LEVELS OF LEAD IN SOLVENT-BASED PAINT FOR HOME USE IN MALAWI, LEVELS OF SELECTED HEAVY METALS IN MUDI RIVER WATER AND SEDIMENTS AND ENVIRONMENTAL IMPACTS OF MUDI RIVER SEDIMENTS

MSc. (ENVIRONMENTAL SCIENCES) THESIS

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UNIVERSITY OF MALAWI

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MSc. (ENVIRONMENTAL SCIENCE) THESIS

By

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DECLARATION

The work presented in this thesis is my original work, which has not been submitted to any other institution for similar purposes. Information from other people's works has been fully acknowledged.

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CERTIFICATE OF APPROVAL

The undersigned certifies that this thesis represents the student's work and effort and has been submitted with our approval.

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DEDICATION

I dedicate this thesis to my Daughter Sharon, my mum, and my dad for their wonderful support and love during my studies.

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Above all, I thank God for everything.

ABSTRACT

The presence of heavy metals in soils, water, and air, among others, has been reported by several researchers in Malawi in recent years. However, there is little documentation about their existence in sediments and paints. This study assessed lead levels in solvent-based paint for home use in Malawi, levels of selected heavy metals in Mudi River Water and Sediments and their Environmental and Ecological Impacts. Lead levels in paint ranged from below the detection limit (< 60 ppm) to 17,000 ppm, with an average of 2,561.04 ppm. 57% of the analysed paints contained lead concentration exceeding the new US and WHO limit of Pb in paint of 90 ppm, and 4% contained lead concentration greater than 10,000 ppm. The results also showed that lead content varied with the brand and colour of the paint. The research also found that, on average, the concentration of heavy metals in both sediments and water samples of Mudi River were below WHO, USEPA and MBS standards. On average, higher concentrations of heavy metals were detected during the dry season than in the wet season in both water and sediment samples. During the dry season, the average concentration of heavy metals in the surface water of Mud Rive was as follows: Fe = 2.08mg/l, Zn = 0.108mg/l, Cu = 0.015mg/l, Pb = 0.011 mg/l, and Cd = 0.005mg/l while the concentration of Cr was below the detection limit (< 0.006). During the wet season, the concentration of surface water of all the studied heavy metals was below the detection limit. During the wet season, on average, a high concentration of Fe (28mg/kg), followed by Zn (0.318 mg/kg), Pb (0.097 mg/kg) and Cu (0.030 mg/kg) were detected in the sediment's samples. The potential ecological risk index (RI) indicated that the sediments posed low ecological environmental risk.

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LIST OF ACRONYMS AND ABBREVIATIONS

AAS: Atomic Absorption Spectroscopy

UNICEF: United Nations Children's Fund

USEPA: United States Environmental Protection Agency

TDS: Total Dissolved Solids

WHO: World Health Organization

EC: Electro conductivity

pH: Power of Hydrogen

BLL: Blood lead level

MBS: Malawi Bureau of Standards

UNEP: United Nations Environmental Program

IPEN: International POPs Elimination Network

B-Cd: Blood cadmium

U-Cd: Urine cadmium

EPA: Environmental protection agency

NGOs: Non-governmental Organizations

CF: Contamination Factor

EF: Enrichment Factor

SPSS: Statistical package for social science

BPb: Blood lead level

UNICEF: United Nations Children's Fund

LIST OF SYMBOLS

Cr: Chromium

Zn: Zinc

Pb: Lead

Cu: Copper

Fe: Iron

Cd: Cadmium

RI: Sum of all risk factors in the sediment samples

E_i: Monomial potential ecological risk factor for individual factors.

T_i: Metal toxic response factor

F_i: The metal pollution factor

C_i: Measured concentration of heavy metal in the sediment sample

C_b: Value of reference metal ion

C_d: Degree of contamination

I_{geo}: Geo-accumulation index

C_n: Content of the toxic metal n,

B_n: Background data of the toxic metal n

C_m: Concentration of a given metal

CHAPTER ONE

INTRODUCTION

1.1 Chapter overview

This chapter explains the general overview of heavy metals, their toxicity in the human body, and their presence in paints, water and sediments. Furthermore, the chapter also discusses the research problem, justification for the study, significance of the present study its aims and objectives.

1.2 Background Introduction

Pollution caused by heavy metals is considered a serious risk to the river environment because of its nature, toxicity, non-biodegradability and bioaccumulation (Malsiu *et al*., 2020; Zhang *et al*., 2020; Mandeng *et al*., 2019;). Heavy metals in polluted habitats can accumulate in river flora and fauna, which may eventually enter the food chain and cause serious health problems (Malsiu *et al*., 2020; Nwineewii *et al*., 2018). Heavy metals are metals with a high density greater than 5 g/cm^3 and have lethal effects even at very low concentrations (Abbas *et al*., 2018). The toxicities and health effects of heavy metals in humans and the environment have been well documented (Godwill *et al*., 2019 Abdullah *et al*., 2015;). Primarily, heavy metals occur naturally on the Earth's crust (Majid *et al*., 2019). Natural sources of heavy metal pollution include volcanic activity, metal corrosion, metal evaporation from soil and water, sediment re-suspension, soil erosion, and geological weathering (Allen *et al*., 2021). However, the most environmental contamination and human exposure to heavy metals is attributed to anthropogenic activities such as, mining and smelting operations, paints, industrial production and use (Allen *et al*., 2021).

Furthermore, the use of domestic and agricultural metals and metal-containing compounds, and the leaching of metals from different sources such as landfills, waste dumps, excretion, livestock manure, runoffs, and automobiles, elevate heavy metal concentrations in the environment (Adimalla & Wang, 2018; Makokha *et al*., 2011). Although heavy metals have been used for more than 5000 years and their severe health and environmental effects have been known for centuries; however, their use in industrial, domestic, agricultural, medical and technological applications has rapidly increased since the middle of the 19th Century, resulting to their wide distribution in the environment leading to the cause-effect phenomenon at a faster rate (Luo *et al*., 2009; Arantes *et al*., 2016). Heavy metals, such as Chromium (Cr), Cadmium (Cd) and Lead (Pb), are the most potentially hazardous in both combined and elemental forms; hence, they are considered priority metals that are of public health concern (Cui & Meng, 2019; WHO, 2007). The United States Environmental Protection Agency and the International Agency for Research on Cancer have considered the above heavy metals as human carcinogens and systemic toxicants are reported to induce multiple organ damage, even at lower levels of exposure (Milivojević, 2016). Heavy metals may accumulate in the human body through ingestion, inhalation or across the placenta in children (Satarug *et al*., 2000; Godt *et al*., 2006; Buchet & Werys, 1983). In the body, most heavy metals bind to cellular structures, thereby injuring the performance of essential biological functions (Godwill *et al*., 2019; Godt *et al*., 2006). Figure 1, shows the circulation of heavy metals in the human body and the pathways they take. Severe health effects of heavy metals exposure in human bodies include causing damage to essential organs such as the brain, lungs, kidneys, and bones and damage to the central nervous system (Edwards *et al*., 2018; Huo *et al*., 2018; Hassaan *et al*., 2016; Karakaya *et al*., 2015). Several factors, such as time of exposure, dosage, age, nutrition status, size of particles, and the health status of the people exposed, determine the level of heavy metal toxicity in the human body (Bernhoft 2013). The Institute for Health Metrics and Evaluation (IHME), for example, estimated that lead exposure accounted for 1.06 million deaths worldwide (UNICEF, 2020). That is almost as many deaths as result from malaria (620,000) or natural disasters (90,000) (UNICEF, 2020; WHO, 2016).

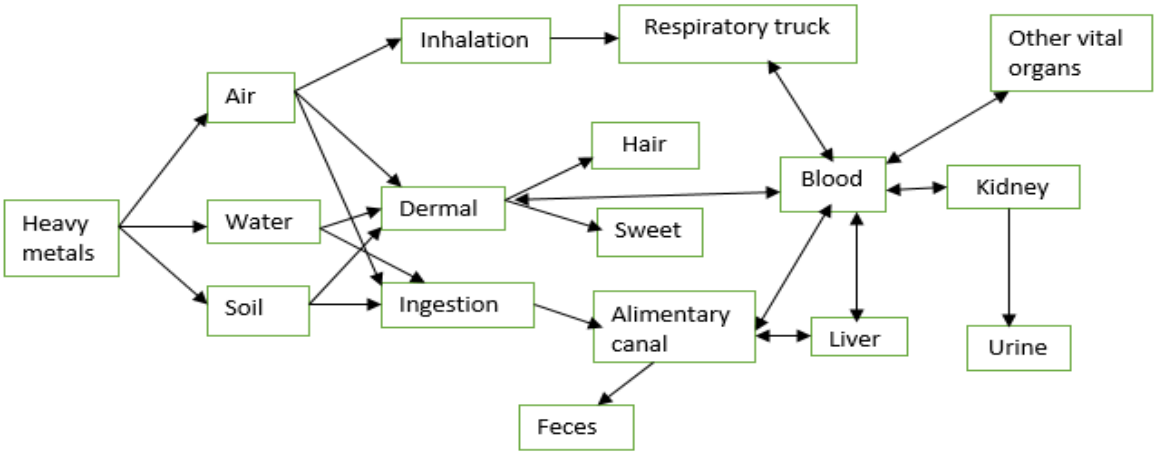

Figure 1 Circulation of heavy metals in the human body and Pathway they take. Modified from (Sharma et al. 2015).

1.3 General toxicity of heavy metals

Heavy metals accumulate in the human body through ingestion, inhalation or across the placenta in children (Buchet & Werys, 1983; Godt *et al*., 2006; Satarug *et al*., 2000). In the body, most heavy metals bind to cellular structures, thereby injuring the performance of essential biological functions (Godt *et al*., 2006; Godwill *et al*., 2019). The level of toxicity of heavy metals depends on several factors, such as time of exposure, dosage, age, nutrition status, size of particles and the health status of the people exposed (Bernhoft, 2013; OSPAR, 2004; WHO, 2000). Heavy metals such as lead and cadmium interact with sulfhydryl groups and other proteins in the body, compromising many enzymatic processes (Saikia *et al*., 2009; Utembe, 2016). Most of the heavy metals commonly interferes with proteins that bind Ca^{2+} and Zn^{2+} ions and gets adhered to the proteins after which they are transported through blood and other vital parts. Heavy metals may damage the lungs, kidneys, bones as well as cardiovascular systems damages among others (Godt *et al*., 2006; Jaishankar *et al*., 2014; Majid *et al*., 2019; Tchounwou *et al*., 2014).

1.4 Heavy metals in paints, surface water and sediments

Several studies have been conducted on heavy metals, for example, lead used in consumer products such as paints, petrol, oils and plastics. The overwhelming evidence of a high lead concentration in these products and publicity has successfully led to the total phase-out of lead in petrol (Adebamowo *et al*., 2007). However, the global attention that affected lead phase-out in petrol has so far not achieved the same result in lead used in paints (Mathee *et al*., 2014). Lead is added to paint to provide colour, increase the paint's durability, and to reduce the drying time (Adebamowo *et al*., 2007; Utembe, 2016). Leaded paint is defined as any paint to which one or more lead compounds have been intentionally added by the manufacturer to obtain specific characteristics (Attina & Trasande, 2013; Liu & Rong, 2020). Despite an effort to ban leaded paints globally, several studies have documented that leaded paints are still available on the market in many countries (Megertu & Bayissa, 2020). In Malawi, a study by Utembe (2016), showed that leaded paints are still available on the market in the country. However, the Malawi Bureau Standards MS280 and MS388 (MBS, 2020), stipulate the prohibition of lead in paint.

Furthermore, published reports in Malawi and elsewhere have indicated that lead, chromium, zinc iron, copper and cadmium ions are also found in water and sediments due to industrial wastewater and municipal sewage discharge into rivers and soils (Kaonga *et al*., 2021). The reviewed data from Malawi, which was published in 2017, has shown that some soils, sediments and water samples which were analysed for heavy metals had higher heavy metal concentrations exceeding permissible limits set by the World Health Organization (WHO) and Malawi Bureau of Standards (MBS) (Kaonga *et al*., 2021). Sediments are mostly mixtures of several components which include different mineral species and organic debris (Abdullah *et al*., 2015; Eum *et al*., 2014; Muller, 1986). Literature has reported that sediments are the main sinks for heavy metals which are discharged into the environment, resulting in heavy metal accumulation, hence bringing in several environmental and health difficulties to both plants and living organisms (Malsiu *et al*., 2020; Sharma *et al*., 2018).

1.5 Research problem

Accumulating heavy metals such as cadmium, chromium, zinc, iron, copper and lead in the environment has received increased attention worldwide in recent years (UNICEF 2020). This is due to their acute and chronic toxicities affecting plants and animals. In Malawi, a recent report by UNICEF and WHO, for example, indicated that 35% (3.4 million) of children in Malawi have lead poisoning with blood lead levels greater than 5µg/dL, a level that can cause serious health problems later in life (Attina & Trasande, 2013; UNICEF, 2020). The UNICEF report estimated that the level of lead poisoning experienced by children is sufficient to reduce their intelligence by 5 IQ points (Attina & Trasande 2013; UNICEF 2020).

Additionally, in 2011, it was modelled that the reduced intelligence and subsequent reduced earning potential caused by childhood lead exposure was responsible for a 6.2% loss to Malawi's GDP (Attina & Trasande 2013; UNICEF 2020; WHO 2020), of which lead paint was considered the primary source of lead exposure. Reducing such environmental health hazards is one of the eight main goals of the United Nations' Millennium Development Goals and Malawi's growth development strategy (Government of Malawi 2017). However, despite the existing evidence of the dangers of heavy metals and their presence in paints, water and sediments, there is little documentation regarding their presence in sediments and paints and their ecological and environmental impacts on humans and the environment. Henceforth, the study was conducted to analyse levels of selected heavy metals in paints, Mudi River water and sediments and to assess their ecological and environmental impacts in order to bring updated information on the status of heavy metals in leaded paints water and sediments.

1.6 Justification of the study

The study achieves one of the key issues of the Malawi Environmental Act of 2017, which stipulates the need for a clean environment for every Malawi citizen. The study also promotes Millennium Development Goal 7 and Malawi Growth Development Strategy III,

which aim to reduce environmental health hazards. Furthermore, it Provides updated information on the status of heavy metals in Mudi River water, sediments and leaded paint.

1.7 Objectives

The objectives of the study were as follows:

1. To determine the concentration of Pb in solvent-based paints for home use currently sold in Malawi and to compare its content in different brands and colours.
2. To determine the Zn, Cd, Cr, Pb, Cu and Fe concentrations in Mudi River water and sediments**.**
3. To determine the contamination levels of Zn, Cd, Cr, Pb, Cu and Fe in Mudi River sediments using different pollution indices.
4. To assess the environmental and ecological risk of Zn, Cd, Cr Cu, Pb and Fe in Mudi River due to contamination of the sediments.

1.8 Significance of the study

a) The study aims to provide up-to-date information about the content of heavy metals in paints currently sold in Malawi, and Mudi River sediments and water.
b) The study assesses the contamination level and ecological risk of selected heavy metals in surface water and sediments from the Mudi River.

1.9 Hypothesis

The research had the following hypothesis.

a) Both Sediments and Solvent paint in Malawi contain high levels of heavy metals.
b) Mudi River sediments posed environmental and ecological risks to the environment.

1.10 Limitations of the Study

Some of the targeted paint colours of other brands were missing during the sampling time, hence creating an imbalance between paint colours and brands among the targeted paint samples. Furthermore, the flooding of the Mudi River during the 2021 rain season disturbed the sampling time and likely diluted the water and sediment samples.

CHAPTER 2

LITERATURE REVIEW

2.1 Chapter overview

The chapter provides a general overview of heavy metals in the environment, paints, sediments and surface water. It also discusses sources of heavy metals, their path into the human body and their health effects. The chapter further discusses the absorption, distribution and elimination of Lead, Chromium, Cadmium, Zinc, Iron, and Copper.

2.2 General overview of heavy metals

Due to rapid industrialization and economic development, heavy metals continue to be introduced into the environment via different pathways such as irrigation, rivers, runoff atmospheric deposition, and point sources, where metals are produced from metal mining, refining, and refinishing by-products (Barakat, 2011). Heavy metal contamination in rivers, wastewater and sediments is of major concern due to their profusion, persistence, toxicity and bioaccumulation (Kosek-hoehne e*t al*., 2017; Makokha *et al*., 2011). Studies have shown that soils and sediments are usually the main sink for heavy metals discharged into the environment. Sediments can be sensitive indicators for monitoring the contamination of heavy metals in aquatic environments (Bahiru, 2020). Heavy metals can be defined differently based on their density, atomic number, weight, chemical properties as well as their toxicity. There are about forty (40) heavy metals, but the exact number depends on the definition (Barakat, 2011; Biswas *et al*., 2017). According to Abbas *et al*., (2018) heavy metals are metals with a high density greater than 5 g/cm^3 and have toxic effects even at very low concentrations. Heavy metals occur naturally, mainly in rocks and are important to life but can become toxic through accumulation in organisms, even at low levels. WHO classifies arsenic, cadmium, chromium, copper, nickel, lead, and mercury as the most common heavy metals which can pollute the environment more than other metals (WHO, 2007).

Mercury, lead, cadmium and chromium are of greatest concern because of their ability to travel longer distances in the atmosphere than other heavy metals (Abbas *et al*., 2018; Shefali *et al*., 2020). However, metals like zinc, manganese, copper, iron and cobalt are essential trace elements for humans, animals and plants. However, they become toxic if the homeostatic mechanisms maintaining their physiological limit are disrupted (Chabukdhara *et al*., 2016; Kalaivanan & Ganeshamurthy, 2015). Research has shown that both natural and anthropogenic activities are responsible for the presence of heavy metals in the environment (Barakat, 2011). Figure 2, shows various sources that add heavy metals to the environment, while Figure 3, shows the pathway representing the transport of metals through biotic and abiotic systems. Natural sources of heavy metals are primarily a result of natural weathering or changes in the pH of soil or water in which the heavy metals present in the rocks, soil and water get solubilized and mobilised and get added into the environment through natural processes such as volcanoes, floods, soil erosion, metal corrosion, and metal evaporation from soil, water and sediment re-suspension (Kalaivanan & Ganeshamurthy, 2015; Sekabira *et al*., 2010).

It is believed that many chemical reactions such as redox reactions, acid/base reactions, and alteration of pH levels that occur in soil and water change the species of metals and convert them to more mobile soluble forms, thus increasing the concentration of heavy toxic metals in the environment (Abbas *et al*., 2018; Ita & Anwana, 2017). Despite their natural presence in the environment, evidence, however, shows that human activities have been the main source of deposits of toxic heavy metals into the environment in recent years due to industrialisation, economic growth and high population growth (Kaonga *et al*., 2017; Nayak & Gupta, 2020; WHO, 2007). Industrial disposal of metals and metal components, leaching of metals from garbage, solid waste heaps, domestic wastewater, sediments, paints, sewage sludge, urban runoff, and mining agrochemicals such as fertilisers and pesticides are some of the well-known anthropogenic sources of heavy metals into rivers, estuaries and coastal waters (Luo *et al*., 2009; Majid *et al*., 2019). Furthermore, a large amount of the total anthropogenic metal input in the sediments in near-shore waters adjacent to urban and industrial growth centres comes from the combustion of fossil fuels, industrial wastewater and municipal dump sites, among others (Cui & Meng, 2019; Sekabira *et al*., 2010). Other notable sources of heavy metals contamination include ports,

harbours, marinas and mooring sites due to their association with recreational, commercial, and occasionally military, boating, and shipping activities around the sites (Denton, *et al*. 1997).

Heavy metals accumulate in the human body through ingestion, inhalation or across the placenta in children (Buchet & Werys, 1983; Godt *et al*., 2006; Satarug *et al*., 2000). In the body, most heavy metals bind to cellular structures, thereby injuring the performance of essential biological functions (Godt *et al*., 2006; Godwill *et al*., 2019). The level of toxicity of heavy metals depends on several factors, such as time of exposure, dosage, age, nutrition status, size of particles and the health status of the people exposed (Bernhoft, 2013; OSPAR Commission, 2004; WHO, 2000). The severe health effects of heavy metals in human bodies cause damage to essential organs such as the brain, lungs, kidneys and bones, among others *(*Edwards *et al., 2018;* Karakaya *et al.*, 2015). Heavy metals like Pb, Cu and Cd cause alteration in the human central nervous system, respiratory system and endocrine system, brain and kidney damage of developing foetus, cancer, miscarriages in pregnant women, high blood pressure, vomiting, diarrhoea, skin rashes and eye irritation. Exposure to very high concentrations of heavy metals may cause death (Jaishankar *et al*., 2014). The most fatal heavy metals are arsenic, mercury, copper, lead and cadmium (Buchet & Werys, 1983; Godt *et al*., 2006; Godwill *et al*., 2019).

