

BINDURA UNIVERSITY OF SCIENCE EDUCATION
DEPARTMENT OF NATURAL RESOURCES MANAGEMENT

**AN ASSESSMENT OF HEAVY METAL (CD, PB, ZN, FE) CONCENTRATIONS IN
WATER AND SEDIMENTS FROM MAZOWE RIVER.**



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Dedication

This dissertation is dedicated to Maposa family.

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Abstract

The purpose of this study was to determine heavy metal (Pb, Fe, Cd and Zn) concentrations in Mazowe River's water, sediments and their concentrations in the maize plants that were being irrigated using Mazowe River water. Water and sediment samples were collected from the chosen sampling sites and were taken to the laboratory for the analysis of heavy metals using Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES) Plant samples were analysed using Atomic Adsorption Spectrometry machine (AAS). The mean concentrations of Lead in water from site 1, 2, 3 and 4 were 0.015mg/l, 0.01mg/l, 0.01mg/l and 0.0225mg/l, respectively. Zinc concentrations for site 1, 2,3 and 4 were 0.015mg/l, 0.0475mg/l, 0.035mg/l and 0.01mg/l, respectively. Iron concentrations were 6.2775mg/l, 12.89mg/l, 8.8075mg/l, 10.8925 mg/l, respectively. Cadmium concentrations were 0.0175mg/l at all the sites. The mean concentrations of Iron in sediments from site 1, 2, 3 and 4 were 1283.39mg/l, 1375.22mg/l, 1305.81mg/l and 1293.92mg/l respectively. In sediments Lead concentrations from site 1, 2,3 and 4 were 401.25 mg/l, 581.07 mg/l, 519.29mg/l and 50643 mg/l respectively. In maize plants heavy metals (Pb, Zn, Fe and Cd) accumulated more in the roots as compared to other parts of the plant. Concentrations in plant parts were as follows roots>leaves>stem>fruit (cob). All the concentrations from samples taken were above FAO /WHO guidelines of heavy metals in water and food crops. Recommendations from this study include regular assessment of heavy metals at different stages of the plant. Also assessments should be carried out on different season (dry and wet) to determine seasonal variations of heavy metal concentrations in water and sediments. The major factor contributing to the differences in metal concentrations was discussed.

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List of acronyms

Cd	Cadmium
Fe	Iron
IDM	Iron Duke Mine
Pb	Lead
Std-error	Standard Deviation
WHO	World Health Organization
Zn	Zinc

CHAPTER 1

1.0 INTRODUCTION

Rivers serve as a hub for a variety of human endeavours around the world, including mining, fishing, and providing irrigation water for crops. The ecology, hydrology, and the sediment dynamics of the aquatic resources have all been significantly impacted by the extensive contamination of water bodies by heavy metals (Fernandes *et al.*, 2016). Mining operations are one of the major sources of point and non-point water pollution, which severely harms riverine ecosystems and many catchments (Hering *et al.*, 2010). Due to heavy metal contamination, biodiversity has declined in the majority of rivers (Hamilton *et al.*, 2016)

In the United Kingdom (UK), Acid Mine Drainage has been transported as dissolved and associated forms into water bodies, influencing water as well as the quality of sediments in Rivers (Tame *et al.*, 2017). Ecological as well as global public concern has escalated as heavy metals can be transferred, bio-accumulated as well as magnified via the food chain to higher trophic levels, giving critical threats to human health (Valencia-Avellan, 2017). If the concentration of contaminants is very high in food items, species on top levels of the trophic web may be exposed to toxic heavy metals. Humans are more vulnerable to serious health problems due to an increase in heavy metals concentrations in the food chain.

Environmental contamination in Africa portrayed that toxic metal contaminations reached extreme levels (Yabe *et al.*, 2010). It was reported that heavy metals such as lead (Pb) and cadmium (Cd) were observed in aquatic sources across the continent (Yabe *et al.*, 2010). Humans are exposed to the effects of heavy metals through inhalation, dermal contact as well as drinking contaminated water. In Eastern Africa, Lake Victoria of Kenya heavy metal concentrations were as a result of industrial, domestic waste and artisanal gold mining activities that utilise mercury around the lake (Jumba *et al.*, 2007; Yabe *et al.*, 2010).

Also, heavy metal concentrations in soil and irrigation water can contaminate food sources, including fruits, vegetables and fish (Saiful *et al.*, 2015). Human exposure to heavy metals also inflicts extreme health effects such as reduced growth and development, nervous system damage as well as in extreme cases, death. Other reports alluded that the exposure to heavy metals such as mercury and lead may also result in auto-immunity, in which the immune system

of an individual can be a threat to its own cells (Saiful *et al.*, 2015). Subsequently, there is increased development of diseases such as kidney diseases, circulatory system and the nervous system (Saiful *et al.*, 2015).

In Zambia, heavy metal pollution is common in the Copper belt area, where they are transported by water to downstream areas by the Kafue River (Ikenaka *et al.*, 2010). In Zimbabwe, rapid urbanisation and industrialisation have escalated the contamination of water resources by heavy metals (Asaduzzaman *et al.*, 2016). The availability of heavy metals were also noted in Sebakwe River in Kwekwe (Chibanda 2019). Sebakwe River serves as the main fishing source as well as a source of drinking water for people living in the vicinity of the river (Chibanda 2019). The rapid expansion of urban, agricultural as well as industrial activities that releases excessive amounts of contaminated waste to the environment and water bodies (Utete *et al.*, 2018).

