THE IMPACT OF WORKINGTON INDUSTRIAL EFFLUENT ON THE SURFACE WATER QUALITY OF MARIMBA RIVER, HARARE, ZIMBABWE.

BY

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**Declaration**

I MUTASA NYASHA.A. (R121214X) do hereby declare that this research project is a result of my own efforts and investigations under the supervision of **Dr A MUNODAWAFA** (Lecturer) and the research project has not been presented elsewhere for the purpose of any higher degree save for Midlands State University, Department of Land and Water Resources Management. All sources of information used herein are formally cited in the body of text and listed in the references section of this document. Notwithstanding any evidence to the contrary herein before, I reserve my right to publish the findings of this study with a Publisher of my choice.

Signed……………………this……day of …….2015

(Author)
DECLARATION

I declare and certify that I have supervised Mutasa Nyasha’s thesis with the topic Impact of Industrial Effluent on the water quality of Marimba River, Harare, Zimbabwe.

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ABSTRACT

Pollution of water bodies due to human activities such as industrial waste disposal is a serious challenge facing most developing countries in the world today. Thus the management and supply of freshwater to the public is compromised and the ecological integrity of these rivers is lost due to adverse impacts such as eutrophicaton with algal blooms proliferating in these rivers. This could be due to such factors as pre-treatment costs, costs of having pre-treatment plants and ineffective and irregular monitoring of companies by responsible authorities. This study is an analysis of the effects of industrial effluent from Workington Industrial effluent on the water quality of Marimba River. Workington Industrial Area consists of such companies as Omnia and Windmill fertiliser companies, Exide Battery Company and ZESA. The study aimed at analysing the following water quality parameters which are BOD$_5$, COD, phosphates, nitrates, lead, copper, temperature, pH and Pv4hr. The effluent was also measured against the EMA industrial effluent discharge limits. Samples were taken upstream of the river, about 3.22 km from discharge point, in the storm drain, about 3.05 km from discharge point and downstream 4.39 km away from discharge point. The upstream of the river was taken as the control. Result from the study showed that there was high nutrient loading of the river in the effluent from the industries with phosphates (4.67 mg/l), nitrates (5.31mg/l), which also lead to high oxygen demand of BOD (85.72 mg/l), COD (101.1 mg/l) and Pv4hr of (12.95mg/l). Recommendations are that there should be effective and regular monitoring of the area by the responsible authorities and also regular river monitoring.
DEDICATON

This study is dedicated first to thank God for this far He has taken me, to my parents for the opportunity they have given me to learn against all odds and to everyone that has put a hand in my life to better it.
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ACRONYMS

BOD-Biochemical Oxygen Demand
COD-Chemical Oxygen Demand
EMA-Environmental Management Agency
Pv4hr-Oxygen absorbed by potassium permanganate in 4 hours
pH-power of hydrogen
Cu-Copper
Pb-Lead
UMCA-Upper Manyame Catchment Area
WHO-World Health Organisation
DNA-Di ribo Nucleic Acid
IWRM-Integrated Water Resources Management
GWP-Global Water Partnership.
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CHAPTER ONE

1.1 INTRODUCTION

Water is one of the most essential and basic need for mankind and is by far an important natural resource for life that is likely to become a scarce resource in the years to come if proper sustainable management practices are not done, (Agrawal, 2013). Water is necessary for a number of purposes such as domestic uses, industrial, agriculture, power generation, waste disposal and transportation (Bhatia, 2003). According to Hirji et al 2002, water is an essential force in ecological life-support systems and is the cornerstone to which all sustainable social and economic development is based on. It is life for every living organism and the elementary value of freshwater can never be compromised for anything (Chinhanga, 2010). The issue of water pollution continues to emerge as a major threat to all water bodies, (Agrawal, 2013), with challenges of water pollution being faced all around the world and the major contributions coming from municipal sewage, industrial waste, domestic waste, and agro-chemical runoff from agricultural fields. Taking into consideration the exponential growth of the human population, according to Chinhanga, 2010, the consequences of claiming the degraded resource and dealing with unpredicted conflicts over water shortages may be very high for future generations to come.

Water pollution can be defined as the alterations or changes in the composition and condition of water due to the introduction of substances with relative quantities, making it harmful or unsuitable for its purposes, (Bhatia, 2003). According to Agrawal, (2003), growth of industrialisation, the rising of public and private sectors have subjected the natural resources to ecological stresses, that is giving rise to water pollution. There are two major sources of water pollution which are point source and non-point source pollution. In point source pollution substances are released directly into the water way from an identified source for example a pipeline from an industrial site discharging effluent directly into a river. Non point source pollution is as a result of many polluting substances coming through from a large area for example pollutants from agricultural activities such as nutrients from fertilisers, pesticides, soil particles from erosion and storm water runoff which are carried into the river system by surface runoff, (Woodford, 2014).
Water pollution however, has led to the deterioration of water bodies, (Vyas et al, 1982), for example, 300 gallons, that is 1135.623 litres of raw sewage produced every day in Britain were dumped into the sea (Woodford, 2014). The Thames River of England was also once named the sewer of Europe because of the massive disposal of sewage waste in the river, (Wells, 1975). High levels of pollution were also reported in Canada’s receiving lakes where sewage effluent was directly disposed in its tributaries, (Wells, 1975). However, industrial effluent among all the causes of water pollution also poses a greater threat to water sources especially in developing countries and this is because of the presence of heavy metals and non-biodegradable pollutants that are discharged in the effluent, (Agrawal, 2013). This can be noticed in countries such as India where most of the rivers have become polluted due to industrial activity (Khropkar, 2011). According to Agarwal, (2013), about 5000 large and medium scaled industries in India were responsible for the pollution of their water bodies. In Zimbabwe, industrial pollution once contributed to the increased number of fish death by loading of heavy metals in Lake Chivero, (Moyo, 1997). During March to April 1996, a plethora of fish deaths were once also recorded in the Lake due to the contamination of the water by industrial waste (Moyo, 1997).