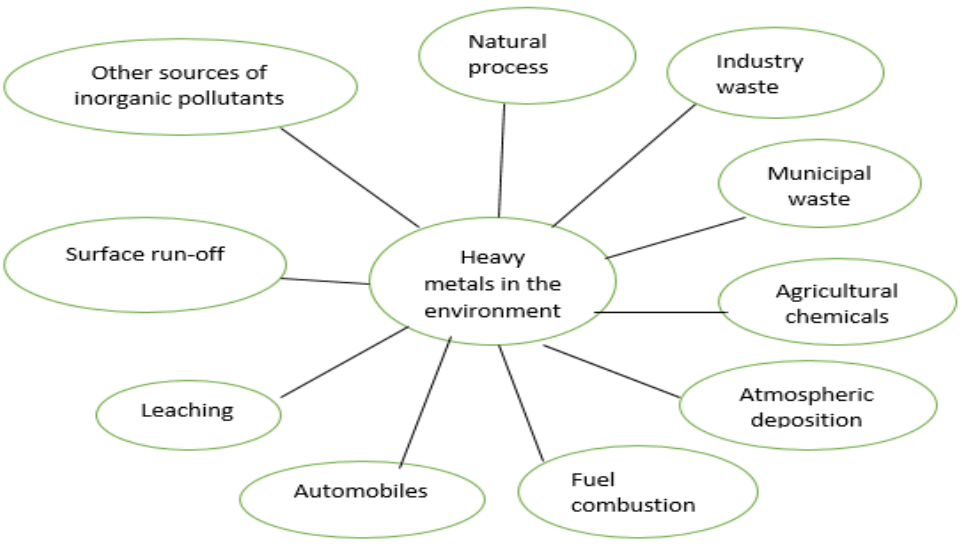

Figure 2 Various sources that add heavy metals to the environment. Modified from (Sharma et al., 2018)

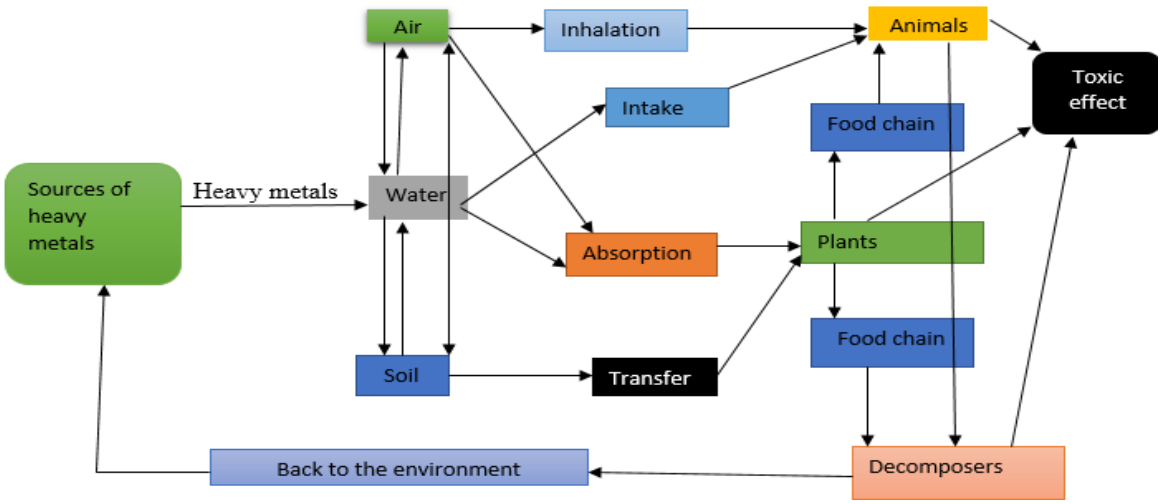

Figure 3 Pathway representing transport of metals through biotic and abiotic systems. Modified from (Sharma et al., 2018)

2.2.1 Paint, surface water and sediments

2.2.1.1 Paints and its compositions

Paint is any liquid, liquefiable, or mastic composition that is converted to an opaque solid film after application to a substrate in a thin layer. Paint is used to protect, decorate (such as adding colour), or add functionality to an object or surface by covering it with a pigmented coating (Adebamowo *et al*., 2007; Saikia *et al*., 2009). The basic ingredients that make up paints are pigment, a binder and a solvent (thinner), which is added to change the application characteristics of the liquid. The combination of the binder and solvent is called the paint vehicle (Saikia *et al*., 2009). The amount of each constituent differs from one brand of paint to another. However, solvents comprise about 60% of the total formulation (Clark *et al*., 2009, 2015). Binders account for 30%, pigments for 7% to 8%, and additives for 2% to 3% (Saikia *et al*., 2009). Pigments are insoluble solids incorporated into the paint to contribute colour, texture and other characteristics. Opaque pigments give the paint its hiding or covering capacity, and colour pigments give the paint its colour. Pigments may be inorganic, such as chrome green, chrome yellow, and iron oxide, or organic, such as toluidine red (Saikia *et al*., 2009). White lead, red lead, leaded zinc oxide, and chrome green are the main lead pigments. Lead is present in these pigments as oxides, carbonates, hydroxides and chromates (Adebamowo *et al*., 2007; Clark *et al*., 2009; Saikia *et al*., 2009).

Transparent pigments present in paint are responsible for bulk and control the application properties, durability, and resistance. Furthermore, many paints contain other pigments responsible for controlling heat resistance, corrosion and reflection of light (Saikia *et al*., 2009). Binders hold the pigment together and cause paint to adhere to a surface. In general, paint durability is determined by the resistance of the binder to the exposure conditions. The most common binder is linseed, which, however, has been replaced with alkyl resins. Other synthetic resins used in paint manufacturing include phenolic resin, vinyl, epoxy, urethane, polyester, and chlorinated rubber (Saikia *et al*., 2009). Solvents are thinners that are used to adjust the consistency of the material so that it can be applied readily to the surface. The solvent evaporates, contributing nothing further to the film (Naicker, 2012). The most used solvents are naphtha and mineral spirit. Lead is found in the waste solvent-based paint sludge in paint manufacture, which typically contains 27.5% pigment, 25% binders, and 47.5% organic solvents (Ali *et al*., 2017). Paint can also be classified into further subgroups, namely, decorative and industrial paint (Philip, 2018; Saikia *et al*., 2009). Decorative paints are acrylic emulsions used mostly in the cities and cater to the housing sector (Naicker, 2012). The medium range consists of enamels, which are commonly used in smaller cities and towns. Industrial Paints include powder coatings, high-performance coating, and automotive and marine paints used mostly in industries (Clark *et al*., 2015; WHO, 2008).

2.2.2 Water and Sediments

Sediments are naturally occurring solid materials that settle at the bottom of a liquid and are broken down by the action of weathering and erosion. They are subsequently transported by the action of water, wind or ice or by the force of gravity acting on the particles (Abbas *et al*., 2018; Eum *et al*., 2014). Sediments are transported in the environment based on the strength of the flow that carries them and their own size, volume, density and shape (Malsiu e*t al*., 2020; Sekabira *et al*., 2010). Stronger flows will increase the lift and drag on the particles, causing them to rise, while larger particles usually fall down through the flow. Sediments are largely taken as environmental indicators for determining metal pollution in the watercourse (Eum *et al*., 2014; Imran *et al*., 2008).

Sediments are an important part of the river basin, with the deviation of habitats and environments (Arantes *et al*., 2016).

Thus, it is necessary to evaluate the concentrations of heavy metals in water and sediments. Furthermore the quality of sediments is a very important factor in defining the pollution forms or nature of rivers or marine systems (Adimalla & Wang, 2018; Arantes *et al*., 2016). This is because they act as both transporters and sinks for environmental pollutants and also provide vital historical information on pollution and the input sources of pollutants into the aquatic systems (Cui & Meng, 2019; Fasano *et al*., 2018; Muhammd, 2018). Since sediments are the final sink for contaminants and pollutants, at certain concentrations, these contaminants or pollutants are re-suspended back to water. Also, they are accumulated most especially on bottom-dwelling biota, which are always closely associated with the sediment (A. Sharma *et al*., 2018; Venter *et al*., 2020). Natural activities such as rock weathering, soil erosion, and dissolution of water-soluble salts as well as anthropogenic sources such as municipal waste-water treatment plants, manufacturing industries, and agricultural activities, contribute heavily to the presence of heavy metals in sediments(Luo *et al*., 2009; Majid *et al*., 2019).

2.2.3 Sources of heavy metal exposure

2.2.3.1 Waste-water and chemical fertilisers

Industrial waste contains high levels of heavy metals, especially if they are not properly treated. Once these wastes are released into the environment, they cause serious problems. Heavy metals in industry waste and municipal sewage sludge usually come from processing companies such as fertiliser manufacturing companies, tannery processing, and textile processing, among others (Kinaichu e*t al*., 2020; Vunain *et al*., 2021). In Malawi, wastewater generation has increased over the years due to increased population, urbanization and industrialization (Kaonga *et al*., 2017). Industrial effluent, for example, is collected in septic tanks or discharged into the sewerage systems (Kaonga *et al*., 2021). Some of these effluent contain heavy metals such as cadmium, lead, copper, zinc and chromium. Kuyeli (2007) analysed industrial effluents in Malawi's city of Blantyre, and found that the concentration of the heavy metals was at least six times higher than the corresponding levels in surface water bodies in the same area. Additionally, heavy

application of certain chemical fertilizers may add heavy metals and other potentially toxic environmental elements (Raven *et al*., 1998). Metals like cadmium, chromium, copper, zinc and iron may be added to the environment from chemical fertiliser applications which are basically manufactured from natural rocks (Majid *et al*., 2019).

2.2.4 Mining and manufacturing of batteries

Mining is an important economic activity (Naicker, 2012; Outa *et al*., 2020) , however it is one of the main sources of heavy metal exposure. During mining, several heavy metals are directly discharged into natural environments such as wetlands, rivers, lakes and soils, resulting in elevated concentrations (Luo *et al*., 2009). Extensive Pb, Zn, Cd and Fe ore mining and smelting have resulted in contamination of the environment in general and pose a risk to human and ecological health (Boboria *et al*., 2021). Evidence shows that many communities have become highly exposed to heavy metals such as lead, chromium and cadmium, with some of the worst incidents of exposure poisoning in the world have occurred around African mining sites such as Zamfara (Nigeria), Aggeneys in South Africa and Kabwe in Zambia (ATSDR, 2018). Fatal results were obtained in Zamfara, which showed that out of the under five years children who had died in the previous year, 25% of them had died from lead poisoning (ATSDR, 2018; WHO, 2016). Battery manufacturing and recycling contribute to the elevated levels of heavy metals in the environment (WHO, 2020). Some heavy metals such as lead, chromium and cadmium are used to manufacture batteries. During the manufacturing and recycling process, poorly disposed people and animals may be exposed to these heavy metals. For example, in Dakar, Senegal, in 2007/8, at least 18 children died from a disease of the central nervous system that health experts related to lead poisoning - as the mothers of several of the children were involved in the recycling of used lead-acid batteries (WHO, 2016).

2.2.5 Paint

Paint is one of the main sources of heavy metal exposure such as lead, cadmium and chromium. Generally, heavy metals are found in paint when the manufacturer intentionally adds them for the paint colour, durability and corrosive resistance. Various researchers have agreed that paint is the main source of lead exposure in the environment after the

banning of leaded petrol. Since 2009, more than 100 studies from 59 countries have shown that lead paints are still widely sold in low- and middle-income countries (IPEN, 2017b). IPEN-affiliated NGOs conducted most of these studies, comprising more than 3,500 solvent-based paints. Many of these paints contained very high levels of lead, above 10,000 ppm of the dry weight of the paint (IPEN, 2017b). Furthermore, research which was conducted by the United Nations Environment Programme (UNEP) on lead in solvent-based paints in 2012 in nine countries, namely Argentina, Azerbaijan, Chile, Cote d'Ivoire, Ethiopia, Ghana, Kyrgyzstan, Tunisia, and Uruguay, showed that out of 234 different paint brands and colours, 67% or more of the paint samples tested had lead content greater than 90 ppm– the regulatory limit in the United States (IPEN, 2017b; UNEP, 2016).

2.2.6 Food and water

Food and water are regarded as among the main sources of heavy metal exposure, as most of the heavy metals are naturally present in water and soil; hence, they find their way into the food chain (Hershko, 2007). For example, the highest level of chromium in food is found in meat, fish, fresh vegetables and crustaceans, with oral intake for infants of one year old being around 33-45 μg/day, for children of eleven years, oral intake is around 123-171 μg/day and for adults it is estimated to be around 246-343 μg/day (Shanker *et al*., 2005). Similarly, the lowest cadmium value of about 1 μg/kg is found in milk, and the highest level of around 100-1000 μg/kg is found in the kidney and liver of mammals (Bernhoft, 2013). Foods such as fish and spinach have been determined to be a pathway of exposure to lead (Gidlow, 2004). Furthermore, elements like zinc, copper and iron are found in many foodstuffs as they are important for plants' growth and development at a normal level (Billings & Schnepel, 2018; Brandão *et al*., 2015). Heavy metals in food may also come from the use of pots and pans fortified with heavy metals or the use of contaminated utensils or apparatuses for food preparation or storage (Utembe, 2016). Water is another source of heavy metal exposure; generally, unpolluted water has a very low estimated concentration of heavy metals, and the levels become high due to human activities (WHO, 2011). Water becomes contaminated with heavy metals because of industrial activities such as electroplating, industrial waste disposal, leather tanning, fertiliser manufacturing, improper waste disposal, soldering pipes and plumbing, among

others. Natural sources of heavy metals entry into water bodies include, leaching from topsoil and rocks, volcanic eruption, soil erosion and weathering of rocks (Clark *et al*., 2015; Saikia *et al*., 2009).

2.2.7 Air and soil

In the air, heavy metals come from both human and natural causes. Activities such as fossil fuel burning, iron, copper, zinc-lead smelting, volcanic activities, and automobile exhaust increase the heavy metal concentration in the air (Adebamowo *et al*., 2007; Philip & Gerson, 1994). For example, coal and oil combustion contribute an estimated 1,723 metric tons of chromium per year to atmospheric emissions in the USA. In comparison, chrome-plating sources were estimated to contribute 700 metric tons of chromium annually to atmospheric pollution (Abbas *et al*., 2018). Naturally, soil contains some levels of heavy metals at relatively small concentrations (Czikkely & Fogarassy, 2018). Human activities have, however, elevated their levels over the past years. Heavy chemical fertiliser applications, poor waste disposal, and municipal sludge tend to increase concentrations of heavy metals in the soil (Abdullah *et al*., 2015; Kaonga *et al*., 2017).

Heavy metals may also originate from crystal rocks that contain lead, iron, copper and cadmium content in the rocks (Mackay *et al*., 2013; Tchounwou *et al*., 2014). Commonly soil pH determines the concentration of most of the heavy metals in the soil with most metals become mobile in low soil pH (Leotsinidis *et al*., 2008). For example, chromium uptake in soils takes place only in a strongly acid and reducing medium (Boboria *et al*., 2021; Sriuttha *et al*., 2017), where it occurs in the form of the Cr^{3+} cations or a strongly basic and oxidizing medium, where it occurs as the CrO_4^{-2} (Tchounwou *et al*., 2014). In Malawi heavy metal levels in soil was found to vary from one city to another and sometimes the variation was also observed between rain and dry season (Kaonga *et al*., 2017). For example, Kaonga *et al*., (2012) reported a 0.18 mg/kgdw, as maximum concentration of cadmium in soils along river bank streams that passes along industry area in Blantyre city and a higher concentration of 4-10mg/kgdw was found in dumpsite soils in Zomba city.

2.2.8 African Traditional Brews and Cultural Practices

Home-brewed alcoholic drinks are popular in many countries in the world, including Africa (WHO, 2020). Home brews are usually made from fermented products, of which several additional constituents are added to it of which some of the constituents contain heavy metals. In Botswana for example, a study of the methods and ingredients used in making of Khadi, a popular traditional African beer, it was found that in some cases, the contents of lead acid batteries were being added to the brew to enhance potency (Brahmbhatt, 2017). Other studies have also shown that high temperature processing, elevated acidity and prolonged storage in metal containers may contribute to the increased levels of heavy metals such as lead, cadmium and zinc in certain African beers (Armstrong e*t al*., 2015). Similar results were found in Dar es Salaam, Tanzania, where it was found that lead levels in local beers ranged from 0 to 0.82 ppm (Nyaruhucha, 2020; WHO, 2016). Cultural practices such as geophagia are another source of heavy metal exposure. Geophagia is the deliberate ingestion of soil, commonly among women (Nyaruhucha, 2020). The reason for the practice is not understood. However religious beliefs, cultural, nutritional and medicinal practices are other reasons. For example, in a study that was done in Dar es Salaam, Tanzania, around 64% of pregnant and breastfeeding women were reported to ingest soil (Nyaruhucha, 2020). Similarly 74% of a group of pregnant women from Nairobi, Kenya, were also reported to have the habit of ingesting soil (WHO, 2020). Studies have shown that soil ingestion may increase exposure to metal contaminants in the soil, such as arsenic and lead. Similar results were found in New York, where women who had a habit of ingesting soil were shown to have higher blood lead levels compared to their counterparts who did not have the habit *(*Popovic *et al*., 2005; WHO, 2016).

2.2.9 Review of the heavy metals under the study

Most heavy metals such as zinc (Zn), copper (Cu) and iron (Fe) pose health and environmental risks at high levels, while metals like lead (Pb), cadmium (Cd), and chromium (Cr) are of great concern even at low levels due to their toxicity and they have been classified by USEPA, UNEP and WHO as carcinogens (USEPA, 1986). A look at their documented properties, toxicity, sources of exposure and health effects to humans and animals following their ingestion and inhalation is therefore of great importance.

2.2.10 Lead

Lead is a transitional element with the symbol Pb (Latin: plumbum). It belongs to group IV A of the periodic table, with atomic number 82 and relative atomic mass 207.2 and has a density of 11.3 g/cm^3 (Clark *et al*., 2015; WHO, 2020). Lead is found in two forms: organic and inorganic lead. Inorganic lead is found in higher lead content paint, soil, dust and various consumer products and is not bio-transformed in the body (Lowry, 2017). The colour varies, depending on the chemical form, and the most common forms are white lead (a lead carbonate compound), yellow lead (lead chromate, lead monoxide) or red lead (lead tetroxide) (Lowry, 2017; WHO, 2008). On the other hand, Organic lead such as Tetraethyl and tetra-methyl lead is the leaded gasoline type used to increase octane rating; unlike inorganic lead, organic lead is metabolized in the liver and extracted through urine. Lead is a soft, malleable metal and has a bluish-white colour when freshly cut, but it tarnishes to a dull greyish colour when it is exposed to air and is shiny chrome silver when melted into a liquid. Ductility, malleability, weathering resistance and low melting point make it simpler to use than other metals (WHO, 2008). Metallic lead does occur rarely in nature (Goyer & Clarkson, 2001; WHO, 2016). It is usually found in ore with zinc, silver and copper and is extracted together with these metals (Makokha *et al*., 2008; Silbergeld, 1990).

Common varieties of lead are Galena (PbS), which contains 86.6% lead, cerussite ($PbCO_3$) and anglesite ($PbSO_4$) (Goyer & Clarkson, 2001; Mason *et al*., 2014). Lead is used in building construction, lead-acid batteries, bullets and shots, pewter, and fusible alloys (IPEN, 2017b). In the past, lead was added to petrol in the form of tetra-ethyl lead ($PbEt_4$) with an anti-knocking function, but it was banned across the world due to health concerns (NAPE & IPEN, 2017; UNEP, 2016). Lead levels in the body are measured as Blood Lead Levels (BLL) in micrograms of lead per deciliter of blood (μg/dL) (Saikia *et al*., 2009). The Centres for Disease Control and Prevention (CDC) in the USA argues that there is no safe blood lead level for children (Lanphear *et al*., 2018; Mason *et al*., 2014). However, the acceptable blood lead level sometimes varies between different countries (Rădulescu & Lundgren, 2019; Utembe, 2016).

2.2.10.1. Toxicokinetics of lead (Absorption, distribution and elimination)

Toxicokinetics explains how lead is absorbed, distributed and eliminated in the body (Mason et al., 2014).

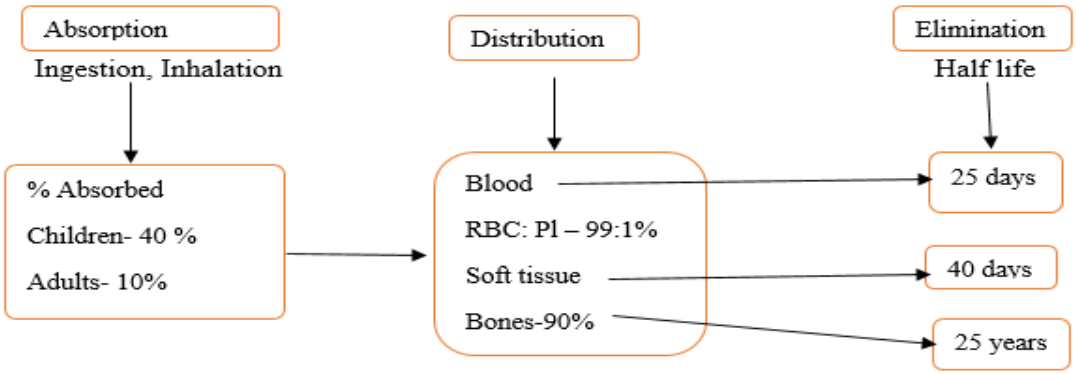

Figure 4 absorption, distribution and elimination of lead in the human body

Figure 4, shows absorption, distribution and elimination of lead in the human body. Lead enters the human body primarily through ingestion (digestive system or gastrointestinal) and inhalation (breathing or airways) via the placenta in children and in small quantities through the skin (Armstrong *et al*., 2015; La-llave-león *et al*., 2016). The absorption rate through the lungs is more efficient than absorption through the gastrointestinal tract (Armstrong *et al*., 2015; Rădulescu & Lundgren, 2019), resulting in higher lead uptake by inhalation than ingestion. The absorption rate depends on factors such as age, gender, nutritional status, and size of lead-containing particles entering the body (La-llave-león *et al*., 2016). For example, children can absorb lead by ingestion up to 40–70%, and pregnant women can also absorb up to 70% of an oral lead dose through the gastrointestinal tract (La-llave-león *et al*., 2016; Popovic *et al*., 2005). In general the absorption rate of adults is lower than in children at around 10 – 20% (Armstrong *et al*., 2015; Popovic *et al*., 2005). Furthermore, ageing adults and children are considered to be a vulnerable population in terms of the effects of lead exposure. The absorption of inhaled lead is influenced by particle size and solubility (Armstrong *et al*., 2015; WHO, 2008). During inhaling inorganic lead, larger particles (>2.5 μm) deposited in the ciliated airways can be

transferred by mucociliary transport into the oesophagus and swallowed. Smaller particles (<1 μm), which can be deposited in the alveolar region, can be absorbed by phagocytic cells after extracellular dissolution or ingestion (Armstrong *et al*., 2015; Labrot *et al*., 1999; Silbergeld, 1990). Being well-malnourished also lowers the rate of absorption (Armstrong *et al*., 2015; Mason *et al*., 2014; WHO, 2016).

