As accumulates in higher concentrations in the liver for both species, followed by gills and muscle tissue. A study by Kah et al. (2015) on the distribution and health assessment of As and other metals in aquaculture sites in Malaysia shows that As is the primary contaminant of heavy metals due to the use of feed pellets enriched with metals.

As is influenced by soil pH, organic matter, soil mineralogy, and arsenic oxidation state (Cagnin et al. 2017; Hooda 2010; Wang et al. 2016). In the natural environment, As can exist in many different forms, whether organic; methylarsonic acid (MMA^{5+}) acid, methylarsonous acid (MMA^{3+}) or inorganic; arsenate (As(V)), arsenite (As(III)) (Rasheed et al., 2016). However, in sediment, the predominantly As speciation in oxidizing conditions is As (V) while As (III) occurs under reducing conditions. Inorganic arsenic is also relatively mobile in the soil, especially in alkaline soils (Hooda 2010; Wang et al. 2016). As (V) is readily bound to the mineral of the sediment and is therefore less mobile and less toxic than As (III). Arsenic (III) is more mobile compared to As (V) which mean it will likely bioaccumulate in the tissues of living biota and is known to be more reactive toward in the tissues of living biota. Arsenic is known to interfere with several enzymatic activities associated with metabolism and nerve transmission (Hussain et al., 2021; Ouattara et al., 2020).

Still, both inorganic As is carcinogenic, mutagenic, and teratogenic (Hatje et al., 2010). This type of inorganic As is the most dangerous type for aquatic organism and human being due to its stability and easily absorbed by gills, liver, gastrointestinal tract, abdominal cavity, and muscle (Bosch et al., 2016; Rasheed et al., 2016). There is also sufficient evidence that ingestion of inorganic As causes bladder and lung cancer in humans (Hassan et al., 2011; Kapaj et al., 2006). Due to its hazardous effect and its widespread use in agriculture and industrial, As is ranked as the number one toxin on the US Environmental Agency's (USEPA) list of pollutants (Hatje et al., 2010).

2.2.2(b) Chromium (Cr)

Cr is glossy, a silver-gray metal that exists in compounds or ions in water but rarely found as an element in the earth's crust (Saha et al., 2011). The density of Cr is 7.15 $g.cm^{-3}$ and it is considered the 21th most abundant element on the earth's surface (Briffa et al., 2020). This metal is a non-essential, non-toxic heavy metal that poses no significant threat to a living organisms, especially when it accumulates below its threshold level. However, if the concentration of the Cr exceeds its threshold value, it may cause alteration of gills morphology, locomotor behavior, mutagenicity and genotoxicity in fish (Begum et al., 2006; Bosch et al., 2016; Kumar et al., 2012; Nagpure et al., 2017). Whereas in humans, high level of Cr is associated with cancer risk, DNA damages, and other damage to major homeostatic organs such as the liver and kidney (Briffa et al., 2020; Resma et al., 2020; Sedman et al., 2006).