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A STUDY OF HEAVY METALS IN FISH FROM THE YELLOW JACKET RIVER, MAZOWE, ZIMBABWE

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Dedication

It is with genuine gratitude and warm regard that I dedicate my work to my mother Miriam Chitiyo, my father Kennedy Chitiyo, my sister Ashleigh Chitiyo and District Superintendent Reverend Heather Jane Zisengwe for their resolute support towards my education financially, spiritually and emotionally. May the Lord bless them.

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Abstract

This study investigated heavy metal concentrations in fish (Clarias gariepinus/catfish and Oreochromis niloticus/Nile tilapia) from the Yellow Jacket River in Mazowe, Mashonaland Central Province, Zimbabwe. The objectives of this study were to determine the levels of heavy metals {nickel (Ni), lead (Pb), zinc (Zn)} in Clarias gariepinus/Catfish and Oreochromis niloticus/Nile Tilapia from the Yellow Jacket River. Twelve (12) Clarias gariepinus/Catfish and eight (8) Oreochromis niloticus/Nile Tilapia were collected from the Yellow Jacket River and analyzed for heavy metal concentration using an Atomic Absorption Spectroscopy (AAS). The results of the study showed that the average zinc concentration in Nile tilapia was (mean = 0.7989 ppm; standard deviation = 0.9204 ppm). The mean nickel concentration was (mean=0.3866 ppm; standard deviation=0.2824 ppm). The average lead concentration was (mean = 1.0046 ppm; standard deviation = 0.11014 ppm). The mean concentration of Zinc in Catfish was (mean = 0.7695 ppm; standard deviation = 0.4500 ppm). The average nickel concentration was (mean=0.2500 ppm; standard deviation=0.12734 ppm). The mean lead concentration was (mean = 0.8421 ppm; standard deviation = 0.39523 ppm). Therefore, this study indicates that the heavy metal concentrations detected in the fish samples examined were above internationally accepted standards such as (WHO, 200, FAO, 2003; USFDA, 1993; EC, 2001).

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CHAPTER ONE

INTRODUCTION

1.0 Background to the study

Heavy metal contamination of aquatic systems from natural anthropogenic sources has become a global problem, threatening ecosystems and natural communities. Therefore, this study examines the effects of heavy metals in freshwater fish. Fish bioaccumulate heavy metals (including nickel, zinc and lead and copper and many others) through various organs such as gills, liver, stomach and intestines. The effect of these heavy metals is highlighted. Pollution of water and sediments by toxic metals is increasingly recognized as a global problem due to its detrimental effects on the aquatic environment due to its toxicity, non-biodegradable and persistent nature and ability to bioaccumulate in the food chain (Barakat and Baghdadi, 2012; Zhang et al., 2014; Wang et al., 2016). Heavy metals enter the aquatic ecosystem mainly through natural influences such as weathering and rock erosion and anthropogenic factors, including urban, industrial and agricultural activities, terrestrial runoff and sewage runoff (Ogoyi et al., 2011; Pandey and Sigh, 2015).

The toxicity of a heavy metal is determined by its concentration in the environment or the media in which it is found in the environment (water, soil, or air), the source (mining or natural rock quarrying), and the acidity of the environment, and whether the metal is present affects alone or as part of larger chemical compounds (khan et al., 2016). Concentrations of heavy metals in aquatic ecosystems are now among the highest reported anywhere in the world and are reaching unprecedented levels (Adham, 2001; Akan et al., 2009). Consumption of foods containing these pollutants by aquatic organisms can affect not only their productivity and reproduction, but also the health of humans who rely on these organisms as a source of protein (Davies et al., 2006).

Several studies on heavy metals have been conducted worldwide and include: mercury, lead, cadmium, zinc, aluminium, copper and nickel among many others (Esmail et al., 2009). The results of these metal pollution studies indicate that these metals are persistent in nature and tend to accumulate and biomagnify in living organisms (Retief et al., 2009). Most of the time, the top carnivores, which include fish, have higher concentrations of the toxic metals, much higher than concentrations in the surrounding water (Sarkar et al., 2008). The overall consequences of trace metal contamination in aquatic ecosystems are a reduction in biological richness and biodiversity, and a change in species composition (Javed, 2005). With this in mind, this study attempts to assess the effects of heavy metals in fish in the Yellow Jacket River.

1.1 Problem Statement

Rivers along mining areas have been contaminated with heavy metals worldwide. The Yellow Jacket River, which flows through the Iron Duke Mine in Bindura, Zimbabwe, is no exception. The water and fish of the Yellow Jacket River can be exposed to heavy metals from acid mine drainage and industrial or mining effluents. This can lead to bioaccumulation of heavy metals in fish and people who use water from this river and eat fish, since its tributaries pass through populated residential areas, cities, industrial and agricultural areas. The assessment of heavy metals containing lead, nickel and zinc in Yellow Jacket River fish is therefore warranted to ensure precautionary use of the water and consumption of Yellow Jacket River fish, as well as a basis for raising awareness among government agencies such as the Environmental Management Authority (EMA) for management of discharge into the Yellow Jacket River.