Once lead is absorbed into the bloodstream, it is rapidly taken in by red blood cells, where it binds to intracellular proteins (Armstrong *et al*., 2015; Goyer & Clarkson, 2001). Approximately 99% of the lead in blood is associated with red blood cells. The remaining 1% resides in blood plasma (Popovic *et al*., 2005; Rădulescu & Lundgren, 2019). After that, the blood lead is widely distributed to soft tissue such as the liver, kidneys, lungs, brain, spleen, muscles, and heart, and mineralising tissues such as bones and teeth (Philip & Gerson, 1994; WHO, 2020). Lead travels in the blood to soft tissues and organs and is later stored in bones and teeth after several weeks (Clark *et al*., 2015; Rădulescu & Lundgren, 2019). Lead has a half-life of 28 to 36 days, 40 and 25 years in the blood, soft tissue and bones, respectively (Armstrong *et al*., 2015; Mason *et al*., 2014; WHO, 2016). Some lead from bones and other tissues may be released back into the bloodstream during times of calcium stress, which may be caused by pregnancy, lactation, menopause and periods of growth (Neda *et al*., 2017; Rădulescu & Lundgren, 2019). Lead is excreted through the urine by the kidney (Goyer & Clarkson, 2001; Neda *et al*., 2017; Tchounwou *et al*., 2014). However, the retained rate differs with children up to 2 years; they retain one-third of the total absorbed dose, while adults retain 1% (Eum *et al*., 2014; Labrot et al., 1999).

2.2.10.2 Mechanisms for lead toxicity

The primary target of lead in the body is the nervous system (Labrot *et al*., 1999). During neurodevelopment, the central nervous system undergoes highly programmed changes involving overall growth in cell number and size in the organ and proliferation and outgrowth of cells to establish connections between cells (Armstrong *et al*., 2015). Many factors regulate these processes, such as growth factors and neuron movement (Mason *et al*., 2014; Philip & Gerson, 1994). Lead in the blood at this stage affects overall regional growth and migration of neurons in the central nervous system by interfering with the

programmed establishment of cell connections, resulting in modification of neuronal circuitry (Gidlow, 2004). Furthermore, lead inhibits the molecular events of cell attachment and interferes with synapse formation, cell communication, and adhesion (WHO, 2008). Lead also interferes with calcium in the central nervous system, disturbing normal functions of calcium in the body. Calcium is a critical component of numerous biochemical and metabolic functions in the brain, and lead may act as a surrogate for calcium (Armstrong *et al*., 2015; Eum *et al*., 2014). The indirect effects of lead on the nervous system result from interference with other body systems that support the nervous system function (Silbergeld, 1990). Lead interferes with neurotransmitter release and signal transduction, disrupting the function of cholinergic systems (A branch of the automatic nervous system which plays an important role in memory, digestion, control of the heartbeat, blood pressure and many other functions) as well as inhibiting Ion channels during the neonatal period (Labrot *et al*., 1999; Uchida *et al*., 2017). Other studies (Lowry, 2015) have shown that lead activates protein kinase C in capillary cells and inhibits Na+/K+-AT Phase in the cell membrane, interfering with energy metabolism. Within the cell, lead appears to interfere with calcium released from the mitochondria, resulting in the formation of reactive oxygen species and speeding mitochondrial self-destruction through the formation of the permeability transition pore (Armstrong *et al*., 2015). Mason *et al*. (2014) reported that lead blocks calcium entry into nerve terminals and inhibits calcium uptake in brain mitochondria, affecting brain functions.

2.2.11 Cadmium

Cadmium (Cd) is a soft, silver-white, blue-tinged, lustrous metal belonging to group IIB of the period table (Kalsi *et al*., 2020; OSPAR, 2004). It has a melting point of 321^0C and a boiling point of 765^0C (Tchounwou *et al*., 2014). Elemental cadmium has an atomic number and atomic weight of 48 and 112.4 g/mol, respectively, with a density of 8.65 g/cm^3 at 20^0C (Bahiru, 2020; Tchounwou *et al*., 2014). It is a post-transition metal with a complete d orbital, and its s orbital has two electrons (Hansen *et al*., 2013; Huo *et al*., 2018). Cadmium has chemical and physical properties similar to those of zinc and mercury, such as being soft, malleable, and ductile (Adimalla & Wang, 2018; Bernhoft, 2013). It has an oxidation state of +2 in most of its compounds. Cadmium metal does not occur naturally,

but it is found in combination with other metals in mineral form, such as zinc sulphides, sphalerite, and wurtzite, in which cadmium occurs as an impurity (Ahamad *et al*., 2020; Tchounwou *et al*., 2014). Cadmium is usually isolated during the production of zinc, and some zinc ores concentrate from sulfidic zinc ores, which contain up to 1.4% of cadmium (Tchounwou *et al*., 2014). Cadmium is highly toxic to most plants and animal species, especially in the free form of cadmium ions, and it is ranked as the seventh most toxic metal by ATSDR (Ahamad *et al*., 2020; Majid *et al*., 2019). It is used in the manufacturing of batteries, fertilisers, electroplating, television screens, cell phones, ceramics and paint, among others (Genchi *et al*., 2020; Sharma *et al*., 2015; Tchounwou *et al*., 2014). Cadmium compounds are also used in printing, textiles, photography, lasers, semiconductors, solar cells, dental amalgams and as pesticides(Tchounwou *et al*., 2014; WHO, 2000). Cadmium is mainly sent into the environment through industrial processes. Considerable human exposure to cadmium happens by the ingestion of contaminated foodstuffs, especially cereals, grains, fruits and leafy vegetables, as well as contaminated beverages (Muhammd, 2018). It is also believed that smoking increases cadmium exposure (Sharma *et al*., 2015).

Studies have shown that in sediments, cadmium is not absorbed by colloidal material but instead by organic matter, which is the main sorption material for the metal (Hansen *et al*., 2013). Cadmium levels in sediments usually increase with the increase in density and decreases in size in terms of partition of sediment samples density and size *(*Adimalla & Wang, 2018; H. Sharma *et al*., 2015; Tchounwou *et al*., 2014). The attachment of cadmium to sediments, and to the clay content, increases with decrease in pH and the release of cadmium from the sediment is influenced by many factors such as acidity, redox conditions and complexing agents in the water (Genchi *et al*., 2020; Huo *et al*., 2018; WHO, 2000). In the US, more than 500,000 workers are exposed to toxic cadmium each year, according to the Agency for Toxic Substances and Disease Registry (Bernard, 2008; Mutlu *et al*., 2012). Studies have shown that in China the total area polluted by cadmium is more than 11,000 hectares and its annual amount of industrial waste of cadmium discharged into the environment is assessed to be more than 680 tons (Huo *et al*., 2018). In Malawi, several studies have documented the presence of cadmium in water, soil and wastewater (Kaonga et a*l*. 2017). Cadmium exposure is expressed in blood cadmium (B-Cd) or urine cadmium (U-Cd). B-Cd is the concentration of cadmium in blood at the present time.

On the other hand, U-Cd shows long time exposure to cadmium and depends on the concentration of cadmium a person has been exposed to (Järup, 2003). Normal B-Cd value is supposed to be less than 5g/ml (Godt *et al*., 2006). An acute toxic is observed when blood levels exceed 500g/ml (Godt *et al*., 2006; Godwill , Engwa *et al*., 2019).

2.2.11.1 Toxicokinetics of cadmium (absorption, distribution and elimination)

Like lead, exposure to cadmium in humans occurs mainly through inhalation, ingestion and skin. Like any other heavy metal, the toxicokinetics of cadmium explain the kinetics of the absorption, distribution and elimination. Figure 5, shows metabolism, storage and excretion of cadmium in human body

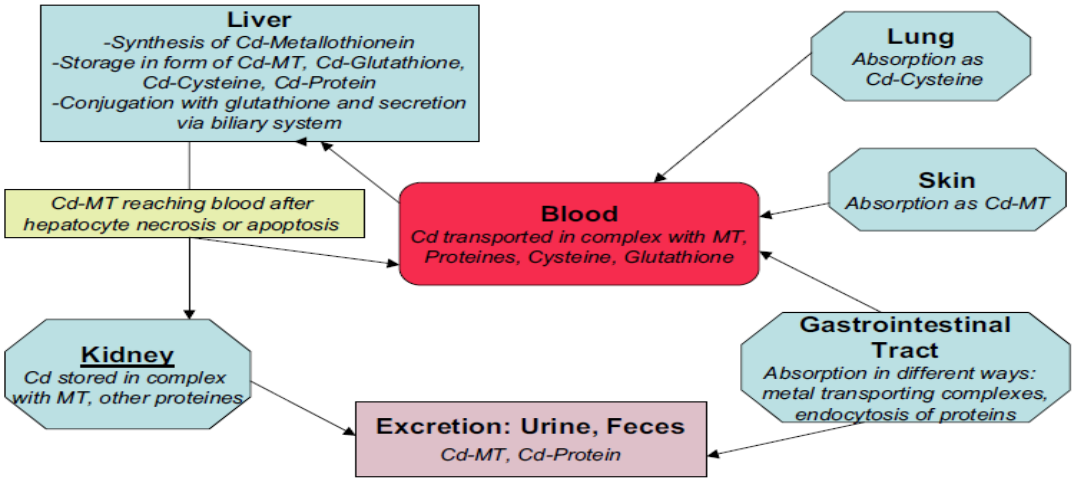

Figure 5 Metabolism, storage and excretion of cadmium in human body. Adopted from (Godt et al., 2006)

Cadmium uptake by humans through gastrointestinal or ingestion is approximately 5% of the total ingested amount (Godt *et al*., 2006). The uptake will also depend on the dose amount and nutritional status of the individual. However, low intake of vitamin D, calcium, and other elements such as zinc and copper increases the ingestion rate in humans (Jaishankar *et al*., 2014). Additionally, a high-fibre diet, such as mushrooms and root crops, increases the dietary cadmium intake (Godt *et al*., 2006; Huo et al., 2018).

Furthermore people with little iron supplies show a 6% higher uptake of cadmium than those with a balanced iron levels which lead to children and menstruating women having high cadmium uptake due to chronic iron deficiency (Kalsi *et al*., 2020).s On the other hand, the main source of inhaled cadmium in humans is cigarette smoke (Jaishankar *et al*., 2014). Human lungs take 40–60% of the cadmium in tobacco smoke (Bernhoft, 2013; Sharma *et al*., 2015). It is estimated that, on average, smokers have cadmium blood levels 4–5 times higher than those of non-smokers (Hansen *et al*., 2013; Huo *et al*., 2018). There is little research on cadmium uptake through dermal absorption. However research that was done by Wester *et al*., in 1991, on the absorption of cadmium from cadmium-contaminated soil and water solutions by human cadaver skin in a diffusion cell model, it was demonstrated that there was a penetration of 8.8 % by soil and 12.7% by water of the applied cadmium dose into the skin suggesting that cadmium intake can also happen via skin (Huo *et al*., 2018; Majid *et al*., 2019; Tchounwou *et al*., 2014). After absorption, it is transported into the blood. From the blood, the first organ to be reached is the liver; about 30% of the total dose is estimated to be deposited into it (Jaishankar *et al*., 2014; Muhammd, 2018). Similarly, another 30% is deposited in the kidneys, and the remaining 40% is distributed throughout the body, with a half-life of twenty-five years. In the kidney, the half-life of cadmium is around 10 years; in the blood, it is believed to be 75 to 128 days (Jaishankar *et al*., 2014; Sharma *et al*., 2015). The blood concentration of cadmium indicates recent exposure, while the urinary concentration shows accumulated past exposure, body burden and renal accumulation; hence, to accurately estimate body burden of cadmium, urine provocation testing is preferred. Cadmium is eliminated through faeces and urine (Godt *et al*., 2006).

2.2.11.2 Mechanism for toxicity of cadmium

The toxicity mechanism of cadmium is not clearly understood. However, its toxic effects on the cells are well documented in some research papers. Its concentration in the body increases 3,000 fold as it binds to the cysteine-rich protein (metallothionein) and forms a cysteine-metallothionein complex. It is believed that the formed complex causes hepatotoxicity in the liver, and it then circulates to the kidney, where it causes

nephrotoxicity (Godt *et al*., 2006; Godwill *et al*., 2019). Furthermore, cadmium can replace zinc and calcium in cells since they have similar oxidation states, thereby inhibiting transport pathways of zinc or calcium within the cells (Jaishankar *et al*., 2014; Majid *et al*., 2019; Muhammd, 2018). Figure 6, shows a summary of cadmium toxicity.

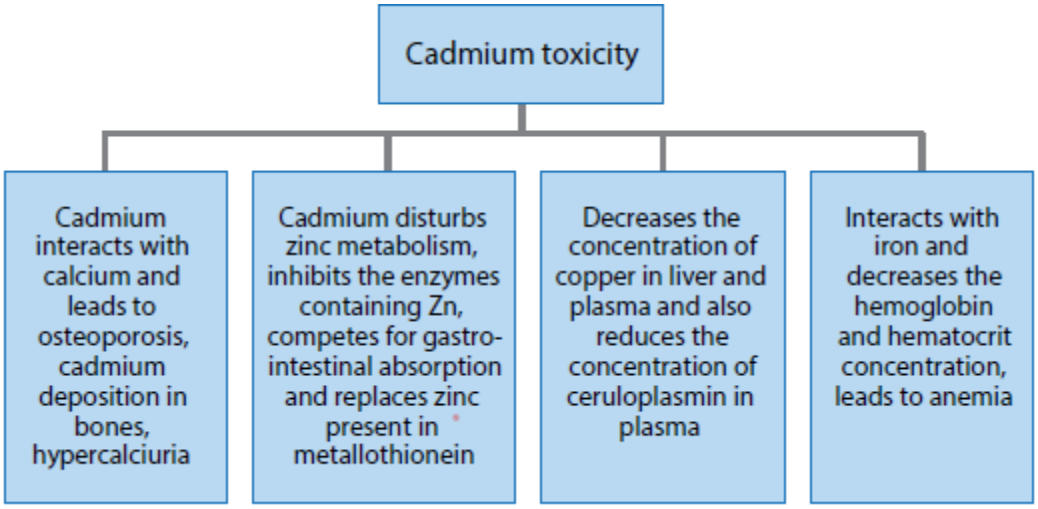

Figure 6 Cadmium toxicity. Adopted from (Jaishankar et al., 2014)

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2.2.12. Chromium

Chromium (Cr), is a silvery white transition metal, mostly residing in the mantle and core (Outa *et al*., 2020). It is ranked as the 21st most abundant element in Earth's crust, with an average concentration of 100 mg/kg (Venkateswarlu, 2011). It is a group 6 metal, period 4, with atomic number 24. Chromium is a solid metal at 20^{o}C with melting and boiling points of 1907^{0}C and 2671^{0}C, respectively (Tumolo *et al*., 2020). Chromium has relative atomic mass of 51.996 and it has three naturally occurring isotopse, namely ^{52}Cr, ^{53}Cr and ^{54}Cr. However ^{52}Cr is the most abundant one with 83.789% natural abundance. Chromium occurs in almost nine oxidation states ranging from -2 to +6. But in the environment, Cr is primarily stable in trivalent (Cr+3) and hexavalent (Cr+6) forms (Outa *et al*., 2020; Tumolo *et al*., 2020). Elemental chromium is biologically inert and does not occur naturally in Earth's crust. Chromium compounds show a wide range of geometries, such as square

planar, tetrahedral, octahedral, and various slanted geometries. Chromium is found in nature predominantly as the chromite ore ($FeCr_2O_4$), mainly in the Cr^{+3} state (Shekhawat *et al*., 2015). The existence of a given oxidation state depends on factors such as pH, redox potentials, and kinetics. Thermodynamically, Cr^{+3} and Cr^{+2} are the most stable states, while Cr^{+3} and Cr^{+6} are the most common and stable oxidation states found in aqueous solution (Tchounwou *et al*., 2014). Kinetically, chromium Cr^{+3} is substitution-ally inert, less toxic, less mobile and is mainly found bound to organic matter in soil and aquatic environment, on the other hand Cr^{+6} is more soluble in water and is more mobile than Cr^{+3} and it is the most toxic form of Chromium to humans than Cr^{+3} (Lamson & Plaza, 2002; Outa *et al*., 2020; Tchounwou *et al*., 2014).

Adverse health effects of chromium in the human body include causing headache, mood change, diabetes, liver diseases, it may irritate the nose, throat and lungs among other impacts. Despite having negative health and environmental impact, at low concentrations, Cr (III) is important in natural human lipid and protein metabolism and other biological process hence very small amounts are needed for normal human life functions (Prasad, 2011; WHO, 2007). Much of the daily intake of chromium, typically around 100 µg, comes from grains, fruits and vegetables, mushrooms and egg yolk, among others (Achmad & Auerkari, 2017; Lamson & Plaza, 2002). Metal chromium is mainly used for making steel and other alloys, while Chromium compounds, such as chromium (III) or chromium (VI), are used for chrome plating, the manufacture of dyes and pigments, leather tannery and tanning, wood preservation, and treatment of cooling tower water among others (Sun *et al*., 2015; Tumolo *et al*., 2020). At low levels, chromium occurs naturally in rocks, animals, plants, soil, and volcanic dust and gases (Achmad & Auerkari, 2017; Venkateswarlu, 2011). However, it is released in large amounts into the environment due to human activities, accounting for 60–70% of the total emissions of atmospheric chromium (Canada, 1994; Lamson & Plaza, 2002). Research shows that industrial activities such as electroplating, leather tanning, and textile industries release large amounts of chromium to surface waters (Flora *et al*., 1997; Kaonga *et al*., 2017; Vunain et al., 2021).

Furthermore, high levels of chromium in soils and sediments come from the disposal of chromium-containing commercial products and coal ash from electric utilities and

improper disposal of solid waste and sludge (Canada, 1994; Tchounwou *et al*., 2014). The primary source of oral exposure to chromium for non-occupational humans comes from food and drinking water. In contrast, occupational exposure occurs via inhalation, and it is estimated that more than 300,000 workers globally are exposed annually to chromium and chromium-containing compounds in the workplace (WHO, 2019). On average, daily intake from air, water, and food is less than 0.2 to 0.4 micrograms (μg), 2.0 μg, and 60 μg, respectively (Shanker *et al*., 2005; Shekhawat *et al*., 2015; Sun *et al*., 2015; Tumolo *et al*., 2020). Chromium levels in food range from <10 to 1300 μg/kg, with the highest amount in meat, fish, fruits, and vegetables (Godwill *et al*., 2019). Chromium concentration in uncontaminated water is about 1–10 μg/L in rivers and lakes and 0.2–1 μg/L in rainwater. Chromium compounds are very much persistent in water sediments (Ahamad *et al*., 2020; Prasad, 2011; Shekhawat *et al*., 2015).

2.2.12.1 Toxicokinetic of chromium

The principal route of human exposure to chromium is inhalation, despite absorption, which also happens through ingestion and skin contact. Evidence shows that Cr (VI) is absorbed more easily than Cr (III) through inhalation and ingestion (Achmad & Auerkari, 2017; Sun *et al*., 2015; Venkateswarlu, 2011). Similar results have been reported in occupational studies, which showed that Cr (VI) is easily absorbed through the skin while Cr (III) shows poor skin absorption (Achmad & Auerkari, 2017). Once Cr (VI) enters the cell via anion transporters, it undergoes a series of metabolic reductions and forms intermediate Cr species such as Cr (V) and Cr (IV) and finally reduces to Cr (III) (Sun *et al*., 2015). When Cr (VI) enters the bloodstream, it is quickly taken up by RBC where it is reduced to Cr (III) and spread to other vital organs of the body such as the liver, kidney and spleen (Godwill *et al*., 2019; Shrivastava *et al*., 2002). Cr (VI) quickly penetrates into the RBC because of its bioavailability. It is converted into Cr (III) which binds to the cellular components and then it is unable to leave RBC (Shrivastava *et al*., 2002). Absorption of Cr depends on factors such as particle size, oxidation state and solubility. It is eliminated through urine and faeces with three half-life excretions ranging from 7h, 15-

30 days and 3-5 years, depending on the organ or fluid it is in (Shekhawat *et al*., 2015; Sun *et al*., 2015; Venkateswarlu, 2011).

