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An investigation of heavy metals pollution in Sebakwe River Kwekwe, Zimbabwe.

CHIBANDA MARYLEEN

R153889N

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APPROVAL FORM

This is to certify that the dissertation entitled "**An investigation of heavy metals pollution in Sebakwe River Kwekwe, Zimbabwe.**", submitted in partial fulfillment of the requirements for Bachelor of Science Honors Degree in Applied Biological Sciences and Biotechnology at Midlands State University, is a record of the original research carried out by **MARYLEEN CHIBANDA R153889N** under my supervision and no part of the dissertation has been submitted for any other degree or diploma.

The assistance and the help received during the course of this research have been duly acknowledged. Therefore, I recommend that I will be accepted as fulfilling the dissertation requirements.

Name of supervisor …….

Signature …….

Chairperson signature ……

ABSTRACT

Pollution of aquatic ecosystems with heavy metals is now of global concern due to their effects on human health and persistence in the environment. The study was carried out to determine the heavy metal pollution in Sebakwe River Kwekwe, Zimbabwe. To provide information on heavy metals chromium, lead, copper, magnesium and iron concentrations in water and sediments, samples were collected at five sites in January 2019 and in February 2019. The samples were acid digested and analysed with an atomic absorption spectrophotometer (AAS). The results showed that all studied metals were present in water and sediment samples and the mean concentrations of all metals occurred in the order Pb> Mg > Fe > Cu > Cr for both samples. There were significant differences in levels of Pb, Cr and Cu in water and Pb, Cr, Mg and Fe in sediments among the 5 sites. Correlation analysis showed a positive relationship between heavy metals in water and those in sediments. The highest contamination degree of the sediment was observed at site 3, the point of sewage discharge and lowest at site 5. Pollution load index (PLI) showed that sediments were uncontaminated to moderately contaminated. Levels of Pb were above permissible limits of SAZ and WHO in water posing a potential health hazard to the aquatic organisms and human inhabitants of the area that use this water resource directly for domestic or agricultural purposes. The results of metal concentration in water and sediments from this study are important as a baseline for future monitoring studies.

DEDICATION

This dissertation is dedicated to my beloved family, my mother and my siblings Amanda Ncube and Nikke Ncube who have supported me not only financially but also emotionally with their words of wisdom which gave me strength through the challenges.

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ACRONYMS

AAS - Atomic Absorption Spectrophotometer

ANOVA - Analysis of Variance

EIA - Environmental Impact Assessment

EMA - Environmental Management Act

mg/L - milligram per litre

mm - Millimeter

MPL - Maximum Permissible Level

Ppm - Part per million

USEPA - United States Environmental Protection Agency

WHO - World Health Organization

SAZ - Standard Association of Zimbabwe

ZINWA - Zimbabwe National Water Authority

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CHAPTER 1: INTRODUCTION

1.1: BACKGROUND

The pollution of aquatic resources is of global concern as it has resulted in the dwindling of freshwater resources, increased pollution load, human health problems and reduced ecosystem resilience which pose significant threat to sustainable development (Hope *et al.,* 2006). Heavy metals are among the pollutants of major concern due to their persistence in the environment and health effect on human beings (Zepeng 2018). Industrial processes, mostly in cities, have been cited as significant sources of heavy metals into the environment through effluent discharges (Ali *et al.,* 2016). Currently, anthropogenic input of metals exceeds natural input from natural geological weathering of rocks and soil (Utete *et al.,* 2018). The high level of heavy metals such as chromium (Cr), Copper (Cu), Lead (Pb), Magnesium (Mg) and Iron (Fe) can act as ecological toxins in aquatic and terrestrial ecosystems (Liu *et al.,* 2011). Artisanal gold mining is an additional source of heavy metal pollution especially mercury which is used in the recovery of gold (Krika and Krika 2018). Urban surface run-off is also normally contaminated with heavy metals due to the use of leaded gasoline and the corrosion or wear of metals from automobiles (Hou *et al.,* 2013). These activities cause a continual introduction of wide range of contaminants into most water bodies, and the associated toxicity poses great threat to aquatic biota. Research has shown that most peri-urban water bodies are at risk of excessive metal pollution due to human activities (Utete *et al*., 2018).

When heavy metals are in the aquatic environment, they are adsorbed onto inorganic and organic particulate deposits and are incorporated into sediment resulting in elevated levels of heavy metals in bottom sediment (Esmaeilzadeh *et al*., 2016; Dube *et al*., 2019). The

accumulation of heavy metals in the sediments is through adsorption and sedimentation processes by suspended matter (Cheng *et al*., 2017). A large amount of heavy metal input therefore accumulate in estuarine and coastal waters since these are important sinks of suspended matter and associated land derived contaminants (de Castro-Catala *et al*., 2016; Verhaert *et al* 2019). Heavy metals are persistent in the environment and they tend to shift from one compartment of the ecosystem to another. In the aquatic environment, the metals shift from aqeous phase to the sediments and then the biota (Zepeng 2018). For example, when heavy metals in the aquatic environment are adsorbed onto suspended matter and sediments, their bio-availability in dissolved state is lowered (Utete *et al*., 2018). Re-suspension of sediments by bioturbation might cause the release of metals back into the water column posing potential threat to the aquatic ecosystems (Ibrahim *et al*., 2018). Therefore sediments may act as both a sink and secondary source of metal contaminants in the aquatic environment. High levels of the metals are often found in sediments with high clay and organic carbon content (Ochieng 2007). The heavy metals in water can be absorbed by aquatic organisms and bio-magnify in food chains resulting in sub-lethal effects to aquatic organisms (Teta *et al*. 2017; Utete *et al.* 2018; Verhaert *et al*. 2019).

Heavy metals have been categorised as pollutants of high importance by most regulatory agencies such as US Environmental Protection Agency and World Health Organization. The metals affect individual aquatic organisms by inhibiting enzymes on the gills or gill-like structures resulting in toxicity through the disruption of ion and water balance (Brenner *et al.*, 2012). Some of the adverse effects of metals include interfering with the embryonic development of fish, genotoxicity and interfering with metabolism (Perez *et al*., 2016). Furthermore, continued exposure of aquatic organisms to high concentration of metals may lead to increased

mortality (de Castro-Catala *et al.*, 2016). In humans, Pb, Cu and Cr have serious health effects such as neurological, kidney and brain damage (WHO 2011). Characteristically, metals also accumulate in tissues of organisms, such as fish, snails (Ibrahim *et al*., 2016) and plants (Liu *et al*. 2011; Dube *et al*., 2019), making their toxicities of significance along the entire food chains, including humans (Wogu and Okaka 2011). These toxic substances are released into the environment and contribute to a variety of toxic effects on living organisms in food chain by bioaccumulation (Asaduzzaman *et al* 2006). Most rivers have lost their biodiversity due to the heavy metal pollution (Hamilton *et al.*, 2016). The accumulation of metals in aquatic ecosystems may impact species diversity, modify community composition and genetic diversity (Hamilton *et al* 2016; Zepeng 2018).

Sebakwe River serves as a major fishing and drinking water resource for people living along the banks of the entire stretch of the river in Kwekwe. Rapid urbanization and industrialization in many developing countries have given rise to the contamination of water resources (Abdel-Khalek 2015; Asaduzzaman *et al*. 2016). The fast expansion of urban, agricultural and industrial activities produces vast amounts of waste potentially contaminated with heavy metals (Utete *et al* 2018). Unfortunately, managing this waste has been a challenge for many countries. In Zimbabwe, technical, financial and institutional constraints have compounded this problem. For example, improperly designed solid waste disposal facilities and landfill sites contribute to contamination of surface and underground water resources. To the best of our knowledge, no studies have been done on heavy metal pollution in Sebakwe River. Most of the research on heavy metal contamination in Zimbabwe has focused on dams in large cities such as Bulawayo (Teta *et al.*, 2017) and Harare (Utete *et al*., 2018). This work is part of a multi-disciplinary research assessing the ecological health of Sebakwe River in the region.

1.2: PROBLEM STATEMENT

Zimbabwe aims to be an upper middle class economy by 2030. This aim cannot be achieved without an efficient and effective management system of waste for the sustainable development of water resources so as to ensure full socio-economic benefits for present and future generations. However, the water management system in Zimbabwe is still a major developmental challenge as human activities have contributed to the pollution of aquatic resources. Sebakwe Reservoir and Sebakwe River are the main sources of water for people living in Kwekwe and its peri-urban settlements. Rapid urbanization and industrialization in Kwekwe has the potential to contaminate water resources. Small scale gold mining, also termed artisanal gold mining (AGM) is practiced along the Sebakwe River where gold is extracted from alluvial deposits in rivers, waterways, outcrops and subsurface sediments along the side of dried-up valleys through Hg amalgamation technique (Simul and Muhammad 2017). Similar studies have shown that inland waters act as receptors of industrial and municipal waters containing varying loads of trace metals and other contaminants from the catchment (Kouame *et al.,* 2014). Along the Sebakwe River, there is a sewage treatment plant (KSTP) and water treatment plant (WTP) discharging their effluent into the river. The KSTP plant is not designed to remove heavy metals but some organic (e.g. aromatic hydrocarbons, preservatives and antioxidants) and inorganic (e.g. chlorides, nitrates, phosphates and sulphates) pollutants. Among the inorganic contaminants, heavy metals are of great concern because of their non-degradable nature and their potential to accumulate through the trophic level (Hou *et al.* 2013). The pollution of water in Sebakwe River poses a health threat to the local people that depend upon these water sources for their daily

requirements. Therefore, monitoring heavy metal pollution is important for safety assessment of the environment and human health in this region.

1.3: JUSTIFICATION OF THE STUDY

The rapid population growth along the Sebakwe River has necessitated proper conservation and efficient utilization of freshwater bodies for sustainable development. This is necessary because there has been deterioration of water quality in the river because of increased domestic, municipal and agricultural activities. The heavy metals iron (Fe), copper (Cu), chromium (Cr), lead (Pb), and magnesium (Mg) were selected for this study because of their common environmental concern, potential health hazards to human beings and aquatic life (Teta *et al.* 2017; W.H.O. 2017). Therefore, continual monitoring and assessment of the heavy metals is important to ecological and human health.

Heavy metal pollution monitoring is needed in order to provide baseline data which can be used by the local authorities such as Kwekwe City Council and Environmental Management Agency for environmental management. Nearly every government around the world advocates for an environment free from harmful contamination for their citizens, therefore these results would serve as baseline data against which future impact assessments will be evaluated. The university richly benefits from having a varied base for future ecological studies.

1.4: OBJECTIVES

1.4.1: MAIN OBJECTIVE

The main aim of the study was to determine the heavy metal concentrations (Cr, Cu, Fe, Mg and Pb) in water and sediments from Sebakwe River in Kwekwe.

1.4.2: SPECIFIC OBJECTIVES

- To determine the spatial variation of heavy metals (Cr, Cu, Fe, Mg and Pb) concentration in water and sediment along Sebakwe River.
- To compare metal concentration in water and sediments.
- To determine the degree of heavy metal contamination and pollution using contamination factor (CF), pollution load index (PLI) and geo- accumulation indices (Igeo).
- To compare the heavy metal concentration in water with WHO and SAZ standards.

CHAPTER 2: LITERATURE REVIEW

2.1: WATER QUALITY

Water quality refers to the chemical, physical and biological characteristics of water. It involves the process of evaluation of the physical, chemical and biological nature in relation to natural quality, human effects and intended uses, particularly uses which may affect human health and aquatic ecosystem (Saiful *et al.,* 2015). The availability of good water quality for drinking purpose is essential for a healthy human society (Khan *et al.*, 2016). Many rivers and streams in developing countries are heavily polluted with industrial and sewage discharge (Krika and Krika 2018). Water Quality Standards such as the World Health Organization (WHO) and SAZ guideline for Drinking Water have been established to regulate substances that potentially affect human health, environment and aesthetic qualities of water. Water quality standards for surface waters vary significantly due to different environmental conditions. Seasonal variations in agricultural activity, storm water runoff, interflow and atmospheric deposition have strong effects on river water quality (Simul 2017).

2.2: ANTHROPOGENIC IMPACTS ON WATER QUALITY

People living along the river use water for many purposes like fishing, drinking, irrigation and recreational and sport activities such as water sports (Zepeng 2018). However, the surface water quality is deteriorating due to industrialization, farming activities, transportation, urbanization, animal and human excretions and domestic waste (Teta *et al.*, 2014). The introduction of sewage effluent into streams severely impacts aquatic ecosystems through habitat destruction and impairment of water quality (Harendra *et al*., 2016). This eventually leads to a reduction in biodiversity of a given aquatic ecosystem and its ability to sustain life (Dube *et al.,* 2019). The

extent of damage depends on a variety of factors including the frequency of influx, volume and chemistry of the drainage and the buffering capacity of the receiving stream (Teta *et al.*, 2017).

2.3.0: HEAVY METALS

Heavy metals are metallic elements with a high atomic weight and density which is five times greater than water (Harendra 2017). These include the transition metals, some metalloids, lanthanides and actinides. More than 20 metals generally exist in a positively charged form and can bind on to negatively-charged organic molecules (Krika and Krika 2018). Heavy metals are usually present in trace amounts in natural waters but many of them are toxic even at very low concentration because they cannot be degraded or destroyed, therefore their stability make them persistent toxic substances in environment (Dube *et al.*, 2019).

2.3.1: TYPES OF HEAVY METALS

Heavy metals are natural constituents of natural waters and are present at low concentrations. Some metals like Cu, Co, Fe, Mg, Ni and Zn are essential as micronutrients for life processes in plants and microorganisms while many other non-essential metals like Cd, Cr and Pb have no known physiological activity but have been proved to be detrimental beyond certain limits (Islam *et al*., 2014). Excessive metal concentrations in surface water can pose health problems to both humans and the aquatic biota, thus it is necessary to restore and conserve surface water resources for the sake of their inevitable role in sustaining both aquatic and terrestrial life forms (Singovska *et al*., 2017).

2.3.2: SOURCES OF HEAVY METALS

Heavy metals enter natural waters from various sources. The natural geological weathering of rocks and soil, directly exposed to surface waters, is usually the largest natural source. The major sources of pollutants affecting aquatic ecosystems are mining, agricultural, industrial and domestic effluent (Bonsignore *et al*., 2018). Rapid industrial growth throughout the world to meet the population demands exerts negative impacts to the environment. Discharge of contaminated effluents without adequate treatment into the aquatic environment creates such implication. Industrial wastewater associated with automobile manufacture, metal purification, electroplating, galvanizing, coating, paint, electronics, pharmaceutical, chemicals and battery manufacturing are the most common source of heavy metal pollution (Ochieng *et al*., 2007). Arsenic, cadmium, copper, chromium, lead, mercury, nickel and zinc are normally found in heavy metal contaminated wastewater (Zepeng 2018).

Significant quantities of heavy metals are discharged into rivers, accumulate and biomagnify in water, sediment, and aquatic food chain, resulting in sublethal effects or death in local fish populations (Liu *et al*., 2011). Metals can heavily accumulate in sediments, as a sink, or be released from sediments, acting as a source back to overlying water via natural or anthropogenic disturbance. The effects of metal pollution on local environments and organisms can be substantial and long lasting in spite of years of restoration efforts. Suspended sediments absorb pollutants from the water, thus lowering their concentration in the water column; heavy metals are inert in the sediment environment and are often considered to be conservative pollutants although they may be released into the water column in response to certain disturbances causing potential threat to ecosystems (Davies *et al.*, 2006; Hope 2006).

2.3.3: EFFECT OF METALS ON AQUATIC LIFE

In present-day, river pollution is a serious and emerging problem in the majority of developing countries. Due to rapid industrialization, there has been an increase in the amount of effluent being disposed to natural water bodies. Industrial effluents and untreated sewage entering the water bodies are one of the prime sources of environmental toxicity, which endangers aquatic biota and deteriorates water quality (Cheng *et al*., 2017). Heavy metal effects on both living organisms and the environment have been observed since water functions as the medium of transport for pollutants (Ochieng *et al.*, 2007). Bottom sediments provide habitats and a food source for benthic fauna. The occurrence of large amount of heavy metal pollutants in surface water and sediment can affect the self-purifying nature of rivers. Diatom community structure can be affected by high levels of micro pollutants, and in particular by metals, which are often found in rivers (Bonsignore *et al*., 2018). Thus, aquatic flora and fauna are exposed to contaminants through direct uptake from the water phase, indirect uptake through food or both. The direct uptake is influenced by the total concentration and the bioavailability of the contaminant, as well as by the physiological factors of the individual organisms (Davies *et al*., 2006). The bioavailability and subsequent bioaccumulation of metals is related to the chemical specification of the elements, which is influenced by the physicochemical conditions of the environment (e.g., pH, conductivity, dissolved oxygen) which may be altered by the input of wastewaters (Ahmed *et al.*, 2009).

Most aquatic organisms are not adapted to deal with trace elements when they occur above threshold concentrations (Ochieng *et al.*, 2017).The most toxic metals such as Pb, Cu and Cd have been subjects of ecotoxicological research for long (Wogu and Okaka 2011; Ochieng *et al.*, 2017). Trace elements such as arsenic, cadmium, copper, lead and selenium are toxic to aquatic biota because plankton has the ability to concentrate heavy metals from their aquatic

environment (Utete *et al.*, 2018). This occurs either because the chemical is taken up faster than it can be used, or because the chemical cannot be broken down for use by the organism, that is, the chemical cannot be metabolized. The metal accumulation levels vary widely among organisms, and have different distributions between tissues and organs in the body (Ibrahim *et al.*, 2016). Aquatic organisms living in the same habitat may have different body concentrations of trace metals, even within closely related species (Yaylutas *et al.*, 2007).

More importantly, toxic metals can be taken up by rooted aquatic macrophytes and other aquatic organisms entering the food chain and be potentially transferred to the upper trophic levels, which can eventually lead to adverse effects on humans due to the consumption of contaminated food (Hoang *et al.*, 2018). Food in the form of plankton is an important source for heavy metal enrichment in fish body potentially leading to bio-magnification (Wogu and Okaka 2011). For example, predators tend to live longer than prey species and have more time to accumulate some contaminants than do prey. The result may be higher concentrations in predators than in prey (Alsop and Wood 2011). Lower food web organisms tend to grow faster than those higher in the food web resulting in low tissue concentration of contaminant pronounced at lower levels than at higher levels (Dube and Sigauke 2015). Predators are often larger than prey and allometric effects on bioaccumulation can result in higher concentrations of some contaminants in predators relative to prey (Hossain *et al.*, 2015). If contaminant concentrations are very high in food item, species further up the trophic web might still be exposed to concentrations sufficient to produce an adverse effect as was the case of Japanese afflicted with itai-itai disease (Teta *et al*., 2017).

Biomagnification, defined as the increasing concentration of a contaminant with increasing trophic level in a food web, has been widely documented for methylmercury in aquatic ecosystems (Singovska *et al*., 2017). Patterns of methylmercury bio-magnifications in aquatic

food webs are similar, even among aquatic systems that differ in ecosystem type, mercury source, and pollution intensity. The dietary uptake of methylmercury in fish is influenced by their size, diet, and trophic position (Ibrahim *et al.,* 2016). In piscivorous species, such as the *Sander vitreus* and *Salvelinus namaycush* the methylmercury content of the diet and associated rate of mercury accumulation can increase with age, accelerating abruptly when the fish become large enough to switch from a diet of invertebrates to prey fish (Hamilton *et al*., 2016). In adult fish, females often contain higher mercury concentrations than males because they must consume more food than males to support the energy requirements of egg production (Verhaert *et al.,* 2019). The increased feeding rates in females cause greater dietary uptake of methylmercury, and only a small fraction of the accumulated methylmercury is transferred to the egg mass and eliminated during spawning (Hoang *et al.,* 2018). Fish can tolerate ten times as much methylmercury as humans and are more tolerant than their wildlife predator (Ibrahim *et al.,* 2016). Storage of methylmercury in the muscle tissue of fish may detoxify it and reduce the exposure of brain tissue to it (Teta *et al*., 2017). However, high levels of methylmercury may cause decreased hatching rate of fish, waterfowl, and marine bird eggs and reduced growth and development of the fish fry and nestlings (Ibrahim *et al*., 2016). These impacts can have severe repercussions at the population and ecosystem levels because food chains will be impacted and there will be a shift in the species composition of the ecosystem (Verhaert *et al.,* 2019).

One of the most important factors influencing the aquatic toxicity of lead is the free ionic concentration and the availability of lead to organisms. However, the toxicity of lead depends upon many factors including fish age, pH and hardness of the water (Ibrahim *et al.,* 2016; Hamilton 2016). When lead concentrations exceed 100 ppb, gill function is affected (Ibrahim 2016). Embryos and fry are more sensitive to the toxic effects of lead than are adults or eggs

(Islam *et al*., 2014). Lead is more toxic at lower pH and in soft water (Brenner and Hoekstra 2012; Hoang *et al*., 2018). As is the case with other metals, the toxicity of lead to fish depends in part on the species. *Carassius auratus* are relatively resistant because they can excrete lead via their gills (Bonsignore *et al.*, 2018). Typical symptoms of lead toxicity include spinal deformity and blackening of the tail region. Lead is unlikely to affect aquatic plants at levels that might be found in the general environment (Esmaeilzadeh *et al*., 2016). In aquatic invertebrates, adaptation to low oxygen conditions can be hindered by high lead concentrations.

Low concentrations of hexavalent chromium cause sublethal toxic effects in aquatic plants and animals. For example, 62 ppb inhibits growth in algae and 16 ppb inhibits growth in *Oncorhyncus tshawytscha* showing that aquatic animals are more sensitive to metals than are aquatic plants (Praveeva *et al*., 2007; Hou *et al.,* 2013). Chromium toxicity to aquatic organisms increases as water temperature increases and as pH and salinity decrease (Krika and Krika 2018) additionally, chromium is more toxic in soft water than in hard water and there are species differences in sensitivity. For example, *Pimephale spromelas* are more sensitive than *Carassius auratus*. The concentration of chromium that caused death in 50% of the exposed population was 3 ppm in soft water and 72 ppm in hard water for *Pimephale spromela* and 18 ppm in soft water and 133 ppm in hard water for *Carassius auratus* (Ibrahim *et al.*, 2016). Water contaminated with chromium will not build up in fish when consumed, but will accumulate on the gills, thus, causing negative health effects for aquatic animals; chromium uptake results in increased mortality rates in fish due to contamination (Pourahmad *et al*., 2005). The gills of the fish act as a mechanical filter, and small particles of Cr are trapped in the gill lamella therefore toxicity of iron depend on species and size of the fish.

2.3.4: HUMAN HEALTH EFFECTS OF HEAVY METALS

Humans are always exposed to the natural levels of trace elements. Under normal circumstances the body is able to control some of these amounts. However, continuous exposure to elevated levels of metals causes serious illness or death (Kouame *et al*., 2014). Increased exposure may occur through inhalation of air borne particles or through ingestion of contaminated soil by children or by absorption through the skin (WHO, 2011). Humans as organisms feeding at the highest level are more prone to serious health problems because concentrations of heavy metals increase in the food chain (Saiful *et al*., 2015). Metals and their compounds can accumulate in the body's tissues, such as bones or nerves. They can cross the placenta and harm an unborn child in pregnant women (Hamilton *et al.*, 2016). Children are the most susceptible to health problems caused by heavy metals, because their bodies are smaller and still developing (Wogu and Okaka 2011). The health hazards presented by heavy metals depend on the level and the length of exposure (Utete *et al.*, 2018). In some cases, the health effects are immediately apparent; in others, the effects are delayed. High levels of toxic metals deposited in body tissues and subsequently in the brain, may cause significant developmental and neurological damage, including depression, increased irritability, anxiety, insomnia, hallucination, memory loss, aggression and many other disorders (Verhaert *et al*., 2019).

Lead is one of the most potent heavy metal that poses significant threat to human health and the environment even in small quantities (Alsop and Wood 2011). The concentrations of lead and exposure time are key factors in lead toxicity measurement. Acute poisoning occurs when one is exposed to high concentration of lead for a short duration and the adverse effects are high and severe (Hamilton *et al.*, 2016). Acute condition can lead to seizures, coma and death in a short time. Long term and low level exposure of chronic poisoning is commonly found in case studies (Hou *et al*., 2013). Lead toxicity leads to diseases such as anaemia, neurotoxicity, hemotoxicity,

nephrotoxicity and toxic metabolic encephalopathy (Ibrahim *et al.*, 2016). It targets organs and tissues including the heart, bones, intestines, kidneys and the reproductive system, thus making it capable of disrupting metabolic processes and threatening human life (Ochieng *et al.*, 2007). Furthermore, lead toxicity may cause brain damage and mental retardation in children (deCastro-Catala *et al*., 2016). Lead can also substitute for zinc in several enzymes that function as transcriptional regulators reducing the binding of these proteins to recognition elements in genomic DNA which suggests an epigenetic involvement of lead in altered gene expression (Hamilton *et al*., 2016).

Copper concentrations as low as 1-2 µg/L have been shown to have adverse effects on aquatic organisms (Yaylutas *et al.*, 2007). Copper can affect the reproduction, physiology and behavior in a variety of aquatic organisms. Moreover, high intakes of copper have been associated with liver failure and gastrointestinal problems in humans (Ali *et al.*, 2016). Continued inhalation of copper-containing sprays is linked with an increase in lung cancer (Wogu and Okaka 2011). People with Wilson's disease are at greater risk for health effects from overexposure to copper. Long-term exposure to copper can cause irritation of the nose, mouth and eyes and headaches, stomachaches, dizziness, vomiting and diarrhoea. Intentionally high uptakes of copper may cause liver and kidney damage and even death (Zepeng 2018). Industrial exposure to copper fumes, dusts, or mists may result in metal fume fever with atrophic changes in nasal mucous membrane (Utete *et al.* 2018). Iron has been shown to be mutagenic, and carcinogenic at high concentrations. IARC found acceptable evidence for local sarcoma attributable to iron carbohydrate complexes, especially iron dextran, in several animal species (Perez *et al.*, 2016).

Chromium is bio-persistent and, once absorbed by an organism, remains resident for many years (over decades for humans) although it is eventually excreted (Islam *et al.*, 2014). Chromium may

also produce bone defects (osteomalacia, osteoporosis) in humans and animals (Hamilton *et al*., 2016).When chromium is present in soils it can be extremely dangerous, as the uptake through food will increase (Hossain *et al*., 2015). Soils that are acidified enhance the chromium uptake by plants. Chromium transported to the liver binds with proteins and form complexes that are transported to the kidneys where it is likely to damage the filtering mechanism (Perez *et al.*, 2013). This causes the excretion of essential proteins and sugars from the body further damaging the kidney. The highest concentration of chromium is found in liver and kidney tissues through its strong binding with cystine residue of metallothionin, with somewhat lower concentration in pancreas and spleen (Islam *et al*., 2014).

Ingestion of small amount of chromium for extended periods may lead to the accumulation of acutely toxic levels of chromium in body tissues (Praveena *et al.*, 2007). It takes time before chromium that has accumulated in kidneys is excreted from a human body. Other health effects that can be caused by chromium are: diarrhea, stomach pains and severe vomiting, bone fracture, reproductive failure and possibly even infertility, damage to the central nervous system, damage to the immune system, psychological disorders and possibly DNA damage or cancer development (Hamilton *et al.*, 2016).