1.2 Aim of the Study

The aim of the study was to determine the level of heavy metal concentrations in fish *(Clarias gariepinus/Catfish and Oreochromis niloticus/Nile Tilapia)* from the Yellow Jacket River in Mazowe, Mashonaland Central Province, Zimbabwe.

1.3 Specific Objective

- To determine the level of heavy metals {Nickel (Ni), Lead (Pb), Zinc (Zn)} in *Clarias gariepinus/Catfish and Oreochromis niloticus/Nile Tilapia* from the Yellow Jacket River.

1.4 Research Question

- What are the concentrations of heavy metals {Nickel (Ni), Lead (Pb), Zinc (Zn)} in Clarias gariepinus/Catfish and Oreochromis niloticus/Nile Tilapia from the Yellow Jacket River?

1.5 Significance of the study

This study is significant in assessing whether the concentrations of heavy metals in two fish species (*Clarias gariepinus/Catfish and Oreochromis niloticus/Nile Tilapia*) are below or above the recommended concentrations of food fish.

1.6 Delimitations of the study

The scope of the study is limited to the investigation of the concentration of heavy metals on two fish species from the Yellow Jacket River in Mazowe, Central Mashonaland in Zimbabwe. The heavy metals studied are only nickel (Ni), zinc (Zn) and lead (Pb), all other metal elements are not part of this study. The study is also limited to examining only two species of fish, namely Clarias gariepinus/Catfish and Oreochromis niloticus/Nile Tilapia. All other fish species are not considered in this study. In addition, the studied fish species are taken from the Yellow Jacket River. Therefore, no fish from any river other than the Yellow Jacket River qualify for this study.

CHAPTER TWO

LITERATURE REVIEW

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2.1 Bioaccumulation and effects in aquatic organisms

Bioaccumulation is the process by which a compound from elements in its environment, such as water, food and sediment, is taken up and accumulated in an organism (Refief et al., 2009). The analysis of biological tissues that accumulate toxic residues over many years, in particular fish and mammalian tissues, is a method to allow a very long-term integration of the environmental conditions, in particular the presence of these toxic residues (Kudirat, 2008). Metals are not biodegradable and are considered to be important environmental pollutants, causing cytotoxic, mutagenic and carcinogenic effects in animals (More et al., 2003). Small increases in concentrations of heavy or trace metals in the aquatic environment can lead to a reduction in biodiversity and ultimately loss of nutrient cycling in streams and lakes (Rauf et al., 2009). From this section it is concluded that bioaccumulation occurs in fish as well as other aquatic organisms and that environmental conditions play an important role in enhancing the bioavailability of these metals to the organisms. It is therefore becoming increasingly difficult to ignore the urgent need for a thorough assessment of the environment to which fish are exposed on a daily basis, i.e. the sediments and the water, and the fish themselves in the Yellow Jacket River, in terms of heavy metal pollution.

Bioaccumulation is the net accumulation of substances from water in an aquatic organism as a result of increased uptake and slow elimination of such substances (Bhattacharya et al., 2009). Heavy metals are conservative pollutants because they degrade over such a long period of time that they effectively become permanent additions to the aquatic environment (Mason, 1996). Because heavy metals bioaccumulate and have deleterious effects on aquatic ecosystems (Roux, 1994; Ezemonye et al., 2006), bioaccumulation measurements are required. Bioaccumulation measurements refer to studies to monitor the uptake and retention of pollutants such as metals or pesticides in organs or tissues of organisms such as fish (Roux, 1994). Hence Olaifa et al. (2004) and Vinodhini and Narayanan (2008) reported that among aquatic animal species, fish cannot escape the harmful effects of these pollutants. This affects the health, growth, development and survival of the fish (Ibemenuga, 2013).

The defining feature of heavy metals is their strong attraction to biological tissues and, in general, their slow elimination from biological systems (Nwani et al., 2009). It has been established that the uptake of heavy metals in fish occurs through absorption via the gill surface or through the intestinal wall tract (Obasohan, 2007; Nwani et al., 2009). Diffusion-facilitated transport or absorption in gills and surface mucus are the mechanisms of water uptake (Oguzie, 2003). The bioaccumulation of metals reflects the amount taken up by organisms, the manner in which the metals have been distributed to different tissues, and the extent to which the metals are retained in each tissue type (Murugan, et al., 2008). Against this background, this study attempts to address issues related to the bioaccumulation of some heavy metals in fish.

2.3 Heavy metals in aquatic ecosystem and their toxicity

Heavy metals refer to any metallic chemical element that has a relatively high density with a specific gravity at least 5 times the specific gravity of water (Lars, 2003). According to Dianne and William (1999), a heavy metal includes any metal exposure that is clinically undesirable and that poses a potential hazard. The presence of heavy metals in the aquatic environment is a major concern due to their toxicity and threat to plants and animals, disrupting the natural ecological balance (Bhattacharya et al., 2008). The rate at which heavy metals are entering aquatic systems is alarming. The presence of heavy metals in aquatic ecosystems in excess of natural levels has become a widespread problem and concern over the years (Voegborlo et al., 1999; Canli et al., 1998; Dirilgen, 2001; Vutukuru, 2005). The sources of toxic heavy metals in the aquatic environment can be attributed to both natural and anthropogenic sources, as changes caused by anthropogenic activities have taken place in the aquatic ecosystem, affecting aquatic habitat (Olomukoro and Ezemonye, 2011) and fish, the main component of the diet , affect the chain leading to man (Mason, 1996). Human activities such as industrialization, urbanization and agriculture discharge effluents into water systems either directly or through runoff, leaching or infiltration (Ezemonye and Kadiri, 2000). Heavy metals and organic compounds can bioaccumulate in aquatic life (USEPA, 1991) and biomagnify in food chains.