2.2.12.2 Mechanism of chromium toxicity

The toxicity of chromium compounds is mainly determined by there different oxidation states and solubility (Lamson & Plaza, 2002; Shrivastava *et al*., 2002). Cr (VI) compounds are powerful oxidising agents and more toxic than Cr (III) compounds, given similar amounts and solubility. Although the mechanisms of biological interaction are not well understood, the toxicity difference may be related to the ease with which Cr (VI) passes through cell membranes and its ability to be reduced and forms intermediates (Canada 2012; Flora *et al*., 1997; Lamson & Plaza, 2002). The reduction of Cr (VI) is considered a detoxification process when it occurs at a distance from the target site. At the same time, it is considered toxic when the reduction happens near the cell nucleus or target organs (Flora *et al*., 1997; Godwill *et al*., 2019; Lamson & Plaza, 2002; Tchounwou *et al*., 2014; Venkateswarlu, 2011). The balance that exists between extracellular Cr (VI) and intracellular Cr (III) is what ultimately dictates the amount and rate at which Cr (VI) can enter cells and impart its toxic effects into the body (Genchi *et al*., 2020).

2.2.13. Copper (Cu)

Copper is a reddish transitional metal with a face-centred cubic crystalline structure. It reflects red and orange light but absorbs other frequencies in the visible spectrum (Aguilar *et al*., 2014). It is malleable and ductile and is a very good conductor of both heat and electricity (Gaetke *et al*., 2015). Copper belongs to period 4 and group 1B of the periodic table. Its atomic number is 29, mass number 63.5, and it has oxidation state of +1 and +2 however the most abundant is +2. Its melting and boiling points are 1083^{o}c and 2595^{o}c, respectively (Anant & Bhagat, 2018). In the lithosphere, it is estimated to have a mean concentration of about 39 µg/g, and it is the third most used metal in the world [OBJ]. Copper is widely distributed in nature in a free state, in sulphides, chlorides and carbonates. Copper is used in making electrical wires and its alloys are used in various industrial applications

such as fungicides and pesticides (Aguilar *et al*., 2014; Thit *et al*., 2015). At low or recommended levels, copper is an essential micronutrient for the growth of both plants and animals; however, at high concentrations, it becomes toxic, causing problems for both plants and animals. Long-term exposure to copper in humans results in nose, mouth, and eyes irritation. It may also cause dizziness, vomiting diarrhoea and headache (Anant & Bhagat, 2018; Gaetke *et al*., 2015). Long and high-level exposure causes anemia, liver and kidney dysfunctions, brain damage and decline in intelligence in young adolescents. The human body is believed to contain copper at the level of about 1.4 to 2.1 mg per kg of the body mass (Aguilar *et al*., 2014; Gaetke *et al*., 2015; Thit *et al*., 2015). The recommended concentration in drinking water by WHO and EPA is 0.05 mg/l (WHO, 2011). Copper enters the natural environment from natural and anthropogenic activities such as erosion, mineral deposit, mining, smelting, domestic and industrial wastewaters, steam electrical production, incinerator emissions, and the dumping of sewage sludge (Gaetke *et al*., 2015).

2.2.13.1 Toxicokinetics of Copper (Absorption, distribution and elimination)

Copper absorption primarily occurs in the small intestine through active and passive transport and a small amount in the stomach (Gaetke *et al*., 2015). Once absorbed, it enters the bloodstream via the plasma and goes to the liver, where its metabolism is controlled (Anant & Bhagat, 2018; Gaetke *et al., 2015)*. Usually, the blood contains 60–95% of the total absorbed dose(Aguilar *et al*., 2014; Thit et al., 2015). The uptake level from the intestines is affected by the amount of copper in the diet, the presence of other metals such as zinc and iron, and the presence of dietary proteins, complexing or precipitating anions and fructose (Gaetke *et al*., 2015; Thit *et al*., 2015). Moreover, copper uptake varies significantly among individuals depending on food choices and dietary customs. After ingestion, the concentration of copper in the blood increases rapidly. The absorbed copper is then transported to the liver, where it is transported to other tissues of the body (Aguilar *et al*., 2014; Anant & Bhagat, 2018). Copper has a half-life of 3.9 and 21 days in the liver, 5.4 and 35 days in the kidney, 23 - 662 days in the heart and 457 days in the brain. Absorbed amount of copper is stored in the liver and it is excreted in the bile, faeces, sweat, hair, and

urine. However, in humans, the major excretory path way is the bile; less than 3% of the daily copper intake is excreted in the urine (Aguilar *et al*., 2014; Gaetke *et al*., 2015).

2.2.13.2 Mechanism for copper toxicity

Copper toxicity has generally been associated with its ability to cycle between an oxidation state, Cu (II), and a reduced state, Cu (I), which generates other radicals such as hydroxyl radicals. Formation of new radicals during copper transition is toxic to cells. Furthermore, evidence shows that copper displaces iron in iron-sulphur cluster proteins, causing toxic effects in the body (Anant & Bhagat, 2018).

2.2.14 Iron (Fe)

Iron (Fe) is a lustrous, ductile, malleable, silver-grey chemical element with atomic number 26; it belongs to group VIII and period 4 of the periodic table. Its density is 7.874 g/cm^3 at room temperature, and it has melting and boiling points of 1538^{0}c and 2862^{0}c respectively (Casida & Frey, 2007)., By mass it is the most common element on Earth, forming much of Earth's outer and inner core. Iron has four stable isotopes, namely ^{54}Fe (5.845% of natural iron), ^{56}Fe (91.754%), ^{57}Fe (2.119%) and ^{58}Fe (0.282) (Hershko, 2007). Iron exists in a wide range of oxidation states ranging from −2 to +6, but +2 and +3 are the most common (Albretsen, 2006; Tenenbein, 2016). Iron (II) compounds are commonly called ferrous, while iron (III) compounds are called ferric. Iron is the body's most abundant trace mineral and an essential element in most biological systems (Tandara & Salamunic, 2012). Iron binds with haemoglobin and myoglobin, which help transport oxygen to the body. About 70% of the iron in mammals is found in haemoglobin, and about 5% to 10% is found in myoglobin and 1 per cent in the various enzymes that control intracellular oxidation. The rest is stored in the liver, spleen and bone marrow for future conversion to haemoglobin (Hershko, 2007; Tandara & Salamunic, 2012). Red meat, egg yolk, carrots, fruit, whole wheat, and green vegetables contribute most of the 10–20 milligrams of iron required daily in the average adult. It is estimated that the human body has approximately 4 grams of iron on average (Albretsen, 2006; Hershko, 2007). Men need about 7 mg of iron daily, whereas

women require 11 mg; the difference is maintained by the menstrual cycle. The body absorbs approximately 25% of all iron present in food (Albretsen, 2006). In industry, iron is used to manufacture steel, while in civil engineering is used to reinforce concrete. Iron is also used in making alloy steels like carbon steels, which are used in making bridges, electricity pylons, bicycle chains and cutting tools. Iron exists naturally in rivers, lakes, and underground water (Hershko, 2007; WHO, 2011). However, in recent years, its concentration has increased due to human activities, which release iron from industrial wastes, refining of iron ores, and corrosion of iron-containing metals. In lakes and rivers iron is contained in heterogeneous sediments and approximately 0.5-1 ppm of iron is found in unpolluted rivers while groundwater contains about 100 ppm (Tandara & Salamunic, 2012). Despite being a biologically important element however, high dose ingestion of iron causes problems to both plants and animals; for example, in plants, high iron content causes leaf discolouration and stunted root system, while in animals such as humans, high dose ingestion of iron can damage the gastrointestinal system among other problems (Morris & Levenson, 2012).

2.2.14.1 Toxicokinetics of iron

Iron enters the human body mainly through the ingestion of iron, which contains food and water. Iron ions are absorbed into the blood from the intestine, mainly in the duodenum and upper jejunum (Tenenbein, 2016). Ferrous iron is better absorbed than ferric iron because ferric iron precipitates out of solution at around pH7 or under normal physiologic conditions (Tenenbein, 2016). However, iron (II) and (III) can be absorbed if ionized. The rate of absorption is increased by taking a diet high in sugar and vitamin C, while a high-phosphate diet reduces iron absorption (Albretsen, 2006). Once absorbed, it is transferred into the blood and transported to other tissues such as liver and spleen (Casida & Frey, 2007; Morris & Levenson, 2012). Iron is mainly stored in the liver and bone marrow, and it is eliminated from the body through the removal of dead skin cells from the outer layer of the skin, the bile and sometimes through menstruation, blood loss and bleeding (Albretsen, 2006; Casida & Frey, 2007).

2.2.14.2 Mechanism for Iron Toxicity

Iron toxicity happens due to the formation of various harmful free radicals in the blood, which is usually caused by overdoses of ingested iron (Tenenbein, 2016). The formed free iron ions penetrate and damage the cells of the liver, heart and brain, causing adverse effects that include coma, metabolic acidosis, shock, liver failure, and adult respiratory distress syndrome (Saito, 2014). Furthermore, free radicals produced by excess iron result in cellular damage, mutations in DNA and malignant transformation, which in turn causes different diseases in the environment, with high concentrations reported close to mines and smelters.

2.2.15 Zinc(Zn)

Most of the zinc in rivers and streams does not dissolve but settles to the bottom (Arantes *et al*., 2016; Outa *et al*., 2020). Sediments from uncontaminated waters typically contain zinc concentrations of 5-50 μg/g. The lithosphere is estimated to have approximately 80 μg/g zinc content. In soil, high levels of zinc may result from the improper disposal of zinc-containing wastes by metal manufacturing industries and electric utilities (Arantes *et al*., 2016; Outa *et al*., 2020). Zinc is commonly used in coating steel, iron, and other metals to prevent rust and corrosion. Zinc is an essential nutrient the body needs for growth, development of bones, metabolism and wound healing. Although humans can handle proportionally large concentrations of zinc, too much zinc can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia (Arantes *et al*., 2016; Kim *et al*., 2020; Plum *et al*., 2010).

2.2.15.1 Toxicokinetics of zinc

Inhalation and ingestion are the primary entry roots of zinc into the human body (Kim *et al*., 2020; Plum *et al*., 2010). However, most studies show that a high absorption rate happens through ingestion. Zinc uptake from a regular diet ranges from 26-33% (Plum *et al*., 2010). Under normal physiological conditions, 20–30% of ingested zinc is absorbed (Kim *et al*., 2020; Outa *et al*., 2020). Zinc is primarily absorbed in the small intestine; approximately 60% of the absorption occurs in the duodenum, 30% in the ileum, 8% in the

jejunum, and 3% through the colon and cecum (Ogunbileje *et al*., 2013). The absorption rate is affected by the solubility of the zinc compounds, the presence of zinc in an individual's body and other metals such as calcium and phosphorus (Ogunbileje *et al*., 2013; Plum *et al*., 2010). Once absorbed, zinc is widely distributed in all tissues in the body (Tchounwou *et al*., 2014). The highest zinc content is found in the prostate gland, muscle, bone, gastrointestinal tract, kidney, brain, skin, lung, heart, and pancreas. Primarily, zinc is excreted in the faeces, 70-80% of an ingested dose, and small amounts are found in urine, sweat, and semen.

2.2.15.2 Mechanism for zinc toxicity.

Zinc is one of the essential elements needed by the body, and usually, it is found in all tissues and tissue fluids where it supports over 300 enzyme systems. However, it may become toxic at high concentrations (Kim *et al*., 2020; Plum *et al*., 2010). Usually, there is a debate on its mechanisms for toxicity. A critical element of zinc toxicity is its ability to generate oxidative stress by free radicals and reactive oxygen species, which damages the neurons and even causes death (Arantes *et al*., 2016; Kim *et al*., 2020; Plum *et al*., 2010). Other studies have suggested that zinc interferes with other metals, such as iron, in the body, disturbing normal cell function (Plum *et al*., 2010).

2.3 Health effects of heavy metals

2.3.1 Neurological and Hematologic effect

Most heavy metals such as lead, cadmium, chromium, zinc and copper cause neuron and blood damage (Albretsen, 2006; Gidlow, 2004; Plum *et al*., 2010.). Lead, cadmium, zinc and iron for example, have been found to increase the risk of numerous conditions that may have adverse effects on nervous system function, including hypertension, impaired renal function, impaired thyroid function, vitamin D deficiency, and preterm birth (Philip & Gerson, 1994; Schroeder, 1979) even at blood lead levels of 80 – 100μg/dL in children and 100 - 120μg/dL (Goyer & Clarkson, 2001).

Hematologic effects are the effects of heavy metals on blood, blood-forming organs, and blood disease . Most heavy metals, such as lead, zinc, copper, and cadmium, are believed to induce anaemia by damaging red blood cells and hindering their normal development and functioning. Heavy metals may cause an increased number of immature red blood cells with small coloured grains, impairing the normal functioning of the blood (Armstrong *et al*., 2015; Godt *et al*., 2006; Philip & Gerson, 1994).

2.3.2 Reproductive effect and endocrine disruption

Clinically, heavy metal toxicity has been associated with sterility in both animal and human studies (Gidlow, 2004; Goyer & Clarkson, 2001; Ogunbileje *et al*., 2013). Some clinical studies have shown a positive relationship between lead dose and sterility; for example, battery manufacturing workers with blood lead levels above 60 g/dL were found to have a reduction in sperm counts and abnormal sperm motility and morphology (Godwill , Engwa *et al*., 2019). In another study in rats, cadmium was noted to interfere with the ovarian pathway (Genchi *et al*., 2020; Sharma *et al*., 2015) The same study revealed that the production of progesterone and testosterone was also significantly affected (Sharma *et al*., 2015)—furthermore, maternal exposure to cadmium resulted in low birth weight and an increase in abortion (Godt *et a*l., 2006; Godwill *et al*., 2019). Several studies have shown that high levels of heavy metals in the body are associated with thyroid, pituitary, and testicular hormone changes (Lowry, 2015). L,ead for example, is believed to change circulating levels of thyroid hormones at mean blood lead levels of ≥40–60 μg/dL (Armstrong *et al*., 2015), while in reproductive hormones, it has been suggested that a blood lead level of 30-40 μg/dL is sufficient to alter the serum level of the reproductive hormones (Armstrong *et al*., 2015).

2.3.3 Immunological and Cardiovascular Effects

Heavy metals have been reported to lower the immune system in humans by decreasing the absolute count of B lymphocytes and suppressing the T helper cells. Evidence also

shows that workers associated with heavy metals mining and smelting cadmium, chromium and zinc may be more susceptible to cold (La-llave-león *et al*., 2016; Makokha *et al*., 2008). Epidemiological data from other studies have proved that most of the heavy metals cause cardiovascular problems such as blood pressure. Literature suggests that both lead and cadmium play a role in causing hypertension and diabetes. Other scholars have also linked cadmium exposure with sudden cardiac death and arterial diseases (Adimalla & Wang, 2018; Bernhoft, 2013). Lead is believed to contribute to high blood pressure due to its role in the depletion of nitric oxide (which plays a role in regulating blood pressure) and the disturbance of cell-signalling mechanisms in endothelial cells (Eum *et al*., 2014).

2.3.4 Kidney damages

Exposure to high levels of heavy metals may damage the kidneys. It is believed that high exposure to heavy metals such as cadmium, chromium, copper and iron results in characteristic microscopic change and formation of kidney stones, which may damage the kidney *(Karthika et al*., 2021; Philip & Gerson, 1994) Other studies have suggested that lead forms inclusion bodies in the cytoplasm of kidney cells grown in culture and tends to migrate into nuclei, secondarily causing kidney problems (Philip, 2018). Furthermore, the kidney is the main target of cadmium chronic exposure, as 30% of the total absorbed dose is deposited in the kidney (Jaishankar *et al*., 2014). Cadmium reaches the kidney in the form of cadmium-metallothionein (Cd-MT). It is filtrated in the glomerulus, then reabsorbed in the tubules, where it remains and forms a significant part of the cadmium body burden (Edwards *et al*., 2018; Jaishankar *et al*., 2014). Human research has shown that high levels of cadmium in the kidney lead to disturbances in calcium metabolism, which results in renal stone formation, thereby causing kidney damage (Godt *et al*., 2006; Kosek *et al*., 2017).

2.3.5 Skeletal damages

Heavy metals can cause bone mineralisation through bone damage or renal dysfunction (Sharma *et al*., 2015). Both present and past studies on humans and animals have revealed that skeletal damage is among the critical effects of heavy metal exposure, such as cadmium (Bernhoft, 2013). For example, in a survey that was conducted in Japan in the

1940s, cadmium was shown to be associated with occurrences of Itai-Itai, a disease under which patients show a wide range of symptoms such as low grade of bone mineralisation, high rate of fractures, and intense bone associated pain (Jaishankar *et al*., 2014; WHO, 2000). Affected patients showed the characteristic symptoms after eating rice grown in fields irrigated with highly cadmium-polluted water (Huo *et al*., 2018; H. Sharma *et al*., 2015).

2.3.6 Respiratory problems

Most heavy metals are believed to cause severe lung damage on higher inhaling levels, leading to shortness of breath, lung oedema and destruction of mucous membranes, and stomach irritation, which usually may result in vomiting and diarrhoea (Godt *et al*., 2006; Godwill , Engwa *et al*., 2019). Furthermore, the respiratory tract is the primary target organ for hexavalent chromium Cr (VI) toxicity for short-term and long-term inhalation exposures (Achmad & Auerkari, 2017). Shortness of breath, coughing, wheezing, perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, pneumonia, and asthma have been reported in cases where an individual inhaled very high concentrations of Cr (VI) for an extended period. Extensive exposure to zinc chloride and copper can cause respiratory disorders (ATSDR, 2011).

2.4 Cancer

Literature from both animal and human medical experiments has proven that heavy metals such as lead, cadmium and chromium may cause cancer (Godt *et al*., 2006; WHO, 2000). In rats, for example, it was demonstrated that subcutaneous injection of cadmium chloride caused prostate cancer (Allen *et al*., 2021; Godt *et al*., 2006). Data elsewhere indicates that there is an association between cadmium and renal cancer in humans (Bernhoft, 2013; Godt *et al*., 2006). The latest studies and reviews of several epidemiological and clinical studies by the International Agency for Research on Cancer have classified cadmium, lead, and chromium as human carcinogen elements (Tchounwou *et al*., 2014; Venter *et al*., 2020).

Data of workers from chromium-related companies have established that inhaled chromium (VI), for example, is a human carcinogen, possibly causing an increased risk of different types of cancer such as lung cancer, nasal and sinus (Shekhawat *et al*., 2015; Sun *et al*., 2015). Other studies elsewhere have reported different kinds of cancer originating from oral exposure to Cr (VI), such as stomach and liver cancer. Studies from China and Greece have reported an increase in stomach and liver cancer mortality in residential areas where the drinking water was heavily contaminated with Cr (VI) (Bernhoft, 2013; Shekhawat *et al*., 2015).

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Chapter overview

This chapter outlines the research design, methods, study area, and sample population. It also discusses the sample collection process, analysis, and sampling technique used. Furthermore, the chapter discusses the assessment of sediment contamination using different pollution indices.

3.2 Research design and methodology

Research design is the procedure for collecting, analysing, interpreting and reporting data in research studies. It is the overall plan for connecting the conceptual research problems with the relevant empirical research (Bernhoft, 2013; Shekhawat *et al*., 2015). In other words, the research design sets the procedure for the required data, the methods to collect and analyse the data, and how the research question will be answered. The research adopted a mixed research design as experimental and descriptive methods were used. Descriptive research involves collection, recording, describing and analysing the facts related to the study (Shekhawat *et al*., 2015. It tries to find a phenomenon's existing status, trend and state of affairs. Descriptive research involves surveys, but they are not merely data collection as they also involve measurement, classification, analysis, comparison and interpretation, and the variables under study are uncontrollable and it was preferred to describe the data obtained from both experiments and surveys.

Experimental, on the other hand, deals with what will be. The variables involved are carefully and scientifically controlled and manipulated, and they were used to obtain the actual concentration of heavy metals in targeted samples.

Research methodology, on the other hand, is the science of studying how research is carried out. The procedures by which researchers describe, explain and predict outcomes by which knowledge is gained (Shekhawat *et al*., 2015. Some well-known- research methodologies employed in research include quantitative, qualitative and mixed research methodologies. Quantitative research is based on quantitative variables, which can be measured in appropriate units. These involve objects and individuals that vary in size, quantity, amount, scale or degree. On the other hand, qualitative research is based on qualitative variables, which vary in quality and type. The variables cannot be measured on a scale or in any units, while mixed research combines quantitative and qualitative approaches. However, this study adopted a mixed research methodology using quantitative and qualitative research methodologies. Qualitative methodology was used to describe the results obtained, while quantitative methods measured and quantified heavy metal concentration in sediments, paints and water.

Furthermore, several research methods were used to collect, analyse and interpret data. Research methods are the various procedures, schemes, algorithms, etc., used in research. They are planned, scientific and value-neutral. They include theoretical procedures, experimental studies, numerical schemes and statistical approaches. This study used experimental, survey, and statistical methods. The experimental method was used to collect and analyse the data obtained during the research. A survey was used to assess the types of paints available in Malawi and why they are familiar and preferred. Mean, mode, median and pearson square correlation are statistical models that were used to quantify the data for straightforward interpretation.

3.3 Study area and sample population

The study was conducted in Malawi, Blantyre City at Mudi River, Lilongwe and Zomba City. For sediments and water samples, samples were taken from Mudi River at 12 different sampling points along the river (figure 7). Mudi River is located at 15^0 51'30''S and 34^0 52' 55''E with an elevation of 1125 meters above sea level. The river is found in the southern part of Malawi in the commercial City of Blantyre. It originates from the Mudi dam, flows north to south through Makata Industrial Area to Blantyre Market, and ends at Stella Maris. The district's site selection was based on industries around the Makata Industrial Area, which was believed to cause pollution in the river and surrounding areas. For paint samples, 23 samples of solvent-based paints intended for home use were purchased from several paint retail stores in three major cities of Malawi (Lilongwe, Blantyre, and Zomba) between November and December 2020. The choice of 3 major cities was based on getting the actual paints that most local Malawians likely buy to get the paint used in all other parts of the country. Furthermore, 24 water samples and 24 sediment samples, making a total of 48 samples, were sampled for analysis.

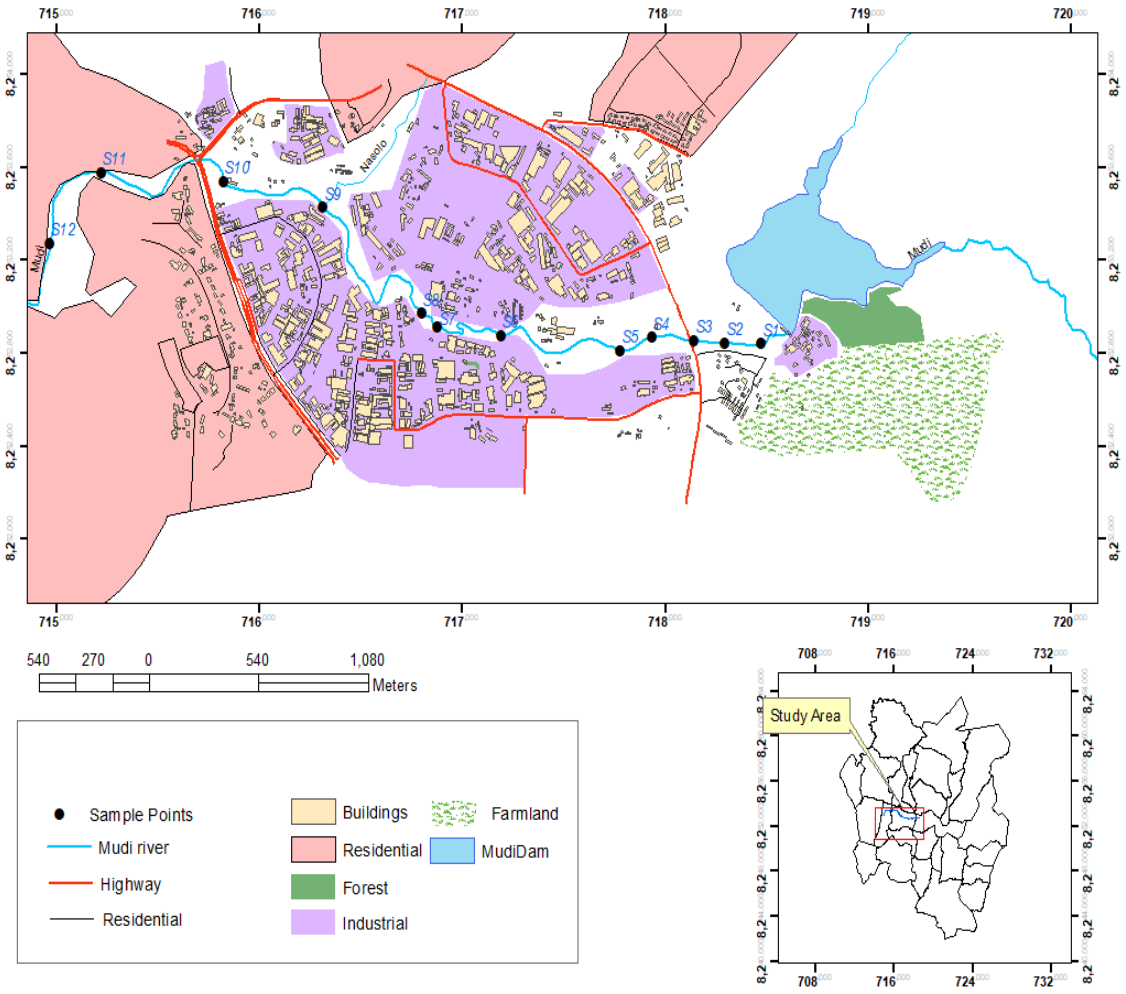

Figure 7 Study area where sediments and water samples were taken by the author (2021)using ArcGIS 10.8.

3.3 Sample collection

For paints samples, twenty-three samples of solvent-based paints intended for home use were purchased from several paint retail stores in 3 major cities of Malawi (Lilongwe, Blantyre, and Zomba) between November and December 2020. Twenty (20) stores were visited, and all available home-use solvent-based paints were included. The paints carried labels of 8 brands, namely Coral, Rainbow, Medal, Plascon, Monolux, Crown Valmore, Nuroc, and Dulux (Figure 8) and White, green, yellow, and red coloured paint were sampled for each.

Figure 8 Paint cans used in the analysis

For sediments and water samples, a total of twelve (12) sediments and twelve (12) water samples making twenty-four (24) samples were collected from Mudi River at twelve (12) different sampling points within the Mudi River during dry season in 2021 and wet season in 2022. Figure 9, shows some section of Mudi River, where sediments and water samples were taken during sample collection. Sediment samples from the targeted sites were collected at 0 to 10 cm deep using a polypropylene spatula and about 1 kg of sediments samples were collected at each selected site and packed in clearly labelled cleaned polyvinyl plastic bags. Similarly, 500ml of water from the river were collected at the selected sites using clearly labeled plastic bottles and 2 ml of nitric acid was added to preserve the samples for analysis. Both water and sediments samples were transported to the chemistry laboratory at the University of Malawi for further treatment and analysis.

Figure 9 Some section of the Mudi River

3.5 Sample preparation and analysis

Each paint was mixed by stirring thoroughly using an untreated wooden stirring utensil. A lead-free 10 cm by 10 cm polypropylene surface was labeled for each painting with the corresponding unique number on the paint can. The paint was applied to the polypropylene surface in a 0.5-1mm coating using the untreated wooden stirring utensil. Each stirring utensil was used only once, fresh nitrile gloves were worn for each application, and care was taken to avoid cross-contamination (Figure 10). After drying at ambient temperature for seven days (For full curing), the paint was peeled from the polypropylene surface, placed in individually labelled polyethene (Ziploc) plastic bags, and shipped for lead content analysis at the Wisconsin Occupational Health Laboratory, United States of America. The paint scrapings were extracted with nitric acid and hydrogen peroxide according to standard operating procedures for Lead in Paint by Hotplate or Microwave-based Acid Digestions and Atomic Absorption or Inductively Coupled Plasma Emission Spectroscopy, EPA, PB92-114172, September 1991 (Adebamowo *et al*., 2007; Clark *et al*., 2009). The digested samples and the reagents were analysed for total lead content by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, NIOSH 7303). The laboratory's analytical methods and certifications are consistent with those recommended by the World Health Organization for measuring lead in paint samples with concentrations below the detection limit of the analytical procedures used, which were

reported as < 60 ppm. For sediment samples, the large stones and other coarse debris were removed manually from the samples. The sediment samples were air-dried for 15 days, followed by oven drying at 100^{o}C for 24 hours to evaporate water. The dried samples were homogenised and ground using a pestle and mortar and allowed to pass through a sieve of 2-mm mesh. Then, 3g of the sediment samples were accurately weighed using an electronic balance and placed in a dry, clean beaker for digestion. For the evaluation of metal contents, 2.5 ml of HNO_3 (65%), 7.5 ml of HCl (37%), and 2 ml H_2O_2 (37%) were added to the samples for digestion at high temperatures in an oven (Abdullah *et al*., 2015). After digestion, 150 ml of distilled water was added to each sample for dilution and then cooled at room temperature. Finally, water and sediment samples were filtered using Whatman No.1 filter paper (0.45 µm).

Figure 10 Sample preparation and air drying of paint samples

Both water and digested sediment samples and reagent blank were analysed for total Cd, Cr, Pb, Zn, Fe, and Cu content by Atomic Absorption Spectrometer (AAS). pH,

temperature, and EC were measured on-site using a combined conductivity/pH/temperature/turbidity meter.

3.6 Sampling technique

The study used both purposive and random sampling. The random sampling technique was used to collect sediments and water samples, while purposive sampling was used to collect paint samples since the research targeted oil-based paints only.

3.7 Assessing metal contamination in sediments

Four indicators were calculated, namely, contamination factor, degree of contamination, enrichment factor, and Geo-accumulation index, to assess the levels of sediment contamination of the Mudi River**.** On the other hand, an ecological risk index was further computed to assess the ecological impact of the Mudi River sediments on the environment and humans in general.

3.7.1. Contamination Factor

The contamination factor (CF) is an indicator of sediment contamination used to evaluate pollution in an aquatic environment by a given toxic substance (Cesar *et al*., 2018). Thus, to evaluate the level of heavy metal contamination in sediments, CF was calculated using equation 1.

$$\mathrm{CF} = \frac{\mathrm{C_m\ Sample}}{\mathrm{C_m Background}} \qquad (1)$$

C_m Sample refers to the concentration of a given metal ion in the sediment, and C_m Background refers to the value of a reference of that particular metal. The CF values are categorised into 4: CF<1 indicates low contamination, CF 1-3 is moderate contamination, CF 3-6 is considerable contamination, and CF>6 is very high contamination (Cesar *et al*., 2018).

On the other hand, the degree of contamination (C_d) is defined as the sum of all contamination factors. Cd values are categorised into 4, where Cd <6 = low degree of contamination, 6 to <12= moderate degree of contamination, 12 to <24, considerable degree of contamination, and Cd≥24 =Very high degree of contamination.

3.7.2 Enrichment factor (EF)

The enrichment factor (EF) is generally used as an appropriate method to discriminate between natural and anthropogenic sources and to reflect the status of environmental contamination by utilising a normalisation element to improve the variations produced by heterogeneous sediments (Gong *et al.*, 2008). He was used as a reference metal for normalisation, and the EF of metals in the sediments was calculated using Equation 2.

$$\mathrm{EF} = \frac{\mathrm{M/Fe\ (Sample)}}{\mathrm{M/Fe\ (background)}} \qquad \textbf{(2)}$$

The M sample and M background are the contents of the investigated metals in the sediment samples and the uncontaminated background, respectively, and the Fe sample and Fe background are the contents of Fe in the sediment samples and the uncontaminated background, respectively. The EF values were interpreted with the following categories, where EF<1 indicates no enrichment, <3 is minor enrichment, 3-5 is moderate enrichment, 5-10 is moderately severe enrichment, 10-25 is severe enrichment, 25-50 is severe enrichment, and >50 is highly severe enrichment (Gong *et al.*, 2008).

3.7. 3 Geo-accumulation index (I_{geo})

The geo-accumulation index (Igeo) is used to determine the extent of metal accumulation in sediments and was calculated using the proposed formula (Muller, 1986).

$$\mathrm{I_{geo}} = \log 2\ \left(\frac{\mathrm{Cn}}{1.5\ \mathrm{Bn}}\right) \qquad \textbf{(3)}$$

Where C_n expresses the content of the toxic metal n, B_n expresses the background data of the toxic metal n, and 1.5 is a factor of possible lithological changes. The *I*geo consists of 7 classes ranging from practically uncontaminated to extremely polluted: I_{geo} <0-0 = uncontaminated, I_{geo} 0 -1 uncontaminated to moderately contaminated, I_{geo} 1-2 = moderately contaminated, I_{geo} 2-3= moderately to heavily contaminated, I_{geo} 3-4 = heavily contaminated, I_{geo} 4-5= heavily to extremely contaminated, I_{geo} 5 above = extremely contaminated (Muller, 1986).

3.7.4 Ecological risk factor (E_{ri}).

The ecological risk factor is used to quantitatively assess the degree of heavy metal pollution in sediments, according to metal toxicity and the environment's response. It was suggested by Hakanson (1980). The ecological risk factor was calculated using equation 4.

$$RI = \sum E_i$$

$$E_i = T_i f_i$$

$$F_i = C_i / C_b \qquad \textbf{(4)}$$

Where RI refers to the sum of all risk factors in the sediment samples, and E_i is the monomial potential ecological risk factor for individual factors. Ti refers to the metal toxic response factor, F_i refers to the metal pollution factor, C_i is the measured concentration of heavy metal in the sediment sample, and C_b is the value of the reference metal ion. T_i refers to the metal toxic response factor (i.e., Cu = Pb=5, Cr = 2, Zn = 1, Cd = 10). The RI values are categorised as follows: I<150 indicates low ecological risk. RI; 150-300 = moderate ecological risk, RI; 300- 600 = considerable ecological risk, and RI≥ 600 indicates very high ecological risk for the sediment (Hakanson, 1980).

3.8 Statistical Data Analysis

The data was analysed using the Statistical Package for Social Science (version 22) and Excel Statistical Packages. Person correlation (r) analysis was performed to determine the strength of the interrelationship between target metals and other environmental factors,

such as pH and EC, in the sediments. Pearson correlation (r) values were also calculated to hypothesise whether the metals had a common source of origin based on the assumption that two or more components may correlate due to a common origin or atmospheric behaviour.

3.9. Apparatuses and chemicals

The following materials and apparatus were used during this study: Cr, Cd, Pb, Cu, Fe and Zn standard solutions, Nitric acid, Hydrogen peroxide, Whatman filter paper, beakers, funnels, test tubes, pipette, distilled water, oven, volumetric flask, plastic bag, spatula, markers, hot plate, conical flask, measuring cylinder and groves.

3.10 Working Principle of ICPAES and AAS

In ICPAES, the sample is introduced into the centre of the plasma as an aerosol with the help of a nebuliser using argon flow, and the sample is usually transported into the instrument as a stream of liquid. Inside the instrument, the liquid is converted into an aerosol through a process known as nebulisation. The sample aerosol is then transported to the plasma and subjected to a temperature of about 5000 to 10000K, desolvated, vaporised, atomised, excited and ionised by the plasma (Adebamowo *et al*., 2007; Clark *et al*., 2009). This high-temperature results in almost complete dissociation of molecules and a significant reduction in chemical interferences. The excited atoms and ions emit their characteristic radiation, which is collected by a device that sorts the radiation by wavelength. The radiation is detected and turned into electronic signals converted into concentration information for the analyst. To generate plasma, first, argon gas is supplied to the torch coil, and a high-frequency electric current is applied to the work coil at the tip of the torch tube. Using the electromagnetic field created in the torch tube by the high-frequency current, argon gas is ionised, and plasma is generated. This plasma has a high electron density and temperature (10000K), and this energy is used to excite the sample (Adebamowo *et al*., 2007; Clark *et al*., 2009).

On the other hand, AAS is a method of analysis based on radiation absorption by atoms when a solution of metallic salt or metals is aspirated (drawing) into a flame. In AAS, a monochromatic light for a particular element is produced by a hollow cathode lamp utilising that element as the cathode. The monochromatic light produced by the lamp is beamed through a long flame into which is aspirated the solution to be analysed (Adebamowo *et al*., 2007; Clark *et al*., 2009). The heat energy dissociates the molecules and converts the components to atoms' flame temperature. Some atoms in the solution are activated, but most of the atoms remain in the ground state. The sample to be analysed is aspirated into a hot flame to break the molecules into their atomic states. The atom cloud required for atomic absorption measurements is produced by supplying enough thermal energy to the sample to dissociate the chemical compounds into free atoms. The high temperature of the flame excites a valence electron to a higher-energy orbital. The atom then emits energy in the form of light as the electron falls back into the lower energy orbital (ground state). The intensity of the absorbed light is proportional to the concentration of the element in the flame; hence, its concentration is measured (Adebamowo *et al*., 2007; Clark *et al*., 2009).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Chapter overview

This chapter presents the findings and discussions of the results obtained in the study. The results are presented in two sections, thus concentration of lead in solvent based paints and concentration of Zn, Cd, Cr, Pb, Cu and Fe in Mudi River surface water and sediments.

4.2 Overall Lead concentration in solvent-based paints in Malawi

Lead was detected in 70% of the analysed paints, and the results showed that Pb levels in paints produced and marketed in Malawi exceed the standard limit of Pb in paint in most developed and developing countries. The new US and WHO limit of Pb in paint is 90 ppm, and China, South Africa, and India have a limit of 600 ppm Pb concentration in paint (WHO 2021; IPEN 2017d). 13 out of 23 of the analysed samples (57%) exceeded the WHO and USA legal limits of lead in paints of 90 ppm. 57% of the analysed paint samples (13 out of 23) had lead content exceeding the South Africa, China, Singapore, Uruguay, and Brazil limit of 600 ppm lead in paints. Further, 4% of the analysed samples (1 out of 23) contained exceedingly high lead concentrations greater than 10000 ppm (figure 11).

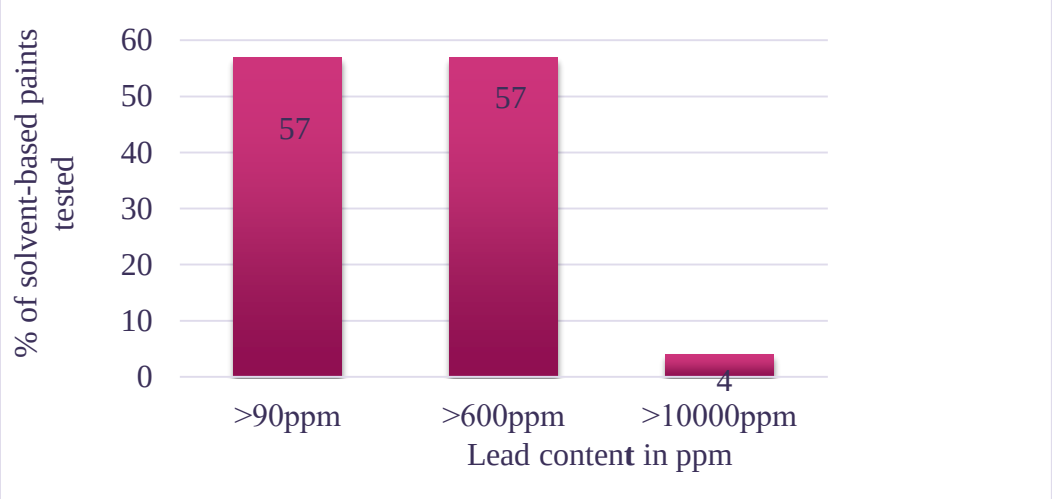

Figure 11 Overall lead content in parts per million

Table 1 Overall lead content in paint in parts per million (ppm) and other vital information

Code	Brand Label	Colour	Lead in ppm	Manufacture	Label information
1.1	Coral	Red	260	Insignia Africa	paint is ventilated
1.2	Coral	Green	3900	Insignia Africa	paint is ventilated
1.3	Coral	White	60	Insignia Africa	paint is ventilated
2.1	Rainbow	Red	17000	Rainbow paint	keep out of children
2.2	Rainbow	Yellow	4200	Rainbow paint	keep out of children
2.3	Rainbow	White	61	Rainbow paint	keep out of children
3.1	Medal	Red	3300	Rainbow paint	keep out of children
3.2	Medal	Green	60	Rainbow paint	keep out of children
3.3	Medal	White	<60	Rainbow paint	keep out of children
4.1	Monolux	Red	8100	Monolux paint	none
4.2	Monolux	Yellow	7600	Monolux paint	none
4.3	Monolux	White	1700	Monolux paint	None
5.1	Nuroc	Red	1800	Monolux paint	None
5.2	Nuroc	Green	1600	Monolux paint	None
5.3	Nuroc	Cream	2600	Monolux paint	None
6.1	Crown, Valmore	Red	3600	Valmore paint	None
6.2	Crown, Valmore	Yellow	10000	Valmore paint	None
6.3	Crown, Valmore	Cream	<60	Valmore paint	None
7.1	Plascon	Red	<60	Kansail plascon	None
7.2	Plascon	Yellow	<60	Kansail plascon	None
7.3	Plascon	White	<60	Kansail plascon	None
8.1	Dulax	Red	<60	Dulux Malawi	This paint is toxic
8.2	Dulux	Yellow	63	Dulux south Africa	No added lead

Generally, the results show variations in lead levels in paints from different labels, irrespective of manufacturer. Pb was not detected only in Dulux (Red) and Plascon and Crown Valmore (Cream) labelled paints whereas), the other six brand labels showed lead content at 90 ppm levels (Table 1). Despite being made by the same manufacturer, rainbow paints showed a higher Pb content, as high as six times the standard limit of lead in paint, than Medal paint.

4.2.1. Distribution of lead concentration by colour and brand

Previous studies have documented that lead concentration in solvent-based paint varies with the colour of the paint (Clark et al., 2015; La-llave-león et al., 2016). Therefore, a comparison was done to check the difference in lead concentration in paints of different colours. The study involved five different colours of solvent-based paints: white, cream, green, yellow, and red. The average lead content of all five colours exceeded the USA, UN, and WHO legal limit of 90 ppm. The total average for red colour had the highest value of 4296.25 ppm. This is followed by yellow (3016.40 ppm) and green (1853.33 ppm) (Figure 12). The colours red, yellow, green, and cream have 100% of their samples registering values greater than 1000 ppm. Only the white colour had 100% of its samples, which registered the lowest total average of lead concentration below 600 ppm. Generally, the red paint showed the highest average lead concentration in solvent-based paint sold in Malawi.

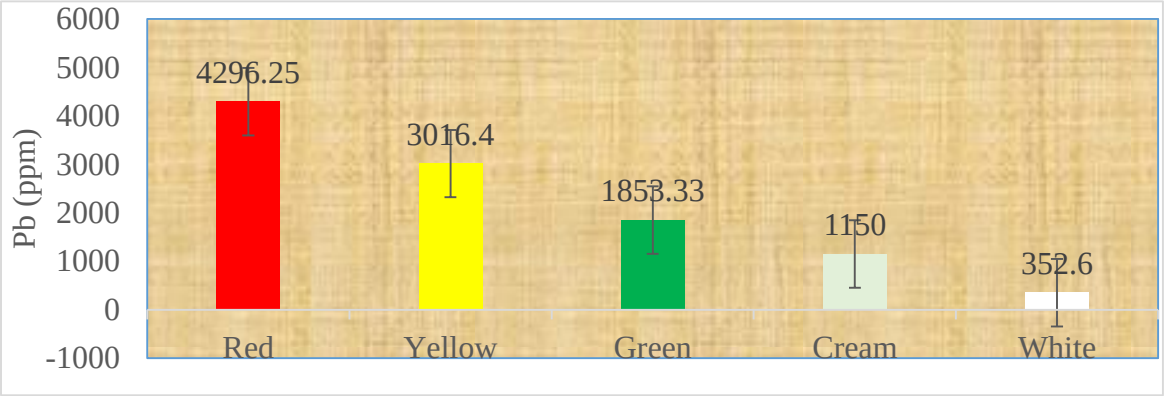

Figure 12 Variation of lead content in analysed paints grouped by colour.

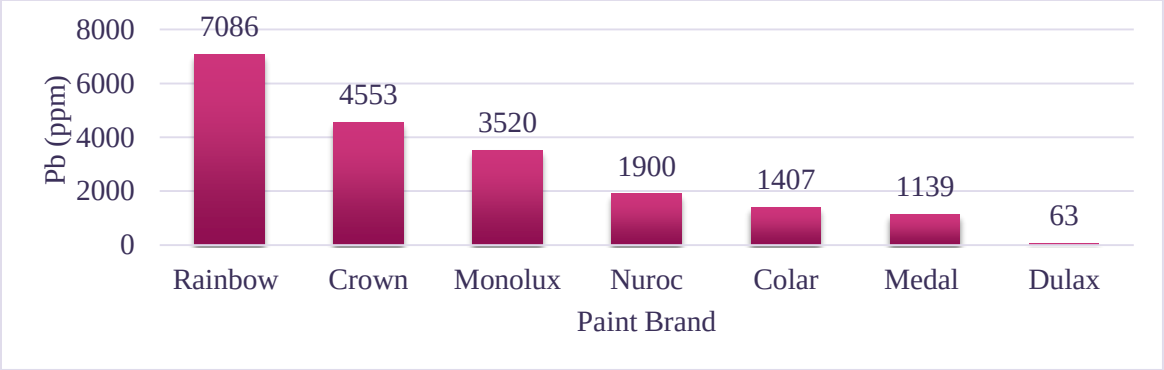

Figure 13 Variation of lead in analysed paints grouped by brand

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From the results, it is clear that coloured paints contained dangerous lead content which may cause serious health effects to humans especially children and pregnant women and the environment in general. For example, one red colour paint was observed to have as high as 17000 ppm lead content (Figure 12). Furthermore, the results showed that there is variation in lead levels in paint from different brands of different companies. The results also indicated a variation in lead content from brands manufactured by the same company (Figure 13), for example, Medal and Rainbow are both manufactured by Rainbow Paints, however Rainball paints showed very high lead content as higher as six times than medal .On average Dulux paints showed the lowest lead content of 63 ppm while the highest concentration was obtained in Rainbow paints with an average lead content of 7086 ppm. These findings of a high level of lead concentration in coloured paints indicate that lead pigments may be the source as it may be intentionally added to the paint during manufacturing, contravening the Malawi Bureau of Standards (MBS, 2020). Lead compounds are traditionally used as pigments for paints such as white lead [$2PbCO_3.Pb(OH)_2$], lead sulphate [$2PbSO_4.PbO$], red and orange lead [Pb_3O4] and lead chromes [e.g., PbCrO4 and PbO.PbCO4]. Since the study included all the main and popular brands in Malawi, these results are somewhat representative of solvent-based paints available on the market in Malawi as of December 2020.

The findings of this study correlate with those reported by Utembe (2016) in which he found out that 56 % of the paint samples analyzed in Blantyre city in Malawi contained

lead content above 90 ppm while 37.5% were above 600 ppm. Utembe (2016) also found out that children around Blantyre city had an average blood lead level (BPb) of 6.9 ± 5.3 μg/dl, with 71.7% of the children having BPb ≥ 5 μg/dL and 22.8% of children showing a BPb ≥ 10 μg/dl. The authors concluded that apart from food as number one cause of children exposure to lead, the paint sold in Blantyre city was highly believed to be one of the causes of children lead exposure in the city of Blantyre. In addition, our results are comparable to those reported elsewhere. The United Nations Environmental Protection (UNEP) (UNEP 2016) reported similar results of high lead content in a study conducted in Argentina, Azerbaijan, Cote d'Ivoire, Ethiopia, Ghana, Kyrgyzstan, Chile, Uruguay, and Tunisia. In this UNEP report, seven countries showed high lead concentrations greater than 10,000 ppm (UNEP 2016). Further, a significant variation by brand was noted in a study in Ethiopia, in which one of the six brand labels sampled showed lead content > 90 ppm. In contrast, other brand levels contained lead levels of > 5000 ppm (Megertu and Bayissa 2020). Similarly, in a separate study carried out in 2017 by the International POPs Elimination Network (IPEN) in Africa, 55 % of 593 analysed samples for solvent-based paints showed a lead content above 90 ppm (IPEN 2017c, 2017a). High lead content in paint was also reported in China in 2009, in which 29 of 58 (50%) new solvent-based paints tested for lead content exceeded recommended levels of 600 ppm for total lead content in new paint (IPEN 2017c, 2017a). Adebamowo *et al*., (2007) and Ahamefuna *et al*., (2014) reported similar results of high lead content in paint in Nigeria. A study in India also revealed that 72% of paint analysed showed an elevated lead concentration in solvent-based paints above 1000 ppm (Clark *et al* . 2009). Similar results of high lead content in paints have also been reported in Kenya, Ethiopia, Uganda, Mozambique, Ghana, Tanzania, and Zambia (IPEN 2017; IPEN 2017c; Megertu and Bayissa 2020; UNEP 2018; WHO 2016). Analysis of lead content in different coloured paint from other countries in Africa and Asia registered the highest lead level in yellow paints, followed by red, green, blue, and white colours (Clark *et al*., 2006, 2009). The study noted 57% of lead in red paint and 55% in red paint with values above 10,000 ppm (Clark *et al*., 2009). A similar study conducted in Paraguay, Brazil, Russia, Kazakhstan, and Egypt showed a variation pattern in the lead content in different colours (Adebamowo *et al*., 2007). In another study,

conducted in Tunisia, the green and yellow paints were found to have the highest average lead concentrations of 7500 ppm and 47,860 ppm, respectively (UNEP 2016).

Table 2 compares the present study and other studies carried out elsewhere in Africa to examine the level of lead content. It is seen from Table 2 that most African countries, just like Malawi, in which the solvent-based paints, used for household contained high lead levels beyond the internationally recommended limit of 90 ppm. The lowest percentage of lead in paint samples above 90 ppm was detected in paints from Mozambique, while the highest percentage of 70 % was observed in paints from Tunisia.

Table 2 Comparison of lead content in paints in other African countries.

Country	**Number of samples**	**% >90ppm**	**% >600ppm**	**%>10000ppm**	**Year of the study**	**Reference**
Mozambique	32	25	25	12	2017	(IPEN 2017a)
Zambia	39	36	33	18	2017	(IPEN 2017)
Tanzania	46	46	37	22	2017	(IPEN 2017)
Uganda	30	67	57	37	2017	(IPEN 2018)
Kenya	51	69	55	33	2017	(IPEN 2017b)
Ivory Coast	43	63	59	27	2017	(IPEN 2017)
Gambia	39	62	59	41	2017	(IPEN 2017b)
Tunisia	30	70	63	27	2013	(UNEP 2013)
Morocco	28	39	39	18	2017	(IPEN 2017a)
Ghana	18	33	28	17	2013	(IPEN 2017a)
Guinea	18	28	not available	0	2017	(IPEN 2017a)
Egypt	20	65	65	Not available	2006	(IPEN 2017)
Malawi	23	57	52	9	2020	**(This study)**

4.2.2 Caution information on the can labels

It was noted that only 11 out of 23 paints (47.8 per cent of solvent-based paints) provided information about lead on can labels, and most of the paints analysed carried little information about ingredients. Five recorded more than 90 ppm lead in the eleven samples; one paint even contained as high as 17,000 ppm lead. Coral, Rainbow, Dulux, and Medal provided information on their cans. Coral had a can label that read ‘paint in the ventilated environment’ while Medal and Rainbow’s had can labels read ‘keep out of reach of children’. Dulux Malawi's can label read, ‘This paint is toxic’. At the same time, Dulux South Africa showed a can label that read ‘contains no added lead’, which upon analysis showed a lead content below 60 ppm, a development that seemed to agree with the information on the label. None of the analysed samples carried any sign on the product label that the product is “lead-free”. Most paints carried only the brand names with no further details with on the type of solvents or pigments (organic or inorganic) provided by manufacturers. Six paint-card labels showed warning symbols “keep out of reach of children”, but no precautionary warnings on the effects of lead on children were provided (Table 2). However, all other brand labels had no warning symbols on the paint cans to indicate the flammability of the paints and precautionary warnings on the effects of lead dust on humans, especially children and pregnant women, contrary to WHO guidelines (WHO 2019). Nineteen of the twenty-three paints analysed (83%) contained a manufacturing date or batch number, while four had no batch number or manufacturing date. Similar results were reported in Uganda by IPEN, where only three out of fifty-one paints (6%) provided information about lead on can labels, and most paints had little information about ingredients (IPEN 2017), whereby some manufacturers claimed lead-free on the can labels, and the contrary was observed after analysis with very high lead content seen in the paint.

4.3. Heavy metal concentration in Mudi River water and sediments

4.3.1. Physical parameters

Some physical parameters of water and sediments, such as temperature, pH, and electrical conductivity (EC) were measured during both dry and wet season at all the sampling points. The results are presented in figure 14, 15, 16, 17 and 18 respectively.

4.3.1.1 Temperature

For water samples, the surface water temperature was higher during dry season than the values recorded during wet season (figure 17). On average during dry season temperature of surface water was 25.9 ^{0}c while average temperature for wet season was 20.08 ^{o}c. Temperature is essential in controlling vital process such as metabolic rate and reproductive system, hence drastic change in temperature might affect such process in the aquatic system.

4.3.1.2 EC

Electrical conductive of water is a functional of the concentration of dissolved ions. Though conductivity is not of health concern however it can be used as an indicator of other water quality product. This study showed high values of electro conductivity during dry season than wet season. An average electro conductivity values of surface water during dry and wet season was 264.8μS/cm and 200μS/cm respectively (figure 18). Generally evaporation rate is higher in dry season which increases ions concentration and hence increase EC while during wet season there is dilution of ions due to rainwater infiltration and can increase water volumes resulting in a decrease in EC. Similarly in sediments, high EC values were obtained during dry season than wet season with an average value of 661μS/cm (figure 15) during dry season. The average EC value during wet season was 103.3μS/cm (figure 15). In general, Mudi River sediments showed high values of EC than water during both seasons.

4.3.1.3 pH

The pH indicates hydrogen concentration in the water which is affected by dissolved gases and salts. pH values of the surface water during dry season was 5.1 and it increased during

the wet season with an average value of 7.4 (figure 16) this indicates that the surface water of Mudi River were acidic during dry season and become basic during the wet season. Mudi River sediments were acidic during the dry season with an average pH value of 6.23 (figure 14) and they were slightly basic during the wet season with an average pH value of 7.5 (figure 14). In general, the results showed that there was no variation in pH in both water and sediment samples during both seasons.

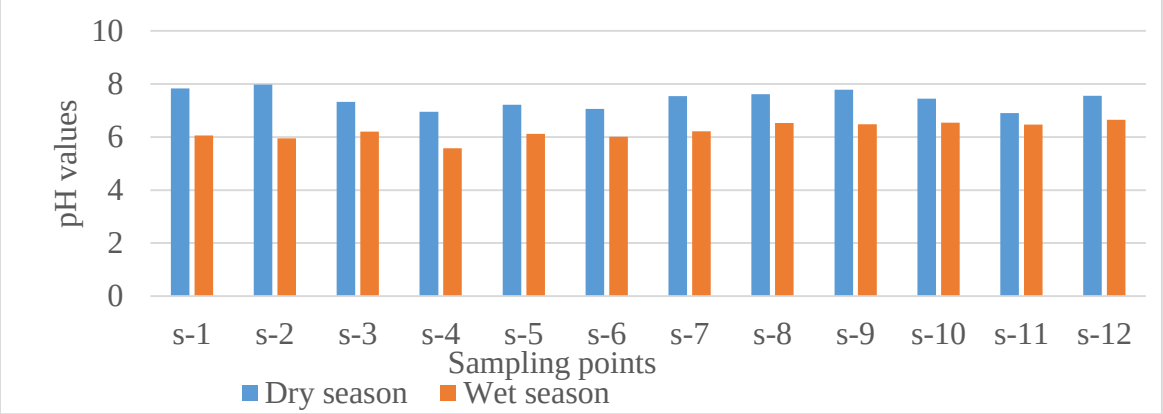

Figure 14 pH values of Mudi River sediments during dry and wet season

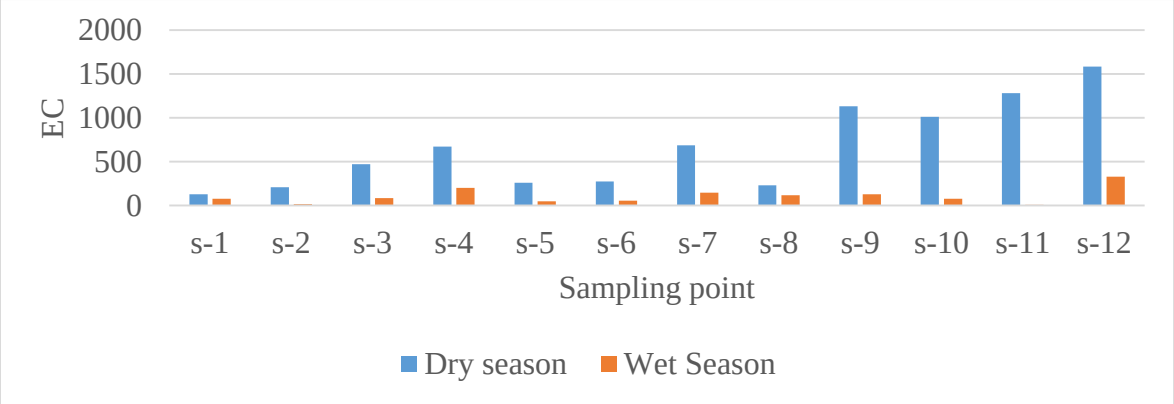

Figure 15 EC values of Mudi River sediments during dry and wet season

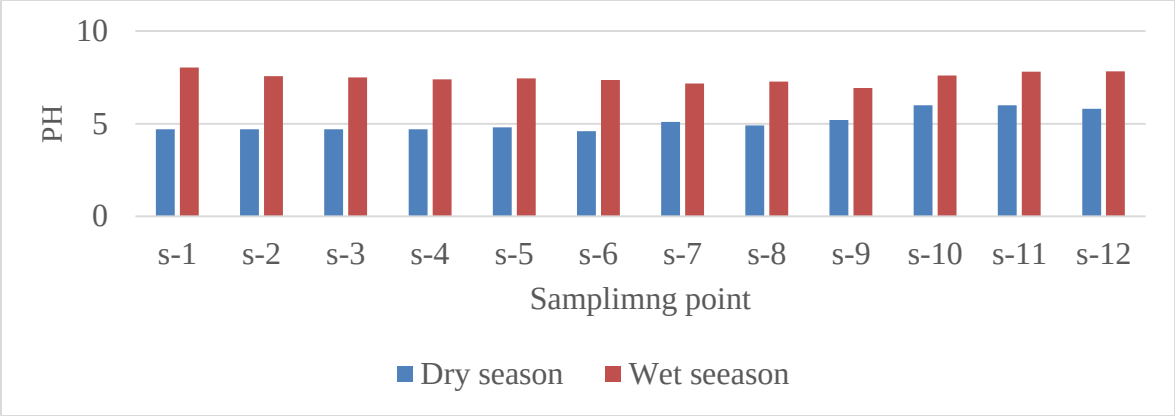

Figure 16 pH values of Surface water in Mudi River during both dry and wet season.

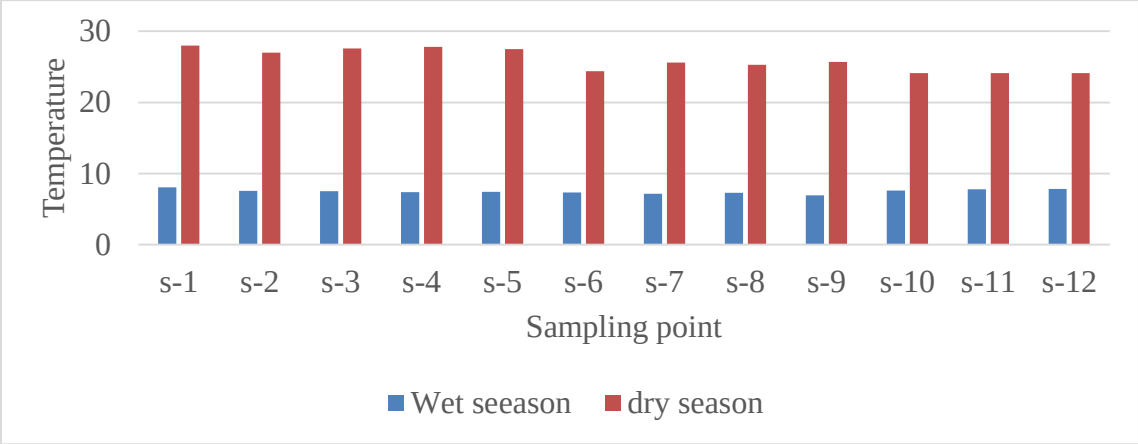

Figure 17 Temperature values of surface water in Mudi River during dry and wet season.

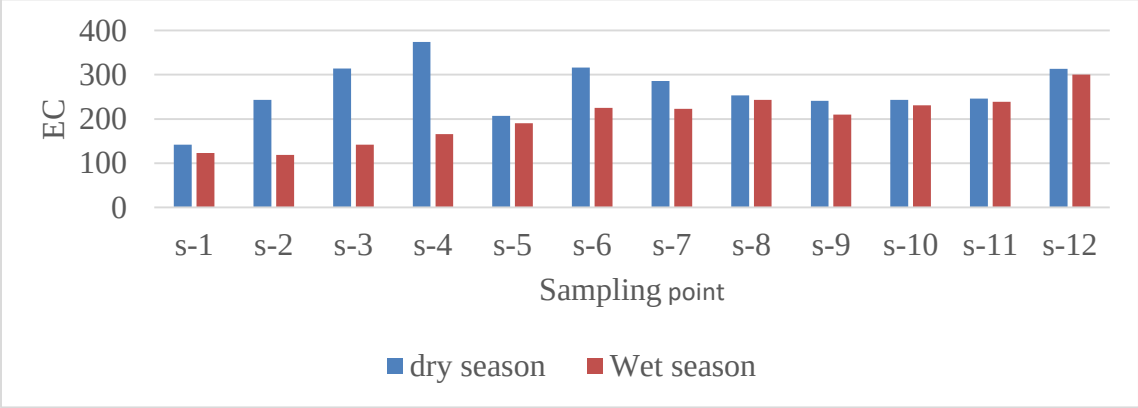

Figure 18 EC values of surface water in Mudi River during both dry and wet season.

4.4 Heavy Metal Concentration in Mudi River Surface Water

The results of the toxic metal concentrations in the surface waters of Mudi River are presented in Table 13 and 14. On average the concentration of all the studied heavy metals were below WHO and USEP legal limits of heavy metals in surface water during both dry and wet season. Notably the concentration of all the studied heavy metals during wet season was below detected limit. During dry season, the concentration of Fe in water ranged from ND (<0.006) -14 mg/L with an average of 2.08 mg/L. Zn showed concentration ranged from 0.007- 0.55 mg/l with a mean value of 0.108mg/l. Concentration of Cu ranged from ND (<0.003) - 006mg/l, with mean concentration of 0.015 mg/l. The Pb concentration in the water ranged from ND (<0.001) -0.015 mg/l with an average concentration of 0.011mg/l. Concentration of Cd ranged from ND (<0.002) - 0.006 mg/l with a mean concentration of 0.005mg/l. The concentration of Cr was below the detection limit (<0.006) at all sampling points. Average concentration of heavy metals in the surface water of Mudi river during dry season was in the decreasing order of Fe >Zn > Cu> Pb>Cd >Cr.

During dry season Fe showed the highest concentration among all the metals at all the sampling points, with the maximum and minimum concentration of 14mg/l at S-6 and ND (< 0.006mg/l) at S-5 respectively. Concentration of Fe at S-2, S-3, S-4, S-7, S-8, S-10 and S-12 were; 0.5815, 0.698, 0.6995, 4.071, 2.709, 0.804, 0.5845 mg/l respectively. Concentration of Fe at S-1, S-9 and S-11 were; 0.195 mg/l, 0.01 mg/l and 0.045 mg/l respectively.

The highest concentration of Zn was 0.55 mg/l at S-6 while the lowest was 0.007 mg/l at S-5. Zn content at S-1, S-2, S-3, S-4, S-7, S-8, S-9, S-10, S-11 and S-12 were as follows; 0.05115, 0.03645, 0.0265, 0.01985, 0.24075, 0.15045, 0.00885, 0.1096, 0.01835, 0.0716 mg/l respectively. These figures are below the MBS standards (3.0-5.0 mg/l) for total Zn content in surface water.

Concentration of Cu at all the sampling points were below MBS (0.5 – 1.0 mg/l), WHO (2 mg/l) and USEPA (1.3mg/l) standards for Cu in surface water. The highest concentration was recorded at S-11(0.006). Cu concentration were as follows; 0.0085, 0.0215, 0.006, 0.004, 0.005, 0.063, 0.0285, 0.022, 0.011, and 0.013 mg/l at S-1, S-2, S-3, S-4, S-7, S-8, S-10, and S-12 respectively. Cu values were below detection limit (<0.003 mg/l) at S-9 and

S- 10 respectively.

Pb was only detected at three sampling points (S-5, S-6 and S-7) with total Pb concentration of 0.005, 0.014, 0.015 mg/l respectively. Detection of Pb at these three places may be contributed by the presence of a match's factory close to the sites in which lead additives might have added to matches manufacturing process and find their way into the surface water through several processes such as leaching. At S-1, S-2, S-3, S-4, S-8, S-9, S-10 and S-11, Pb concentration was below detection limit.

Concentration of Cd at S-1 to S-10 was below detection limit. However a concentration above WHO limit (0.003 mg/l) of 0.006 and 0.004mg/l was detected at S-11 and S-12 respectively. The sources of Cd in the last two points may be mainly attributed to metal processing operations, phosphate fertilizers and deposition of metal products around the Blantyre market and surrounding areas These concentration however were within both MBS (0.003-0.005 mg/l) and USEPA (0.003 mg/l) limits of Cd in surface water.

Chromium concentration at all the twelve sampling points (S-1 to S-12) was below detection limit (<0.006) This means that surface water contains very low levels of chromium which could not be detected by the instruments used during the analysis.

The results of the present study were compared to other four similar studies that have been done on the same Mudi River. On average the results of the present study showed that concentration of the most of the studied heavy metals were lower than those reported by other researchers on the same study area. This shows that there is a slight decrease in heavy metal concentration in the waters of Mudi River as of April 2022. Table 15 shows comparison of the present result and those that were reported by Chikabvumbwa *et al*., (2021), Kaonga, (2012), Kumwenda *et al*., (2012) and Sajidu et al., (2007) from the same Mudi River.

Table 3 Concentrations of metals in surface water in mg/L, PH, T, and EC during dry season compared to WHO (2011), USEPA (199), and MBS (2008) recommendations for drinking water

Sampling Points	Zn	Cr	Cd	Pb	Cu	Fe	PH	T	EC
S-1	<0.001	<0.006	<0.002	<0.001	<0.003	<0.006	8	19.6	123
S-2	<0.001	<0.006	<0.002	<0.001	<0.003	<0.006	7.5	19	119
S-3	<0.001	<0.006	<0.002	<0.001	<0.003	<0.006	7.4	18.5	142
S-4	<0.001	<0.006	<0.002	<0.001	<0.003	<0.006	7.4	20.5	166
S-5	<0.001	<0.006	<0.002	<0.001	<0.003	<0.006	7.2	20	190
S-6	<0.001	<0.006	<0.002	<0.001	<0.003	<0.006	7.3	20.5	225
S-7	<0.001	<0.006	<0.002	<0.001	<0.003	<0.006	7.2	21.5	300
S-8	<0.001	<0.006	<0.002	<0.001	<0.003	<0.006	7.6	21.2	276
S-9	<0.001	<0.006	<0.002	<0.001	<0.003	<0.006	7	21	470
S-10	<0.001	<0.006	<0.002	<0.001	<0.003	<0.006	7.6	22.7	485
S-11	<0.001	<0.006	<0.002	<0.001	<0.003	<0.006	7.8	22.8	486
S-12	<0.001	<0.006	<0.002	<0.001	<0.003	<0.006	7.8	22	478
Mean	-	-	-	-	-	-	7.5	20.8	290
WHO	-	0.05	0.003	0.01	2	-	6.5–8.5	-	700-1500
USEPA	-	0.10	0.005	0.015	1.3	-	-	-	-
MBS	3-5.0	0.005-0.010	0.003-0.005	0.01-0.05	0.5-1.0	0.01-0.02	5-9.5	-	-

S = Sampling point, WHO = World Health Organization, USEPA= United states Environmental Protection agency, MBS = Malawi burial standards.

Table 4 Concentrations of metals in surface water in mg/L, PH, T, and EC during dry season compared to WHO (2011), USEPA (199), and MBS (2008) recommendations for drinking water

Sampling Points	Zn	Cr	Cd	Pb	Cu	Fe	PH	T	EC
S-1	0.05115	<0.006	<0.002	<0.001	0.0085	0.1955	4.7	28	142
S-2	0.03645	<0.006	<0.002	<0.001	0.0215	0.5815	4.7	27	243
S-3	0.065	<0.006	<0.002	<0.001	0.006	0.698	4.7	27.6	314
S-4	0.01985	<0.006	<0.002	<0.001	0.004	0.6995	4.7	27.8	374
S-5	0.00745	<0.006	<0.002	0.005	0.005	<0.006	4.8	27.5	207
S-6	0.5594	<0.006	<0.002	0.014	0.063	14.568	4.6	24.4	316
S-7	0.24075	<0.006	<0.002	0.015	0.0285	4.071	5.1	25.6	286
S-8	0.15045	<0.006	<0.002	<0.001	0.022	2.709	4.9	25.3	253
S-9	0.00885	<0.006	<0.002	<0.001	<0.003	0.01	5.2	25.7	241
S-10	0.1096	<0.006	<0.002	<0.001	0.011	0.804	6	24.1	243
S-11	0.01835	<0.006	0.006	<0.001	<0.003	0.0455	6	24.1	246
S-12	0.0716	<0.006	0.004	<0.001	0.013	0.5845	5.8	24.1	313
Mean	0.1083	-	0.005	0.011	0.015	2.08	5.1	25.9	265
WHO	-	0.05	0.003	0.01	2	-	6.5–8.5	-	700-1500
USEPA	-	0.10	0.005	0.015	1.3	-	-	-	-
MBS	3-5.0	0.005-0.010	0.003-0.005	0.01-0.05	0.5-1.0	0.01-0.02	5-9.5	-	-

Table 5 Comparison of the present results with other study from the same area (Mudi River) on heavy metal concentration of surface water in mg/L.

Reference	Parameter								
	Zn	Cr	Cd	Pb	Cu	Fe	pH	EC	T
Present study D	0.108	ND	0.005	0.011	0.015	2.08	5.1	264.83	25.9
W	ND	ND	ND	ND	ND	ND	7.4	200	20.08
(Sajidu *et al*., 2007)	0.24	0.064	0.032	0.027	0.017	4.923	7	-	-
(Kumwenda *et al*., 2012)	0.12	0.22	0.01	0.56	0.07	-	7.46	389.49	24.11
(Chikabvumbwa *et al*., 2021)	0.149	0.133	-	0.63	0.086	-	-	350.3	25.63
(Kaonga , 2012**)**	0.010	0.39	0.048	0.085	0.025	-	7.38	-	-

D = dry season, W = wet season

4.5. Heavy metal concentration of Mudi River sediments

The total metal concentration in sediments of the Mudi River during dry and wet season are presented in Table 6 and 7 respectively. Generally the concentration of all the studied heavy metals during both dry and wet season were below the USEPA and EU standard limits of heavy mental in sediments. However the metals showed high concentration during dry than wet season. The variation in metal concentration might have been as a result of dilution during the wet season. During the dry season the concentrations of the studied heavy metals were in the following range: Fe = 215.2 – 419.2 mg/l, Zn = 1-9.54 mg/l, Pb = 1.57-2.92 mg/l, Cu = 0.46 – 2.07 mg/l and Cr = 0.34 to 1.64 mg/l. On average, Fe showed the highest concentration of 330.67 mg/kg, followed by Zn with 2.34mg/kg, while Cd had

the lowest value of 0.1mg/kg. Average concentrations of Pb, Cu, and Cr were 2.23, 1, and 0.7 mg/kg, respectively. The highest concentration of all metal were observed at S-12 and this may be due to several human activities that happens within the area as it is a market place leading to disposal of waste into the river, which might have accumulated in the sediments.

The highest and lowest concentrations of Fe were 419.2 at S-12 and 215.2 at S-3. Concentration of Fe at S-1, S-2, S-4, S-5 S-6, S-7, S-8, S-9, S-10 and S-11 were; 324.73, 391.02, 363.19, 427.08, 308.78, 389.35, 326.78, 228.33, 258.85, 315.48 mg/kg respectively. The Fe values obtained in this study were all below the USEPA, EU and Canada international guidelines of sediments, hence posing no real risk to humans. However Fe had the highest value among all the metals at all the sampling stations suggesting the natural abundance of Fe as it is the most common element on the earth crust and it comes mostly from the geochemical rock structured within the earth.

The maximum and minimum concentrations of Zn were observed at S-12 (9.54 mg/kg) and S-4 (1 mg/kg) respectively. Concentration of Zn at S-1, S-2, S-3, S-5 S-6, S-7, S-8, S-9, S-10 and S-11 were; 1.501, 1.096, 0.738, 1.953, 1.283, 3.514, 1.044, 2.409, 1.952, 2.519, 9.5 mg/kg respectively. High concentration of zinc at S-12 may be attributed to activities at Brantley market such as poor waste disposal which might have led to high zinc level at the location.

Lead had the highest and lowest concentration of 2.92 at S-12 and 1.57 at S-3 mg/kg respectively. Concentration of Pb at S-1, S-2, S-4, S-5 S-6, S-7, S-8, S-9, S-10 and S-11 were; 1.728, 2.01, 2.252, 2.405, 2.007, 2.41, 2.313, 2.301, 2.622 and 2.313 mg/kg respectively. Pb in the sediments might have originated from industrial area around the river especially the leopard matches company which manufactured leopard matches in which Pb additives are added.

Maximum and minimum concentrations of Cu were 2.07 at S-12 and 0.46 at S-3 mg/kg respectively. Concentration of Cu at S-1, S-2, S-4, S-5 S-6, S-7, S-8, S-9, S-10 and S-11

were; 0.505, 0.776, 0.697, 0.941, 0.617, 1.475, 0.557, 0.886, 1.861 and 1.342 mg/kg respectively.

The highest and lowest concentrations of Cr were 1.64 at S-12 and 0.34 at S-1. Concentration of Cr at S-2, S-3, S-4, S-5 S-6, S-7, S-8, S-9, S-10 and S-11 were; 0.819, 0.368, 0.548, 0.647, 0.713, 0.964, 0.522, 0.706, 0.584 and 0.631 mg/kg respectively.

Maximum and minimum concentrations of Cd were 0.159 at S-12 and 0.097 at S-3 mg/kg respectively. Concentration of Cd at S-2, S-4, S-4, S-5 S-6, S-7, S-8, S-9, S-10 and S-11 were; 0.109, 0.121, 0.132, 0.154, 0.128, 0.126, 0.121, 0.123, 0.13 and 0.122 mg/kg respectively.

During wet season the concentration of the studied heavy metals were in the following ranges; Fe = 1.83-108.61, Zn = 0.29-1.54 mg/kg, Cu = 0.044- 0.143mg/kg, Pb = ND (<0.001) - 0.23 mg/kg, Cd and Cr had their concentration below detected limit. On average Fe had the highest concentration of 28mg/g, followed by Zn with 0.318 mg/kg while Pb and Cu had an average concentration of 0.097 mg/kg and 0.030 respectively.

Maximum and minimum values of Fe during wet season were 108.61 at S-1 and 1.83 at S-10 respectively. Concentration of Fe at S-2, S-3, S-4, S-5, S-6, S-7, S-8, S-9, S-11 and S-12 were; 45.82, 29.68, 39.51, 6.11, 6.59, 19.12, 4.54, 2.67, 24.58 and 14.44 mg/kg respectively.

Zn showed maximum concentration at S-11 of 1.54 mg/kg while the lowest value was obtained at S-3 (0.295 mg/kg). Concentration of Zn at S-1, S-2, S-4, S-5, S-6, S-7, S-8, S-9, S-10 and S-12 were; 0.78, 0.34, 0.36, 0.52, 0.50, 0.69, 0.43, 0.62, 0.69, 0.43, 0.62, 0.48 and 0.43 mg/kg respectively.

The highest and lowest values of Pb were 0.239 (S-12). Pb concentration at S-9, S-10 and S-12 were 0.661, 0.0079 and 0.043 mg/kg respectively. Concentration of Pb at S-1, S-2, S-4, S-5, S-6, S-7 and S-8, were below detecting limit.

Results from this study are lower than those revealed by other scholars in Malawi especially in soil samples. For example, a study by Braun (2015) on agricultural soils close to a dumpsite and wastewater treatment facility in Zomba City, Malawi found high content

of heavy metals ranging from 4-11 mg/kg dw Cd, 5 69 mg/kg dw Cu, 14693-17592 mg/kg dw Fe and 183 to 231 mg/kg dw Pb. Similar high concentration of heavy metals were also reported in the same city of Zomba, Malawi in a study by Orvestedt (2015) in soils around the city in the following ranges,14700 to 17600 mg/kg dw Fe,130 to 210 mg/kg dw Zn, 4-10 mg/kg dw Cd, 5 to 69 mg/kg dw Cu (Kaonga *et al*., 2017). Furthermore, high levels of heavy metals than those found in the present study were revealed by Kaonga and Monjerezi (2012) in a study of river bank soils along streams that pass through industrial areas in Blantyre, Malawi, where maximum concentrations of heavy metals were reported as; 0.18, 8.19, 10.13, 82.82, 3.49, 17.45 mg/kg dw for Cd, Cr, Cu, Fe, Pb and Zn respectively.

Table 6 Comparison of the present results with other study from the same area (Mudi River) on heavy metal concentration of surface water in mg/L.

Sampling points	Zn mg/kg	Cr mg/kg	Cd mg/kg	Pb mg/kg	Cu mg/kg	Fe mg/kg
S -1	1.501	0.343	0.109	1.728	0.505	324.73
S -2	1.096	0.819	0.121	2.01	0.776	391.02
S- 3	0.738	0.368	0.097	1.578	0.461	215.24
S -4	1.044	0.548	0.132	2.252	0.697	363.19
S -5	1.953	0.647	0.154	2.405	0.941	427.08
S- 6	1.283	0.713	0.128	2.007	0.617	308.78
S- 7	3.514	0.964	0.126	2.41	1.475	389.35
S -8	1.044	0.522	0.121	2.313	0.557	326.78
S -9	2.409	0.706	0.123	2.301	0.886	228.33
S -10	1.952	0.584	0.132	2.622	1.861	258.85
S -11	2.519	0.631	0.122	2.313	1.342	315.48
S -12	9.542	1.641	0.159	2.925	2.07	419.24
Mean	2.383	0.707	0.127	2.238	1.015	330.67
Std	2.289	0.327	0.016	0.353	0.522	67.7
USEPA	110	26	0.6	31	16	36700
EU	300	-	0.3	300	40	-

Table 7 Heavy metal content (in mg/kg dw) in the sediment of the Mudi river during wet season and comparison with different international guidelines

Sampling points	Zn	Cr	Cd	Cu	Pb	Fe	PH	EC
S-1	0.78115	<0.006	<0.002	0.127	<0.001	108.615	7.83	75
S-2	0.34655	<0.006	<0.002	0.0975	<0.001	45.82	7.97	14
S-3	0.2953	<0.006	<0.002	0.048	<0.001	29.685	7.33	83
S-4	0.3687	<0.006	<0.002	0.0595	<0.001	39.51	6.95	200
S-5	0.52965	<0.006	<0.002	0.054	<0.001	6.115	7.22	48
S-6	0.50895	<0.006	<0.002	0.046	<0.001	6.595	7.06	54
S-7	0.69075	<0.006	<0.002	0.063	<0.001	19.125	7.54	146
S-8	0.4394	<0.006	<0.002	0.0695	<0.001	4.545	7.61	116
S-9	0.65295	<0.006	<0.002	0.0695	0.0061	2.67	7.78	127
S-10	0.487	<0.006	<0.002	0.058	0.00795	1.83	7.45	76
S-11	1.54165	<0.006	<0.002	0.143	0.03455	24.585	6.9	8.2
S-12	0.43375	<0.006	<0.002	0.044	0.2391	14.445	7.55	329
Mean	0.589	-	-	0.07325	0.071925	25.295	7.43	106.34
Std	0.318	-	-	0.030	0.097	28	0.33	85.24
USEPA	110	26	0.6	16	31	36700	-	-
EU	300	-	0.3	40	300	-	-	-

4.6 Comparison of heavy metal concentration in sediments and surface water of Mudi River

To assess the difference in heavy metal contamination between sediments and water, the results of the heavy metal content of sediments were compared to those of water. Table 8 provides a summary of the mean results of sediments and water.

Table 8 Concentration of heavy metals in sediments compared to surface water of Mudi River

		Zn	Cr	Cd	Pb	Cu	Fe
Sediments	D	2.38	0.707	0.12	2.23	1.015	330.67
	W	0.58	ND	ND	0.071	0.073	25
water	D	0.1083	ND	0.005	0.011	0.015	2.01
	W	ND	ND	ND	ND	ND	ND

D = dry season, W = wet season ND = not detected

From the results obtained in Table 8, it is clear that heavy metal concentration was higher in sediments than in water samples, with all the studied heavy metals occurring during both seasons. During the dry season, the average concentration of metals in sediment (mg/kg) /water (mg/l) were as follows: Zn = 2.38/0.108, Cr = 0.707/ND, Cd = 0.1/0.005, Pb = 2.23/0.011, Cu = 1.015/0.015, Fe = 330.67/2.08. During the wet season, the average concentration of metals in sediment (mg/kg) /water (mg/l) were as follows: Zn = 0.58/ND, Cr = ND/ND, Cd = ND/ND, Pb = 0.071/ND, Cu = 0.073/ND, Fe = 25/ND. High values of heavy metals in sediments may be attributed to sediments being sinks for heavy metals, unlike water. Once heavy metals have been released into the environment, they are mainly deposited and accumulate in sediments and soils; hence, they may stay in the sediments longer than in surface water.

4.7 Comparisons of the concentration of metals in the sediments of the Mudi River with different rivers of the world from the literature

The results of the present study, which provide valuable insights into the heavy metal contamination in the Mudi River, were compared with those of other worldwide rivers. This comparison underscores the global relevance of our findings and their potential implications for water pollution management. It was noted that the results from this study

are lower than those reported in Balok river sediment, Pahang, Malaysia, in which the metal contents ranged over the following concentrations: Cd: 0.4 – 1.0 mg/kg, Cr: 23.4 – 59.2 mg/kg and Cu: 10.6 – 41.6 mg/kg (Abdullah *et al*., 2015). In Nigeria, heavy metals in sediments from New Calabar River had the following mean values: Fe, 147.84±90.13; Zn, 5.49±2.01; Cr, 3.42±1.00; Cu, 2.48±1.11; Pb, 2.42±1.09; Cd, 0.089±0.12 and As, 0.006±0.005 mg/Kg (Nwineewii *et al*., 2018). Furthermore, a study conducted in an urban river in the Philippines also found higher levels of heavy metal concentration than those reported in this study (Cesar *et al*., 2018). Moreover, the results from this study were also lower than those reported for the sediments of the Tigris River in Turkey, the Indian River, the Songhua River in China and the Mefou River in Cameroon (Mandeng *et al*., 2019). Additionally, in a study of sediments of Laucala Bay, Suva, Fiji, a higher concentration of heavy metals was also reported than those found in the present study (Pratap *et al*., 2020). Table 9 compares the results of the present study with those of other rivers worldwide.

Table 9 Concentration of metals in sediments of the Mudi River compared with different Rivers of the world from the literature (mg/kg).

River		Zn	Cr	Cd	Pb	Cu	Fe	Reference
Mudi River, Malawi	D	2.38	0.70	0.12	2.23	1.01	330.67	**This study**
	W	0.589	ND	ND	0.071	0.1073	25.29	
New Calabar River, Nigeria		5.49	3.42	0.089	2.42	2.48	147.84	*(*Nwineewii *et al*., 2018)
Weihe River, China		103.4	109.98	-	24.44	52.44		*(*Ahamad *et al*. 2020)
Balok River, Malaysia		152.1	24.21	0.541	30.3	55.7	-	*(*Abdullah *et al*., 2015)
Mangonbangon River, the Philippines		213.7	89.45	-	-	116.36	22006	(Cesar *et al*. 2018)
Abiete River, Cameron		46.66	-	0.128	5.856	24.19	-	(Mandeng *et al*., 2019)
Sitalakhya River Bangladesh,		86.92	28.60	0.04	30.72	35.46	-	(Rahman 2017)

D = dry season, W = wet season, ND = not detected

4.8 Discussion on the assessment of sediment contamination or Quality

4.8.1 Introduction

This study employed a comprehensive range of methods, including pollution indices and ecological indexes, to assess the level of pollution in river sediments. The use of these well-established and widely accepted methods enhances the credibility of our findings and ensures the robustness of our conclusions. The pollution indices used in this study include contamination factors, degree of contamination, enrichment factor, degree of contamination, and geo-accumulation index. Ecological risk assessment and Pearson's correlation were also used to evaluate the level of contamination and source of heavy metals.

4.8.2 Contamination Factor (CF) and degree of contamination (C_d).

The contamination factor and degree of contamination for Mudi River sediments were calculated as Tomlinson et al. propose (1980). Due to the absence of any documented background concentration of metals in the study area, this study applied the geochemical average shale reference values of metals described by Turekian *et al*. (1961). The values used in mg/kg are 0.3 = Cd, 90 = Cr, 50 = Cu, 20 = Pb, 95 = Zn, and 46700 = Fe. Results of the contamination factor and degree of contamination for the dry and wet seasons are presented in Tables 10 and 11, respectively. CF values of all the metals in the sediments of the Mudi River during both dry and wet seasons were less than 1, showing less contamination factor at all selected sites. However, the studied metals showed a higher contamination factor and degree of contamination during the dry than in the wet season. During the dry season, on average, Cd had the highest CF value of 0.42, followed by Pb with 0.11, while Fe had the lowest CF value of 0.007. Average CF values for Zn, Cu, and Cr were 0.025, 0.20 and 0.008, respectively. The maximum CF values of Cd, Pb, Zn, Cu and Cr were detected at S-12 with the following values: 0.53, 0.15, 0.1, 0.041 and 0.018, respectively, while the minimum values of the metals were detected at S-3 with the following values; Cd = 0.32, Pb = 0.08, Zn = 0.008, Cu = 0.009 and Cr = 0.004. On average, during the wet season, Zn had the highest CF value of 0.0062, followed by Cu,

which had a CF value of 0.0015. Fe had a CF value of 0.00049. Maximum CF values of Zn, Cu, Pb and Fe were 0.165 (S-11), 0.0029 (S-11), 0.0012 (S-12) and 0.023 (S-1).

Similarly, all the studied metals showed a low degree of contamination (C_d<6) at all the sampling points along the river during both seasons. During the dry season, the maximum and minimum values of the recorded contamination degree were 0.8 at S-12 and 0.43 at S-3. The C_d values at S-1, S-2, S-4, S-5, S-6, S-7, S-8, S-9, S1-10 and S-11 were 0.48, 0.55, 0.59, 0.69, 0.57, 0.63, 0.55, 0.58, 0.64 and 0.59 respectively. Maximum and minimum C_d values during the wet season were detected at S-11 (0.021) and S-3 (0.0047). The C_d values at S-1, S-2, S-4, S-5, S-6, S-7, S-8, S-9, S1-10 and S-12 were 0.013, 0.0062, 0.0059, 0.0067, 0.0064, 0.0089, 0.0060, 0.0085, 0.0066 and 0.017 respectively.

Table 10 Contamination factors and degree of contamination of Mudi River sediments during dry season.

	Contamination factor (CF)						C_d
Sampling points	Zn	Cr	Cd	Pb	Cu	Fe	
S-1	0.016	0.004	0.362	0.086	0.01	0.007	0.48
S-2	0.012	0.009	0.402	0.1	0.016	0.008	0.55
S-3	0.008	0.004	0.323	0.079	0.009	0.005	0.43
S-4	0.011	0.006	0.438	0.113	0.014	0.008	0.59
S-5	0.021	0.007	0.512	0.12	0.019	0.009	0.69
S-6	0.014	0.008	0.427	0.1	0.012	0.007	0.57
S-7	0.037	0.011	0.42	0.12	0.029	0.008	0.63
S-8	0.011	0.006	0.402	0.116	0.011	0.007	0.55
S-9	0.025	0.008	0.408	0.115	0.018	0.005	0.58
S-10	0.021	0.006	0.44	0.131	0.037	0.006	0.64
S-11	0.027	0.007	0.407	0.116	0.027	0.007	0.59
S-12	0.1	0.018	0.528	0.146	0.041	0.009	0.84
Mean	0.025	0.008	0.422	0.112	0.02	0.007	

Table 11 Contamination factor and degree of contamination of Mudi River sediments during wet season.

Contamination factor							C_d
Sampling point	Zn	Cr	Cd	Cu	Pb	Fe	
S-1	0.0082	-	-	0.0025	-	0.0023	0.0130
S-2	0.0036	-	-	0.002	-	0.00063	0.0062
S-3	0.0031	-	-	0.001	-	0.00063	0.0047
S-4	0.0039	-	-	0.0012	-	0.00084	0.0059
S-5	0.0056	-	-	0.0011	-	0.00013	0.0067
S-6	0.0054	-	-	0.0009	-	0.00014	0.0064
S-7	0.0073	-	-	0.0013	-	0.00041	0.0089
S-8	0.0046	-	-	0.0014	-	0.000009	0.0060
S-9	0.0069	-	-	0.0014	0.0003	0.000005	0.0085
S-10	0.0051	-	-	0.0012	0.0004	0.000003	0.0066
S-11	0.0162	-	-	0.0029	0.0017	0.00052	0.021
S-12	0.0046	-	-	0.0009	0.012	0.00030	0.017
Mean	0.0062	-	-	0.0015	0.0012	0.00049	0.0015

4.8.3 Enrichment factor (EF)

EF is usually used to discriminate between natural and anthropogenic sources of heavy metals. In this study, Fe was used as a normalisation element. Geochemical average shale reference values of metals described by Turekian *et al*. (1961) were used as reference values. The calculated EF values of the present study are given in Table 12 for the dry season and 13 for the wet season. During the dry season, river sediments were highly enriched with Cd, severely enriched with Pb, moderately enriched with Zn, and minorly enriched with Cu and Cr. On the other hand, during the wet season, the sediments were severely enriched with Zn, moderately severely enriched with Cu and moderately enriched with Pb.

During the dry season, Cd was extremely severely enriched at all the sampling points, except S-2, where it was very severely enriched. The Cd maximum EF value was noted at S-9 (83.52), and the lowest was at S-2 (47.95).

Pb was severely enriched at all sampling points. The maximum and minimum EF values of Pb observed were 23 at S-10 and 12 at S-2.

The results show that Zn was severely enriched at S-12, moderately enriched at S-7, S-9, S-10 and S-11 and was minor enriched at S-1, S-6 and S-8. The maximum and minimum EF values were 11.38 (S-12) and 1.40 (S-2) respectively.

There was minor enrichment with Cu at S1-, S-6 and S-8. Moderate enrichment with Cu was noted at S-7, S-9, S-11 and S-12. However, Cu was moderately to severely enriched at S-12. Cu's maximum and minimum EF values were 6.71 at S-10 and 1.45 at S-1, respectively.

Cr was severely enriched at S-12. Minor enrichment with Cr was noted at S-1 to S-6 and S-8 while moderate enrichment with Cr was observed at S-7, S-9, S-11 and S-12 respectively

During the wet season, Zn was highly enriched at S-9 and S-10 and severely enriched at S-5, S-6, S-8 and S-11. It was severely enriched at S-7, S-10 and S-12. However, Zn was moderately enriched at S-1, S-2, S-3 and S-4. Zn's maximum and minimum EF values were 131.1(S-10) and 3.54 (S-1), respectively.

During the wet season, the river sediments were highly enriched with Cu at S-6, very severely enriched at S-10 and severely enriched at S-8 and S-9.

The sediments were moderately severely enriched with Cu at S-5 and S-11. However, it was moderately enriched at S-1, S-4, S-7, and S-12. The highest EF value of Cu was detected at S-6 (72.12), while the lowest was detected at S-1 (1.093).

During the wet season, Pb was severely enriched at S-12, severely enriched at S-10, moderate-severe enriched at S-9, and moderately enriched at S-11.

Table 12 Enrichment of Mudi River sediments at different sampling points during dry season.

	Enrichment factor				
Sampling Point	Zn	Cr	Cd	Pb	Cu
S-1	2.31	0.55	52.01	12.42	1.45
S-2	1.402	1.09	47.97	12	1.85
S-3	1.715	0.89	70.15	17.11	2
S-4	1.438	0.78	56.36	14.48	1.79
S-5	2.286	0.79	55.95	13.15	2.06
S-6	2.078	1.2	64.53	15.18	1.86
S-7	4.513	1.28	50.38	14.45	3.54
S-8	1.598	0.83	57.4	16.52	1.59
S-9	5.275	1.6	83.52	23.53	3.62
S-10	3.771	1.17	79.38	23.65	6.71
S-11	3.993	1.04	60.2	17.12	3.97
S-12	11.38	2.03	58.85	16.29	4.61
Mean	3.48	1.1	61.39	16.32	2.92

The table 13 shows the enrichment factor of Mudi River sediments at different sampling points during the wet season.

Enrichment factor					
Sampling point	Zn	Cr	Cd	Cu	Pb
S-1	3.543	-	-	1.093	-
S-2	3.726	-	-	1.989	-
S-3	4.9	-	-	1.511	-
S-4	4.597	-	-	1.407	-
S-5	42.67	-	-	8.253	-
S-6	38.02	-	-	72.12	-
S-7	17.79	-	-	3.079	-
S-8	47.62	-	-	14.29	-
S-9	120.5	-	-	24.33	5.313
S-10	131.1	-	-	29.62	10.1
S-11	30.89	-	-	5.436	3.268
S-12	14.79	-	-	1.626	38.49
Mean	38.34	-	-	13.72	4.76

4.8.4 Geo-accumulation index (I_{geo}).

The geo-accumulation index was used to explain the quality of sediments. Igeo values for dry and wet seasons are represented in Tables 14 and 15. During the dry season, all Igeo values of the studied metals in Mudi River sediments fell between 0-1, indicating that the Mudi River sediments were uncontaminated to moderately contaminated with Zn, Cr, Cd, Pb and Fe. On average, Cd showed the highest Igeo value of 0.084, while Fe had the lowest I*geo* value of 0.0014. On average, Igeo values for the wet season showed that the river sediments were uncontaminated to moderately contaminated with Fe, Cu and Pb.

During the dry season, Igeo values varied from 0.02 - 0.002 for Zn, 0.0078- 0.0008 for Cr, 0.106 - 0.065 for Cd, 0.029 -0.016 for Pb, 0.0083- 0.0018 for Cu, and 0.0018 - 0.0009 for Fe (Table 14).

Igeo values for the wet season ranged from 0.0016-0.0006 for Zn, 0.0006-0.0002 for Cu, 0.00239-ND for Pb, and 0.00047-ND for Fe. Cr and Cd had values below the detecting limit; hence, their Igeo values were not calculated.

Table 14 Geo-accumulation index (Igeo) at different sampling stations during dry season in the Mudi River during dry season

	Geo-accumulation index					
Sampling points	Zn	Cr	Cd	Pb	Cu	Fe
S-1	0.003	0.0008	0.073	0.017	0.002	0.0014
S-2	0.002	0.0018	0.081	0.02	0.0031	0.0017
S-3	0.002	0.0008	0.065	0.016	0.0018	0.0009
S-4	0.002	0.0012	0.088	0.023	0.0028	0.0016
S-5	0.004	0.0014	0.103	0.024	0.0038	0.0018
S-6	0.003	0.0016	0.084	0.02	0.0025	0.0013
S-7	0.007	0.0078	0.081	0.024	0.0059	0.0017
S-8	0.002	0.0012	0.081	0.023	0.0022	0.0014
S-9	0.005	0.0016	0.082	0.023	0.0036	0.001
S-10	0.004	0.0013	0.088	0.026	0.0075	0.0011
S-11	0.005	0.0014	0.082	0.023	0.0054	0.0014
S-12	0.02	0.0037	0.106	0.029	0.0083	0.0018
Mean	0.005	0.002	0.084	0.022	0.0041	0.0014

Table 15 Geo-accumulation index at different sampling stations in Mudi River during wet season.

Sampling points	Zn	Cr	Cd	Cu	Pb	Fe
S-1	0.0016	-	-	0.0005	-	0.00047
S-2	0.0007	-	-	0.0004	-	0.0002
S-3	0.0006	-	-	0.0002	-	0.00013
S-4	0.0008		-	0.0002	-	0.00017
S-5	0.0011	-	-	0.0002	-	-
S-6	0.0011	-	-	0.0002	-	-
S-7	0.0015	-	-	0.0003	-	-
S-8	0.0009	-	-	0.0003	-	-
S-9	0.0014	-	-	0.0003	-	-
S-10	0.001	-	-	0.0002	-	-
S-11	0.0032	-	-	0.0006	0.000346	-
S-12	0.0009	-	-	0.0002	0.002391	-
Mean	0.0012	-	-	0.0003	0.00024	0.00011

4.8.5 Ecological risk assessment.

To determine the potential risk of the studied heavy metals, the potential ecological risk index (Er) and IR were calculated for the studied metals as proposed by Hakanson (1980). Geochemical average shale reference values of metals described by Turekian et al., (1961) were used in this study. The ecological risk values for both dry and wet season are presented in table 16 and 17 respectively. Both RI and E_i values for the studied heavy metals at all the sampling points during both dry and wet season were below 150, suggesting that the sediments in the Mudi River posed low ecological risk to the environment. On average RI values were much lower during wet season than dry season at all the sampling points.

Calculated E_i values of studied heavy metals ,during dry season are presented in table 4.16. From the table 4.16, Cd showed the highest E_i values which ranged from 9.7-15.85 while Cr had the lowest E_i values ranged from 0.0076 – 0.036. S-12 was noted to have the maximum IR value of 16.93 while the lowest IR value of 10.16 was observed at S-3. IR value at S-1, S-2, S-4, S-5, S-6, S-7, S-8, S-9, S-10, and S-11 were 11.36, 12.66, 13.81, 16.08, 13.39, 13.41, 12.71, 12.95, 14.08 and 12.95 respectively.

During wet season, Igeo values of the studied heavy metals ranged from 0.003-0.0016 for Zn, 0.0088-0.028 for Cu and ND- 0.05 for Pb. Sampling point (S-12) had the highest RI value of 0.0731 and the lowest RI value was detected at S-3 (0.0127). IR value at S-1, S-2, S-4, S-5, S-6, S-7, S-8, S-9, S-10, and S-11were: 0.033, 0.023, 0.015, 0.016, 0.0146, 0.0199, 0.018, 0.022, 0.018, 0.053, 0.053 respectively.

Table 16 Ecological risk index for selected heavy metals of Mudi River sediments at different sampling points during dry season.

	E_i					RI
Sampling points	Zn	Cr	Cd	Pb	Cu	
S-1	0.016	0.0076	10.85	0.432	0.0505	11.356
S-2	0.012	0.0182	12.05	0.502	0.0776	12.66
S-3	0.008	0.0082	9.7	0.394	0.0461	10.156
S-4	0.011	0.0122	13.15	0.563	0.0697	13.806
S-5	0.021	0.0144	15.35	0.601	0.0941	16.08
S-6	0.014	0.0158	12.8	0.502	0.0617	13.393
S-7	0.037	0.0214	12.6	0.602	0.1475	13.408
S-8	0.011	0.0116	12.05	0.578	0.0557	12.706
S-9	0.025	0.0157	12.25	0.575	0.0886	12.955
S-10	0.021	0.013	13.2	0.655	0.1861	14.075
S-11	0.027	0.014	12.2	0.578	0.1342	12.953
S-12	0.1	0.0365	15.85	0.731	0.207	16.925
Mean	0.025	0.0157	12.67	0.56	0.1015	13.37

Table 17 Ecological risk index for selected heavy metals of Mudi River sediments at different sampling points during wet season.

	E_i					RI
Sampling points	Zn	Cr	Cd	Cu	Pb	
S-1	0.0082	-	-	0.0254	-	0.0336
S-2	0.0036	-	-	0.0195	-	0.0231
S-3	0.0031	-	-	0.0096	-	0.0127
S-4	0.0039	-	-	0.0119	-	0.0158
S-5	0.0056	-	-	0.0108	-	0.0164
S-6	0.0054	-	-	0.0092	-	0.0146
S-7	0.0073	-	-	0.0126	-	0.0199
S-8	0.0046	-	-	0.0139	-	0.0185
S-9	0.0069	-	-	0.0139	0.0015	0.0223
S-10	0.0051	-	-	0.0116	0.002	0.0187
S-11	0.0162	-	-	0.0286	0.0086	0.0535
S-12	0.0046	-	-	0.0088	0.0598	0.0731
Mean	0.0062	-	-	0.0147	0.006	0.0269

4.9 Pearson correlation (r).

The results of Pearson correlation analysis during dry season are presented in Table 18. Pearson correlation (r) values were calculated to hypothesise whether the metals had a common source of origin based on the assumption that two or more components may correlate either, due to a common origin or atmospheric behaviour. The results showed that there was a strong positive correction among all metals except Fe, which correlated with Cd only. The strong positive correlation between these heavy metals indicates common pollutant sources or similarity in geochemical behaviour except for Fe which might have a different source of pollution. Similarly a strong positive correlation was observed between EC and all other metals except Cd. pH correlated only with Cu. This may suggest that metal ions may have caused increased electrical conductivity in the sediments in addition to other factors. Pearson correlation values for wet season were not calculated since some metals were not detected.

Table 18 Pearson's correlation matrix of heavy metals in sediments and related environmental parameters.

	Zn	Cr	Cd	Pb	Cu	Fe	EC	pH
Zn	1							
Cr	0.917**	1						
Cd	0.646*	0.697*	1					
Pb	0.707*	0.715**	0.839**	1				
Cu	0.763**	0.713**	0.623*	0.845**	1			
Fe	0.424	0.548	0.672*	0.428	0.286	1		
EC	0.712**	0.594*	0.398	0.680*	0.785**	-0.080	1	
PH	0.511	0.362	0.178	0.514	0.576*	-0.230	0.583	1

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed)

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1. Chapter overview

This chapter provides the major conclusions of the present study and recommendations for further studies.

5.2. Conclusions

This study was conducted to assess levels of lead in solvent based paint for home use in Malawi, levels of selected heavy metals in Mudi River Water and Sediments and their Environment and Ecological Impacts. This study has demonstrated that solvent-based paint available in Malawi for home use contains a high concentration of lead since the paints sampled for this study are brands commonly sold in retail stores all over Malawi. The lead concentration in solvent-based paint for household use in Malawi ranged from <60 ppm to 17000 ppm with an average content of 2570 ppm. The study reveals that 57% of the samples analysed contained high levels of lead (>90 ppm), 57% of the paint analysed showed a lead content greater than 600 ppm, while 4% of the analysed paint showed a lead content greater than 10000 ppm. The results also shows that lead content in paint varied by brand label and colour. Rainbow paint had the highest average lead concentration of 7086 ppm, while no lead was detected in Plascon and Dulux. Further, the average lead concentrations of Coral, Medal, Monolux, and Nuroc were 1407, 1680, 3520, and 1900 ppm, respectively. The results also show a higher level of lead concentration in colored paint than in white paint. The study shows that the color of the paint was related to the lead content, with the red paint showing the highest mean lead content of 4296.25 ppm while the white paint showed the lowest lead content.

In addition, only 48% of the analysed paint had information on their can labels. Most existing Malawian houses likely contain a very high level of lead, so it is critical from a health perspective that immediate efforts be made to assess the presence of lead in houses. These findings clearly show that solvent-based paints in Malawi contain higher lead levels, thus increasing the risk of lead exposure to children, pregnant women, the human population, and the environment.

Furthermore, the present study has shown that the concentration of the studied heavy metals in both water and sediments samples were below, USEPA, EU and MBS guidelines for heavy metals in surface water and sediments during both dry and wet season. However, the present study shows that the studied metals had high concentration during the dry season than wet season. This might be attributed to dilution factor during the wet season, as a result of heavy rains during the previous rain season. The study further shows that sediments samples had high heavy metal concentration compared to water samples taken at the same sampling points during both seasons. Furthermore, the results of the present study are lower in comparison to other rivers of the world from the literatures. On average, the concentration of heavy metals in the sediments of Mudi River was in the decreasing order of Fe > Zn > Pb> Cu> Cd> Cr. Average concentration of heavy metals in the surface water of Mudi River was in the decreasing order of Fe >Zn > Cu> Pb>Cd >Cr. Both CF and C_d values showed that it was less contaminated at all the selected sites. On average Mudi River sediments were extremely enriched with Cd, severely enriched with Pb, moderately enriched with Zn, and minor enriched with both Cu and Cr. I_{geo} values of the studied metals in Mudi River sediments were between 0-1, indicating that the river was uncontaminated to moderately contaminate with the studied metals during both seasons. Both RI and E_i values for the studied heavy metals at all the sampling points were below 150, suggesting that the sediments in the river posed low ecological risk to the environment. Pearson correlation analysis showed a strong positive correlation among all metals expected for Fe, which suggested that, the metals under the present study originated from a common source of pollution.

5.3. Recommendations

Based on the results from this study; the researcher makes the following recommendations. First, the study serves to highlight the need to monitor quality of paint products manufactured and sold in Malawi and the SADC region in order to protect public health, given the severe harm associated with children's exposure to lead paint. The results provide a strong justification to adopt and enforce regulation that will ban the manufacture, import, distribution, sale and use of solvent-based paint with concentration greater than 90 ppm in Malawi.

Second, there is an urgent need to determine the extent of leaded paints in existing housing stock in Malawi as well as its effects on children's blood lead levels, and to develop intervention programs to reduce the risk of exposure.

Third, serious measures to increase awareness and enforce regulations leading to the total elimination of lead in solvent-based paint need to be employed. Public health groups, consumer organizations and Non-governmental organization (NGO) should support the elimination of lead paint, and conduct awareness campaigns to sensitize and protect children from lead exposure through lead paint, lead in dust and soil, and other sources of lead. The elimination of lead paint now brings future economic benefits in terms of preventing losses as a result of reduced productivity and avoiding the huge health impacts of lead toxicity. Alternatively, non-lead-based ingredients are available that can be used to formulate paint and, of course, paints produced without lead have been in the markets for decades in many countries, more especially in those countries with proper paint laws, legislation and policies

Fourth, the study recommends that more intensive sampling and analysis, including sampling of sediment from different depths, different sections of the river and more special locations should be carried out.

Firth, the study recommend that a different sampling procedure on paint sampling in order to include storage conditions, duration, expire dates of the paints and large sample size of the paint from different brands and colour.

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