DETERMINATION OF SELECTED HEAVY METAL LEVELS IN UNDERGROUND WATER AND SOIL AND ANALYSIS OF WATER HARDNESS SOURCES IN NYATIKE-KARUNGU DIVISIONS, MIGORI DISTRICT, KENYA.

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A thesis submitted to the Graduate School in partial fulfilment of the requirement for the award of Master of Science Degree in Chemistry of Egerton University.

EGERTON UNIVERSITY

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DECLARATION AND RECOMMENDATION

DECLARATION

This thesis is my original work and has not been presented in part or as a whole for any academic award in any other university.

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RECOMMENDATION

This thesis has been submitted with our approval as university supervisors.

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DEDICATION

This work is dedicated to my Father Abdallah and the late Mother Sellah and my wife Janet and daughter Princess.

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ABSTRACT

Intensive mining activities and highly mineralised rock formations have a significant impact on both surface and underground water. Mining activities shuffle the rock formations creating fissures and cracks enhancing greater percolation and movement of water underground. Macalder mines(gold mining region) in Nyatike –Karungu Divisions was divided into two regions (Epicentre and surrounding).This research sought to determine the concentration levels of Zn, Cu, Pb, Fe, and water hardness levels and sources. Quantitative determination of heavy metal levels were performed using FAAS and water hardness determined using EDTA titration method. The interpretations of the analytical results were performed using Excel spreadsheet and SPSS statistical packages. The range of the mean metal concentration in water during the dry season was Zn (0.04-0.19) mgl^{-1}, Cu (0.01-0.04) mgl^{-1}, Pb (0.63-2.48) mgl^{-1}, and Fe (0.44-1.63) mgl^{-1}. The range of mean metal concentration in water during the wet season was Zn (0.03-0.37) mgl^{-1}, Cu (0.01-0.05) mgl^{-1}, Pb (0.51-4.02) mg^{-1} and Fe (0.44-2.43) mgl^{-1}. The range of the mean metal concentration in soil during the dry season was Zn (0.08-2.64) ppm, Cu (0.2-1.12) ppm, Pb (0.22-2.28) ppm, Fe (0.50-2.00) ppm. The range of mean metal concentration in soil during the wet season was Zn (0.09-0.19) ppm, Cu (0.08-0.66) ppm, Pb (0.25-2.37) ppm and Fe (0.27-1.78) ppm. The pH of the borehole waters were determined in situ and ranged from 6.5-7.2 thus an average of 6.7. The range for the mean water hardness during the dry season was (75.83-658.6) mg/L of $CaCO_3$ and wet season (71.60-585.83) mg/L of $CaCO_3$. Concentrations of Zn, Cu and Fe were within the WHO water quality guidelines except for Pb levels that were above the admissible threshold. Nyatike-Karungu divisions lie along a geological fault line with volcanic igneous rock type, dolomite, limestone and dolerite rocks predominant. The net effect of the solubility of these rocks was the hardness of water in the boreholes and wells however, lake water samples showed low hardness levels ranging from (75.8-99.4) during dry season and (71.6-95.1) mg/L of $CaCO_3$ during wet season.

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ABBREVIATIONS

μg/g	Micrograms per gram
AAS	Atomic Absorption Spectrometer
ANOVA	Analysis of Variance
APHA	American Public Health Association
DDDW	Deionised Double Distilled Water
E	Exponential (10^x)
EDTA	Ethylenediaminetetraacetate
LBDA	Lake Basin Development Authority
mg/L	Milligrams per litre
pH	Potential Hydrogen
ppm	Parts per million
std	Standard
SWL	Static Water Level
TH	Total Hardness
UNEP	United Nations Environmental Programme
WHO	World Health Organisation
WSL	Water Struck Level

CHAPTER ONE

INTRODUCTION

1.1 Background information

Water is among the most essential requisites that nature provides to sustain life for plants and animals. The use of water by man, plants and animals is universal and that without it there can be no life. In homes, whether in the city or rural, potable water within the environment is vital for cleanliness and health. Water having secured first priority amongst man's needs, it is also the life-blood of industry namely: manufacturing, generation of electric power, transportation and recreation. (McDonald and Kay, 1988). The demand for water is increasing rapidly with the growing population thus creating acute shortage of both surface and underground waters in many localities.

Pollution and contamination of streams, lakes and underground sources has greatly impaired the quality of water available for use. (Wright, 1956). Ground water is often called underground water, which occurs below the surface of the earth. The formation of underground water takes place when under hydrostatic pressure the permeable rocks get saturated with water. (Singh and Dhillon, 1994). The character and quality of groundwater largely depends on the nature of the soil through which water percolates and the nature of the rock comprising the aquifer. Most aquifers in England have hard water. Limestone and chalk aquifers contain high concentrations of calcium hydrogen carbonate; dolomite aquifers are often rich in sodium chloride (Grey, 1994). Economically, groundwater is much cheaper, has good quality free from suspended solids, and except in limited areas where it has been affected by pollution free from bacteria and other pathogens (Grey, 1994).

The clean up of underground water, unlike surface water is very different. In underground water, clean up takes place through the porous structures of the geology. What both underground water and surface water share in common is that they both clean up when pollution stops. The water body namely a river and a lake clean itself once pollution stops. However, groundwater is not able to clean itself at a rapid rate hence clean up usually targets the source of pollutants and the aquifer itself. Underground water can be contaminated when organic and inorganic contaminants are released to the ground. The main force on the movement of compounds underground is gravity. Porosity of the soil and viscosity of the materials spilled onto the ground are contributing to the leaching of contaminants.(Duffus, 1998)

Water hardness.

Water hardness is primarily due to the amount of calcium, magnesium and to a lesser extent, iron in the water. Water hardness can be determined by adding up the concentrations of calcium, magnesium and converting its value to an equivalent concentration of calcium carbonate ($CaCO_3$) in milligrams per litre (mg/L) of water. Water hardness in most groundwater is naturally occurring from weathering of limestone, sedimentary rock and calcium bearing minerals. Hardness can also occur locally in ground water from chemical and mining industry effluent or excessive application of lime to the soil in agricultural areas. (Well stewardship information series, 2002).

1.1.1 Environmental health concerns of hard water.

Hard water is mainly an aesthetic concern because of the unpleasant taste caused by high concentration of calcium and other ions in water. It also reduces the ability of the soap to produce lather and causes scale formation in pipes and on plumbing fixtures. Hard water can cause pipe corrosion and may increase the solubility of heavy metals such as copper, zinc, lead and cadmium in water whose concentrations above the admissible levels may cause health problems. In some agricultural areas where lime and fertilizers are frequently applied on the land, excessive hardness may indicate the presence of other chemicals such as nitrates. (British Columbia ministry of health services, health file 45,[1995], Well stewardship and information series, [2002]).

Nyatike and Karungu divisions are generally high potential region for ground water. Many boreholes and shallow wells were sunk in Nyatike region. The location of these boreholes and wells are widespread and easily accessible to schools, health facilities, social gathering centers and homes. Some of these boreholes and wells which are machine drilled or man-dug have a yield of between 1m^3/hr and 10 m^3/hr, with an exception of a few boreholes that can produce up to 20 m^3/hr. The boreholes are usually perennial even though they may experience water table fluctuations of a few meters most borehole depths range between 40 m-90 m. (LBDA, water and sanitation report, 1988.)

The water production of wells in the area is generally good and varies according to the type of aquifer (confined or non-confined), rate of recharge and depth of penetration into the aquifer. Most of these wells have seasonal characteristics and their water depths are less than 0.5 m depending on water table fluctuations. The high yields, perennial character and good water quality even though slightly saline in taste, boreholes and wells are considered excellent water sources especially in rural areas that should be protected from whatever form of pollution. (Yehdegho *et al*, 1997).

1.2. Geology of Karungu-Gwasi area.

The rock system includes Precambrian volcanic rocks, meta-sediments and shallow intrusions of the Nyanzian system. These rocks are mildly metamorphosed and have been invaded by granites and dykes of various types. The rocks found represent intrusive, tectonic, volcanic and depositional activity that occurred many years ago. After a number of ring complexes containing alkaline igneous rocks and carbonatites associated with explosion vents that had been emplaced prior to the lower Miocene, volcanic activity commenced on a large scale, a vast volcanic cone being raised up in Kaksingri and great exposes being covered with nephelinitic lavas. (McCall, 1958).

Faulting in the upper Miocene slightly later gave rise to a south-westerly trend, which enclosed its explosive diatremes and associated ring complexes. This normal gravity faulting was followed by the outbursts of renewed volcanic activity a series of phonolitic clays being emplaced along the major faults and along subsidiary fracture lines. Two periods of sedimentary deposition were recognized. Lakebeds were first deposited in the Lake Victoria basin in the lower Miocene and have yielded a wealth of faunal remains. Later, thick sediments were deposited in the Lambwe valley and less extensive deposits at Karungu. Unusually, radioactive ironstones are present at Ruri and may overlie deposits of Uranium – thorium minerals.

Macalder is a mineral potential region as shown in the geological map of Gwasi area (McCall, 1958). Mining activities were incepted in the area in early 1960’s in small scale however by mid 1980’s mining activities got to climax then later subsided. Geologically, the minerals present include copper, cobalt silver, zinc, lead and gold. Gold mining has been prominent with inclusion of toxic materials like iron, sodium cyanide and mercury used in the formation of gold amalgam for easier separation and purification of gold and silver (Davies, 1993). Over time, few land excavations and landfills resulted from the activities.

1.3 Statement of the problem.

Heavy metals such as lead, copper, zinc and iron may be present in an environment through natural and anthropogenic causes and their presence in trace concentrations is important both to the animal and plant development. On the contrary, if the concentration of these heavy metals surpasses the maximum admissible levels as stipulated by various organisations such as World Health Organization (WHO), American Public health Association (APHA, 1989), then plant and animal developments may be retarded because of malfunctions caused by bio-concentration of the heavy metals. For instance, lead accumulation in the body adversely affects many enzymatic systems causing lead poisoning of the heme system. High levels of iron in the body can cause a condition known as hemochromatosis, affecting the liver, pancreas and heart (Kaplan and Pesce, 1989). Macalder region in Migori district is endowed with a variety of minerals like zinc, silver, copper and lead as exemplified in the geological map. Mining activities have been prominent in this region since 1960s. The open caves, cracks along the fault lines and excavations exposed deeper rocks rich in minerals hence increased chances of contact with agricultural sub- soil as well as underground water.

1.4 General objective.

To determine water hardness and the concentration levels of some selected heavy metals in soil and underground water in Nyatike-Karungu area.

1.4.1 Specific objectives.

1. To determine the concentrations of Copper, Zinc, Lead and Iron in soil and underground water in Nyatike-Karungu area.
2. To analyse spatial variations in concentrations of each heavy metal in water and soil with respect to region and seasons around the mining site (a radius of 70 km).
3. To establish the extent to which the geology of the area influences water hardness levels of the underground water from boreholes and other sampling points.

1.5 Hypotheses.

1. Underground water and sub-soils in Nyatike and Karungu do not contain soluble heavy metals in concentrations that surpass the guidelines by WHO, APHA and other organisation guidelines.
2. Selected heavy metal concentrations do not increase further away from macalder (epicentre of the mining activities).
3. The geology of the area does not influence water hardness of boreholes and wells.

1.6 Justification.

The surface waters adjacent to Lake Victoria have substantially changed over a short period because of the increased anthropogenic activities in the lake and its catchments. The lakeshore and some sections of the inflowing rivers are heavily polluted by municipal and industrial discharges (Omole, 2003). Some of the industries responsible for the pollution include tannery, fish processing, sugar mills, abattoirs (LVEMP, 1999). Macalder was/is an active mine site for Gold, Copper and Silver. The presence of such minerals is associated with other trace metals such as Zinc, Lead and Iron ores. It is therefore imperative that groundwater quality be monitored and assessed regularly for inorganic and organic pollutants.

World Health Organisation (WHO) has guidelines pertaining to the maximum concentration limits (MCL) for all the heavy metals in both water and soil. The presence of these heavy metals in drinking water and soil surpassing the given limits poses a health risk to plants, animals and humanity in general. A chemical and environmental assessment giving an analytical account of the concentration levels of some selected heavy metals was imperative. Water is an important commodity to humanity and animals and should be safe from any sort of elemental pollution. Soil remains the medium through which plants get their nutrients in a soluble form. It therefore means that polluted soil passes on the pollutants to the plants.

CHAPTER TWO

LITERATURE REVIEW

Groundwater is precious and the most widely distributed resource of the earth and unlike any other mineral resource, it gets its annual replenishment from meteoric precipitation. The world's total water resources are estimated at 1,370,323 x 10^3 km^2. Of this global water resource, about 97.2% is salt water mainly in oceans and only 2.8% is available as fresh water at any time on planet earth (Duffus, 1998). Ground water within 800 m from the ground surface is over 30 times the amount in stream channels at any one time. Presently, one fifth of all the water used in the world is obtained from ground water resources (Ellis, 1989).

2.1 Relative abundance of Cu, Zn and Pb in the earth's crust.

Heavy metals refer to a group of metals and metalloids which have densities >5g/cm^3 and exhibit atomic number >64. They are in most cases associated with pollution and toxicity of water and soil (Alloway and Ayres, 1997). Examples of heavy metals include lead, mercury, zinc, cobalt, nickel, copper, cadmium, iron, chromium and manganese. Heavy metals, such as copper, lead, mercury, and selenium, get into water from many sources, including industries, automobile exhaust, mines, and even natural soil and rocks. The average elemental composition of rocks and soils is given in the table 2.1 below. Like pesticides, heavy metals become more concentrated as animals feed on plants and are consumed in turn by other animals (bio-concentration). When they reach high levels in the body, heavy metals can be immediately poisonous, or can result in long-term health problems similar to those caused by pesticides and herbicides (Alloway and Ayres, 1997).

Table: 2.1 Average elemental compositions of rocks and soils in (ppm).

Element	**Igneous rock**	**Sedimentary rock**	**Earth soil**
Zinc	100	160	200
Copper	55	57	20
Lead	12.5	20	10

Source: (Valkovic, 1975)

The guidelines for drinking water quality supporting documents on hardness divide hardness into four categories as illustrated in the appendix 1.

The optimum range of hardness in drinking water is 80-100 mg/L of $CaCO_3$. Water with hardness greater than 200 mg/L of $CaCO_3$ was considered poor in most regions of Canada and water with hardness greater than 500 mg/L of $CaCO_3$ is considered unacceptable for domestic purposes. On average, water in British Columbia has been found to range in hardness from less than 10 mg/L to 180 mg/L of $CaCO_3$. Groundwater tends to be harder than surface water and can range to greater than 1000 mg/L. (Well stewardship information series, 2002).

2.2 Movement of ground water.

Few rock formations are impervious to water; even crystalline igneous formations such as granite usually contain discontinuities such as fissures, faults or joint planes along which water can migrate. Water also moves through granular strata via pore spaces or interstices between the component minerals or grains of the rock. Finally, water moves to rock formations, which both store and transmit water and which are called aquifers. (Duff, 1998).
Ground water moves from levels of higher energy to levels of lower energy, its energy being essentially the result of elevation and pressure. The flow is often laminar as found by Henry Darcy, a French engineer. Darcy's law states that velocity of the ground water depended upon the hydraulic head of the water and permeability of the material that the water is moving through.

Darcy's law states that ground water velocity = permeability x hydraulic gradient

$$V = K\frac{h}{L}$$

Where V = velocity ground water flow.
K = hydraulic conductivity or permeability.
h = difference in elevation
L= distance moved by water (Plummer et al, 1999).

2.3 Ground water as an erosive agent.

Water is the most active naturally occurring chemical compound and can dissolve a huge range of substances. It does not decay and can demonstrate an infinite range of flow conditions from laminar to turbulent (Duff, 1998). Water falling as precipitation dissolves small quantities of carbon dioxide (CO_2) from the atmosphere, the water becomes weakly acidic by liberation of hydrogen ions;

$$H_2O + CO_2 \longrightarrow (HCO_3)^- + H^+$$

Rainwater has an approximate pH of 5.5-6.0 as it falls on the ground. When it migrates through soils and bedrock, the water reacts with the rock and cementitious minerals and become a complex solution, which exhibits chemical characteristics. Where rock forming minerals or intergranular cement is calcareous or otherwise susceptible to solution by water, fissures due to faults, joints and bedding planes can be opened out to create conduits for water movement (Duffus, 1998).

2.4 Metal poisoning.

The presence of excessive amounts of a metal in living organisms is responsible for a variety of syndromes. For example, Wilson's disease, symptoms of which are a malfunctioning liver, neurological damage and brown or green rings in the cornea of the eyes, are caused by a copper overload due to genetically inherited metabolic defect. Excessive amounts of calcium results in calcification of tissue, cateract, kidney stones and gallstones. (Thomas, 2002). Metal poisoning occurs when the body's metal management system allows the concentration of the metal to reach toxic levels in sensitive areas of the body. The metal can enter the body in a number of ways ranging from accidental ingestion, pollution of the blood chain, skin absorption and breathed in as atmospheric pollutants. Treatment is based on the use of chelating agents that form stable complexes with the excess metal and are either easily excreted or deposited as non- harmful solids (Alloway and Ayres, 1997).

2.5 Pollution of ground water.

Ground water in its natural state tends to be relatively free from contaminants in most areas. Because it is a widely used source of drinking water, pollution of ground water can be very serious problem. Pesticides and herbicides such as DDT and 2, 4-D applied to agricultural crops can find their way into ground water when rain or irrigation water leaches the poison downwards into the soil. Fertilizer such as nitrate is harmful in even small quantities in drinking water. Zhang *et al*, (1996) in their research on nitrate pollution of groundwater in Northern China found that in vegetable producing areas and farm yards nitrate content in ground and drinking water were measured at 300 $mgNO_3/L$ far much beyond the acceptable level of 50 $mgNO_3/L$. Rain can also leach pollutants from city dumps into ground water supplies. Heavy metal such as mercury, lead, chromium, copper and cadmium together with other household chemicals can all be concentrated in ground water supplies. Carey *et al*, (1996) researched on leaching of copper, chromium and arsenic through free draining New Zealand soils and found that 2%w/v solution containing cupric, dichromate and arsenic ions leached through surface and sub-surface horizons of two free draining New Zealand soils.

(Sadiq *et al*, 1994) carried out arsenic chemistry in groundwater aquifer; underneath an industrial complex in Eastern, province of Saudi Arabia and their findings were that arsenic concentrations in groundwater samples varied between 0.18 and 11.14 µg/L depending on sampling locations. Liquid and solid wastes from septic tanks, sewage plants and animal feedlots may contain bacteria, viruses and parasites that can contaminate ground water.
Acid mines drainage from coal and metal mines can contaminate both surface and ground water. The acid water draining from long abandoned mines and factory effluents often kills fish and plants. Pinta (1998) notes the Minammata case where effluents from a nearby factory were found to contain HgS and which led to bio-concentration in fish and subsequently taken by fishermen. This led to health complications among the consumers of such fish. Radioactive waste is both an existing and a very serious potential source of ground water pollution.

Generally, not all sources of ground water pollution are man-made; naturally occurring minerals within rocks and soil may contain elements such as arsenic, selenium, mercury and other toxic metals. Circulating ground water can leach these elements out of the minerals and raise their concentrations to harmful levels within the water (Plummer *et al*, 1999).

Mbila (2000) carried out a comparative research on concentrations of Zn and Pb on abandoned mines in Spain. Results obtained showed that concentrations of total Zn and Pb were 10 to 20 fold greater in spoil than the undisturbed soils.

2.5.1 Small-scale gold mining-high mercury risk, Tanzania.

A pilot project entitled, an integrated approach to mineral exploration and environmental assessment in southern and eastern Africa, comprised compilation and integrated evaluation of existing geo-science and environmental data from western Tanzania. The fieldwork comprised detailed studies and sampling of numerous small gold deposits. All mining, crushing and grinding are done by hand and the ground ore is treated with metallic mercury, whereby the very fine-grained gold amalgamates with the mercury. The mercury is subsequently burned off over small fires.

Large quantities of mercury are released into the environment during the amalgamation. Some of this mercury is inhaled by amalgamists and nearby villagers. The remaining mercury enters the drainage system where it is incorporated in the food chain. Samples of fish, porridge and human hair were collected. The analysis showed that several of these miners had very high contents of mercury in their hair. The mercury used in amalgation poses serious health problems to the population of west Tanzania (UNEP, 1993).

2.6 Lead (Pb).

Lead is an element, which is extensively used and is one of the most wide spread metal in the environment largely due to human activities. The main lead ores that are mined are *galena* (PbS), *Cerrusites* ($PbCO_3$) and *anglesite* ($PbSO_4$). On a global basis, about a quarter of total production of lead is from lead scrap. The world chief producers of Pb are USA, Australia and Canada. Other sources of lead in the environment include smelting and refining of lead, burning of lead based petroleum fuels containing lead additives. To a lesser extent the melting of other metals and the burning of coal and oil also contribute as sources of lead in the environment (Alloway and Ayres, 1997)

Lead compounds are used in a variety of commercial products and industrial materials including plastics, storage batteries bearing alloys, ceramics, cable sheathing and even paints. Lead enters the human body system through three major pathways:

i. Inhalation
ii. Ingestion
iii. Skin contact

Inhaling Lead based gasoline or petrol can lead to poisoning if the gasoline has tetraethyl lead and tetramethyllead. The total concentration of tetraethyl lead in the brain, lungs, liver and spleen are 10 mg/Kg, 22 mg/Kg, 41mg/Kg and 12 mg/Kg respectively. Toxic concentration can accumulate in the marrow, where the red blood cell formation (haematopoiesis) occurs. Lead affects at least five stages in the formation of haem part of the haemoglobin but the two enzymes affected are *δ-amino laevulinic dehydratase* (ALAD) and *ferrochelatase* (Alloway and Ayres, 1997).This inhibition of haem synthesis results into anaemia. Kidney damage also occurs because of exposure to lead. Lead, like mercury, is a powerful neurotoxin and a range of pathological conditions associated with acute lead poisoning may induce behavioural abnormalities, including learning difficulties. The fatal inorganic lead concentrations in the brain, liver, kidney, flat bone and long bone are 5.8 mg/Kg, 40 mg/Kg, 8.8 mg/Kg, 268 mg/Kg and 132 mg/Kg respectively (Higgins and burns, 1992).

2.7 Copper (Cu).

Copper (element), symbol Cu, brownish-red metallic element that is one of the most widely used of metals. Copper is one of the transition elements of the periodic table. The atomic number of copper is 29. Copper occupies the same family as silver and gold since they all have one s-orbital electron on top of a filled electron shell. This similarity in electron structure makes them similar in many characteristics. All have malleability characteristics and very high thermal and electrical conductivity. There are two stable isotopes ^{63}Cu and ^{65}Cu.In terms of corrosion, copper is a metal that does not react with water but oxygen of the air will react slowly at room temperature to form a layer of copper oxide on copper metal.

2.7.1 Biological role of copper.

Copper is essential in all plants and animals. It is mostly carried in the bloodstream on a plasma protein called *ceruloplasmin.* When copper is first absorbed in the gut, it is transported to the liver bound to albumin. Copper is also found in a variety of enzymes. A normal healthy adult should take an average of 0.9 mg/day of copper however, research on the subject recommends 3.0 mg/day copper intake. Because of its role in facilitating iron uptake, copper deficiency can often cause anaemia related symptoms (Alloway and Ayres, 1997).

2.7.2 Toxicity of copper.

Copper is toxic in uncontrolled quantities. The suggested safe level of copper in drinking water for humans varies depending on the source, but pegged at 1.5 to 2mg/L. In toxicity, copper can inhibit the enzyme *dihydrophil hydrase,* an enzyme involved in *haemopoiesis*. A significant portion of the toxicity of copper comes from its ability to accept and donate single electron as it changes oxidation state. This catalyses the production of very reactive radical ions such as hydroxyl radical. The enzymes use this catalytic activity of copper and that it is associated with and is thus only toxic when unsequestered and unmediated. An inherited condition called Wilson's disease causes the body to retain copper since the liver into the bile does not excrete it. This disease if not treated can lead to brain and liver damage. Mental illness such as *schizophrenia* is because of heightened levels of copper. High levels of copper in water have also been found to damage marine life. In fish, it damages gills, liver, kidney and the nervous system.

2.8 Zinc (Zn).

Zinc pollution is often associated with mining and smelting. Usually cadmium is often found as a guest element in ZnS and other ores. Zinc readily undergoes oxidation to Zn^{2+}. ZnS (sphalerite) ore often occurs together with PbS (galena), the main ore of Pb. Zn pollution is often associated with lead and copper (Alloway and Ayres, 1997). Soils and water from areas of historical or active lead- zinc mining tend to have higher concentrations of these heavy metals than other areas where mining has not occurred. These trace element concentrations decrease with increasing distance down-stream from the mining activity (Espana *et al*, 2006).

Table: 2.2 Lead and Zinc concentration in water and soil in Ozark Plateau, Arkansas.

SITE	**LEAD**		**ZINC**	
	Water (ppm)	**Soil (ppm)**	**Water (ppm)**	**Soil (ppm)**
Centre Creek	1	1.7	1.3	1.7
Big River	1	1.8	1.4	1.6
Strother Creek	1	1.5	1	1.3
Background	<1	<1	<1	<1

2.9 Iron (Fe).

Iron forms ferrous compounds in which it has a valence of +2 and ferric compounds in which it has a valence of +3. Ferrous compounds are easily oxidized to ferric compounds. The most important ferrous compound is ferrous sulphate ($FeSO_4$), called green vitriol or copperas; it usually occurs as pale-green crystals containing seven molecules of water of hydration. The ferrous and ferric ions combine with cyanides to form complex cyanide compounds. Ferric ferrocyanide ($Fe_4[Fe(CN)_6]_3$), a dark-blue, amorphous solid formed by the reaction of potassium ferrocyanide with a ferric salt called Prussian blue. It is used as a pigment in paint and in laundry bluing to correct the yellowish tint left by the ferrous salts in water. Potassium ferrocyanide ($K_3Fe(CN)_6$), called red prussiate of potash which is obtained from ferrous ferrocyanide ($Fe_3[Fe(CN)_6])_2$ also called Turnbull's blue, It is used in processing blueprint paper. Iron also undergoes physiochemical reactions with carbon that are essential to the formation of steel.

Corrosion is partial or complete wearing away, dissolving or softening of any substance by chemical or electrochemical reaction with its environment. The term corrosion specifically applies to the gradual action of natural agents, such as air or salt water, on metals. The most familiar example of corrosion is the rusting of iron, a complex chemical reaction in which the iron combines with both oxygen and water to form hydrated iron oxide. Iron is used in processed forms such as wrought iron, cast iron, and steel. Commercially pure iron is used for the production of galvanized sheet metal. Iron compounds are employed for medicinal purposes in the treatment of anaemia, when the amount of haemoglobin lowers.

2.10 Atomic absorption spectrometric technique.

Many analytical methods, both quantitative and qualitative, involve the interaction of matter and radiant energy. Atomic absorption spectrometry (AAS) is an analytical method for the quantitative determination of elements based upon the absorption of radiation, (Skoog and West, 1982 and Alloway and Ayres, 1997).

2.11 Wet digestion/acid oxidation.

There are four different categories of wet oxidation methods. These methods are used for digestion in the initial stages of sample decomposition, however, their results are the same (Allen, 1989).The characteristics of various wet oxidation methods are illustrated below:

Table: 2.3 Characteristics of wet oxidation mixtures.

Digestion reagent.	**Applicability to organic-matrix.**	**Remarks.**
H_2SO_4/HNO_3	Vegetable origin.	The most used, danger of volatilization as in the determination of As, Se and Hg.
$HClO_4$ alone	Biological origin.	Catalysts $(NH_4)_2$ MO_4
$H_2SO_4/HClO_4$	Biological origin.	Suitable only for small samples, danger of explosion.
$HNO_3/HClO_4$	Protein carbonate (No fat).	Less explosive and loss of lead.
HNO_3 alone	General: also fat	Applied directly to most materials.

Adapted from (Allen, 1989).

2.11.1 Wet Digestion (Acid oxidation).

There are numerous wet oxidation procedures proposed, but they all fall into four categories differing only in the digestion mixture used:

- Sulphuric acid and hydrogen peroxide
- Nitric acid and sulphuric acid
- Perchloric acid and nitric acid or sulphuric acid
- Nitric acid.

Amina (1997) in his research on comparison of the results of four different analytical procedures for heavy metals determination in superficial sediments concluded that digestion with a mixture of HCl/HNO_3 on a 4:1 ratio was the most efficient.

2.12 Total hardness (TH).

Water is a good solvent and picks up impurities easily. Pure water is often referred to as universal solvent. When water combines with carbon dioxide to form very weak carbonic acid becomes even a better solvent. Practically, all natural ground waters contain minerals. The kind and extent of mineral content varies widely with the exposure of the water to various sources of soluble minerals as it flows over and through the earth's crust. As water moves through soil and rock, it dissolves very small amounts of minerals and holds them in solution (Oram, 2005). Water hardness is measured by adding up the concentrations of calcium, magnesium and converting this value to an equivalent concentration of calcium carbonate ($CaCO_3$) in milligrams per litre (Mg/L) of water (Wright, 1956). The hardness of water is the capacity for the precipitation of soap. The soap is precipitated by calcium and magnesium ions in water. It can also be precipitated by other polyvalent metals e.g. Al, Fe, Mn, Zn and even hydrogen ions but only Mg^{2+} and Ca^{2+} are usually present in water in high concentration and hence hardness is expressed as the characteristic of the water to represent total concentration of just Mg^{2+} and Ca^{2+} expressed as carbonate.

2.13 pH.

This refers to the potential hydrogen concentration of hydrogen ions in a solution. Water with a pH value of 6.5 – 9.5 supports normal aquatic life. The degree of acidity or alkalinity is mostly measured using pH electrode, which is an example of a selective ion electrode (Stewart, 1989). Natural rainwater rarely has a pH lower than 5.6 (Raven and Johnson, 1992). This is because of atmospheric pollution (oxides of nitrogen and sulphur) from vehicles and thermal power stations leading to acid rains. However, sewage and industrial effluents can also affect the pH balance of river and lake waters. pH is a very important factor in the oxidation and reduction of trace elements. Laboratory oxidation studies performed with samples from mine effluents have confirmed that oxidation rate is maximum at temperatures between 27-35^{0}C (Espana *et al*, 2006).

CHAPTER THREE

MATERIALS AND METHODS.

3.1 Study area.

Macalder is situated in Nyatike division, Migori district. It borders Karungu division to the West, Suba East and Suba West to the East while Muhuru and Uriri divisions to the South and North respectively. Macalder is on longitude 34^0 East of Greenwich meridian and latitude 1^0 South of the equator. The region is characterised by dry and hot climate with an average annual rainfall of below 650 mm and an average temperature of 33^0C and 22^0C on high and low respectively. The soil type is stony-black loam. The topography is steep, low towards the lakeshore with plain basin at the borders of Karungu and Muhuru divisions.

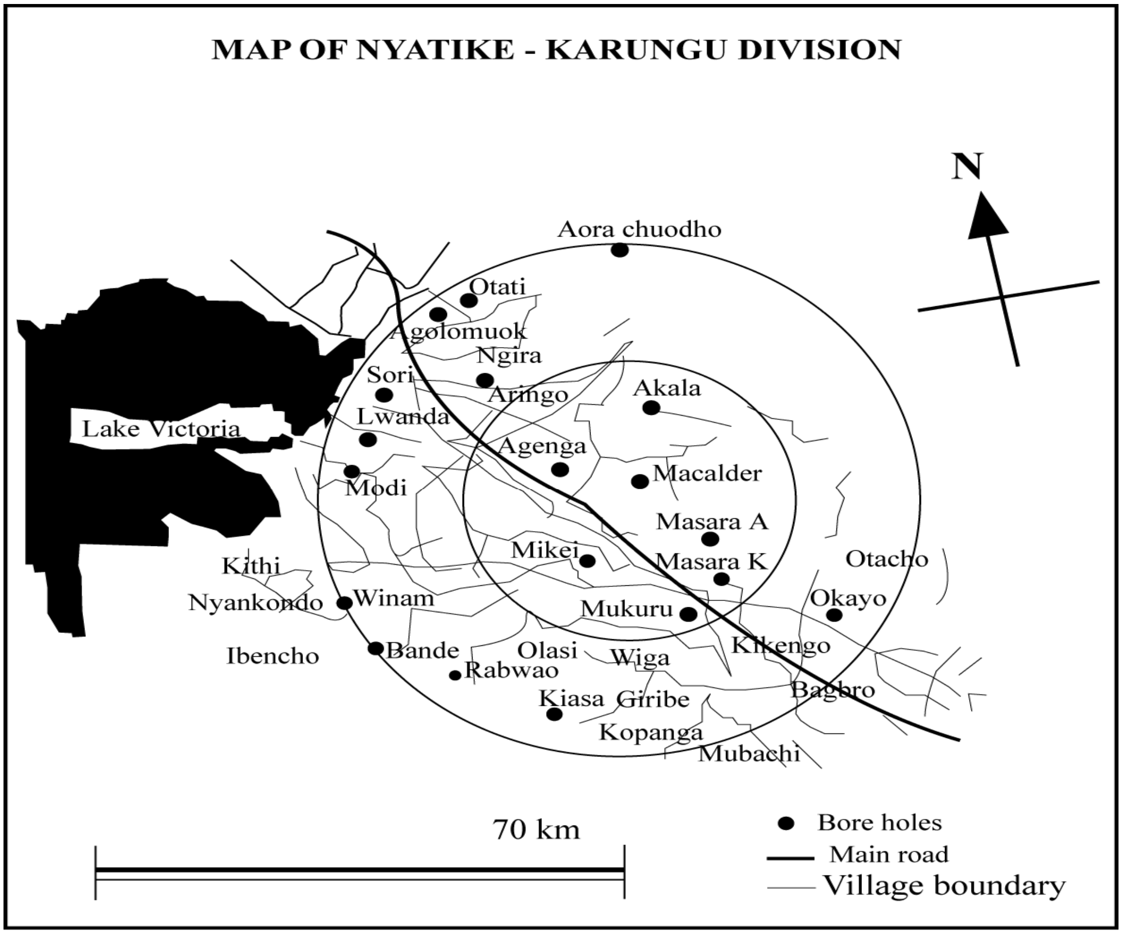


Fig 1: Map of Nyatike -Karungu Divisions.

3.2 The geology of Macalder area.

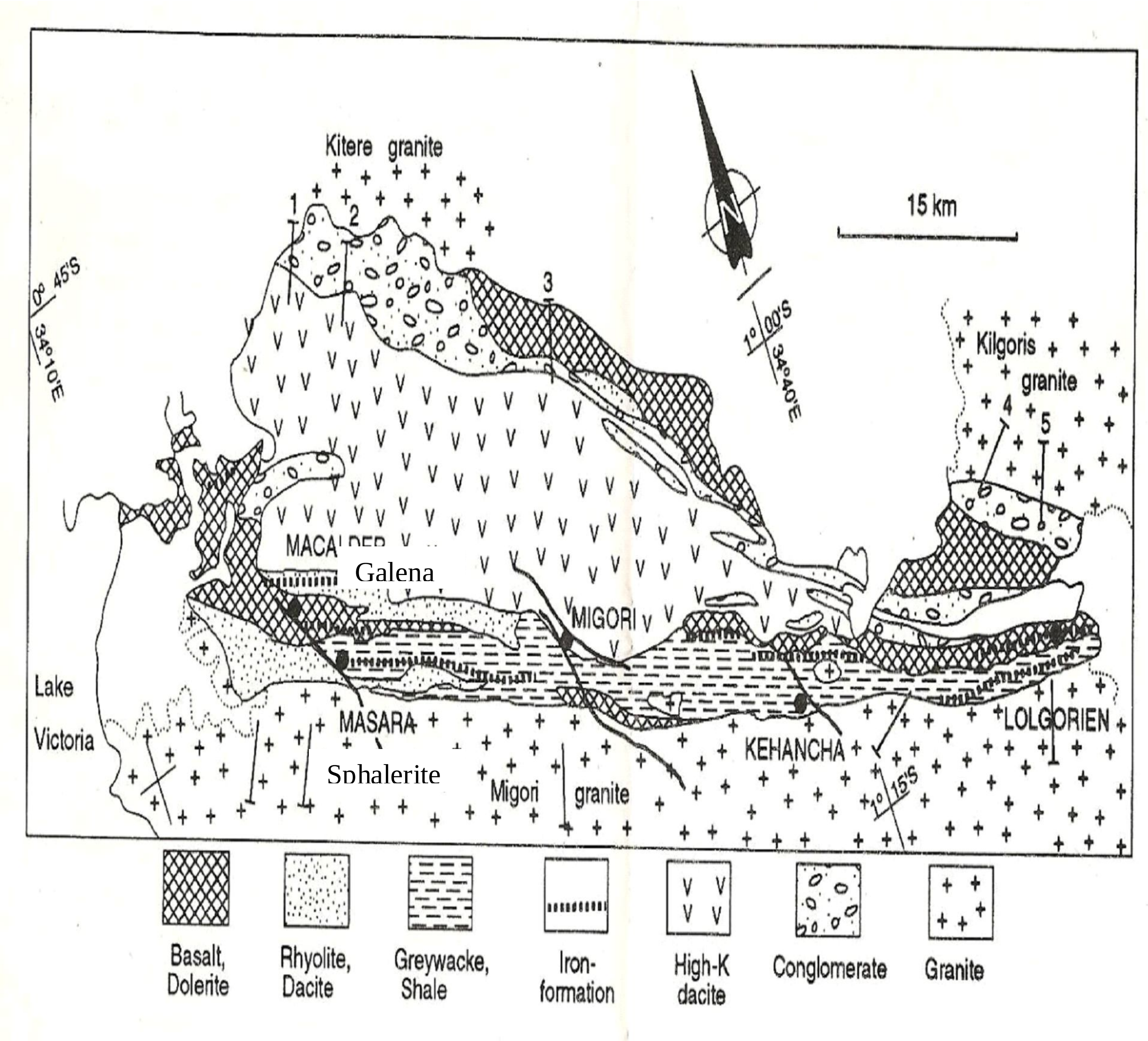
The geological details of the Macalder area as contained in Gwassi geological map showed that Macalder was a high mineral potential region. The Migori segment forms about a third of the portion of the Nyanza greenstone belt to the south of the Winam rift and is located just north of the Kenya-Tanzania border. The 80 km South-Western margin of the segment with the Migori Granite parallels the North-West to South-East strike of the marine volcano – sedimentary greenstones of the Migori gold belt, which forms the South-Eastern portion. The Macalder Zn-Cu-Ag massive sulphide deposite and numerous small gold occurrences are restricted to greenstone of the gold belt. These rocks consist of tholeiitic and calcium-alkaline volcanics, sills, dykes, as well as greywacke turbidites (Ichang'i, (1992), Shackleton, 1951). Mineralogy studies carried out in Macalder by Ogola, (1996) showed the presence of Lead and Zinc ores. The primary sources of lead, zinc and copper were sulphide minerals disseminated in the limestone and dolomites in the underlying rocks. Sulphide minerals mined included Sphalerite (ZnS), Galena (PbS), Chalcopyrite (Cu_2S) and Pyrite (FeS_2). Oxidation of these minerals through the mining process or after can release soluble metals in an acidic solution as below,

$$4FeS_2 + 15O_2 + 14H_2O \longrightarrow 4Fe(OH)_3 + 8SO_4^{-2} + 16H^+$$

$$2ZnS + 4O_2 + 4H_2O \longrightarrow 2Zn(OH)_2 + 2SO_4^{-2} + 4H^+$$

$$2PbS + 4\,O_2 + 4H_2O \longrightarrow 2Pb(OH)_2 + 2SO_4^{-2} + 4H^+$$

Similar reactions are possible with sulphides of Copper (Pyrite) .Boreholes in the abandoned mines or water which has been discharged from such areas is potential source of contamination for aquifers in the area. Other trace metals associated with these ores may also be released into solution by similar oxidation-reduction reactions (Mize and Deacon, 2003). A composite ore sample averaged 5.1% Zn, 3.8% Cu, 0.9% Pb, 0.3% Co, 5 g/tonne Au, and 95% Ag (Shackleton, 1951).



Adapted from proceedings of fifth conference on geology of Kenya. (Ichang'i D.W, 1992)

Fig 2: Geology of macalder segment.

3.3 Hydro-geological information of sampled boreholes.

The rock type that covers the region was made up of sediments covered by sandy and clay soils. Generally, the first Water Struck Level (WSL) is at around 35-55 m. Main aquifer struck at around 70-90 m. Most boreholes have a Static Water Level (SWL) of approximately 33.5 m and a Pumping Water Level (PWL) of around 82.5 m. Average water discharge is approximately 6 L per minute (LBDA, 1988).

3.4 Sampling.

Sampling of both water and soil was done at nearly the same points approximately 5 m apart. Soil samples were used for elemental analysis of the heavy metals while water samples were used for both elemental analysis of the heavy metals and determination of the water hardness. Sampling was done during the wet season (May-June 2007) and dry season (December 2007-February 2008) in triplicates (N).

3.4.1 Water Sampling and HCl/HNO_3 acid wet oxidation method.

Sampling of the borehole and well water were done in three regions. Region 1(*epicentre*) comprised boreholes that lie within 0-20 km radius from the epicentre (Macalder-mines). Region 2 (*surrounding*) comprised water points that lie between 20-50 km radii from the epicentre. Region 3 (control) comprised a borehole 100 km away from the epicentre and which also served as the control water point. Twenty-one boreholes were sampled in the months of May and December, which represent the peak of wet and dry seasons in Nyatike-Karungu.

Water samples were contained in half litre plastic bottles. The water samples were preserved by adding 5 ml concentrated HNO_3 per litre to each sample. The samples were then transported and stored in a refrigerator at 4^0C to prevent any change in volume due to evaporation(APHA,1989).100 ml of each water sample was transferred into 250 ml beaker and digested on a hot plate using a mixture of concentrated HNO3/HCl in the ratio of 3:1until a light coloured clear solution was formed. The digested solution was transferred into a 100 ml volumetric flask. The beaker was rinsed twice with about 10 ml of distilled water and the rinsing water also transferred into the 100 ml volumetric flask. The solution was then diluted to the mark with distilled water and mixed thoroughly. The same procedure was repeated for reagent blank containing distilled water. Portions of the resulting solutions and the blank were separately for the concentration of the heavy metals using atomic absorption spectrophotometer (APHA, 1989).

Measurements of physical parameters like temperature and pH were done in situ using an electrochemical analyser kit (Model: Jenway 3405 Electrochemical analyser).

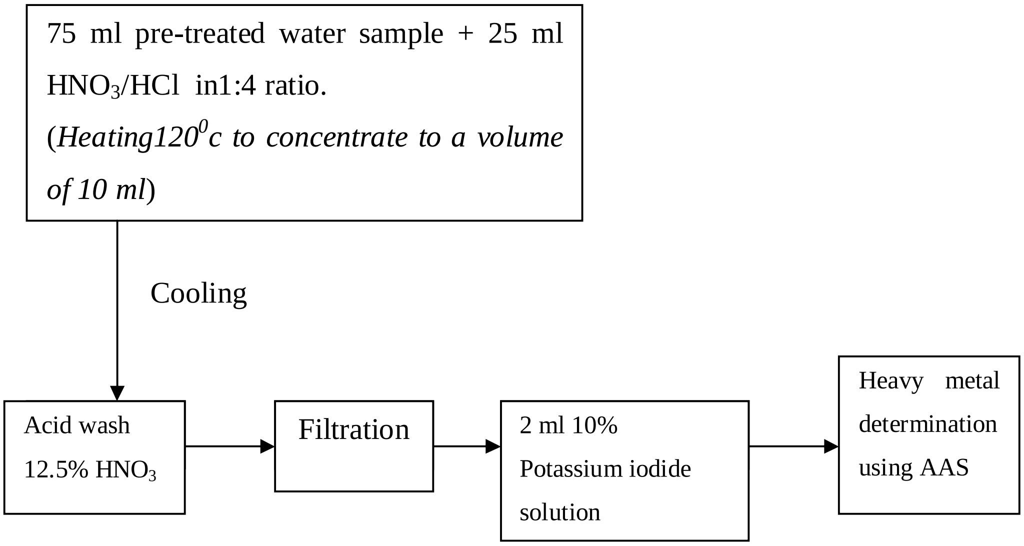


Fig: 3 Sequence of steps for preparation and analysis of water samples on the basis of digestion with a mixture of HNO_3/HCl.

3.4.2 Soil sampling

Sampling of the soil was done at twenty-one sites beside the boreholes and wells and divided in three regions as illustrated in the study area map. Soil was sampled by a van veen grab at a depth of 20 cm in all sites using a stratified method. About 20 g was sampled and packed in dry polyethylene bags.

Soil sampling.

Soils adjacent to the twenty-one water points were sampled using a standard Van Veen grab with an effective grasping area of 25 cm^2. About 20 g soil samples were taken in three replicates in the months of May and December 2007. The three samples collected from each site was analysed separately. The heavy metal concentration levels obtained were measured in µg/g dry weight.

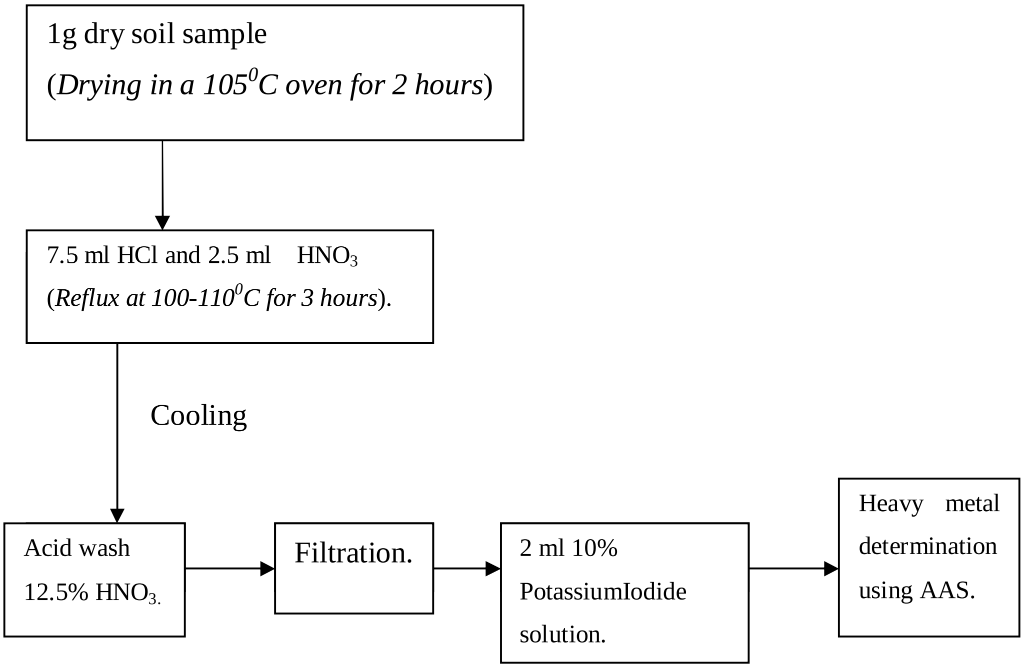


Fig 4: Sequence of steps for preparation and analysis of soil samples for digestion with a mixture of HNO_3/HCl.

2 g of each soil sample were bench dried for 5 days in the laboratory then crushed in a mortar with pestle to fineness. The ground soil sample was sieved through a 10-mesh (2 mm) sieve and moisture dried in the oven separately at 105^0C until constant weight was obtained. The wet digestion was done by reflux digestion of 1 g sub-sample with 10 ml of concentrated HCl/HNO_3 in 1:4 ratios. A few boiling chips were added and temperature regulated at 100^0C for 3 hours by using Aluminium digestion block. The mixture was cooled and acid washed with 12.5% v/v HNO_3 then filtered.

Throughout the analytical work, double distilled water (DDW) was used. Reagents were of analar grade. All the lab wares used were washed first in detergent and tap water then soaked in 15% v/v HNO_3 for 24 hours followed by rinsing repeatedly in DDW. With each sample set, a reference material and two blanks were also run. All analyses for each sampling sites were taken in triplicates and the mean values calculated. For elimination of matrix interferences a 10% v/v potassium iodide solution was added to all standards and sample solutions and elemental concentrations determined by Thermo-Jarrel Double Beam Atomic Absorption Spectrometer. Deuterium source, automatic background correction was used throughout the analytical program. The AAS system used had 10 cm one-slit burner head and uses standard air-acetylene flame. Wavelengths of 217.0, 324.8, 248.3 and 213.9 nm were used for lead, copper, iron and zinc respectively. Single element hollow cathode lamps and an automatic background correction mechanism were used for all elements. The instrument settings and other experimental conditions were in accordance with the manufacturer specification.

3.5 Preparation of standards.

Standards for Cu, Pb, Fe and Zn were available in 1000 ppm concentration in analytical grades. The linear ranges for Fe and Cu were 1 ppm ≤ Fe / Cu ≤ 5 ppm while Pb had a linear range of 2 ppm ≤ Pb ≤ 10 ppm. Zn also had a linear range 0.1 ppm ≤ Zn ≤ 0.4 ppm. Standards were prepared in 50 ml volumetric flask. 1 ppm Cu in 50 ml of DDW was prepared by adding 0.05 ml of the standard from self loading micro-pipette in 30 ml of DDW and topped upto 50 cm. The same procedure with the same appropriate dilution was done for Zn, Fe and pb for various concentrations.

1 ml = 1000 ml= 1 ppm
x = 50 ml = 1 ppm
x = 0.05 ml

Table: 3.1 Spectrometric parameters

Metal	**Pb**	**Zn**	**Cu**	**Fe**
Wavelength (nm)	217.0	213.9	324.8	248.3
Slit width (nm)	1.0	1.0	1.0	0.3
Lamp current (mA)	5.0	3.0	3.0	8.0
Sample flow rate (ml/min)	6.0	6.0	6.0	6.0
Oxidant flow rate (ml/min)	8.0	8.0	8.0	8.0
Fuel flow rate (ml/min)	2.0	2.0	2.0	2.0
Burner height (cm)	25.0	25.0	25.0	25.0
Sensitivity (ppm)	0.1760	0.0220	0.3384	0.2095
Flame	Air/C_2H_2	Air/C_2H_2	Air/C_2H_2	Air/C_2H_2

3.6 Spectrometric sensitivity

Sensitivity is the concentration (quoted usually in ppm in aqueous solutions) which absorb 1% of the incident resonance radiation of a given element (Caulcutt and Boddy, 1994). In atomic absorption spectroscopy, sensitivity is the reciprocal of the slope of the calibration curve near the origin and that sensitivity of an instrument can be determined using the formula:

$$\text{Sensitivity} = \frac{\text{Concentration of std (ppm) x 0.0044}}{\text{Measured absorbance}}$$

The sensitivity assists the analyst to know if all instrumental conditions were optimised and the instrument was working up to the manufacturer's specifications.

All solutions were prepared from analytical reagent grade materials in DDW. Stock solutions (1000 ppm) of Pb, Fe, Cu and Zn were prepared by dissolving appropriate amounts of metal salts in DDW. Working solutions of lower concentrations were prepared by appropriate serial dilution of the stock solutions in DDW. All the solutions were contained in polypropylene bottles.