Mining activities at Iron Duke Pyrite Mine resulted in the release of heavy metals such as iron, nickel, copper, lead and zinc was reported in the previous studies done in Mazowe River (Ravengai *et al.*, 2004). The poor water quality was associated with an overall decrease in the diversity of aquatic species (i.e. macro-invertebrates and fish) downstream of the Mine until its confluence with the Mazowe River (Ravengai *et al.*, 2004). Pollution of trans- boundary water systems such as Mazowe River that flows into the Zambezi River in Mozambique has higher ecological risks (Yabe *et al.*, 2010). Mining is considered the main source of environmental contamination in Mazowe River. Therefore, this study seeks to assess heavy metal pollution in Mazowe River, Bindura

1.1 Problem statement

There is a threat of heavy metal pollution due to artisanal gold mining along the Mazowe River. Therefore, this study was aimed at assessing heavy metal pollution in water and sediment as well as in maize plants that are irrigated with water from the Mazowe River.

1.2 Justification

Artisanal gold mining continues unabated along the Mazowe River and hence there is need to assess current concentrations of heavy metals in water sediment and maize plants.

1.3 Objectives

1.3.1 Main objective

- To determine heavy metal concentrations (Cd, Pb, Zn, Fe) in water and sediments from the Mazowe river

1.3.2 Specific objectives

- To quantify the concentration of Cd, Pb, Zn, Fe in Mazowe River's water.
- To quantify the concentration of Cd, Pb, Zn, Fe in Mazowe River's sediments.
- To quantify the concentration of Cd, Pb, Zn, Fe in maize plants that are being irrigated with the Mazowe River's water.

CHAPTER 2: LITERATURE REVIEW

2.1 DEFINITION OF HEAVY METALS

Any metallic element with a relatively high density that is dangerous or poisonous, even at low concentrations is considered a heavy metal (Lenntech 2004). Also can be defined as metallic elements with a high atomic weight as well as density that is five times greater than water (Harendra 2017). It also, includes elements lighter than carbon and can exclude some of the heaviest metals (Dzikowitzky et al., 2013). Transition metals, some metalloids, lanthanides as well as actinides are part and parcel of heavy metals (Krika 2018). Other scholars suggested that the bioavailability of heavy metals and their compounds, that is the methods of uptake through cell membranes, intracellular distribution, and binding to cellular macromolecules is a major factor in determining their toxicity. (Hartwig 2008). From the areas which are not mined, metals are released through the natural rock–water interaction processes (Kimball et al., 2002). The oxidation of heavy metals leads to vast concentration in water bodies, for example, the iron mines in Mazowe Sub catchment, when FeS₂ is exposed to Oxygen then water oxidizes to sulphuric acid and ferrous hydroxide (Ravengai et al., 2005)

2.2 Sources and impacts of:

2.2.1 Lead

Lead is a poisonous heavy metal that can accumulate in the human body and inflicts damage to multiple essential organs (Lotfi *et al.*, 2020). Lead comes from batteries and electrical, pigments and paints, fuel, fertilizers, pesticides, refiners, to name but a few. The leaded petrol combustion in motor vehicles as well as automobiles also inflicts a widespread release of lead globally (Fifield and Haines, 2000; Yahya *et al.*, 2018).

Globally, its utilisation has led to environmental pollution, human exposure as well as extreme public health calamities (Lofti *et al.*, 2020). Researches reflected that chronic exposure is associated with health calamities, including anaemia, hypertension in adults, kidney as well as brain destruction in males as well as the formation of cataracts (Fatima *et al.*, 2014).

The availability of low amounts of lead in water (i.e. <0.05mg/l) can result in destruction of nervous system, hearing challenges and learning disabilities in infants as well as young children

(Lotfi *et al.*,2020). Lead usually target organs as well as tissues inclusive of reproductive system, subsequently threatening human life. Extreme levels of toxic metals such as lead (Pb) may be deposited in body tissues and as a result in the brain, may inflict neurological destruction such as depression, anxiety as well as memory loss (Verhaet *et al.*, 2019).

2.2.2 Zinc

Zinc, it is a necessary component of our diet. Too much zinc can also be harmful to your health. Children who are toxic to significant quantities of zinc experience nausea and vomiting. Humans may experience anaemia and cholesterol issues if their zinc levels are too high. The main sources of zinc in the air, soil, and water are mining, metallurgical processing of zinc ores, and its industrial application. Additionally, coal burning produces it (Ravindra *et al.*, 2014)

Zinc exists naturally in the air, water as well as soil, but can be released artificially in large quantities by human activities and reflect human health dangers (Lotfi *et al.*,2020). Heavy metals such as zinc exist as natural constituents of the rocks as well as soils. Soil and sediments have some detrimental heavy metals (i.e. zinc) adsorbed within the structural lattice of crystalline minerals as primary constituent (Yahya *et al.*,2017). They are persistent environmental contaminants in nature since they cannot be destroyed. Industrial processes including mining, coal combustion and waste from the steel industry are the major sources of artificial zinc (Tirkey 2017).Despite zinc being a critical requirement for a health body, excess of it can be detrimental and result in zinc toxicity. Zinc bio accumulates in the wide range of tissues as per different trends of bioaccumulation factors (Fatima and Usani 2013). It was asserted that free zinc ion solution is highly harmful to plants, invertebrates as well as vertebrate fish (Addae 2013).

2.2.3 Cadmium

Cadmium occupies position seven in the priority list of hazardous substances and it generally occurs as an isometric trace element in sphalerite (ATSDR 1999). Heavy metals such as cadmium (Cd), copper (Cu), mercury (Hg), arsenic (As) as well as zinc (Zn) reflected to have potential effects of entering the environment at high concentrations attributed to agricultural activities (Alloway 2013). Cadmium is a toxic element and has harmful effects on aquatic environment as well as human health. Cadmium comes from batteries and electrical, pigments and paints, fuel, fertilizers, pesticides and refiners. Several researches reflected that the

consumption of extremely high quantities of cadmium can inflict lung as well as prostate cancer (Lofti *et al.*, 2020). In Japan, it was noticed that, renal dysfunction as well as bone diseases including Itai-itai may develop due to the accumulation of cadmium (Ravindra *et al.*, 2014).