Aquatic ecosystems receive continuously increasing concentrations of heavy metals, with anthropogenic sources identified as the main sources of heavy metal contamination in aquatic systems (Linnikand Zubenko, 2000; Farkas, 2000; WHO, 2000). In fish, gills are considered to be the dominant site for pollutant uptake due to their anatomical and physiological properties that maximize absorption efficiency from the water (Tawari-Fufeyin and Ekaye, 2007). Sediments are important sinks for various pollutants such as pesticides and herbicides, while heavy metals in surface water can exist as simple hydrated ions, as well as inorganic and organic complexes (Linnila, 2000; Rashed, 2001). This study focuses on the effects of lead, zinc and nickel on selected fish species.

2.3.1 Lead (Pb)

Lead is of particular concern because of its toxicity and ability to bioaccumulate in aquatic ecosystems, as well as its persistence in the natural environment (Miller et al., 2002; Animet al., 2010). Lead is known to accumulate in fish tissues such as bones, gills, liver, kidneys and scales, while gas exchange via the gills into the bloodstream is reported to be the main uptake mechanism (Oguzie, 2003; Tawari-Fufeyin and Ekaye, 2007).). Because fish can bioaccumulate metals over a long period of time, the level of metal ions at any given time may not give accurate information about the concentration at that particular time.

Various studies on the effects of heavy metals on fish have been conducted in African rivers. Lead levels measured in the Ogba, Warri and Ikpoba rivers were below the WHO and FEPA standard limit of 2.0 mg/kg for edible fish, meaning these river fish were safe to consume in terms of Pb contamination (Oguzie, 2003; Obasohan, 2008). High concentrations in fish above 2.0 mg/kg during the dry season have been attributed to the high water temperatures associated with the dry season (Obasohan, 2008). Higher temperatures can result in higher rates of activity and aeration in fish and tend to decrease blood oxygen affinity and thus increase the rate of contaminant accumulation (Nussey et al., 2000; Obasohan, 2008). Higher temperature could also lead to higher metabolic rates, which could lead to more food intake and thus increased metal concentration if the metals are taken up through the food chain (Nussey et al., 2000). Mean Pb levels in sediments from the Tyume River have been reported to range from 0.040.005 to 0.067.003 mg/kg, and Pb in sediments from the Nile River showed a wide range from 3.1 to 76.9 mg/kg, the was higher than the allowable limit of 35 mg/kg, meaning the Nile was polluted and needed constant monitoring and assessment (Awofolu et al., 2005; WHO, 2008; Alaa and Osman, 2010).

Elevated Pb concentrations could adversely affect aquatic ecosystem health directly and humans indirectly. The sediments could be a contributing source of these heavy metals in the water, so continuous assessment was extremely important (Awofolu et al., 2005). Agatha (2010) also recorded mean Pb levels of 9.43 mg/kg from the Forcados River in sediment samples, below the WHO recommended limit of 35 mg/kg. Decreasing concentrations of Pb metal away from the point of pollution were recorded, which was attributed to the dilution effect by runoff or stormwater, releasing a large fraction of the heavy metals in sediments back into the aquatic compartment during the remobilization process (Kar et al., 2008; ztrk et al ., 2009; Agatha, 2010). Studies from the Ikpoba River showed a mean Pb concentration of 0.035 mg/l in the water, and mean Pb concentrations of 0.1 mg/l were also obtained from the Nairobi River, which exceeds the WHO (WHO, 2003) exceeded the recommended limit of 0.01 mg/l for drinking water ; Kithiia, 2006; Oguzie and Izevbigie, 2009).

2.3.2 Impact of Lead (Pb) on fish

According to Mason (1996), lead residues are rich in heavy metals, which leads to significant contamination of freshwater systems. Lead is mainly released into the environment through car tailpipes as it is contained in petrol (Nsofor et al., 2007). Fish bioaccumulate lead through various organs including gills, stomach, liver and intestines. Lead is a highly toxic metal in the aquatic environment (Lee et al., 2019). Fish are at the top of the food chain in most aquatic environments and are the most susceptible to the toxic effects of Pb exposure. In addition, fish are one of the most abundant vertebrates and can directly affect humans through food intake. Therefore, fish can be used to assess the level of pollution in an aquatic environment.

Pb-induced toxicity in fish exposed to toxins is mainly induced by bioaccumulation in specific tissues, and mechanisms of accumulation vary with aquatic habitat (freshwater or marine water) and route (aquatic or dietary exposure). Pb accumulation in fish tissues causes oxidative stress due to excessive ROS production (Lee et al., 2019). Oxidative stress from Pb exposure induces synaptic damage and neurotransmitter dysfunction in fish as neurotoxicity. In addition, as an immunotoxic agent, Pb exposure affects immune responses in fish. Olaifa and Lewis (2003) assessed the toxic stress of lead on Clarias gariepinus. Toxic exposure to lead in fish was tested using a 96-hour bioassay. Lead in the form of lead chloride was used to prepare the stock solution. The lead concentrations used for the experiment were 0, 1.8, 3.2 and 5.6 and 10.0 mg/l. The lethal concentration (LC50) was estimated using the logarithmic method and was 0.6, 0.58, and 0.62 mg/l for replicates 1, 2, and 3, respectively. Therefore, the purpose of this study is to determine the levels of heavy metals, Pb contained in fish (Clarias gariepinus and Nile tilapia) from the Yellow Jacket River.

2.3.3 Nickel (Ni)

The toxicity of nickel is generally low, but elevated concentrations have been reported to have sublethal effects (Nussey et al., 2000). It is known that fish accumulate Ni in various tissues when exposed to increased concentrations in their environment (Nussey et al., 2000; Obasohan and Oronsaye, 2004). Studies on heavy metal concentrations in fish from the Dhaleswari and Buriganga rivers in Bangladesh found mean concentrations of 9.55 to 13.35 mg/kg and 0.09 to 0.48 mg/kg, respectively (Ahmad et al., 2009; Ahmed et al., 2009b). Other results from the Ikpoba River showed a mean Ni concentration of 0.02 mg/kg in the gills of chrysichthys nigrodigitatus in the rainy season, which posed no immediate danger as it was below the levels recommended by the Food for Fish and Fishery Products of 0.4 mg/kg fell and United Nations Agricultural Organization (FAO, 1984; Oguzie and Izevbigie, 2009).

Studies in river water have revealed different Ni concentrations compared to the WHO recommended limit of 0.07 mg/l Ni in drinking water (WHO, 2003; Awofolu et al., 2005; Wachira, 2007). Awofolu et al. (2005) determined mean Ni values in water ranging from 0.201 to 1.777 mg/l of the Tyume River. Mean nickel values of 0.03 mg/l were measured in the Nairobi River (Wachira, 2007). Awofolu et al., (2005) suggested that possible sources of Ni in surface water include anthropogenic activities, fossil fuel burning, waste battery waste, car parts, old coins and many other items containing stainless steel and other Ni alloys. Elevated Ni concentrations in the Tyume River water could be a contributing source to the concentrations in irrigated vegetables, so continuous assessment was extremely important (Awofolu et al., 2005). Wachira (2007) concluded that the water of the Nairobi River is not unsafe for human consumption as far as Ni is concerned.

2.3.4 Impact of Nickel on fish

Al-Ghanim (2011) investigated the influence of nickel (Ni) on hematological parameters and behavioral changes in Cyprinus carpio. The fish were exposed to nickel for 96 hours and the influence of nickel on haematological parameters and behavior was examined. The fish were administered different doses (0, 6, 9, 12, 15 and 18 (mg/l)) of nickel sulphate following a normal screening process. The results showed that with increasing nickel concentrations, the mortality rate of the experimental fish decreased. Using the logarithmic method and the dose-mortality regression line y = 188.224x, the 96-hour mean lethal concentration (96-hour LC50) was 12.44 mg Ni /L The dissolved oxygen concentration decreased with increasing Ni amount, resulting in a value of -86.52 (Al-Ghanim, 2011).

Furthermore, Ololade and Oginni (2010) evaluated the effects of nickel on the behavior and some blood parameters of African catfish to determine the safe concentration effect on the fish's metallophysiological functions. The mortality rate increased with increasing concentrations of toxins. The 96-h median lethal concentration (96-h LC50) was 8.87 mg Ni/L using the logarithmic method with dose-mortality regression line Y (% mortality) = 174.74 (log concentration) - 97.711. All blood parameters (erythrocytes, leukocytes, hematocrit and hemoglobin count) decreased with increasing toxicant concentration and became significantly lower at higher concentration compared to control ($P < 0.05$). The derived hematological indices mean corpuscular volume (MCV), mean corpuscular hemoglobin (MCH) and mean corpuscular hemoglobin concentration (MCHC) were equally reduced. It is believed that the observed reductions in hematocrit and hemoglobin levels, together with reduced and deformed erythrocytes, are obvious signs of anemia. The observed changes indicated that hematological parameters can be used as an indicator of Ni-related stress in fish exposed to elevated Ni concentrations (Ololade and Oginni, 2010).

2.3.5 Zinc (Zn)

Zinc, an essential element, is one of the most common heavy metal contaminants of river waters (Kori-Siakpere et al., 2008). Zinc is an essential element that acts as a structural component and has properties necessary for life (Bengari and Patil, 1986; Murugan et al., 2008). The sources of zinc and other heavy metals in natural waters can be from geological rock weathering or from human activities such as industrial and domestic effluents and animals, where it has a constituent function in maintaining cytoplasmic integrity (Weatherly et al., 1980; Kori- Siakpere et al., 2008). Since zinc is an unnatural substance, it can remain undecomposed for years. Zinc is toxic to fish and macroinvertebrates at sublethal concentrations (Folorunsho and Oronsaye, 1990; Ajiwe et al., 2000; Nsofor et al., 2007). Although zinc is an essential element (Dimari et al., 2008), it is a potential toxicant for fish (Everall et al., 1989; Murugan et al., 2008) with adverse effects. Liver and kidney are the main sites of zinc accumulation (Murugan et al., 2008). Zinc toxicity is the result of excessive absorption that suppresses copper and iron absorption, while free Zn2+ ion in solution is highly toxic to plants, invertebrates and even fish (FAO/WHO, 2011).

2.3.6 Impact of Zinc (Zn) on fish

Mean zinc levels in fish were measured in various rivers, which were below the recommended limit of 75 mg/kg for fish and fish products. In Egyptian Nile sediments, zinc concentrations of 91.5 to 307 mg/kg were measured during the dry season. 34.61 mg/kg from Forcados River sediments and 126.33-307.00 mg/kg from Nairobi River sediments were obtained, some of which posed no immediate threat to aquatic fauna and humans (Kage, 2003; Alaa and Osman, 2010; Agatha, 2010). A concentration of 0.60 mg/kg zinc from the Nairobi River was found to be below the recommended limit of 123 mg/kg for Zn in sediment (Wachira, 2007). However, constant monitoring of contamination levels to assess the impact of heavy metals in the aquatic system has been recommended (Wachira 2007; Agatha, 2010).

Zinc levels in rivers flowing through industrial or mining areas can be as high as 20 mg/L, while soils contaminated with zinc from mining of zinciferous ores, refining, or use of zinciferous sludge as fertilizer may contain several grams of zinc per kilogram of dry soil (Emsley, 2001). A higher mean zinc content of 76.25 mg/l than the recommended limit of 3 mg/l was measured in the Forcados River, while lower mean values of 0.085 mg/l during the dry season and 0.716 mg/l during the wet season were found in the river's water Gangas and 1.0 mg/l from the water of the Nairobi Rivers were recorded (WHO, 2003; Kithiia, 2006; Kar et al., 2008; Agatha, 2010). This level has been attributed to land use activities such as the farming system and runoff from residential and industrial areas. A decrease in water pollutants downstream was observed and attributed to the dilution effect and self-cleaning. Constant monitoring of contamination levels to assess the impact of the heavy metal on the aquatic system and the use of riverine vegetation has been recommended as a useful means of absorbing heavy metals as a means of purification (Kithiia, 2006; Agatha, 2010).

CHAPTER 3

METHODOLOGY

3.1 Study Area

This study was conducted on the Yellow Jacket River in Mazowe, Mashonaland Central Province, Zimbabwe. The Yellow Jacket River flows north through the Iron Duke Mine (IDM). The mine complex itself is to the south, the landfill (Tailings Dam) and evaporation ponds to the north. Pond 1 is for mine complex effluent, ponds 2 and 3 (now defunct) were used for underground mine effluent, and northern ponds 4 and 5 are new ponds replacing ponds 2 and 3 (Smith and Williams, 2000). . The area is part of Zimbabwe's Highveld and receives an average rainfall of 800 to 1 000 mm/a, which usually falls between November and April (Chizvondo, 2007). Average daily temperatures range from 15°C in winter to 30°C in summer (Gratwicke, 1999).

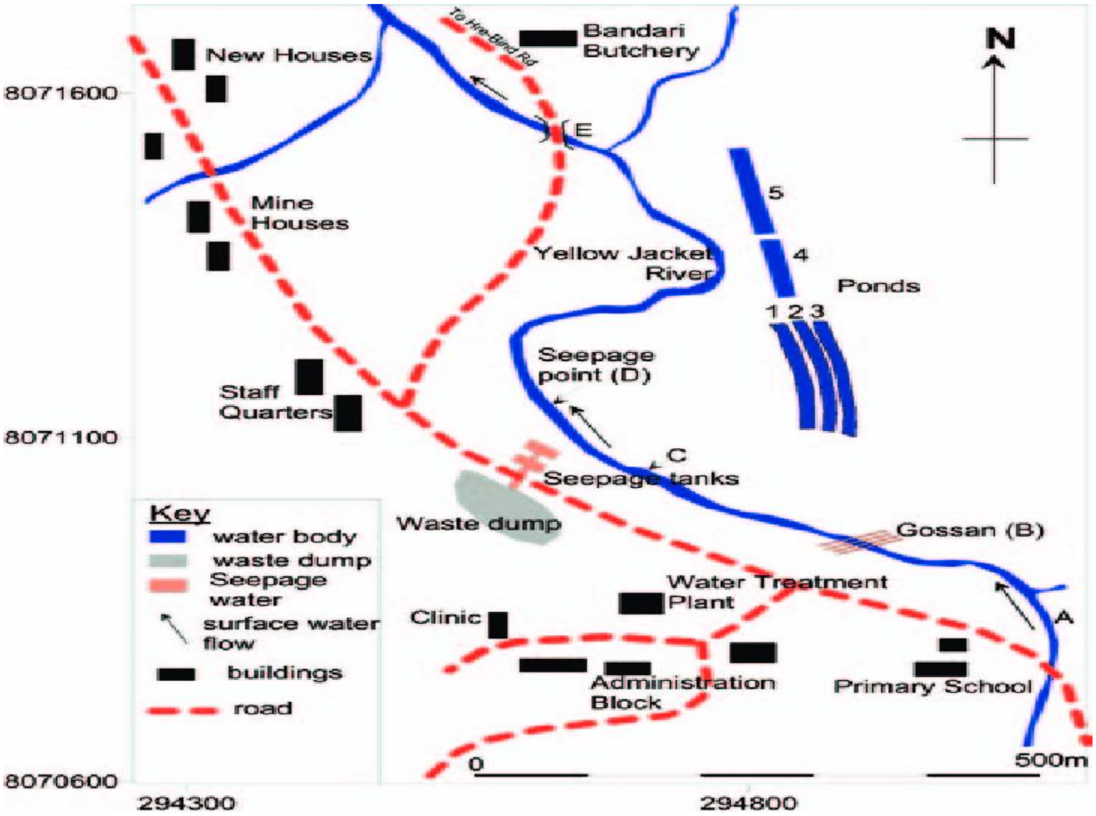

Figure 3.1: Surface Plan of Iron Duke Mine Infrastructure in Relation to the Yellow Jacket River (Source: Ravengai et al., 2005)

The IDM was opened in 1914 as a gold mine. Quarrying of iron pyrites began around 1940. The quarrying process also generates large amounts of waste, which in the past has been dumped as rock piles and landfill (Tailings Dam). In the past, the acid, which came from both underground workings and surface rock dumps, was discharged into the Yellow Jacket River as the mine had an exemption from the Zimbabwe Ministry of Water Development to discharge 170 m3/d effluent with a pH of 1 underground mine (Gratwicke, 1999). This permit expired in 1990 and the mine subsequently constructed evaporation ponds into which the effluent is pumped and evaporated (Gratwicke, 1999). The study area is located in the economically productive Harare-Bindura-Shamva greenstone belt (Vinyu et al., 1996) with extensive gold mining and agricultural activities. Mine effluent from the Iron Duke mine is believed to be the primary contributor to heavy metal contamination of the Yellow Jacket River

3.2 Materials

Sharp blade; 10 glass petri dishes; 10 conical flasks; 10 * 50ml volumetric flasks

Heraeus oven; Mellerware kitchen blender; Adam electronic scale; 10ml measuring cylinder

Concentrated sulphuric acid (H_2SO_4); concentrated nitric acid (HNO_3); Distilled water;

Hydrogen peroxide (H_2O_2). Larger hot plate; Fish: 8 Oreochromis Niloticus (Nile tilapia) and 12 Clarias Gariepinus (Cat fish)

3.3 Sampling and Sample Preparation

The fish samples of fresh 8 *Oreochromis niloticus* (Nile tilapia) and 12 *Clarias gariepinus* (Catfish), were bought from fishermen at the Yellow Jacket River. The samples were labelled accordingly, packed in clean zipped polythene plastics and transported to the SDRC laboratory in an ice chest. Upon arrival, fish samples were stored in the laboratory freezer prior to analysis. Fish tissues (muscle dorsal) where cut using a sharp blade and put into glass petri dishes. Then the samples were dried in a Heareus oven (UK) at 110 ^{o}C to a constant weight. After that they were ground to powder form using a Mellerware kitchen blender and packed into small zip lock bags.

3.4 Sample Digestion

i. Before analysis, all glassware was previously soaked in dilute nitric acid for 24 hours and rinsed in distilled water.
ii. 5 g of the dried sample was weighed into a conical flask using an Adam scale.
iii. Then 5ml of HNO_3 and 5ml H_2SO_4 (Merck, Germany) were added to the sample.
iv. When the sample has stopped reacting with the acids, place flask on the hot and heat at 60^{o}C for 30 minutes. Allow beaker to cool.
v. Then 10ml of HNO_3 (Merck, Germany) were added before returning to hot plate and heating slowly and gradually increasing temperature to 150 ^{o}C until the samples turn black.
vi. The samples were removed from hot place and allowed to cool.
vii. Then H_2O_2 (Merck, Germany) was added until the sample is clear.
viii. Lastly the contents were transferred into a 50ml volumetric flask and diluted to the mark using distilled water.

ix. Standards for Zn, Ni and Pb (Merck, Germany) of 1ppm, 3 ppm, 5 ppm were prepared for analysis using AAS GBC, Australia. All steps were performed in a fume hood.

x. The samples were analyzed using AAS and results recorded.

3.5 Statistical Analysis

The data obtained in this study were statistically analyzed using a Statistical Package for Social Sciences (SPSSv.26) (Descriptive Statistics) for comparing the different mean concentration values of the three heavy metals (Zinc, Nickel and Lead) tested in two fish species (Clarias gariepinus/Catfish and Oreochromis niloticus/Nile Tilapia)) from the Yellow Jacket River.

CHAPTER FOUR

RESULTS

4.1 Concentration of Heavy Metals in Oreochromis niloticus (Nile Tilapia)

The concentrations of heavy metals in *Oreochromis niloticus* (Nile tilapia) were tested using AAS for heavy metals and minerals test.

4.1.1 Zinc (Zn)

The results show that for Nile tilapia fish samples, the highest zinc concentration was observed in sample 4 (0.90 ppm), followed by sample 7 (0.89 ppm) and sample 6 (0.88 ppm), respectively. The lowest concentration was observed in sample 2 (0.64 ppm). The results of this study show that the zinc concentration in the Nile tilapia samples ranged from 0.64 ppm to 0.90 ppm as shown in Appendix 1.

4.1.2 Nickel (Ni)

The results of this study show that in Nile tilapia fish samples, the highest concentration of nickel was observed in sample 5 (0.76 ppm), followed by sample 7 (0.71 ppm) and sample 8 (0.66 ppm). The lowest concentration was observed in sample 1 (<0.01 ppm). In addition, the results of this study show that the concentration of nickel in Nile tilapia fish samples ranged from <0.01 ppm to 0.76 ppm.

4.1.3 Lead (Pb)

The results of the study showed that in Nile tilapia fish samples, the maximum concentration of lead was observed in sample 4 (1.17 ppm), followed by sample 5 (1.11 ppm) and sample 7 (1.06 ppm), while the minimum concentrations were recorded in samples 3 (0.88 ppm) and 6 (0.88 ppm). Lead concentrations in Nile tilapia are shown to range from 0.88 ppm to 1.17 ppm.

The table below, indicates the descriptive statistics showing the mean concentrations of heavy metals in Oreochromis niloticus (Nile Tilapia).

Table 4.1:Mean Concentrations of Heavy Metals in Oreochromis niloticus (ppm)

Metal	Zinc	Nickel	Lead
Mean Concentration (ppm)	0.7989	0.3866	1.0046
Std. Deviation	0.9204	0.2824	0.11014

4.2 Concentration of Heavy Metals in Clarias gariepinus (Catfish)

The concentrations of heavy metals in Clarias gariepinus (Catfish) were tested using AAS for the Heavy Metals and Minerals Test.

4.2.1 Zinc (Zn)

The results of this study showed that the highest zinc concentration in catfish was observed in sample 7 (0.75 ppm), followed by sample 11 (0.73 ppm) and sample 4 (0.72 ppm). The results also show that the lowest zinc concentration in catfish samples was observed in sample 12 (0.58 ppm). The results further show that the zinc concentration in catfish samples ranges from 0.58 ppm to 0.75 ppm as shown in Appendix 3.

4.2.2 Nickel (Ni)

In terms of nickel concentrations in catfish samples, the study results show that Sample 3 (0.38 ppm) had the highest concentration, followed by Samples 8 and 9 each (0.35 ppm). Minimum nickel concentrations in catfish were observed in samples 1 and 2 with concentrations of (<0.01 ppm) each. Study results have shown that nickel concentrations in catfish samples range from 0.00 ppm to 0.38 ppm.

4.2.3 Lead (Pb)

The results of the study show that for lead, the maximum concentration values were observed in sample 11 (1.10 ppm) followed by sample 12 (1.04 ppm), while the minimum concentrations were observed in samples 1 (<0.01 ppm) and 2 (<0.01ppm). The study also indicates that lead concentrations in catfish samples range from 0.00 ppm to 1.10 ppm.

The table below indicates the descriptive statistics showing the mean concentrations of heavy metals in Clarias gariepinus (Catfish).

Table 4.2: Mean Concentrations of Heavy Metals in Clarias gariepinus (ppm)

Metal	Zinc	Nickel	Lead
Mean Concentration (ppm)	0.7695	0.2500	0.8421
Std. Deviation	0.4500	0.12734	0.39523

CHAPTER FIVE

DISCUSSION

The study highlighted zinc, nickel and lead pollution in Yellow Jacket River fish. It provides an average concentration each heavy metal in two fish species under study. It was indicated that on average, the concentration of Zinc in Oreochromis niloticus was (Mean=0.7989ppm) while in Clarias gariepinus was (Mean=0.7695ppm). According to the Egyptian Chemical Standards, the maximum permissible limits of heavy metal in fish or surface water are 5.0ppm for Zinc. Hence, in this study it is shown that the mean concentrations of Zinc in both Clarias gariepinus and Oreochromis niloticus samples were greater than the acceptable limit for consumption by international standards. Eisler (1993), argues that fish can accumulate zinc from their diet as well as from their surrounding water and habitats. However, it is vital to state that, although zinc is an essential element, at high concentrations, it can be toxic to fish, leading to a variety of deleterious effects including mortality, growth retardation and reproductive impairment (Sorenson, 1991). Therefore one is inclined to argue that the findings of this study are a cause for concern, because Clarias gariepinus and Oreochromis niloticus fish constitute a major diet for the communities in Mazowe and they pose a serious threat upon consumption of these species of fish from the Yellow Jacket River.

More so, the mean concentration of Lead in Oreochromis niloticus was (Mean=1.0046ppm) while in Clarias gariepinus was (Mean=0.8421ppm). This indicates that the concentration of Lead (Pb) in both fish species (Oreochromis niloticus and Clarias gariepinus were higher than the acceptable limit for consumption by international standards (FAO, 2003; USFDA, 1993; EC, 2001). Lead concentrations above permissible standards pose a threat to fish and human being as they not only affect the aquatic life but human beings whose diet is also dependent on fish. Therefore one may comment that the fish from the Yellow Jacket River are not recommended for human consumption. In addition to that, the authorities must look into ways of conserving environment particularly the Yellow Jacket River from further accumulation of heavy metals from the mining effluent.

Furthermore, the mean concentration of Nickel was in Oreochromis niloticus was (Mean=0.3866ppm) while in Clarias gariepinus was (Mean=0.2500ppm). According to Baumann and May (1984), nickel mean concentration levels of 0.70ppm in fish is considered potentially harmful to fish and humans that consume them Nickel is a low toxicity element. The nickel content in natural fresh water is 0.001-0.003 ppm (Effendi, 2003); while in marine waters it is between 0.005 and 0.007 ppm. Therefore, to protect the life of fish and humans, the nickel content should not be more than 0.025 ppm (Effendi, 2003). Therefore, one is inclined to conclude that the nickel concentration for Oreochromis niloticus and Clarias gariepinus in the Yellow Jacket River is higher than acceptable standards (FAO, 2003; USFDA, 1993; EC, 2001).

CHAPTER SIX

CONCLUSIONS

6.1 Conclusions

The results of this investigation indicated that the Yellow Jacket River have been polluted by mining effluents from the Iron Duke Mine. This has been evidenced by the presence of heavy metal contamination in Yellow Jacket River fish, which have reached high concentration levels sufficient to render the fish unfit for human consumption. The results of this study also confirm that effluents from mining activities are a significant source of heavy metal pollution. Heavy metals were measured in fish and the mean values of each metal tested were recorded; Nile tilapia (zinc-6.39 ppm; nickel-3.09 ppm; lead-8.04 ppm) while catfish (zinc-0.6795; nickel-0.2500 ppm; lead-0.84210 ppm). These averages exceeded the WHO safe limits for fish because all fish tested had higher metal levels and were unfit for human consumption.

6.2 Implications of the study

The Yellow Jacket River can be considered a dead river based on concentration levels of heavy metals (zinc, nickel, and lead) above allowable standards. Heavy metal pollutants above allowable limits will cause the Yellow Jacket River to cease to perform its ecological functions, rendering it unable to support any life form such as fish and aquatic plants. More so, it is vital to note that heavy metal contamination does not only affects individual aquatic species, but also people who rely on fish as part of their food chain (EMA, 2015).

Heavy metal pollution leads to the disruption of the natural food chain, pollutants such as zinc, lead and nickel are eaten by microorganisms. Later, these animals are consumed by fish, the fish are eaten by humans, and the food chain continues to be broken at all higher levels. Humans are also affected by this process; People can get diseases like hepatitis from eating poisoned seafood. Aquatic ecosystems can be severely altered or destroyed by water pollution. Many areas are now affected by careless human pollution and this pollution is coming back and harming people in many ways.

6 References

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Appendix 1: Heavy Metal Concentration in Oreochromis niloticus (Nile Tilapia)

Fish Species	***Heavy Metal Concentration (ppm)***		
Oreochromis niloticus (Nile tilapia)	**Zinc (Zn)** ***(ppm)***	**Nickel (Ni)** ***(ppm)***	**Lead (Pb)** ***(ppm)***
Sample 1	0.82	<0.01	0.90
Sample 2	0.71	0.24	1.03
Sample 3	0.81	0.19	0.88
Sample 4	0.90	0.24	1.17
Sample 5	0.74	0.76	1.11
Sample 6	0.88	0.29	0.88
Sample 7	0.89	0.71	1.06
Sample 8	0.64	0.66	1.00

Appendix 2: Mean Concentrations of Heavy Metals in Oreochromis niloticus (Nile Tilapia)

Descriptive Statistics

	N	Minimum	Maximum	Sum	Mean	Std. Deviation
Zinc in Oreochromis niloticus	8	.64	.90	6.39	.7989	.09204
Nickel in Oreochromis niloticus	8	.00	.76	3.09	.3866	.28242
Lead in Oreochromis niloticus	8	.88	1.17	8.04	1.0046	.11014
Valid N (listwise)	8					

Appendix 3: Heavy Metal Concentrations in Clarias gariepinus (Catfish)

Fish Species	***Heavy Metal Concentration (ppm)***		
Clarias gariepinus (Cat fish)	**Zinc (Zn) *(ppm)***	**Nickel (Ni) *(ppm)***	**Lead (Pb) *(ppm)***
Sample 1	0.65	<0.01	<0.01
Sample 2	0.65	<0.01	<0.01
Sample 3	0.68	0.38	1.02
Sample 4	0.72	0.29	1.03
Sample 5	0.65	0.30	0.94
Sample 6	0.70	0.20	1.00
Sample 7	0.75	0.32	0.98
Sample 8	0.65	0.35	1.00
Sample 9	0.68	0.35	1.00
Sample 10	0.70	0.23	1.03
Sample 11	0.73	0.32	1.10

Sample 12	0.58	0.26	1.04

Appendix 4: Mean Concentrations of Heavy Metals on Clarias gariepinus(Catfish)

Descriptive Statistics

	N	Minimum	Maximum	Sum	Mean	Std. Deviation
Zinc in Clarias gariepinus	12	.58	.75	8.15	.6795	.04500
Nickel in Clarias gariepinus	12	.00	.38	3.00	.2500	.12734
Lead in Clarias gariepinus	12	.00	1.10	10.11	.8421	.39523
Valid N (listwise)	12					