3.7 Determination of water Hardness.

Hardness in water is as a result of the presence of Calcium and Magnesium salts in water. Total hardness is the sum of dissolution of both Calcium and Magnesium salts in water. Water hardness can be determined in two ways,

- By an AAS where ammonium acetate extracts are directly analysed for Calcium and Magnesium. The spectrophotometric standards are prepared in the ammonium acetate solution and both the standard and extracts are read against ammonium acetate as blank.
- By complexometric titrations using Ethylene diamine tetraacetic acid (EDTA). This was the method chosen for the determination of water hardness in this research.

EDTA titration method.

This method makes use of chelating properties of EDTA solution which forms soluble complexes with metal cations. Chelating ligands are commonly formed by linking donor groups via organic linkers. A classic *bi*dentate ligand is ethylenediamine, which is derived by the linking of two ammonia groups with an ethylene ($-CH_2CH_2-$) linker. A classic example of a polydentate ligand is the hexadentate chelating agent EDTA, which is able to bond through six sites, completely surrounding some metals. The structure of EDTA is shown in fig. Below.

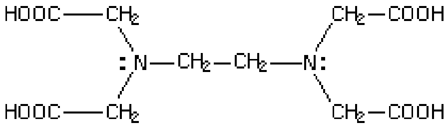


Fig.5: Ethylene diamine tetraacetic acid (EDTA)

Each of the acetic acid groups give up a proton, yielding an anion with a -4 charge. The two nitrogens has a pair of non-bonding electrons such that in the most basic form, the EDTA anion has six points at which it can attach to a central atom. This occurs by wrapping itself around the central atom to exhibit an octahedral coordination. EDTA molecule therefore, bind to metal ions by forming six bonds to it (two from nitrogen atoms in amino groups and four from oxygen atoms in carboxyl groups) and can co-ordinate with calcium ion as below.

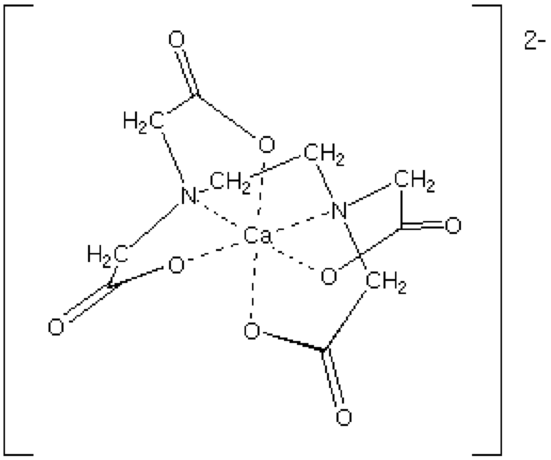


Fig.6: Ethylenediaminetetraacetatocalcium ion $[Ca(EDTA)]^{2-}$

Buffer preparation for the hardness titration.

A mixture of 1.18 g of Disodium ethylene diamine tetraacetate (EDTA, analytical reagent grade) and 0.78 g of Magnesium sulphate were dissolved in 50 ml of DDW and added to a 250 ml volumetric flask with 16.90 g of Ammonium chloride. The electronic weighing balance had an accuracy of 0.01. Then 143 ml of concentrated ammonium hydroxide was added and mixture stirred and made up to 250 ml mark. The resultant solution was the standard EDTA titrant or the hardness buffer.

1 ml of buffer solution was added to 50 ml of each water sample followed by a few granules of the indicator (Erio-chrome T black mixture). Standard EDTA titrant was added drop by drop through titration while continuously stirring until the last reddish tinge (pink) disappeared from the solution.

Calculation formulae.

$$Hardness\ EDTA\left(\frac{mg}{L}\right) = \frac{A \times B \times 50{,}000}{V}$$

Where: - A = Volume of EDTA titrant.

B = Mass (mg) carbonate equivalent 1 ml EDTA titrated.

V = Volume of water sample .

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Results for determination of metal concentration in soil.

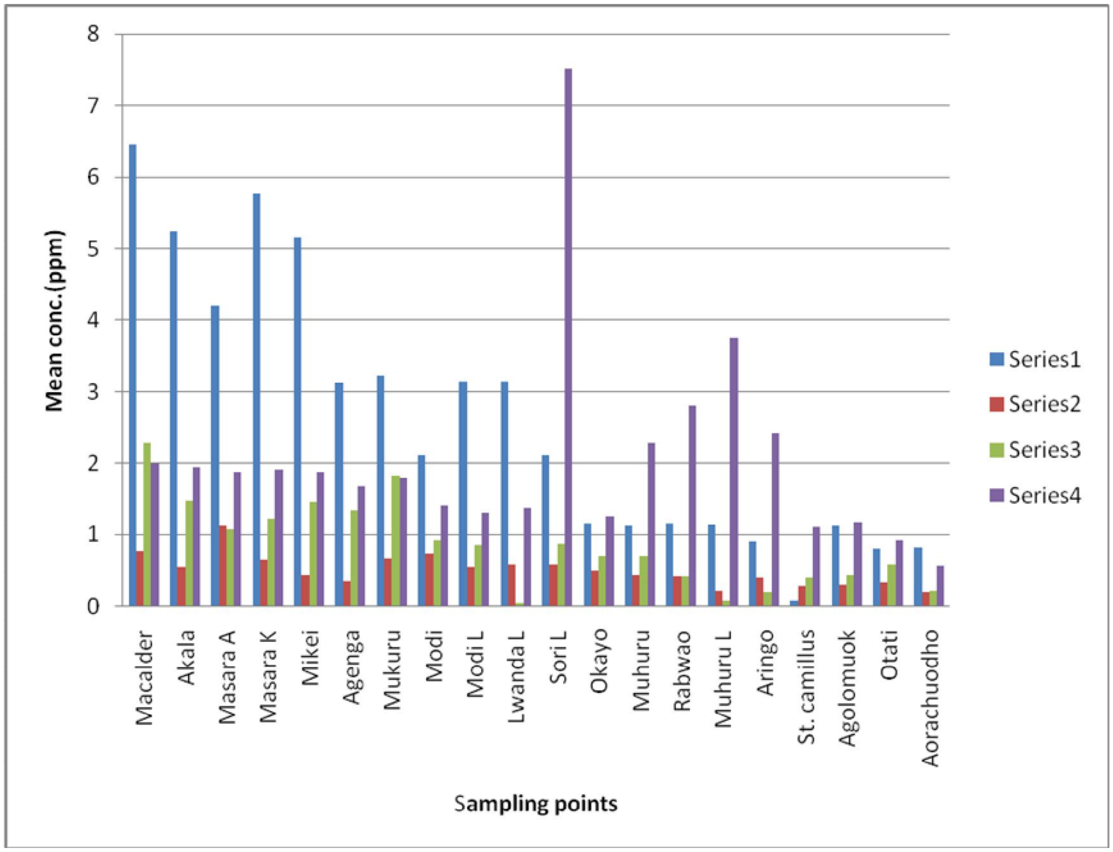
Metal levels in soil are usually expressed in µg/g dry weight however, for uniformity and comparative purposes the units were converted to ppm, whereas concentrations in water were expressed in mg/L. Results obtained for mean metal concentrations in soil and water samples are illustrated in table 4.1 and 4.2 below.

Table 4.1: Mean metal concentration (ppm) in soil during dry season (N=3)

Sampling points	Zn	Cu	Pb	Fe
Macalder	6.45 ±0.18	0.78 ±0.24	2.28 ±0.43	2.00 ±0.03
Akala	5.24 ±0.06	0.55 ±0.07	1.48 ±0.45	1.95 ±0.19
Masara arombe	4.20 ±0.02	1.12 ±0.24	1.08 ±0.23	1.88 ±0.13
Masara kakelo	5.76 ±0.19	0.65 ±0.15	1.23 ±0.73	1.92 ±0.22
Mikei	5.16 ±0.01	0.44 ±0.05	1.46 ±0.70	1.89 ±0.13
Agenga	3.13 ±0.03	0.35 ±0.01	1.35 ±0.70	1.68 ±0.16
Mukuru	3.23 ±0.08	0.67 ±0.04	1.84 ±1.45	1.80 ±0.07
Modi	2.12 ±0.02	0.74 ±0.03	0.92 ±0.21	1.41 ±0.03
Modi lake	3.14 ±0.03	0.56 ±0.01	0.86 ±0.22	1.31 ±0.30
Lwanda lake	3.15 ±0.01	0.59 ±0.01	0.05 ±0.16	1.38 ±0.04
Sori lake	2.11 ±0.03	0.59 ±0.01	0.88 ±0.07	7.51 ±1.16
Okayo	1.16 ±0.08	0.50 ±0.02	0.70 ±0.27	1.26 ±0.08
Muhuru	1.12 ±0.04	0.44 ±0.06	0.70 ±0.65	2.29 ±0.16
Rabwao	1.16 ±0.07	0.42 ±0.10	0.42 ±0.66	2.81 ±0.04
Muhuru lake	1.14 ±0.01	0.22 ±0.02	0.08 ±0.03	3.74 ±0.20
Aringo	0.90 ±0.03	0.40 ±0.01	0.20 ±0.39	2.42 ±0.50

Sampling points	**Zn**	**Cu**	**Pb**	**Fe**
St.camillus	0.09 ±0.01	0.29 ±0.01	0.40 ±0.20	1.11 ±0.36
Agolomuok	1.13 ±0.05	0.30 ±0.01	0.43 ±0.22	1.17 ±0.03
Otati	0.82 ±0.02	0.33 ±0.06	0.58 ±0.62	0.92 ±0.23
Aorachuodho	0.80 ±0.04	0.20 ±0.03	0.22 ±0.27	0.57 ±0.06

(Relative standard deviation was calculated at 95% confidence level. N is number of sample replicates.)



🟦 Zn 🟥 Cu 🟩 Pb 🟪 Fe

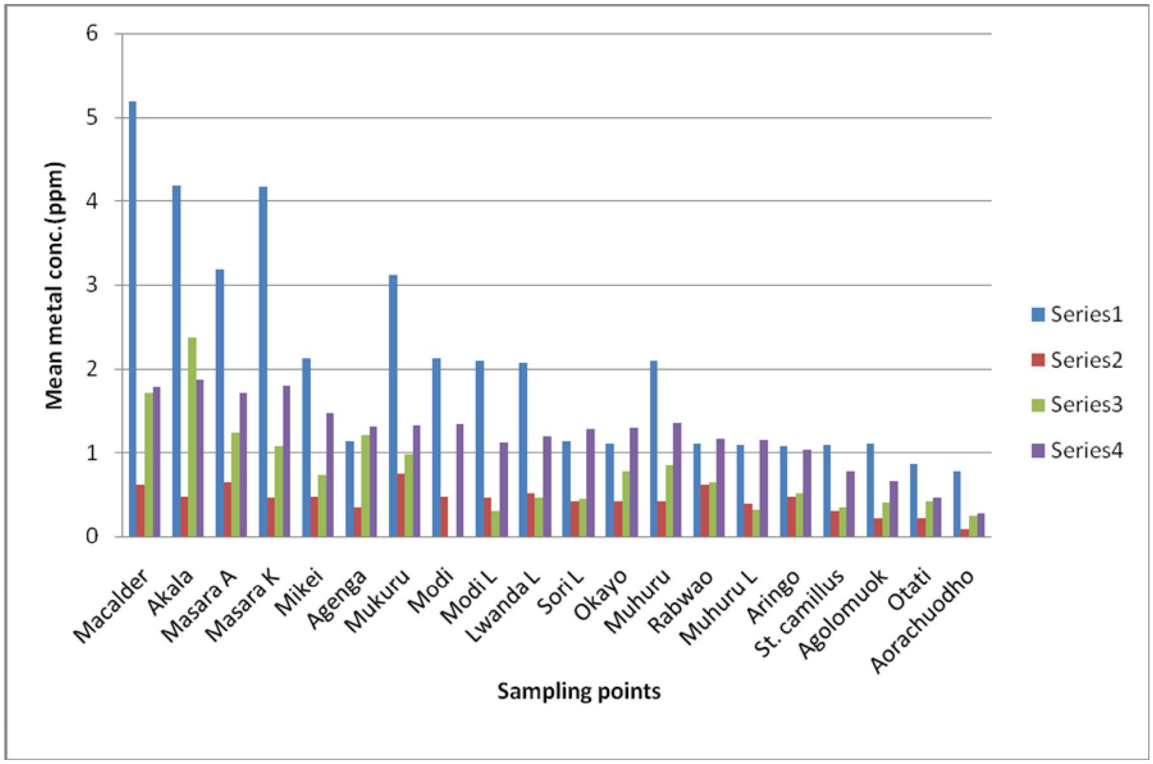
Fig. 7: Summary of mean concentration (ppm) of Zn, Pb, Cu and Fe in soil during dry season.

The range of the mean metal concentration for Zn was (6.45-0.09) ppm. Generally there was a decline in Zn metal concentration in the soil from Macalder mines to Aorachuodho during the dry season. The range of the metal concentration for Cu was (1.12-0.20) ppm. A slight decline in Cu metal concentration in soil from Macalder mines to Aorachuodho during the dry season. The range of the mean Pb metal concentration in soil was (2.28-0.08) ppm. A decreasing trend was exhibited from Macalder mines to Aorachuodho in the soil during the dry season with soil samples besides the lake giving the lowest Pb metal concentration However, Fe metal mean concentrations were rather constant from Macalder mines to Aorachuodho with a mean range of (7.51-0.57) ppm. Sori lake sampling point showed the highest mean Fe concentration since it was next to the pier made of Steel and iron metal bars.

Table 4.2: Mean metal concentration (ppm) in soil during wet season (N=3)

Sampling points	Zn	Cu	Pb	Fe
Macalder	5.18	0.62	1.71	1.78
	±0.01	±0.03	±0.17	±0.06
Akala	4.18	0.47	2.37	1.86
	±0.01	±0.09	±0.62	±0.17
Masara arombe	3.19	0.65	1.23	1.71
	±0.02	±0.06	±0.78	±0.04
Masara kakelo	4.16	0.46	1.08	1.80
	±0.01	±0.08	±0.28	±0.26
Mikei	2.13	0.48	0.73	1.46
	±0.01	±0.02	±0.37	±0.09
Agenga	1.13	0.34	1.20	1.30
	±0.01	±0.02	±0.03	±0.07
Mukuru	3.12	0.74	0.98	1.32
	±0.02	±0.05	±0.19	±0.08
Modi	2.12	0.47	0.7 2	1.34
	±0.01	±0.05	±0.20	±0.01
Modi lake	2.10	0.46	0.30	1.12
	±0.02	±0.01	±0.02	±0.10
Lwanda lake	2.07	0.52	0.46	1.19
	±0.04	±0.03	±0.03	±0.03
Sori lake	1.13	0.42	0.44	1.28
	±0.01	±0.06	±0.04	±0.06
Okayo	1.10	0.41	0.78	1.29
	±0.02	±0.03	±0.08	±0.01
Muhuru	2.10	0.41	0.84	1.35
	±0.35	±0.02	±0.10	±0.05
Rabwao	1.10	0.62	0.64	1.16
	±0.02	±0.04	±0.23	±0.02
Muhuru lake	1.09	0.39	0.31	1.15
	±0.02	±0.02	±0.10	±0.02
Aringo	1.08	0.47	0.52	1.04
	±0.01	±0.02	±0.17	±0.08
St,camillus	1.09	0.30	0.34	0.77
	±0.02	±0.01	±0.02	±0.05

Agolomuok	1.10 ±0.03	0.22 ±0.03	0.40 ±0.04	0.66 ±0.06
Otati	0.86 ±0.02	0.21 ±0.04	0.41 ±0.09	0.46 ±0.07
Aorachuodho	0.77 ±0.01	0.08 ±0.01	0.25 ±0.06	0.27 ±0.06



🟦 Zn 🟥 Cu 🟩 Pb 🟪 Fe

Fig. 8: Summary of mean concentration (ppm) of Zn, Pb, Cu and Fe in soil during wet season.

Generally, the mean Zn metal concentration in soil during the wet season showed a declining trend from Macalder mines to Aorachuodho a mean concentration range of (0.19-0.09) ppm. The same declining trend was also exhibited by Pb with a mean concentration range of (2.37-0.2) ppm. Cu and Fe exhibited a rather constant mean concentration across the sampling region giving a mean range concentration of Cu (0.66-0.08) ppm and Fe (1.78-0.27) ppm.

An analysis of variance (ANOVA) between the mean metal concentration of Zn, Cu, Pb and Fe in soil during the dry and wet seasons.

Table 4.3: ANOVA of mean metal concentration between dry and wet seasons in soil

Metal		Sum of Squares	df	Mean Square	F	p value
Zn	Treatment	0.161	1	0.161	11.044	0.001
	Error	1.724	118	0.015		
Cu	Treatment	0.151	1	0.151	3.871	0.054
	Error	4.589	118	0.039		
Pb	Treatment	91.508	1	91.508	8.320	0.005
	Error	1297.828	118	10.999		
Fe	Treatment	20.900	1	20.900	17.570	0.003
	Error	140.364	118	1.190		

The results of the ANOVA above clearly shows that during dry season, mean metal concentrations for Zn, Pb and Fe were significantly higher in soil compared to mean metal concentration during the wet season for all the values of ($p<0.05$) at 95% significance level except for Cu. This may be attributed to the facts that during the dry season much of the metal remains as atoms unlike during the wet season when much of the metal dissolve in water and undergo leaching into the ground.