High concentrations of cadmium have been noted in sewage irrigation water as well as vegetables grown in some regions in India (Omar, 2013). This has led to stones development in the gallbladder. Chromium can also be accumulated in the bodies of animals via the food chain and it potentially inflicts DNA destruction as well as carcinogenic effects attributed to their mutagenic ability. Planktons usually give a critical source of heavy metal concentration in fish the circulatory system, resulting in bio-magnificant (Alsop and Wood, 2011).

2.2.4 Iron

Iron (Fe) has also reflected mutagenic as well as carcinogenic at extremely high concentrations (Peez *et al.*, 2016; Chibanda, 2019). The availability of iron in water is related to its abundance in the earth's crust. The presence of heavy metals in water ecosystems resulted in the contamination of rivers as well as irrigation water (Chibanda 2019). Main sources of heavy metals in aquatic ecosystem emanates from human civilisation as well as other modern technologies. Iron emanates from pigments and paints, fuel, refineries as well as from textile industries.

In Egypt, heavy metal concentrations including iron among others were observed in fish muscles of *Clarias gariepinus* obtained from six areas linked to river Nile (Omar 2013). The aquatic species are exposed to pollutants via direct uptake from the water phase as well as indirect uptake via food or both. Direct uptake of heavy metals by aquatic organisms is affected by pH, conductivity as well as dissolved oxygen in water that may be changed by the entry of waste waters (Chibanda 2019). Biochemical, physiological responses as well as geochemistry of heavy metals are responsible for heavy metal concentrations noted in several populations of aquatic organisms.

2.3 Previous studies of heavy metals in Mazowe River

The study area of Mazowe River lies in the most essential green stone belt which is highly economical and productive accompanied by vast extensive gold mining as well as agricultural activities, (Vinyu *et al.* 1996). Other previous studies of Cd, Pb, Zn, Fe concentrations showed

that seasonal variations of these metals within Yellow Jacket and Mazowe River were also considered (Magadza and Masendu 1986, Gratewicke 1999). The drainage from acute acid mine at the Iron Duke Mine waste dump was also polluting Mazowe and Yellow Jacket river, (Williams and Smith 2000). The results showed that these ponds at IDM were producing acid in large quantities (Ravengai et al 2000c). There is need of managing the impacts of mining operations concerning the quality of both surface and ground water because it is essential for mining operational sustainability (Ashton et al 2001). The waste dump produced AMD that had the pH which is below 0.52 (Williams and Smith 2000). The acid mine drainage which was produced from the waste rock dump was also reported by some of the researchers (Nyamadzawo 2000, Ravengai 2004, Meck et al 2006, Ntengwe and Maseka 2006, Nyamadzawo et al 2008). Iron Duke Pyrite mine (IDPM) discharges highly acidic effluent into evaporation ponds at the mining place, therefore, increasing the presence of heavy metals including iron, nickel, copper, cobalt, lead as well as zinc, (Ravengai et al 2004).

Acidic Mine drainage combined with heavy metal contamination, usually persist for a long period of time and may lead to extreme environmental deterioration if not resolved accordingly (Ashton *et al.*, 2001; Ravengai *et al.*, 2004). Studies revealed that Mazowe water quality deteriorated as a result of heavy metal pollution from Iron Duke Pyrite mine. Mazowe River is directly linked to the Yellow jacket River located in Mashonaland central that is categorised as a dead river because of heavy metal contamination from Iron Duke Mine, (Tazvivinga *et al.* 2012)

Also, the presence of cadmium and copper in Mazowe River was noted. Their concentrations for downstream as well as midstream were exceeding the irrigation standards as per Food and Agriculture Organization of the United Nations (Masunungure and Michael 2018). Scholars further recommended routine monitoring of water quality and determination of heavy metal concentrations in Mazowe River. The pH in the River from the mine ranged from 7.5 upstream to 3.0 downstream, this trend experienced during dry seasons (Nyamadzawo 2007).

CHAPTER 3: METHODOLOGY

3.1 Study site

Mazowe River is one of the most essential freshwater bodies in Zimbabwe located in Bindura in Mashonaland central of Zimbabwe. It rises 14 kilometres north of Harare at an estimated altitude of 530 metres above sea level. Mazowe River flows in a north-easterly direction past Bindura town until its confluence with the Murodzi River 59 kilometres downstream.

3.2 Study area map

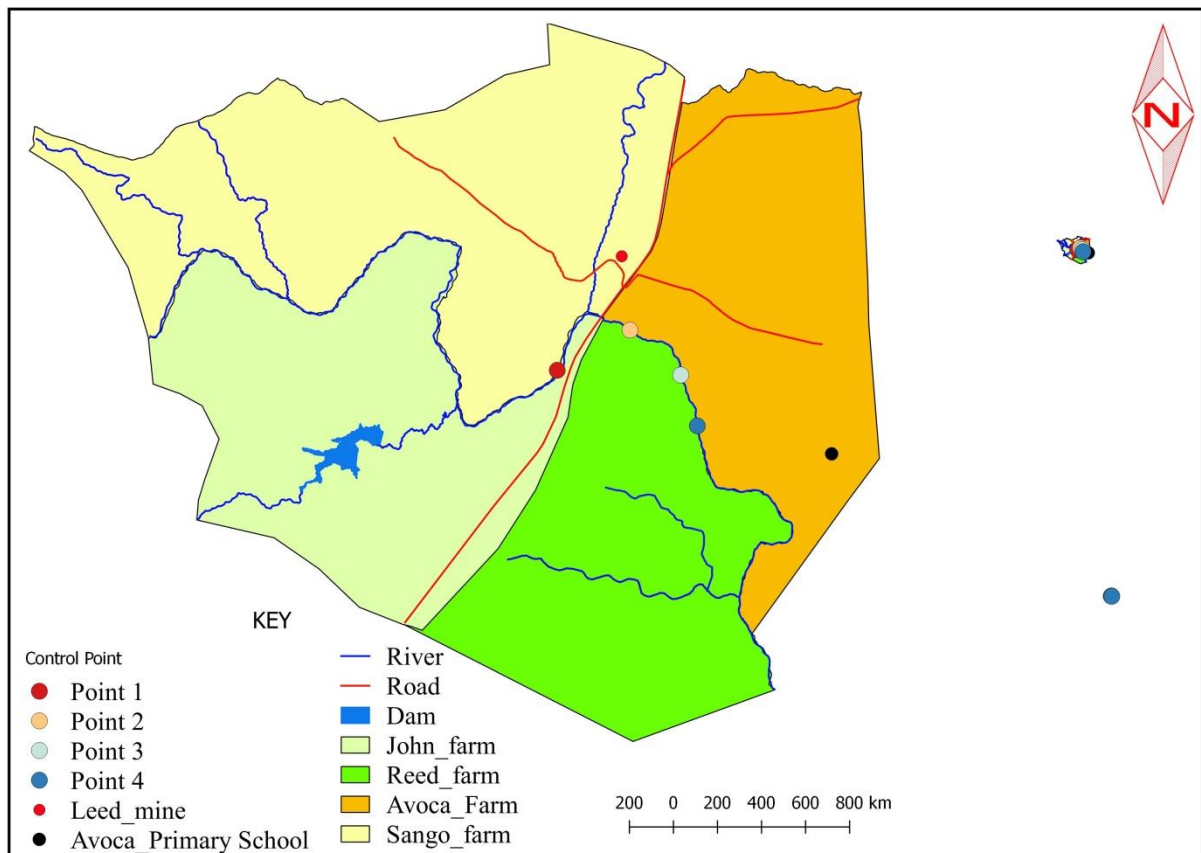


Figure 1: Study area map

3.3 Sampling design

Water and sediment samples were collected from upstream of the mining areas and also on farming areas. A total of four sites were chosen for sampling 2km apart, 2 sites before Mazowe Bridge and the other 2 sites after the Bridge downwards along the stream. The mine is located downstream of the first 2 sampling sites. On each sampling trip, 4 samples were collected at each site. Water samples were collected weekly, for 4 weeks plant samples were collected on

4 farms along Mazowe River. Maize plants were uprooted in KCC area, at 2 sites, namely Johns farm and Sango farm, the third site was at Masawi farm and the fourth one at Shown farm. Maize samples were collected once on the first trip. The plant samples were analysed from the roots, stem, leaves and fruit (cob). The total of 4 plants will be collected per each site. 5 grams of each sample will be used for the analysis. Samples were analysed at Trojan Nickel Mine Laboratory.

3.3.1 Water sampling and analysis

The sample collection bottles were rinsed thrice with river water to avoid sample contamination. At each site, a sample was taken with a pre-acid washed 500ml polypropylene bottle attached to a plastic pole. Sampling bottles were tightly closed soon after sample collection to avoid contamination of samples by surrounding environment. The sampling bottles were labelled immediately after sampling according to the sampling sites to avoid incorrect labeling of the samples. The water samples were stored in a cooler box under 4°C, and were taken to the Laboratory for analysis.

The samples were filtered to remove all suspended solids and to eliminate dissolved pollutants that may interfere with the chemistry of water. 10ml of each sample was transferred into 100ml volumetric flasks. The standard solution was added to the sample by pipette. The solution was then diluted by distilled water to make it 100ml. The sample diluted sample was then mixed to form homogeneous sample prior the analysis.

3.3.2 Sediment sampling and digestion

Sediment samples were collected on the same sites together with water samples. Sediments were put into small plastic bags. In the laboratory, sediment samples were transferred from the plastic bags into the drying pans. Samples were put into the oven overnight to remove all excess moisture. The dried samples were cooled to make them ready for crushing. The sample was grounded to a fine powder using the ring mill to 85% passing 75µm. The sample was then packed into labelled sample packs.

Soon after the samples were crushed, they were taken to the balance room to weigh the required mass for fluxing. The sample was fluxed for it to be soluble in a diluted acid solution. Flux is a substance that is nearly inert at room temperature but which poses a strong reducing property at elevated temperatures and in this case prevents the formation of metal oxides. A mass of

0.25g of all the samples was weighed, 3g sodium peroxide and 0.5g of sodium carbonate and mixed together in zirconium crucibles to decompose through fusion. Fusion was achieved by heating the flux together with the suitable sample amount. The sample was allowed to react in the molten mixture after it has been heated to a temperature above the melting point of the flux. The sample was fused at 650 degrees in a furnace. The melt was leached by adding 50ml of water into a beaker and 10ml of hydrochloric acid was added. The solution was gently heated on the hot plate for about 2 to 3 minutes. After boiling the beaker was placed on a water bath to allow it to cool to room temperature. After cooling the 250ppm of the solution was pipetted into a 250ml volumetric flask. The sample solution was diluted to volume by deionized water. The solution was shaken to homogenise the sample. The sample was analysed using Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES) machine Model 150 Varian.

3.3.3 Plant sample preparation and digestion

Plant samples were uprooted and cleansed the residual materials and other contaminants with clean running water. Plant samples were washed using deionized water for final cleaning. Each plant sample was divided into 4 parts which are the roots, stem, leaves and fruit(cob) and oven dried at 70° for 12 hours (Raymond et al. 2022). It was grounded in a mill prior to further analysis and metal determination. The sample passed through a 1.5mm sieve. A sample of 1g was taken from each part and placed into zirconium crucibles and was put into the oven for 2 hours. The crucibles were then put into beakers and the sample was washed. 0.5ml of nitric acid was added to the sample and placed on a hot plate and was boiled. Samples were allowed to cool. The 10ml of the solution was pipetted into a 250ml volumetric flask. 100ml of hydrochloric acid was added to the sample (Onyedika, et al 2008). The solution was diluted with deionized water to volume. The solution was then analysed for heavy metals (Pb, Fe, Cd and Zn) using Atomic Adsorption Spectrometry (AAS) Perkin-Elmer Model Analyst 400. Atomic Absorption Spectrometry (AAS) is a technique used mostly for quantifying chemical elements available in samples by measuring the absorbed radiation as per individual elements. The obtained results were being compared with FAO \WHO standards to see if they are not exceeding the permissible standards of each heavy metal.