2.3.5: LEGISTLATIVE ISSUES

Wastewater and sewage sludge are the main sources of heavy metal water pollution, strengthening the monitoring and control of heavy metals and metalloids in waste water treatment plants can play a substantial role in improving environmental quality and reducing environmental risks. Everyone has the right to live in an environment which is safe and unlikely to pose any deleterious effects to their health. The Clean Water Act addresses water pollution

and water quality of surface waters and includes sections addressing both point and nonpoint sources of pollution, as well as the establishment of beneficial uses of waters and water quality criteria to protect those uses (Brenner and Hoekstra 2012). EMA states that no local authority operating a sewerage system or industrial undertaking operating within the jurisdiction of two or contiguous local authorities shall discharge any effluents or other pollutants into the environment without an effluent discharge licence issued by the board (Haper *et al.,* 1998). Every person whose activities generate waste shall employ measures essential to minimize waste through treatment, reclamation and recycling. Any person who disposes of any waste in contravention of standards prescribed in terms of section sixty-nine; or who transports any waste otherwise than in accordance with a valid licence issued shall be guilty of an offence and shall be liable to imprisonment or to a fine or to both fine and imprisonment (EMA 2002).

Effluent and solid waste disposal regulations SI 6, 2007 provides the water quality standards in which the effluent should be discharged into the environment. A lot of work regarding effluent and waste standards and management has already been done following the amendments to the Water Act in 1998 and the subsequent passing of the Effluent and Waste Standards Statutory Instrument 274/2000 (ZINWA, 2000). Effluent standards are classified by color coding into: blue, for that which is environmentally safe; green, low environmental hazard, yellow, medium environmental hazard; and red, high environmental hazard. All the categories attract some disposal fees ranging from US$130 to US$400 (blue to red) as of Government exchange rate for December 2002 (Figure 2.1).

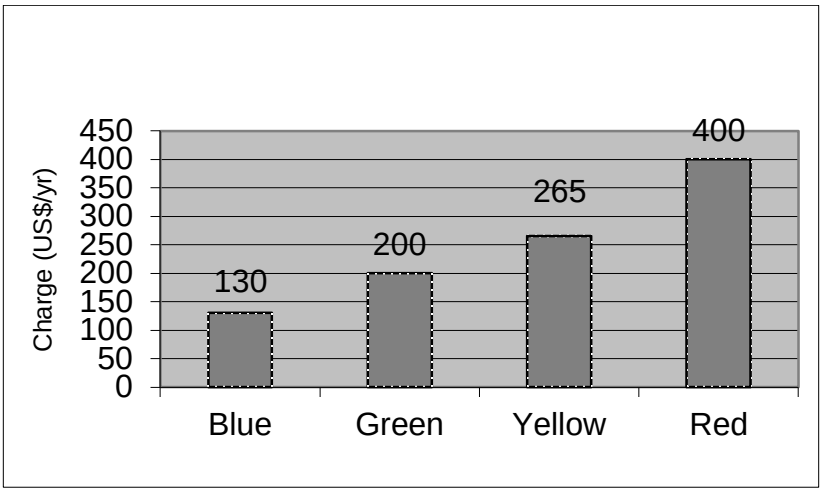

Figure 2.1: Effluent Monitoring Charges (Mubvami 200)

In addition to monitoring charges, different environmental fees are charged per mega litre of effluent for the green (US 50 cents) yellow (US$ 1.20 and for the red category (US$ 2.10). The red colour code also attracts a penalty charge of US 50 cents per mega litre of effluent. Monitoring charges for disposing solid wastes on land are double those of effluent with a 25% penalty fee set for wastes falling in the red category (Mubvami 2002).

CHAPTER 3: METHODS

3.1: STUDY AREA

Sebakwe River is one of the most important freshwater bodies in Zimbabwe located in Kwekwe in the Midlands Province of Zimbabwe. The town receives mean annual rainfall range 600 to 699 mm (Change 2000). The river has a length 150 km from source to mouth and is a tributary of Munyati River which it joins in Zhombe East. Kwekwe is one of the most populated and fast growing metropolis in Zimbabwe with a population of ninety-nine thousand one hundred and forty nine (99 149) people ( ). Sebakwe River is the main recipient of waste from the city of Kwekwe. Agricultural waste, fertilizers, and raw sewage effluents constitute the predominant anthropogenic pollution sources in the area. Communities around the Sebakwe River abstract water from the river for human and animal consumption. The pollution in Sebakwe is evidenced by the proliferation of macrophytes such as *Azolla filiculoides Lam*, *Typha domingensis* and *Eichhornia crassipes Solms*.

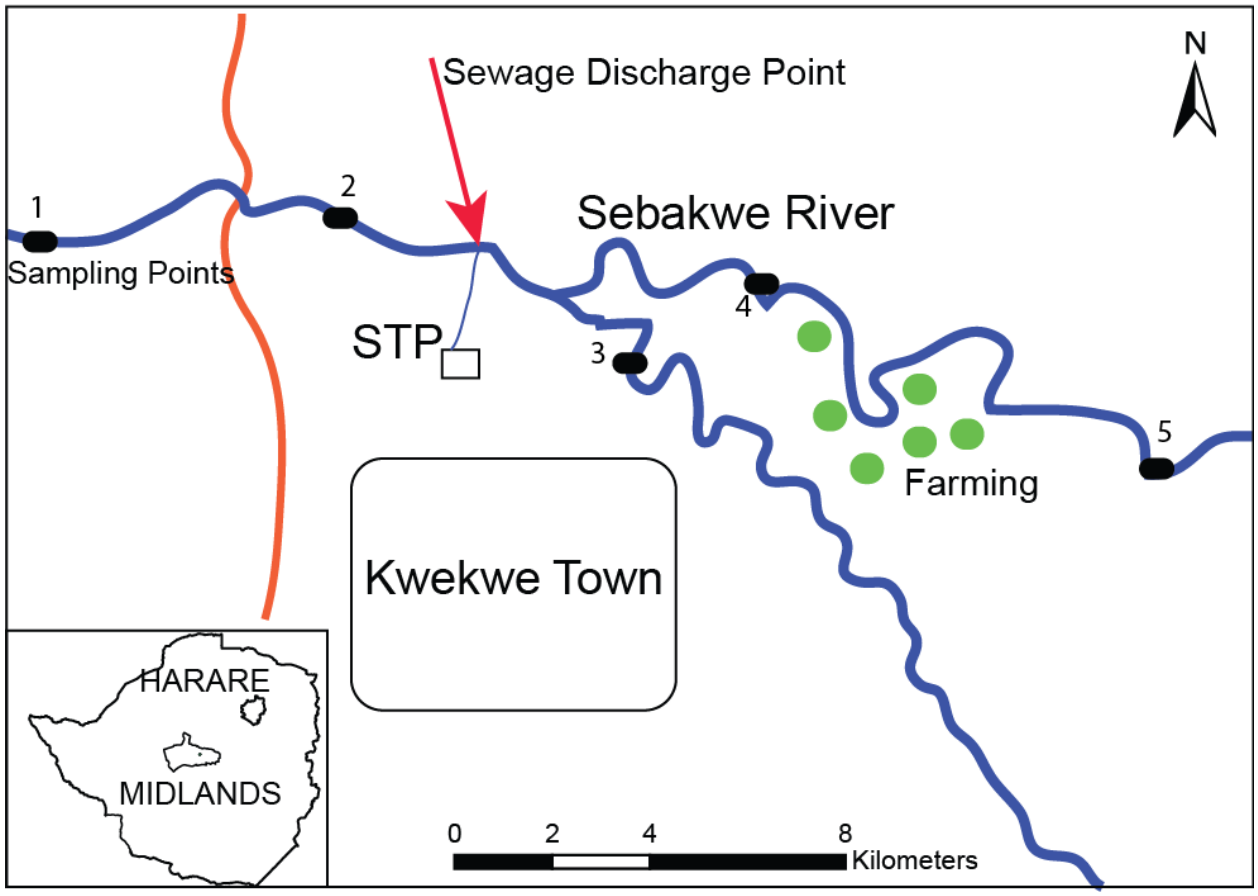

Figure 3.1: Location of different sampling sites along Sebakwe River

3.2: SAMPLING DESIGN

Water and sediment samples were collected in January 2019 and February 2019. Sample points were located and recorded using GPS. Site selection along the river was done to capture different activities occurring in the catchment. The water and sediment samples were collected at 5 sites along Sebakwe River. Sites 1-3 were located below the point where Kwekwe sewage treatment plant discharges its effluent. Sites 4 and 5 were located above the discharge point where artisanal mining and farming activities are concentrated.

3.3: WATER AND SEDIMENT COLLECTION

Water samples were collected from surface to below the water surface. Two water samples were collected from each site. The samples were placed in sterile polythene bottles, acidified with 10% nitric acid (pH = 2) to keep metal ions in the dissolved state, and also prevent microbial activities. The water samples were kept in an ice cooler-box to maintain them at a temperature below 4 °C during transfer from the field to the laboratory (USEPA, 1996). 500 g of sediment samples were collected from a depth of 20 cm under the river bed with a soil auger. At each point, a composite sediment sample was collected using standard protocol (USEPA, 1996). The sediments were placed in ziplock plastic bag and transported to the laboratory for analysis.

3.4 PREPARATION OF SOLUTIONS

3.4.1 STOCK SOLUTIONS

Lead stock solution was prepared by dissolving 1.60 g of lead nitrate [$Pb(NO_3)_2$] in 100 ml of deionised water then diluting to 1L in a volumetric flask with deionised water forming a colorless solution. For copper, 3.80 g of Cu $(NO_3)_2.3H_2O$ was dissolved in 250 ml of deionised water then diluted to 1L in a volumetric flask with deionised water to form a blue solution. For chromium, 1.000 g of pure metal was weighed using an analytical balance and transferred into a beaker. The metal was dissolved by partially heating in concentrated nitric acid (HNO_3) and hydrochloric (HCL) acid at a ratio 1:3 respectively then diluted to 1 L in a volumetric flask with deionised water to form a dark green solution. For Fe, 0.864 g of ammonium ferric sulphate was dissolved in 5 ml of concentrated sulphuric acid and made up with deionised water in 100 ml standard flask. Magnesium stock solution was prepared by dissolving 3.96 g in deionised water then diluting to 1 L in a volumetric flask.

3.4.2 STANDARD SOLUTION

The instrument calibration standards were prepared by diluting standard (1000 ppm) obtained from Merck for all 5 metals. The stock solutions were used to calculate the required volumes for concentrations of 10, 20, 30 and 40 ppm in final volumes of 100 ml. The formula used was:

$C_1 V_1 = C_2 V_2$ where C_1 (standard concentration of 1000 ppm), V_1 (the required volume to be calculated), C_2 (different concentrations of 10, 20, 30, 40ppm, V_2 (volumetric flask used 100ml). After calculating the required volumes for each metal and pippeting these volumes into 100ml flasks, the flasks were filled with deionised water.

3.5.1: DIGESTION PROCEDURE FOR WATER

Water samples were filtered through a Millipore Filtration Assembly, using 0.45 mm membrane filter. The filtrate was then acidified with concentrated HNO_3 to a pH of <2. 50 mL of well mixed, acidified sample was poured in a beaker. 5 mL of concentrated HNO_3 was added and heated at 130 ℃ on hot plate till the volume came to 25–30 mL and light color. The addition of HNO_3 and heating were repeated till solution became light colored or clear. After cooling, the volume was made to 1 L with deionised water passing through the Whatman no. 41 filter paper. Total dissolved metals were determined by atomic absorption spectrophotometre. The average values of two replicates were taken for each determination.

3.5.2: DIGESTION PROCEDURE FOR SEDIMENT

A procedure recommended by Environmental Protection Agency (EPA, Method 3050B) was used as the conventional acid extraction method. The sediment was sieved and ground with mortar and pestle until fine particles (< 200 μm) were obtained (USEPA 1996). About 1 g of sample was placed in 250 ml flask for digestion. The first step was to heat the sample to 95 ℃

with 10 ml of 50 % HNO_3 without boiling. After cooling the sample, it was refluxed with repeated additions of 65 % HNO_3 until no brown fumes were given off by the sample. The solution was then allowed to evaporate until the volume was reduced to 5 ml. After cooling, 10 ml of 30 % H_2O_2 was added slowly. The mixture was refluxed with 10 ml of 37 % HCl at 95 ℃ for 15 minutes (USEPA 1996). The digested sediment was then passed through Whatman no. 41 filter paper and washed with a 0.1 M HNO_3 solution and made to 100 mL volume using deionized water (Ali *et al*. 2016).

3.6: SAMPLE ANALYSES (AAS)

The heavy metals for all prepared samples [chromium (Cr), Iron (Fe), magnesium (Mg), lead (Pb) and copper (Cu)] were determined using an air-acetylene flame atomic absorption spectrometer (AAS) Perkin-Elmer Model AAnalyst 400. Atomic Absorption Spectrometry (AAS) is a technique used mostly for measuring quantities of chemical elements present in samples by measuring the absorbed radiation by the chemical element of interest. The operating conditions adjusted in the spectrometer were carried out according to the Standard guidelines of the manufacturers. A 10 cm long slot-burner head, a lamp and an air/acetylene flame were used. An acetylene–air flame was used; the gas flow rates and the burner height were adjusted in order to obtain the maximum absorbance signal for each element. Argon 99.96% (v/v) was used as gas through the FAAS. The analytical reagent blanks were prepared together with each batch of digestion set and analyzed for the same element of the samples. All reagents used were of the analytical grade from MES Equipment. De-ionized ultrapure water was used for the experimental procedure. All glass and plastic wares were cleaned by soaking them in warm 5% (V/V) aqueous nitric acid for 6–7h and rinsed with ultrapure deionised water. The standard for

the ASS calibration was prepared by diluting standard (1000ppm). Matrix Spike recovery was in the range of 85–100%. The calibration of the AAS was done daily.

3.7:0: STATISTICAL ANALYSIS AND DATA ANALYISIS

3.7.1: SPATIAL VARIATION

3.7.1.1:ONE-WAY ANOVA

Data were analyzed in SPSS (ver 17.0). The data generated from the chemical analysis was subjected to descriptive statistical analysis (mean, range and standard deviation at 95% confident limit). The measured concentrations of all the five metals were analyzed using one-way (ANOVA) to test if there were significant differences in the concentrations of heavy metals in water and sediments among the different sampling sites ($p< 0.05$). One–way (ANOVA) was used since there was one independent variable (sampling sites) and one dependent variable (concentration of heavy metals). Turkey post hoc analysis was used to detect the sites that differed in metal concentration.

3.7.1.2: PRINCIPAL COMPONENT ANALYSIS (PCA)

PCA was used for exploratory analysis to better understand the spatial occurrence of metals among the five sites. The PCA was performed in PAST (ver 20). This procedure reduces overall dimensionality of the linearly correlated data by using a smaller number of new independent variables, called principal components (PC). The factor loadings, which can be regarded as combination between the elements, were then computed after rotating the original principal component solution according to Kaiser's varimax criterion (Praveena, *et al.*, 2007).

3.7.1.3: CLUSTER ANALYSIS (CA)

Cluster analysis was also used for investigating the similarities in heavy metal concentration from sediments and water samples among sites by means of Ward's linkage method using squared Euclidean distances. The CA was performed in PAST. Cluster analysis groups the objects into classes on the basis of similarities within a class and dissimilarities between different classes (Praveena, *et al.,* 2007). The results of cluster analysis help in interpreting the data and indicate common patterns of metal occurrence (Harendra *et al.,* 2017). The core concept is to regard each individual as one cluster and combine two clusters with highest similarity as a new cluster, then combine this new cluster with another most similar cluster as another new cluster. This process is repeated over and over again until all clusters become one cluster.

3.7.2.0: COMPARISON OF METAL CONCENTRATION IN WATER AND SEDIMENTS

3.7.2.1: EXCHANGE FACTOR (CE)

The CE water-sediment for each heavy metal was calculated as the heavy metal concentration in water (Cw) divided by the heavy metal concentration in sediment (Cs):

CE =Cw/Cs (Kouame*et al.,* 2014):

3.7.2.2: PEARSON CORRELATION

Pearson correlation analysis was performed between metal concentration in sediments and water using SPSS software. The Pearson correlation coefficient of variation was used to measure the strength of a linear relationship between metal concentration in water and sediments on a scale of -1 (perfect inverse relation) through 0 (no relation) to +1 (perfect sympatric relation) (Kouame *et al*., 2014).

3.7.3.0: CONTAMINATION FACTOR, POLLUTION LOAD INDEX AND GEO-ACCUMULATION INDEX OF HEAVY METALS IN SEDIMENTS.

3.7.3.1: METAL CONTAMINANT FACTOR (CF)

CF metals are the measured concentration to the value measured before the sewage discharge of a given metal (Yu *et al.,* 2011). CF metals were determined by the following equation:

CF metals=C metal/C before sewage discharge

(CF) was classified into four grades for monitoring the pollution of one single metal over a period of time (Islam *et al.,* 2015): low degree ($CF < 1$), moderate degree ($1 \leq CF < 3$), considerable degree ($3 \leq CF < 6$), and very high degree ($CF \geq 6$) (Hakanson, 1980). The CF values were used to monitor the enrichment of one given metal in sediments.

3.7.3:2: POLLUTION LOAD INDEX (PLI)

To evaluate the sediment quality for each site, combined approaches of pollution load index of the five metals were calculated (Islam *et al.* 2015). The PLI for a single site was the *n*th root of n number multiplying the factor (CF values) together. PLI for each site was determined by the following equation:

PLI = $n \sqrt{}$ (CF_1 XCF_2… … …X CF_n), where n is CF = C metal/ C before sewage discharge

PLI value of zero indicates excellence, a value of one indicates the presence of only baseline level of pollutants and values above one indicate progressive deterioration of the site (Tomilson *et al*., 1980). The PLI gave an evaluation of the overall toxicity status of the sample and also it is a consequence of the contribution of the studied five metals.

3.7.3.3: INDEX OF GEO- ACCUMULATION (I_{geo})

Geo- accumulation index was calculated to assess the anthropogenic impact as follows:

$I_{geo} = \log 2 (C_n / 1.5B_n)$

Where C_n is the measured concentration of a metal n in sediments and B_n is the value measured before sewage discharge and 1.5 is the background matrix correction factor due to lithogenic effects. I_{geo} consists of 7 grades (0- 6) ranging from unpolluted to very high polluted sediment quality. Class0 (uncontaminated): $I_{geo} \leq 0$; Class 1 (uncontaminated to moderately contaminated): $0 < I_{geo} < 1$; Class 2 (moderately contaminated sediments): $1 < I_{geo} < 2$; Class 3 (moderately to strongly contaminated): $2 < I_{geo} < 3$; Class 4 (strongly contaminated): $3 < I_{geo} < 4$; Class 5 (strongly to extremely contaminated): $4 < I_{geo} 5$; Class 6 (extremely contaminated): $5 < I_{geo}$. Class 6 is an open class and contains all values of the index above class 5.

3.7.4.0: COMPARISON OF HEAVY METAL CONCENTRATION IN WATER WITH WHO (2008) AND SAZ (2015) STANDARDS.

Heavy metal concentration in water at each site were compared with WHO (2008) and SAZ (2015) standards.

CHAPTER FOUR: RESULTS

4.1.0: SPATIAL VARIATION OF HEAVY METALS

4.1.1: SPATIAL VARIATION OF HEAVY METAL CONCENTRATION IN WATER

The concentrations of metals varied within a range of: Mg (0.03-0.10) mg L^{-1}, Fe (0.01-0.07) mg L^{-1}, Cu (0.02-0.16) mg L^{-1}, Cr (0.01-0.08) mg L^{-1}, and Pb (0.06-0.14) mg L^{-1} (Figure 4.1). Site 2 after the discharge of sewage effluent had the highest concentration of Pb (0.12 ± 0.02) mg L^{-1} compared to all other sites. The levels of Mg were generally high among all the sites with S1 (0.08 ± 0.01) mg L^{-1}, S2 (0.07 ± 0.01) mg L^{-1}, S3 (0.08 ± 0.02) mg L^{-1}, S4 (0.05 ± 0.02) mg L^{-1} and S5 (0.19 ± 0.27) mg L^{-1}. The average concentration of all metals studied was found at S3 in Sebakwe River. There was a significant difference in Pb (ANOVA: $F = 8.38$, $p = 0.01$), Cr (ANOVA: $F = 10.82$, $p = 0.00$), and Cu (ANOVA: $F = 18.36$, $p = 0.00$), concentrations among the 5 sites. A Turkeys post hoc test revealed that S1 and 4 ($p = 0.02$), S1 and 5 ($p = 0.002$), S2 and S4 ($p = 0.03$), S2 and S5 ($p = 0.04$) and S1 and S3 ($p = 0.03$) were significantly different from each other for Pb. S1 and S3 ($p = 0.01$),S4 and S3 ($p = 0.004$), S5 and S3($p= 0.00$) were significantly different from each other for Cr. S3 and S1 ($p = 0.00$), S2 and S3 ($p = 0.00$), S4 and S3 ($p = 0.00$) and S5 and S3 ($p = 0.001$) for Cu. Overall, the concentrations of all heavy metals occurred in the order Pb> Mg > Fe > Cu > Cr. There were no statistically significant differences in the concentrations of the Mg ($F = 0.87$; $p = 0.50$) and Fe ($F = 0.74$; $p = 0.58$) at all sites (Fig 4).

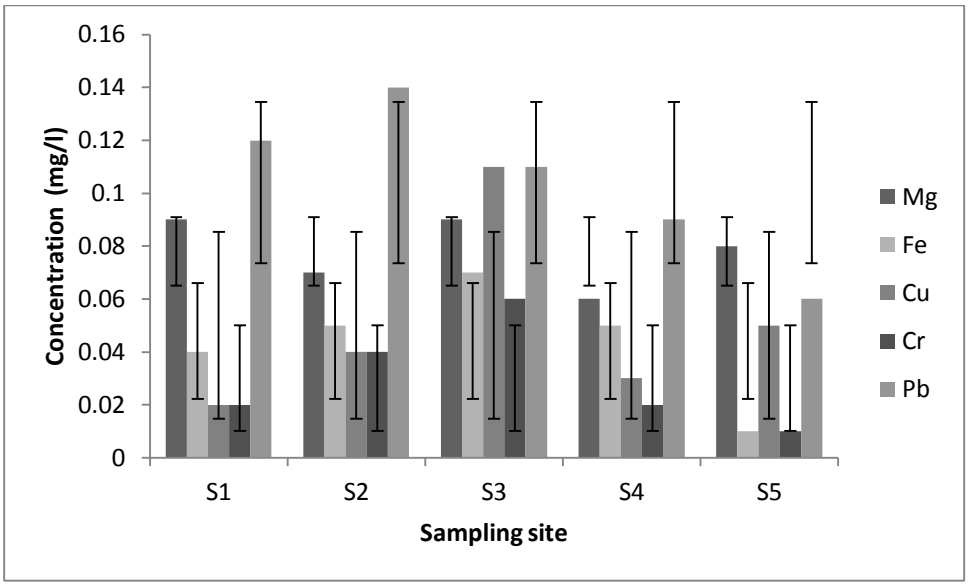

Figure4.1: Heavy metal concentrations in water from different sampling sites.

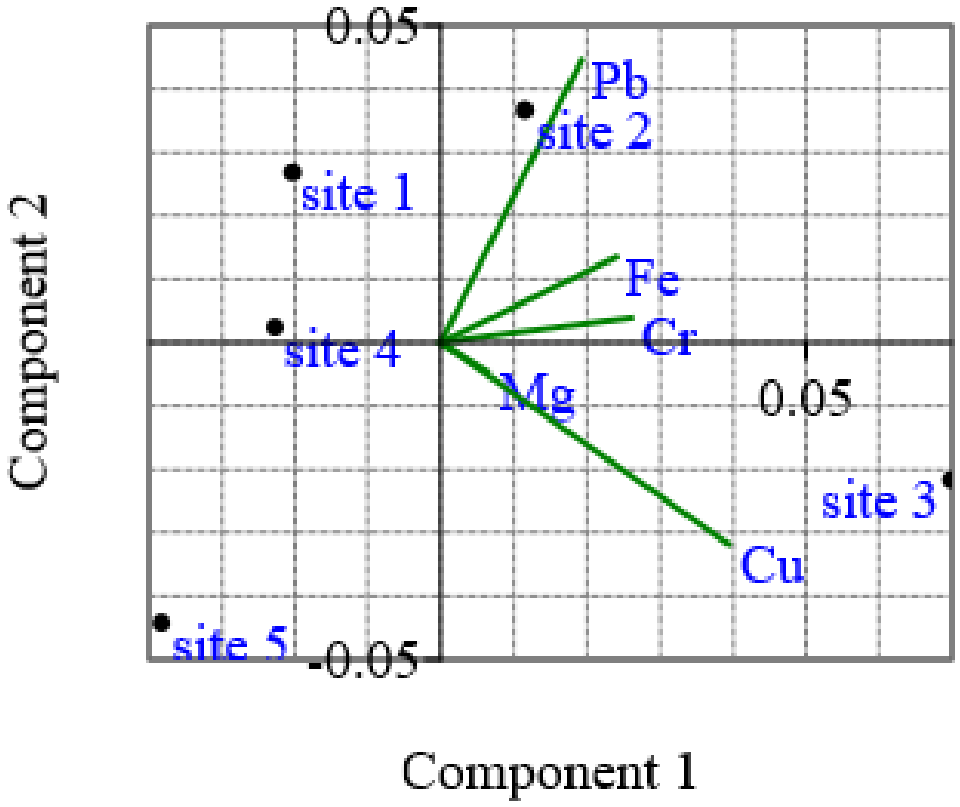

Figure4. 2: Spatial variation of metals in water using PCA

PC 1 and PC 2 explained 57.3% and 34.7% variation respectively in metal concentration among the sites. PCA separated sites 2 and 3 from sites 1, 4 and 5 along the PC 1 (Figure 4.2). The PCA could not completely separate the downstream sites 1, 2 and 3 from the upstream sites 4 and 5.The PCA shows that site 2 had high Pb concentrations while site 3 had high Cu concentration. Pb and Cu are the major variables responsible for separation along PC1.

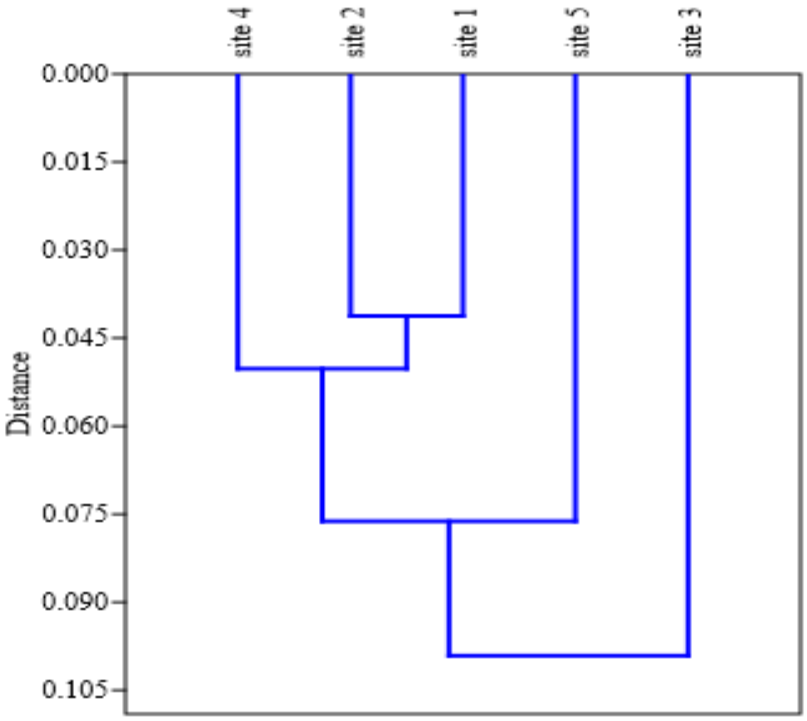

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Figure4.3: Dendrogram showing spatial similarities of heavy metal concentration in water

Cluster 1 included S 1, 2 and 4. The sampling site 4 located upstream showed similar metal contaminations with site 1 and site 2 due to low levels of Cu. Cluster 2 consisted of site 5 and cluster 3 of site 3 respectively.

4.1.2: CONCENTRATION OF HEAVY METALS IN SEDIMENTS

Overall, difference for metal level in sediments varied significantly among sampling points (Figure 4.4). The metal concentration in sediments was in the ranges: Mg (0.09 -0.23) mg $L^{-}1$, Cu (0.02-0.13) mg L^{-1}, Cr (0.01- 0.09) mg L^{-1}, Fe (0.01 – 0.11) mg L^{-1} and Pb (0.03 - 0.24) mg L^{-1}. A similar trend with metal concentration in water was observed in which highest levels of Pb

was at site 2 (0.20 ± 0.26) mg L^{-1} compared to other sites. There were significant differences in Pb (ANOVA:F = 18.08, p = 0.00), Cr (ANOVA:F = 15.64, p = 0.00), Mg (ANOVA:F = 6.22, p = 0.04) and Fe (ANOVA:F = 9.13, p = 0.01) among the sites. A Turkeys post hoc analysis showed that S1and S3 (p = 0.00), S2 and S3 (p = 0.004), S5 and S3 (p = 0.00) were significantly different for Cr. S3 and S4 (p = 0.004), S3 and S5 (p = 0.004), S2 and S5 (p = 0,004) were significantly different for Fe. S3 and S2 (p = 0.003), S3 and S4 (p = 0.01), S3 and S5 (p = 0.04) were significantly different for Mg. S5 and S3 (p = 0.004), S5 and S2 (p= 0.00), S5 and S1 (p = 0.00) and S4 and S2 (p = 0.001) were different from each other for Pb where as S1 and S4 (p= 0.05) were marginally significant. The results show that there were no significant differences in Cu levels among all the studied sites (ANOVA: F = 0.10, p = 0.44). Overall, concentration of heavy metal in sediments was in the order: Pb> Mg> Fe> Cu> Cr.

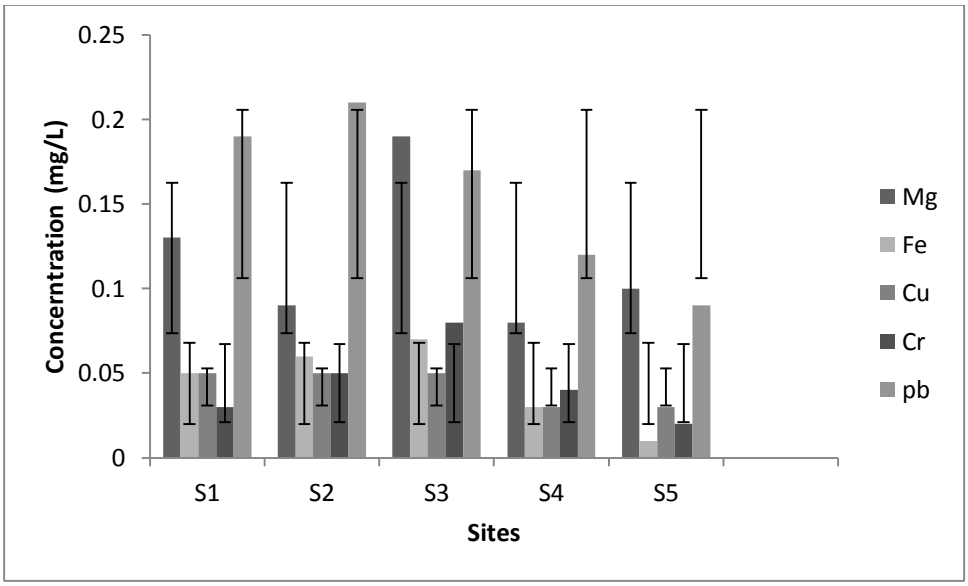

Figure4.4 Heavy metal concentrations in sediments from the five sampling sites.

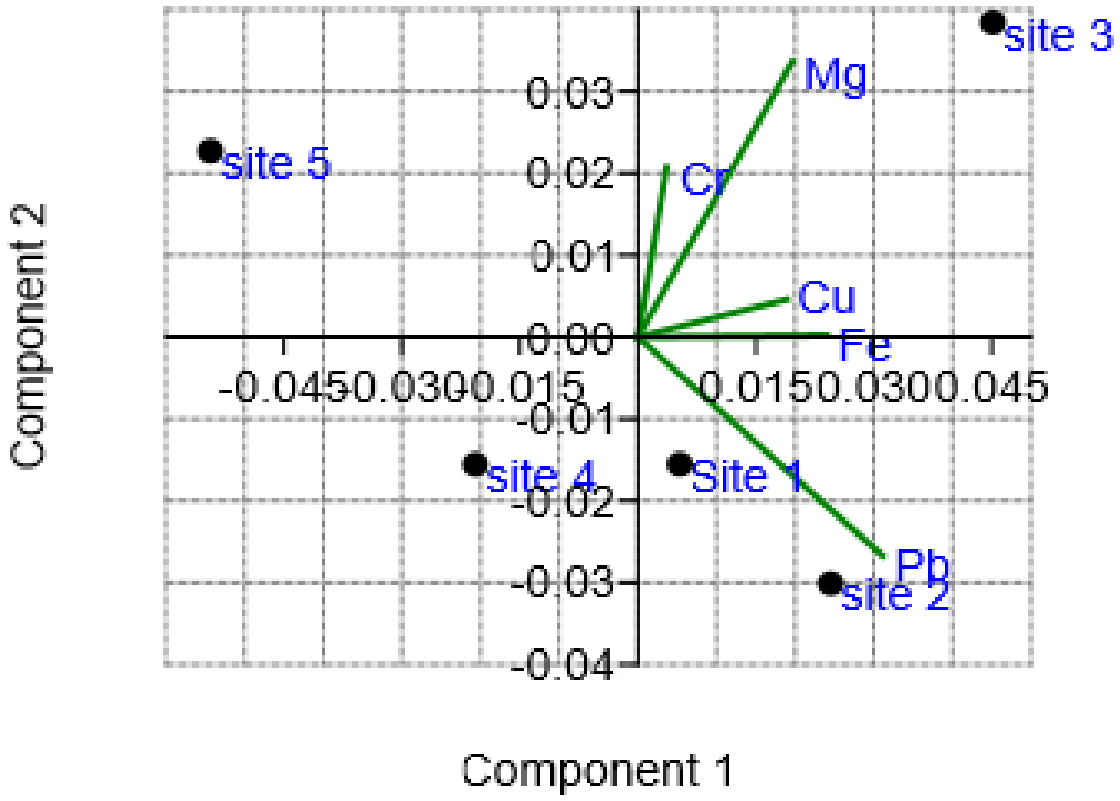

Figure4.5: Spatial variations of metals in sediments using PCA

The first PC separated sites 1, 2 and 3 downstream of the Sebakwe river from site 4 and site 5 (Figure 4.5) located upstream of the sewage disposal point. Sites (1 and 2) are separated from other sites due to high concentration of Pb and site 3 isolated due to elevated levels of Mg. PC 1 explained 78.52% and PC 2 explained 10.16% respectively of total variation of metal concentration in sediments. Mg and Pb were the major variables responsible for the separation of sites along PC 1.

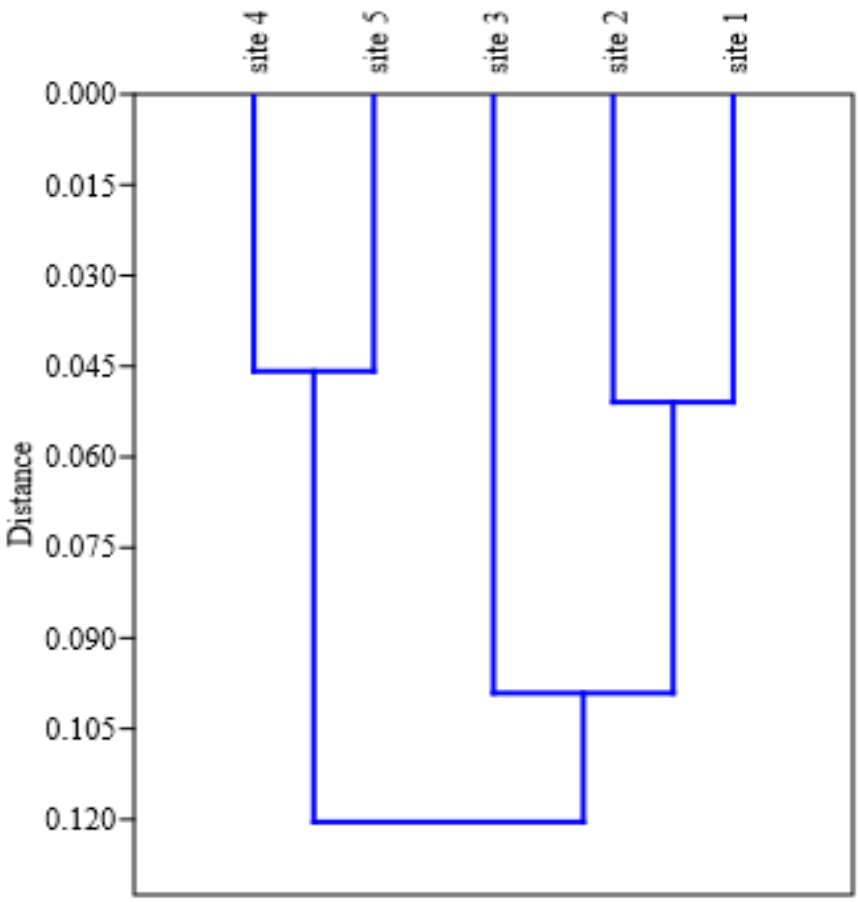

Figure 4.6: Dendrogram showing spatial similarities of sediment in different sampling sites

Cluster analysis showed that all sampling sites cluster into three clusters (figure 4.6). Cluster 1 consists of sites 4 and 5 that are located upstream of the sewage discharge point along Sebakwe River. Cluster 2 composed by site 3 which is separated from other downstream sites as it has elevated levels of Mg. The third cluster is formed by sites 1and 2 that are located downstream of the urban waste water discharge with similar levels of Fe and Pb concentrations.

4.2:0: COMPARISON OF METAL CONCENTRATION IN WATER AND SEDIMENTS

4.2.1: EXCHANGE FACTOR

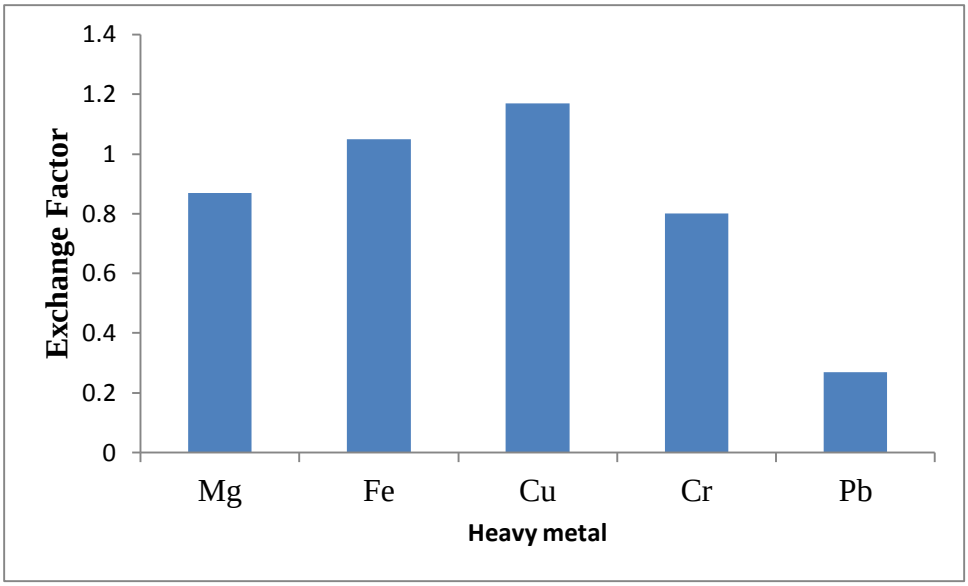

Figure 4.7: Exchange factor of water and sediment in the Sebakwe River.

The CE was higher for all heavy metals (> 0.8) except Pb (Figure 4.7), showing greater mobility of Mg, Cr, Cu and Fe in water towards the sediments. Mg, Fe and Cu showed high significant correlations ($r > 0.8$; $p < 0.05$) between metals in water and sediment (Table 1).

Table 4.1: Correlation between metal concentration in water and sediments

Metal	**Pearson r**	**P- value**
Fe	0.947	0.01
Cu	0.546	0.34
Cr	0.862	0.06
Pb	0.812	0.9
Mg	0.984	0.00

4.3: CONTAMINATION FACTOR, POLLUTION LOAD INDEX AND GEO-ACCUMULATION INDEX OF HEAVY METALS IN SEDIMENTS.

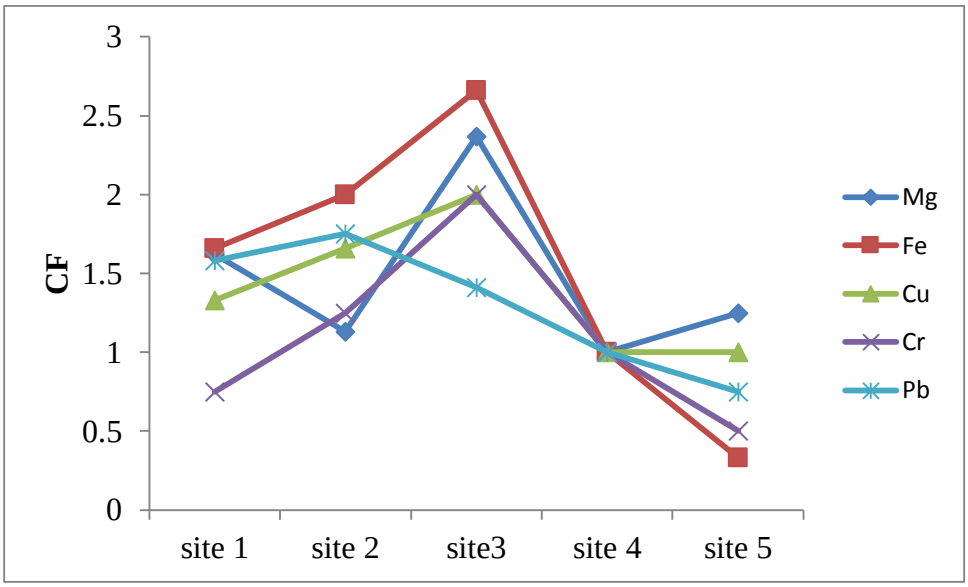

Figure4.8: CF of sediment samples

Sites 1-4 were moderately contaminated with Cu, Pb, Fe, Mg, Cr with contamination factor ranging from 1-3 except for site 1 with Cu having a contamination value less than 1 (0.75) indicating a low degree of contamination. The overall PLI indicates that site 4 was less contaminated with all studied metals (Figure 4.8).

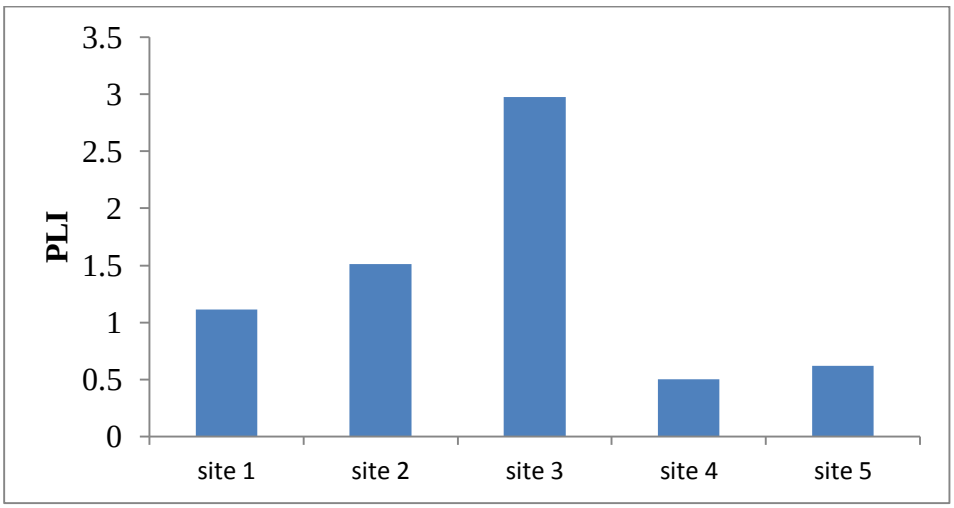

Figure4.9 Pollution Load at different sampling sites

The PLI indicate that metal concentrations among sites do not show pollution. Sites 4 and 5 upstream of the sewage discharge point had the least PLI of 0.5 and 0.62 respectively (Figure 4.9). Sites 1 and 2 downstream of the sewage discharge point were moderately contaminated while S3 was heavily contaminated with all studied metals**.**

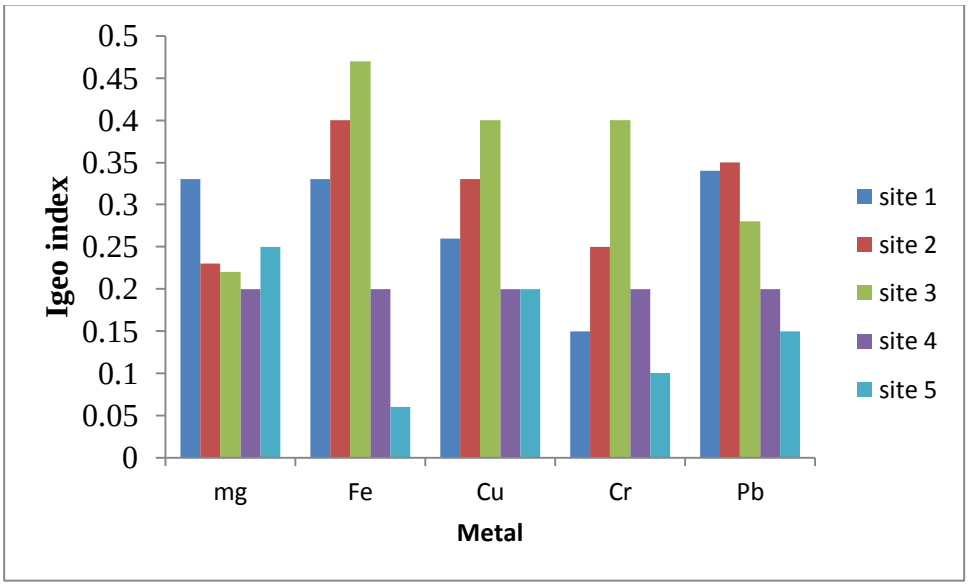

Figure 4.10: I Geo index at different sampling sites

Results showed that all the studied sites were uncontaminated to moderately contaminated (i.e.0 < I_{geo} < 1 which shows that they were uncontaminated to moderately contaminated. S 1, 2, and 3 were moderately contaminated with Fe, Cu, Cr and Pb while site 4 and site 5 was generally uncontaminated (Figure 4.10).

4.4: COMPARISON OF HEAVY METAL CONCENTRATION IN WATER WITH WHO (2008) AND SAZ (2005) STANDARDS.

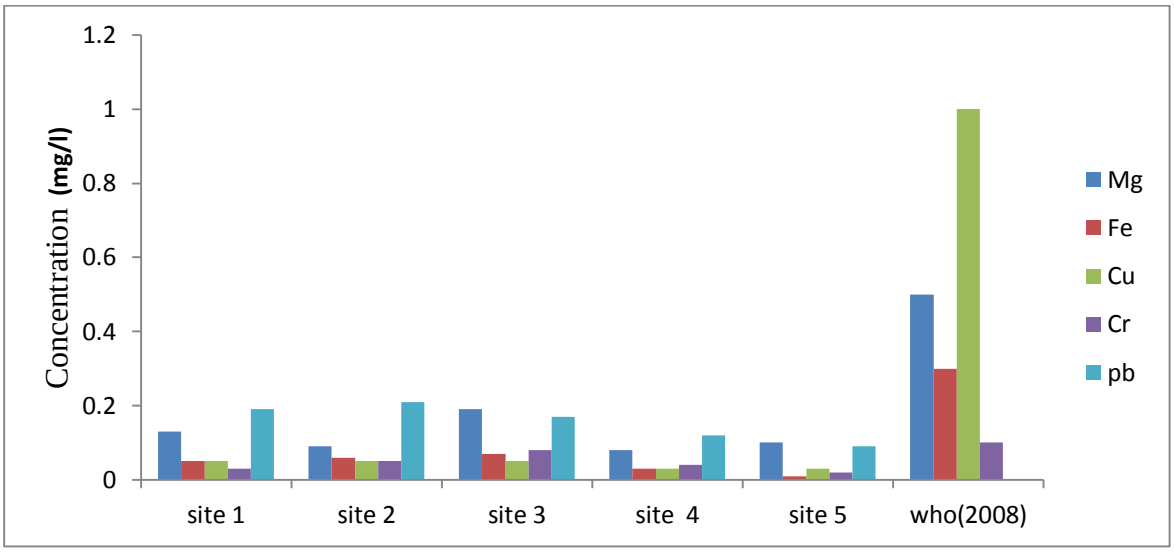

Figure 4.11: Comparison of metal concentrations with WHO (2008) standards.

The concentration of Pb at all sampling sites was above the permissible limits recommended by WHO (Figure 4.11) indicating a bad condition of the river quality. Mg, Fe, Cu, Cr were all below the WHO standards.

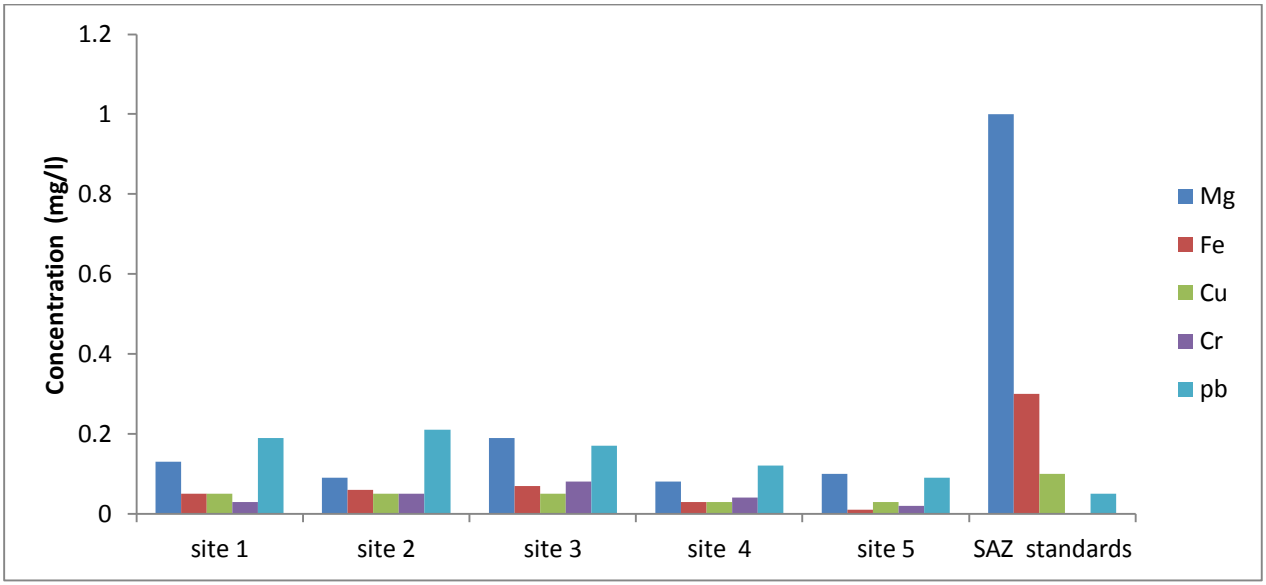

Figure 4.12: Comparison of metal concentrations with SAZ (2015) standards.

Mg, Fe, Cu and Cr were well below the permissible limits recommended by SAZ where Pb was above the SAZ permissible limit at all studied sites (Figure 4.12).

5.0 CHAPTER FIVE: DISCUSSION

5.1: SPATIAL VARIATION OF HEAVY METAL CONCENTRATION IN WATER AND SEDIMENTS

The study showed that the heavy metal concentrations in water were in the order Pb > Mg > Fe > Cu > Cr. The metal concentration in upstream sites could not be separated from downstream sites. There were significant differences in Pb, Cr and Cu but no significant differences were observed in Mg and Fe concentration among the studied sites. The high levels of Cu and Cr in water at site 3 could be attributed to domestic and sewage industrial effluent from Kwekwe Sewage Treatment Plant (KSTP). The study also showed that the heavy metal concentration in sediments were in the order Pb > Mg > Fe > Cu > Cr and there were significant differences in Pb, Cr, Fe and Mg. Similar patterns with water were observed in which the concentration of metals in sediments were higher in downstream compared to upstream sites (Figure 4.4). The results from this study confirm findings from similar studies where high levels of metals were observed in rivers due to sewage effluent e.g. (Ochieng *et al.,* 2007; Ibrahim *et al* 2016; Teta *et al.,* 2017; Utete *et al*., 2018). The differences in metal concentration upstream and downstream can be attributed to the improper discharge of partially treated industrial waste water and domestic sewage water that are loaded with metals from various industries. Some industries in Kwekwe discharge waste water effluents with heavy metals into KSTP which is not designed to remove metal pollutants but mainly nutrients, TSS and TDS. The results from this study confirm findings from similar studies in which sites after effluent discharge had elevated levels of Cr and Fe and Pb compared to sites before the discharge (Perez *et al.*, 2016; Simul and Muhammad 2017).

This study also showed that high levels of Pb, Cu and Cr were observed at site 2 downstream of site 3. Site 2 was located under the bridge along the Kwekwe-Harare highway which is characterized by high volumes of traffic. Other studies have showed that the combustion of petrol in vehicles containing anti-knocking additive lead is a major source of atmospheric lead which can be deposited into the surface water (Saiful *et al*., 2015; Singovszka *et al*., 2017).

Furthermore, the catchment of Sebakwe River is characterized by artisanal gold mining (AGM) which also contributes to metals upstream ( ). Runoffs pass through the mines tailings and become acidified by contacting sulfur – containing rock (Singovszka *et al.*, 2017). This result in high levels of metals being leached from rocks by the acidic water and then discharged into the river. A decrease in pH may increase solubility of toxic heavy metal resulting in elevated levels in water body and the less soluble forms are accumulated in the suspended or sedimented phase. Acid generation and discharge continue to occur even after the mining is ceased. This causes serious threat to human health and ecological systems since heavy metals are not biodegradable and thus tends to accumulate in living organisms causing various diseases and disorders (Verhaet *et al*., 2019). The low pH of mine drainage results in solubility of heavy metals in water and support only severely reduced animal and plant diversity (Singovszka *et al*., 2017). Acute exposure to high metal levels result in death of an organism while prolonged exposure to lower metal levels can cause stunted growth, lower reproduction rates, deformities and lesions (Pourahmad *et al*., 2005).

5.2: COMPARISON OF METAL CONCENTRATION IN WATER AND SEDIMENTS

The results from this study showed a positive correlation between metals in water and sediments suggesting that heavy metal concentration in water influence those in sediments (Table 4.1).

Similar studies have shown that metals (e.g. Cu, Zn, Cd and Pb) in water and sediments were positively correlated for the samples collected from Bietri Bay River (Kouame 2014). Sediments are an ultimate sink for metals in aquatic environment (Esmaeilzadeh *et al*., 2016). However, a change in the ecological conditions such as pH, temperature, salinity, conductivity and dissolved oxygen will cause the sediments to release the metals into the water column (Yayintas *et al.*, 2007). In this study, the heavy metal concentration in water was composed of both the dissolved and the suspended metals due to the formation of a strong aqueous complex with dissolved sulfides which is a mechanism facilitating the mobilization of metals from sediment. Other studies have shown that some of the suspended metals in water come from the sediments, producing a correlation between sediment and suspended metal concentrations (Pourahmad *et al.,* 2005; Singovszka *et al.,* 2017). The positive relationship between metal concentration in sediments and aqueous is because most metals are insoluble at neutral to alkaline pH ranges, hence they precipitate and accumulate in sediments (Pourahmad *et al*., 2005). At the same time, heavy metals can be released into the aqueous phase depending on the redox potential and bioturbation of the sediment (Bonsignore *et al.,* 2018). Therefore, aquatic sediments are important when monitoring environmental pollution in the rivers.

The mobility of heavy metal from water towards the sediments was also shown by the high exchange factor (CE) for all the studied metals except Pb (Figure 4.7). The CE values showed a decreasing pattern of Cu > Fe > Mg > Cr > Pb. The higher metal concentrations in sediments coincided with an increasing amount of fine-grained fraction and organic carbon downstream of the Sebakwe River from the sewage discharge. In addition, the binding of metals with insoluble iron sulphides might explain the high concentrations of heavy metals in sediment at the sampling sites after the sewage discharge along the Sebakwe River. These insoluble iron sulphides may be

released from the Kwekwe Water Treatment Plant as sludge. Similar studies have shown that accumulation of heavy metals in sediment is related to high clay and organic carbon content (Ochieng *et al*., 2007, Ahmed *et al*., 2009).

High levels of heavy metal concentrations in sediments have an impact on the aquatic ecosystems because sediments are an integral component of aquatic environment providing habitat, feeding, spawning and rearing areas for many organisms (de Castro-Catala *et al*., 2016). Several studies have shown that heavy metals bioaccumulate in the aquatic food chain and their impact varies from individual organisms to community composition (Bonsignore *et al*., 2018; Verhaert *et al*., 2019). For example, the metals affect individual organisms by inhibiting enzymes on the gills or gill-like structures resulting in toxicity through the disruption of ion and water balance (Pourahamad *et al.,* 2006). Heavy metals accumulates in fish organs especially the gills which act as a filter causing deleterious effects at sub cellular, cellular, organ, and system levels (Ibrahim *et al.,* 2016). These effects are exhibited through effects on reproduction (especially in the form of teratogenesis) and reduced survival of young fish as well as effects on health, physiology, and survival of older fish. In aquatic invertebrates, adaptation to low oxygen conditions can be hindered by high metal concentrations (Bonsignore *et al.,* 2018). The toxicity of these elements is due to their ability to cause, oxidative damage to living tissues. Heavy metals bind strongly to functional sites that are usually occupied by essential functional groups of biologically important molecules thereby disrupting the integrity of entire cells and their membranes, making them inactive, decomposing essential metabolites and changing the osmotic balance around the cells (Ibrahim *et al.,* 2016). The degeneration and morphological alterations of the cells reflect one aspect of the cytotoxic impacts after exposure to pollutants and serve as an index of cytotoxicity (Ibrahim *et al.,* 2016). Other effects of continued exposure to heavy

metals of aquatic organisms include decreased respiration, reproductive capacity, kidney failure, neurological effects, bone fragility and mutagenesis (deCastro-Catala *et al*., 2016). These impacts can have implications at the population and ecosystem levels because food chains will be affected and there will be a shift in the species composition, species diversity and genetic diversity of the ecosystem (Hamilton *et al.*, 2016). Sebakwe River provides fish to local human communities through established fishing cooperatives. Similar studies have reported an accumulation of heavy metals in the tissues of fish living in polluted water (Utete *et al.* 2018; Verhaert *et al*., 2019; Dube *et al*., 2019).

5.3: CONTAMINATION FACTOR, POLLUTION LOAD INDEX OF HEAVY METALS IN SEDIMENTS.

The contamination factor (CF) of metals in Sebakwe River were above 1 (CF > 1) and in the order Fe > Mg > Cu > Pb > Cr indicating that the sediment samples were moderately contaminated. Similarly, Igeo (class 0) indices indicate that the sediments are uncontaminated to moderately contaminated. The sediment metal levels in present study were lower compared to polluted rivers and dams in the region (Teta *et al.* 2017; Utete *et al.* 2018). The Pollution Load Index (PLI) of heavy metals in sediments was in the decreasing order of S3 > S2 > S1 > S5 > S4. Sites 1, 2 and 3 after the sewage effluent discharge in Sebakwe River experienced progressive deteriorations (PLI > 1) due to anthropogenic inputs hence they need to be monitored (Tomilsonn *et al*., 1980, Esmaeilzadeh *et al*., 2016). Findings from the present study indicate that the river sediment is slightly contaminated and may increase. The results form a baseline for future monitoring of metal pollutants in Sebakwe River. The continued release of metals in Sebakwe River would result in accumulation to higher levels which have negative impacts on biota.

5.4: EFFECTS OF METAL POLLUTION ON HUMAN HEALTH

The comparison of the heavy metals concentrations in the Sebakwe River water with the WHO and SAZ standards of drinking water suggest that the level of Cu, Mg, Fe and Cr in water were within the acceptable range recommended. The concentrations of Pb at each studied site were above the permissible limit of both SAZ and WHO standards. High levels of heavy metal concentrations in water may cause health problems because human communities along the Sebakwe River are using water for domestic purposes. Although Pb is not a nutritionally essential element, its monitoring is important because of its toxicity to human health (Zepeng *et al.,* 2018). Acute exposure to lead induces brain damage and central nervous system to cause coma, kidney damage, convulsions and even death, and gastrointestinal diseases, while chronic exposure may cause adverse effects on the blood, central nervous system, blood pressure, kidneys, and vitamin D metabolism (Zepeng *et al*., 2007). This makes the water unsuitable for human consumption as Pb is known to be toxic even at low levels with resultant ill-health effects as chronic exposure has been linked to growth retardation in children **(**WHO, 2011; Ibrahim *et al.,* 2016). Lead exposure can have serious consequences for the health of children because they absorb 4–5 times as much ingested lead as adults from a given source (Wogu and Okaka 2011). Children who survive severe lead poisoning may be left with mental retardation and behavioral disorders. At lower levels of exposure lead can affect children's brain development resulting in reduced intelligence quotient (IQ), behavioural changes such as reduced attention span and increased antisocial behaviour, and reduced educational attainment (deCastro-Catala *et al*., 2016). Lead exposure also causes anaemia, hypertension, renal impairment, immunotoxicity and toxicity to the reproductive organs (Verhaert *et al.,* 2019).

5.5: CONCLUSION

The contamination factor (CF), pollution load index (PLI) and geo-accumulation index (Igeo) exposed that sediments were unpolluted to extremely polluted by heavy metals. When the quality of the river is compared with the WHO and SAZ standards recommended limits for source of water supply, the river was found to contain Pb above the recommended limits, indicating pollution. Rapid urbanization and increased industrialisation followed by releasing of untreated industrial effluents into the river played a significant role in deteriorating the water quality of the Sebakwe River. In this study water and sediment samples taken from five sampling sites confirmed that the river has been polluted with Cr, Fe, Pb, Mg and Cu. The result demonstrated that heavy metals have originated from various sources; however, the main anthropogenic sources were industrial waste, municipal waste, run–off from agricultural fields and artisanal mining activities practiced near the river. Because this area is populated with many industries and the final drainage of this river ends into the sea hence the water quality and pollution status of the river system is of great concern. Management of domestic and industrial waste is required to lower the accumulation, contamination and subsequent pollution of such metals in water and sediments, and to minimize environmental degradation. This should be achieved by installing municipal solid waste landfills, and proper treatment of municipal and industrial wastewater before being released to the environment, improvements in agricultural practices and also in artisanal mining activities especially when there is low flow rate.

5.6: RECOMMENDATIONS

To control water contamination, legislative measures must be taken, legally binding the individual industries, outlawing the discharge of untreated or poorly treated industrial effluents.

Lowering the quality of water health due to these industries can only be restricted if a zero discharge system of effluent is implemented. Immediate steps including regular monitoring of toxic metals in the river waters is needed to check the environmental quality. Wastewater discharged from municipal sewage could be recycled for the remediation of pollution in a sustainable and eco-specific way. Improvement of conditions and industrial effluent is needed and domestic sewage discharge should be reduced. Moreover different remediation measures should be taken promptly to remove existing metal contaminants.

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APPENDICES

Appendix 1: AAS results of the concentrations of Pb, Fe, Cr, Cu and Mg at different sites in water

	Sites	January		February	
metals		1	2	1	2
Mg	1	0.09	0.08	0.07	0.06
	2	0.07	0.08	0.06	0.08
	3	0.09	0.10	0.08	0.05
	4	0.06	0.08	0.04	0.03
	5	0.08	0.06	0.06	0.04
Fe	1	0.04	0.04	0.03	0.04
	2	0.05	0.05	0.05	0.05
	3	0.07	0.06	0.06	0.07
	4	0.05	0.04	0.04	0.05
	5	0.01	0.02	0.01	0.01
Cu	1	0.02	0.01	0.02	0.02
	2	0.04	0.03	0.03	0.04
	3	0.11	0.08	0.16	0.11
	4	0.03	0.05	0.02	0.03
	5	0.05	0.03	0.07	0.05
Cr	1	0.02	0.03	0.02	0.01
	2	0.04	0.05	0.04	0.02
	3	0.06	0.08	0.07	0.04
	4	0.02	0.04	0.03	0.01
	5	0.01	0.04	0.01	0.01
Pb	1	0.12	0.08	0.19	0.13
	2	0.14	0.10	0.15	0.11
	3	0.11	0.09	0.09	0.10
	4	0.09	0.05	0.07	0.04
	5	0.06	0.05	0.04	0.02

Appendix 1.2

AAS results of the concentrations of Pb, Fe, Cr, Cu and Mg at different sites in sediments

metals	Sites	January		February	
		1	2	1	2
Mg	1	0.13	0.10	0.15	0.11
	2	0.09	0.07	0.10	0.07
	3	0.19	0.15	0.23	0.16
	4	0.08	0.06	0.15	0.10
	5	0.10	0.07	0.13	0.15
Fe	1	0.05	0.04	0.08	0.05
	2	0.06	0.05	0.11	0.07
	3	0.08	0.10	0.09	0.08
	4	0.03	0.04	0.05	0.07
	5	0.01	0.02	0.03	0.02
Cu	1	0.05	0.03	0.08	0.05
	2	0.05	0.06	0.06	0.07
	3	0.06	0.04	0.10	0.13
	4	0.03	0.02	0.06	0.08
	5	0.03	0.01	0.04	0.03
Cr	1	0.03	0.02	0.04	0.02
	2	0.05	0.06	0.07	0.03
	3	0.08	0.09	0.10	0.06
	4	0.04	0.03	0.05	0.02
	5	0.02	0.01	0.01	0.02
Pb	1	0.19	0.15	0.22	0.18
	2	0.21	0.18	0.24	0.19
	3	0.17	0.10	0.18	0.12
	4	0.12	0.09	0.11	0.08
	5	0.09	0.05	0.05	0.03

Appendix 2: SPSS output

Appendix 2.1: One WAY ANOVA

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
pb	Between Groups	.024	4	.006	8.384	.001
	Within Groups	.011	15	.001		
	Total	.034	19			
cr	Between Groups	.006	4	.002	10.818	.000
	Within Groups	.002	15	.000		
	Total	.008	19			
mg	Between Groups	.052	4	.013	.870	.505
	Within Groups	.223	15	.015		
	Total	.275	19			
cu	Between Groups	.023	4	.006	18.355	.000
	Within Groups	.005	15	.000		
	Total	.028	19			
fe	Between Groups	.144	4	.036	.737	.581
	Within Groups	.730	15	.049		
	Total	.874	19			

Appendix 2.1.2: Multiple Comparisons

Multiple Comparisons

Tukey HSD

Dependent Variable	(I) treatment	(J) treatment	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
pb concentration	site 1	site 2	.00500	.01873	.999	-.0528	.0628
		site 3	.03250	.01873	.443	-.0253	.0903
		site 4	.06750*	.01873	.019	.0097	.1253

		site 5	.08750*	.01873	.002	.0297	.1453
		site 1	-.00500	.01873	.999	-.0628	.0528
		site 3	.02750	.01873	.597	-.0303	.0853
	site 2	site 4	.06250*	.01873	.031	.0047	.1203
		site 5	.08250*	.01873	.004	.0247	.1403
		site 1	-.03250	.01873	.443	-.0903	.0253
		site 2	-.02750	.01873	.597	-.0853	.0303
	site 3	site 4	.03500	.01873	.374	-.0228	.0928
		site 5	.05500	.01873	.066	-.0028	.1128
		site 1	-.06750*	.01873	.019	-.1253	-.0097
		site 2	-.06250*	.01873	.031	-.1203	-.0047
	site 4	site 3	-.03500	.01873	.374	-.0928	.0228
		site 5	.02000	.01873	.820	-.0378	.0778
		site 1	-.08750*	.01873	.002	-.1453	-.0297
		site 2	-.08250*	.01873	.004	-.1403	-.0247
	site 5	site 3	-.05500	.01873	.066	-.1128	.0028
		site 4	-.02000	.01873	.820	-.0778	.0378
		site 2	-.01750	.00842	.278	-.0435	.0085
		site 3	-.04250*	.00842	.001	-.0685	-.0165
	site 1	site 4	-.00500	.00842	.974	-.0310	.0210
		site 5	.00750	.00842	.896	-.0185	.0335
		site 1	.01750	.00842	.278	-.0085	.0435
		site 3	-.02500	.00842	.062	-.0510	.0010
	site 2	site 4	.01250	.00842	.586	-.0135	.0385
		site 5	.02500	.00842	.062	-.0010	.0510
		site 1	.04250*	.00842	.001	.0165	.0685
		site 2	.02500	.00842	.062	-.0010	.0510
Cr	site 3	site 4	.03750*	.00842	.004	.0115	.0635
		site 5	.05000*	.00842	.000	.0240	.0760
		site 1	.00500	.00842	.974	-.0210	.0310
		site 2	-.01250	.00842	.586	-.0385	.0135
	site 4	site 3	-.03750*	.00842	.004	-.0635	-.0115
		site 5	.01250	.00842	.586	-.0135	.0385
		site 1	-.00750	.00842	.896	-.0335	.0185
		site 2	-.02500	.00842	.062	-.0510	.0010
	site 5	site 3	-.05000*	.00842	.000	-.0760	-.0240
		site 4	-.01250	.00842	.586	-.0385	.0135
mg	site 1	site 2	.00250	.08625	1.000	-.2638	.2688

		site 3	-.00500	.08625	1.000	-.2713	.2613
		site 4	.02250	.08625	.999	-.2438	.2888
		site 5	-.12000	.08625	.642	-.3863	.1463
		site 1	-.00250	.08625	1.000	-.2688	.2638
	site 2	site 3	-.00750	.08625	1.000	-.2738	.2588
		site 4	.02000	.08625	.999	-.2463	.2863
		site 5	-.12250	.08625	.625	-.3888	.1438
		site 1	.00500	.08625	1.000	-.2613	.2713
	site 3	site 2	.00750	.08625	1.000	-.2588	.2738
		site 4	.02750	.08625	.997	-.2388	.2938
		site 5	-.11500	.08625	.676	-.3813	.1513
		site 1	-.02250	.08625	.999	-.2888	.2438
	site 4	site 2	-.02000	.08625	.999	-.2863	.2463
		site 3	-.02750	.08625	.997	-.2938	.2388
		site 5	-.14250	.08625	.489	-.4088	.1238
		site 1	.12000	.08625	.642	-.1463	.3863
	site 5	site 2	.12250	.08625	.625	-.1438	.3888
		site 3	.11500	.08625	.676	-.1513	.3813
		site 4	.14250	.08625	.489	-.1238	.4088
		site 2	-.01750	.01258	.642	-.0564	.0214
	site 1	site 3	-.09750*	.01258	.000	-.1364	-.0586
		site 4	-.01500	.01258	.756	-.0539	.0239
		site 5	-.03250	.01258	.124	-.0714	.0064
		site 1	.01750	.01258	.642	-.0214	.0564
	site 2	site 3	-.08000*	.01258	.000	-.1189	-.0411
		site 4	.00250	.01258	1.000	-.0364	.0414
		site 5	-.01500	.01258	.756	-.0539	.0239
		site 1	.09750*	.01258	.000	.0586	.1364
		site 2	.08000*	.01258	.000	.0411	.1189
cu	site 3	site 4	.08250*	.01258	.000	.0436	.1214
		site 5	.06500*	.01258	.001	.0261	.1039
		site 1	.01500	.01258	.756	-.0239	.0539
	site 4	site 2	-.00250	.01258	1.000	-.0414	.0364
		site 3	-.08250*	.01258	.000	-.1214	-.0436
		site 5	-.01750	.01258	.642	-.0564	.0214
		site 1	.03250	.01258	.124	-.0064	.0714
	site 5	site 2	.01500	.01258	.756	-.0239	.0539
		site 3	-.06500*	.01258	.001	-.1039	-.0261
		site 4	.01750	.01258	.642	-.0214	.0564
fe	site 1	site 2	-.01250	.15604	1.000	-.4943	.4693

		site 3	-.02750	.15604	1.000	-.5093	.4543
		site 4	-.00750	.15604	1.000	-.4893	.4743
		site 5	-.22250	.15604	.622	-.7043	.2593
		site 1	.01250	.15604	1.000	-.4693	.4943
	site 2	site 3	-.01500	.15604	1.000	-.4968	.4668
		site 4	.00500	.15604	1.000	-.4768	.4868
		site 5	-.21000	.15604	.669	-.6918	.2718
		site 1	.02750	.15604	1.000	-.4543	.5093
	site 3	site 2	.01500	.15604	1.000	-.4668	.4968
		site 4	.02000	.15604	1.000	-.4618	.5018
		site 5	-.19500	.15604	.724	-.6768	.2868
		site 1	.00750	.15604	1.000	-.4743	.4893
	site 4	site 2	-.00500	.15604	1.000	-.4868	.4768
		site 3	-.02000	.15604	1.000	-.5018	.4618
		site 5	-.21500	.15604	.650	-.6968	.2668
		site 1	.22250	.15604	.622	-.2593	.7043
	site 5	site 2	.21000	.15604	.669	-.2718	.6918
		site 3	.19500	.15604	.724	-.2868	.6768
		site 4	.21500	.15604	.650	-.2668	.6968

***. The mean difference is significant at the 0.05 level.**

Appendix2.2SPSS output for Sediments

Appendix 2.2.1: Levenes' Test of Equality of Error

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
pb	Between Groups	.061	4	.015	18.077	.000
	Within Groups	.013	15	.001		
	Total	.074	19			
cr	Between Groups	.011	4	.003	15.643	.000
	Within Groups	.003	15	.000		
	Total	.014	19			

	Between Groups	.011	4	.003	9.130	.001
fe	Within Groups	.004	15	.000		
	Total	.015	19			
	Between Groups	4.892	4	1.223	.999	.438
cu	Within Groups	18.361	15	1.224		
	Total	23.253	19			
	Between Groups	.024	4	.006	6.222	.004
mg	Within Groups	.014	15	.001		
	Total	.038	19			

Appendix 2.2.2: Multiple Comparisons

Tukey HSD

Dependent Variable	(I) treatment	(J) treatment	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
pb	site 1	site 2	-.02000	.02055	.863	-.0835	.0435
		site 3	.04000	.02055	.337	-.0235	.1035
		site 4	.08750*	.02055	.005	.0240	.1510
		site 5	.13000*	.02055	.000	.0665	.1935
	site 2	site 1	.02000	.02055	.863	-.0435	.0835
		site 3	.06000	.02055	.068	-.0035	.1235
		site 4	.10750*	.02055	.001	.0440	.1710
		site 5	.15000*	.02055	.000	.0865	.2135
	site 3	site 1	-.04000	.02055	.337	-.1035	.0235
		site 2	-.06000	.02055	.068	-.1235	.0035
		site 4	.04750	.02055	.195	-.0160	.1110
		site 5	.09000*	.02055	.004	.0265	.1535
	site 4	site 1	-.08750*	.02055	.005	-.1510	-.0240
		site 2	-.10750*	.02055	.001	-.1710	-.0440
		site 3	-.04750	.02055	.195	-.1110	.0160
		site 5	.04250	.02055	.283	-.0210	.1060
	site 5	site 1	-.13000*	.02055	.000	-.1935	-.0665
		site 2	-.15000*	.02055	.000	-.2135	-.0865
		site 3	-.09000*	.02055	.004	-.1535	-.0265
		site 4	-.04250	.02055	.283	-.1060	.0210
cr	site 1	site 2	-.02500	.00935	.106	-.0539	.0039
		site 3	-.05500*	.00935	.000	-.0839	-.0261
		site 4	-.00750	.00935	.926	-.0364	.0214
		site 5	.01250	.00935	.674	-.0164	.0414
	site 2	site 1	.02500	.00935	.106	-.0039	.0539
		site 3	-.03000*	.00935	.040	-.0589	-.0011
		site 4	.01750	.00935	.373	-.0114	.0464
		site 5	.03750*	.00935	.009	.0086	.0664
	site 3	site 1	.05500*	.00935	.000	.0261	.0839
		site 2	.03000*	.00935	.040	.0011	.0589
		site 4	.04750*	.00935	.001	.0186	.0764
		site 5	.06750*	.00935	.000	.0386	.0964
	site 4	site 1	.00750	.00935	.926	-.0214	.0364
		site 2	-.01750	.00935	.373	-.0464	.0114
		site 3	-.04750*	.00935	.001	-.0764	-.0186
		site 5	.02000	.00935	.255	-.0089	.0489
	site 5	site 1	-.01250	.00935	.674	-.0414	.0164
		site 2	-.03750*	.00935	.009	-.0664	-.0086

		site 3	-.06750*	.00935	.000	-.0964	-.0386
		site 4	-.02000	.00935	.255	-.0489	.0089
		site 2	-.01750	.01201	.603	-.0546	.0196
	site 1	site 3	-.03250	.01201	.100	-.0696	.0046
		site 4	.00750	.01201	.969	-.0296	.0446
		site 5	.03500	.01201	.069	-.0021	.0721
		site 1	.01750	.01201	.603	-.0196	.0546
	site 2	site 3	-.01500	.01201	.724	-.0521	.0221
		site 4	.02500	.01201	.277	-.0121	.0621
		site 5	.05250*	.01201	.004	.0154	.0896
		site 1	.03250	.01201	.100	-.0046	.0696
	site 3	site 2	.01500	.01201	.724	-.0221	.0521
fe		site 4	.04000*	.01201	.032	.0029	.0771
		site 5	.06750*	.01201	.000	.0304	.1046
		site 1	-.00750	.01201	.969	-.0446	.0296
	site 4	site 2	-.02500	.01201	.277	-.0621	.0121
		site 3	-.04000*	.01201	.032	-.0771	-.0029
		site 5	.02750	.01201	.201	-.0096	.0646
		site 1	-.03500	.01201	.069	-.0721	.0021
	site 5	site 2	-.05250*	.01201	.004	-.0896	-.0154
		site 3	-.06750*	.01201	.000	-.1046	-.0304
		site 4	-.02750	.01201	.201	-.0646	.0096
		site 2	1.23000	.78233	.535	-1.1858	3.6458
	site 1	site 3	1.20750	.78233	.552	-1.2083	3.6233
		site 4	1.24250	.78233	.526	-1.1733	3.6583
		site 5	1.26250	.78233	.511	-1.1533	3.6783
		site 1	-1.23000	.78233	.535	-3.6458	1.1858
	site 2	site 3	-.02250	.78233	1.000	-2.4383	2.3933
		site 4	.01250	.78233	1.000	-2.4033	2.4283
		site 5	.03250	.78233	1.000	-2.3833	2.4483
		site 1	-1.20750	.78233	.552	-3.6233	1.2083
	site 3	site 2	.02250	.78233	1.000	-2.3933	2.4383
cu		site 4	.03500	.78233	1.000	-2.3808	2.4508
		site 5	.05500	.78233	1.000	-2.3608	2.4708
		site 1	-1.24250	.78233	.526	-3.6583	1.1733
	site 4	site 2	-.01250	.78233	1.000	-2.4283	2.4033
		site 3	-.03500	.78233	1.000	-2.4508	2.3808
		site 5	.02000	.78233	1.000	-2.3958	2.4358
		site 1	-1.26250	.78233	.511	-3.6783	1.1533
	site 5	site 2	-.03250	.78233	1.000	-2.4483	2.3833
		site 3	-.05500	.78233	1.000	-2.4708	2.3608
		site 4	-.02000	.78233	1.000	-2.4358	2.3958
		site 2	.04000	.02174	.388	-.0271	.1071
	site 1	site 3	-.06000	.02174	.091	-.1271	.0071
mg		site 4	.02500	.02174	.778	-.0421	.0921
		site 5	.01000	.02174	.990	-.0571	.0771

site 2	site 1	-.04000	.02174	.388	-.1071	.0271
	site 3	-.10000*	.02174	.003	-.1671	-.0329
	site 4	-.01500	.02174	.956	-.0821	.0521
	site 5	-.03000	.02174	.649	-.0971	.0371
site 3	site 1	.06000	.02174	.091	-.0071	.1271
	site 2	.10000*	.02174	.003	.0329	.1671
	site 4	.08500*	.02174	.010	.0179	.1521
	site 5	.07000*	.02174	.039	.0029	.1371
site 4	site 1	-.02500	.02174	.778	-.0921	.0421
	site 2	.01500	.02174	.956	-.0521	.0821
	site 3	-.08500*	.02174	.010	-.1521	-.0179
	site 5	-.01500	.02174	.956	-.0821	.0521
site 5	site 1	-.01000	.02174	.990	-.0771	.0571
	site 2	.03000	.02174	.649	-.0371	.0971
	site 3	-.07000*	.02174	.039	-.1371	-.0029
	site 4	.01500	.02174	.956	-.0521	.0821

*. The mean difference is significant at the 0.05 level.

Appendix 3: Permissible limits in domestic water

Metals	WHO(2008)	SAZ(1997)
Magnesium	0.5	10
Chromium	0.05	_
Copper	1	0.1
Iron	0.03	0.3
lead	0	0.05