Water pollution has serious effects on the quality of water and has caused negative impacts on the health of the public, also affecting ecosystems and imposing effects on the economy and on the cost of treating the water (Moyo, 2007). Globally according to Corcorn, et al, 2010, about two million tons of sewage, industrial and agricultural waste is directly being discharged into surface bodies and thus due to this about 1.8 million children die all around the world under the age of five, one in every twenty seconds suffering from water related diseases. Recently, an increased awareness of and concern about water pollution has risen all over the world with new approaches towards sustainable management being developed (Helner and Hespanhol, n.d). The Dublin Principles, Agenda 21, Vision 21 and the Millennium Development Goals, and the recent Sustainable Development Goals for example, provide the basis for development of holistic and sustainable approaches, (Nhapi, 2005) despite the fact that project proponents continue degrading the aquatic ecosystems. The approaches however, towards sustainable management can only be effective as the ability to enforce them thus they can be planned and undertaken provided only if the levels of pollution caused and impacts are known.
Over 70% of the earth’s surface is covered with water and of this fraction 97.5% is salty water leaving a fraction of 2.5% as freshwater and nearly 70% of the freshwater is frozen in icecaps, thus leaving about 1% as fresh accessible water for direct human use. However, even with these statistics of the available freshwater, industrial pollution in most developing countries continues to pose inevitable water pollution problems, degrading even further to the extremes the precious resource (Adekunle et al, 2008). Workington industrial site is one area in Harare, Zimbabwe that through discharge of partially-treated and untreated industrial effluent into Marimba River is having a great influence on the chemical and even the physical quality of the river in terms of pollution. Workington Industrial Area is a light industry area with companies such as Omnia Fertiliser Company, Windmill Fertiliser Company and Exide Battery Company.

According to Nyamangara et al, 2013, although Marimba River may account for the lowest volumes input into Lake Chivero, it is however the major contributor of nitrate and phosphate loading in the lake thus making it a major source of pollution and eutrophication. According to Mazhandu.R, (2010), all the industrial effluent from Workington Industrial area is treated at Crowbrough Sewage Treatment Plant thus however giving ignorance as to wether there is any effluent that is illegally being disposed directly into Marimba River.

Due to the challenges going on with the responsible authorities in monitoring effluent discharges, the author therefore will take a period to monitor and determine the quality of effluent discharged from Workington Industrial Area, into Marimba River and the effects the effluent is having on the quality of the water. The findings in this study will help the responsible authorities in taking more action to enforce legislations on effluent discharge into water sources.

1.2 JUSTIFICATION
Water disposal and management are the major challenges threatening urban water sources in nearly all countries in the world (Miller 1994). With the current economic situation in Zimbabwe, most manufacturing industries have been causing massive pollution to the receiving waters. The expenses of having a pre-treatment plant, the cost of pre-treating the effluent, inadequate pollution monitoring schemes and also the fact that pollution of rivers has a much lower penalty than the cost of processing it, are some of the economic factors that have led to the pollution of surface water bodies (Muchena, 1998).
According to the EMA Act (20:27), any person who discharges or applies poisonous, toxic or noxious substances to the environment in contradiction with the water pollution control standards and without a discharging permit shall be guilty of an offence and is liable to charges and in addition shall also imposed on him the cost of removal of the substance or restoration of the damaged environment which may be incurred. Despite the presence of such legislation, the degree of pollution continues to increase as responsible authorities such as municipal councils are facing financial problems causing them to inadequately monitor the discharge of effluent due to challenges such as lack of adequate transport facilities, trade inspectors and also reagents including materials and equipment to use during the monitoring.

As defined in Johannesburg by the Global Water Partnership (GWP), Integrated Water Resources Management (IWRM) is a process which promotes the coordinated development and management of water, land and related resources in order to maximise the resultant economic and social welfare in an equitable manner without compromising the sustainability of vital ecosystems,(Rahaman and Varis, 2005). The lack of coordination or an integration of ideas between the responsible authorities (public sector) and the private sector is also an issue that is causing the ineffectiveness of policies and implementation of proper monitoring schemes.

Another factor that has also led to the ineffectiveness of pollution monitoring schemes is that he who controls the means of production, that is the company owners, controls the mental production that is they are the decision makers as the board of responsible authorities. Thus corruption has crippled the water governance sector as it is difficult to sue or fine an industry that is owned by a member of the responsible authority.

Though many factors may be attributed to justify the lack of monitoring of effluent disposal into water sources, the fact that this is causing serious threats and stress to the resources should not be denied. This study therefore seeks to bring to an awareness of the impact of the lack of proper monitoring on the quality of water in Marimba River and though fully aware that some of the challenges underlying this can be beyond one’s control, serious action must be taken to curb for this before most rivers and streams in Zimbabwe become ‘dead’. Monitoring of effluent disposal into waterways can help to effectively manage and help in achieving a healthy state of rivers.
1.3 OBJECTIVES

1.3.1 Main objective
➢ To determine the impacts of unmonitored effluent disposal on the quality of water in Marimba River.

1.3.2 Specific objectives
➢ To determine the quality of water in the river, upstream and downstream of the industrial zone by analysing for the following water quality parameters; BOD, COD, 4hr Permanganate Value (4hr P V), pH, temperature, phosphates, nitrates, copper and lead.
➢ To evaluate the quality of the river water in comparison with the EMA industrial effluent hazard classification standards.

1.4 HYPOTHESIS
➢ $H_0$: There is a significant difference in the quality of water in the river, upstream, within the industrial zone and downstream.
➢ $H_0$: There is a significant difference between the pollution levels introduced into the river water and the EMA industrial effluent discharge limits.
CHAPTER TWO

2.1 LITERATURE REVIEW
This section gives further information on the impact of partially-treated industrial effluent disposal in water sources and detailed information on the physico-chemical parameters used to analyse the quality of water in Marimba River in this project.

2.2 Industrial effluent
Industrial effluent is any waste generated from an industrial activity or process and the effluent however effluent produced is industry specific and the nature of the effluent differs from industry to industry due to the process and activities in that particular industry. According to (Ogedengbe and Akinbile, 2004, industrial waste water is the most common source of water pollution in our world today and continues to increase yearly due to the fact that most countries are still developing and thus using industrialisation to upgrade and sustain their economies, (Adekunle et al, 2008). Over the past years, an increasing attention has been given towards the health implications of large industrial establishments. Modern industrial development has resulted in many benefits stemming from socioeconomic development but it has also resulted in environmental contamination and adverse impacts on the health of the public, (Mudu et al, and 2014).

Adekunle et al, 2008, notes that wastewater, due to its high nutritional content, can be used for agricultural purposes but these nutrients however can inflict serious effects on the communities, their health and on their ecosystems. Some of the problems associated with waste water discharge into water bodies are eutrophication, which triggers the proliferation of algae, an increased water treatment cost, reduction in the recreational value of the water, health risks to humans and livestock, reduction in the available oxygen and undesirable loss of aquatic life. Water bodies such as rivers, lakes and dams are the major destinations of effluent disposal and the prospective adverse effects of polluted wastewater discharge on the quality of receiving water bodies are many and are only dependent on the volume of the discharge, the chemical and microbiological concentrations and composition of the discharge. Nhapi et al 2006, notes that contaminated or untreated waste water is an ecological threat unless pre-treatment of the waste water is done.
2.3 Wastewater Pre-treatment

Wastewater pre-treatment is the semi removal or reduction of its pollutants before it is discharged into a municipal treatment works or directly into the environment, (Fakayode, 2005). The major reasons for waste water treatment can be classified as to, prevent the rapid degradation of the environment, to protect the public health as the waste water can contain disease producing-organisms and so as to meet the set standards of environmental regulations, (Nagpal et al, 2003).

2.4 Effects on water bodies and the environment

Industrialisation is the centrepiece of economic growth for most countries especially developing nations and therefore its pollution and effects to the environment continues to be on the rise in Africa as most countries in this continent are still developing. Now over the years water bodies such as rivers, streams and dams have been the major destination of effluent discharge from mainly these manufacturing industries (Adekunle et al 2008). Large volumes of untreated or semi-treated effluents are finding their way unregulated mainly into rivers flowing through cities and towns, (Olaniyi, 2012). According to Chinhenga 2012, many industries continue to degrade the precious and scarce resource irregardless of the presence of other alternatives that can be adopted for waste water management.

With a rough 90% estimate of all the wastewater that is being discharged into water bodies in developing countries, there is an increase of de-oxygenated dead zones rapidly growing in oceans and seas, with 245 000km² of marine ecosystems affected, (Corcoran et al, 2010). Information of water sources, its quality and pollution is very vital for the effective implementation of sustainable management strategy, (Zhou et al 2007).

According to Phiri 2005, the nature of effluent from different manufacturers is industry specific due to the type of production; however, the pollution caused can reduce the potential of the water as a resource for various uses. This pollution disturbs the balance of the ecosystem inside the water bodies resulting in the death of plant and animal species present. In reference to such a scenario, the biodiversity of Lake Victoria in Uganda has been threatened by heavy industrial effluent pollution Nakawa-Ntinda industrial area in Kampala town, (Walakira and Okoto-okuma, 2011).
In Zimbabwe, according to Chinhanga, 2010, water resources are also under serious threat of pollution as the discharge of partially or untreated effluent continues to increase. Nyamangara, 2008 assets that increased concentrations of pollutants that include nitrates and phosphates have been reported in most rivers that drain into the Upper Manyame Catchment Area (UMCA) from agro-processing fertilizer manufacturers in Harare. This has caused problems such as proliferation of algal blooms, invasive species and fish kills due to loss of oxygen and reduction of biological diversity, (Nyamangara et al, 2013). In the town of Kwekwe, the health of Kwekwe River is being threatened due to the discharge of high quantities of iron, sulphur, oil and tar into the river from the iron and steel company, (Chinhanga, 2010).

Industrial effluent is dangerous in that it primarily contains toxic chemicals that if they infiltrate or find their way into the environment, they have persistence in it for a long time. Most rivers in India such as Sati, Gaga and Damodor, have been reported to have high levels of contamination of high levels of heavy metals and a mixture of chemicals. According to a survey of the industrial zones, it also proved that ground water sources had been contaminated and have also reported high levels of toxic chemicals.

Another environmental impact of untreated wastewater effluent, which at times can be linked to health, is the occurrence of bioaccumulation and biomagnifications of contaminants. Due to the occurrence of bioaccumulation, certain substances which are in low concentrations or barely measurable in water can sometimes be found in high concentrations in plant and animal tissues. According to Ogedengbe and Akinbile, 2004, as long as localization of industry is used as an economic anchoring tool, the risk of environmental pollution will also be brought along with it. According to Irin 2007, water bodies have the ability of self purification in them but however this mechanism is affected by the interferences of different anthropogenic activities.

2.5 Effects on human health
The principle reason for waste water treatment is to protect the public from the spread of diseases and to prevent pollution of water sources. According to Adekenhle 2010, undesirable effluent disposal is detrimental to animal and human health and according to estimation by the World Health Organisation (WHO) in 2010, about a quarter of the diseases facing mankind today, occur due to prolonged exposure to water pollution. The effect of industrial
pollutants on human health is based on the amount of concentration and the amount of time the individual is exposed to, however, studies have shown that even metals; such as lead, copper and zinc in their low concentrations can cause serious damages to the human kidney and liver (HO.Y.C et al 2012) and can be carcinogenic in high concentrations, (O’Brien et al 2003).

All around the world there is a history of cases of diseases that have arisen due to industrial pollution or contamination of water bodies. Such cases as the Minamata disease of Japan in a period from 1950-1956, a neurological syndrome that was caused by the release of methylmercury in industrial water from Chisso Corporation’s chemical factory.

Industrial effluent over the past years has found its use as irrigation water in agricultural fields, however, depending on the nature of industry, the effluent can contain high concentrations of heavy metals, toxic substances which can be taken up by plants and as these plants are consumed they likely to affect the endocrine system, these metals also can be passed on affecting generations to come through the DNA.

2.6. Effects on the economy
Industrialisation is the backbone of economic growth in most developing countries (Bello et al. 2013) especially in Africa where its activities are the major economic contributors, however, in much eager for growth, as positive impacts are made, negative impacts are also associated. While industrial production can affect the quality of water in a receiving water body, poor water quality supply can also affect industrial production in a negative way in that water plays a very vital role in industrial processes such as heating, cooling, cleaning or generation of steam. Therefore water quality in an environment may cause an industry to halt production, relocate to a different area or decrease its production and this in turn has an impact on the economy of that particular area, (Chiramba and Manyara, nd).

According to the World Health Organisation (WHO), 2004, it is estimated that an area of 20 million hectares of land is irrigated with effluent from industrial waste that is partially treated or untreated and this results in contamination of the crops due to the nature of the effluent giving an impact on the overall produce (Chicago et al 2012). This is mainly due to the fact that, for plants to attain maximum growth and give a good yield, they require nutrients only in certain amounts in which exceeded yield and growth begin to decline. Use of effluent for agricultural purposes also affect the soils to which it is applied on thus affecting the chemical composition of the soil making it either more alkaline or acidic depending on the nature of
the effluent. However, this can be caused by the unavailability of alternative sources of water for irrigating the crops.

The overall costs of treating waste water has also been highly increased due to discharging of partially treated or untreated waste water into water ways with the City of Harare alone spending close to 3 million dollars each month on treatment chemicals and this in relation to our current economy is having a serious impact on the economy of the nation as whole.

2.7. WATER QUALITY PARAMETERS

2.7.1. Biochemical Oxygen Demand (BOD)
Also known as biological oxygen demand, is a measure of the dissolved oxygen consumed by a micro-organism during the oxidation of reduced substances in water and waste, (Penn.R et al , nd). The oxygen is used in the aerobic breakdown of organic material present in a given water sample at a certain temperature over a specific time period. The presence of this sufficient oxygen promotes the aerobic biological decomposition of an organic waste (Metcalf and Eddy, 2003).

BOD levels are used to measure the strength of an effluent, therefore it gives a measure of the degree of water pollution. Thus the greater the BOD, the more concentrated an effluent would be with pollutants. BOD can be determined as either carbonaceous BOD (CBOD) or nitrogenaceous BOD (NBOD). The higher the amount of organic material found in the stream, the more the oxygen used for aerobic oxidation. This depletes the amount of dissolved oxygen available to other aquatic life. Thus a low BOD is an indicator of a good quality of the water and a high BOD indicates a proof of the pollution of the water, (Ramu, 2012). This measurement is obtained over a period of five days, and is expressed in mg/l. The 5- day BOD (BOD₅) is the most commonly organic pollution parameter useful to wastewater.

2.7.2 Chemical Oxygen Demand (COD)
COD is the amount of oxygen required by one litre of a sample to oxidize all the organic matter in the sample to carbon dioxide and water. This parameter measures the amount of oxygen consumed for the breakdown of organic matter in a water body under the catalyst of a chemical oxidant. It also gives a measure of the organic matter that does not decompose in 5 days but eventually would decompose and affect water quality (Harrison, 1999). The COD
will always be higher than the BOD. This is because the COD measures substances that are both chemically and biologically oxidized, (Akpor, O.B and Muchie, M, 2011).

2.7.3.4hour Permanganate Value
It is the amount of oxygen absorbed by a litre of sample from N/80 potassium permanganate in 4 hours in order to oxidise the organic matter in the sample. Potassium is an oxidising agent therefore it is added to the sample to provide the oxygen and it is then reduced during the process. Very pure waste absorbs little oxygen whilst inorganic constituents of the waste such as nitrates and sulphides absorbs higher.

2.7.4. pH
The term pH means power of hydrogen and is used to measure the concentration of hydrogen ions in water, thus it is used to determine the acidity or alkalinity of the water. (Nyasulu, 2010). A scale of readings 0-14 is used to determine the pH of the water ,with the reading of zero is taken as neutral, the readings below 7 as acidic and the readings above 7 as alkaline. The pH of water is of much importance as it has an effect on the solubility and availability of metals and nutrients and also how these can be utilised by aquatic organisms (Chapman 1996). A change in the pH of the water cause may increase the solubility of phosphorous making it easily available for the growth of plants and thus resulting in a higher demand for dissolve oxygen.

2.7.5. Temperature
Temperature is a parameter critical to water quality measures which determines how hot or cold the water is and it is measure in units of degrees Celsius (°C). Temperature has a direct influence on the amount of dissolved oxygen that can be available for aquatic organisms (Nyasulu, T, 2010). As temperature can also have an effect on BOD levels because as oxygen consumption increases, temperature also increases. Discharge of industrial cooling system effluent into rivers may cause the temperature of the river water to rise as well. According to Krenekel and Novoty, 1980, the effect of heated water on receiving water bodies can be equated to that of sewage or other organic waste since both pollutants may cause a decrease in the available oxygen of the receiving body. Increased temperatures in a water body also usually results in a decrease in the self purification capacity of a water body causing unwanted growth of algae, (Krenekel and Novoty, 1980).
2.7.6. Nitrates
Nitrates are an oxidised form of nitrogen and they occur naturally in soils and water but however an excess of them is considered to be a contaminant in ground and surface waters. The major sources of excess levels of nitrogen can be agricultural activities, human waste and industrial pollution from industrial plants and agricultural processing operations. High levels of nitrate, along with phosphate, can trigger the proliferation of algal growth and aquatic plants and this gives rise to the consumption high levels of dissolved oxygen by these plants as they die, causing the death of fish and other aquatic organisms due to the unavailability of oxygen, a process called eutrophication, (Ansar and Khad, 2005). Nitrogen does not limit growth in plants because phosphorous is already a limiting factor but it accelerates depletion of oxygen as it is converted to nitrogen gas.

When high levels of nitrates are consumed in a human body, they can interfere with the ability of the red blood cells to carry oxygen. However, the risk of nitrate poisoning is common in infants than in elderly people where children can suffer from baby blue syndrome biologically known as methemoglobinemia and can cause brain damage or death (Dr Basu.A, 2012). Methemoglobinemia is the most significant disease common with high nitrogen levels in water. Blood contains haemoglobin an iron based compound that carries oxygen, thus when nitrite is present, this compound can be converted to methemoglobin, inhibiting it carry oxygen, (WHO, 1997; Akpor, B and Muchie, M, 2011). Despite the fact that nitrate levels that affect infants do not pose a direct threat to older children and adults, they indicate the presence of other serious residential or agricultural contaminants, such as bacteria and pesticides (McCasland et al., 2008).

2.7.7. Phosphates
Phosphates are an inorganic form of phosphorous and these can enter surface water bodies from such sources as inorganic fertilisers, waste water treatments from municipal sources, soaps and detergents and from industrial process. Phosphates are the primary limiting factor in fresh water plants and algal growth as they are necessary for plants in their energy cycle. However, high levels of phosphates as in nitrates can lead to eutrophication. Water bodies with high levels of phosphates usually have high BOD levels due to the bacteria consuming the organic plant waste thus resulting in low dissolved oxygen levels, (Hooper, 1998). Phosphorous initially stimulates aquatic plant growth which unlocks even more phosphorous
from bottom sediments. Phosphates however, are not toxic to humans or animals unless when they are presented in very high levels as they can cause digestive problems, (Nyasulu, 2010).

2.7.8. Lead (Pb)
Lead is a heavy toxic metal and is one of the most abundant heavy metals that occur in nature and is used at a larger scale. According to Nyasulu, 2010, lead is mainly produced in metallic form in cell batteries, cable sheathing sheets and pipes; lead solders, lead based paints and lead gasoline. Lead has adverse human health effects and an excess exposure to lead can damage the nervous systems and can cause blood and brain disorders, in pregnant women lead can lead to miscarriages (Gurruswammy, 2000).

2.7.9. Copper (Cu)
Copper is a toxic metal widely used for engineering purposes and can also be used in ceramics and paints. Copper can enter into the environment through both anthropogenic and natural sources. It is discharged via sources such as industrial effluents of various industries such as; paints and dyes, fertilisers, pesticides and steel industries,(Shrivastava.A.K,2009).When consumed beyond permissible limits, copper can lead to a disease known as Wilson’s disease,(Shrivastava.A.K,2009). Copper toxicity can cause hepatic and renal damage together with irritations n the central nervous system (Krishnamurthy et al, 1991).

2.8 EMA Hazard Classification of Waste Water

This is a legislative instrument that regulates the discharge of waste into the environment, thus according to section 5(2) of the act, ‘any person willing to dispose of wastewater of effluent into the environment shall submit an application for a blue, green or yellow permit. However, an industry should have a pre-treatment plant on site and is thus given a permit to discharge into the environment but when channelling waste water into municipal sewer systems one is not liable to a permit.

The permits have set standards for each parameter that could be found in the effluent .The standards are then further classified according to the level of hazard that could be could be caused on the environment as follows:
2.8.1 Blue Class (Safe)
Quality of effluent discharged has no significant risk to the environment therefore it meets blue standard for sensitive areas or normal areas.

2.8.2 Green Class (Low hazard)
The quality of the effluent discharged presents or has a low risk or impact on the environment to which it is disposed, the effluent exceeds blue standards in one or more parameters, blue permit conditions not met.

2.8.3 Yellow Class (Medium hazard)
The effluent discharged exceeds green standards thus it has risks to the quality of the environment or on the water resources; green permit conditions not met.

2.8.4 Red Class (High hazard)
The quality of effluent exceeds yellow standards thus permit can only be issued on condition of imposed improvement by the authorities, the waste disposed presents a high risk of water pollution and environmental damage. Yellow permit conditions not met.
CHAPTER 3:

3.1 MATERIALS AND METHODS

3.1.1 STUDY AREA DESCRIPTION
Marimba River is a sub-catchment in the Upper Manyame Catchment Area (UMCA) covers a length of about 189 km and stretches for a width of about 25km (Nhapi and Tirivarombo, 2004). It originates from the University of Zimbabwe area and flows past Avondale shopping centre and down to Kensington shopping centre into Monavale vlei. The river then passes through the National sports stadium, Warren Park 1, Kambuzuma, Workington Industrial Area, Marimba Park and finally near Mufakose area before reaching Lake Chivero (Mathuthu et al, 1976). Workington Industrial Area is a light industrial area that comprises of the following partially listed companies which are; Windmill Fertiliser Company, Dairy Marketing Board, Omnia Fertiliser Company, Exide Battery Company, ZUPCO Bus Company and Olivine Oil Company.

![Map of study area: Marimba River](image)

Figure 1 Map of study area: Marimba River, 12:15pm, 20/08/15

3.1.2 Sample collection
A total of six samples were collected for a period of three months which are June, July and August from three sampling sites along the stream. The first sampling point was upstream of
the river approximately 3.22 km from the discharge point, along Samora Machaele road at the Bulawayo road bridge.

Figure 2 Marimba River, sample point 1

The second point was approximately 3.05 km from the discharge point, along Coventry road.

Figure 3 Storm drain, sample point 2

The third site was down stream approximately 4.39 km from the discharge point near Kambuzuma residential area.
Sampling sites were selected at random due to the inaccessibility of some parts along the river.

Two litre plastic bottles were used as containers for sample collection. The bottles were sterilised with 1% HNO$_3$ (nitric acid) and were rinsed with distilled water and dried before collection of samples. Clear labelling of sample bottles was also done before collecting samples. After sample taking, bottles were tightly sealed and transported to the laboratory immediately after were analysis commenced. The following parameters were determined BOD$_5$, COD, pH, temperature, iron, copper, phosphates, nitrates, lead and 4hr permanganate value.

3.1.3 MATERIALS
This section includes an overview of the methods used to carry out the research. The SAZ discharge limits on industrial effluent are shown in appendix section.

A LASANY model thermometer was used to take the temperature of the samples. Power of hydrogen, pH was determined using a PHS-3E Chinese model pH meter. Total phosphate and nitrate determination was done based on ISO 6878: Part 1:1986 methods. Determination of Chemical Oxygen Demand (COD) was done based on Clause 22 of CAS Z21:1972. Permanganate Value Determination (4hr) was determined based on Clause 23 of CAS Z21:1972. Determination of Biochemical Oxygen Demand (BOD) was done based on SAZ methods of 1998.
3.1.4 Statistical Approach
Analysis of Variance was done using Genstat 14th edition.
CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 pH trends

Results from fig 6 indicates pH values ranging from 6.59 to 6.72 for upstream, 7.11 to 7.24 for storm drain and 6.71 to 6.76 for downstream with average means of 6.647, 7.180 and 6.733 respectively. pH values varied significantly across all treatments at p<0.01. The s.drain had the highest pH value of 7.180, followed by down stream with a pH value of 6.733 then lastly upstream with a pH value of 6.647. Classifying the pH means according to the EMA hazard classification (standard), the upper stream, s.drain and down stream had figures within the blue safe class.

Figure 5 mean pH value for upstream, s.drain and d.stream.

Results on pH as outline above were within the acceptable blue safe class. The values were more neutral to alkaline for all positions (upstream, d.stream and s.drain). This may have been because of the direct disposal of waste water containing cleaning detergents and chemicals containing phosphates from Longchen plaza mall. The pH in the storm drain could also have been raised by cleaning chemicals such as lime and caustic soda used by other
companies in pre-treatment processes and also chemical spillages from other companies, (Musiiwa et al., 2006; Nyasulu, 2009). The decrease in pH downstream can be due to mixing and the dilution effect of the waste effluent with river water, (Nagpal, 2003), as there is an increase in the hydrogen ions as the effluent enters the river.

**TABLE 1: MEAN VALUES FOR THE PHYSICO-CHEMICAL PARAMETERS**

<table>
<thead>
<tr>
<th>TREATMENTS</th>
<th>UPSTREAM</th>
<th>S.DRAIN</th>
<th>D.STREAM</th>
<th>P.VALUE</th>
<th>C.V%</th>
<th>LSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEMPERATURE(°C)</td>
<td>21.55&lt;sup&gt;a&lt;/sup&gt;</td>
<td>26.03&lt;sup&gt;b&lt;/sup&gt;</td>
<td>25.20&lt;sup&gt;b&lt;/sup&gt;</td>
<td>&lt;0.01</td>
<td>2.8</td>
<td>0.85</td>
</tr>
<tr>
<td>Ph</td>
<td>6.647&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7.180&lt;sup&gt;b&lt;/sup&gt;</td>
<td>6.733&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&lt;0.01</td>
<td>0.6</td>
<td>0.05</td>
</tr>
<tr>
<td>PHOSPHATES(mg/l)</td>
<td>1.60&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.67&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3.13&lt;sup&gt;b&lt;/sup&gt;</td>
<td>&lt;0.01</td>
<td>8.7</td>
<td>0.33</td>
</tr>
<tr>
<td>LEAD(mg/l)</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>PV4HR(mg/l)</td>
<td>5.48&lt;sup&gt;a&lt;/sup&gt;</td>
<td>12.95&lt;sup&gt;b&lt;/sup&gt;</td>
<td>17.05&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&lt;0.01</td>
<td>3.1</td>
<td>0.44</td>
</tr>
<tr>
<td>BOD(mg/l)</td>
<td>46.6&lt;sup&gt;a&lt;/sup&gt;</td>
<td>85.72&lt;sup&gt;b&lt;/sup&gt;</td>
<td>95.58&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&lt;0.01</td>
<td>2.6</td>
<td>2.47</td>
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<tr>
<td>COD(mg/l)</td>
<td>74.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>101.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>138.3&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&lt;0.01</td>
<td>5.7</td>
<td>7.39</td>
</tr>
<tr>
<td>COPPER(mg/l)</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>NITRATES(mg/l)</td>
<td>2.133&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.317&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3.617&lt;sup&gt;b&lt;/sup&gt;</td>
<td>&lt;0.01</td>
<td>8.2</td>
<td>0.37</td>
</tr>
</tbody>
</table>

- Numbers with the same superscript letter have no significant difference.

Waste classification according to EMA can be due to the reasons stated in the table below.

**EMA HAZARD CLASSIFICATION**

<table>
<thead>
<tr>
<th>Classification</th>
<th>Risk</th>
<th>Reasons for classification.</th>
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<tbody>
<tr>
<td>Blue</td>
<td>Safe</td>
<td>Complies with blue standards.</td>
</tr>
<tr>
<td>Green</td>
<td>Low hazard</td>
<td>Waste meets green standard, or blue licence conditions not being met.</td>
</tr>
<tr>
<td>Yellow</td>
<td>Medium hazard</td>
<td>Waste meets yellow standard, or green licence, conditions not being met.</td>
</tr>
<tr>
<td>Red</td>
<td>High hazard</td>
<td>Waste meets red standard, or yellow licence conditions not being met.</td>
</tr>
</tbody>
</table>

*Figure 6 Description of EMA hazard classification*
The table below shows the limits to which each class is defined in milligram/litre and in degrees Celsius for temperature.

Table 2: EMA STANDARD LIMITS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>EMA standard limit (mg/l)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>BLUE</td>
</tr>
<tr>
<td>Ph</td>
<td>6.0--9.0</td>
</tr>
<tr>
<td>BOD</td>
<td>≤30</td>
</tr>
<tr>
<td>COD</td>
<td>≤60</td>
</tr>
<tr>
<td>Lead</td>
<td>≤0.05</td>
</tr>
<tr>
<td>Copper</td>
<td>≤1.0</td>
</tr>
<tr>
<td>Total phosphates</td>
<td>≤0.5</td>
</tr>
<tr>
<td>Nitrates</td>
<td>≤3</td>
</tr>
<tr>
<td>Temperature</td>
<td>&lt;35</td>
</tr>
<tr>
<td>Pv4hr (Oxygen Absorbed)</td>
<td>≤10</td>
</tr>
</tbody>
</table>

4.1.1 TEMPERATURE
Results from fig 7 showed that temperature values ranged from 21.1°C to 22.3°C for upstream, 24.1°C to 27°C in the s.drain and 25.1°C to 25.4°C for downstream. The average values were 21.55°C, 26.03°C and 25.20°C respectively. Temperature values varied significantly across all treatments from the standard at p<0.01. The highest value of temperature was s.drain (26.03°C), followed by d.stream (25.20°C) then lastly upstream with 21.55°C. From the statistics it also showed that there was no significant difference between s. drain values (26.03°C)\(^b\) and d.stream values (25.20°C)\(^b\). According to the EMA classification,
temperature values from upstream, s.drain and d.stream were all in the acceptable safe standard blue class.

![Bar chart showing mean temperature for standard, upstream, s.drain, and d.stream.]

**Figure 7** mean temperature, upstream, s.drain and d.stream.

Temperature affects the chemical and biological reactions in water but however, the values showed that temperature was also in the blue safe zone and this can explain that companies involved in thermal cooling processes were not discharging their waste effluent directly into the storm drain. However there was an increase in temperature in the effluent from the storm drain and a slight decrease further downstream, this in turn could have had a bearing in the decrease of nutrients downstream as an increase in temperature from the storm drain increases microbial activity and may increase nutrient uptake, (McClain et al, 1998)

### 4.1.2 NITRATES

The nitrate values ranged from 1.8 mg/l to 2.4 mg/l upstream, 4.9mg/l to 6mg/l in the s.drain and 3.3 mg/l to 3.9 mg/l downstream. The mean levels were of 2.13 mg/l, 5.13mg/l and 3.617mg/l respectively. From the statistical analysis it showed that there were significant differences on the mean nitrate values across all treatments at a p value of <0.01. Nitrate values from the s.drain recorded the highest mean of 5.13mg/l followed by downstream with 3.617mg/l and lastly upstream with 2.13mg/l. According to the EMA hazard classification, it was clear that upstream nitrate values were in the blue-safe class (below 3mg/l). However,
storm drain nitrate values were in the yellow-medium hazard class (≤ 8mg/l) and the nitrate values downstream were in the green-low hazard class (≤ 5mg/l).

![NITRATES](image)

**Figure 8** mean nitrate values, upstream, s.drain and d.stream.

Nitrogen levels upstream were within the blue safe class as shown in fig 8 above and this might be because there is no evidence of major sources of nitrogen into the river. However the levels increased in the storm drain as shown in the graph above and this could be the fact that nitrates are used as major components in fertiliser production this agrees with the EPA report 2008 on behaviour of nitrates in water that the fertilizer production companies are one of the major sources of nitrogen in surface waters. As we went down stream the nitrogen levels began to decrease and this is because of the breaking down of the nutrient as they are being taken up by plants and also because of the self purification system of the stream, (Bere, 2005).
4.1.3 PHOSPHATES
Phosphate values ranged from 1.2mg/l to 2mg/l upstream, 4.3mg/l to 5mg/l in the s.drain and 2.9 mg/l to 3.4 mg/l downstream with average values of 1.6mg/l, 4.6 mg/l and 3.13mg/l respectively. From the statistics data generated by Genstat, it was clear that there were significant differences on the phosphate levels across all treatments from that of the EMA standard at p < 0.01. The storm drain Phosphate value was the highest recording 4.6mg/l followed by d.stream with 3.13mg/l and then upstream with 1.6mg/l. Classification according to the EMA hazard classification highlighted that the s.drain values were in the red category (5mg/l) indicating that the levels were way beyond the acceptable limits or safe zone. A red class indicates a high hazard threat to the environment. Downstream phosphate values were in the yellow category (3mg/l) posing a medium threat to the environment and upstream phosphate values were in the green category (1.5mg/l) posing a low environmental hazard.

![Figure 9 mean phosphate values in mg/l](image-url)
The phosphate levels upstream though with a low hazard risk to the environment were quite high and this could be because phosphates are used as major component of domestic detergents, industrial detergents and also in industrial cleaning products (Vaccarin, 2009). The increase in the phosphate levels in the storm drain can be explained by the phosphorous and phosphoric acid products that might be the major products being used in fertiliser production, (Bruce et al., 2008). The decrease in the phosphate values downstream could be due to the breaking down of the inorganic material by organisms during transportation away from the source, the uptake of the nutrient by aquatic plant and also because the stream might have a self purification processes.

4.1.4 BOD
Biochemical oxygen demand levels ranged from 50 mg/l to 56.1 mg/l upstream, 83.38mg/l, to 85.2mg/l, in the s.drain and from 92.2 g/l to 98.4mg/l d.stream with average values 86.2 mg/l, 85.72 mg/l and 95.58 mg/l respectively. From the Genstat output, it shows that were also significant differences on the BOD levels upstream, in the storm drain and downstream at $p<0.01$. The highest BOD value was recorded downstream (95.58mg/l), followed by the storm drain (85.72mg/l) and then upstream (83.38mg/l). However, according to the EMA colour classification as shown in fig 7 below, the BOD levels upstream were in the green class indicating a low hazard to the environment ($\leq 50$mg/l). The BOD levels in the storm drain and downstream were both classified under the yellow class ($\leq 100$mg/l) which indicates a medium threat to the environment.

From the fig 10 $BOD_5$ levels began to increase more from samples in the storm drain as shown in the graph and this could have been through the introduction of a high load of inorganic pollutants that promote the growth of decomposer organisms that may lead to the depletion of dissolved oxygen (DO) of the water in the river therefore increasing the BOD$_5$, (Gyawali et al., 2012). The high BOD levels also proved that there is pollution from industrial waste into the river as is with the findings of Gyawali et al., 2012. Downstream there also shows an increase in the BOD and this concurs with the findings of EPA, 2015 that the increase proves that there is rapid depletion of the oxygen in the stream as more is used in the breakdown of the organic material in the river.
4.1.5 COD
The COD values ranged from 71.9mg/l to 74.7mg/l upstream, 100.2mg/l to102.6mg/l in the s.drain and 130.1mg/l to 137.6 downstream with mean levels of 74.5mg/l, 101.1 mg/l and of 138.3mg/l respectively. From the graph, downstream COD values were the highest followed by the s.drain values and lastly from upstream. It statistically showed that there was a significant difference in the COD levels in the river and with the EMA standard at a p<0.01. It also showed that there were statistical differences in the mean COD levels upstream,(74.5a) and COD levels it he storm drain(101.1b) and also from downstream(138.3c).According to the EMA hazard classification as shown in the fig 11 below COD values upstream and downstream were in the green class (≤ 90mg/l) indicating a low hazard to the environment and. In the storm drain the levels increased though they were still classified in the yellow class.

COD indicates the organic and inorganic pollution loads in water, therefore increases in the COD levels from upstream can imply that there is also an increase in the organic and inorganic content from chemicals in the industrial waste water, this is in agreement with Nyamangara et al 2007. The COD values also correlated with the BOD values as in the findings of Harrison,1999, as COD was higher than BOD, this is because COD shows the

![BOD levels in mg/l](image-url)

**Figure 10 BOD levels in mg/l**
total biodegradable organic matter that normally is decomposed by micro-organisms during a 5-day period of BOD and biodegradable organic matter that is decomposed with the help of chemical catalyst (Nyasulu, 2010).

![Graph showing COD mean levels mg/l](image)

**Figure 11 COD mean levels mg/l**

4.1.6 PV4hr (Oxygen Demand)
Oxygen demand levels (PV4hr) ranged from 5.0mg/l to 6.2mg/l upstream, 12.4mg/l to 13.5 mg/l in the s.drain and 16.8mg/l to 7.3mg/l downstream with mean levels of 5.48mg/l, 12.9mg/l and 17.5mg/l respectively. Downstream PV4hr levels were the highest followed by values from the s.drain and lastly upstream. From statistics it showed that there were significant differences in the oxygen demand levels, upstream, downstream and in the s.drain with that of the standard EMA values at a (p<0.01). According to the EMA hazard classification, the PV4hr levels upstream were within the acceptable safe blue class (≤10mg/l), the levels increased in the storm drain and were in the green class (≤15mg/l) as shown in the graph below thus indicating a low hazard to the environment. Downstream the oxygen absorbed levels increased and were within the yellow class (≤25mg/l) indicating medium hazard to the environment.
Figure 12 Pv4hr mean levels mg/l

4.1.7 COPPER AND LEADER
Copper and lead were below detectable limits therefore the methods of pre-treatment used were effective. These two are heavy metals and have carcinogenic effects to the human body if consumed thus are very sensitive to environmental disposal, (Gurruswammy, 2000).
CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion
From the results obtained in the above chapter (four), it shows that the quality of water in Marimba River is greatly affected with the effluent from Workington Industrial Area that contains a load of nutrients such as phosphates and nitrate, irregardless of the fact that further downstream there will be an influx of nutrient loading from Crowbrough Sewage Treatment Plant. Some of the parameters such as temperature, pH, copper and lead were within the EMA blue normal class thus it can be concluded that methods of disposal and treatment used by such companies as ZESA and Exide battery company may be effective in reducing pollution to the environment and surface waters. Other parameters such as nitrates, BOD, COD and oxygen absorbed ranged in the green to yellow classes and thus having effects on the environment. Total phosphates from the storm drain were in the red class thus posing a very high environmental hazard if this is not looked into, this support Nyamangara et al, 2013 that Marimba though with the lowest flow of water into Lake Chivero, it is the major contributor of nutrients into the Lake. It can be concluded that these nutrients might be coming from fertiliser companies which are in the industrial area and thus there should be closer monitoring of the methods of waste disposal used by these companies.

5.1.2 Recommendations
- There should be a more regular and effective monitoring on every company in the area and also on the processes and methods of disposal used. This is because at some point in time when monitoring authorities are relaxed, industries will tend to dispose effluent in the best economic way they can.
- For a more effective monitoring there should be a more coordinated approach between EMA and the City of Harare in pollution control. This will also increase the number of inspectors to do the work.
- The penalty fee for environmental pollution should be increased so that direct environmental disposal of waste should not be an option over pre-treatment of waste effluent.
- There should be a redesigning of permit procedures so as to award companies that are complying with the blue normal class in the effluent they discharge by giving subsidies. National recognition and publicity should be increased for outstanding companies that are complying with safe standards so as to motivate other companies.
- Industries should be involved in pollution monitoring projects and workshops this will help them in understanding the importance and impacts of pollution on the environment.
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APPENDICES

A: ANOVA TABLE FOR pH

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>d.f.</th>
<th>s.s.</th>
<th>m.s.</th>
<th>v.r.</th>
<th>F pr.</th>
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</thead>
<tbody>
<tr>
<td>Treatments</td>
<td>2</td>
<td>0.982933</td>
<td>0.491467</td>
<td>294.10</td>
<td>&lt;.001</td>
</tr>
<tr>
<td>Residual</td>
<td>15</td>
<td>0.025067</td>
<td>0.001671</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>17</td>
<td>1.008000</td>
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B: ANOVA TABLE FOR BOD

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<th>m.s.</th>
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<tr>
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<td>8053.663</td>
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<td>1288.54</td>
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<td>Residual</td>
<td>15</td>
<td>46.877</td>
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<td>17</td>
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C: ANOVA TABLE FOR COD

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<td>Total</td>
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D: ANOVA TABLE FOR Copper

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<th>F pr.</th>
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<td>0.</td>
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<tr>
<td>Residual</td>
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<td>.</td>
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<tr>
<td>Total</td>
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E: ANOVA TABLE FOR Nitrates

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F: ANOVA TABLE FOR PV4Hr

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<th>d.f.</th>
<th>s.s.</th>
<th>m.s.</th>
<th>v.r.</th>
<th>F pr.</th>
</tr>
</thead>
<tbody>
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G: ANOVA TABLE FOR Temperature

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H: ANOVA TABLE FOR Phosphates

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