3.4 Standard solution preparation.

The instrument calibration standards were prepared by diluting standard (1000ppm) obtained from Merck for all metals. The stock solution was used to calculate the needed volumes for

concentration of 10, 20, 30, 40 and 50ppm in final volumes of 100ml. The formula below was used:

$$C_1V_1 = C_2V_2$$

Where: C1= standard concentration of 1000ppm

V1= the required volume to be calculated

C2=different concentration of 10, 20, 30, 40 and 50ppm

V2=volumetric flask used (100ml)

After calculating the needed volumes for each metal and pipetting these volumes into 100ml flasks, the flask was filled with deionised water.

3.5 Data analysis

The data was be subjected to Microsoft Excel 2010 for analysis. The heavy metal concentrations will be used to detect the sites with differences in metal concentration. Mean concentrations and standard deviation was calculated using Excel. The obtained information was presented in tables according to each metal and the sites.

CHAPTER 4: RESULTS

Table 1: Mean concentration of Lead in water samples.

Lead	Site 1	2	3	4
Mean(mg/l)	0.015	0.01	0.01	0.0225
Std-error	0.005774	0.005774	0.005774	0.25

In Table 1, the mean Lead concentration was generally similar for sites 1, 2, and 3 but differed from Site 4.

Table 2: mean concentrations of Zinc in water samples

Zinc	Site 1	2	3	4
Mean(mg/l)	0.015	0.0475	0.035	0.01
Std-error	0.005774	0.062383	0.020817	0.005

In Table 2, the mean Zinc concentration was generally similar for sites 1 and 4 but differed from 2 and 3. Site 2 has higher concentration as compared to other sites.

Table 3: mean concentrations of Iron in water samples.

Iron	Site 1	2	3	4
Mean(mg/l)	6.2775	12.89	8.8075	10.8925
Std-error	3.994633	0.746726	0.901457	3.345677

In Table 3, Iron concentration was fluctuating across the sampling sites. Site 1 has the least concentrations followed by site 3, 4 and site 2 has the highest concentration.

Table 4: Mean concentrations of Cadmium in water samples.

Cadmium	Site 1	2	3	4
Mean (mg/l)	0.0175	0.0175	0.0175	0.0175
Std-error	0.005	0.005	0.005	0.005

In Table 4, Cadmium concentrations were generally the same on all sampling sites.

Table 5: mean concentrations of Lead in sediment samples.

Lead	Site1.	Site2	Site3	Site4
Mean mg/l	401.25	581.07	519.29	506.43
Std-error	140.1481	221.61	184.4477	171.294

In Table 5, Lead concentrations varied across the sites with site 2 recorded the highest concentration followed by site 3, 4 and 1.

Table 6: mean concentrations of iron in sediments

Iron	Site 1	Site2	Site3	Site4
Mean mg/l	1283.39	1375.22	1305.81	1293.92
Ste-error	43.59003	53.17707	51.904034	46.1275

In Table 6, Iron concentrations in sediments were generally similar on site 1 and 4 as well as for site 2 and 3.

Table7: mean concentrations and standard error of Cadmium in Mazowe River

Cadmium	site 1	2	3	4
Mean mg/l	1.77	2.01	1.96	1.95
Std-error	0.114	0.266	0.214	0.201

In Table 7, Cadmium concentrations in sediments were the lowest as compared to other metals. The concentrations were slightly different at all sites.

Table 8: Mean concentrations of Zinc in sediments

Zinc	1	2	3	4
Mean mg/l	42.2	54.71	52.58	45.98
Std error	4.897315	18.94321	14.96446	3.675342

In Table 8, Zinc concentrations in sediments were higher on site 2 followed by site 3, 4 and 1.

Table 9: Mean concentrations of Zinc in maize plants

	Farm A	Farm B	Farm C	Farm D
Root	1.21 (0.20)	1.20 (0.21)	1.21(0.22)	1.18(0.21)
Stem	0.27 (0.42)	0.36 (1.32)	0.17(0.11)	0.16(0.09)
Leaves	0.16 (0.99)	0.41 (2.42)	0.38(0.12)	0.28(0.21)
Fruit	0.12 (0.09)	0.26 (0.15)	0.07(0.04)	0.02(0.01)

Note: Values in brackets are standard errors of the mean

In Table 9, Zinc concentrations were similar in roots from farm A, B and C but differed slightly from farm D

Table 10: Mean concentrations of Iron in maize parts

	Farm A	Farm B	Farm C	Farm D
Root	1.05 (0.29)	1.60 (0.210)	2.15(0.02)	1.50(0.21)
Stem	0.12 (0.02)	0.49 (0.07)	0.70(0.11)	0.09(0.09)
Leaves	0.16 (0.11)	1.25 (0.26)	0.85(0.12)	0.28(0.23)
Fruit	0.10 (0.05)	0.26 (0.15)	0.07(0.04)	0.01(0.01)

Note: Values in brackets are standard errors of the mean.

In Table 10, Iron concentrations in maize plant organs slightly differed across the sites

Table 11: Mean concentrations of lead in maize parts

	Farm A	Farm B	Farm C	Farm D
Stem	0.21 (0.04)	0.11 (0.06)	0.52(0.11)	0.62(0.12)
Leaves	0.34 (0.33)	0.45 (0.15)	0.71(0.12)	0.80(0.21)
Fruit	0.18 (0.01)	0.02 (0.005)	0.08(0.04)	0.25(0.01)
Root	1.64(0.50)	1.27(0.39)	1.18 (0.20)	0.98(0.25)

Note: Values in brackets are standard errors of the mean

In Table 11, Lead concentrations in maize plants parts varied from across the farms. Concentrations followed a

Table 12: Cadmium concentrations in maize parts

	Farm A	Farm B	Farm C	Farm D
Root	1.45(0.42)	2.00 (0.23)	1.36(0.17)	1.50(0.26)
Stem	0.20 (0.05)	0.36 (0.28)	0.65(0.11)	0.15(0.09)
Leaves	0. 60(0.08)	0.41 (0.10)	0.90(0.12)	0.18(0.21)
Fruit	0.02 (0.01)	0.26 (0.06)	0.17(0.04)	0.32(0.01)

Note: Values in brackets are standard errors of the mean

In Table 12, Cadmium concentrations in the roots were generally similar for all maize samples collected along Mazowe River.

Bioaccumulation of heavy metals in water is $\frac{\text{Metal concentration in water}}{\text{Metal concentration in sediments}}$

Zinc bio-concentration in water

Site 1	$0.015 / 54.71 = 0.000274$
Site 2	$0.0475 / 54.71 = 0.000868$
Site 3	$0.035 / 52.58 = 0.000666$
Site 4	$0.01 / 45.98 = 0.000217$
Mean	0.000506

Iron bio-concentration factor

Site 1	$6.2775 / 1283.39 = 0.00489$
Site 2	$12.89 / 1375.22 = 0.00937$
Site 3	$8.8075 / 1305.81 = 0.00674$
Site 4	$10.8925 / 1293.92 = 0.00842$
Mean	0.007355

Lead bio-concentration factor

Site 1	$0.015 / 401.25 = 0.0000374$
--------	------------------------------

Site2	$0.01 / 581.07 = 0.0000172$
Site3	$0.01 / 519.29 = 0.0000193$
Site4	$0.0225 / 506.43 = 0.0000444$
Mean	0.0000432

Cadmium Bio-Concentration Factor

Site 1	$0.0175 / 1.77 = 0.00989$
Site 2	$0.0175 / 2.01 = 0.00871$
Site 3	$0.0175 / 1.96 = 0.00893$
Site 4	$0.0175 / 1.95 = 0.00897$
Mean	0.009125

Bioaccumulation factor of maize is calculated as $\frac{\text{Metal concentration in maize part}}{\text{Metal concentration in water}}$

Iron bio- concentration in maize Parts

Farm A roots	$1.05 / 6.2775 = 0.167$
Farm B roots	$1.60 / 12.89 = 0.124$
Farm C roots	$2.15 / 8.8075 = 0.244$
Farm D	$1.50 / 10.8925 = 0.1377$
Mean	0.168175

Farm A stem	$0.12 / 6.2775 = 0.019$
Farm B	$0.49 / 12.89 = 0.038$
Farm C	$0.70 / 8.8075 = 0.0795$
Farm D	$0.09 / 10.8925 = 0.00826$
Mean	0.03619

Farm A leaves	$0.16 / 6.2775 = 0.0255$
Farm B leaves	$1.25 / 12.89 = 0.0970$
Farm C leaves	$0.85 / 8.8075 = 0.0965$

Farm D leaves $0.28 / 10.8925 = 0.0257$

Mean 0.061175

Farm A fruit $0.10 / 6.2775 = 0.0159$

Farm B fruit $0.26 / 12.89 = 0.0202$

Farm C fruit $0.07 / 8.8075 = 0.00795$

Farm D fruit $0.01 / 10.8925 = 0.000918$

Mean 0.0110355

Zinc bio-concentrations in maize parts

Farm A roots $1.21 / 0.015 = 80.667$

Farm B roots $1.20 / 0.0475 = 25.263$

Farm C roots $1.21 / 0.035 = 34.571$

Farm D roots $1.18 / 0.01 = 118$

Mean 35.42025

Farm A stem $0.27 / 0.015 = 18$

Farm B stem $0.36 / 0.0475 = 7.579$

Farm C stem $0.17 / 0.035 = 4.857$

Farm D stem $0.16 / 0.01 = 16$

Mean 11.6135

Farm A leaves $0.16 / 0.015 = 10.667$

Farm B leaves $0.41 / 0.0475 = 8.632$

Farm C leaves $0.38 / 0.035 = 10.857$

Farm D leaves $0.28 / 0.01 = 28$

Mean 14.539

Farm A fruit	$0.12 / 0.015 = 8$
Farm B	$0.26 / 0.045 = 5.778$
Farm C	$0.07 / 0.035 = 2$
Farm D	$0.02 / 0.01 = 2$
Mean	4.4445

Lead bio-concentration in maize parts

Farm A roots	$1.64 / 0.015 = 10.93$
Farm B roots	$1.27 / 0.01 = 127$
Farm C roots	$1.18 / 0.01 = 118$
Farm D roots	$0.98 / 0.0225 = 43.556$
Mean	14.234

Farm A stem	$0.21 / 0.015 = 14$
Farm B stem	$0.11 / 0.01 = 11$
Farm C stem	$0.52 / 0.01 = 52$
Farm D stem	$0.62 / 0.0225 = 27.556$
Mean	26.139

Farm A leaves	$0.34 / 0.015 = 22.667$
Farm B	$0.45 / 0.01 = 45$
Farm C	$0.71 / 0.01 = 71$
Farm D	$0.80 / 0.0225 = 35.556$
Mean	43.55575

Farm A fruit	$0.18 / 0.015 = 12$
Farm B	$0.02 / 0.01 = 2$
Farm C	$0.08 / 0.01 = 8$
Farm D	$0.25 / 0.0225 = 11.11$
Mean	8.2775

Cadmium bio-concentration in maize parts

Farm A roots	$1.45 / 0.0175 = 82.8571$
Farm B	$2 / 0.0175 = 114.286$
Farm C	$1.36 / 0.0175 = 77.714$
Farm D	$1.50 / 0.0175 = 85.714$
Mean	90.14275

Farm A stem	$0.20 / 0.0175 = 14.429$
Farm B	$0.36 / 0.0175 = 20.571$
Farm C	$0.65 / 0.0175 = 37.143$
Farm D	$0.15 / 0.0175 = 8.571$
Mean	20.1785

Farm A Leaves	$0.60 / 0.0175 = 34.286$
Farm B	$0.41 / 0.0175 = 23.429$
Farm C	$0.90 / 0.0175 = 51.429$
Farm D	$0.18 / 0.0175 = 10.286$
Mean	29.8575

Farm A fruit	$0.02 / 0.0175 = 1.143$
Farm B	$0.26 / 0.0175 = 14.857$
Farm C	$0.17 / 0.0175 = 9.714$
Farm D	$0.32 / 0.0175 = 18.286$
Mean	11

CHAPTER 5: DISCUSSION

Because of their human toxicity and bioaccumulative effect, heavy metal contamination in rivers and lakes is of a great concern in any ecosystem, particularly in wetlands and water masses. Heavy metal pollution Mazowe River is of particular concern in this regard due to its economic and domestic uses in households near Mazowe River. The results from the study indicated that heavy metals concentrations in sediments were higher than those in plant and water samples. This study shows a higher concentration at site two as compared to the other three sites and this may be attributed to the impacts of artisanal mining operations along the river.

5.1.1 Lead concentration in water

Table 1 shows the mean concentration of lead in water samples collected downstream the river shows that there was a significant difference in the lead quantities at all the sites during the study period. The highest concentration was recorded on week 4 as compared to other weeks. The highest concentration was 0.0225mg/l which is lower than WHO permissible limits of 0.1mg/l (WHO 2017). This shows that there was no point source pollution of lead on the sampling sites under the period of study. Also, there was not discharge of lead contaminants into the stream. The concentration followed the sequence site 4 > site3 > site1 and site. A slight increase in lead quantities might be as a result of a slight lead pollution along the river. However, lead has potential effects even if in its lowest quantities. People who are living near Mazowe River are being exposed to the effects of lead because they use this water for domestic purposes. When lead is ingested it has a higher risk of cancer and brain damage.

Lead levels from the three sampling sites (boreholes) that drains water from Yellow Jacket River was high with the minimum of 0.49mg/l (Gratwicke et al 2005). These levels were above WHO and (MRRWD 2000).

5.1.2Cadmium concentration in water samples

The concentrations of Cadmium were the low on all the sites as compared to other heavy metals analysed during the study. The results were same and this can be as a result of low Cadmium content in the parent rock along Mazowe River. The concentration was within the range of WHO guidelines.

5.1.3 Lead concentration in water samples

This study shows that lead concentration was constant at all the sampling sites. The concentration is 0.0175mg/l and the WHO maximum permissible limit is 0.01mg/l in drinking water (WHO 2007). Some of the studies done on Mazowe valley in Yellow Jacket river shows that Cd levels were 3.7mg/l and it was as a result of Acid Mine Drainage (Nyamadzawo et al., 2007). Also, other passive bio-monitoring of Mazowe and Yellow Jacket river was done in 2011 and the Cd levels were ranging from 0.01 to 0.51 mg/l (Tazvizinnga et al., 2012). This shows that upstream of Mazowe River is heavily polluted.

5.1.3 Zinc concentration in water samples

Zinc concentrations in water samples were generally similar across all the sampling sites. The lowest levels of Zinc concentrations can be attributed to the absence of Zinc in the chemicals used for ore processing along Mazowe River. Also, it might be as a result of metals sinking into the sediments leaving small quantities in water.

5.1.4 Iron concentrations in water samples

The mean concentration for Fe 6.2775mg/l to 12.89mg/l were extremely above the WHO standards. The permissible limit for iron in drinking water is 0.3mg/l. These results were higher as compared to other previous studies done in other rivers. Other water bodies that were assessed for heavy metal concentration recorded Fe concentration that ranges from 0.4 to 2.37mg/l in Mushambanyama River (Shamva) and were slightly higher than WHO standards.

5.2 Heavy metals in sediments

The concentrations were high in sediment samples maybe due to point source solution and the pollutants sink into the river sediments. Studies done about heavy metal concentration in the Yellow jacket River shows that, the stream directly discharges water into the Mazowe River (Nyamadzawo 2007). Iron concentration in sediments was higher at site 3 with the mean range of 1375.22 followed by site 1 with 1305.81 followed by site 2 with 1293.92 and site 4 with 1283.39. Heavy metals concentrations in sediments can be attributed to different causes. Sediments serve sink of heavy metals. Also, the chemical composition, grain size and total organic matter influence the concentrations of heavy metals in sediments (Hazrat et al., 2019).

The concentrations were higher in sediment samples maybe due to the point source solution and the pollutants that sink into the river sediments. Studies that were previously done about heavy metal concentrations in Yellow jacket River shows that, the stream directly discharges its water into the Mazowe River (Nyamadzawo 2007). Heavy metals concentrations across all the sampling sites in sediments as compared to water samples, this might be as a result of sediments being sink of heavy metals (Hazret et., al 2019). Also, the chemical composition, grain size and total organic matter in sediments influences the concentrations of heavy metals (Hazrat et., al 2019)

Heavy metals concentrations in sediments were higher as compared those in water and this can be attributed to the presence of dead plants which absorbed heavy metals in the past and now releasing it back into the sediments. There are other natural factors that might be attributed to the increase in heavy metals concentrations in sediments as compared to those in water. Iron had highest concentrations at all sites because it is naturally found in the environment (Halli, 2014). Lead contamination can be attributed to urban pollution by runoff and lead recycling plant disposal. Also, it can be as a result of traffic related sources (Mukai et al., 1994). Cadmium concentrations in Mazowe river sediments were very low followed by zinc concentrations on this study. Other studies done in Rivers showed that Cadmium has the lowest concentration levels for example, studies done in Pristine River (Meybeck 2013). The levels of Cd on this study were also low, this can be as a result of absence of cadmium in the parent rock. In addition, other studies were undertaken to understand the major sources, transfers and state of heavy metal contamination for example River Seine basin (Meybeck et al., 2007, Thevenot et al., 2007). Heavy metals in sediments were as follows $Fe > Pb > Zn > Cd$

5.3 Heavy metals concentration in maize plant tissues

Heavy metals accumulated differently in different parts of the maize plant (*zea mays*). The highest concentration was found in the roots because they are the ones that absorb metals from the soil (Delbari and kulkarni 2001). These concentrations can be as a result of phytoextraction of metals by plants. The maize plant is capable of continuous phytoextraction of metals from contaminated soils by translocating them from the roots to the shoots (Nascimento and Xing, 2006). Maize plants are capable of phytoremediation. Phytoremediation is the process of using green plants to remove pollutants from the environment to make them less harmful (Raskin, 1997, Weller, 2000). Contaminated irrigation water by heavy metals from artisanal mining operations in Mazowe River can be the major source of heavy metals concentrations in field crops.

Translocation of metals takes place in different parts of the plant. These metals have effects on the growth and development of the plant if excessively absorbed (Gupta et al. 2019). The lowest concentrations were identified in the fruit because it is the last part to develop on the plant heavy metals accumulates less as compared to other plant organs. Heavy metals concentration in maize plants analysis that was done on the period of study was presented on table 9 to table 12. The concentration was higher than the permissible limits except for Zn. The standard error for heavy metals concentrations are presented in the same tables with mean in brackets. The concentration of zinc in maize fruit (cobs) from different farms are as follows farm D > C > A and B. The concentration varied from 0.16 to 0.60 and it was above the WHO and FAO permissible limits of zinc in crops. Cadmium levels were slightly above the permissible limits of 0.01ppm (WHO 2011). The difference in heavy metals uptake from the selected sites can be related to textural classes and soil Ph of the farms (Stevenson 1992) concentration. These metals concentrations are of a major concern because people and livestock are being exposed to it when they consume the maize products. WHO and FAO standards for heavy metals in maize plant are as follows Fe 0.5mg/kg, Zn 3mg/kg, cd 0.1mg/kg and Pb 0.2mg/kg (FAO/WHO 2002, 2011). Other studies done on plants grown along Nairobi River shows that accumulation of Zn and Cd levels were moderately elevated (Owiti 2015). Heavy metals distributions in plants are influenced by plant species, metal species and soil features (Yoon, Cao 2006). Heavy metals uptake can be affected by metal concentration in soil, soil Ph, plant age, cation exchange capacity and organic matter content (Jung 2008).

CHAPTER 6: CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion.

Mazowe River, is one of the Rivers that are being affected by artisanal mining activities along the river. These activities are contributing to high concentrations of heavy metals (Pb, Zn, Fe and Cd) in Mazowe River water and sediments. Also, the study shows high concentrations of these heavy metals in maize plants that are being irrigated using Mazowe river water. The obtained levels were compared to WHO and FAO guidelines and they were higher than the permissible limits. The mean concentrations of these metals in plant tissues were as follows roots> leaves>stem>fruit.

6.2 Recommendations

- Regular assessment of heavy metal concentration in Mazowe River water and sediments.
- The study should be carried out in different seasons (dry and wet) to determine seasonal variations of heavy metals accumulation in water and sediments.

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APPENDICIES

Appendix 1: Materials used for water samples collection and preparation

- 500ml bottles
- Filter papers
- Pipette
- Vascular tubes

Appendix2: Materials used for sediment sample collection and preparation

- Small labelled plastic bag
- Sample drying plates
- Oven
- Balance scale
- 500ml Beakers
- Zirconium crucibles
- Hot plates

Appendix 3: Materials used for heavy metals analysis

- 500ml Beakers.
- 64 cuvettes.
- Distilled water.
- Inductively Coupled Plasma Atomic Emission Spectrometry (ICPOS)
- Atomic Adsorption Spectrometry (AAS)

Appendix 3A : Methodology for water samples

- Water samples collection and labelling
- Filtration
- Standard solution addition
- ICPO- ES analysis

Appendix3B: Methodology for plant and sediment samples preparation

- Sample collection
- Sample cleaning
- Sample drying
- Weighing and mixing
- Sodium peroxide fusion
- Leaching

- Dissolution
- Dilution
- ASS Instrument analysis

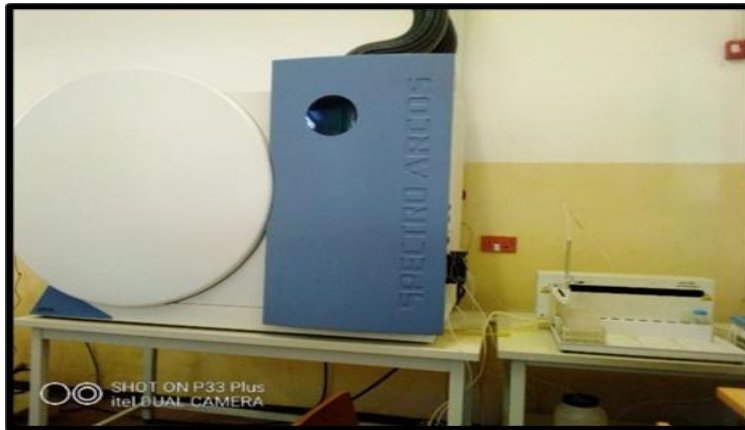


Figure 1: ICPOS Instrument



Figure 2 zirconium crucibles in the oven



Figure 3 AAS instrument

Appendix 4: WHO/FAO permissible limits for heavy metals (2002, 2011)

Parameter	Permissible limits in water	Permissible limits in plants
Fe	3 mg/l	0.5 mg/kg
Pb	0.01mg/l	0.1mg/kg
Cd	0.01mg/l	0.03 mg/kg
Zn	1 mg/l	3 mg/kg