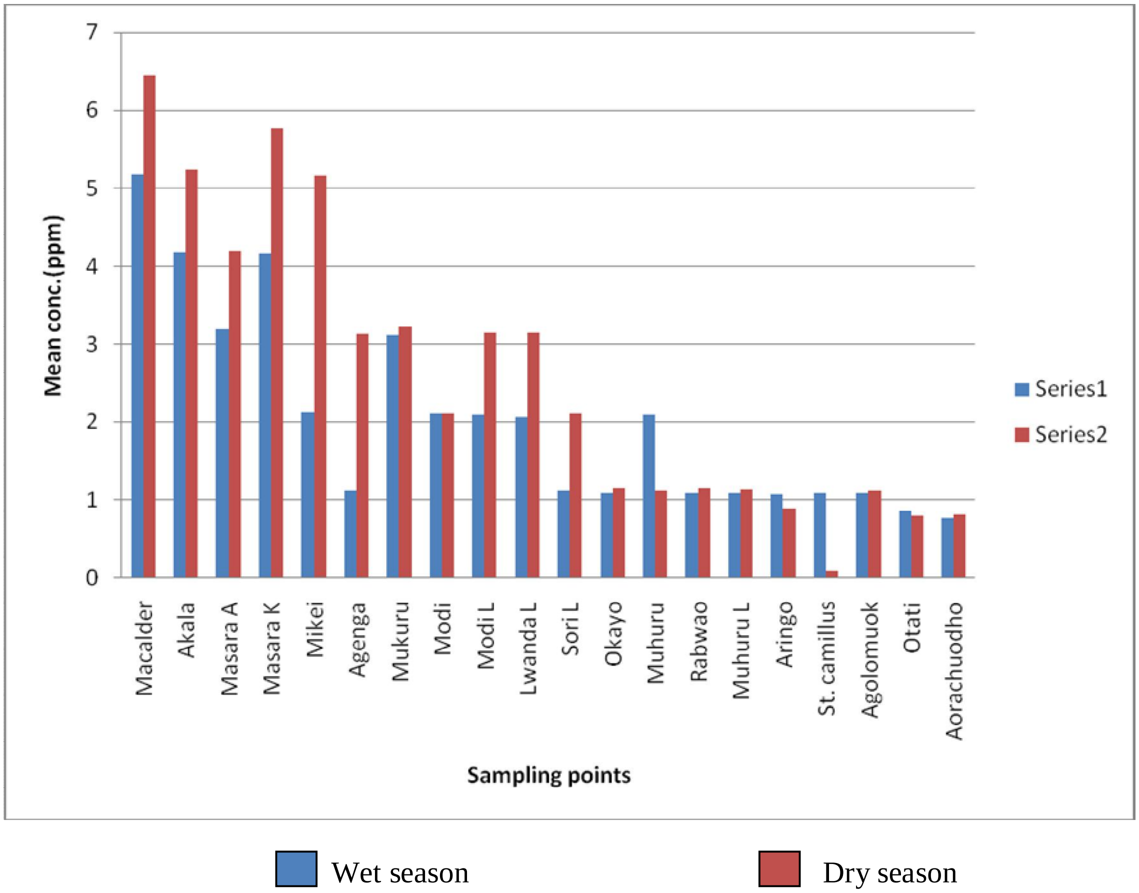


Fig. 9: Mean concentration of Zn in soil during wet and dry seasons.

4.2 Results for determination of metal concentration in water

Table 4.4: Mean metal concentration in water during wet season (mg/L) (N=3)

Sampling points	Zn	Cu	Pb	Fe
Macalder	0.37	0.12	4.00	1.33
	±0.03	0±.01	±0.06	±0.05
Akala	0.36	0.10	4.02	1.32
	±0.04	±0.02	±0.18	±0.03
Masara arombe	0.18	0.08	4.05	1.28
	±0.06	±0.01	±0.06	±0.04
Masara kakelo	0.28	0.07	4.01	1.26
	±0.03	±0.01	±0.03	±0.04
Mikei	0.17	0.09	3.67	1.30
	±0.03	±0.01	±0.18	±0.09
Agenga	0.12	0.07	3.68	1.10
	±0.05	±0.01	±0.32	±0.08
Mukuru	0.10	0.08	3.76	1.19
	±0.04	±0.02	±0.38	±0.02
Modi	0.07	0.05	2.93	1.12
	±0.02	±0.01	±0.12	±0.02
Modi lake	0.11	0.06	0.92	0.38
	±0.02	±0.01	±0.09	±0.12
Lwanda lake	0.10	0.07	0.82	0.41
	±0.01	±0.03	±0.12	±0.04
Sori lake	0.10	0.09	0.89	2.43
	±0.01	±0.02	±0.19	±0.28
Okayo	0.06	0.04	2.07	1.05
	±0.05	±0.05	±0.30	±0.10
Muhuru	0.08	0.04	1.68	0.99
	±0.01	±0.01	±0.06	±0.14
Rabwao	0.07	0.06	1.5	0.86
	±0.01	±0.02	±0.14	±0.05
Muhuru lake	0.12	0.03	0.87	0.40
	±0.01	±0.01	±0.07	±0.09
Aringo	0.05	0.03	1.21	0.94
	±0.01	±0.01	±0.16	±0.07
St,camillus	0.05	0.02	1.03	0.75
	±0.01	±0.01	±0.25	±0.02
Agolomuok	0.04	0.01	0.52	0.62
	±0.01	±0.01	±0.13	±0.01
Otati	0.04	0.01	0.68	0.59
	±0.01	±0.01	±0.10	±0.14
Aorachuodho	0.03	0.01	0.51	0.44
	±0.01	±0.01	±0.06	±0.03

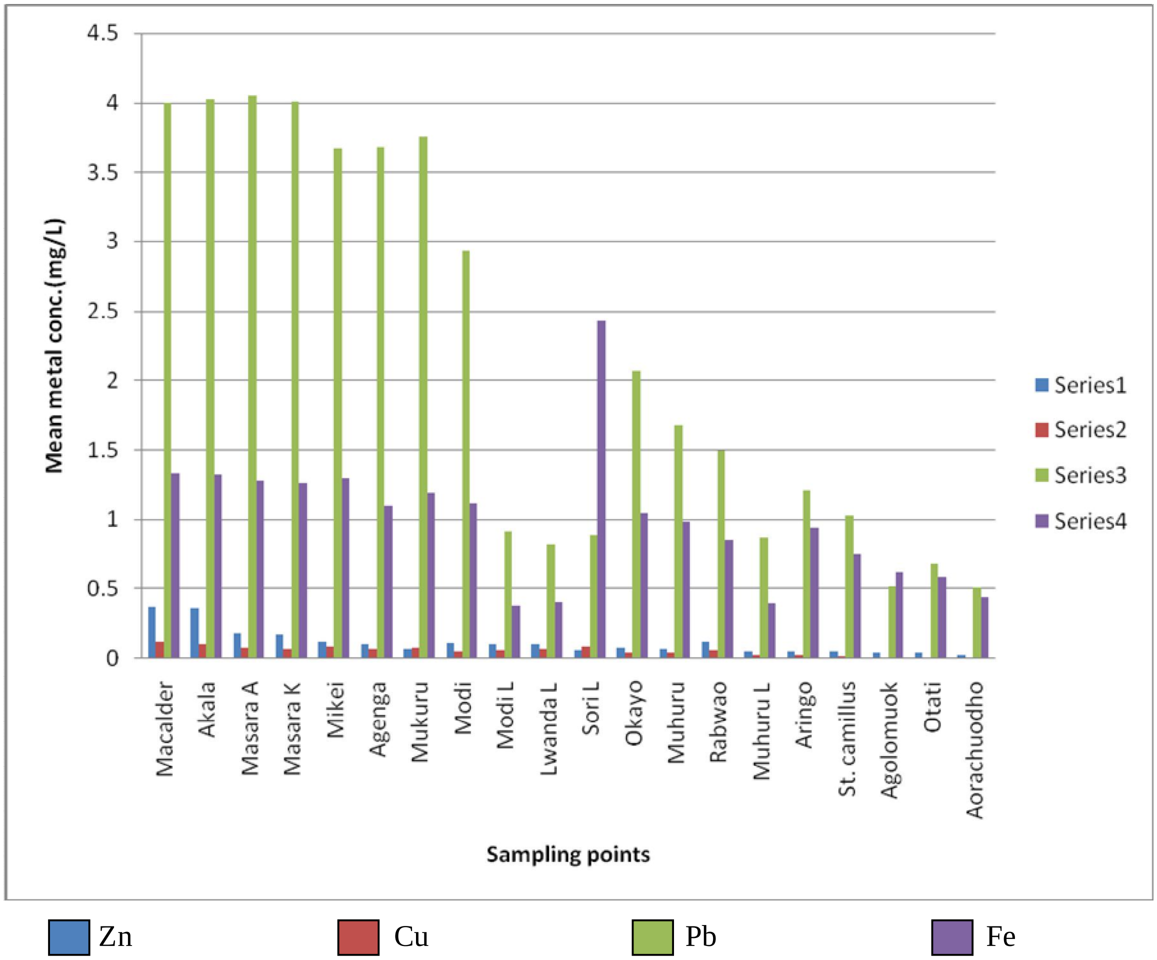


Fig. 10: Summary of mean concentration (ppm) of Zn, Cu, Pb and Fe during wet season in water.

The range of mean metal concentration in water during the wet season for Zn (0.37-0.03) mg/l, Cu (0.05-0.01) mg/l, Pb (2.48-0.63) mg/l and Fe (1.63-0.44) mg/l. Sori Lake during the dry and wet seasons showed an extraordinarily higher concentration in Fe (2.43) mg/l, this was because the pier was built using iron metal bars and that ship and boats anchor around the pier for long. Spontaneous rusting of the iron bars and the ability of hydrated ferrous (III) oxide to dissolve in water at lower pH caused the high concentrations. The mean pH of water samples during the wet season was 6.82 while the mean pH of the same during the dry season was 7.31. This meant that water samples were relatively acidic during the wet season and a little alkaline during the dry season. The acidic nature of ground water during the wet season could be attributed to the higher velocity of the ground water between the fissures and cracks in the underground rocks and a higher hydraulic gradient due to the rise in the water table hence a higher hydrolysis of the ore-salt according to the equation below (Mavura *et al*, 2005)

$$\mathrm{Zn(H_2O)_6^{2+}} \longrightarrow \mathrm{[Zn(H_2O)_5OH]^+ + H^+}$$

$$\mathrm{[Zn(H_2O)_5OH]^+} \longrightarrow \mathrm{[Zn(H_2O)_4(OH)_2] + 2\,H^+}$$

$Fe(H_2O)_6$ hydrolyses quite easily and therefore would be expected to lower the pH of water especially during the wet season when there is a lot of water (rise in water table).

Table 4.5: Mean metal concentration in water during dry season (mg/L)

Sampling points	Zn	Cu	Pb	Fe
Macalder	0.19	0.04	2.48	1.60
	±0.02	±0.01	±0.11	±0.07
Akala	0.15	0.03	2.44	1.63
	±0.02	±0.01	±0.05	±0.11
Masara arombe	0.13	0.02	2.36	1.58
	±0.02	±0.01	±0.04	±0.03
Masara kakelo	0.17	0.02	2.25	1.53
	±0.02	±0.01	±0.32	±0.05
Mikei	0.11	0.02	2.01	1.36
	±0.02	±0.02	±0.04	±0.08
Agenga	0.09	0.02	2.08	1.58
	±0.02	±0.01	±0.25	±0.07
Mukuru	0.08	0.02	1.97	1.44
	±0.02	±0.01	±0.05	±0.04
Modi	0.06	0.01	1.92	1.40
	±0.01	±0.01	±0.07	±0.02
Modi lake	0.10	0.01	0.86	1.07
	±0.01	±0.01	±0.07	±0.30
Lwanda lake	0.12	0.01	0.95	0.98
	±0.01	±0.01	±0.23	±0.21
Sori lake	0.09	0.01	1.02	8.61
	±0.02	±0.01	±0.54	±1.01
Okayo	0.07	0.03	2.00	1.32
	±0.01	±0.01	±0.26	±0.03
Muhuru	0.06	0.02	1.63	1.32
	±0.01	±0.01	±0.10	±0.12
Rabwao	0.06	0.01	1.58	1.15
	±0.02	±0.01	±0.18	±0.14
Muhuru lake	0.09	0.01	0.89	1.27
	±0.01	±0.01	±0.03	±0.18
Aringo	0.05	0.02	1.52	1.31
	±0.01	±0.01	±0.09	±0.38
St,camillus	0.04	0.01	1.21	1.09
	±0.01	±0.01	±0.17	±0.24
Agolomuok	0.05	0.02	1.04	0.67

	±0.01	±0.01	±0.18	±0.13
Otati	0.05	0.01	0.91	0.51
	±0.01	±0.01	±0.22	±0.19
Aorachuodho	0.04	0.01	0.62	0.44
	±0.01	±0.01	±0.04	±0.15

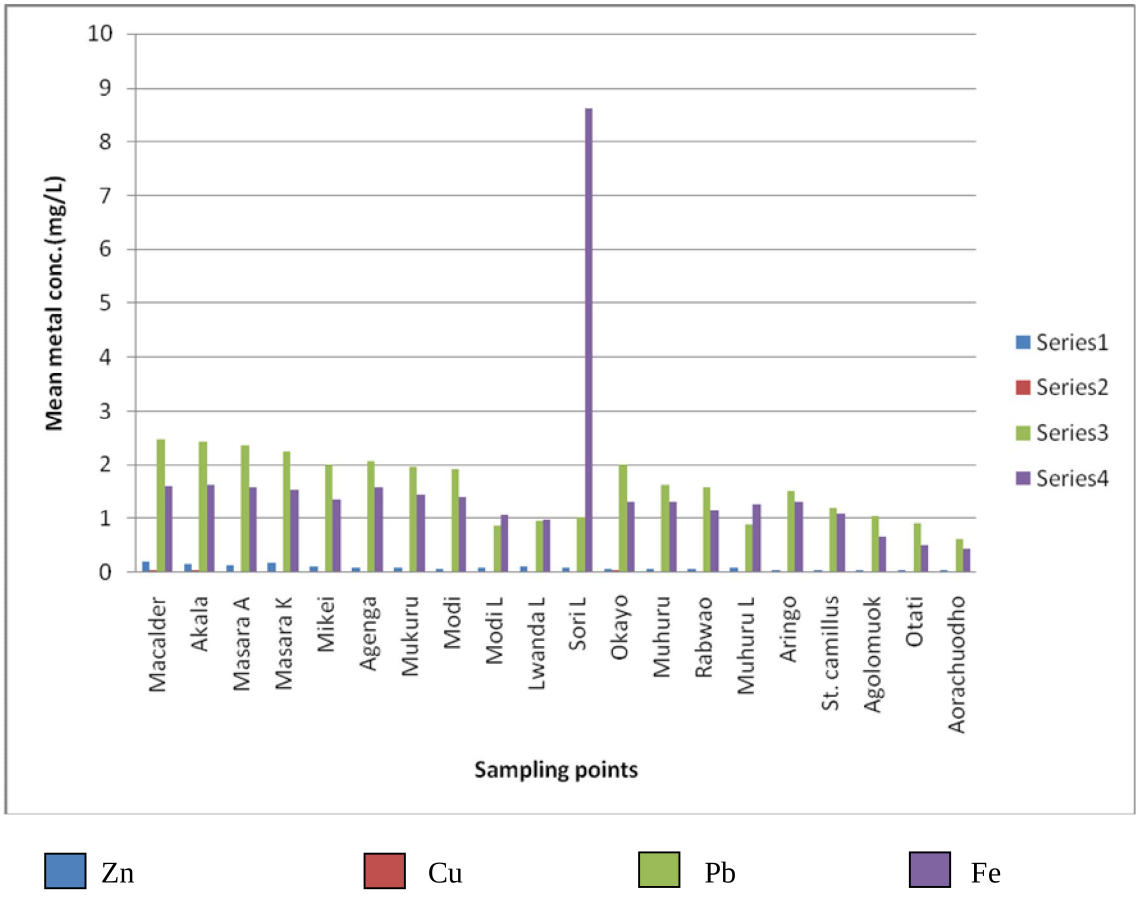


Fig. 11: Summary of mean concentration (ppm) of Zn, Pb, Cu and Fe during dry season in water.

The ranges of the mean metal concentration in water during the dry season were Zn (0.19-0.04) mg/l, Cu (0.04-0.01) mg/l , Pb (2.48-0.63) mg/l, Fe (1.63-0.44) mg/l. Generally there was constant trend in mean concentrations of all the metal across Macalder mines to Aorachuodho. There was evidently an abnormal shoot in the mean concentration for Fe metal due to the proximity of the sampling point to the pier made of Iron bars resulting into higher dissolution of Iron atoms into hydrated Iron ions at lower pH of 6.28.

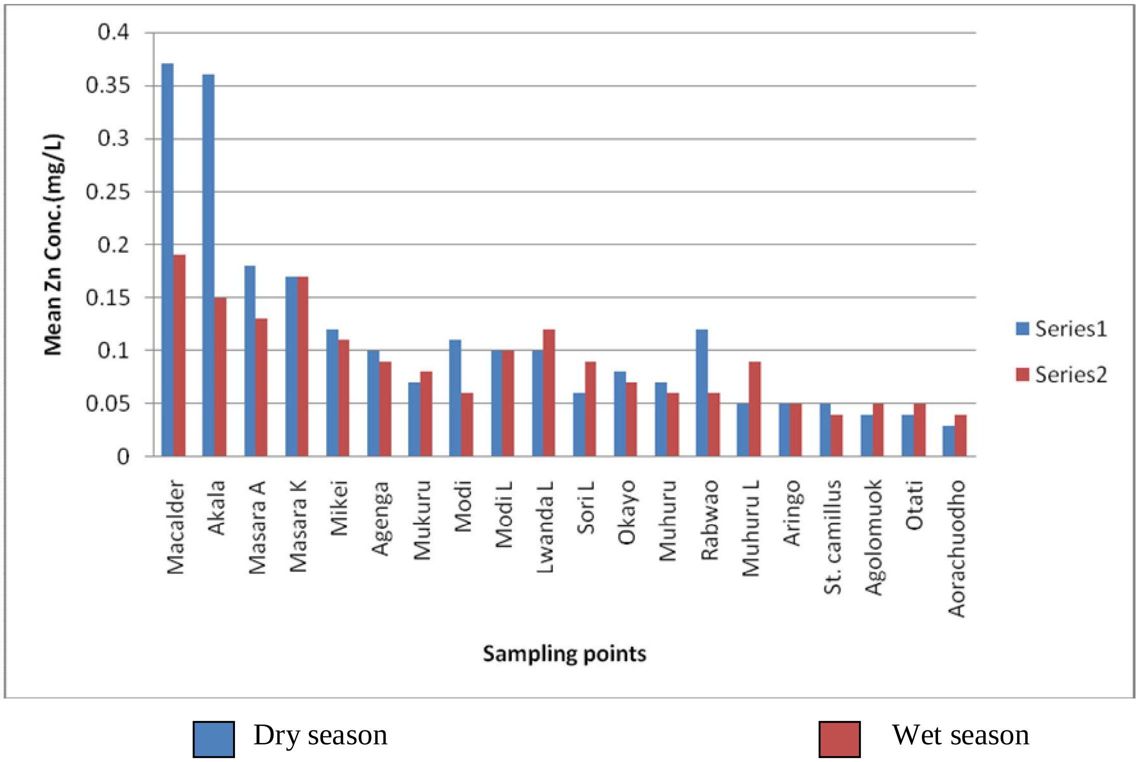


Fig: 12: Mean Zn metal concentrationsin water during dry and wet seasons.

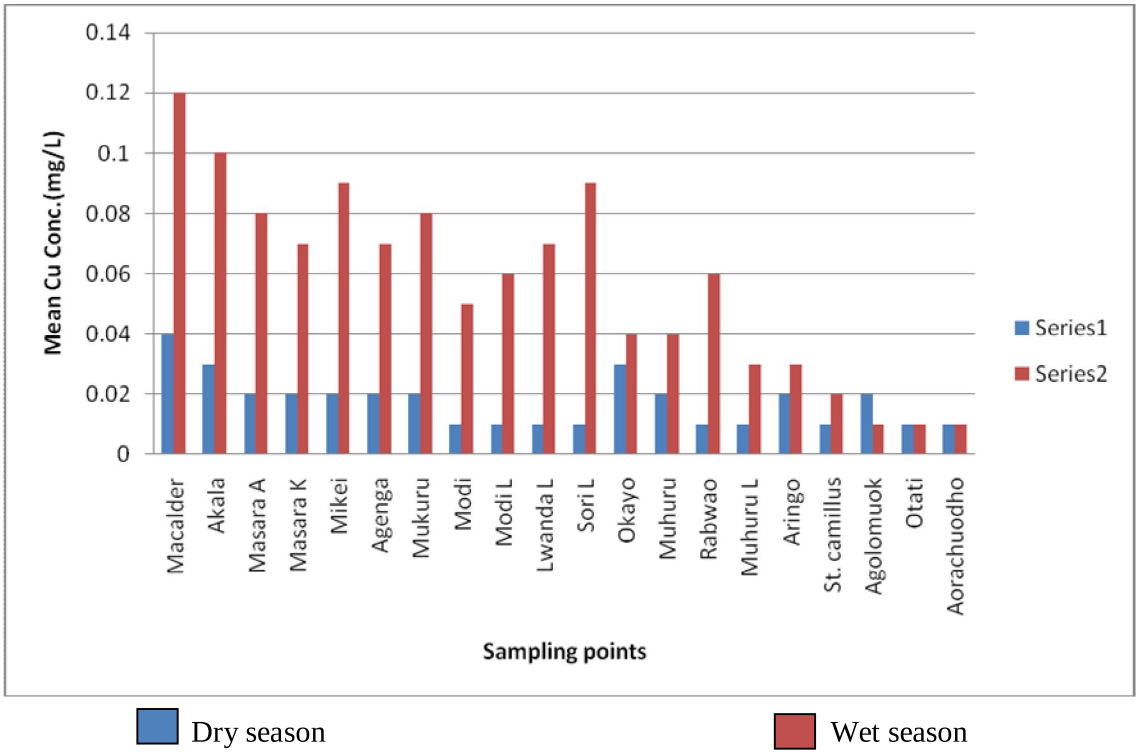


Fig: 13: Mean Cu metal concentrationsin water during dry and wet seasons.

It was statistically prudent that the differences in mean metal concentrations in water during the dry season and wet seasons were strongly significant in Zn, Cu, Pb and Fe. The concentration levels in the region for Zn and Cu were within the permissible threshold; nevertheless, Pb levels were much above the recommended level. The recommended level as given by WHO is 0.01 mg/L however, the higher concentrations were obtained in borehole waters in Macalder, Akala, Masara above 4.0 mg/L. The comparison between means of metal concentrations in water and means of metal concentration in soil was performed using paired sample T-Test and the results in table 4.6 below were obtained.

4.3 Comparing mean metal concentrations in water and soil.

Table 4.6: Comparing means of metal conc. in water and soil

Paired Sample t-test.

	Mean	**95% confidence interval of the difference**		**t**	**df**	**Sig.(2-tailed)**
		Lower	**Upper**			
Zns-Znw	0.04 ±0.12	0.02	0.07	4.12	119	0.001
Cus-Cuw	0.44 ±0.19	0.40	0.47	24.58	119	0.002
Pbs-Pbw	0.04 ±0.08	0.20	0.89	13.29	119	0.001
Fes-Few	0.34 ±0.06	0.22	0.45	5.86	119	0.003

The above-paired sample t-test analysis indicated with confidence that the mean metal concentrations for Zn, Cu, Pb and Fe in soil were significantly higher than mean metal concentrations of the same metals in water. Thus, metal concentrations in soil were higher than concentrations in water. This could be due to the fact that in soil, most metal ions exist in solid inorganic complexes and hence during the rainy season they partly dissolve in water. (Alloway and Ayres, 1997). Water therefore exhibits a comparatively lower metal concentration due to dilution effect. The ANOVA table 4.7 below illustrates.

Table 4.7: ANOVA of mean metal concentration during the dry and wet seasons in water.

Metal		Sum of Squares	df	Mean Square	F	p value
Zn	Treatment	0.050	1	0.050	8.036	0.005
	Error	0.729	118	0.006		
Cu	Treatment	0.054	1	0.054	79.199	0.009
	Error	0.080	118	0.001		
Pb	Treatment	9.280	1	2.280	7.786	0.006
	Error	140.638	118	1.192		
Fe	Treatment	11.133	1	11.133	7.338	0.008
	Error	179.009	118	1.517		

4.4 Water hardness results

Table 4.8: Mean of water hardness (mg/L of $CaCO_3$) during dry season (N=3).

Sampling points	Mean	Sampling points	Mean
Macalder	102.83 ±26.62	Sori lake	99.40 ±9.73
Akala	421.00 ±19.05	Okayo	237.96 ±34.78
Masara Arombe	564.20 ±16.31	Muhuru	275.56 ±7.89
Masara kakelo	478.83 ±7.18	Rabwao	238.76 ±7.16
Mikei	514.00 ±11.95	Muhuru lake	86.00 ±6.67
Agenga	658.66 ±12.47	Aringo	200.53 ±4.64
Mukuru	498.20 ±13.78	St,camillus	214.46 ±13.99
Modi	253.86 ±32.29	Agolomuok	199.90 ±11.20
Modi lake	79.23 ±13.80	Otati	143.10 ±7.99
Lwanda lake	75.83 ±10.00	Aorachuodho	82.23 ±11.73

Table 4.9: Mean of water hardness (mg/L of $CaCO_3$) during wet season (N=3).

Sampling points	Mean	Sampling points	Mean
Macalder	97.63 ±7.55	Sori lake	95.16 ±3.80
Akala	376.63 ±14.67	Okayo	226.70 ±22.54
Masara Arombe	574.23 ±30.81	Muhuru	268.53 ±12.01
Masara kakelo	447.03 ±10.34	Rabwao	219.83 ±16.68
Mikei	549.60 ±11.40	Muhuru lake	79.36 ±8.22
Agenga	585.83 ±23.18	Aringo	192.63 ±10.36
Mukuru	437.43 ±16.28	St,camillus	176.70 ±14.92
Modi	222.33 ±21.57	Agolomuok	184.03 ±8.25
Modi lake	89.40 ±17.00	Otati	136.23 ±12.72
Lwanda lake	71.60 ±21.43	Aorachuodho	91.56 ±10.14

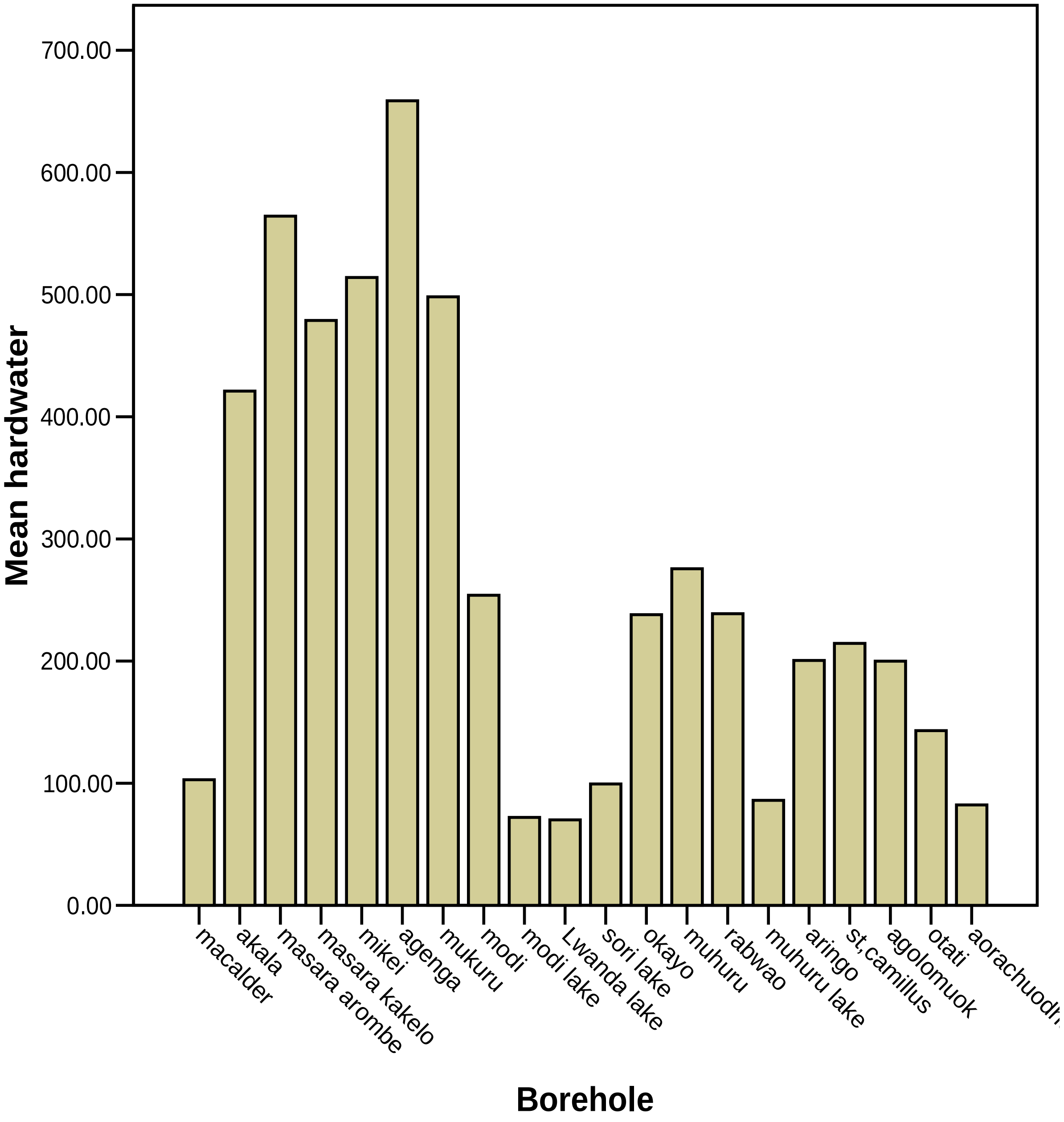


Fig 14: Mean of water hardness (mg/L of $CaCO_3$) during dry Season

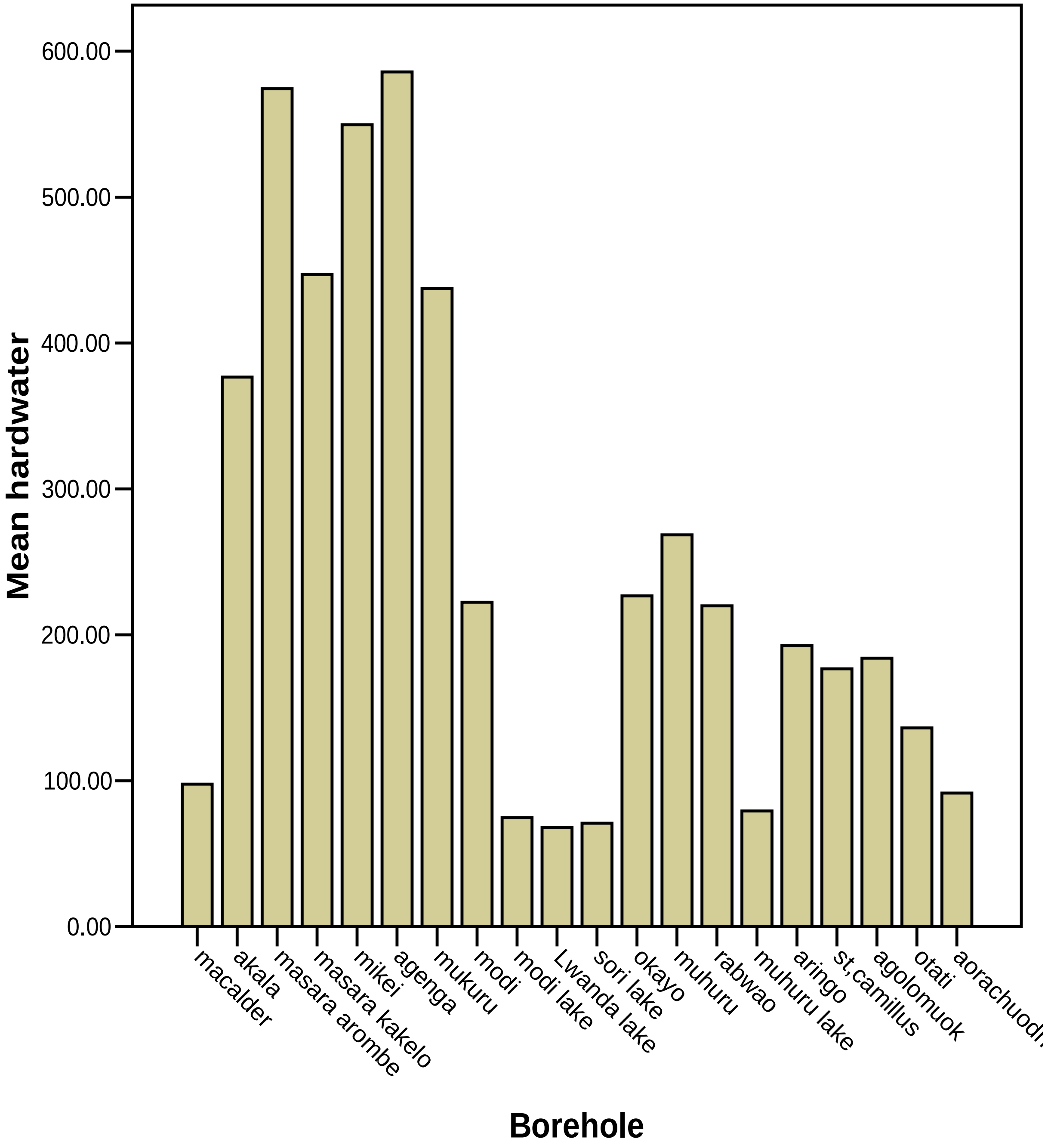


Fig 15: Mean of water hardness (mg/L of $CaCO_3$) during wet Season

The range for the mean water hardness during the dry season was (75.83-658.66) mg/L of $CaCO_3$ and wet season (71.60-585.83) mg/L of $CaCO_3$.From least to highest the borehole waters can be categorised as medium hard and very hard respectively (Canadian drinking water quality guideline, 1979). From the table above, water hardness of lake water samples from modi, lwanda, muhuru and sori showed comparatively low hardness levels ranging between 60-90 mg/L of $CaCO_3$.This confirmed the fresh status of the lake water and therefore the reason why most lakeshore dwellers prefer to do their washing using lake water to borehole waters. The dry season exhibited the highest hardness level of 658.6 mg/L of $CaCO_3$ however, statistically, the difference in hardness during the dry and wet seasons was insignificant giving (F=0.302) and the p= 0.584 at 95% significance level.

Table 4.10: ANOVA for means of hardness between dry and wet seasons

	Sum of Squares	**df**	**Mean Square**	**F**	**P value**
Treatment	8421.901	1	8421.901	0.302	0.584
Error	3292703.4	118	27904.266		
Total	3301125.3	119			

The mean metal concentrations were also analyzed in terms of zones. The differences in mean metal concentration between zones 1 and zone 2 showed a strong significance for Zn, Cu and Pb. However, Fe was insignificantly different. This indicates that the mean metal concentrations in the epicenter region were significantly higher than the surrounding region. The epicenter region was like the nucleus of the heavy metals because of the intense mining operations that took/take place in the region mineral mines (Mize *et al*, 2003). The zonal means were compared using one-way ANOVA. The table 4.11 below illustrates

4.5 Comparing metal means in water and soil between regions.

Table 4.11: ANOVA for mean metal concentration in water between epicenter and surrounding

Metal		Sum of Squares	df	Mean Square	F	Sig.
Zn	Treatment	0.335	1	0.335	89.297	0.045
	Error	0.443	118	0.004		
Cu	Treatment	0.023	1	0.023	25.052	0.009
	Error	0.110	118	0.001		
Pb	Treatment	92.377	1	92.377	189.441	0.038
	Error	57.540	118	0.488		
Fe	Treatment	0.663	1	0.663	0.413	0.522
	Error	189.478	118	1.606		

The differences in mean metal concentrations in soil showed a strong significance for Zn and Cu with (F=33.44 and 30.55) and p value of 0.025 and 0.049 respectively. This indicates that Zn and Cu exhibited significantly higher mean concentrations in epicenter and significantly low mean concentrations in surrounding region. However, Fe and Pb mean concentrations in the two regions were insignificant. This has been illustrated in the 4.12 table below.

Table 4.12: ANOVA of mean metal concentration in soil in the epicenter and surrounding regions

Metal		Sum of Squares	df	Mean Square	F	p value
Fe	Treatment	0.727	1	0.727	0.534	0.466
	Error	160.537	118	1.360		
Pb	Treatment	921.896	1	921.896	232.723	0.067
	Error	467.440	118	3.961		
Cu	Treatment	0.975	1	0.975	30.553	0.049
	Error	3.765	118	0.032		
Zn	Treatment	0.416	1	0.416	33.441	0.025
	Error	1.469	118	0.012		

Variation of metal concentration levels with distance from macalder (epicentre) to Aora-chuodho is as shown below in the regression equations table 4.13 and 4.14 below.

4.6 Regression analysis.

Table 4.13: Regression equations for metal concentrations in water against distance for dry and wet seasons. (E = exponential 10^x)

Metal	Regression equation during dry season	Regression equation during wet season
Zn	$y = -8E\text{-}07x^3 + 0.0001x^2 - 0.0057x + 0.1911$ $R^2 = 0.8289$	$y = -3E\text{-}06x^3 + 0.0004x^2 - 0.0183x + 0.4044$ $R^2 = 0.8951$
Cu	$y = -5E\text{-}07x^3 + 6E\text{-}05x^2 - 0.0023x + 0.0398$ $R^2 = 0.7027$	$y = -6E\text{-}07x^3 + 6E\text{-}05x^2 - 0.0027x + 0.1134$ $R^2 = 0.8518$
Pb	$y = 4E\text{-}05x^3 - 0.0042x^2 + 0.038x + 4.0609$ $R^2 = 0.8276$	$y = -5E\text{-}06x^3 + 0.0006x^2 - 0.0449x + 2.654$ $R^2 = 0.6832$
Fe	$y = -2E\text{-}05x^3 + 0.0013x^2 - 0.0369x + 1.7517$ $R^2 = 0.8078$	$y = -4E\text{-}07x^3 + 5E\text{-}05x^2 - 0.0149x + 1.4072$ $R^2 = 0.5468$

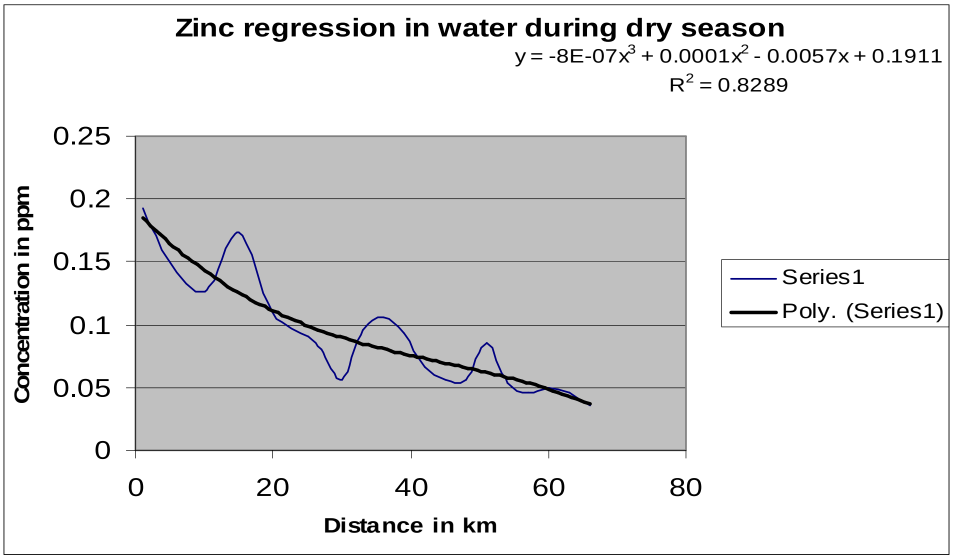


Fig 16: Zinc regression in water during dry season.

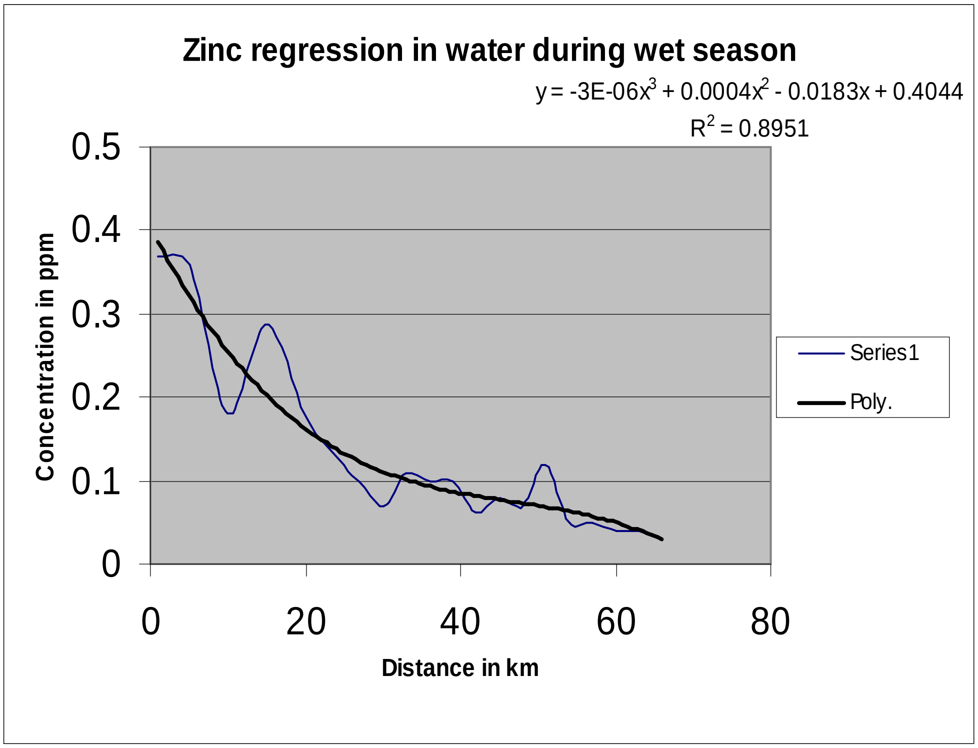


Fig 17: Zinc regressions in water during wet season.

Table 4.14: Regression equations for metal concentrations in soil against distance for dry and wet seasons

Metal	Regression equation (dry season)	Regression equation (wet season)
Zn	$y = 4E\text{-}05x^3 - 0.0029x^2 - 0.0447x + 5.9985$ $R^2 = 0.9078$	$y = -2E\text{-}05x^3 + 0.0029x^2 - 0.1758x + 5.1673$ $R^2 = 0.8383$
Cu	$y = -4E\text{-}08x^3 - 5E\text{-}05x^2 - 0.0051x + 0.7739$ $R^2 = 0.5671$	$y = -4E\text{-}06x^3 + 0.0003x^2 - 0.0054x + 0.6063$ $R^2 = 0.5811$
Pb	$y = 7E\text{-}06x^3 - 0.0005x^2 - 0.0211x + 1.8614$ $R^2 = 0.6878$	$y = -1E\text{-}05x^3 + 0.0015x^2 - 0.0845x + 2.1314$ $R^2 = 0.7933$
Fe	$y = -2E\text{-}05x^3 + 0.0014x^2 - 0.0494x + 1.9983$ $R^2 = 0.9272$	$y = -2E\text{-}06x^3 + 7E\text{-}06x^2 - 0.0078x + 2.0111$ $R^2 = 0.6403$

Regression analysis was performed using the polynomial model of order 3 since it satisfied to a greater level of high concentration region (Macalder) lying along the major geological fault line and two other minor fault lines (fissures). This consequently showed three regions of non-uniform metal concentrations across the area radii. Polynomial model calculates the least squares fit through points based on the equation:

$$Y= b+ C_1X^1+C_2X^2+C_3X^3\ldots\ldots CnX^n$$

Where b, $C_1\ldots Cn$ are constants.

This was so because of the higher R^2 values compared to other models. The concentration of Zn, Cu, Pb and Fe in water decreased with increasing distance from the epicentre (macalder mines) according to the regression equations shown in the table above. The far most borehole (Aorachuodho borehole) from the epicentre (Macalder borehole) was approximately 70 km. The regression equations for Zn, Cu, Pb and Fe could be used to predict the concentration variations in water during dry and wet season. Taking (y) as the probable metal concentration and (x) as the distance (km) of the borehole in reference from Macalder. Generally, as the distance (x) from the first borehole (Macalder) increases, the probable metal concentration (y) decreases as the regression equations.

4.7 Reliability

In order to test the reliability of the flame atomic spectroscopic method (FAAS) in the determination of heavy metals in water and soil samples, recoveries of spiked pure metal samples were determined by performing four standard addition procedures to four water and soil samples. Specific quantities of metal standard solutions were added prior to the digestion process.

Table 4.15: Amounts of metal present, metal added and recoveries for soil and water samples

Metal	Amount present (ppm)	Amount added (ppm)	Amount recovered (ppm)	% recovered
Pb	5.045	0.100	5.142	98.11 %
	5.045	0.200	5.249	96.11%
	5.045	0.300	5.344	94.40%
	5.045	0.400	5.443	92.69%
Zn	0.837	0.500	1.333	99.70%
	0.837	1.000	1.836	99.94%
	0.837	1.500	2.338	100.04%
	0.837	2.000	2.829	99.72%
Cu	0.216	0.400	0.605	98.21%
	0.216	0.800	1.006	99.01%
	0.216	1.200	1.401	98.94%
	0.216	1.600	1.818	100.11%
Fe	1.552	1.000	2.485	97.37%
	1.552	2.000	3.521	99.13%
	1.552	3.000	4.563	100.24%
	1.552	4.000	5.500	99.06%

The results of the recoveries process show that Pb recovery ranged between 92-98%, Zn recovery ranged between 99-101%, Cu recovery ranged between 98-100% and recovery for Fe ranged between 97-100.4%. The results obtained were satisfactory with a mean percentage recovery of 98.29%. These mean percentage recovery was above the 95% threshold and consequently the results produced by the AAS were fairly reproducible.

4.8 Conclusion.

Sampled water points in Nyatike-Karungu region has mean concentrations 0.15 mg/l for Zn, and 0.47 mg/l for Cu which were within the WHO water quality guidelines. WHO recommended admissible limits for Cu (2 mg/l), Fe (0.3 mg/l), Pb (0.01mg/l) and Zn (3 mg/l) However, Fe (1.63 mg/l) and Pb (0.845 mg/l) were above the admissible levels. Water collection for drinking purposes near the pier made of iron metals posed danger to animals consuming it including those who use it for drinking purposes since Fe metal concentration at Sori Lake was ranging between (2-8) ppm, which was far beyond recommended admissible limits. Zn, Cu, Pb and Fe mean concentration trends decreased with increase in distance from Macalder, for instance, mean concentration of Zn in soil during the dry season at Macalder was (0.45 ±0.187) and (0.08 ±0.04) ppm at Aorachuodho. This trend was in tandem with the results obtained by (Espana *et al*, 2006). A polynomial regression model of order 3 showing a decline in mean concentrations could predict the spatial concentration pattern of the four heavy metals. Similarly, Cu, Pb and Fe exhibited decline in concentration from Macalder to Aorachuodho

Water is a good solvent and picks up impurities easily. As water moves through soil and rock, it dissolves very small amounts of minerals and holds them in solution. It was established that the rock structure around Nyatike region comprise of volcanic igneous rocks with prominent intrusive dolomite ($MgCO_3.CaCO_3$) rocks, limestone ($CaCO_3$) rocks and carbonatite rocks which dissolve and cause hardness in water. The geological formation of Gwassi-Nyatike area had a greater influence in the water hardness in the region. This was attributed to the presence of Ca and Mg ions in the rocks as cations and presence of a combination of carbonate and sulphate anions in the geochemistry of the underground rocks (Ichangi, 1992) and other polyvalent metal ions such as Al^{3+} ions. The water hardness may be categorised as very hard for borehole cases and soft for lake water cases (Canadian water drinking quality guidelines, 1979). Even though, the water hardness may not have raised negative health concerns other than unpleasant taste due to high salinity. The water hardness was however limited to lake basin region.

4.9 Recommendation

Portable drinking water boreholes, wells and lake water around Nyatike –Karungu divisions was safe with respect to Zn, Cu and even hardness. Subsequently, it was recommended that procurement of water by people for drinking purposes at home and even for use by animals around the pier should cease.

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APPENDICES

Appendix 1. Hardness category equivalent concentration of $CaCO_3$

Type of water	Concentration in (mg/L)
Soft	< 60
Medium hard	60-120
Hard	120-180
Very hard	>180

Guidelines for Canadian Drinking Water Quality document (1979).

Appendix 2: Guideline and maximum acceptable concentrations for metal in water for human consumption.(1993).

HEAVY METAL	WHO Guide Concentration(mg/L)	EC Guide Concentration(mg/L)
Cu	2	3
Fe	0.3	0.05
Pb	0.01	_
Zn	3	0.1

Adapted from WHO (1993) and EC (1980). EC- European Commission

Appendix 3: Selected values from Canadian environmental quality criteria.(1993)

HEAVY METALS IN SOIL	Agricultural concentration (µg/g)	Residential Concentration (µg/g)
Cu	**150**	**100**
Pb	**375**	**500**
Ag	**20**	**20**
Zn	**600**	**500**

Appendix 4: Concentration (ppm) of selected heavy metals in ground water around Egerton University.

Sample	Zn	Fe	Cu	Pb	pH
Ng'ondu BH	0.004	1.14	0.006	0.001	8.45
Kihingo well	0.161	6.55	0.001	0.01	7.2

(Adapted from Egerton university journal, Paper presented by Mavura et al, 2005).

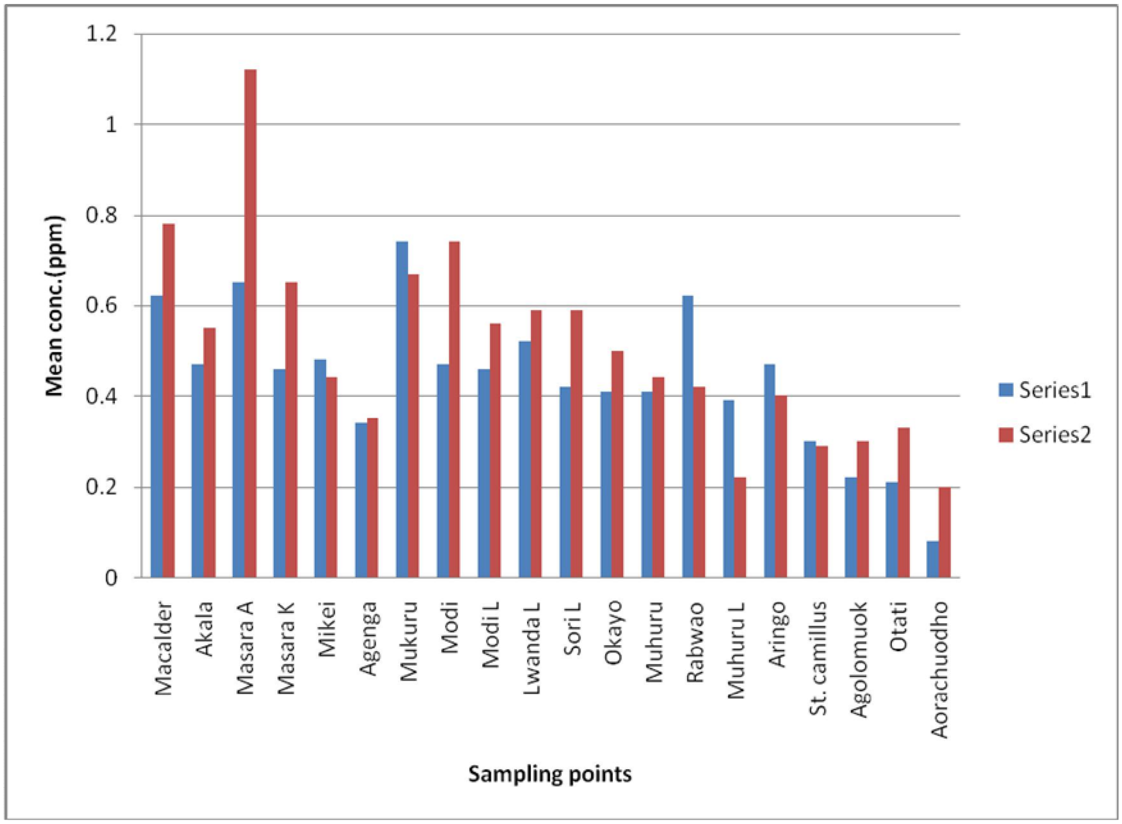
Appendix:5 Laboratory results for physico-chemical parameters of selected water points in Nyatike

PARAMETER	WATER POINTS									
	Tuk Pr.Schl	Macalder Pr.Schl	Mukuru W-MC029	Masara W-MC069	Mariba BH-MC092	Angugo W-MC207	Oganga BH-MC081	Kakelo BH-C7173	Agen'ga BH-C5215	Otati BH-ND52
Temp(^{o}C)	27.5	27	28	26	25.3	27	26	25	29.5	29
Conductivity µs/cm	750	1970	600	70	1100	1200	1600	7000	2800	1400
pH	7	7	6.5	6.5	7.3	7.5	6.0	6.5	6.5	7
Turbidity (NTU)	100	140	4.2	0.8	10	5	2.1	3.1	8.0	250
T.Hardness (mg/L)	92.3	616.6	-	120	430	340	560	-	-	190
Iron (mg/L)	ND	0.01	0.05	ND	0.4	0.5	0.6	1.3	0.3	-

(Adapted from: LBDA-Rural Domestic Water Supply and Sanitation Programme, 1988).

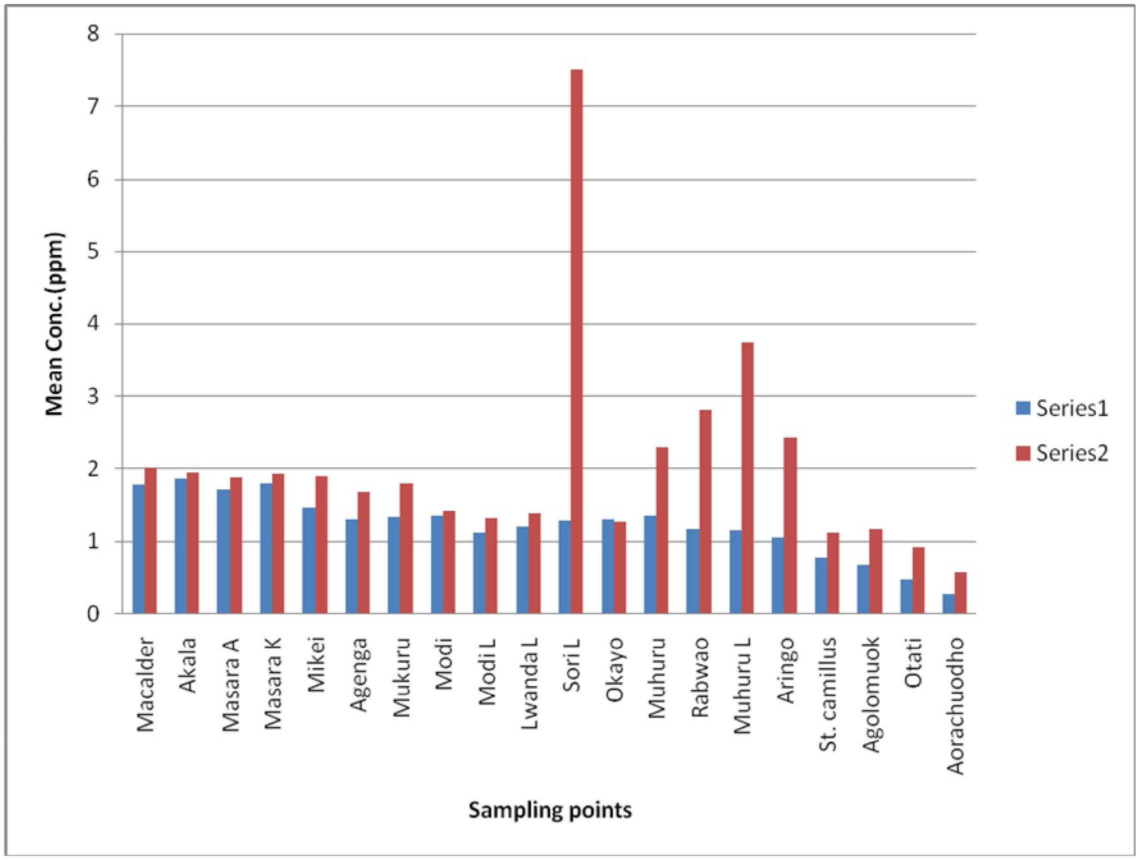
ND – Not detected

Appendix 6: Mean concentration of Cu in soil during wet and dry seasons.



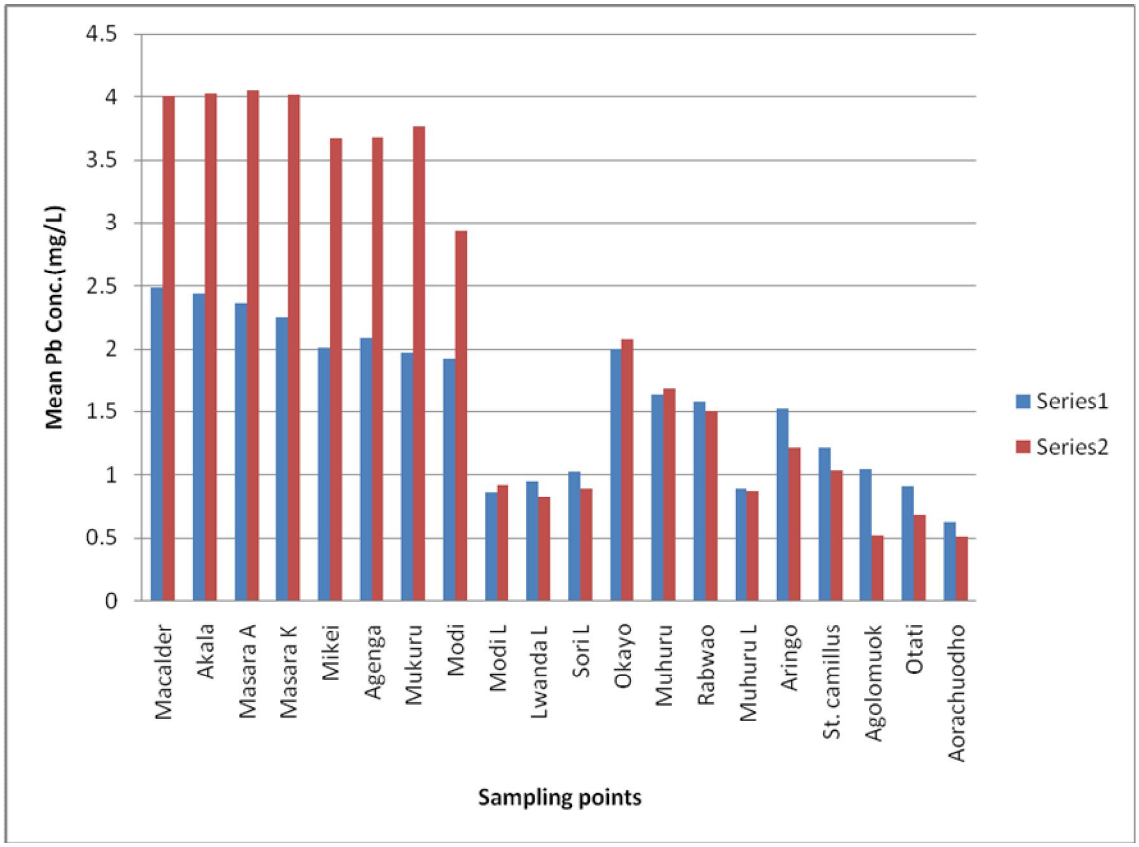
🟦 Wet season 🟥 Dry season

Appendix 7: Mean concentration of Fe in soil during wet and dry seasons.

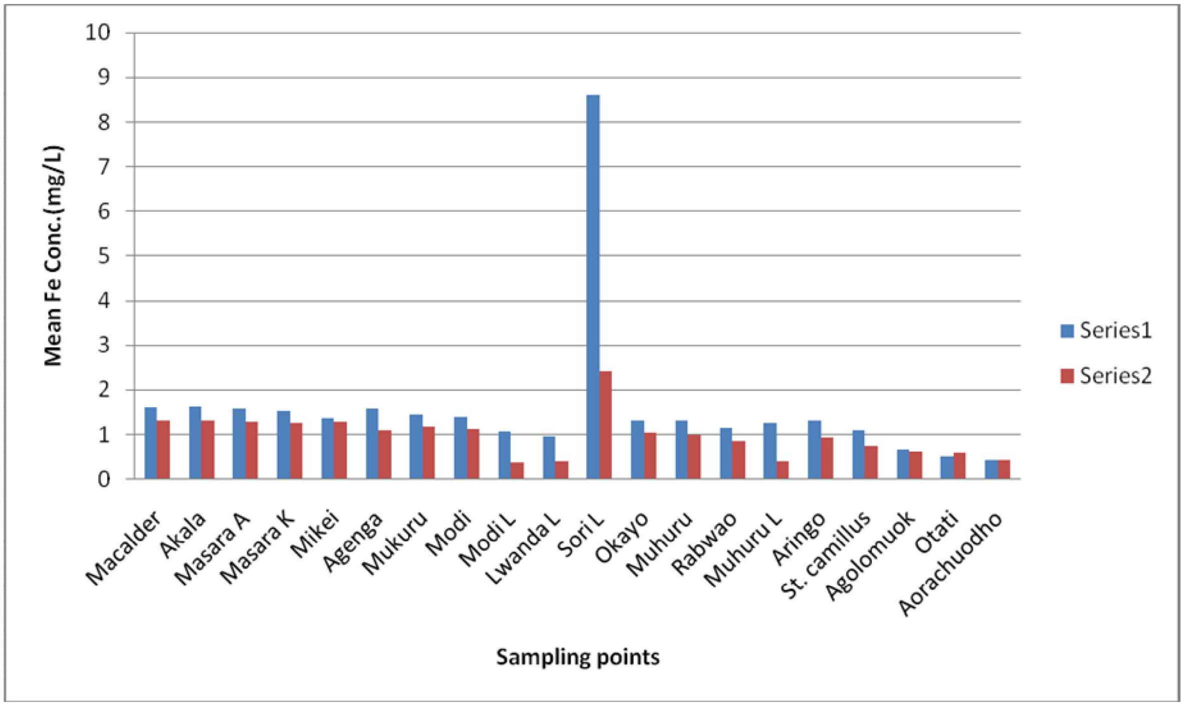


🟦 Wet season 🟥 Dry season

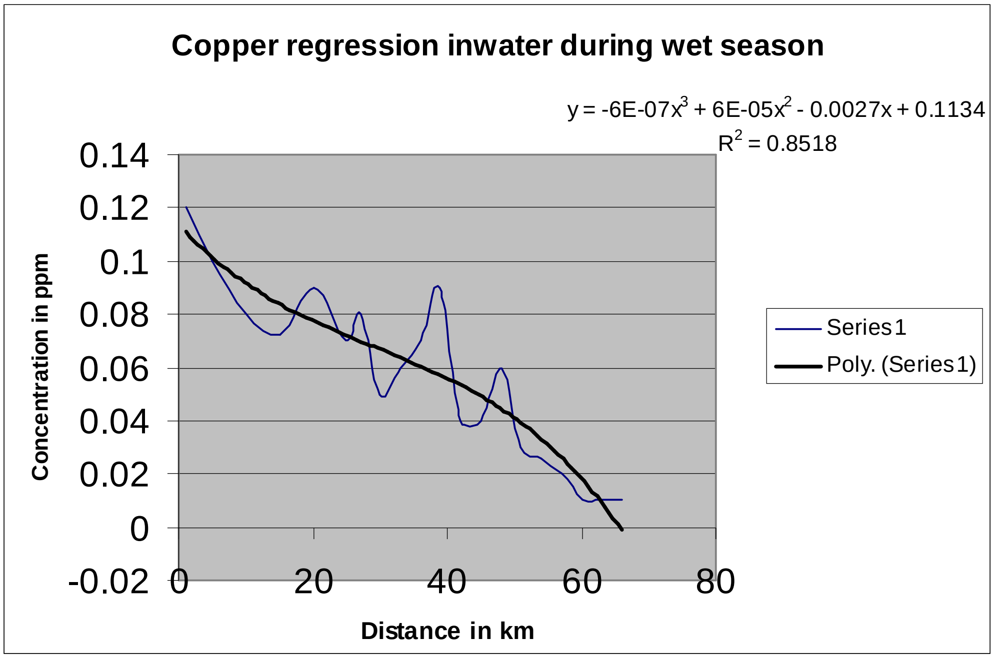
Appendix 8: Mean concentration of Pb in soil during wet and dry seasons.



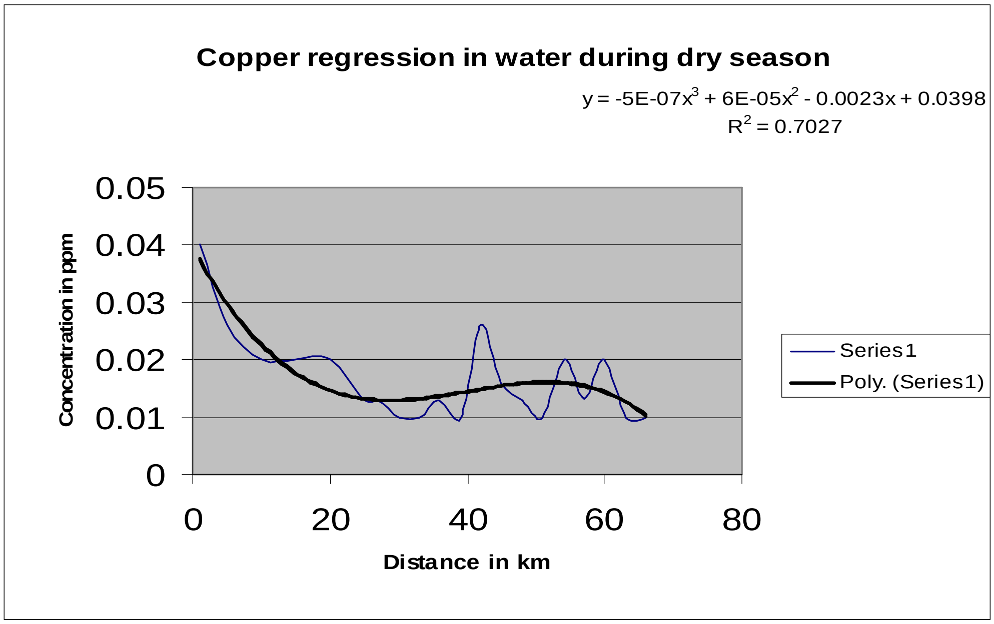
Appendix 9: Mean concentration of Fe in water during wet and dry seasons.



Appendix 10: Copper regression in water during wet season.



Appendix 11: Copper regression in water during dry season.



GLOSSARY

Aquifer: Underground rock segment saturated with water.

Buffer: A solution that resists change in pH when an acid or alkali is added or when the solution is diluted.

Epicentre: A 20 km radius region from Macalder mines.

Lake Basin region: Lakeshore stripe about 50km in breadth.

R- Squared value: An indicator from 0 to 1 that shows how closely the estimated values for the trendline correspond to the actual data.

Regression: Analysis tool that uses least squares method to fit a line through a set of observations

Spectroscopy: The study of the methods of producing and analysing spectra using spectroscope, spectrometer and spectrographs.

Surrounding: A region within 20-60 km radius from Macalder mines.

Underground water: Used interchangeably with groundwater. It refers to water found within the aquifer.