University of Nairobi

Institute of Nuclear Science and Technology

DISTRIBUTION OF HEAVY METALS IN WATER AND SEDIMENTS OF LOWER RIVER NZOIA

OMONDI CAVIN

S56/61784/2013

A thesis submitted in partial fulfillment for the degree of Master of Science in Nuclear Science of the University of Nairobi.

2017

DECLARATION

This thesis is my original work and has not been submitted in support of award of any degree or qualification at the University of Nairobi or any other university or institution of higher learning.

Signature ……………………….. Date……………………………………..

Omondi Cavin - S56/61784/2103

This thesis has been submitted with the approval of my supervisors,

Mr. David M. Maina Signature ....

Institute of Nuclear Science and Technology Date ....

University of Nairobi

Prof. John M. Onyari Signature ……………………………

Department of Chemistry Date ……………………………………..

University of Nairobi

DEDICATION

This research work is dedicated to my family for the continued love and support and always believing in me.

ACKNOWLEDGEMENTS

I am greatly indebted to the Almighty God who has provided me with good health and great sound mind and giving me protection to go through and complete this research work.

I wish to thank my supervisors Mr. David M. Maina and Prof. John M. Onyari for their encouragement and invaluable support without which this work would not have seen the light of the day. I would also wish to thank Mr. Simon Bartilol for assisting in the analysis where necessary by providing vital information if and when required.

Lastly, I would wish to appreciate Kenya Nuclear Electricity Board for offering me a scholarship to pursue this course and the project.

ABSTRACT

Heavy metals are major pollutants of aquatic systems due to their bio-accumulative nature. Overreliance on agro based farm inputs to improve agricultural yield, discharge of industrial waste and lack of proper sewerage system within the towns that the lower section of Nzoia River passes through has resulted to an increased amount of pollutants including heavy metals being deposited into the river. With the water from the river being used for irrigation purposes, drinking by human beings and livestock as well as recreational areas, concerns have been raised on the suitability of the river to serve the above purpose as well as the safety of the produce that depend on the river. This study aimed at investigating whether the waters and sediments along lower Nzoia River have been contaminated with heavy metals. In this study, sediment and water samples were collected and analyzed. Sediment samples were collected at depths of 30 cm, 50 cm and 100 cm on either side of the river at thirty sampling sites to give a total of 180 samples. Water samples were also collected at both sides of the river at the exact locations sediments were collected to make a total of 60 water samples. The collected water samples were analyzed using TXRF whiles the sediment samples were analyzed using EDXRF. Trends in variation of concentrations with depth were evaluated as well as observing the trends in the concentration of metals downstream. The mean concentrations (mg kg^{-1}) in sediments ranged: Mn (520 – 2060), Fe (2.7% – 8.3%), Cu (250 – 390), Ni (260 – 510), V (150 – 380), Cr (85 – 320), Zn (40 – 100), Pb (7 – 30) and As (10 – 15). Metal concentration levels in sediment samples increased downstream with a significant variation ($p < 0.05$) being observed between the sampling points. The mean concentrations of Mn, Fe, Cu, Cr and Ni were above the USEPA guidelines; Mn (30), Fe (30), Cu (16), Cr (25) and Ni (16). Metal concentrations in water samples were largely below the WHO guidelines except for copper that had higher amounts indicating that the waters are polluted with copper; Mn (100), Fe (2000), Cu (20), Zn (20), Pb (100) and Ni (20). The mean water concentrations reported in μg l^{-1} were Mn (78), Fe (6144), Ni (13.7), Cu (26.5), Zn (161) and Pb (11.2). Lower river Nzoia sediments were determined to be contaminated with Mn, Fe, Cu, Cr and Ni with the concentrations in sediments being higher than those reported for water.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

LIST OF ABBREVIATIONS AND ACCRONYMS

ANOVA – Analysis of Variance

ASTSDR – Agency for Toxic Substances and Disease Registry

ATP - Adenosine Tri Phosphate

AXIL – Analysis of X-ray Spectra by Interactive Least - Square fitting

CRM - Certified Reference Material

EDTA – Ethylene Diamine Tetraacetic Acid

DNA- Deoxy Ribonucleic Acid

EDXRF – Energy Dispersive X-Ray Fluorescence

GPS – Global Positioning System

IAEA – International Atomic Energy Agency

IQ – Intelligence Quotient

IARC- International Agency for Research on Cancer

mg kg^{-1}- milligrams per kilogram

NEMA- National Environment Management Authority

NRBMI – Nzoia River Basin Management Initiative

ppm – Parts per million

TXRF – Total Reflection X-Ray Fluorescence

UNEP – United Nations Environmental Program

USEPA – United States Environmental Protection Agency

WHO – World Health Organization

CHAPTER ONE

INTRODUCTION

1.1 Background

Particles may be produced through various means. Some of these ways include land disturbing activities such as road construction, mining, farming, real estate development, water drilling, erosion and weathering. These particles may then be transported by water, wind or ice where they are eventually deposited in streams, lakes, wetlands and oceans (Lalah et al., 2008). These particles are known as sediments and their size range from about 0.00195 mm- 1.5 mm (Shuhaimi, 2008).These particles have been studied greatly in recent times.

Sediments have a lot of significance in aquatic ecosystems where they enable addition of nutrients, provide spawning areas, habitat and transport of essential nutrients. Sediments can however also carry contaminants and pollutants such as heavy metals hence acting as a reservoir for pollutants in the water column. The pollutants can then pose a great risk to the aquatic habitat and human beings through the food chain (Forstner and Wiltman, 1983).

Studies on sediments has been done to determine the quantity of contaminants in them, provide information on impact of pollution sources as well as to know the patterns of pollution of aquatic systems. These studies can also help to give an insight into the history of pollution of the analyzed ecosystem (Shuhaimi, 2008).This is based on the fact that sediments act as sinks as well as reservoirs for various pollutants of the fauna and flora such as heavy metals by absorbing harmful substances resulting to concentrations that exceed those in the water column (Milekonvic et al., 2005). The amount of contaminants retained by sediments is normally influenced by the size of the grain, partition coefficient, the concentration of organic matter in the sediment and cation exchange (Forstner and Wiltman, 1983). One of the major contaminants contained in sediments is heavy metals.

The distribution of heavy metals is determined by the geological set up of the system which constitutes background levels. Their concentrations can however be disturbed due to human-influenced activities such as use of farm inputs containing these metals. This makes them of special interest since some are poisonous, persist and bio-accumulate in nature (Tam and Wong, 2000) and may result to pollution.

Pollution caused by heavy metals is mainly via natural and anthropogenic sources with the latter being more pronounced. The natural sources of heavy metal pollution include; weathering away of rocks that bear ores, windblown dust (Ross, 1994), volcanic eruptions and fires that occur in the forests (Seaward and Richardson, 1990). The anthropogenic sources include extraction of minerals from the earth, extracting metals from their ores and coating of metal surfaces with other metals and industrial processes that produce wastes that contain the heavy metals (Lalah et al., 2008). Some industrial processes such as electroplating also produce large volumes of metal-rich effluents which are more likely metal polluters than say the food processing industries. Lead acid manufacturing also generates effluents that are rich in metals which can subsequently be deposited in surface waters and eventually to the sediments. Coal fired power generation which is currently gaining momentum in Kenya is also another potential source of heavy metal pollution (De Gregori et al., 1996).

Other anthropogenic sources of heavy metal pollution include; applications of substances that contain metal pollutants in the informal (Jua Kali) metal construction and scraping industries which are then discharged into aquatic resources (Lalah et al., 2008). Agricultural activities also produce heavy metals through farm inputs like fertilizers and pesticides which can form part of agricultural drainage that are washed off as surface runoffs to water bodies (Marcovecchio et al., 2007). Raw sewage and discharge from industries are some of the high contributors of heavy metal pollution to water bodies (Santos et al., 2005). Streams and rivers receive pollutants from surface runoffs and through release of sewage and untreated industrial discharge which are then transported to water bodies that provide water for drinking where they are eventually deposited into the bottom sediments of rivers, seas and lakes (Skeat, 1969). These heavy metals may then find their way to plants, animals and human beings when they are exposed to the pollutants.

Human beings are mainly exposed to heavy metals through the food chain. Exposure to heavy metals affects both human beings and other terrestrial organisms. In human beings exposure to heavy metals has been known to contribute to reduced growth rate, damage of the kidney, cancer, reduced IQ and loss of life in case of interaction with levels that exceed the normal allowable limits in human beings (Aderinola et al., 2009). Exposure of terrestrial organisms to heavy metals can result in reduced fertility, damaged kidneys, slow growth and development and to some cases even death for high concentration levels (Aderinola et al., 2009).

Plants require some heavy metals in certain concentrations for their biological processes. The metals are referred to as essential metals and include Zn, Cu, Mn and Fe. These processes include helping enzymes to function and increase the rate of enzyme catalyzed reactions. However, at higher concentrations of heavy metals these processes might be interfered with resulting in stunted growth and in some cases death of plants (Choi et al., 1996). The level to which heavy metals affect plant is known as heavy metal toxicity. It is a factor of the type of plant, concentration of the specific metal, soil composition and pH (Patients Medical, 2013).

River Nzoia is one of the numerous fresh water bodies that drain its water into Lake Victoria. It receives pollutants from household discharge into the river, effluents from industries such as Nzoia Sugar Company, Mumias Sugar Company and Webuye Panpaper Mills, agricultural drainage from the farms adjacent to the river and urban run offs from the municipalities it transverses (Mwamburi, 2003). The river transverses three fundamental zones as it flows to Lake Victoria namely upper, middle and lower Nzoia catchment areas. The upper catchment is mainly dominated by agricultural activities hence agro based chemicals are the potential source of heavy metals. The middle catchment is characterized by heavy industrial activity and industrial discharge is a potential source for heavy metal contamination (Achoka, 1998). The lower catchment area is dominated by small scale agricultural activities such maize and millet farming, here the river again absorbs agrochemical based pollutants which act as the main source of contaminants.

It is important to determine the levels of heavy metal contamination in Nzoia water sediments and also to determine the effect of these contaminations to the aquatic life and ecosystem in general. This study covers sampling of sediment and analysis to establish the level of contamination of heavy metals in the lower section of River Nzoia.

1.2 Problem Statement

River Nzoia flows through several towns, industrial zones, informal sector (jua kali) zones, agricultural zones which mainly rely on the use of agrochemicals and informal settlements. As the water passes through these areas it collects domestic and industrial waste which is discharged into it or washed down through run-offs into the river basin. This process results in contaminants such as heavy metals accumulating in the river waters and eventually settling at the bottom sediment. The river waters have variable uses such as irrigation, commercial, industrial and domestic uses and the sediments providing pawning sites for aquatic organisms. Concerns have, however, been raised over the safety of some of the products obtained from the river since aquatic plants and animals as well as crops irrigated by such waters could absorb and accumulate the heavy metals hence posing a risk to consumers. There is therefore need for regular studies to determine the heavy metal concentrations levels in such area. With this background understanding, the study was undertaken whereby water and sediment samples from the lower Nzoia (Mumias Bridge to Sigiri cross point) were collected and analyzed for total heavy metal concentration levels.

1.3 Objectives of the study

The main objective of the study was to investigate the extent of pollution of water and sediments of the lower section of River Nzoia with heavy metals.

The specific objectives were:

i. To determine levels of concentration of selected heavy metals in water samples from the Lower Nzoia River.
ii. To determine the concentrations levels of selected heavy metals in sediments along the Lower Nzoia River.
iii. To assess the spatial and vertical distribution patterns of selected heavy metals in sediments along the Lower Nzoia River.

Figure 1.1 Some activities that occur along the Nzoia River some of which introduce pollutants into the river.

1.4 Justification and significance of the research project

The lower section of River Nzoia experiences intensive agricultural activities where there are large sugar plantations in Mumias sub county and some parts of Ugenya sub county. In the other areas food crops such as maize (*Zea mays*), millet (*Pennisetum glaucum*), beans (*Phaseolus vulgaris*), sorghum (*Sorghum bicolour*), sweet potatoes (*Ipomoea batatas*) and cassava (*Manihot esculenta*) are grown both for domestic consumption and commercial purposes. There is intensive use of farm inputs such as fertilizers, herbicides and pesticides. Some of these might be enriched with heavy metals given that some of them are essential for biological processes in plants. The heavy metals are eventually washed into the river through runoffs when it rains. The river also collects pollutants from wastewater from industrial and residential areas as it passes through towns and areas of informal settlement. These pollutants eventually find their way to human beings through the food chain yet there is inadequate information on heavy metals concentration levels in the section of the river being studied. The few studies available have focused only on heavy metals in the sugarcane farms (Pembere et al., 2015) or single selected sampling points along the river (Mutuku et al., 2014; Lalah et al., 2008; Mwamburi, 2003). To determine the suitability of the river in serving its purpose and the safety of its produce, it is essential to determine the heavy metal concentration levels in water and sediment and their distribution patterns in sediment.

In this study, concentration levels of heavy metals in sediments were investigated by determining the deposition over a period of time. The concentration levels of the heavy metals in water were also determined. The results obtained from this study have provided a much improved understanding of the pollution by heavy metals of the lower Nzoia River and the suitability of the use of the waters for production. The study has also given an insight into the past levels of contamination, trends and the risks posed by such contaminants. Assessment of pollution control programs established to reclaim the river can also be done based on the results of this study as well as improving environmental management policies and strategies.

CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy Metals

Heavy metals can be considered as metallic elements of relatively high density and are usually poisonous at even minimal concentrations (Lenntech, 2004). They are intrinsic, natural constituents of the environment (Aderinola et al., 2009). The heavy metals consist of transition metals, metalloids, lanthanides and actinides. Some heavy metals such as Cu, Fe, Cr, and Ni are essential and are needed by plants, animals and human beings as they are necessary for biological ecosystems. On the other hand heavy metals such as Cd and Pb are non-essential and have no known biological role and are harmful even in low concentrations (Fernandes et al., 2008).

In the last decade, investigation of heavy metals in water bodies, fish and sediments have been of great concern to scientists. This is because they are non-biodegradable; at certain concentrations they are toxic and can find their way to human beings via the food chain through consumption of foods contaminated by heavy metals (Opaluwa et al., 2012). Once consumed, these metals are normally incorporated into the body, stored and accumulated by the human body causing discomfort of the digestive system, diarrhea and chronic problems (Dinesh and Kunwar, 2002). Monitoring of heavy metals in aquatic ecosystems can be done through measurement of their concentrations in water and sediments.

2.1.1 Sources of heavy metals

Heavy metals exist within the earth’s geological structure which makes up the background levels for heavy metals. However, the concentrations of these metals may be increased through the introduction of heavy metals into the environment. There are two major ways through which heavy metals are introduced into the environment; natural sources and anthropogenic sources. The natural sources of heavy metals include weathering of heavy metal bearing rocks, windblown dust, volcanic eruptions, acid rain and dew (Harikumar et al., 2009, Bazrafshan et al., 2015).

The major contributor to elevated levels of heavy metal concentration beyond the background levels has been anthropogenic sources which include waste from industries and municipalities, erosion of metals through oxidation and leached agricultural chemicals (Mwamburi, 2003). Other sources include Jua Kali metal fabrication and scrapping industries (Lalah et al., 2008) mining, smelting, electroplating and non-point source surface runoffs (Milenkovic et al., 2005). Agricultural activities also produce heavy metals that can also find their way to the aquatic system through farm inputs like fertilizers, herbicides, fungicides and pesticides which form part of agricultural drainage that are washed as surface runoffs to water bodies (Marcovecchio et al., 2007). Sewage and industrial effluents are some of the high contributors of heavy metal contamination to rivers and lakes (Santos et al., 2005). These heavy metals once introduced into the environment eventually find their way into the aquatic ecosystem through being washed by rain water and runoffs where they are deposited in the surface water and eventually settle to the bottom sediments.

2.1.2 Heavy metals in surface water

Water is an essential resource that supports human life. The major sources of water include rivers, lakes, springs and oceans. Rivers act as water resources in terms of providing drinking water, recreational and sporting activities as well as fishing activities. There is therefore need to investigate entry sources and effects of pollutants in rivers. Initially rivers in developing countries were viewed to be the least polluted but this has rapidly changed as a result of increased industrial activities in the developing countries Kenya included (Neal et al., 2000, Kiithia, 2006). This has resulted to introduction of contaminants such as heavy metals to water bodies and hence posing a great threat to the naturally existing water resources. Animals that consume water from contaminated rivers accumulate these metals in their tissues and human beings can be exposed by consuming such meat from animals leading to undesirable biochemical disorders in their system (Duruibe et al., 2007).

There are various ways through which heavy metals maybe introduced to the surface waters. These include; urban and industrial waste discharge, agro-based chemicals such as fertilizers, pesticides and herbicides as well as deposition of domestic effluents and solid waste (Marcovecchio et al., 2007) which are washed off to the rivers. All heavy metals present in surface water occur in form of particulates, colloids and dissolved phases which are however generally low (Kenneish, 1992). Water has been known to possess unique chemical properties since it is polar in addition to possessing the hydrogen bond and thus is capable of dissolving, absorbing, adsorbing or even suspending many different compounds (WHO, 2007). The solubility of the heavy metals that end up in surface water is dependent on pH, metal ion present, oxidation state and concentration (Warren et al., 2005; Grosbois et al., 2006). Kiithia (2012) reports that pollutants in rivers increase downstream and consequently the concentration levels of heavy metals also increase downstream. The increase in concentration levels of metals in the lower zones of the river can be viewed to be as a result of increased suspension, dilution and the settling of particulate materials.

2.1.3 Heavy metals in sediments

Sediment refers to particles that normally settle at the bottom of an aquatic ecosystem. Sediments are of significance in the development of aquatic ecosystem through the replenishment of nutrients, creation of benthic habitat and provision of spawning areas. They are also however, important sinks and reservoirs for several contaminants such as pesticides, leached chemicals and heavy metals. They are essential in the re- introduction of pollutants in aquatic systems when optimal conditions are provided (Öztürk et al., 2009). Enhanced levels of heavy metals in sediments are pointers to disturbances due to human activities as compared to natural enrichment through weathering (Binning and Baird, 2001; Eja et al., 2003). Sediments thus serve as both carriers and sources of pollutants in rivers and lakes (Shuhaimi, 2008). The analysis of sediments for heavy metal levels enables the detection of heavy metals that could be missing or in minimal concentrations in the water column (Aderinola et al., 2009). It also permits the detection of pollution and deteriorating water quality while providing information about the critical sites of the water system (Fabbri et al., 2001; Bordes and Bourg, 2001). According to USEPA criteria, chromium, lead and zinc in the sediment are categorized as ‘non-pollutant’, nickel is a ‘moderate pollutant’ while copper is categorized as a ‘heavy pollutant’.

There are various mechanisms by which sediments take up heavy metals. These may include; biological uptake by organic matter in the sediments, physiochemical adsorption by the water column and physical accumulation of particles enriched by heavy metals. Spatial distribution of heavy metals in river sediments is thus important in the determination of the history of contamination of the river (Birch et al., 2001). Concentration of heavy metals at different depths gives an insight into the addition and accumulation changes over time of the heavy metals in the river (White et al., 2005). This then results to pollution which has been caused by the heavy metals present in the sediments. Mateu et al., (1996) concluded that trace metal levels can be pointers to concentration of other contaminants they might be associated within the ecosystem. Studies have indicated that almost all metal content in rivers and lakes are found in the water sediments (Ademoroti, 1996)

2.2 Effects of heavy metals

The potential hazard of pollutants in any ecosystem is a factor of their concentration and their ability to last long in the system. Pollutants that have the ability to continue existing in the environment like heavy metals remains in the environment unaltered for a long period of time where they bio-accumulate and thus pose a risk to aquatic plants and animals including human beings who may ingest them via the food chain. The effects of these metals normally occur when contact is established between the contaminant and living organism producing undesirable biochemical effects. These effects are presented in the following sections.

2.2.1 Effects of heavy metals on plants

Zn, Cu and Fe are some of the heavy metals that have an important significance in the biological and physiological processes of aquatic plants and are hence considered necessary to aquatic life. These essential micronutrients help in plant growth by playing an essential function in CO_2 conversion and ATP formation (Thomas et al., 1998). However, a deficiency or excess of these ions can result to some undesirable consequences on the development of the plant. Such effects range from but are not limited to retarded growth and development, leaf chlorosis, inhibition of seed germination and a reduction in photosynthetic rate and low amounts of yield.

Some heavy metals including cadmium, lead, arsenic as well as chromium have got no known biochemical importance in plants and as such are harmful to the plant at any concentration. Their accumulation in the plant tissues is detrimental to the proper development of the plant and may result in decreased growth and yields in the plant.

2.2.2 Effects of heavy metals on human health

Human beings get exposed to heavy metals occurring in an aquatic ecosystem mainly via the food chain where animals may over time consume water contaminated with heavy metals which then accumulate in their tissues (Fig. 2.1). These animals may then be eaten by human beings who in turn get exposed to these contaminants or through consuming plants grown in areas polluted by heavy metals. Alternatively, exposure may also result from direct intake where human beings drink water that is contaminated by heavy metals. The extent by which a heavy metal can be absorbed by human beings is dependent on the concentration of the metals in river or lake water and sediments (Wintz et al., 2002).

Heavy metals in the human body can be categorized into essential or non- essential. The essential heavy metals such as zinc, manganese, iron and copper are necessary for the human body’s biochemical processes. Consequently, an excessive dosage of these metals in the body can result to heavy metal toxicity which is the immoderate accumulation of heavy metals and can eventually lead to drastic health issues in adults and children (Patients Medical, 2013). The quantity of essential nutrients required by the body is controlled homeostatically with their uptake determined by its demand.

The non-essential heavy metals are those which are not required in the body in any amount because they have no any biological role. Such metals include mercury, lead, arsenic and cadmium. They are toxic to human beings at minimal concentrations when exposure is established between the contaminant and human beings. Exposure however is not a consequence of there being a potentially dangerous agent in the ecosystem only but contact has to be established between the agent and the outermost layer of the human body hence for exposure to occur heavy metals and man must co-exist (Patients Medical, 2013). The effects of some selected metals are presented in the following section.

Figure 2.1 Cows drinking water at the shores of River Nzoia.

Cadmium

Cadmium occurs within the earth’s crust with a mean background concentration of 0.1 – 5 ppm. It exists mainly in combined form with sulfide minerals associated with zinc ores, lead ores as well as copper- lead – zinc ores (Morrow, 2001)

Cadmium remains in the body for many years where it piles up especially in the kidney and liver (UNEP, 2008). Cadmium exposure has been shown to cause skeletal damage in people who drank cadmium- contaminated water in Japan in 1950 (Järup, 2003). Cadmium interferes with metabolism of calcium and phosphorous resulting to a painful bone disease (Lenntech, 2004).

Copper

Copper occurs naturally in both plants and animals as well as in rocks, soil, water and sediments. It is an essential element required by the body for biological processes when taken in the right amounts. It also forms the oxygen carrying part of the blood cell (ATSDR, 2004). It is also responsible for production of chemicals that help to regulate blood pressure, pulse and healing process.

Exposure to copper has been associated with liver and kidney destruction as well as uncomfortable stimulation of the stomach and intestines (Lenntech, 2004). Other unhealthy effects associated to copper poisoning include anorexia, fatigue, depression, anxiety, childhood hyperactivity and learning disorders (USEPA, 2001; Sadiq et al., 2003).

Iron

It is an abundant element as it forms most of the earth's outer and inner core. It is majorly occurring due to its production by fusion in high mass stars (Rana et al., 2012). Iron is a micronutrient element with many functions in the body. For instance, it is an essential part of hemoglobin - the part of our blood that carries oxygen and used by the body to make ligaments and tendons (Inam *et al*., 2012). Certain chemicals in our brain are controlled by the presence or absence of iron. Iron deficiency (anemia) which affects at least five hundred million people in the world is probably the most common nutritional disease (Inam *et al*., 2012). The unhealthy effects of excessive iron exposure on human beings include; ingestion, elevated blood pressure, growth retardation as well as cognitive and neurobehavioral effects in adults and children (Järup, 2003).

Lead

Lead is one of the nonessential heavy metals that have no known biological functions either in human beings, animals and plants. It induces toxic effects in human beings at even very low doses. Symptoms of lead poisoning which is the presence of too much lead in the body in human beings include colic, anemia, headache, brain damage and nervous disorders (Inam et al., 2012). Exposure to lead mainly affects children under the age of five years where some of the effects include developmental delays, hyperactivity, learning disorders and behavioral problems.

Exposure to small children is mainly due to the fact that they put things such as toys into their mouths, chew on painted objects and spend most of their time on the floor where leaded products may be found.

Lead mainly bio-accumulates in the tissues and may result to other effects such as convulsions, renal failure, coma and even death in case of chronic exposure (USTSDR, 1999). It may also result to deficit in mental development in children (Banks et al., 1997; WHO, 1995). Short-lived lead poisoning may result in pain in the head, irritability and pain in the abdomen. It is considered as an accumulative lethal substance which has the possibility to cause cancer in human beings (Bakare-Odunola, 2005). In general lead affects every organ and/or system in the body of human beings and animals.

Zinc

Zinc is an essential element required by plants, animals and human beings. It is involved in about one hundred different biological and physiological reactions in the human body (Inam et al., 2012). These reactions are those that help our bodies construct and maintain DNA, the molecule that controls how every single part of our bodies is made and works. The author also states that zinc deficiency can result in undesirable effects on our health. According to the author, some of the symptoms of zinc deficiency include hair loss, mental apathy and damage to reproductive organs. Decreased growth rate and impaired mental capacity are other symptoms. Additionally, one can lose most of his/her senses of taste and smell, and develop mental disorders.

Arsenic

Arsenic is known to accumulate in soft tissues in parts of the body such as the liver, spleen, kidneys and lungs; however, it is eventually stored in the tissues rich in keratin such as skin, hair and nails. Long-term exposure results in peripheral nerve damage which exhibits itself in the form of reduced sensitivity to stimulation as well as causing the hands and feet to be weak. Studies by WHO have shown that when contact is established with arsenic via consumption of contaminated water, it may result to cancer of the lungs, kidney, bladder and skin (WHO, 2001)

Chromium

Chromium gets its way into rivers, lakes and other water bodies mainly through aerial deposition or run offs where it finally gets deposited to the sediments (Adriano, 2001). Chromium has the ability to cause cancer as well as being capable of causing genetic mutation in living tissues. It is also known to cause short and long term disorders, nephritic damage, and accumulation of air in the lungs, high blood pressure and reduced functionality of the testicles (Bazrafshan et al., 2015).

2.3 Nzoia River Pollution

River Nzoia has its source at Cherengani Hills which is at an elevation of 2300 m and drains into Lake Victoria. Its flow is generally in the south-west direction and transverses through Trans Nzoia, Bungoma, Kakamega, Siaya and Busia counties in the western part of Kenya. It provides water for rural and urban use. It also provides water for agricultural, commercial sectors and industrial establishments like Pan Paper Mills, Nzoia Sugar Company, Mumias Sugar Company and West Kenya Sugar (NRBMI, 2006). River Nzoia provides water for day to day human practices like fishing, sand harvesting and to residences within the proximity of the river banks for bathing, washing and drinking water by animals and man. It is thus mainly polluted by run-off from urban and agricultural areas, effluent from residential and industrial sectors as well as point sources with variable chemical composition (Mwamburi, 2003).

In the recent past, death of fish on a large scale has been noted especially on the lower sections of river Nzoia with the main cause being pollution of the rivers waters that was evident even from the foul smell that was emanating from the river (Daily Nation, 2015). An analysis of the water at the time indicated high levels of chemicals in the water. This has not only affected fish but even individuals who engage in sand harvesting whose skins have become cracked and pale with the locals blaming the pollution on poor agricultural practices and discharge of chemicals which contain heavy metals into the river by factories (Daily Nation, 2015).

There have been no intensive researches on pollution by heavy metals on River Nzoia water and sediments with the few studies available only being for selected sites along the river. A study by Mwamburi (2003), to determine the changes in trace elements in bottom sediments of rivers in Lake Victoria’s basin, Kenya, sampled sediments at Nyadorera and Ugunja which showed high copper levels of 110 μg g^{-1} with the concentration of Fe, Mn, Pb, and Cr being within the permissible limits. Cadmium was however not found in any of the samples collected. The study of heavy metals in lakes and rivers has generally shown minimal levels though more work need to be done to provide a more in-depth knowledge on the same.

A study by Lalah et al., (2008) to determine the input of heavy metal into Winam Gulf, Kenya, analyzed for heavy metals at two sites along the Nzoia River at Rwambwa Bridge and Nzoia Bridge with the levels of Cd, Co, Cr and Cu indicating higher values than those determined by Mwamburi in 2003. It is noted that Cd which was initially not detected was now available in the ecosystem at concentrations of 0.27 ± 0.21 μg/g. This might either be from a point source in the sampling site or actually originated from upstream of the river. The study revealed an enrichment of the river with Cd and Pb at the sampling points. The concentrations determined for water were Cu (20.0 μg/l), Mn (50.00 μg/l), Ni (13.0 μg/l), Pb (15.0 μg/l) and Zn (40.0 μg/l)

The analysis of heavy metals in water and bottom sediments of upper and lower Nzoia by Mutuku et al., (2014), showed that sediment samples recorded high levels of metals concentration as compared to water confirming the fact that sediments act as sinks for heavy metals where they bio-accumulate over time. The mean concentrations were for Pb (0.81μg/l), Mn (0.31 μg/l), Zn (0.23 μg/l), Ni (0.03 μg/l) and Cu (0.52 μg/l) in water and Pb (32.5), Mn (307), Zn (4.8), Ni (12.4), Cu (6.93), Cr (14.0) and Co (17.02) in sediments in mg kg^{-1}. The levels determined for manganese, cadmium and lead were above the permissible limits with regard to WHO (1985) and KEBS (1996) standards. They observed that the river acts as a sink to effluents originating from both industries and municipalities transversed by the river.

Several studies have been done on the Lake Victoria Basin for rivers that drain its waters into the lake. Mwamburi and Oloo (1997) reported mean concentrations in sediments as Fe (16100 – 55500 μg/g), Mn (290 – 1810 μg/g), Zn (31.8 – 136.4 μg/g) and Pb (13.6 – 122.7 μg/g). High concentration levels were observed in the river mouths with Nzoia recording the maximum values for copper, iron and manganese. Elevated levels for Cu was also reported (50 μg/g) which was mainly due to effluent discharge by Pan-Paper mills. Other factors cited for the high concentrations in the study included use of paints as well as leaded fuel at the year of the study in

1997. A similar study by Orata (2003) recorded high levels of concentration than those previously recorded by Mwamburi and Oloo (1997) with the range of concentrations in mg kg^{-1} being Cu (11.8 – 749.2), Cd (0.50- 1.998), Cr (13.74 – 98.17), Zn (58.79 – 453.8) and Pb (6.99 – 424.2). The reported concentrations were attributed to anthropogenic sources. The increased range of pollutants points to the fact that pollutants indeed accumulate within the ecosystem and specifically for this case sediments. Onyari (1985) and Onyari and Wandiga (1989) had also reported lower levels of concentration for a similar study than those previously reported earlier.

A study by Oyenkule et al., (2013) of Asunle River in Nigeria, reported that high concentrations of metals in sediments could be due to proximity of the river to a dumpsite where these metals could be washed into the river from the nearby dumpsite. A decrease in concentrations downstream was also reported and this could be explained by the dilution effect owing to widening and volume increase of the river. Other contributing factors include discharge of waste from residential areas, urban garbage, sewage sludge as well as deposition of solid waste.

2.4 EDXRF theory

Is a technique that works on the fact that atoms in a sample are excited by X-rays and they in turn emit x-rays that are characteristic of each element present in the sample. The energies and intensities of the x-rays produced are then measured by a detector and thus giving the identity of the element present and the corresponding concentration of the element. The working of EDXRF can be explained as; a source reduces photons which in turn irradiate the sample causing its atoms to be excited. The atoms then de-excite by producing x-rays corresponding to the concentration of the element present in the sample. The x-rays are then passed through a detector where they release pulse of charge directly proportional to the amount of energy produced. The processor then adds the pulses to give out an energy spectrum whose peaks are characteristic of the elements present in the sample (Appendix C). The peaks are then analyzed in software that is able to give concentrations in each sample based on the intensity of the recorded peaks. The instrumentation is represented by the figure below and a photo of the machine used. (Redus R, 2008)

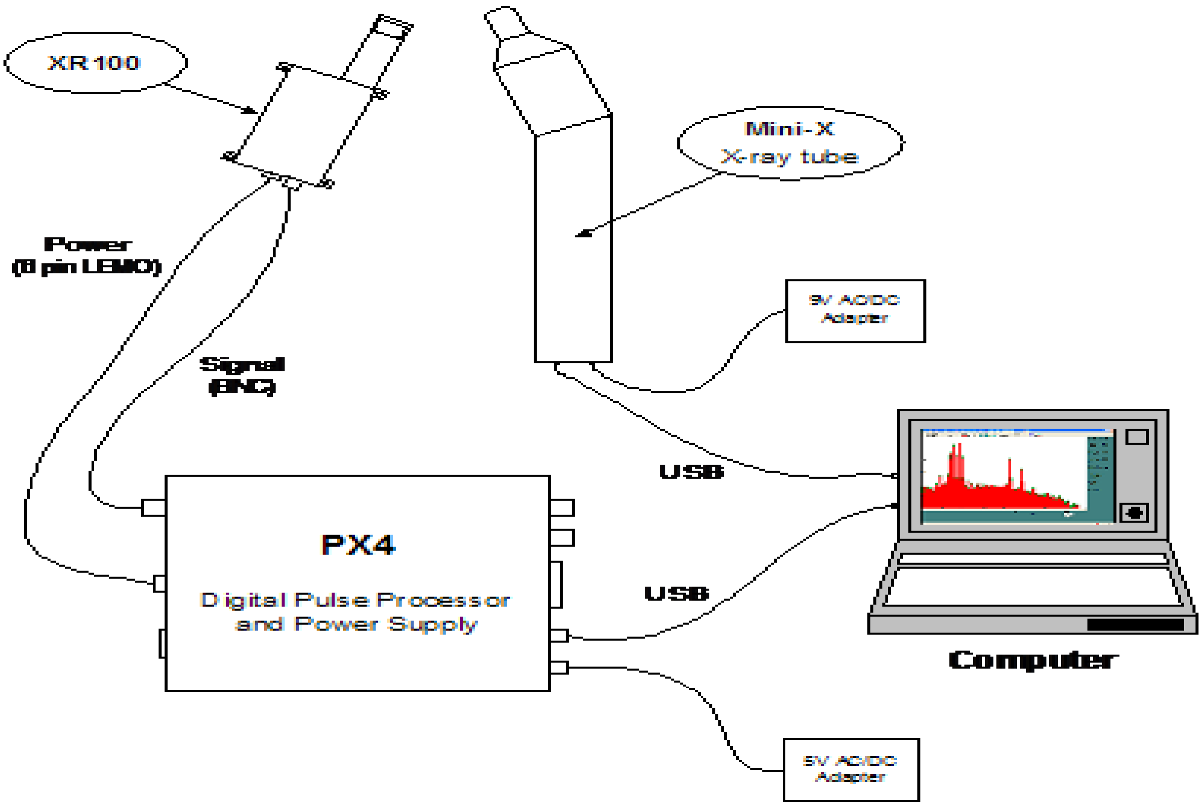


Figure 2.2: Block diagram of EDXRF instrumentation (R. Redus, 2008)

2.5 TXRF theory

TXRF works on the principle of total internal reflection as well as Snell's law of reflection. Incident photons strike the surface at a small angle where they are the reflected externally without penetrating the sample at an equally small angle where they create a standing wave and electrons at the surface can then be excited and then decay by emitting fluorescence x-rays in all directions accompanied by Thomson scattering as well as Bremsstrahlung radiation.

It relies on scatter properties close to the Bragg angle. It relies on long collimator so as to maintain the angle at a one lower than the Bragg angle. The detector is then placed above the surface where the sample has been placed at an angle and height.

An X-Ray beam generated by a Molybdenum tube is reflected onto a Ni/C-multilayer producing a beam that has one energy. This beam is then passed through a sample holder which carries the sample at an angle of about 0.3-0.6˚ resulting to total reflection of the beam which is then detected and the intensity measured through amplification.

The complete analysis and quantification process is described as; all elements that can be detected are measured all at once by the complete spectrum, the elements which are present are then quantified by evaluating the measured spectra through spectra deconvolution where the overall degree of strength of the peaks are determined by correlating line overlaps, background factors and escape peak correction (Klockenkamper, 1997).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Description of the study area

River Nzoia originates from the highlands of Cherengani hills and Mount Elgon. It passes through Trans Nzoia, Uasin Gishu, Bungoma, Siaya and Busia Counties. The river transverses three fundamental zones i.e. upper, middle and lower catchment areas. The upper catchment area is a rich agricultural area and is dominated by large scale agricultural activities mainly involving sugarcane and maize growing hence the main source of pollution is in this area is from agrochemicals used in the farms. The middle catchment area has major urban areas hence the river receives industrial discharge from industries such as Nzoia Sugar Company, Mumias Sugar Company and the Webuye Pan-Paper Mills which discharge their wastes into the river (Achoka, 1998) and urban run offs. The lower catchment area which forms the main study area of this work is dominated by several large scale and small scale agricultural activities such as sugar cane plantations and cultivation of maize, beans, sorghum, cassava, potatoes, groundnuts and millet.

The economy of the lower catchment area is largely rural with a greater portion of the locals earning its living from subsistence farming and livestock rearing. The land is mostly private owned though few large commercial farms are also available mainly for sugarcane growing and in the Bunyala irrigation scheme. This region covers mainly Kakamega, Siaya and Busia counties. The Busia part of the river is mainly characterized by flooding especially in the Budalangi area.

Nzoia River provides water for use in the industries and large-scale farms within the Nzoia Basin all year round. The lower section thus acts as a sink where most pollutants from upstream are deposited. Also during flooding, silt is deposited in the adjacent farms. Some of the deposited wastes include nitrogenous and phosphorous fertilizers which farmers use to improve their crop yield, agrochemicals, fertilizers and pesticides which contribute to pollution of the river when washed to the river as surface runoff.

It also receives pollutants from household discharges and other sources that are normally generated by urban runoffs. In the areas where industries are located, the river absorbs a lot of effluent from the sugar and paper factories. Other minor sources of pollution include coffee roasting, flower farming, jaggery (crude sugar) factories. The problems affecting this region are therefore soil erosion, sedimentation and river bank cultivation (NRBMI, 2006). These pollutants then get their way to human beings through the food chain since the water is used for domestic purpose, washing of utensils and clothes and also when consumed by cows which accumulate the metals in their tissues and milk if lactating.

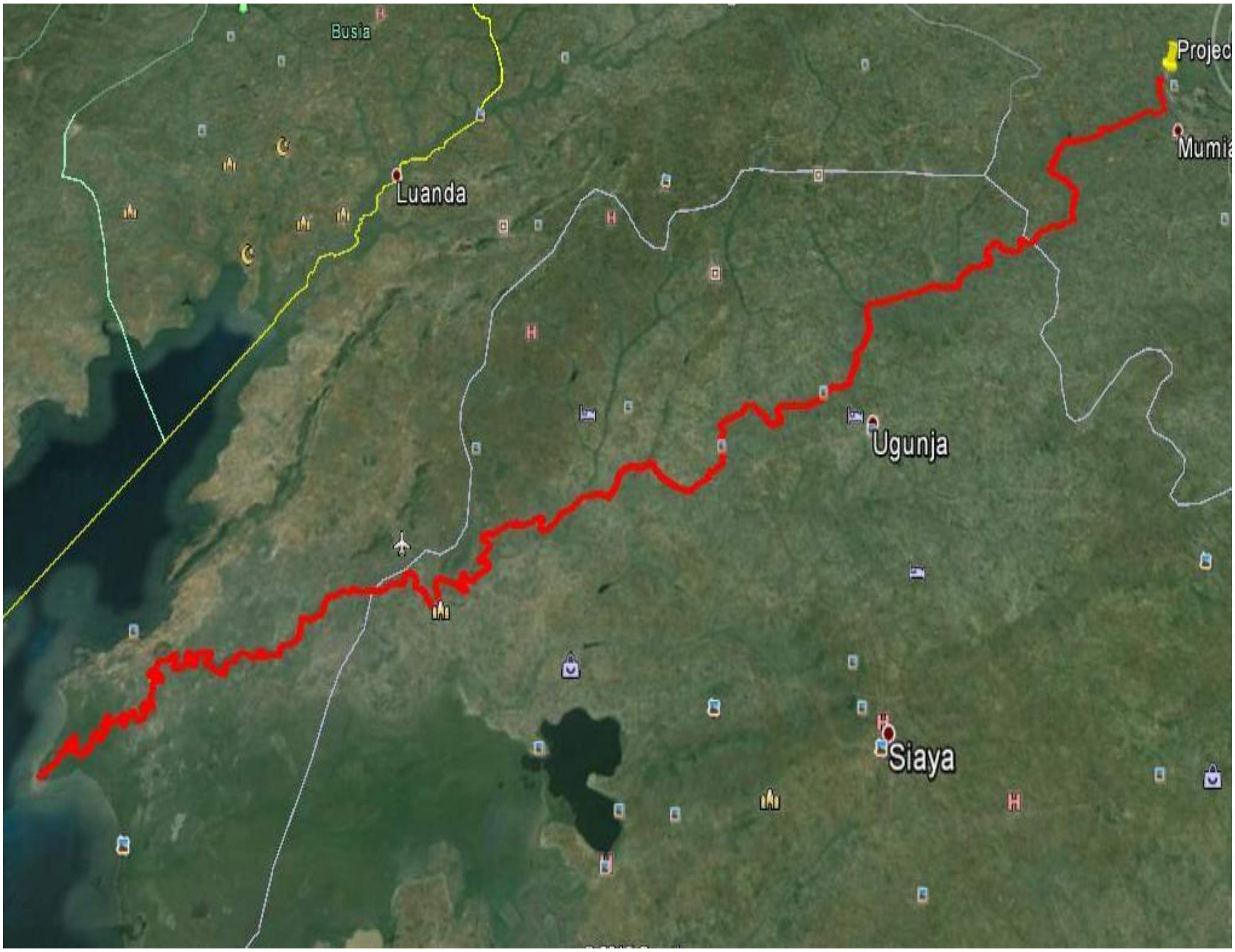


Figure 3.1: Map showing the section of River Nzoia covered by the study

3.2 Description of the sampling sites

Thirty sampling sites along the Nzoia River were selected from the Mumias Bridge to Sigiri crossing point. The selection of these points were based upon human activities taking place near the river banks and in the river such as sand harvesting and farming, geographical proximity of industrial and urban discharges of effluent to the river, proximity of residential areas near the river banks, inflow regions of the river, drainage patterns and accessibility. In Kakamega and part of Siaya region, the areas surrounding the sites were mainly characterized by sugar plantations which were grown on either side of the river with the farmers heavily relying on fertilizers to improve yield. The other areas had subsistence farming where food crops were grown with the applications of fertilizers, fungicides as well as pesticides which are major contributors to pollutants. Sampling sites 1, 5, 9, 10, 11 and 21 were located along major roads where they were most likely to receive pollutants from automobiles. Sampling site 20 was located near a busy market centre that had no proper sewerage systems hence likelihood of waste disposal and urban discharge being deposited to the river. Sampling site 30 served as a busy crossing point serving a large population on a daily basis and motorcycles were available just within the river banks which could also introduce pollutants mainly due to oil spillage into the river or during cleaning of the motorcycles in the river. The rest of the sampling sites were generally areas of intensive sugarcane growing (sites 2, 3, 4, 6, 7, 8) and cultivation of food crops (sites 12-19 and 22-29). All these relied on heavy use of farm inputs which was witnessed during sampling and these are likely introducers of heavy metals into the river.

3.3 Sampling

Samples that were collected included surface water and sediment samples at depths of 30 cm, 50 cm and 100 cm on either side of the river at every sampling point. The coordinates of the sampling area were obtained by the aid of a hand held GPS gadget. Consistent sediment collection, holding time consideration as well as sediment manipulation and storage procedures were strictly adhered to in order to have high quality samples.

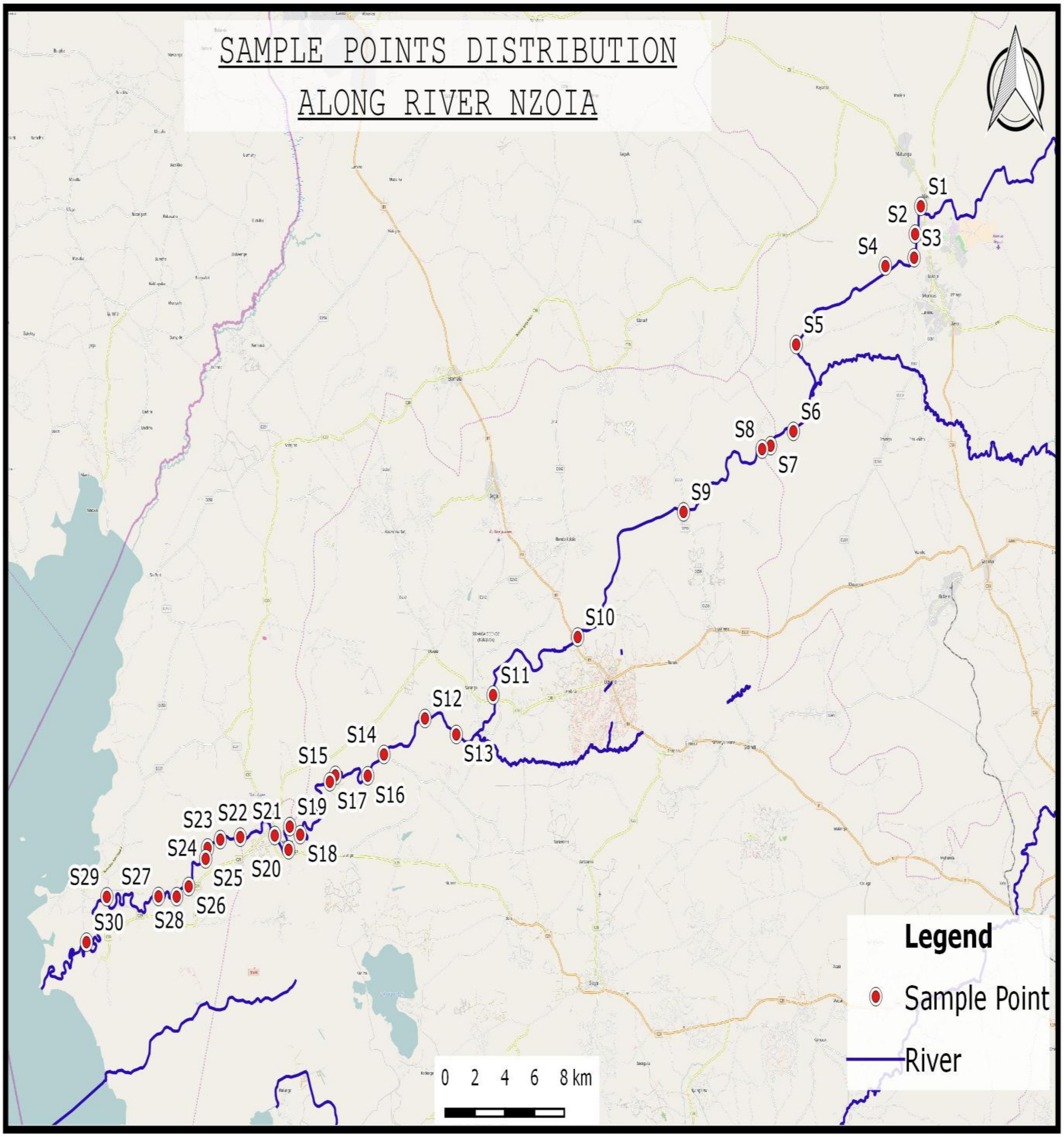


Figure 3.2: Map showing sampling sites along River Nzoia

3.3.1 Sediment sampling and preparation.

At each of the thirty sampling points, sediment samples were taken at depths of 30 cm, 50 cm and 100 cm with the aid of an auger hence six samples were collected at each sampling point to give a total of 180 samples. Each sample of sediment collected was then placed in a separate clean polythene bag, sealed, labeled, packed and transported to the laboratory awaiting preparation and processing prior to being analyzed.

In the laboratory, sediment samples were air dried for five days after which they were ground to fine particles that could go through a 2 mm sieve so as to remove any large particles such as roots and rock particles. The samples were further reduced in size using pestle and mortar after which they were sieved in a 75 μm sieve, mixed depending on the depth to form a composite sample after which it was placed in clean polythene bag, sealed and labeled for the subsequent procedure.

A portion of each of the fine sediment (about 1.6 g) was then mixed with starch binder analar grade (about 0.4 g) to make a ratio of 1:4 or 20 % starch. The mixture was then thoroughly mixed to homogeneity after which three pellets each weighing about 350 - 400 mg were prepared using a hydraulic press from each sample for EDXRF analysis (IAEA Operational Guide, 1995).

3.3.2 Water sampling and preparation

Water samples were collected on either side of the river at every site by grab method making a total of sixty samples. The collected samples were placed into pre-cleaned plastic bottles, sealed, labeled and moved to the laboratory for preparation and analysis.

In the laboratory, the two samples at each sampling point were mixed to make a composite sample after which about 300 mls of the mixture was stored in pre-cleaned plastic bottles. 5mls analar grade hydrochloric acid was added to the mixture to prevent adsorption of the metal cations.

The prepared samples were then prepared in three replicates for analysis. Twenty (20 ml) of each sample was measured into a sample vial using a pipette and a pipette filler which had been cleaned with distilled water and rinsed with small amount of the sample after every sample after which 10 µl of gallium was added to act as an internal standard and the mixture shaken to homogeneity to give a final concentration of 0.5 µg l^{-1} for the internal standard.

Ten (10µl) of the mixture from the sample vial was then pipette onto a pre-cleaned sample carrier and the sample evaporated on a hot plate leaving a thin film for analysis with TXRF (IAEA Operational Guide, 1995).

3.4 Heavy metal analysis of sediment samples

Total elemental concentrations in sediment samples were determined using Amptek EXP-1 EDXRF spectrometer available at the Institute of Nuclear Science and Technology in the University of Nairobi. The prepared sediment pellets were irradiated for 200 seconds in the spectrometer and a spectrum which was saved and the sample again irradiated for 100 seconds with the target and the spectra obtained saved. The duration for irradiation was obtained through optimization.

The spectra saved were then de-convoluted and quantification done using AXIL which involved spectrum format conversion from MCA to SPE format, spectrum fitting and eventually qualitative analysis to give the concentrations.

3.4.1 Energy calibration

The effectiveness of analysis by EDXRF depends on identifying peaks at their correct energy positions. This was ascertained by performing energy calibration using an internal standard A750 twice a week. Here, Cu-Kα position should be in the range of 8.00-8.08 keV with Sn-Lα, Al-Kα and Ni-Kα peaks present.

3.4.2 Quality assurance

Verification of the accuracy of the method of analysis was done by using certified reference materials (CRM) whereby river clay CRM from IAEA was prepared and analyzed in a similar way as the other samples for this particular study. The values obtained were then compared to reported values. Also precision and purity of the analyses was controlled by analyzing three replicates per sample.

3.5 Heavy metal analysis of water samples

Elemental concentration of metals in water samples were determined by the use of an S2 Picofox TXRF spectrometer available at the Institute of Nuclear Science and Technology in the University of Nairobi in which an X-ray beam produced by a Molybdenum tube is reflected onto a Ni/C-multilayer producing a beam with only one energy. This beam is then passed through a sample holder which carries the sample at an angle of about 0.3-0.6°resulting to total reflection of the beam.

The complete analysis and quantification process is described as; all elements that can be detected are measured all at once by the complete spectrum, the elements which are present are then quantified by evaluating the measured spectra through spectra deconvolution where the overall degree of strength of the peaks are determined by correlating line overlaps, background factors and escape peak correction (Klockenkamper, 1997). The concentrations can then be found using;

$$C_x = \frac{N_x/S_x \times C_{is}}{N_{is}/S_{is}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textit{Equation 3.1}$$

where,

C_x → analyte concentration

C_{is} → internal standard concentration

N_x → analyte net intensity

N_{is} → internal standard net intensity

S_x → analyte relative sensitivity

S_{is} → is the internal standard's relative sensitivity

The water samples were irradiated for 1000 seconds using a voltage of 50 kV and a current of 1000 μA and the spectra obtained deconvoluted by inbuilt software with the concentrations determined by equation 3.1.

3.5.1 Procedure

The carriers which held the samples for analysis were cleaned thoroughly using distilled water, heated in EDTA and HNO_3 at 100˚C respectively for one hour. The carriers were then dried in a hot plate and wiped with a soft tissue paper soaked in ethanol and irradiated for 100 seconds to ascertain that no elemental peaks apart from those of silicon, argon and molybdenum appear with intensities higher than Ar K_β- line. Disposable pipette tips were used in pipetting each sample onto the clean carrier.

Before commencement of analysis, resolution, sensitivity and count rate of the TXRF Spectrometer was determined daily for the period of analysis. This was done by analyzing 1μg of Mn standard for resolution, 1μg of Ni standard for sensitivity and 1μg of As standard for count rate. All the three samples were irradiated for 1000 seconds. The indicated duration for irradiating the sample was obtained through optimization.

A multi-elemental standard reference material from Bernd Kraft was analyzed to validate the analytical procedure and observed values compared to certified values.

3.6 Statistical analysis

The mean heavy metal concentration values were calculated and reported with their standard deviations. One way ANOVA was used to determine if the variation was significant in the mean heavy metal concentration between sampling depths and between sampling points.

The data obtained was also subjected to Pearson’s correlation analysis to test if the correlation was significant between the concentrations of water and the corresponding sediment samples.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.0 Introduction

In this chapter, the results of this study are presented. First, the quality assurance of the procedure is reported. Secondly, the results obtained for concentrations in water are reported and finally the concentrations in sediments are presented and discussed.

4.1 Quality Assurance

The reference concentration for Bernd Kraft certified reference material was 10 mg l^{-1} (Table 4.1). The analysis of multi- element certified reference material using TXRF showed concentration values that were close to the certified values (Table 4.1).

Table 4.1 Results of analysis of Bernd Kraft certified reference material

Element	Experimental value (mg l^{-1})	Certified value (mg l^{-1})	Percentage Deviation	Detection Limits (mg l^{-1})
Ca	10.7 ± 0.82	10.0 ± 0.03	1.2%	0.165
Ti	9.1± 0.91	10.0 ± 0.03	0.1%	0.090
V	8.9± 0.74	10.0 ± 0.03	3.6%	0.075
Cr	9.5± 0.69	10.0 ± 0.03	1.6%	0.065
Mn	9.9± 0.76	10.0 ± 0.03	9%	0.050
Fe	9.3± 0.88	10.0 ± 0.03	2%	0.045
Ni	11.0± 0.93	10.0 ± 0.03	0.4%	0.025
Cu	10.0± 0.00	10.0 ± 0.03	0%	0.025
Zn	10.3± 0.48	10.0 ± 0.03	3%	0.020

The average concentration for the experimental value was determined to be 9.8 mg l^{-1}. A one tailed paired sample t-test showed that the experimental values (m = 9.94, s = 0.74) and the certified values (m = 10.0, s = 0.03), were statistically similar, t (9) = -0.23, $p > 0.05$. Based on the results of the analyses of the Certified Reference Material (CRM) using EDXRF spectroscopy (Table 4.2), it is evident that the concentrations for most elements lie within the confidence interval of the certified values, except copper and titanium, which recorded slightly higher concentrations. These could be attributed to sample inhomogeneity or closeness of the expected concentration levels to the detection limits, particularly for copper (Sirengo, 2001). A one tailed paired sample t-test revealed that the experimental values (m = 7040, s = 10.6) and the certified values (m = 6888, s = 10.5) were statistically similar, t (9) = 1.218, $p > 0.05$.

Table 4.2 Results of the analysis of PTXRF-IAEA09 river clay certified reference material by EDXRF method

Element	Experimental values (mg kg^{-1})	Certified values (mg kg^{-1})	Percentage Deviation	Detection limits (mg kg^{-1})
Ca	13500 ± 805	13270 - 14330	4%	50
Mn	1065 ± 80	940 - 1060	5%	75
Fe	29750 ± 1550	28700 - 30700	-2%	50
Ni	30.6 ± 9.7	35.5 - 40.3	0%	100
Cu	32.3 ± 7.8	18.1 - 22.2	-9%	20
Zn	76 ± 12.4	88.4 - 103.8	0%	15

4.2 Heavy metal concentration levels

4.2.1 Heavy metal concentrations in water

The mean heavy metal concentration levels and the ranges in water samples are presented in Table 4.3. The concentration levels for most of the metals were generally high and this could be explained by the fact that sampling was done at the onset of heavy rains hence the likelihood of overflow from farms and municipal sweeps being washed into the river. Generally concentration levels in water samples were in the order of Fe> Zn> Cd> Mn> Cu>Ni> Pb. The results will be discussed element by element.

Table 4.3 Mean heavy metal concentration levels in water samples (µg l^{-1})

Metal	Mean Concentrations µg l^{-1}	Range µg l^{-1}
Mn	78	44.5±7.75 - 217.5±20.3
Fe	6607	1574±29 - 12314±145
Ni	15.74	<13 - 21±3.8
Cu	27.7	<13 - 92.3±5
Zn	212	28.6±3 - 1399.8±20
Pb	14.94	<10 - 24.25±4

4.2.1.1 Manganese

The mean concentration of Mn in the water samples was observed to be 78 µg l^{-1} with the concentration range being 44 - 217 µg l^{-1} (Table 4.3). Most sampling points, however, had concentration levels that were within the WHO (2004) recommended limits of 100 µg l^{-1} but higher concentration levels were recorded in sites 12, 14, 22, 28, 29 and 30 (Figure 4.1). The high concentrations in site 12 and 14 can be attributed to point sources of pollution upstream, informal settlements, human activities such as businesses or discharge of industrial effluents, runoffs and raw sewage while the last three is due to accumulation from upstream as site 30 had the highest concentration or even deposition of sewage sludge and deposition of solid waste from within the locality.

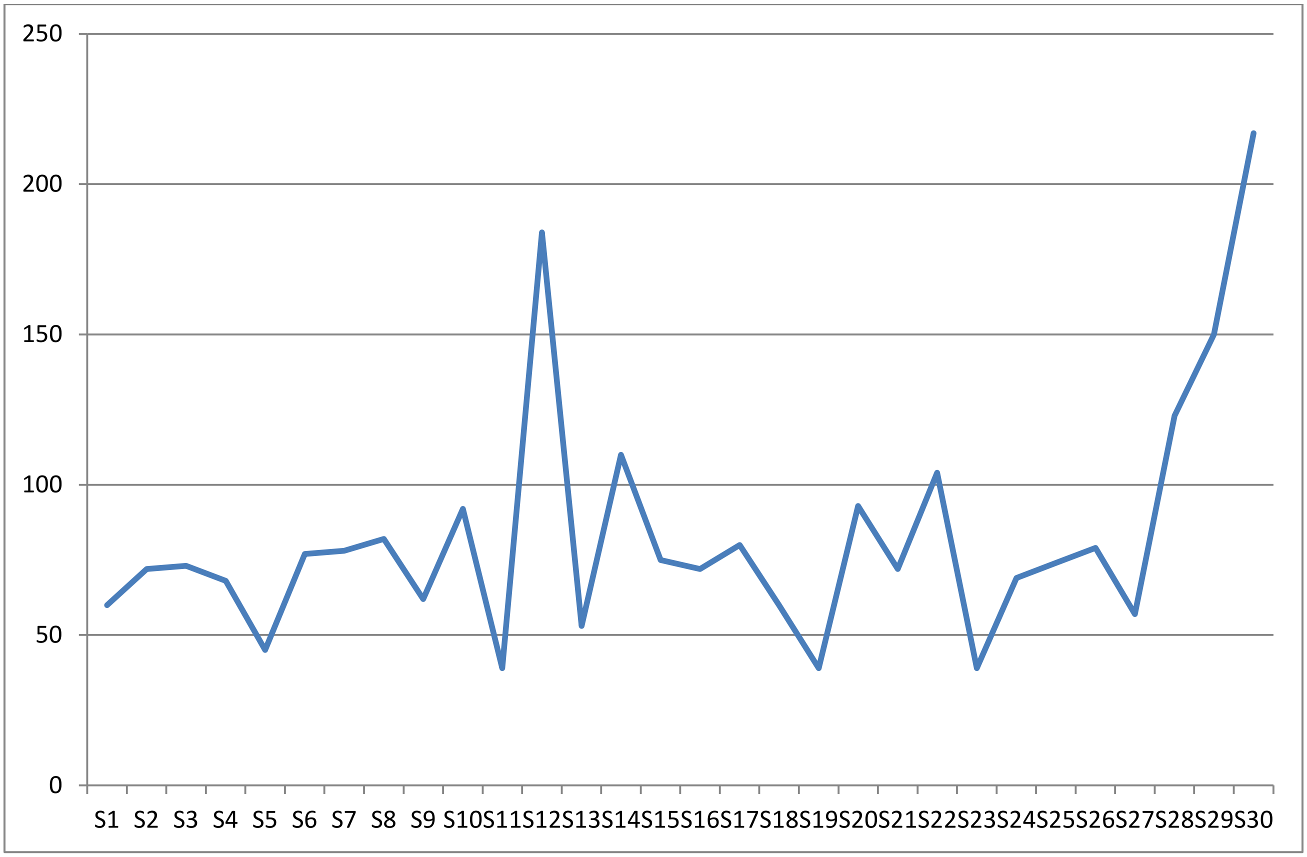


Figure 4.1: Mn concentrations (µg l^{-1}) in water samples of lower Nzoia River

4.2.1.2 Iron

The mean iron concentration in Nzoia water samples ranged between 1574 µg l^{-1} and 12314 µg l^{-1} with a mean concentration of 6607 µg l^{-1} (Table 4.3). The minimum levels of Fe were observed at S23 while maximum levels were observed at S12. High levels of concentration were recorded at sites S12, S14, S28 and S30 that recorded concentration levels that were above 10000 µg l^{-1} (Figure 4.2). The high levels could mainly be attributed to point source of pollution upstream, anthropogenic activities that cause pollution to the river as well as runoffs since the points did not record corresponding high concentrations in sediments as well as accumulation of pollutants from upstream. According to WHO (2004) guidelines for drinking water, the recommended level is 300 µg l^{-1} indicating that the water is not fit for drinking.

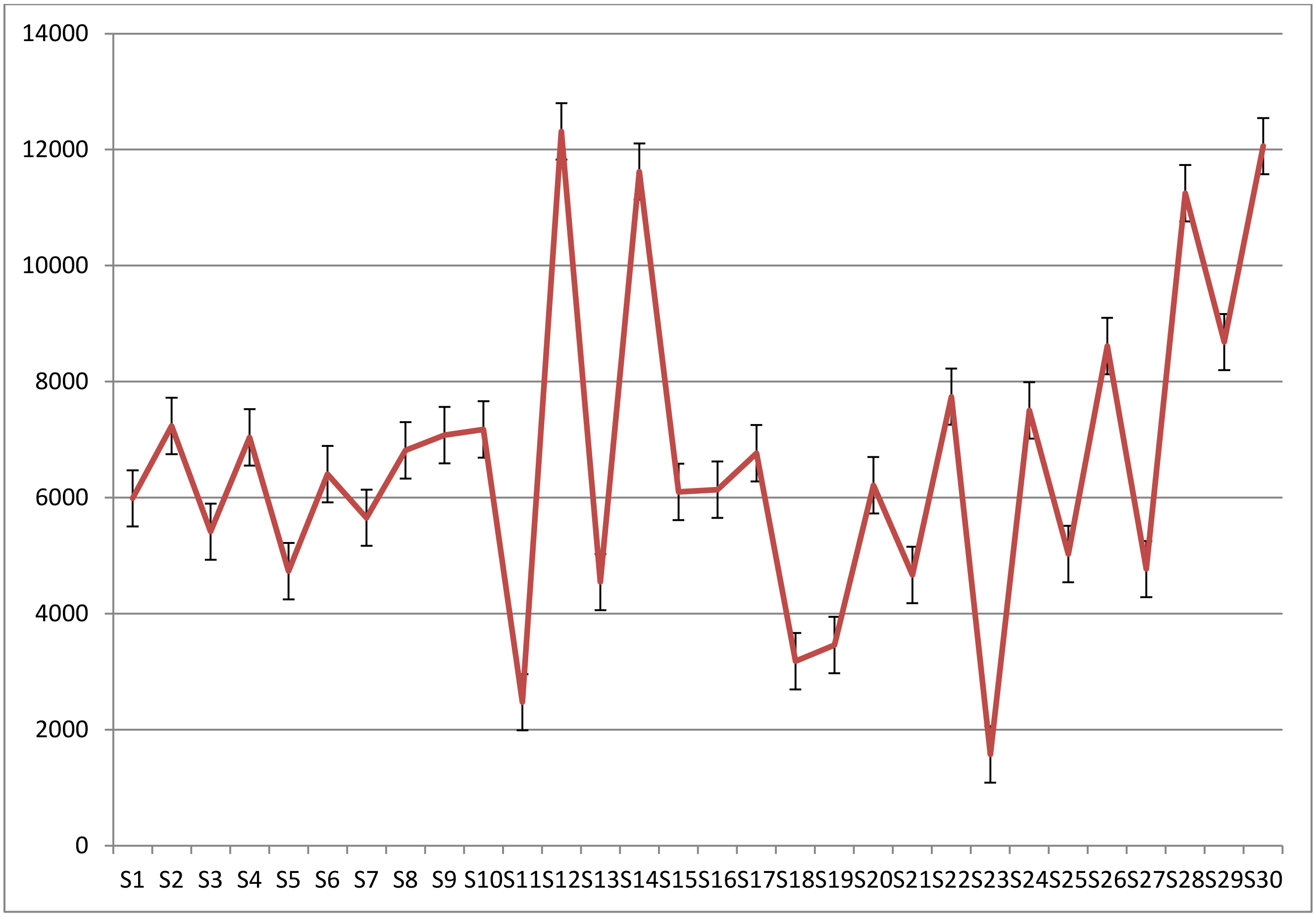


Figure 4.2: Fe concentrations (µg l^{-1}) in water samples of lower Nzoia River

4.2.1.3 Nickel

In water samples, total nickel concentrations ranged between < 13 to 21.0 ± 3.8 µg l^{-1} with a mean concentration of 15.74 µg l^{-1} (Table 4.2). The maximum level of nickel in water was recorded at S7 with the minimum level being recorded at S16 and S24. However, most of the sampling points showed concentration levels that were below the detection limit of 13 µg l^{-1} (Figure 4.3). The concentrations were below the WHO (2004) standard for drinking water which is 70 μg l^{-1} showing that the water is not polluted by Ni. The points that showed slightly higher concentrations could be due to human activities around the sites which are responsible for point sources of pollution.

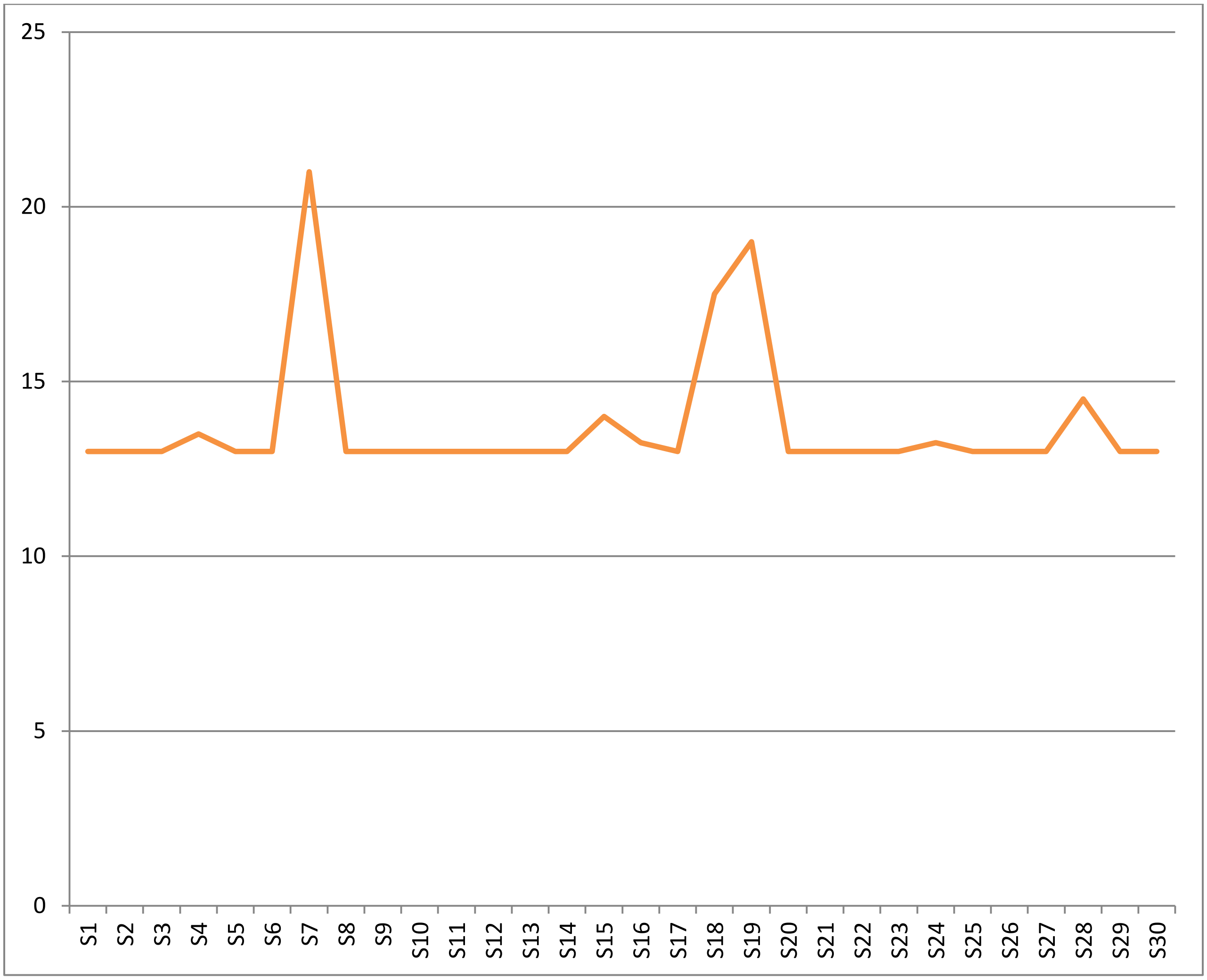


Figure 4.3: Ni concentrations (μg l^{-1}) in water samples of lower Nzoia River

4.2.1.4 Copper

The mean concentrations of copper in water samples ranged between <13 to 92.3 μg l^{-1}, with an overall mean concentration of 27.7 μg l^{-1} (Table 4.2). The levels reported are higher than WHO recommended limits of 20.0 μg l^{-1} for drinking water. The maximum levels reported for Cu was at S19. Significantly high levels were recorded at sites S18, S19, S23, S24 and S29 (Figure 4.4).

These points, however, did not have corresponding high concentrations in sediments indicating the possibility of point sources upstream such as discharge of effluents into the river in the aforementioned areas. The results obtained are comparable to those reported by Lalah et al (2008) where the concentration for Cu was 20.0 ± 1.99 μg l^{-1}.

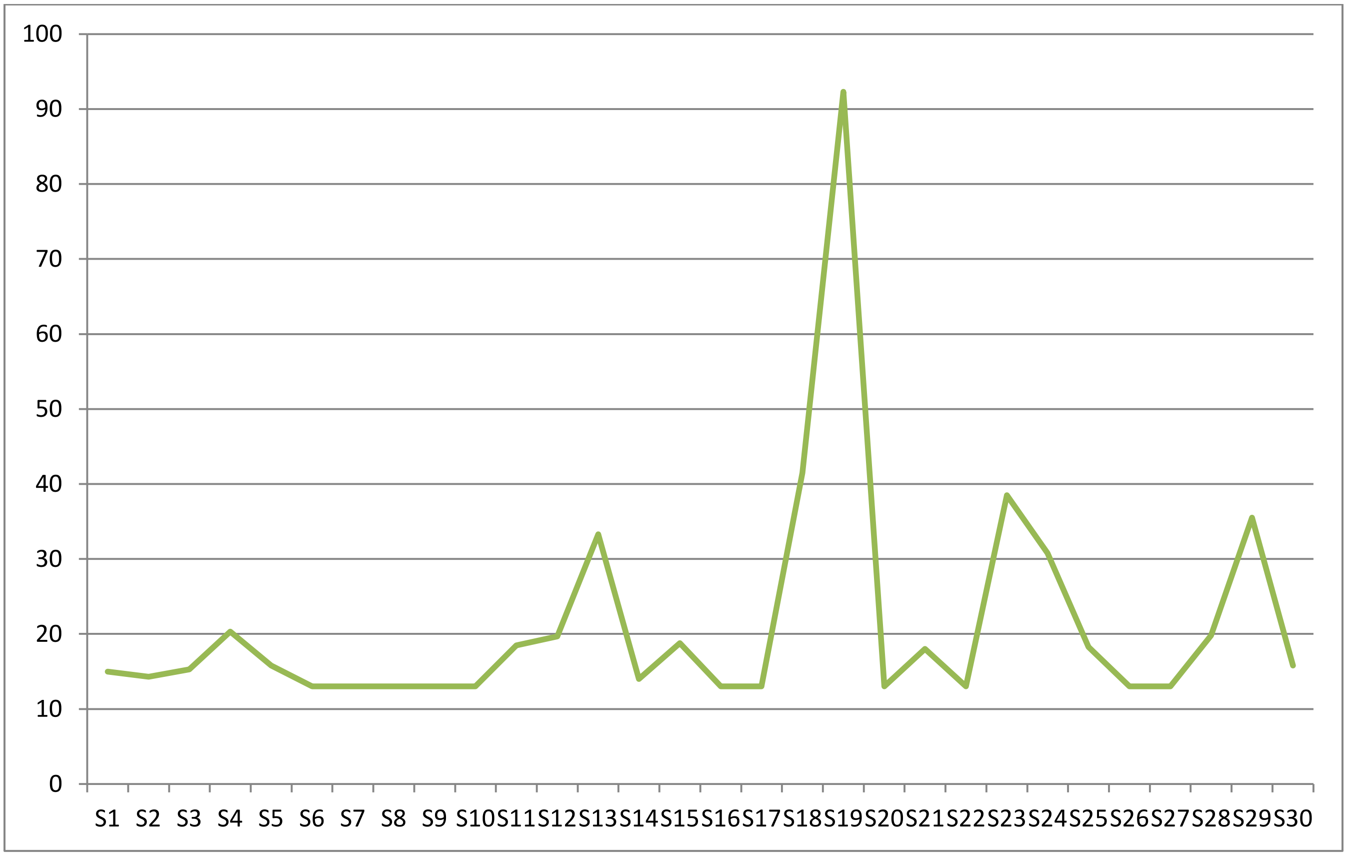


Figure 4.4: Cu concentrations (μg l^{-1}) in water samples of lower Nzoia River

4.2.1.5 Zinc

Mean zinc concentrations recorded for zinc in water was 212 μg $l^{-1}$with concentration ranging from 28.6 to 1399 (Table 4.3). Minimum concentration level of Zn was observed at sampling point S17 with the highest value being observed at S7. Exceptionally high levels of zinc were reported at sites 7, 24 and 29 (Figure 4.5). This could be a pointer to a high influx of zinc at these points from point sources upstream as well as deposition of waste from residential areas. The correlation between zinc content in sediment and water samples was not significant. Zinc is one of the essential micronutrients; however, at high levels Zn may inhibit plant metabolic functions as well as causing deficiencies in copper and manganese (Yadav, 2010). The levels of zinc reported were below those accepted by regulatory bodies.

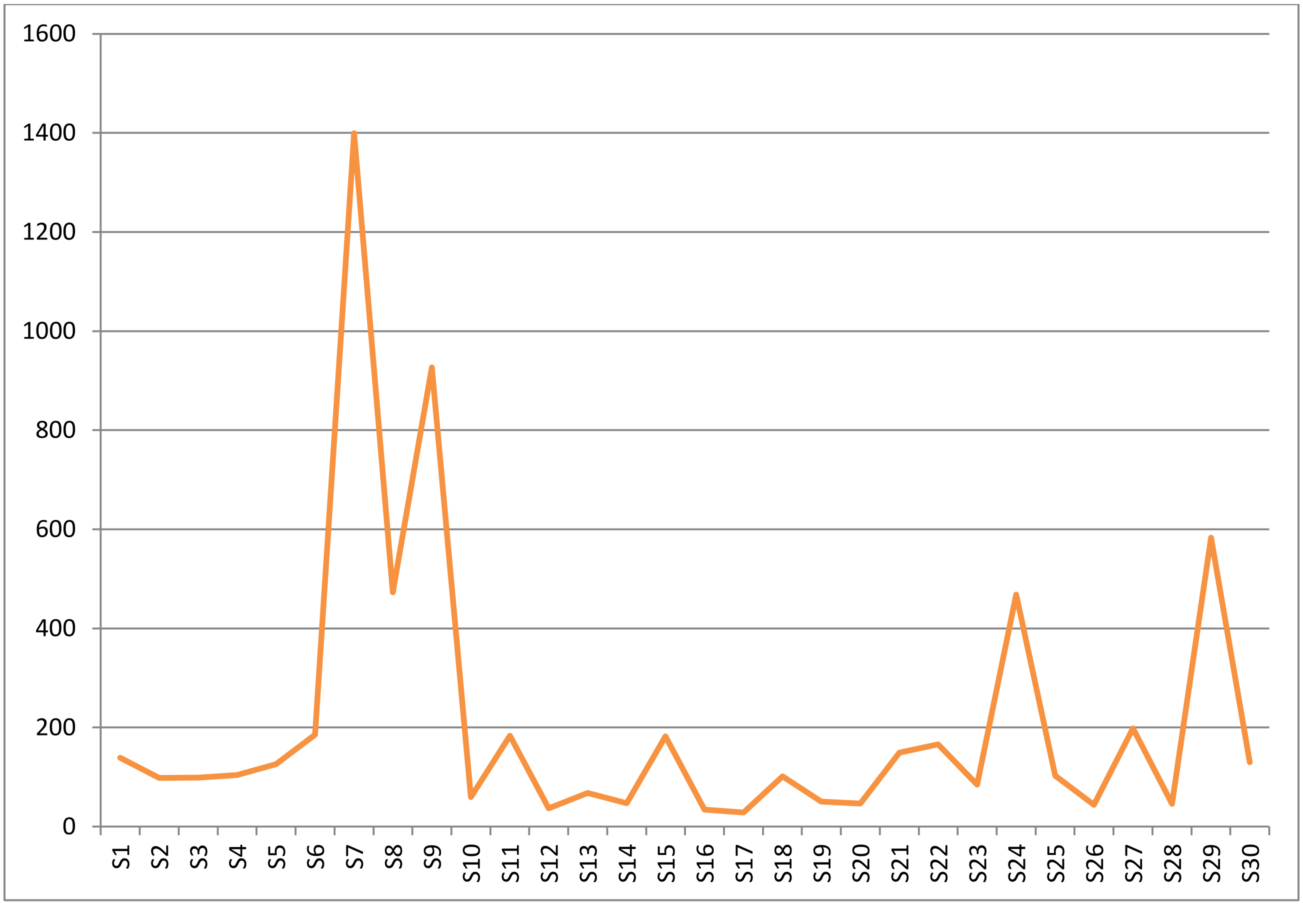


Figure 4.5: Zn concentrations (µg l^{-1}) in water samples of lower Nzoia River

4.2.1.6 Lead

The mean concentrations of lead in water samples was in the range of <10.0 - 24.2 µg l^{-1}(Table 4.2). This was way below the recommended WHO limits for drinking water (100 µg l^{-1}). However, most of the sampling points showed concentration levels that were below the detection limit of 10 µg l^{-1} (Figure 4.5). It was only at S8 and S15 that higher levels of Pb were recorded and it could be a clear indication that there is a pollutant source of Pb at that point or human activities that generate lead as one of the pollutants leading to high levels of lead concentrations in those areas.

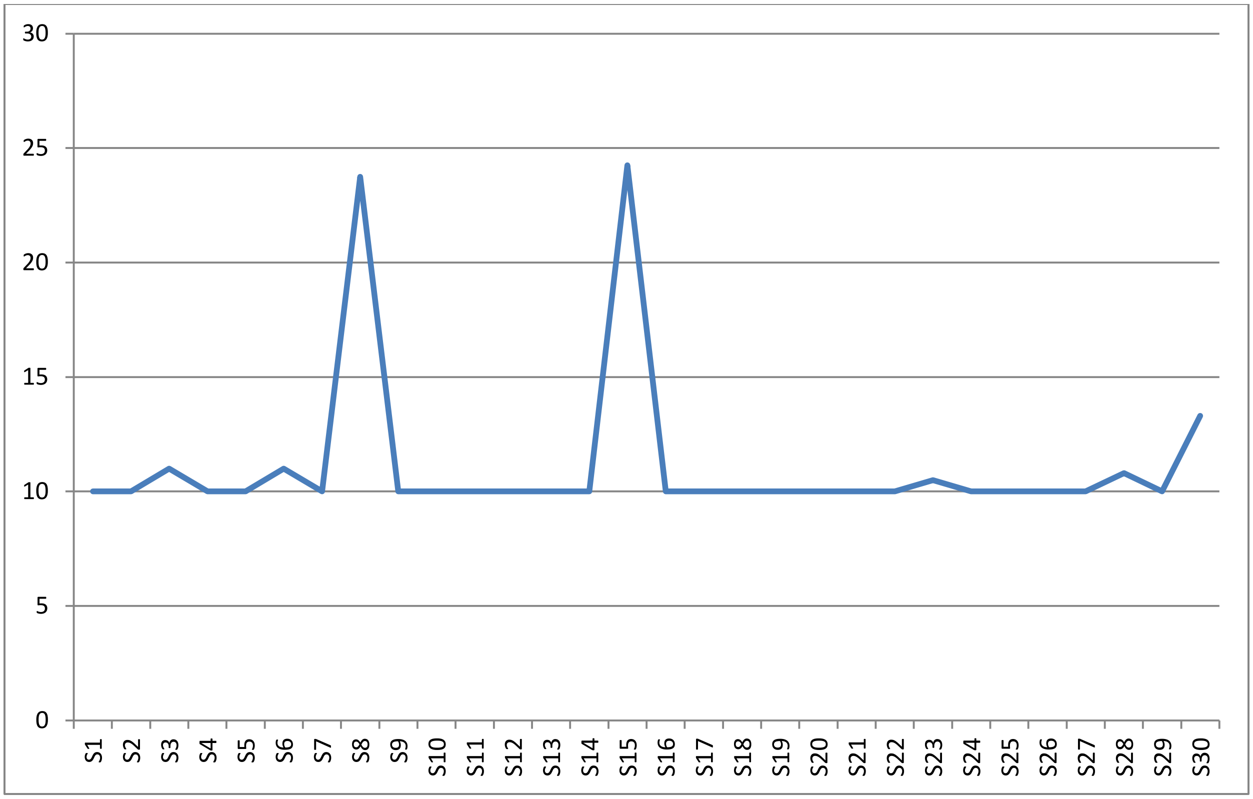


Figure 4.6: Pb concentrations (μg l^{-1}) in water samples of lower Nzoia River

4.2.2 Heavy metal concentrations in sediments

The mean heavy metal concentration levels and the ranges in sediment samples with their comparison to standard guidelines are presented in Table 4.4. The concentration levels for the metals were generally high than those reported for water a clear indication that indeed sediments act as sinks for heavy metals where they then accumulate. Generally concentration levels in water samples were in the order of Fe> Zn> Cd> Mn> Cu>Ni> Pb. The results will be discussed element by element.

Table 4.4 Comparison of metal (mg/kg) in sediments of Nzoia River with different standard values

Metal	Range	Mean	WHO	USEPA
Fe	27000 – 83000	46,190	-	30
Mn	520 – 2065	1163	-	30
Cu	250 – 390	331	25	16
Ni	260 – 510	389	20	16
V	150 – 380	176	-	-
Cr	85 – 3220	122	25	25
Zn	40 – 100	69	123	110
Pb	7 – 30	13	-	40
As	10 – 15	10	-	-

4.2.2.1 Manganese

The mean concentrations of manganese in sediments, the range as well as comparison to standard guidelines are presented in Table 4.4. In general the mean concentrations of manganese in sediments ranged from 519 mg kg^{-1} to 2064 mg kg^{-1} as shown in the table. The trends in concentration along the River Nzoia and variations with depth are shown in Figure 4.7, where the highest concentration was reported at site S21 (Rwambwa) and lowest at site S28 (Burangasi).

Manganese is mainly introduced into the aquatic ecosystem through anthropogenic sources such as municipal waste discharges, sewage sludge and combustion of fossil fuels (WHO, 2004). Rwambwa area is a semi-urban centre with a busy market not far off. The area has no proper drainage and sewerage system hence all wastes produced is washed into the river and thus the

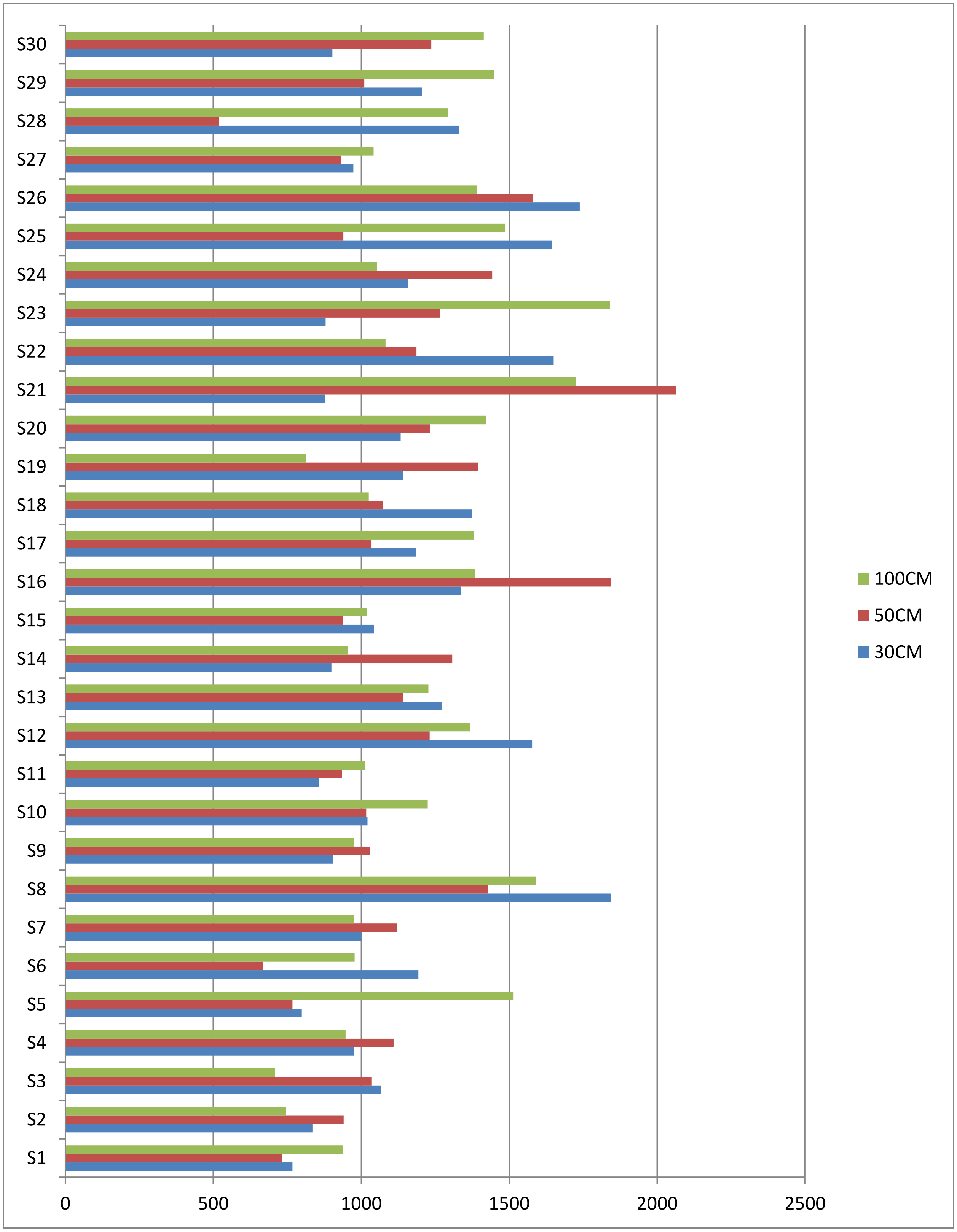


Figure 4.7 Spatial and vertical variation in Manganese concentration in mg kg^{-1} in sediment samples obtained from lower River Nzoia.

high levels of manganese in the area could be a pointer to the introduction of Mn from the urban area. Compounds containing Mn have found wide applications in fertilizers, fungicides and also in supplements for livestock and this could be other means by which it is introduced into the environment as locals embrace modern technology in agriculture.

The difference is not significant between the three sampling depths ($p > 0.05$). It is worth noting however that relatively higher concentrations were reported in lower sediment profiles. The mean values for the depths were at 30 cm 1138 mg kg^{-1}, at 50 cm 1152 mg kg^{-1} and at 100 cm 1199 mg kg^{-1}. The mean Mn level in the sampled points is 1163 mg kg^{-1}.

USEPA limits for sediments samples is 30 μg/g which were clearly exceeded by the results of this study indicating that the river sediments are polluted by Mn. The mean concentrations obtained were higher than those obtained by Lalah et al. (2008) and Mwamburi (2003) an indication to the fact that Mn as one of the heavy metals bioaccumuates in the ecosystem with time hence the reported increase over time. The value was also higher than the world average as well as for those obtained in Ganga and Euphrates River (Table 4.5)

,

4.2.2.2 Iron

The mean concentrations of iron in sediments, the range as well as comparison to standard guidelines are presented in Table 4.4. In general the mean concentrations of iron in sediments ranged from 2.7±0.1 w/w % to 8.3±0.2 w/w %. The trend along the river as well as the variations with depth are shown in Figure 4.8, where the highest concentration was reported in site S5 (Matawa Bridge) and lowest at site S28 (Buranagasi). The levels recorded for iron were generally high and this could be due to high concentrations resulting from weathering as well as anthropogenic inputs from municipalities. The other likely contributors of the high levels of Fe could be discharge from industries, agriculture and real estate through construction and demolition (Jitendra and Rachna, 2015).

Generally, an increase in mean iron concentration with depth was observed with there being no statistical difference ($p > 0.05$) between the three sediment profiles. This could be interpreted to

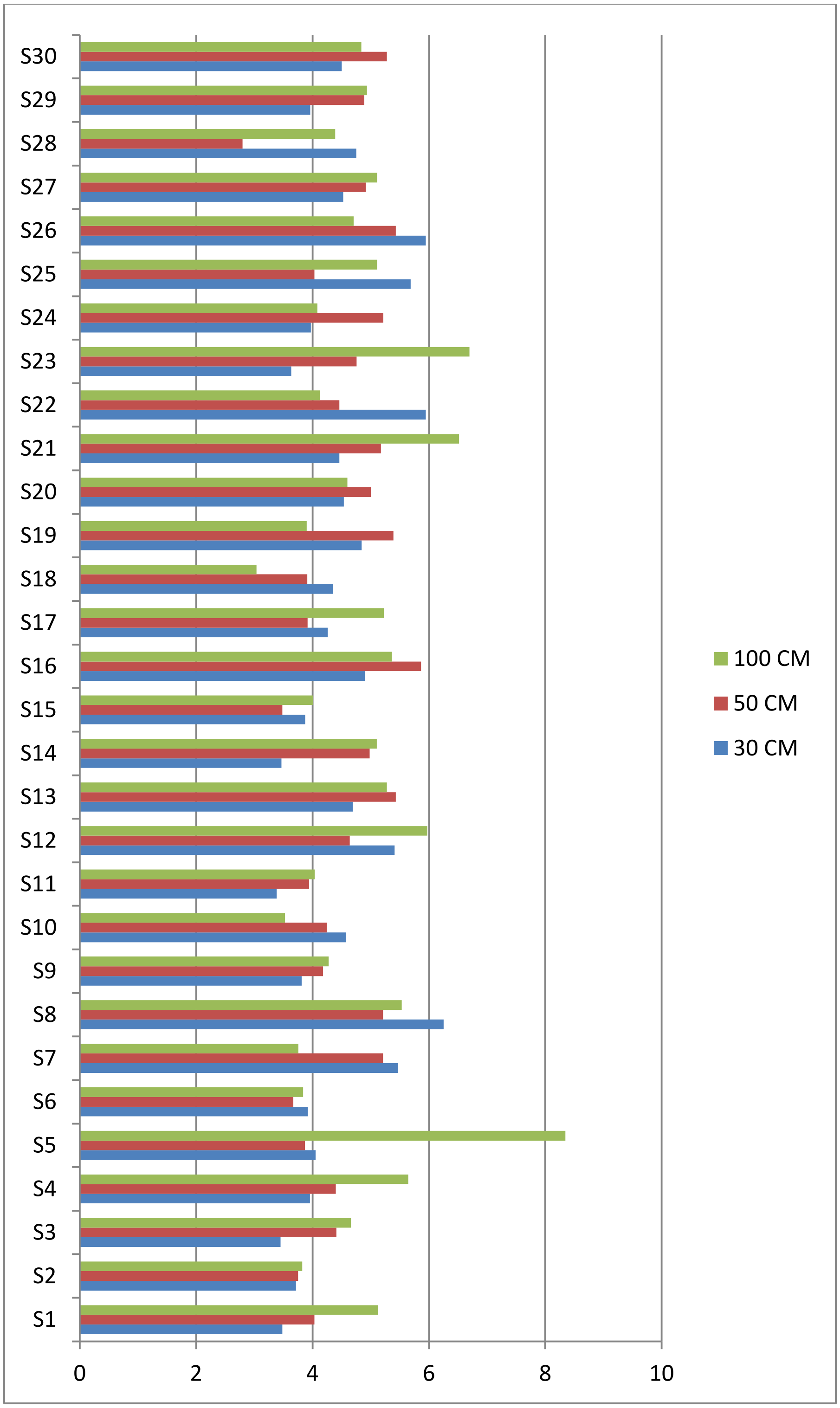


Figure 4.8 Spatial and vertical variation in iron concentration in sediment samples obtained from lower River Nzoia (w/w %)

mean that pollution levels have declined or probably there was a downward mobility of ions to lower sediment profiles. According to Maldonado (2008), iron concentration levels increases with depth and this was explained by the downward mobility of the metal ions. High iron concentration levels that are observed downstream could be as a result of deposition of pollutants which mainly occurs downstream of the river originating from farm inputs and industrial discharges into the river as well as flooding that is mostly witnessed in the area of study.

Acceptable values for Fe in sediments as set by USEPA are 30 μg/g (Table 4.4). Concentrations exceeding the guidelines could lead to haemo-chromatosis (Akan et al. 2010). The results obtained from this study exceeded the set limits indicating severe pollution of River Nzoia by Fe hence high chances for the above mentioned condition occurring in the area. The mean concentrations levels obtained were however lower than the world average (Table 4.5). The levels obtained were comparable to those obtained for Ganga River sediment by Jitendra and Rachna (2015) where the mean concentrations ranged from 21,924 to 41,170 μg/g but lower than those obtained for a similar study in River Euphrates (Table 4.5). The high concentrations of Fe were mainly due to anthropogenic input via urban- industrial release, waste from municipalities as well as agricultural activities.

4.2.2.3 Arsenic

The mean concentrations of arsenic in sediments, the range as well as comparison to standard guidelines are presented in Table 4.4. The concentrations of arsenic in sediments were in the range of < 10 to 15.2 mg kg^{-1}. The trends along the river as well as the variations with depth are shown in Figure 4.8, where the highest concentration was reported in site S10. However, most of the sampling points recorded concentration levels that were below detection limits which was 10 mg kg^{-1} with a significant difference in sampling points ($p < 0.05$) being noted. There is no significant variation in the reported mean arsenic concentrations with depth ($p > 0.05$). River Nzoia sediments can be regarded as not to be polluted by As since the values reported were lower than the set values by WHO which is at 27 μg g^{-1} (Table 4.4).

Figure 4.9 Spatial and vertical variation in arsenic concentration in sediment samples (mg kg^{-1}) obtained from lower River Nzoia

4.2.2.4 Copper

The mean concentrations of copper in sediments, the range as well as comparison to standard guidelines are presented in Table 4.4. The values range from 251 mg kg^{-1} to 392 mg kg^{-1}. The trends along the river as well as the variations with depth are shown in Figure 4.10. There is no significant difference between the three sampling depths ($p > 0.05$). From the results, it is evident that relatively higher concentrations were reported in lower sediment profiles. The mean values of Cu obtained at various depths were 328 mg kg^{-1} (30 cm), 333 mg kg^{-1} (50 cm) and 334 mg kg^{-1} (100 cm). The mean Cu level in the sampled points is 331 mg kg^{-1}.

Copper finds wide applications in electrical wiring, making alloys and pigments, pesticides, fungicides and in wood preservatives (Akan et al. 2010). It is also one of the ingredients in some food additives (Eaton, 2005; WHO, 2004) apart from being used in pipes for distributing waters so as to limit biological growth of bacteria (WHO, 2004). These might be pointers to the high concentrations reported for this study where Cu levels were exceptionally high as the above uses might lead to the increase in Cu levels from urban and agricultural areas. The high Cu levels could also be attributed to discharge of municipal and domestic waste as well as release of industrial effluents to the river and also the Jua kali (informal sector).

The values reported were higher than those set by WHO for survival of aquatic organisms which is 25 µg/g and USEPA (Table 4.4). The sediments of Nzoia River are therefore polluted with Cu. Mwamburi had also previously obtained high Cu levels for sediments sampled at Rwambwa Bridge while lower concentrations have been obtained for sediments in Euphrates River and Ganga River (Table 4.5)

4.2.2.5 Zinc

The mean concentrations of zinc in sediments, the range as well as comparison to standard guidelines are presented in Table 4.4. The mean concentrations of zinc in sediment samples ranged from 42.7 mg kg^{-1} to 99.8 mg kg^{-1} with a mean concentration of 69.0 mg kg^{-1}. The trends along the river as well as the variations with depth are shown in Figure 4.11.The highest and lowest concentrations were recorded at S16 and S28 respectively indicating a significant

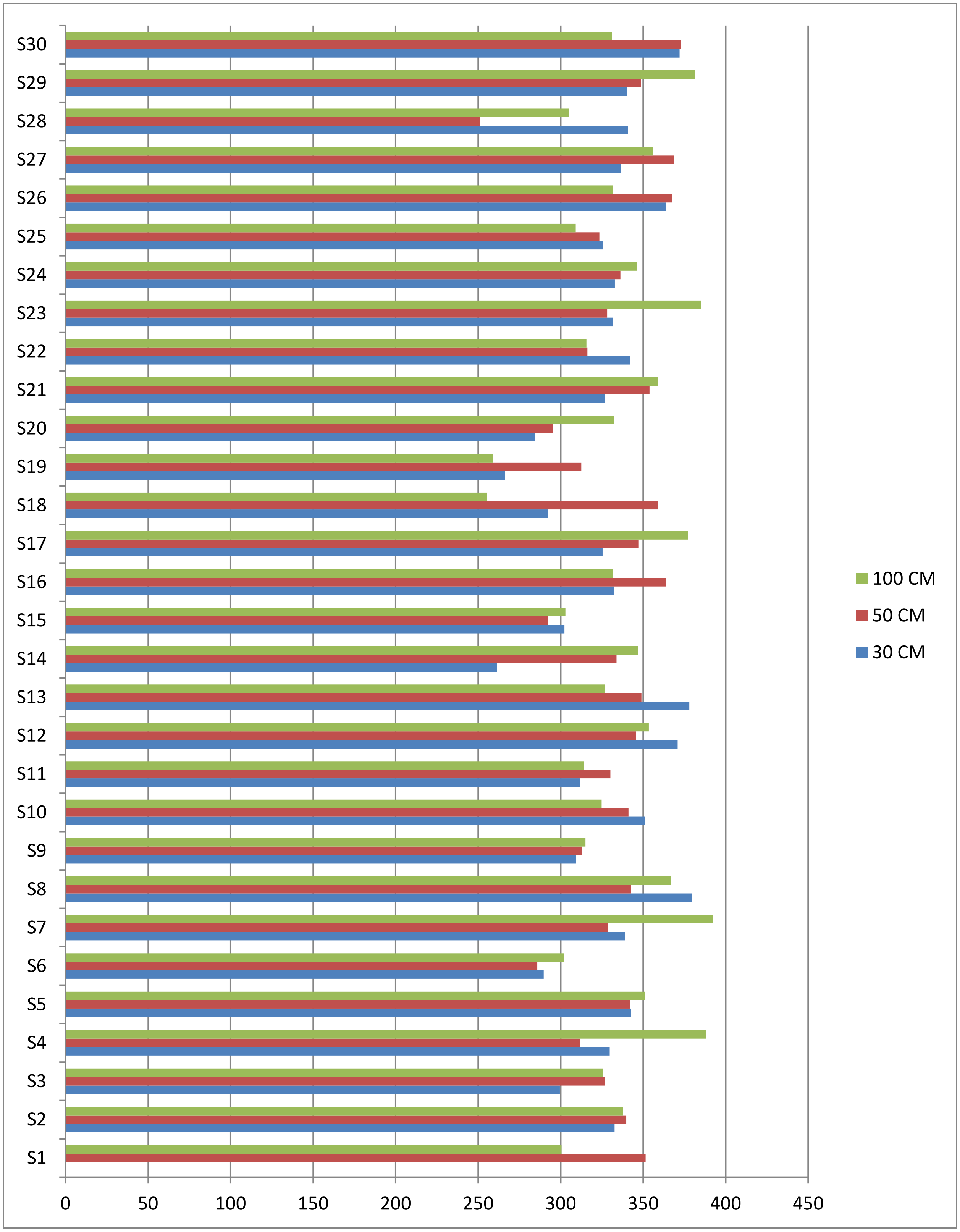


Figure 4.10 Spatial and vertical variation in copper concentration in sediment samples (mg kg^{-1}) obtained from lower River Nzoia

difference between the sampling points ($p < 0.05$). The variation of total Zn concentration with depth was however not significant ($p > 0.05$). The mean concentrations with depth were 67.9 mg kg^{-1}, 71.1 mg kg^{-1} and 68.1 mg kg^{-1} for 30, 50 and 100 centimeters respectively.

The levels of zinc in the sediment samples were below the WHO and USEPA guidelines (Table 4.4) indicating that River Nzoia sediments are not polluted with Zn. The average value obtained for Zn was higher than the average background levels (63.5 µg/g) reported for Liaoning Province in China (Wang et al, 2000). The mean levels reported were comparable to those obtained for a similar study on Ganga River but way much below those for Buriganga River (Table 4.5). The concentrations of Zn in this study were also lower than those reported for Almendares River, Cuba (Olivares-Rieumont et al., 2005) which was (86.1–708.8 µg g^{-1}). The Almendares River is mainly polluted by industrial and agricultural waste (Romic and Romic, 2003). The mean concentration is also lower than the world average value for Zn (Table 4.5)

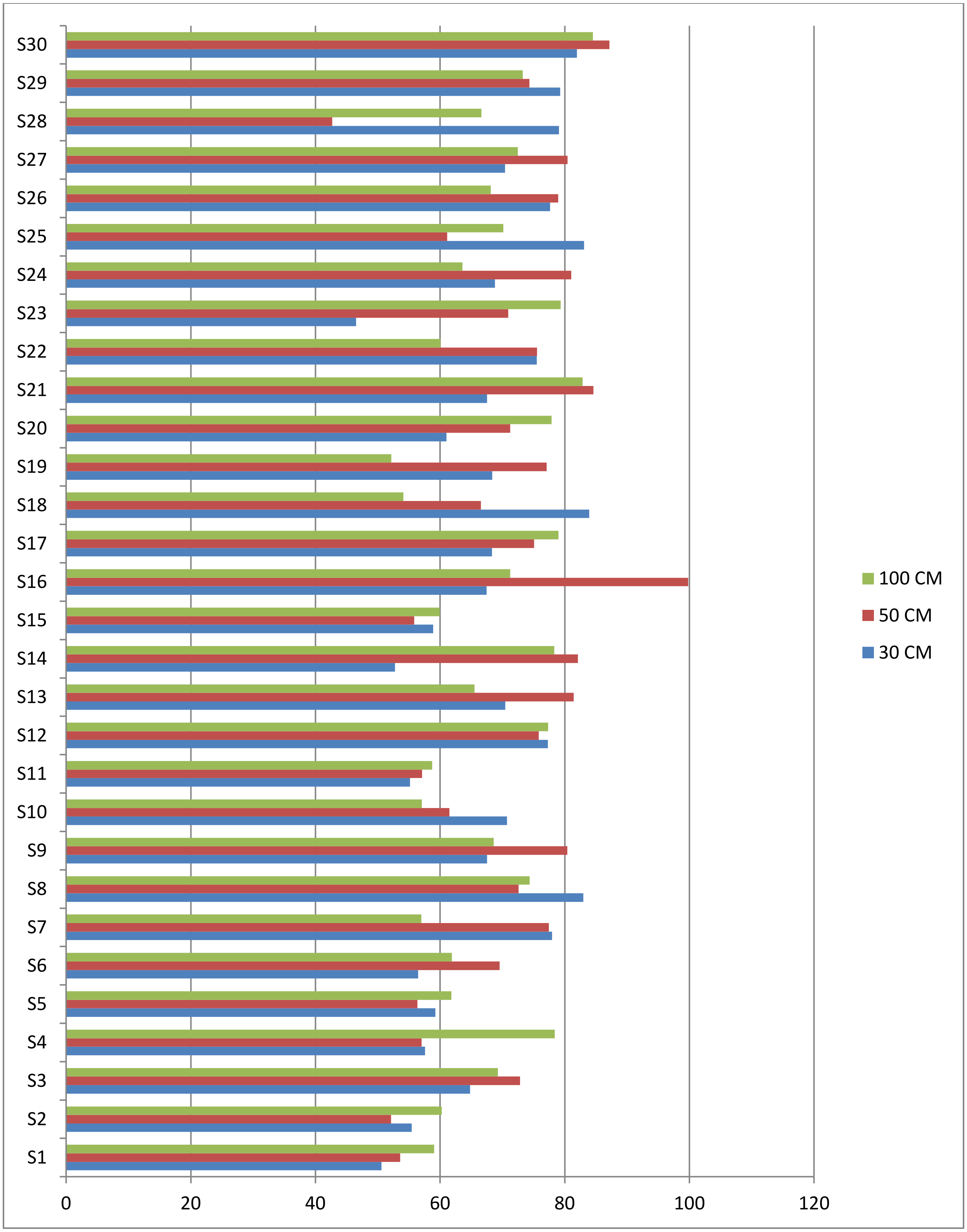


Figure 4.11 Spatial and vertical variation in zinc concentration in sediment samples (mg kg^{-1}) obtained from lower River Nzoia

4.2.2.6 Lead

The mean concentrations of lead in sediments, the range as well as comparison to standard guidelines for the areas covered by this project are presented in Table 4.4. The concentrations of Pb in sediments for the areas covered by this project ranged from 6.7 - 26.0 mg kg^{-1}. The trends along the river as well as the variations with depth are shown in Figure 4.12. The mean concentrations reported with depth are 13.1 mg kg^{-1}, 14.1 mg kg^{-1} and 13.2 mg kg^{-1} for 30, 50 and 100 centimeters respectively. The mean lead concentration of lead in the area of study was 13.5 mg kg^{-1}. Highest values were determined in sediments collected from sampling sites S21 and S16. This could be attributed to deposition of solid waste into the river within the locality of the said areas. There was a significant difference in Pb concentrations between sampling points ($p < 0.05$).

There is no significant variation in the reported mean lead concentrations with depth ($p > 0.05$). A similar study by Oyekunle et al., (2013) reported high levels of Pb in the sediments and this was mainly due to input from nearby human residences within the proximity of the river that dump solid waste to the river as well as erosion that leaches dissolved metal to the river. A decrease in concentration downstream was reported which was attributed to dilution in the river as it widens and the volume increase. The average value obtained for Pb was lower than the average background levels (21.4 μg/g) reported for Liaoning Province in China (Wang et al., 2000) which is a major recipient of municipal waste.

Higher levels for Pb than those for this study have also been reported in Ganga and Euphrates rivers (Table 4.5). This is because Pb is mainly found with Fe–Mn oxide fraction where it is highly retained in sediments (Jitendra and Rachna, 2015). The man - made sources for Pb in the environment include household sewage, waste from industries as well as emissions from vehicles. In comparison with USEPA (Table 4.4) sediment quality guidelines, the mean Pb concentration did not exceed the guidelines showing that Nzoia River sediments are not polluted by Pb. The concentration was also below the world average concentration for Pb (Table 4.5).

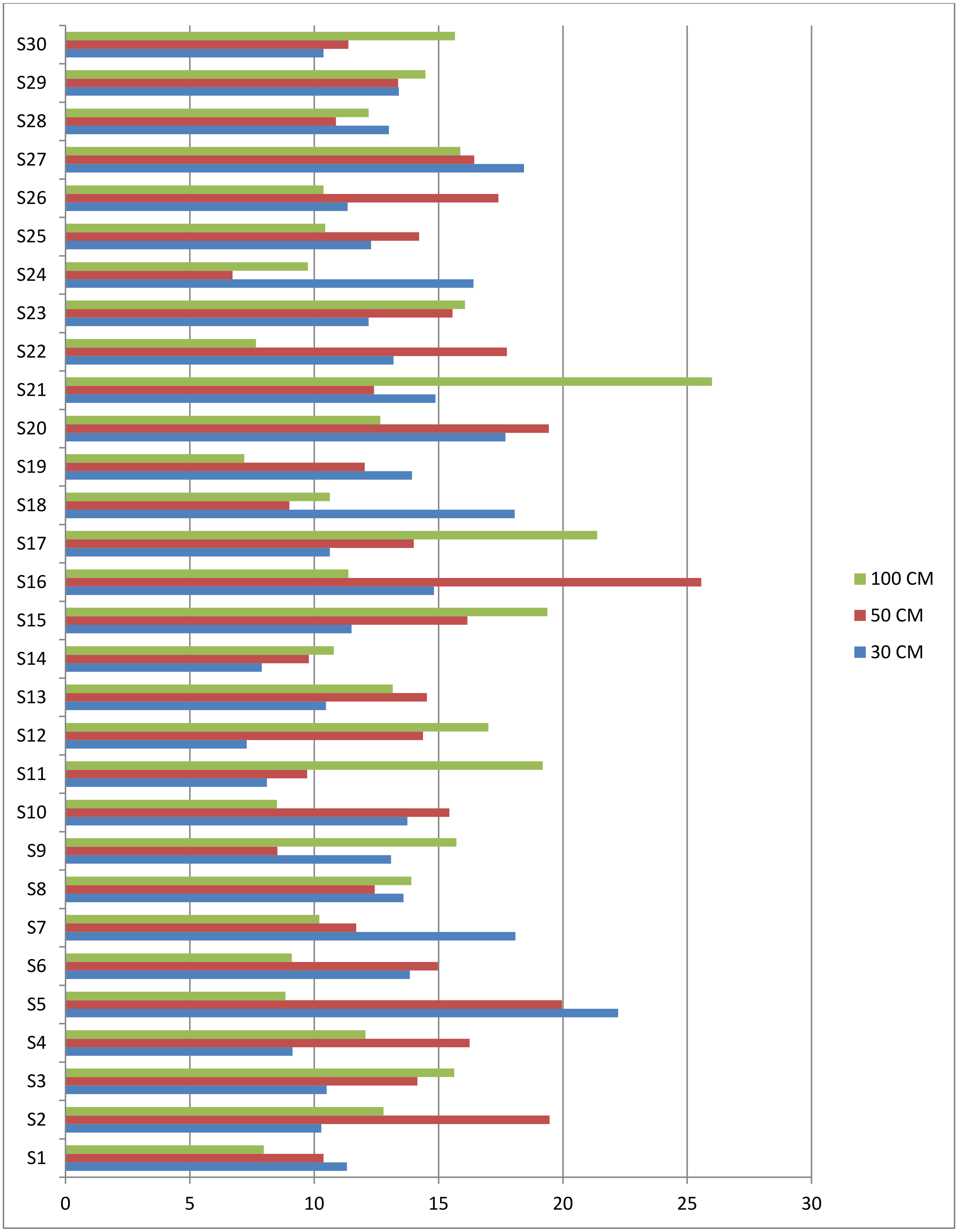


Figure 4.12 Spatial and vertical variation in lead concentration in sediment samples (mg kg^{-1}) obtained from lower River Nzoia

4.2.2.7 Vanadium

The mean concentrations of vanadium in sediments, the range as well as comparison to standard guidelines for the areas covered by this project are presented in Table 4.4. The mean concentrations of vanadium in sediments were in the range of < 150 mg kg^{-1} to 384 mg kg^{-1}. The trends along the river as well as the variations with depth are shown in Figure 4.13. The highest concentration for vanadium was recorded at sampling site S26 which was then followed by S13; however, some of the sampling points recorded concentration levels that were below detection limits of 150 mg kg^{-1} with a significant difference being observed between the sampling points ($p < 0.05$).

There is no significant variation in the reported mean vanadium concentrations with depth ($p > 0.05$). The concentration of vanadium in water samples was, however, below the detection limit of <53 µg l^{-1}. This could imply a possibility of accumulation of vanadium in the sediment over a period of time.

4.2.2.8 Chromium

The mean concentrations of chromium in sediments, the range as well as comparison to standard guidelines for the areas covered by this project are presented in Table 4.4. The mean concentrations of chromium in sediments were in the range of < 85.0 mg kg^{-1} to 322 mg kg^{-1}. The trends along the river as well as the variations with depth are shown in Figure 4.14. The highest concentration for chromium was recorded at sampling site S23 which was then followed by S5, however, some of the sampling points recorded concentration levels that were below detection limits of 85 mg kg^{-1} with a significant difference in sampling points ($p < 0.05$) being noted.

There is no significant variation in the reported mean chromium concentrations with depth ($p > 0.05$). The mean concentrations reported with depth were 110 mg kg^{-1}, 115 mg kg^{-1} and 141 mg kg^{-1} for 30, 50 and 100 centimeters respectively indicating a general increase in concentration with depth. The mean chromium concentration in the area of study was 122 mg kg^{-1}.

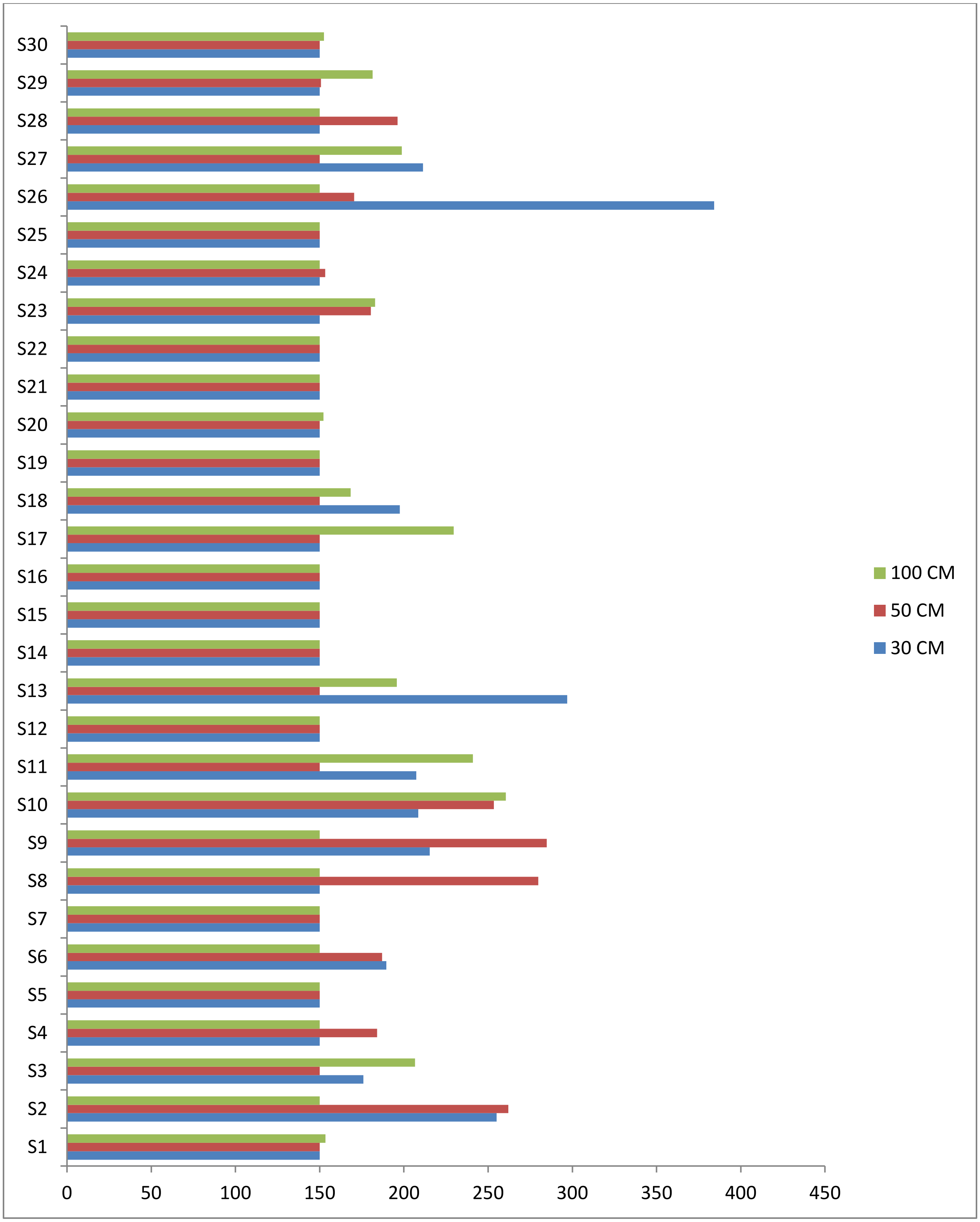


Figure 4.13 Spatial and vertical variation in vanadium concentration in sediment samples (mg kg^{-1}) obtained from lower River Nzoia

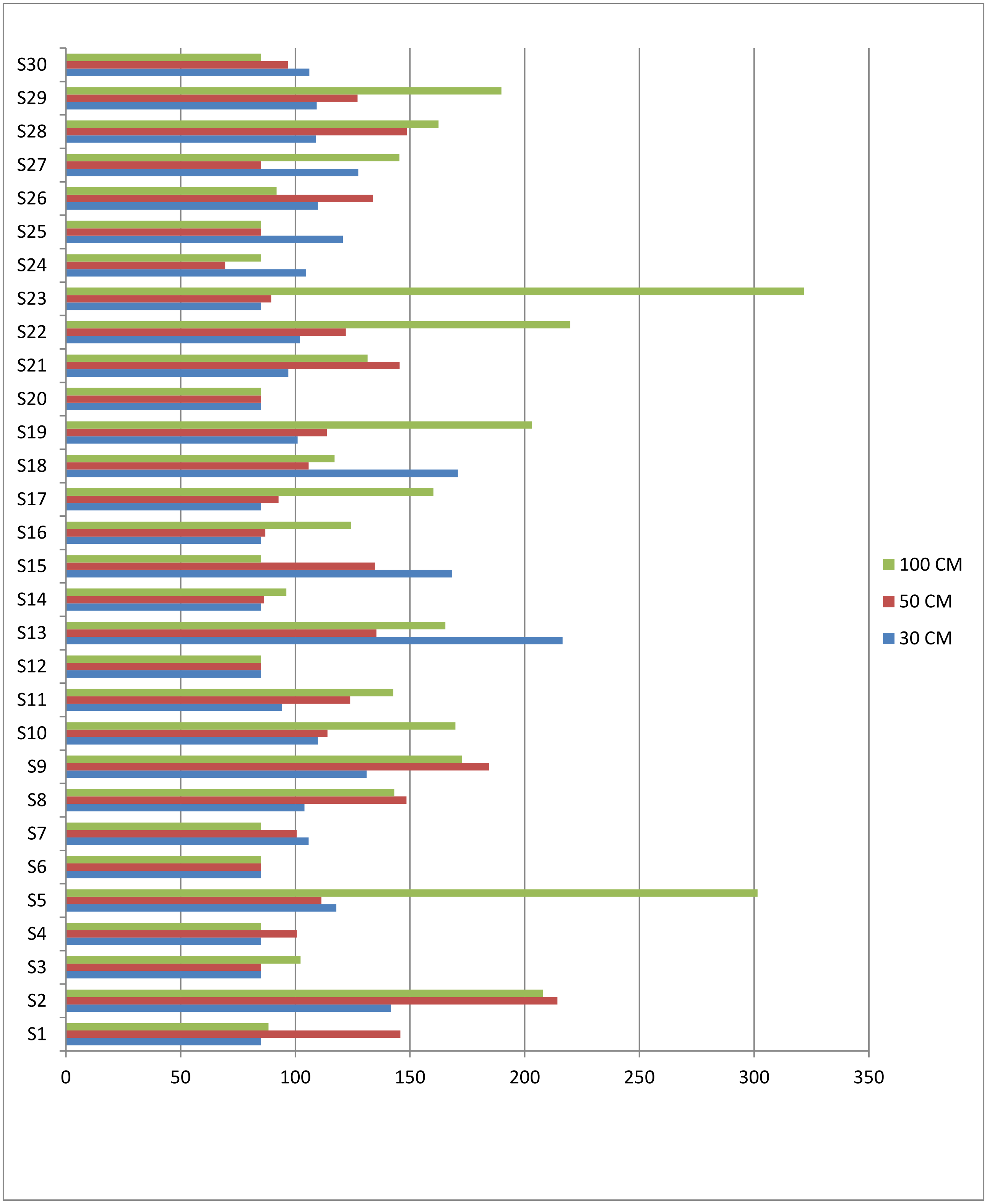


Figure 4.14 Spatial and vertical variation in chromium concentration in sediment samples (mg kg^{-1}) obtained from lower River Nzoia

Based on WHO sediment quality guidelines, River Nzoia sediments are contaminated with Cr. These reported high concentrations might lead to allergic dermatitis (USEPA, 2001).

4.2.2.9 Nickel

Nickel occurs naturally at very low levels in the environment and is basically essential in small doses but is toxic when the allowable limits are exceeded (Wuana and Okieiman, 2011). The mean concentrations of nickel in sediments, the range as well as comparison to standard guidelines for the areas covered by this project are presented in Table 4.4. The concentration ranged from 262 mg kg^{-1} to 509 mg kg^{-1}. The trends along the river as well as the variations with depth are shown in Figure 4.15. Highest values were determined in sediments collected from sampling sites S23, with the least concentration being at S7. There was a significant difference in Ni concentrations between sampling points ($p < 0.05$).

There is no significant variation in the reported mean nickel concentrations with depth ($p > 0.05$). The mean concentrations reported with depth are 389 mg kg^{-1}, 391 mg kg^{-1} and 387 mg kg^{-1} for 30, 50 and 100 centimeters respectively. The mean nickel concentration of lead in the area of study was 389 mg kg^{-1}. This value was higher than both the WHO and USEPA sediment quality guidelines (Table 4.4) a clear indication that the sediments of lower Nzoia River are polluted by Ni. The value for mean Ni concentration obtained was higher than those obtained for similar studies in rivers Ganga and Euphrates with the value being higher than the world average value for Ni (Table 4.5).

Nickel has a high chance of being introduced into the aquatic system from urban areas. This is due to the fact that it is used in wide applications such as in stainless steel, Ni-Cd batteries, coins and as well as electroplating. This could therefore possibly explain the high levels obtained in this study especially from disposal of Ni-Cd batteries.

However, most of the sampling sites (97%, n=30) recorded concentration levels below 20μg l^{-1}, which is the regulatory limit for WHO with respect to nickel in drinking water. Thus, Nzoia waters are not significantly contaminated with nickel. However, there was no significant correlation between nickel concentrations in sediments and water samples.

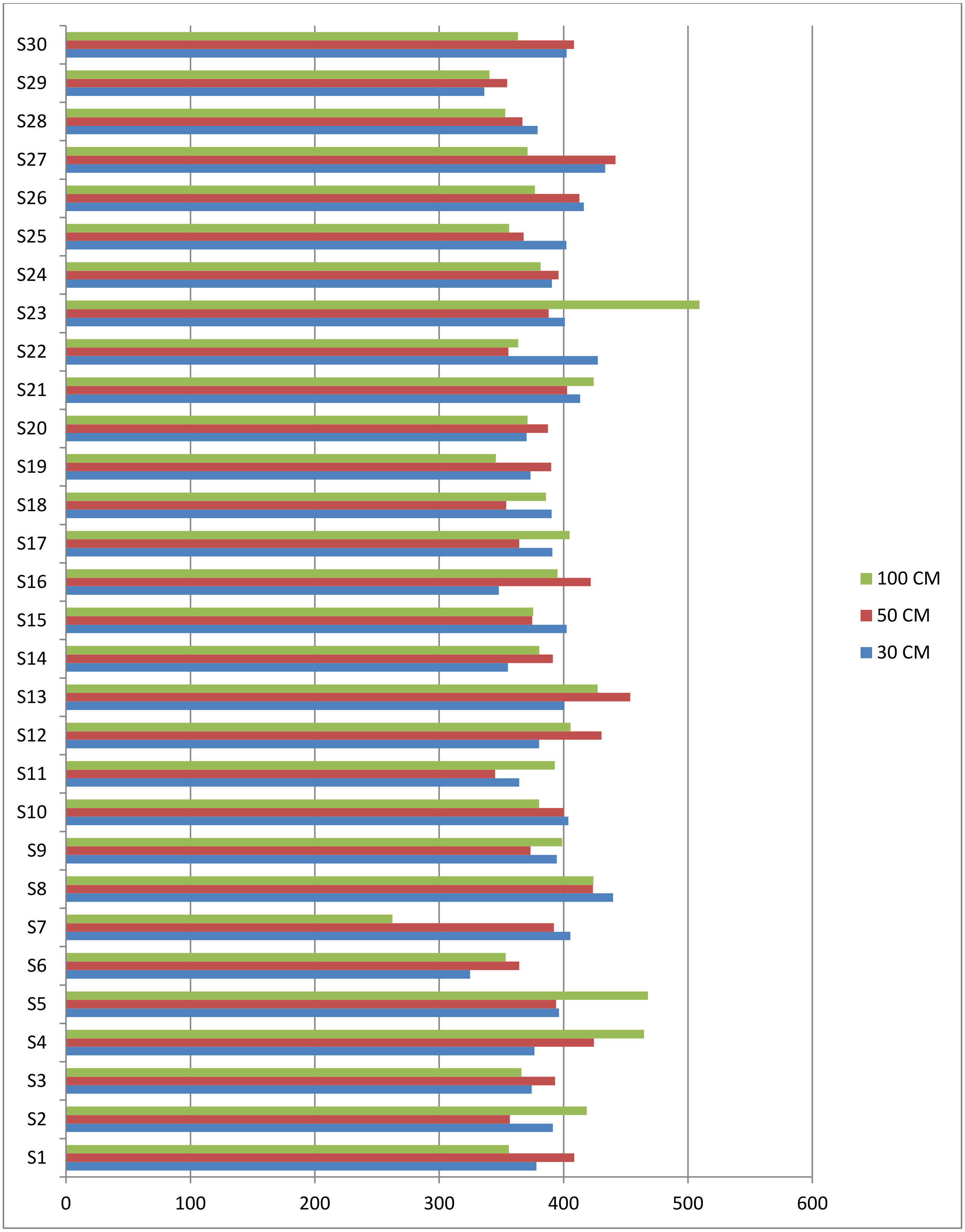


Figure 4.15 Spatial and vertical variation in nickel concentration in sediment samples (mg kg^{-1}) obtained from lower River Nzoia

Discussions

A comparison of the results of this study was done with the previous studies that had been done at some selected points along the river. The values were also compared to other rivers of the world as well as the world average concentrations for the heavy metals as represented in Table 4.5

Table 4.5 Concentrations of heavy metals in the Nzoia River sediments (mg/kg) compared to other local studies, other rivers and world river sediment averages.

River and location	Mn	Fe	Cu	Zn	Pb	As	Cr	V	Ni	Reference
R. Nzoia(Kenya)	1163	46,190	331	69.2	13.6	10.4	122	176	389	Present study
R. Nzoia(Kenya)	838	-	17.5	76.0	15.6	-	3.9	-	-	Lalah et al. (2008)
R. Nzoia(Kenya)	680	20,100	110	3.1	1.9	-	17	-	-	Mwamburi (2003)
Buriganga (Bangladesh)	-	-	184	502	79.8	-	101	-	-	Saha aand Hossain (2010)
Ganga (India)	372	31,989	29.8	67.8	26.7	-	69.9	-	26.7	Jitendra and Rachna (2015)
Euphrates (Iraq)	228	2250	18.9	48.0	22.6	-	58.4	-	67.1	Salah et al. (2012)
World average	975	57,406	123	303	231	-	126	-	102	Martin and Meybeck (1979)

The values obtained for Zn and Cu in this study were found to be higher than those for industrial soils; Zn (44.5 ± 4.1 - 134 ± 10.5) and Cu (21.4 ± 2.0 – 102 ± 10) (Olajire et al., 2007) with the levels reported for Pb being lower. The values obtained for Mn, Cu, Ni, Zn and Pb were lower than those for Asunle River in Nigeria whose mean concentrations were Mn (645 – 3573 μg/g), Cu (88 – 493 μg/g), Ni (265 – 1515 μg/g), Zn (132 – 431 μg/g) and Pb (10 – 34 μg/g). The high concentrations were as a result pollutants being leached into the river owing to its proximity to a dumpsite (Oyenkule et al., 2013). However, the levels obtained for Ni, Pb, and Zn in the lower Nzoia River were higher than the values (Ni, 16.6 ± 5.6 µg/g; Pb, 22.4 ± 10.5 µg/g; Zn, 74.4 ± 29.8 µg/g;) that were reported for the sediments of Waji River which was contaminated with industrial effluents (Leton and Akpila, 2008). This implies that there could be other sources of anthropogenic input into the river such as agricultural discharge. The differences in the geochemistry of the two rivers i.e Nzoia and Waji could also have resulted to the differences in concentrations reported.

The high levels obtained for Mn, Cu, Cr, Zn and Pb are in accordance with similar results reported by Mohamed et al., (2010) for a similar study in the Nile Delta in Egypt. The concentrations were due to agricultural, domestic and industrial effluent discharge a problem that is replicated with the Nzoia River which ironically drains its water to Lake Victoria which is a source of River Nile and this could explain the high concentrations that have been obtained in this study.

Oyenkule et al., (2013) reported a decrease in concentrations of metals in water downstream, an observation he attributed to increase in dilution owing to increase in the volume of water in the river and also absence of point pollutant sources downstream. They also noted that the settling of the metals in the sediments could have led to the decline in concentration levels. The results are consistent with the results of this study as most of the sites towards the mouth of the river did not record higher levels of contaminants. The levels of metals in surface water was also higher than those in sediments as reported by Kennish (1992) indicating that the dissolution of metals in water is lower than in sediments. It also confirms the reported result that sediments act as hosts for metals as well as allowing for the detection of heavy metals whose levels could be low in the water column (Aderinola et al., 2009). The results reported in this study show similar consistency to the studies highlighted in the previous section.

A study by Omwoma et al., (2010) on impact of fertilizers on heavy metal in the Nzoia Nucleus reported that the use of fertilizers was responsible for introduction of heavy metals to the environment. An analysis of fertilizers applied in the farms revealed presence of some heavy metals though not beyond permissible limits. Similar results have been obtained elsewhere notably by Oliver (2004) and Pekey et al., (2004). This could be a pointer to the cause for high concentrations of heavy metals obtained in this study as most of these contaminants are mostly washed and discharged to the river or leached where they bioaccumulate mostly from use of agricultural inputs used in adjacent.

Concentrations values reported earlier by Lalah et al., (2008) for heavy metal concentrations in surface water for the Nzoia River in μg l^{-1} were Cu (20.0 ± 1.99), Mn (50 ± 10) , Ni (13.0 ± 2.34), Pb (15.0 ± 1.44) and Zn (33.0 ± 11). The values are comparable to the mean values obtained for this study indicating there has been no disturbing factor in the concentration of heavy metals in the waters. Similar results have also been obtained by Okonkwo et al., (2005) for rivers in South Africa and Demirak et al., (2006) for studies in streams in Turkey.

In the same study by Lalah et al., (2008) the results reported for sediments in mg kg^{-1} were Cr (3.90 ± 0.44), Cu (17.54 ± 5.41), Mn (838.1 ± 100.4), Ni (25.34 ± 5.44), Pb (15.59 ± 2.11) and Zn (76.01 ± 18.4). The values for Mn, Zn and Pb are comparable to those obtained for the current study while those for Cr, Cu and Ni were lower than the current values and this could be an indication of an influx of these contaminants to the environment owing to the high values reported for them by the current study or an increase in the use of substances containing these pollutants over the last decade. The elevated concentrations of Cu could be due to the use of copper compounds in treatment of wood as well as fungicides and pesticides applied in farms adjacent to the river. However, the values are lower than those for river Kisat (Lalah et al., 2008) which is mainly polluted by sewage and industrial effluent owing to its proximity to the city centre where most of its pollutants originate.

A study by Mutuku et al., (2014) reported concentrations that were lower than those reported in the current study. The sampling was done at the mouth of river Nzoia where it enters Lake Victoria. The low concentrations could be due to dilution of the contaminants as the river widens and increases in volume.

Akan et al., (2010) reported that an increase in concentration levels of heavy metals in River Ngada in Nigeria was due to the discharge of waste water into the river from a treatment plant. According to Akali et al., (2011), Mumias Sugar Company discharges water into the Nzoia River that is a likely carrier of pollutants. This can explain the fact that high concentration of the elements were found in sites that were not far off from the company. The mean concentrations were determined to increase with depth with the results being comparable to those obtained by Akan et al., (2010) who reported that concentrations increased with depth due to leaching and Stephen et al., (2001) who reported that sediments act as sinks for pollutants.

In a study by Saeed et al., (2014) where they investigated the effect of waste disposal into Tembi River, an increase in concentration of pollutants downstream beyond where the pollutants were introduced was observed thus could be a pointer to the high concentration levels which were reported downstream as the river approaches Lake Victoria. Similar study on Warri River by Wogu and Okaka (2011) reported that the concentrations were higher than the set guidelines and this was mainly due to the fact that it received industrial, agricultural and urban sewage. River Nzoia basin has no well developed sewerage system and thus receives urban waste coupled with agricultural waste due to the extensive agricultural activities that occurs within the basin and this compares to the rivers stated previously which also receive urban and agricultural effluents hence the high concentrations that exceed the set guidelines.

Assessment of heavy metals contamination

This was done by comparing the sediment quality with the guidelines proposed by USEPA with the criteria shown in table 4.6.

Table 4.6 USEPA guidelines for sediments contamination (mg/kg dry weights)

Metal	**Not contaminated**	**Moderately contaminated**	**Heavily contaminated**	**Present study concentrations**
Pb	<40	40-60	>60	7-26
Cd	…..	…	>6	……
Cr	<25	25-75	>75	85-320
Cu	<25	25-50	>50	250-390
Zn	<90	90-200	>200	40-100

According to USEPA guidelines, the sediments of River Nzoia are not polluted by Pb, moderately polluted by Zn and heavily polluted with Cu and Cr hence Cu and Cr are responsible for a large amount of heavy metal pollution while Zn is moderately responsible.

CHAPTER

FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Sediment samples collected from lower Nzoia contained the following elements Mn, Fe, Cu, Zn, Pb, Ni, V and Cr. The mean concentrations (mg kg^{-1}) in sediments ranged Mn (519- 2064), Fe (27000 – 83000), Cu (251 – 392), Zn (43 – 100), Pb (7 – 26), Ni (262 – 509), V (150 – 384), Cr (85 – 328) and As (10 – 15).

In general, there was an increase in metal concentrations downstream with variation between sampling points being significant ($p < 0.05$). This could mainly be due to the influx of the metals as one move downstream. The area also experiences perennial flooding and this could also be a major contributor to the increase in concentration levels downstream.

The levels recorded for drinking water were within acceptable WHO limits except for a few exceptions. High levels of concentrations were observed for copper in water samples and consequently the concentrations were also higher in sediment samples.

Local water pollution was, however, found and mainly due to effluent discharge and this could result to deterioration of the water quality posing a risk to aquatic animals as well as human beings who consume the water.

USEPA guidelines were applied to assess the degree of contamination. The Nzoia sediments were determined to be contaminated with Mn, Fe, Cu, Cr and Ni with Pb and Zn being below the guidelines set by USEPA.

5.2 Recommendations

1. Concentrations of water beyond regulatory limits for drinking water were observed. Therefore there is need for greater public awareness to educate the communities that use the water for domestic purposes.
2. Pollution mitigation measures such as the one by NRBMI need to be enhanced to reduce the concentration levels of metals by relevant bodies such as NEMA.
3. Soils adjacent to the river bed need to be analyzed so as to have a quantitative knowledge of their effect on the concentrations reported in sediments.
4. The analysis should be done both for the dry and wet season to show the effects of water evaporation on concentration of heavy metals so as to have a comparative analysis of how the seasons affect concentrations of heavy metals in Nzoia River.
5. The results obtained from this study indicate that focus should be on element re- mobilization since the high levels of metals in the sediments could find their way to the water column hence need to mitigate such kind of pollution and thus the need for continuous studies of Nzoia river water.

REFERENCES

Abdel-Baki AS, Dkhil MA, Al-Quraishy S (2011) Bioaccumulation of some heavy metals in tilapia fish relevant to their concentration in water and sediment of Wadi Hanifah, Saudi Arabia. African Journal of Biotechnology. 10:2541–2547.

Achoka, DJ (1998) Levels of the physico-chemical parameters in the liquid effluents from Pan paper mills at Webuye and in river Nzoia. Doctoral thesis at Moi University Eldoret, Kenya.

Ademoroti CMA, (1996) Environmental Chemistry and Toxicology, Fodulex press Ltd., Ibadan.

Aderonila, OJ, Clarke EO, Olarimonye OM, Ksemiju, V and Anatekhai MA (2009) Heavy metals in surface water, sediments, fish and periwinkles of Lagos Lagoon- American – Eurasian J. Agric and Environ. Sci, 5(5): 609 – 617.

Adriano DC, (2001) Trace Elements in Terrestrial Environments, Springer Verlag, New York, NY.

Agency for Toxic Substances and Disease Registry (ATSDR), (2004) Toxicological profile for Copper. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

Akali N Moses; Nyongesa N Destaings; Neyole EMasinde and Miima, JB (2011) Effluent Discharge by Mumias Sugar Company in Kenya: An Empirical Investigation of the Pollution of River Nzoia Sacha Journal of Environmental Studies, Volume 1 Number 1; 1-30.

Akan JC, Abdulrahman FI, Sodipo OA, Ochanya AE and Askira YK (2010) Heavy metals in sediments from River Ngada, Maiduguri Metropolis, Borno State, Nigeria Journal of Environmental Chemistry and Ecotoxicology Vol. 2(9), 131-140.

Bakare-Odunola MT (2005) Determination of some metallic impurities present in soft drinks marketed in Nigeria. The Nig. J. Pharm., 4(1): 51-54.

Bazrafshan E, Ferdos KM, Morteza E, Gholam RE and Amir HM (2015): Concentration of heavy metals in surface water and sediments of Chah Nimeh water reservoir in Sistan and Baluchestan province, Iran, Desalination and Water Treatment, DOI: 10.1080/19443994.2015.1027958

Banks EC, Ferretti LE and Shucard DW (1997) Effects of low-level lead exposure on cognitive function in children: A review of behavioral, neuropsychological and biological evidence. Neurotoxicology 18: 237-81.

Binning K and Baird D (2001) Survey of heavy metals in the sediments of the Swatkops River estuary, Port Elizabeth South Africa. Water SA, 24: 461-466.

Birch GF, Taylor SE and Matthai C (2001) Small-scale spatial and temporal variance in the concentration of heavy metals in aquatic sediments: a review and some new concepts. Environmental Pollution. 113:357–372.

Bordes, P and Bourg, A (2001) Effect of solid/liquid ratio on the remobilization of Cu, Pb and Zn from polluted river sediment. Water, Air and Soil Pollution 128: 391–400.

Censi P, Spoto SE, Saian F, Sprovieri M, Mazzola S, Nardone G, Di Geronimo SI, Punturo R, and Ottonello D (2006) Heavy metals in coastal water systems. A case study from the northwestern Gulf of Thailand. Chemosphere, 64: 1167–1176.

Choi JM, Pak CH, Lee CW (1996) Micronutrient toxicity in French marigold. J Plant Nutri 19:901–916.

Col M, Col C, Soran A, Sayli BS and Ozturk S. (1999) Arsenic-related Bowen’s disease, palmar keratosis, and skin cancer. Environ Health Perspect 107:687-9.

Connell FA, Roberts TR, Patel K, and Schenck FJ (1984). Dissolved metals speciation, Water Resource Characterization, DSS - Heavy Metals.

Daily Nation Kenya, 2015. Who will clean up River Nzoia Monday 11th May 2015.

De Gregori, I, Pinochet H, Arancibia, M, Vida, A, (1996) Grain size effects on Trace metals distribution in sediment from two coastal Areas of Chile. Bull. Environmental Contamination Toxicology.57: 163-170.

Demirak A, Yilma ZF, Tuna AL and Ozdemir N (2006) Heavy metals in water, sediment and tissues of Leuciscus cephalus from a stream in south western Turkey. Chemosphere 63(9):1451–1458.

Dinesh M and Kunwar PS (2002) Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse-an agricultural waste, Water Res. 36 2304–2318.

Duruibe, J, Ogwuegbu, M and Egwurugwu, J (2007) Heavy metal pollution and human biotoxic effects. International Journal of Physical Sciences, 2(5): 112-118.

Eaton AD (2005). Standard Methods for the Examination of Water and Waste Water. 21st Edn. American Public Health Association,Washington, ISBN. 0875530478. pp. 343-453.

Edris B, Ferdos KM, Morteza E, Gholam Reza E and Amir HM (2015) Concentration of heavy metals in surface water and sediments of Chah Nimeh water reservoir in Sistan and Baluchestan province, Iran, Desalination and Water Treatment, DOI: 10.1080/19443994.2015.1027958.

EPA (1999) Sediment Q,uality Guidelines developed for the national status and trends program. Report No. 6/12/99.http://www.epa.gov/waterscience/cs/pubs.htm (Accessed in May 2016).

Eja CE, Ogri OR and Arikpo GE (2003) Bioconcentration of heavy metals in surface sediments from the Great Kwa river estuary, Calabar, Southeast Nigeria. J. Nig. Environ. Soci., 1: 47-256.

Espinoza – Quinones FR, Zacarkim CE and Palacio SM (2005) Removal of heavy metal from polluted river water using aquatic macrophytes *salvinia sp.* Brazilian Journal of Physics, vol 35(3): 744 – 746.

Fabbri, P, Gabbianelli, G, Locatelli, C, Lubrano, P, Tormbini, C and Vassura, I (2001) Distribution of mercury and other heavy metals in core sediments of northern Adriatic Sea. Water, Air and Soil Pollution 129: 143–153.

Fernandes C, Fontaínhas-Fernandes A, Cabral D and Salgado MA (2008) Heavy metals in water, sediment and tissues of *Liza saliens* from Esmoriz–Paramos lagoon, Portugal. Environ. Monit. Assess.136: 267–275.

Fernandes C, Fontainhas-Fernandes A, Peixoto F and Salgado MA (2007) Bioaccumulation of heavy metals in Liza saliens from the Esomriz-Paramos coastal lagoon, Portugal. Ecotoxicology and Environmental Safety.66:426–431.

Forstner U and Wiltman GT (1983) Metal pollution in aquatic environment. 2nd edu (Springer – Verlag, Berlin).

Grosbois C, Meybeck M, Horowitz A and Ficht A (2006) The spatial and temporal trends of Cd, Cu, Hg, Pb, and Zn in Seine river floodplain deposits (1994–2000). Sci Total Environ 356:22–37.

Gumgum B, Uulu E, Tez Z and Gulsu Z (1994) Heavy metal pollution in water, sediment and fish from the Tigris River in Turkey. Chemosphere 29: 111-116.

Harikumar P, Nasir U and Mujeebu-Rahman P (2009) Distribution of heavy metals in the core sediments of a tropical wetland system. International J. Environ. Sci. Tech., 6 (2), 225-232.

Hawkes JS (1997) Heavy metals. J Chem Edu 74:1369–1374.

Huang KM and Lin S (2003) Consequences and implication of heavy metal spatial variations in sediments of the Keelung river drainage basin, Taiwan. Chemosphere 53:1113–1121.

Inam F, Deo SS, Kadam NS and Mahashabde RP, (2012) Comparative account of heavy metal analysis of selected plant species by ICP-AES. Research Journal of Pharmaceutical, Biological and Chemical Sciences, 3 (2): 57 - 63.

Issa BR, Arimoro FO, Ibrahim M, Birma GH and Fadairo EA (2011) Assessment of Sediment Contamination by Heavy Metals in River Orogodo (Agbor, Delta State , Nigeria). Curr World Environ: 6(1); 29-38.

Järup L. (2003). Hazards of heavy metal contamination. British medical bulletin, 68(1), 167-182.

Jeon BH, Dempsey BA, Burgos WD, Royer RA (2003) Sorption kinetics of Fe(II), Zn(II), Co(II), Ni(II), Cd(II), and Fe(II)/Me(II) onto heamatite. Wat Res 37:4135–4142.

Jha SK, Chavan SB, Pandit GG, Sadasivan S.(2003) Geochronology of Pb and Hg pollution in a coastal marine environment using global fallout ^{137}Cs. Journal of Environmental Radioactivity; 69:145–157.

Jitendra P and Rachna S (2015) Heavy metals in sediments of Ganga River: up- and downstream urban influences Appl Water Sci DOI 10.1007/s13201-015-0334-7

Jordaan, J, Plate EJ, Prins E and Veltrop J (1993) Water in our common future; IHP Committee on water research (COWAR); A research agenda for sustainable development of water resources, Paris UNESCO.

Kenya Bureau of Standards (1996) Kenya Standard Specification for drinking part I. The requirement for drinking water and containerized drinking water. Nairobi, Kenya.

Kennish MJ, (1992) Practical Handbook of Estuarine and Marine Pollution, CRC Press, New York.

Kithiia, SM (1992). Effects of Industries and Landuse Systems on the Water Quality within Nairobi River Sub-Catchments, Kenya (Master's thesis). University of Nairobi.

Kithiia, SM (2006) Effects of land-use types on the Hydrology and water quality of the upper-Athi River Basin, Kenya, unpublished PhD. Thesis materials, University of Nairobi.

Kithiia, SM (2012). Effects of Sediments Loads on Water Quality within the Nairobi River Basins, Kenya. International Journal of Environmental Protection, 2(6):16-20.

Kithiia,SM and GO Khroda (2011) Sediments yields and Transport within the Nairobi River basins, Kenya: In River, Coastal and Estuarine Morphodynamics: RCEM2011 © 2011 Tsinghua University Press, Beijing.

Kishe, MA, and Machiwa JF, (2003), "Distribution of heavy metals in sediments of Mwanza Gulf of Lake Victoria, Tanzania," Environment International, 28, pp. 619– 625.

Klockenkämper (1997). Total-Reflection X-Ray Fluorescence Analysis, John Wiley & Sons

Lalah JO, Wandiga SO and Ochieng EZ (2008), Sources of Heavy Metal Input Into Winam Gulf, Kenya Bull Environ Contam Toxicol 81:277–284.

Leton TG and Akpila SB (2008) An assessment of impact of industrial effluents on sediment quality of Woji River. American-Euroasian J. Agric and Environ. Sci. 4(6): 713-718.

Lenntech Water Treatment and Air Purification (2004) Water treatment Lenntech, Rotterdamseweg, Netherlands (http://www.excelwater.com/thp/filters/Water-Purification.htm) accessed in April 2014.

MacFarlane GB and Burchettt MD (2000). Cellular distribution of Cu, Pb, and Zn in the Grey Mangrove Avicemnia marina (Forsk.). Vierh Aquatic Botanic, 68**:** 45–59.

Maldonado V., Arias H., Quintana R., Saucedo R., Gutierrez M., Ortega J. and Nevarez, G. (2008). Heavy Metal Content in Soils under Different Wastewater Irrigation Patterns in Chihuahua, Mexico. Int. J. Environ. Res. Public Health, 5(5):441-449

Marcovecchio JE, Botte SE and Freije RH (2007). Heavy Metals, Major Metals, Trace Elements. In: Handbook of Water Analysis. L.M. Nollet, (Ed.). 2nd Edn. London: CRC Press, 275-311.

Mateu, J, Forteza, M, Colom-Altes, M and Cerda V (1996) Atmospheric background levels and transport of heavy metals in the Balearic Islands. Water, Air and Soil Pollution Vol 86, 157-172.

Martin J and Meybeck M, “Elemental Mass-Balance of Material Carried by Major World Rivers,” Marine Chemistry, Vol. 7, No. 3, 1979, 178-206.

Mico´C , Recatala´ L , Peris M and Sa´nchez J (1996) Assessing heavy metal sources in agricultural soils of a European Mediterranean area by multivariate analysis, Chemosphere 65:863–872.

Milenkovic N, Damjanovic M and Ristic M (2005), Study of Heavy Metal Pollution in Sediments from the Iron Gate (Danube River), Serbia and Montenegro, Polish Journal of Environmental Studies Vol. 14, No 6:781-787

Mohamed MB, Ahmed AB, Mohamed MY and Eman AM (2010) Heavy metal concentrations in surface river water and bed sediments at Nile Delta in Egypt Suoseura — Finnish Peatland Society Suo 61(1): 1–12.

Morrow, H, (2001) Cadmium and cadmium alloys. In. Kirk–Othmer encyclopedia of chemical technology. Wiley, New York, 471–507.

Mwamburi J (2003) Variations in trace elements in bottom sediments of major rivers in Lake Victoria’s basin, Kenya. Lakes & