MSc Research Project

HEAVY METAL CONTAMINATION AND ITS SPATIAL DISTRIBUTION FROM MINING WASTES IN RECEIVING ENVIRONMENTS OF THE MAZOWE DISTRICT, ZIMBABWE

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DECLARATION

I hereby declare that:

- This research project represents my original work.
- Except as properly attributed through and correct referencing, this research project contains no information that has already been published or authored by a third party.
- I am aware of what plagiarism is, as well as the value of properly and distinctly crediting my sources.
- I have correctly acknowledged all direct quotations and paraphrased content appropriately.
- The work was done under the guidance and supervision of Professor Akpofure Taigbenu and Professor Solomon Newete at the University of the Witwatersrand, Johannesburg.

Signature (Josiah Charema)

27/11/2024

Date

ABSTRACT

The purpose of this study was to investigate heavy metal contamination and its spatial distribution from mining wastes (especially artisanal/informal mining) and the impact of agriculture on heavy metal pollution in receiving environments of the Mazowe district, Zimbabwe. Agriculture and mining have considerably contributed to heavy metal and nutrient concentration into the world's freshwater systems. This study aimed to improve the understanding of the contribution of agriculture and informal mining to heavy metal and nutrients pollution of Mazowe River. Also, the research aimed to establish the contribution of sulphates and phosphorous on heavy metal mobility in agricultural and mining areas. The research was conducted in Mazowe District in Mashonaland Central Province of Zimbabwe. Collection of the samples was carried out at five locations along Mazowe River, from its outlet at Mazowe dam to about 25 km downstream. The samples were preserved using WHO approved preservation methods and transported to a licensed laboratory in Harare for testing and analysis of heavy metals (Hg, Pb, Cr and Cd), extractable sulphates and phosphorus at Zim Labs laboratory, in Harare - Zimbabwe. Heavy metal analysis was done using the flame Atomic Absorption Spectrometer after wet digestion. The results indicated an average concentration of heavy metals in the river sediments ranging from 0.01mg/kg (Hg) to 26.68 mg/kg (Pb) during the wet season. During the dry season the levels of Hg, Pb, Cr and Cd were less than 0.01mg/kg. There were low detectable levels of heavy metals in the water samples for both wet and dry seasons. Significant differences in mean levels of phosphates and extractable sulphate pollutants were observed in the wet and dry season. The average phosphorus levels detected in the sediment samples during the wet season was 14.93mg/kg which was 93.7% higher than that of water samples which was at an average of 0.94 mg/l. The sampling points were small due to budget constraints and limited access to some areas because of property rights' issues and national key points along Mazowe River. Thus, it would imperatively be unjustified to generalise the effects of the research outcome to other locations within Mazowe River Catchment or locations along Mazowe River downstream from the study area, without considering other land use patterns. The results showed that the presence of heavy metals in the sediment samples of Mazowe River could be highly attributed to informal mining along the river while extractable sulphates and phosphorous in both water and sediment samples could be attributed to agricultural activities. These findings may assist the environmental management and mining authorities to regulate the activities of artisanal mining to combat heavy metal contamination of rivers from mining activities.

DEDICATION

First and foremost, I would like to thank God, for giving me the strength and courage that I needed throughout all the challenging moments of completing this research project. I would like to thank my dear wife, Rufaro Charmaine Charema. She is my everything. Without her constant support, guidance, and encouragement I wouldn't have made it this far. I would also like to thank my lovely sons, Jaden Tinaye Charema and Jamian Tamiranashe Charema. They are the reason why I never gave up. I would like to especially thank my mother and my mother-in-law who always made it a point to consistently check up on me. Without the prayers of these two phenomenal women this research project would not have been possible. I cannot thank my in-laws, sisters, and friends enough for their unwavering support. Thank you all, this research project is dedicated to you.

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LIST OF ABBREVIATIONS AND ACRONYMS

As - Arsenic

Cd - Cadmium

Cr - Chromium

Cu - Copper

DTPA - Diethylenetriamine Pentaacetate

Fe - Iron

GDP - Gross Domestic Product

Hg - Mercury

Mn - Manganese

NGO - Non-Governmental Organisation

NDS - National Development Strategy

Ni - Nickel

Pb – Lead

1. INTRODUCTION

Zimbabwe is a mixed economy country that is heavily dependent on both its formal and informal sectors (Castañeda 2018; Pla-Barber et al. 2021). Agriculture and mining are the crucial activities that contribute to the nation's gross domestic product (GDP) (Castañeda 2018). However, despite their meaningful contribution to the economy of the country, their operations take a toll on the environment, especially on water resources. Agricultural activities change the structure of the land significantly through the clearing of vegetation, bringing loose soil to the land surface and use of industrial chemicals (Khatri and Tyagi 2015; Meyer and Turner 1992). These bring about several environmental issues especially when the agricultural activities are done without monitoring and adherence to legislative guidelines. Recent information on farming in Zimbabwe has focused on commercial farming activities and their impact on the socio-economic and environmental issues (Khatri and Tyagi 2015; Torrance et al., 2021). Runoff from mining operations and alluvial gold mining have also played significant roles on river water pollution in Zimbabwe (Nyamangara et al, 2008). There is a lack of focus on the contribution of small scale and informal miners on river pollution in Zimbabwe which is a gap in legislation and research.

The Mazowe River, located in an intensive farming region, has become a recipient of runoff from nearby farms and a significant point of convergence for both the household and industrial effluents from the surrounding areas. There are increasing farm activities and human settlements in and around the area that are largely unplanned and unregulated, and these have contributed to the Mazowe River being one of the most polluted surface water storages in Mashonaland central in Zimbabwe (Nyamangara, 2008). Drainage or wash away water from the farms, pollutants leaking from the septic systems, sewage, leachate from waste dumps and other anthropogenic activities increase the concentrations of organic and inorganic nutrients in the river (Carpenter et al., 1998; Singh and Gupta 2016). The pollution of Mazowe River is of grave concern since it is a known habitat for many different aquatic life forms and a source of fodder for animals (Li 2006; Smith et al., 2003). It is against this background that this study is aimed to assess the contribution of agriculture and mining to heavy metals and nutrients pollution in water and sediment in Mazowe River in Zimbabwe. The study also aims to establish the contribution of phosphorous and sulphates in heavy metal mobility and mineral enrichment of the Mazowe River. Disposal of wastes from sulphate mining operations has been a perennial problem to the environment in many countries, because these wastes produce acid mine drainage (AMD) which increases the toxicity of aquatic ecosystems (Nyamadzawo et al, 2007).

The contamination of Riverian ecosystems is a worldwide environmental concern (Rani et al, 2022). There are some heavy metals such as Fe, Cu, Mn, Zn and Ni which are considered as essential for biotic processes in fauna and flora, but other metals such as Cd, Cr, Hg and Pb are not known to have any physiological activities and they are known to project extreme levels of toxicity even at trace levels (Daoji and Daler 2004; Rahmani and Samarghandi, 2007; Nouri et al., 2009). The biggest contributors of these heavy metals in water are agriculture, geological weathering, and mineralogy (Samarghandi et al., 2007). Despite all these, undertakings such as mining, continued release of untreated waste effluents (which contain heavy metals) into the environment; and metal chelates increase water pollution. Also, the widely uncontrolled use of inorganic fertilizers that contain heavy metals and heavy-metal laden pesticides in the farms, can compound the speed at which heavy metals enter surface water systems such as rivers, dams, ponds, and lakes (Sithole, 2001; Tewari and Kushwaha, 2008).

A great deal of research work has been carried out on the hydrology of Zimbabwe (Chikozho 2014, Mazvimavi, 2010). But the conundrum of extreme heavy metal pollution in rivers (e.g., Mazowe, Save, Runde among others.) is currently increasing based on the Lancet research of 2015 (EMA, 2024). This study assessed the extent of heavy metal pollution in Mazowe River emanating from the nearby farming and mining activities.

1.2 Problem Statement

Informal mining is a significant source of livelihood for many rural people. It provides employment, supports livelihoods of poor rural populations, and contributes to national income, through taxes, export earnings, and provision of raw materials for local industries. Despite the economic gains of artisanal mining, it is known to cause security, safety, and environmental issues such as mercury contamination, land degradation, pollution, and harm to biodiversity (Bansah et al., 2018). It is also reported to cause land disputes and violent confrontations between the artisanal and small-scale miners and large-scale mining firms and/or government security force. Water pollution, from pyrite mines (which are predominant in the study area), is a major international environmental problem that can have a broad array of symptoms. The impacts include modification of pH, elevated salinity, modified stream ionic composition and elevated heavy metals (Wright et al, 2018).

According Reichelt-Brushett et al. (2016) Hg is recognised as a priority hazardous substance due to its high toxicity, mobility, and prolonged residence time, and is identified by the World Health Organisation as a global contaminant which poses a high risk to human health (WHO, 2007). Heavy metals are persistent in the environment and may be dispersed over great distances through atmospheric, oceanic, aquatic, and biotic transport vectors (Reichelt-Brushett et al., 2016). Mazowe district is the breadbasket of Zimbabwe; it is located in the valley along the Iron mask mountain range which has pyrite and nickel mines and successful commercial agriculture. Mazowe district has fertile red medium clay loam soils that produce maize, soyabeans and horticultural produce that provide food to feed millions of Zimbabweans in Harare and other cities. According Reichelt-Brushett et al. (2016), heavy metals in the environment are toxic with high potential to bioconcentrate and biomagnify within the aquatic ecosystems, thereby exposing millions of Zimbabweans who feed on the farm produce from Mazowe farms.

Zimbabwe is a mixed economy country that is heavily dependent on both its formal and informal sectors (Castañeda 2018; Pla-Barber et al., 2021). Agriculture and mining are the crucial activities that contribute to the country's gross domestic product (GDP) (Castañeda 2018). However, despite their meaningful contribution to the economy of the country, their operations take a toll on the environment, especially on water resources. Agricultural activities change the structure of the land significantly through the clearing of vegetation, bringing loose soil to the land surface and use of industrial chemicals (Khatri and Tyagi 2015; Meyer and Turner 1992). These bring about several environmental issues especially when the agricultural activities are done without monitoring. Commercial farming activities in Zimbabwe have received considerable attention in the recent years, and with emerging farmers participating in this commercial venture, it is important to assess their impacts not only on the socio-economic climate but also on the environmental statue of an area (Khatri and Tyagi.; 2015) (Torrance et al., 2021).

This research aims to investigate the effects of mining and farming activities on the water quality of Mazowe River in Mashonaland Central as a case study. The twin scourge of intensive artisanal mining and accelerated semi commercial agricultural activities have an impact on the river water quality. This research will make a comparison between agriculture and mining activities in their varying contributions to pollution of water and sediments with heavy metals, phosphorus and sulphates. This will help shape the government policies in regulating both mining and agriculture to protect the environment. A balance on water quality, water quantity and socioeconomic development should be structured in a scientifically sound manner. This study should be able to demonstrate that balance and inform policy makers on how to ensure sustainable development in this era of water shortages and climate change.

Conducting research on heavy metal pollution of rivers by mining and agriculture will complement efforts to ensure environmental and food safety in urban and rural communities of Africa. This study investigates the levels of heavy metals and contributions interface from both mining and agricultural in Mazowe Catchment area of Zimbabwe.

1.3 Rationale of the study

It is very crucial that organizations in environmental management and rural development become aware of the impacts of heavy metal accumulation in surface water bodies for environmental sustainability. It is also of much significance that environmental and rural development stakeholders are informed about the associated consequences of gold mining activities on the environment, particularly water, so that measures can be taken to avoid pollution. This knowledge of the potential environmental consequences of unsustainable agriculture and mining activities facilitates making of informed, robust, and prudent decisions that can be incorporated into policy blueprints such as the National Development Strategy (NDS 1). If the study is approved and accepted by the relevant authorities, it shall go a long way in mitigating environmental problems caused by ill-informed economic activities in some parts of Mazowe areas with main reference to the Mazowe River which is under threat to the continuing artisanal gold mining in the area and pollution from agricultural activities. This study will also contribute to the body of academic knowledge and be used for reference purposes and open other avenues for future research.

1.4 Hypothesis

Informal mining is causing significant heavy metal, phosphorous and sulphates pollution of the river water and sediments comparable to agricultural activities which release heavy metals, phosphorous and sulphates into the Mazowe River catchment.

1.5 The Aim of the Research

To investigate the current pollutants loadings and chemistry of water and sediments in the receiving environments downstream of mining and agricultural activities over two seasons in Mazowe District of Mashonaland Central in Zimbabwe.

1.6 Research Objectives

1.6.1 Quantify heavy metals (Hg, Pb, Cr, Cd), sulphates and phosphates in Mazowe River water.

1.6.2 Quantify heavy metals (Hg, Pb, Cr, Cd), sulphates and phosphates in Mazowe Riverbed sediments.

1.6.3 Compare the concentration of heavy metals over two seasons and the seasonal variation in sulphates and phosphates in Mazowe River.

2 LITERATURE REVIEW

2.1 Introduction

River water quality has been negatively impacted due to a number of factors such as urbanization, industrial, agricultural and mining activities in Zimbabwe, and in most developing countries. Runoff from mining and agricultural operations has had significant impacts on river water pollution with heavy metals and nutrients like phosphorous and extractable sulphates. With an increase in informal mining activities, increased agricultural activities to meet high food demand due to population growth, and increased urbanization, environmental issues in the form of heavy metals and nutrients polluting rivers will continue to escalate.

2.2 Heavy Metals Described

There could be several definitions of the term “heavy metal”. Heavy metal is synonymously used for trace metals elements, and it includes both metals that are essential and nonessential with high total atom weight and higher density compared to that of water. In chemistry all matter that can donate an electron and valence ion, can switch places with H ions in acids, can form compounds with nonmetals but cannot form compounds with each other and has alkaline oxides; is defined as a heavy metal (Elbeshti et al., 2018). In physics, all matter that can conduct heat and electricity, can be transformed into metal plate and wire, has a metallic colour and lustre and is solid under normal circumstances except mercury is defined as a heavy metal (Tchounwou et al., 2012). But when it comes to the impacts of heavy metals on organisms, despite the definition, any metal may qualify to be called a heavy metal if it has toxic characteristics to any living organism under any conditions or circumstances (Elbeshti et al, 2018).

Metal availability and distribution in the environment is a result of natural processes (volcanoes, bacterial activity, spring water), and anthropogenic activities (fossil fuel combustion, industrial and agricultural activities) (Florea and Busselberg, 2006). Mining and industrial activities are known major contributors of heavy metal pollution in the environment (Naicker et al., 2003).

Heavy metals in the soil have toxicological impacts on the soil microorganisms, which may lower their population and activities (Khan et al., 2010). Mine rock waste or tailing dams are the main sources of heavy metal contaminants in the environment in South Africa (Witkowski 2006; Naicker et al., 2003; Newete and Byrne, 2016). Heavy metals have negative effects on the health of both humans and animals; hence, special attention is needed on heavy metal contamination of the food chain.

Application of agrochemical products inevitably may lead to heavy metals pollution in agricultural soils (Yang et al, 2024). The leaching and runoff from agricultural areas may wash away the heavy metals and deposit them in river channels.

2.3 Global View on Heavy Metal Pollution

Globally, environmental pollution by heavy metals has become a topical issue, affecting the earth to a greater extent compared to the contribution of agriculture to heavy metal pollution in the environment. Heavy metals pollution has become a phenomenon which has resulted in adverse impact on the aquatic environment, and this is mainly because of their toxicity and bioaccumulation by aquatic creatures. There are different anthropogenic activities which are associated with aquatic pollution and among them are domestic activities, farming, and mining. The pollution caused by heavy metals has severe effects on different aquatic life forms (Briffa et al, 2020).

The heavy metal pollutants bio accumulates in food chain and cause antagonistic effects and may even result in increased mortality cases in aquatic species (Santosh et al, 2024). Among the animal species, catastrophic effects of these pollutants can never be negligible for fishes. Fish exist in their diverse forms in the surface water bodies. They rely on water for food and survival. It is water and all its provisional services which sustain the growth of fish in dams, rivers, and lakes. Fish in water act as keystone species that, if they are affected, have considerable impacts on the whole food chain system (Pockberger et al, 2014).

Heavy metals form the most dangerous side of chemical water pollution due to their ability to bio accumulate and bio magnify and cannot be eliminated from the body by metabolic activities. Studies carried out in Pakistan by Chatha et al. (2023) examined the toxicological effects of heavy metals in fish and showed that heavy metals cause severe damage to fish; thus, endangering fish health and ecosystem, posing risks for human health through consumption of heavy metal contaminated fish.

2.4 Sources of Heavy Metals

Heavy metals already naturally exist in the earth's crust, soil, water, air or in organic matter in varying concentrations, and they have been over the years widely dispersed because of natural and human activities that include production of cement, processing metals in the iron and steel industry, steam based power plant, production of glass, waste burning or incineration facilities, surface or underground mining activities, metal smelters and foundries, pipe and tubing, internal combustion and automobiles (Rether, 2002; Sönmez, 2012). Natural activities such as dusty winds/ storms, vulcanicity soil erosion, can help with the spreading out and movement of heavy metals in the environment (Karayakar et al., 2017). The rapid growth of agricultural activities to meet human food needs, exponential growth in population, increased urbanization, and massive industrialization; all driving pollution and corresponding risks to higher levels, are critically affecting the environment (Sönmez et al., 2013). There is no doubt that the most dangerous chemical pollution in water is heavy metal contamination (Sönmez et al., 2012). The ability of heavy metals to accumulate in organisms in the food chain and their toxicity constitute a very significant ecological and health concern. Although having the strong ability to influence the stability of ecosystems, heavy metals have negative effects on humans (Bolognesi et al., 1999). Although some heavy metals such as Iron, zinc, copper and cobalt have an essential role in enzymatic activity and other biological processes at trace levels, when they exceed a certain tolerable limit, they become toxic to organisms. However, some other heavy metals that include Cd, Hg and Pb have no known essential role to play in the living organisms and are known to be extremely toxic even at very low concentrations (Bryan, 1976). In the water, heavy metals do not get suspended, but settle down swiftly at the bottom onto the underlying sediments. This is attributed to their higher density which is greater than that of water. A demonstration on the density of Cd and Cu in water was carried out with the results showing 72 to 97% reduction from their original concentrations after a period of 96 hours under an experimental study (Ghosal and Kaviraj, 2002; Ghosh et al., 2016; Ghosh and Maiti., 2018).

2.4.1 **Agriculture and Heavy Metal Pollution**

Heavy metal contamination in agricultural soils affects the surrounding environment widely (Peng and Yu, 2024). The high population growth and the increasing demand for food means more intensive use of agricultural fields. In order to meet the demand, intensive agriculture has seen increased proportion of chemical substances and preparations being used in agriculture, resulting in an increased accumulation of heavy metals (Tomczyk et al, 2023). Excessive use of fertilizers for a long time resulting in heavy metals accumulation in agricultural soils reduces soil fertility, and consequently decreases plant growth and productivity Agricultural non-point source pollution threatens the quality of the ecological environment, human health, and safety (Zhang et al, 2024). Heavy metals from agricultural areas are washed away through runoff and leaching.

2.5 Effects of Heavy Metals on the Ecosystems

Heavy metals are generally toxic and can cause acute damage to tissues which may become lethal for humans and organisms. Localization of a high amount of heavy metal causes its increased toxicity (Briffa et al., 2020). Heavy metals tend to bioaccumulate or biomagnify in the food chain. Bioaccumulation is defined as an elevated concentration of a xenobiotic in an organism over a period of time in a space compared with the background concentration of the same xenobiotic in the environment (Govind and Madhuri, 2014) whereas; the transfer of a xenobiotic in the food chain from a food source to the organism is referred to biomagnification. This transfer of heavy metals from one organism to the other in a food chain results in significantly higher concentrations in the tissues of the organism than the sources (Rand et al., 1995).Even at lower concentrations, many heavy metals and metalloids (chemical elements whose physical and chemical properties fall in between the metal and the non-metal categories) become toxic and can result in undesirable effects and severe problems to the organism (Memon and Schroder, 2009).

Severe contamination of water sources by human activities leads to loss of aquatic life and therefore causing disruption of the food chain balance (Afshan et al., 2014). Some of the aquatic organisms can store heavy metals up to a certain amount. Even though these heavy metals are not harmful or toxic, they can reach humans via the food chain and affect human health (Merlini and Pozzi 1970). As a general rule, toxicity occurs when heavy metal concentrations reach above levels that may damage DNA (Jaishankar et al., 2014; Briffa et al., 2020). Also, heavy metals deposited in water bodies join the food chain from many stages and threaten ecosystem safety, fish, and human health (Jain et al., 2008; Sönmez et al., 2013).

Furthermore, heavy metals can replace essential metals in pigments or enzymes, disrupting their function for both plants and humans (Oehme, 1978; Shah et al., 2001). Regarding toxicity levels, heavy metals of serious concern are Cd, Hg, Zn, Pb, Sn, As, Cu, and Cr (Callender, 2003). Out of these problematic heavy metals, As, Hg, Pb and Cd are non-essential heavy metals, while on the other hand Zn and Cu have essential roles as trace elements. Different health problems arising from toxic heavy metals affects not only people but both flora and fauna. Insects living and breeding in highly polluted areas have been known to accumulate heavy metals when feeding, in particular Ni and Cu (Heliovaara et al., 1987; Zvereva et al., 2003). Heavy metal pollution affects growth rate of insects (Warrington, 1987) and leads to mortality (Mitterbock and Fuhrer, 1988). Some of these insects are part of the food chain in areas of their occurrence and in the case of Zimbabwe can be a good source of proteins. Also, heavy metals pollution can have harmful effects on immune defence system of plants and animals (Van Ooik, 2008).

2.5.1 Cadmium (Cd)

Cadmium is a naturally occurring element in the earth's crust and is usually found as a mineral that is combined with other elements such as oxygen, chlorine, or sulphur (IARC, 1993). Both, the aquatic environment, and the earth's crust contain very significant concentrations of cadmium (Liu et al., 2022). Cadmium is a highly toxic heavy metal that has a detrimental effect on fish and the survival of other aquatic organisms' (Chatha et al.,2023). Cadmium affects the development, and reproduction of fish through accumulation in tissues, particularly the kidneys, liver, and gills, which can result in several physiological and structural issues (Al-Asgah et al., 2015). Fishes are one of the major primary predators in the aquatic ecosystems, making them more susceptible to Cd pollution. The bioaccumulation of Cd in fish tissues may negatively affect their gills, liver, gonads, and other organs, which may eventually affect metabolism, physiology, and reproduction, as well as cause mortality (Liu et al., 2022). In cadmium (Cd) contaminated aquatic environments, fish can experience stress due to the presence of ROS (reactive oxygen species) and RNS (ribonucleic acid enzymes) (Rehman et al., 2022). Fish can take up cadmium through river sediments and in other aquatic species like algae and accumulate them in humans through the food chain (Norani et al., 2023). The accumulated Cd may affect human health in the long run.

2.5.2 Lead (Pb)

Lead (Pb) is known as a toxic heavy metal that is naturally found in the earth's crust, predominantly as sulphide compound (Chatha et al., 2023). Airborne lead (Pb) can be sourced from emissions originating from processing of ores and metals (in dust or smoke), exhaust gases from piston-engine aircraft that utilize leaded aviation fuel and emissions from vehicles that use leaded fuel. Other significant anthropogenic sources of lead (Pb) pollution include but not limited to waste incinerators, utilities, and manufacturers of lead-acid batteries. Other sources of Pb include old lead pipes in farmlands or urban areas can be another source of aquatic lead pollution, corrosion of pipes, brass metal faucets, artificial turf for stadiums/ carpets, and explosives, leachates from unlined landfills and mine dumps. Lead from these different sources leach into waterways and groundwater; leading to elevated environmental (water and soil) lead levels that are detrimental to the health and vitality of human and aquatic organisms. Low levels of lead in the human body cause serious health issues such as, lowering I.Q (intelligent quotient) and disrupting development in children and high blood pressure and infertility in adults (NRDC, 2023). Children are more vulnerable to Pb toxicity when compared to adults because of the increased hand-to-mouth activity and intestinal absorption (Garcia-Vazquez et al., 2021).

2.5.3 Mercury (Hg)

Mercury (Hg) is a naturally occurring metal which is a shiny silver-white, odourless liquid and becomes colourless and odourless gas when heated. Mercury is found primarily in a light red stone mineral called cinnabar. The cinnabar stone can contain approximately up to 86 percent mercury (USGS, 2003). Mercury is very toxic and exceedingly bio accumulative heavy metal which can be released to the environment through the natural processes of rock weathering and (or) vulcanicity (Jaishankar et al., 2014). However, human activities such as coal-burning in electricity power generation and disposal of industrial waste, are the main source of mercury in the environment (USGS, 2003). When mercury is released to the environment, it can be converted to form of biologically toxic methylmercury (MeHg) by microorganisms that are present both in the soil and in the aquatic environment; and becomes highly toxic to humans, ecosystems, and wildlife (EU Science Hub, 2021). Through bioaccumulation, mercury levels elevate from small levels in small fish and elevated levels in the bigger predator fishes (which humans eat) and have a very negative health effect on humans and on fish-eating wildlife

(USGS, 2003). Mercury is extremely poisonous, absorbed into human body by touch, inhalation, or consumption building up and potentially causing fatalities (Patrick, 2002).

2.5.4 Chromium (Cr)

Chromium (Cr) is a naturally occurring element in the earth's crust and can be found in compounds form or as ions in the case of water; and is a very commonly occurring contaminant of both surface water and groundwater (Bartlett and James, 1988). Chromium can also be released into the environment through anthropogenic sources contributing to major environmental contamination (ATSDR, 2008). Chromium can be introduced to the atmosphere through exhaust gasses from the burning of fossil/ hydrocarbon fuels, production of steel, welding activities, and Cr manufacturing; whereas industrial processes such as electroplating, leather tanning, dyeing of fabric, water treatment, or disposal of coal ash can discharge Cr into water and soil (USEPA 1995; Testa et al., 2004). Cr is highly toxic to humans and can cause cancer, damage the kidneys and liver, and may cause gastritis (ATSDR 2008, 2012)

2.6 Phosphorous and Sulphate Pollution.

The use of phosphates and sulphates-based fertilisers increases the risk of heavy metal mobility (Rani et al, 2022). Phosphorus and sulphates are indispensable soil nutrients which are essential for plant growth, but in excess can cause water pollution when leached or washed away from agricultural and mining areas (Vargese et al, 2024).

2.6.1 Phosphorous

Phosphorus (P) is a nonmetallic chemical element of the nitrogen family and always occurs as phosphate ions or as phosphate salts (Brittanica, 2024). By far the largest use of phosphorus compounds is for the manufacture of fertilizers, thereby making agriculture a major source of phosphorus pollution, both from the production of crops and rearing of animals (UNEP, 2024). Other potential sources of phosphorus can be sewage, discarded food leftovers or waste and other organic or inorganic waste streams polluting water bodies such as rivers, dams, lakes, seas, and the oceans through eutrophication. Phosphorus is widely used in fertilizer synthesis; simultaneously, it plays a significant role in heavy metals accumulation through its application to the soil (Chen et al, 2020). Water-insoluble phosphorus fertilizers have been shown to produce phosphate rocks, which play a major role in the immobilization of metals by precipitation as metal phosphates in the soil (Bolan et al, 2003). Excessive use of fertilizers for a long time resulting in heavy metals accumulation in agricultural soils reduces soil fertility, and consequently decreases plant growth and productivity (Ai et al, 2003).

Eutrophication of the water bodies leads to algal blooms which in turn results in contamination of drinking water supplies and create low or no oxygen zones (oxygen-starved dead zones), which result in the death of aquatic species such as fish. Phosphorus pollution is said to be a prime driver which contributes to the loss of biodiversity and this also in turn contributes to the degradation of the ecosystems which humanity depends on for survival (EPA, 2023). Availability of phosphorous is also influenced by addition of organic materials. Organic materials can release inorganic phosphorous directly and after mineralisation of organic phosphorous (Sharpley and Moyer, 2000). Further, organic amendments influence phosphorous availability indirectly. Firstly, organic acid anions produced during decomposition can exchange bound phosphate from anion exchange sites, releasing phosphorous into the soil solution (Hue, 1991).

2.6.2 Sulphates

Sulphate is a common anion which is widely distributed in various natural environments and plays an important role in biogeochemical cycles (EPA, 2023). Natural formation of dissolved sulphate happens in inland waters when processes like vulcanicity, weathering of rock minerals, organic decay or decomposition and burning of organic matter. Anthropogenic activities such as atmospheric pollution from fossil fuels, the drainage of wetlands, the lowering of groundwater levels for opencast lignite mining, fertilizer leaching from agricultural soils and agricultural and industrial wastewater are primarily responsible for increase in the concentrations of sulphates in water (Wang and Zhang, 2019).

Apart from impairing the quality of the drinking water, sulphate also interferes with the cycles of nitrogen, carbon, and phosphorus (UNEP, 2024). The end results of this interference are increased nutrient enrichment in water bodies and ending up causing algal blooms, growth of plants like hyacinth and impacting food supplies for the aquatic organisms. When plant growth happens in a water body due to eutrophication, dissolved oxygen in the water is reduced, which increases the further phosphates release from the sediment, a vicious cycle (Zak et al., 2021).

Sulphate and bi-products of its degradation, such as hydrogen sulphide, have toxic effects on aquatic life (Degryse et al., 2021).

3 MATERIALS AND METHODS

3.1 Study Area

This research was carried out in the Mazowe District near the Iron Mask Mountain range along the Mazowe River which acts as the main transport vehicle for the pollutants produced by abandoned pyrite mines at Iron Duke and artisanal gold mining activities adjacent and parallel to the river. The waters or acid mine drainage discharging from inside old mine shafts and draining from open pits through a network of tunnels, including the leachates from mine waste dumps, tailing dams and other mining facilities produce liquid pollution, which, upon reaching the Yellow Jacket River, is carried into the receiving Mazowe River. The area is also a prime agricultural area with rich red soils sustaining horticulture, maize, tobacco, and wheat farming. It is from this area where oranges for the famous Mazoe Orange Crush drink are mainly sourced. The river originates North of Harare and flows in the Northeastern direction towards Mozambique. It is very popular with gold panners especially during the wet season where they look for alluvial gold deposits (Chikozho, 2014).

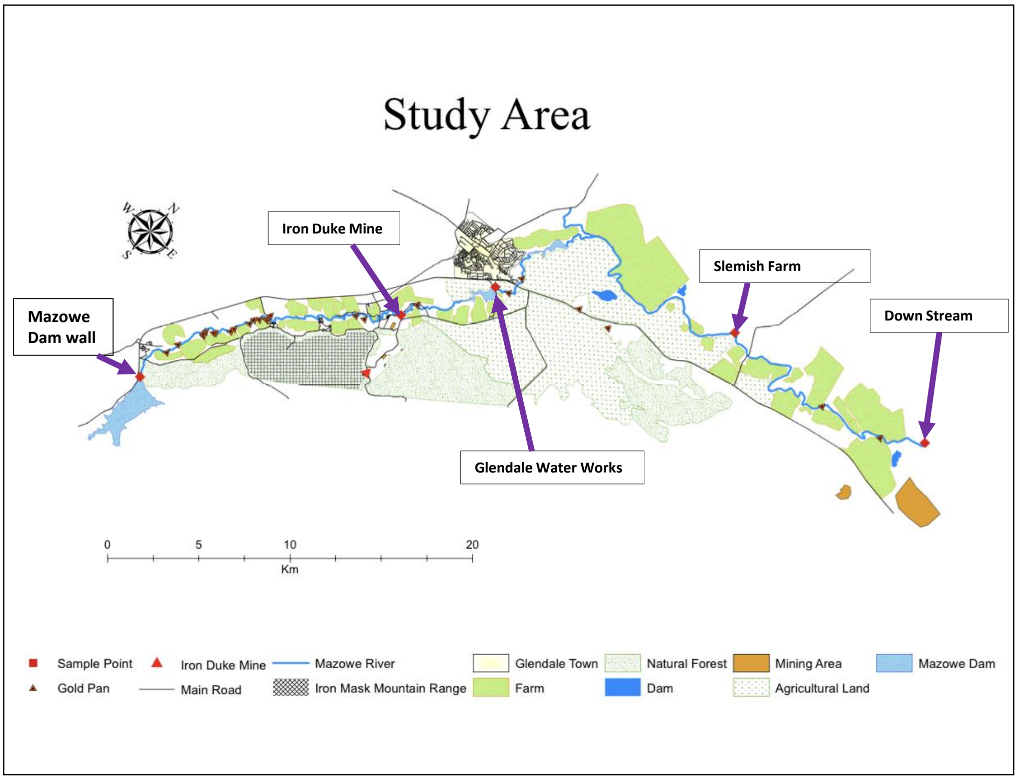

Figure 1. Map of the study are in Mazowe District of the Mashonaland Central Province in Zimbabwe.

The figure provides an ArcGIS generated map of the study area and sampling points. The map also shows the Iron Duke Mine, urban settlements, dams, farmlands, natural forest, and informal mining activities (indicated by brown little triangles on the map) along the Mazowe River in light blue. The natural forest is depicted in green. Blue represents water along Mazowe River.

3.2 Description of the Mazowe Catchment Area

Mazowe catchment is located between 16.470°S latitude and 18.240°S latitude and between 30.680°E longitude and 33.000°E longitude (Key, 1989). The river catchment has a total area of 38937 km^2 and its catchment borders on the West is the Manyame Catchment, and on the South-West and South is the Save Catchment (Fetter, 1994). The Mazowe catchment also straddles over three administrative Zimbabwean provinces of Mashonaland East and Central as well as Manicaland (Figure 2).

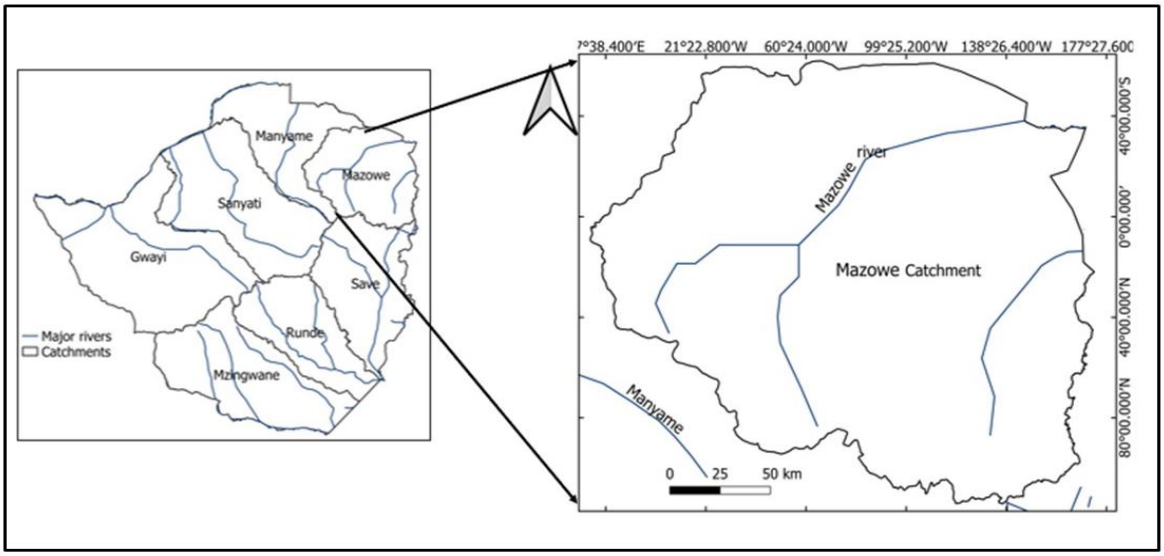

Figure 2. Location of Mazowe River in Zimbabwe

3.3 Sampling Design

The sampling was carefully designed in such a manner to cover a period of two seasons within a year. The water and sediment samples were collected from the sampling sites between the months of February 2021 (wet period) and October 2021 (Dry period). The sampling points for the sediments and water samples were selected in a stratified random sampling way using prior knowledge of the area located immediately downstream of the already known artisanal (informal) gold mining locations and near the confluence/discharge areas of all the small streams, dams and water works. The sampling point upstream of the agricultural and artisanal/informal gold mines was located at Mazowe Dam outlet which is away from the artisanal gold mining area (Figure 1). Three composite samples were collected by the grab bucket sampler at each site across the river cross section. The composite samples were grabbed at the left bank, midstream and right bank of the river, giving 3 samples per location (Figure 3). The left and right banks are viewed in the downstream flow direction of the river. The water samples were collected at about 12 to 15cm below the surface of the river water using the Ruttner sampler (Rahmani and Samarghandi 2007; Nouri et al., 2009; Pedzisa et al., 2015).

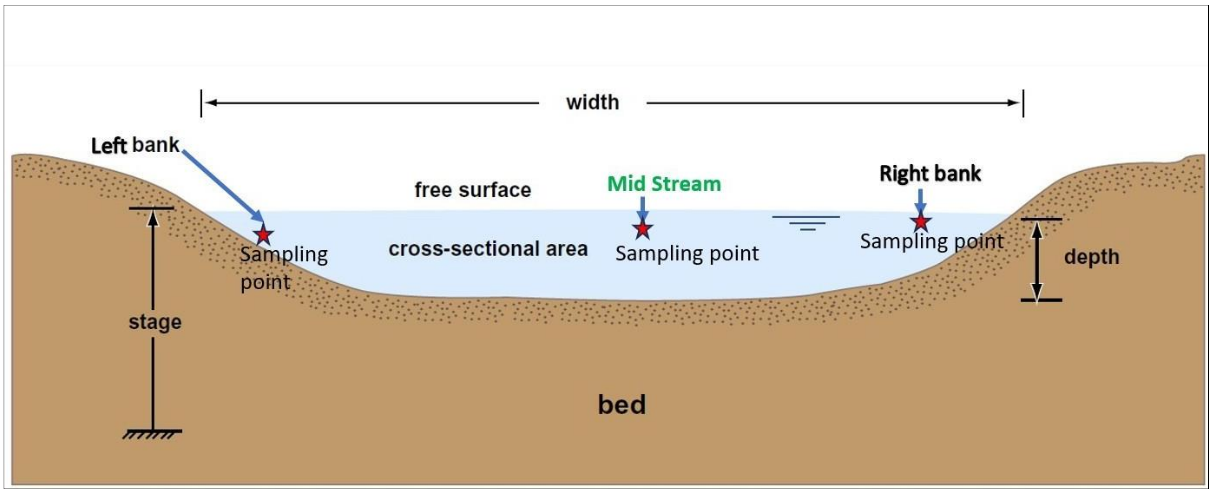

Figure 3. Simplified cross section through a river channel showing sampling points. (Source: John Southard, 2024)

The sample containers consisted of pre-labelled polypropylene bottles which were washed with Nitric acid (10.0% HNO_3) to remove metal contaminants and thoroughly rinsed in distilled water. The samples were all acidified immediately after sampling by adding 0.15 mL concentrated nitric acid (HNO_3) per 100 mL of sample (0.15% vol./vol) to a pH of less than 2 to ensure that the ions of the heavy metals stay in solution and do not adsorb onto the sample container walls during transit and storage before laboratory testing. The same procedure was done for sediments where the collection of the samples was done using the Ekman Dredge sampler that employed the Grab sampling process and were put in polythene bags. After the process, all the collected samples were packed and carefully labelled to avoid mixing up (Nouri et al., 2009; Rahmani and Samarghandi 2007; Pedzisa et al., 2015). All the samples were stored in an ice cooler box with ice to maintain a low temperature (<4˚C) during transportation to the Zimbabwe Laboratories (Zimlabs) located in Harare, Zimbabwe for the laboratory analysis of heavy metal, extractable sulphates, and phosphorous. All the sediments collected from the five different points were dried in an oven, ground, and passed through a 2mm sieve. Then the different elements were analysed using the method articulated by Lindsay and Norvell (1978). Approximately 10g of the processed sediment sample was shaken for exactly 120 minutes with 20mL of extractant (0.005 M DTPA, 0.01 M CaCl2 and 0.1 N TEA buffered at 7.3 pH) on an electrical shaker and the filtrate was analysed for heavy metals using Atomic Absorption Spectrophotometer (ELEMENTAS AAS4141-Electronics Corporation of India Limited). The flame Atomic Absorption Spectrometer was used to analyse metals after wet digestion (Nelson 1982). The calibration curves were prepared for each metal by running different concentrations of standard solutions. The reagent blanks were run on the instrument and the obtained values were statistically analysed. The elements that were obtained from the results included Mercury, Phosphate, Cadmium, Chromium and Lead (Blaker 1978, Lindsay and Norvell 1978). The sulphates analysis was done at a wavelength of 420nm using an advanced microprocessor UV-VIS Spectrophotometer Single Beam 295 while phosphorous absorbance was measured at 880 nm on a UV-VIS spectrophotometer.

3.4 Data Analysis (Quantification of Heavy Metals in Space)

The study quantified the relationship between heavy metal parameters in space. Excel for Microsoft 365 was used for data compilation and analysis. SPSS Statistics 29.0.1 (SPSS Inc. Chicago, IL, USA) was used for the statistical analysis, and, prior to any statistical analysis, the normality (Shapiro-Wilk test) test was first assessed and then the constant variance (Brown-Forsythe test) of the data. The statistical significance of the difference between the average pollutant levels in the wet and dry seasons was done using a Student's t-test at a 0.05 alpha level.

4 RESULTS

4.1 Distribution of Extractable Sulphate and Phosphate in Water and Sediments (Wet vs Dry Season)

The study sought to examine the distribution of phosphates and sulphates downstream from the Mazowe Dam wall (outlet) sampling point to the Downstream sampling point in two different seasons (Fig. 4). Significant differences in mean levels of phosphates and extractable sulphate pollutants were observed in the wet and dry season.

Extractable sulphate was higher in the water samples during the wet season compared to the sediment samples (Fig. 4 A, B, C and D). In the wet season, the Downstream sampling location recorded the highest mean concentration of extractable sulphates in water samples (213.27 mg/l) while Iron Duke Mine sampling location recorded the least (57.3mg/l) (Fig. 4A). Upstream at Mazowe Dam outlet sampling location, the extractable sulphates levels in water samples (119.58mg/l) were higher than that of Iron Duke Mine (119.58mg/l) (Fig. 4 A). During the dry season the extractable sulphates levels in water samples decreased with the highest concentration (62.27mg/l) observed at the Slemish Farm sampling point and the least (35.56mg/l) observed at the Iron Duke Mine site (Fig. 4C). There was a spike of contaminants in the farming areas as seen by higher levels of extractable sulphates at Slemish Farm.

In the sediment samples, extractable sulphates were higher during the dry season compared to the wet season. During the wet season, Glendale Water Works had the highest extractable sulphate concentration in sediment (35.1 mg/kg) while Mazowe Dam outlet had the least (2.15mg/kg) (Fig 4B). The extractable sulphates concentrations in sediments increased in the dry season with the levels at the Downstream site spiking to 55.51mg/kg which was the highest comparing to Iron Duke Mine which had 32.4mg/kg (Fig. 4D).

Phosphates contaminants levels in water samples were lower compared to the sediment samples both during the wet and the dry seasons. Mazowe Dam outlet had the lowest concentration of phosphorous (0.3mg/l), while Slemish farm recorded the highest (1.47mg/l) during the wet Season. In the dry season, Slemish farm had the lowest concentration of phosphates in water (0.54mg/l), while the downstream site had the highest (0.75mg/l). During wet season, Glendale had the highest phosphates concentrations in sediments (23.42mg/kg) while the upstream site at the Mazowe Dam outlet recorded the least (10.25mg/kg) (Fig. 4B).

The dry season concentration of phosphates in sediments decreased slightly with the highest concentration recorded at Iron Duke Mine (9.51mg/kg), while Glendale had the least concentration (7.32mg/kg) (Fig. 4D). The upstream levels of both sulphates and phosphates in water and sediments were lower at Mazowe Dam outlet compared to the downstream levels as indicated by Figs. 4(A, B, C and D).

Laboratory analysis of the water samples showed that higher levels of extractable sulphate were detected in the wet season compared to the dry season at all sampling points ($P<0.01$) (Figs 4 A and B). Iron Duke Mine and Glendale Water Works had lower levels of extractable sulphate than the Mazowe Dam outlet which is the upstream of the study site. There were not any significant differences in the phosphorous levels in the waters sampled between Mazowe Dam outlet, Iron Duke Mine area and Glendale waterworks during the wet season ($P < 0.01$).

There were significant differences in the concentration of sulphates in both water and sediment samples along the river from upstream, midstream, and downstream during both the wet and dry seasons (Fig. 4 A, B, C and D). A significant decrease in sulphates levels in both water and sediment samples was observed between Mazowe Dam outlet and Iron Duke Mine during both wet and dry seasons (Fig. 4 A, B, C and D). There was higher concentration of sulphates in water samples at Mazowe Dam outlet, which is upstream, than that of Iron Duke Mine area in both wet and dry seasons (Fig. 4 A and B). During the wet season, the level of sulphates in water increased from lower levels at Iron Duke Mine, to higher levels at Glendale Water Works, Slemish Farm and Downstream sampling points. During the wet season, water samples recorded significantly higher sulphates at all sampling locations from upstream to downstream compared to sediment samples (Figs 4 A and B). Midstream and downstream sampling locations had significantly higher pollutant levels compared to the upstream locations (Mazowe and Iron Duke Mine) (Fig. 4 A and B).

The average phosphorus levels detected in the sediment samples during the wet season was 14.93mg/kg which was 93.7% higher than that of water samples which was at an average of 0.94 mg/l. During the dry season, the average levels of phosphorous in sediments was 92.05%, higher than that of water ($P<0.01$). The sampling point with the highest levels of phosphorus recorded was at the Glendale Waterworks site. The phosphorous level was significantly greater in the sediments than in the water samples ($P<0.01$). During the wet season, there were significant differences in phosphorous concentrations in both the sediment and water samples, progressively increasing across all the sampling points from the upstream site of the Mazowe Dam outlet to the downstream site of the study area (Figs. 3 and 5). In the dry season, however, there was not any significant difference in phosphate concentrations in water samples at the sampling points of the Mazowe Dam outlet, Iron Duke Mine and Glendale Water works (Fig. 4C).

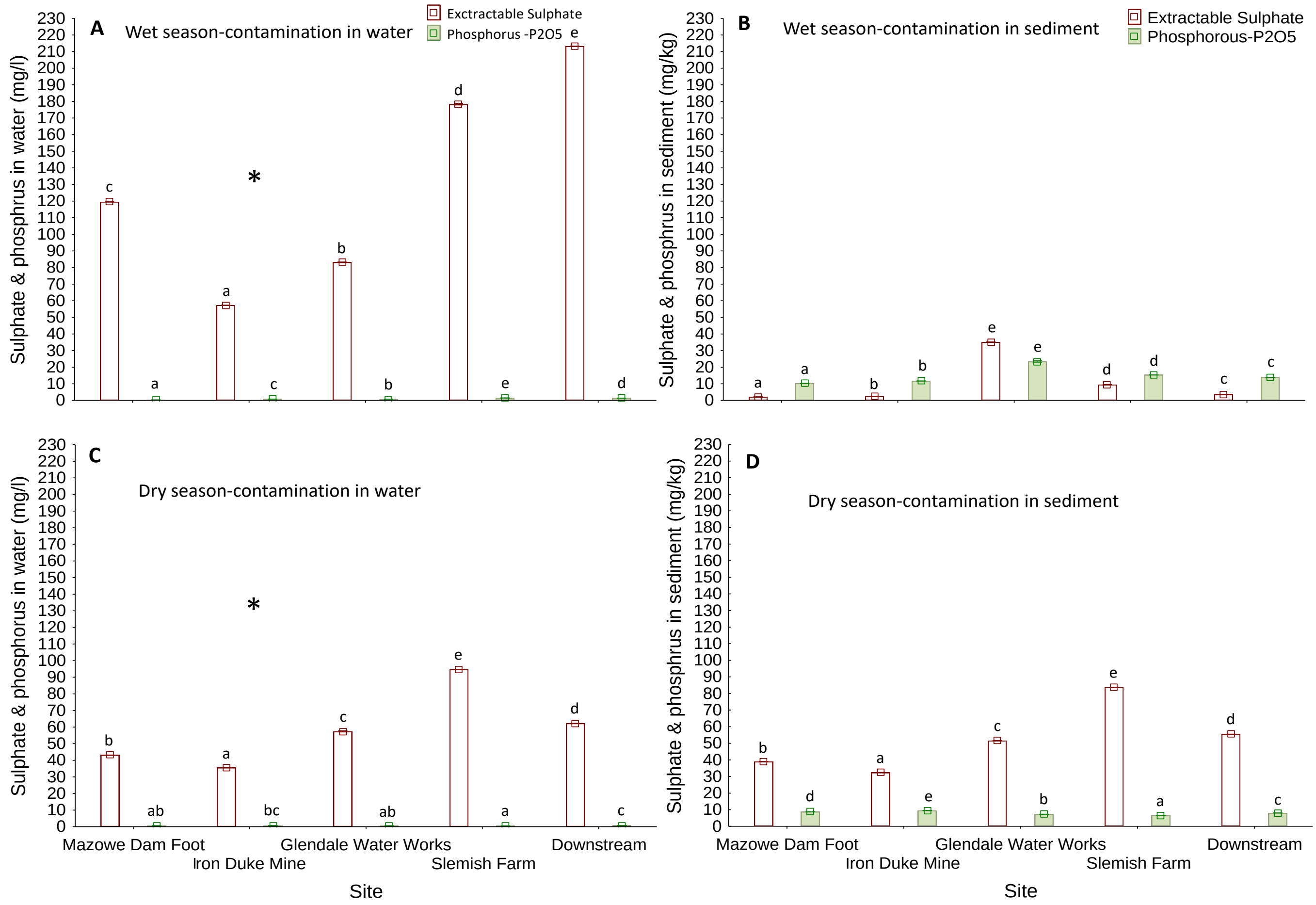

Figure 4. Distribution of extractable sulphate and phosphorous in water and sediments (wet vs dry season)

*(A) extractable sulphates and phosphorus in water during the wet season, (B) extractable sulphates and phosphorus in sediments during wet season, (C) extractable sulphates and phosphorus in water during the dry season, and (D) extractable sulphates and phosphorus in sediments during the dry season. NB: The letters on top of the bars represent significant differences. Levels not connected by same letter are significantly different at 0.05 alpha level. The Asterisk * means that phosphorous levels in water samples were below 5mg/l in graphs A and C.*

4.2 Distribution of Heavy Metals in Water and Sediments (Wet vs Dry Season)

Concentrations of the heavy metal pollutants (Cd, Pb and Hg) detected in water samples during the wet season were all reported as less than 0.01 mg/l showing no significant values or differences between the sampling points on the graphs except for one (Fig. 5A, C and D). In the wet season, Lead, Cadmium, and Mercury were detected in all sediment samples collected from the different sampling locations (Fig. 5B). The heavy metal pollutants in the sediments showed significant differences between the different sampling points during the wet season ($P<0.001$), but not in the dry season since all samples analysed for the metals were found to be <0.01 (Fig. 5 A, C and D). Results from this study showed that Iron Duke Mine sampling point had the highest concentration of heavy metals compared to other locations (Fig 5B). Mercury was the least recorded heavy metal in the sediments during the wet season.

Lead concentration was the highest in Iron Duke while the lowest was recorded in the Flemish farm (Fig. 5B). During the wet season, Pb levels in the sediments at Iron Duke Mine area was about 100% more than the value recorded at Mazowe Dam outlet, which was an upstream sampling point (Fig. 5B. The levels of Pb declined at Glendale by almost 50% from the value recorded at Iron Duke Mine sampling point. Pb levels further declined at Slemish Farm by about 74% from the value recorded at Glendale Water Works. At the Downstream sampling point the lead (Pb) levels increased. There were no significant differences in lead (Pb) concentrations between Mazowe Dam outlet and the Glendale Water Works sampling locations. However, there were significant differences in Pb concentrations between Mazowe Dam outlet and the Iron Duke Mine sampling locations (Fig 5B).

Concentrations of cadmium in sediments during the wet season were less than 2mg/kg at all sampling locations of the study area. There were no significant differences in cadmium concentrations between Slemish Farm and the Downstream sampling locations (Fig. 5B).

During the wet season, chromium (Cr) levels in the sediments only spiked higher at Iron Duke Mine compared to the Cr levels found at the upstream sampling point (Mazowe Dam outlet) and declined at Glendale Water Works and marginally increased at the Slemish Farm and Downstream sampling points (Fig. 5B). There were significant differences in Cr concentrations in sediments in some sampling points during the wet season except for Mazowe dam and Glendale which were not statistically significantly different (Fig 5B).

The concentrations of heavy metals in water were less than 0.01mg/kg during both wet and dry seasons (Fig 5A and C). During the dry season, concentrations of heavy metals in sediments fell to below 0.01mg/kg as indicated in Figure 5D.

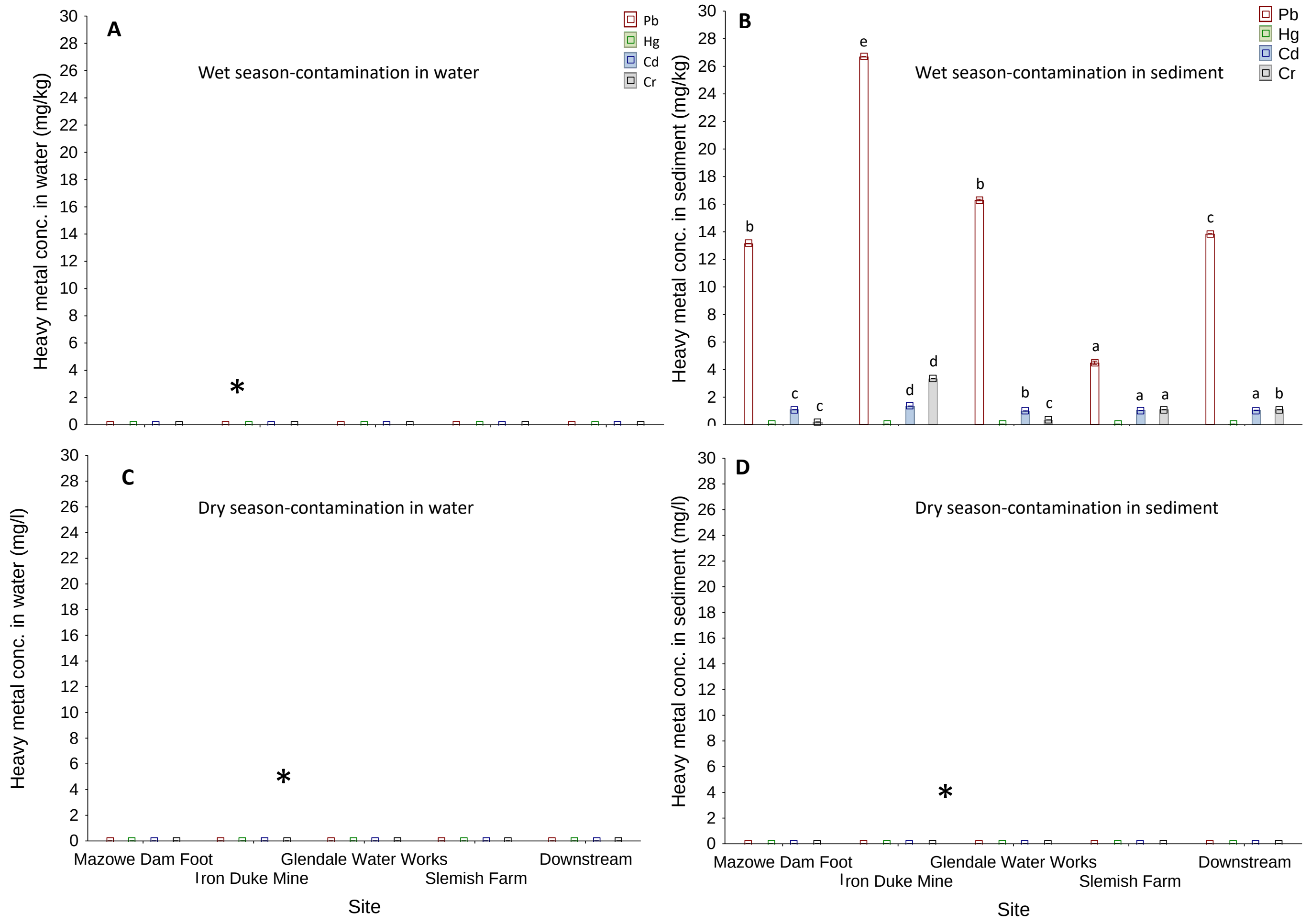

Figure 5. Distribution of heavy metals in water and sediments (wet vs dry season)

*(A) Distribution of heavy metals (Pb, Cr, Cd and Hg) in water during wet season, (B) Distribution of heavy metals (Pb, Cr, Cd and Hg) in sediments during wet season, (C) Distribution of heavy metals (Pb, Cr, Cd and Hg) in water during the dry season, and (D) Distribution of heavy metals (Pb, Cr, Cd and Hg) in sediments during the dry season. NB: The letters on top of the bars represent standards error. Levels not connected by same letter are significantly different at 0.05 alpha level. The Asterisk * means the levels of heavy metals in the samples were below 0.01mg/l or 0.01mg/kg in graphs A, C, and D.*

4.3 Differences in Average Water Pollutant Levels (Wet vs Dry Season)

The percentage changes in the level of the pollutants in water, such as extractable sulphates and phosphorous, were generally positive (Table 1) at all sampling locations along Mazowe River in Zimbabwe, indicating a decrease from higher concentration of contaminants levels in the wet season to lower concentrations of contaminants levels in the dry season. There was a negative percentage change of phosphorous at Mazowe Dam outlet in the dry season representing an increase in pollutant levels. This only happened for phosphorous levels at

Mazowe Dam outlet which is located upstream of the other sampling sites. There were no statistically significant changes in heavy metal pollutants levels in water samples between the wet and dry season at all sampling locations (Table 1). In some cases, especially for heavy metals, there were no significant changes in recorded pollutant levels in water samples.

Table 1. Seasonal differences in average water pollutant levels at different Mazowe River locations (wet and dry season).

Sampling Site	Parameter	Average (Wet Season)	Average (Dry season)	Percentage	p-value
Mazowe Dam Foot (Control)	Extractable Sulphate	119.58	43.15	64%	<0.01 *
	Phosphorous-P2O5	0.30	0.60	-100%	<0.01 *
	Lead	0.01	0.01	0%	N/A
	Mercury	0.01	0.01	0%	N/A
	Cadmium	0.01	0.01	0%	N/A
	Chromium	0.01	0.01	0%	N/A
Iron Duke Mine	Extractable Sulphate	57.30	35.56	38%	<0.01 *
	Phosphorous-P2O5	0.82	0.70	15%	<0.29 *
	Lead	0.01	0.01	0%	N/A
	Mercury	0.01	0.01	0%	N/A
	Cadmium	0.01	0.01	0%	N/A
	Chromium	0.01	0.01	0%	N/A
Glendale Water Works	Extractable Sulphate	83.20	57.38	31%	<0.01 *
	Phosphorous-P2O5	0.73	0.60	18%	<0.02 *
	Lead	0.01	0.01	0%	N/A
	Mercury	0.01	0.01	0%	N/A
	Cadmium	0.01	0.01	0%	N/A
	Chromium	0.01	0.01	0%	N/A
Slemish Farm	Extractable Sulphate	178.28	94.71	47%	<0.01 *
	Phosphorous-P2O5	1.47	0.54	63%	<0.01 *
	Lead	0.01	0.01	0%	N/A
	Mercury	0.01	0.01	0%	N/A
	Cadmium	0.01	0.01	0%	N/A
	Chromium	0.01	0.01	0%	N/A
Downstream	Extractable Sulphate	213.27	62.21	71%	<0.01 *
	Phosphorous-P2O5	1.38	0.75	46%	<0.01 *
	Lead	0.01	0.01	0%	N/A
	Mercury	0.01	0.01	0%	N/A
	Cadmium	0.01	0.01	0%	N/A
	Chromium	0.01	0.01	0%	N/A

*The Asterisk * indicates significant differences. A Student's t-test was used to ascertain whether there were any differences in the average pollutant levels between the different sampling sites during the wet and dry seasons (Table 1).*

The heavy metal (Cd, Hg, Pb and Cr) concentrations found in water in the study area were less than 0.01mg/l. The World Health Organization (WHO) permissible limits for water are presented in Table 2 below.

Table 2. WHO Limits for heavy metals in water (WHO 2006).

Heavy metal	Current study (mg/L)	Standard limits as per WHO guidelines (mg/L)
Cadmium	<0.01	0.003
Mercury	<0.01	0.006
Lead	<0.01	0.001
Chromium	<0.01	0.05

4.4 Differences in Average Sediment Pollutant Levels (Wet vs Dry Season)

A Student’s t-test was conducted to investigate the differences in the mean levels of pollutants during the wet and dry seasons. There were significant differences in the levels of sulphates and phosphorous in sediments between the sampling points ($P<0.01$) (Table 3). Higher levels of heavy metals were detected in the sediment samples from all sampling locations during the wet season. The levels were less than 0.01mg/kg during the dry season and, at some locations, were not detectable.

Table 3. Seasonal differences in average sediment pollutant levels at different Mazowe River locations (wet vs dry season).

NB: Negative percentage changes represent an increase in pollutant levels at the sampling location between the seasons. A positive percentage represents a decline in pollutant levels from wet to dry season. In some cases, especially for heavy metals, there were no significant changes in detected pollutant levels in sediments. Extractable sulphate increased from lower levels during wet season to higher levels during the dry season.

Sampling Site	Parameter	Average (Wet Season)	Average (Dry season)	Percentage	p-value
Mazowe Dam Foot (Control)	Extractable Sulphate	2.15	38.99	-1713.5%	<0.01 *
	Phosphorous-P2O5	10.25	8.78	14.3%	<0.01 *
	Lead	13.15	0.01	99.9%	N/A
	Mercury	0.05	0.01	80.0%	N/A
	Cadmium	1.1	0.01	99.1%	N/A
	Chromium	0.2	0.01	95.0%	N/A
Iron Duke Mine	Extractable Sulphate	2.48	32.4	-1206.5%	<0.01 *
	Phosphorous-P2O5	11.71	9.51	18.8%	<0.01 *
	Lead	26.7	0.01	100.0%	<0.01 *
	Mercury	0.05	0.01	80.0%	N/A
	Cadmium	1.35	0.01	99.3%	<0.01 *
	Chromium	3.35	0.01	99.7%	<0.01 *
Glendale Water Works	Extractable Sulphate	35.1	51.62	-47.1%	<0.01 *
	Phosphorous-P2O5	23.42	7.32	68.7%	<0.01 *
	Lead	16.3	0.01	99.9%	<0.01 *
	Mercury	0.05	0.01	80.0%	<0.01 *
	Cadmium	1	0.01	99.0%	N/A
	Chromium	0.35	0.01	97.1%	<0.01 *
Slemish Farm	Extractable Sulphate	9.5	83.7	-781.1%	<0.01 *
	Phosphorous-P2O5	15.37	6.59	57.1%	<0.01 *
	Lead	4.5	0.01	99.8%	<0.01 *
	Mercury	0.05	0.01	80.0%	<0.01 *
	Cadmium	1.05	0.01	99.0%	N/A
	Chromium	1.1	0.01	99.1%	N/A
Downstream	Extractable Sulphate	3.67	55.51	-1412.5%	<0.01 *
	Phosphorous-P2O5	13.91	8.05	42.1%	<0.01 *
	Lead	13.35	0.01	99.9%	<0.01 *
	Mercury	0.05	0.01	80.0%	<0.01 *
	Cadmium	1.05	0.01	99.0%	<0.01 *
	Chromium	1.1	0.01		N/A *

*The Asterisk * indicates significant differences*.

N.B: *The P-values, with asterisks, represent statistically significant differences in mean levels of pollutants in the wet and dry season at a 0.05 alpha level.*

5 DISCUSSION

Lead (Pb) may occur naturally in soil at low levels in the range of 5 to 100 ppm total lead (UCONN, 2023). In the sediment, high levels of lead (Pb) could be attributed to the contaminated waste from corrosion of old agricultural lead metal pipes and mixing of domestic and industrial wastes (RUGTERS, 2024). In this study, the average level of lead (14.9mg/kg), that was found in the sediment samples of the study area during the wet season, was below the WHO (1996) permissible limits of 85mg/kg. In the water samples, the average detected lead (Pb) levels were less than 0.01mg/l which is below the WHO (2003) limit of 0.01mg/l. Elevated lead (Pb) concentrations from soils may also be attributed to runoff from roadways because of wet or dry deposits of lead in air emissions from vehicles and agricultural machineries that use leaded gasoline. Average cadmium (Cd) levels in the sediment samples during the wet season was 1.11mg/kg which was 27.93% above the WHO (1996) permissible limits of 0.8mg/kg in soils. However, during the wet season, the average chromium (Cr) concentrations in both the sediment and water samples were below the WHO (1996) permissible limits of 100mg/kg and 0.05mg/l respectively.

The average levels of Pb, Cd, Hg, and Cr in water were all less than 0.01mg/l both during the wet and dry seasons. The results could be attributed to settling of heavy metals or the dilution of heavy metals in water when the river discharge is high, especially in rainy season (Surbakti et al., 2021). The danger of heavy metals in water even in trace concentrations is that they have properties of being difficult to decompose and of accumulation and endangering the biota in aquatic environment (Riani, 2015). Heavy metals could be toxic if bioaccumulated in plants and fish over time (Zhang et al., 2023). Also, the lower levels of these metals could be a result of absorption by marshy plants as observed by Lee et al. (1981).

The average concentration of extractable sulphates recorded in water samples was 130.33mg/l during the wet season, which was higher compared to that of the sediments (10.58mg/kg), suggesting that this could be due to extensive leaching and runoff from farming areas which intensively use sulphate related fertilisers, common in commercial farming in Zimbabwe (FAO, 2024). Sulphate related fertilisers can dissolve in water and carried along with the runoff from adjacent farmlands (Degryse et al., 2021). This shows that agriculture has a very huge effect on the water quality of the catchment. Previous research in watershed management indicated that Phosphorous losses in farming lands are highly dependent on run off volume

(Deng 2019; Reid, 2018; Stan 2002). These findings indicate the need for having integrated watershed management practices that ensure that farming activities are regulated and maintained within stipulated buffer zones. Extractable sulphates can come from acid mine drainage generated from the pyrites residues of Iron Duke Mine which could in turn increase the mobility of heavy metals as they alter water pH levels. The heavy metal ions will be leached from the stabilized contaminated soil under sulphate erosion conditions, which gives rise to secondary contamination to the areas around the mine sites (Zhang, et al 2017).

The slightly high concentration of phosphorus in sediments (though below WHO 1996 standards) and elevated extractable sulphates in water need to be addressed as they can potentially lead to eutrophication of the water course. A study by Chen et al. (2021) on the effects of elevated sulphate in waters and sediments established that: higher sulphate levels in water promoted internal phosphorus release under oxic conditions. Previous studies have shown that phosphorus (P) is one of the primary driving factors for eutrophication issues (Carpenter, 2008; Schindler et al., 2008). This can potentially lead to growth of undesirable plants and death of aquatic life (Chen et al., 2021).

5.1 The Difference in Metal Concentrations in Wet and Dry Season

The concentration of heavy metals in sediments was higher in wet season compared to those in the dry season. The differences might be because of reduced transportation of heavy metals through runoff into the river during the dry season. Water acts as a mode of transport of heavy metals from the different sources of pollution such as farms and mining areas. Once they are carried from the pollution points, the heavy metals will be deposited and carried down the course of the river, hence an increase in the high concentration of heavy metals in the sediments as well as the water during the wet season. A study by Zhang et al. (2022) showed that metal transport and partitioning in the rivers were primarily controlled by suspended solids with seasonal flow regimes in river networks and the volumes of metals were higher during wet seasons compared to dry season. Iron Duke Mine, Glendale Water Works, Slemish Farm and Downstream sampling points had relatively higher concentration of heavy metals in the wet season in both water and sediments (this was not demonstrated on the graphs for water analysis during the wet season because of lower concentrations that couldn’t fit on the graphs). This might be because they are located in the middle part of the river course and are surrounded by farming and mining activities which act as major sources of heavy metal pollutants into the river. Iron Duke mine had higher levels of heavy metals (Pb, Cr, CD and Hg) in the sediments during the wet season compared to other sampling locations. In this study, the Iron Duke Mine acted as one of potential major sources of heavy metal pollution of Mazowe River and distribution of heavy metals at each sampling location in the study area. There were also some agricultural fields close to the samples point, and these also act as major sources of pollutants such as phosphorous and sulphates from the fertilizers applied in the field for the crops. This in turn causes eutrophication and increases the mobility of heavy metals from farming areas through leaching. The influence of phosphorous and sulphates on the pH were identified as the primary factors controlling heavy metal release from tailings and agricultural lands in past studies (Tian et al, 2024).

5.2 Erosion and Deposition of Sediments and its Impacts on Pollution Levels

Due to agriculture-related mechanical disturbance of soils, artisanal gold mining and deforestation around Mazowe River, the movement of pollutants in the rivers as sediments, suspended solids or in solution is more pronounced during the wet season. Pollution deposition, however, is generally predicted to happen at the position of low velocity in the river cross section. However, gold panning in the riverbanks distorts this process. Rainfall rapidly transports heavy metals, phosphorous and sulphates from the surface of the tailings and agricultural areas into the surface runoff, thereby increasing heavy metal migration (Li et al., 2024). This probably explains why there was higher pollutants levels in the samples of water during the wet season compared to dry season. Tributaries of major rivers, like Mazowe River, coming from mining and farming areas carry significant pollution load that result in more than expected pollutants deposition at the points of inlet of the runoff to the major river. In Mazowe River, the visual observation of washed-up sands on riverbanks and on the riverbed indicated very complex hydrodynamic processes of the silt-laden river during the wet season that are heavily influenced by uncontrolled riverbank gold panning, which may make it difficult to predict the behaviour of pollutants deposition in the riverbed (Phillips et al., 2022). An alluvial river is naturally a self-organized system that is adjusted by the erosion and deposition of sediments (Dunne and Jerolmack, 2020). However, these processes are directly or indirectly influenced by anthropogenic disturbances caused by intensive damming, mining (organized and unorganized), irrigation, and land-use changes (Best and Darby, 2020).

6 CONCLUSIONS

This study showed that pollution of phosphates and sulphates in Mazowe River may be largely due to commercial agriculture and other sources, while heavy metals pollution was due to informal mining and commercial agriculture. The Pb spike in the sediment and sulphates in water during the wet season were more pronounced at the Iron Duke Mine area, indicating the influence of mines in river water pollution. The land use type also had a bearing on the results as seen by increasing levels of heavy metals in samples collected close to the mining areas and those influenced by runoff from agricultural areas as we move downstream from the control sampling site at Mazowe Dam outlet.

This study focused on four main areas: (a) the total quantities and distribution of Phosphorous and Sulphates; and the heavy metals: Hg, Pb, Cd and Cr in the river sediments, (b) the location (spatial) and temporal (seasonal) variation in the heavy metal, phosphates and sulphates concentrations, (c) source identification of pollutants origins, and (d) investigation of the nexus between mining and agricultural pollutants in general river pollution and mobility of pollutants.

6.1 The major results and outcomes of this study answered the above main and sub-components as follows:

6.1.1 The detected higher concentrations of heavy metals (14,9mg/kg Pb, 1.23mg/kg Cr, 1.11 mg/kg Cd and 0.05mg/kg Hg) in the sediment samples, during the wet season compared to levels of the dry season (less than 0.01mg/kg), are an indication of impacts of poor environmental management in the mining and agricultural environment. The presence of heavy metals in sediment samples from sampling points that exist far away from the main mining area of Iron Duke Mine and other upstream alluvial gold mining may be attributed to agricultural activities. There seems to be a marginally lower contribution of Agriculture in heavy metal mobility in the study area as indicated by lower metal levels during the dry season. Alluvial gold panning during the dry season may be a huge contributing factor to the presence of heavy metals in water and sediment samples.

6.1.2 Mazowe River sediments had significant contamination from heavy metals, particularly from Cd and Cr, which was more than the value for the Mazowe Dam outlet sampling site which acted as the control because of its position of being located before the confluence of the potential sources for pollution such as agriculture, mining, and domestic effluents and or runoffs into the river. Chromium and Pb concentrations in sediments were approximately 10 times higher than the control values during the wet season. Cadmium was detected in the river sediments across all sampling points, including the control, during the wet season. This may be attributed to illegal gold mines along the Mazowe area and other sources like leachate from old unlined landfills like Teviotdale located in North of Harare where Mazowe River originates (Nemadire et al., 2017). The presence of heavy metals during the wet season poses a high threat to the river ecosystem as they become bioavailable and creating a toxicity risk, while Pb, Cr and Hg may find their way into the food chain. Extractable sulphates mainly from acid mine drainage coming from the pyrites residues of Iron Duke Mine increases the mobility of heavy metals as they alter water pH levels. Phosphates however are generally originating from agricultural activities and urban settlements as a product of wastewater treatment facilities. Therefore, the sediment environment, had more pollution levels during the wet than in the dry seasons.

6.1.3 The lower levels of heavy metals in the sediments during the dry season compared to the wet seasons indicate how leaching, soil erosion and siltation of rivers can influence pollution in temporal and spatial scales. A study carried out by Mohammadi et al. (2019) established a correlation in the spatial distribution of heavy metals in the rivers and eroded soils from agricultural areas at temporal and spatial scales.

6.1.4 Iron Duke Mine sampling site recorded the highest concentrations of heavy metals in sediments compared to other sites during both wet and dry periods. The older mine dumps and tailing dams at Iron Duke Mine were singled out as a ‘potential hot spot’ for Cr, Pb, Cd and Hg. Mercury is normally used by artisanal miners for gold extraction during the panning exercise. In addition, spatial patterns varied for different metal fractions, and the dominant metal fractions differed from total concentration distribution patterns across the watershed. Gold panners are highly active during the wet season, targeting alluvial gold deposits hence a significant presence of heavy metals in sediments during the wet season which also have led to extensive siltation of the rivers in Zimbabwe.

6.1.5 The concentrations of heavy metals in water samples were lower compared to sediments. During the dry season, the concentrations of heavy metals in both water and sediment samples were less the 0.01 mg/kg at all sampling sites in the study area, which show seasonal variation in heavy metal pollution of the Mazowe River. It is possible that heavy metal distribution in the river is influenced by pollution from agricultural activities where organic compounds and leached fertilisers affect the mobility of heavy metals. The results from this study showed that the aquatic environment of Mazowe River was not extremely polluted by heavy metals as per the WHO 1996 and 2003 standards, but there was a big difference in the results at each sampling point, and also there was spatial differences in heavy metals (Pb, Cr, Cd and Hg) caused by local sources.

6.1.6 The seasonal changes in the concentration of phosphates in the Mazowe River may be attributed to the contribution of agricultural activities. The different land use types have a greater influence on pollution levels and, if not carefully planned, their impact on river pollution can be detrimental. On the other hand, sulphates are more likely to originate from mining activities, especially acid-mine drainage. However, in the study area (during both wet and dry seasons), there were more sulphates in water samples at Mazowe Dam outlet sampling point (which is upstream of the Iron Duke Mine) than the levels at Iron Duke Mine; indicating that the source of sulphates may be other sources apart from mining activities at Iron Duke Mine.

6.1.7 Informal mining activities is causing heavy metals pollution of the water in Mazowe River while agricultural activities are slightly causing phosphorus and extractable sulphate pollution of Mazowe River water and sediments. The presence of phosphorous upstream of the study area at the control site suggests other sources of pollutants in the river.

7 RECOMMENDATIONS

7.1.1 Control of leaching in farming areas is important to reduce eutrophication and mineral enrichment of rivers. Alternative farming methods that include the employment of technology like drip irrigation, hydroponics and organic farming can go a long way in phosphates reduction. The leaching and washing away of the phosphates may result in algae blooming downstream.

7.1.2 Further studies need to be conducted in the study area to analyse the concentration of these heavy metals in aquatic plants as this might have harmful consequences on both aquatic and human life. Further studies need to be conducted on the growth of heavy metal tolerant plants within the catchment to be able to apply restoration ecology techniques when necessary.

7.1.3 Also, integrated catchment management approaches need to be constantly revised to have sustainable agricultural production, environmental protection, water planning and operations activities that complement each other. There is also a need for a spatial-temporal assessment of heavy metal concentration over at least a two-year period and an in-depth analysis of the heavy metal concentrations is required in future.

7.1.4 Gold panning exacerbates heavy metal contamination of waters and sediments of receiving rivers in the catchment where it is practiced. Banning of streambank mining or gold panning needs to be enforced by the authorities while doing further studies on the impacts of artisanal mining and agriculture on river health. The presence of heavy metals in the sediments downstream of Iron Duke Mine may be attributed to small scale mining along the river and runoff from the mine dumps. Meanwhile, since mining is the source of livelihood in the Mazowe Catchment area, small scale miners need to be issued with environmental permits that are tied to the provision of a valid environmental impact assessment (EIA). These permits are to be periodically monitored and reviewed by relevant government authorities.

7.1.5 Environmentally friendly farming practices need to be emphasized since it has been noted that there are very high levels of phosphates and sulphates in sediment. There seems to be a nexus in elevated phosphates levels and the river mobility and higher concentrations of heavy metals. The combination of poor agricultural activities and poor mining is bad for the environment. This study proposes the review of the types of fertilisers that are used in the commercial farming areas in relation to river pollution and influence in heavy metal mobility in farming areas.

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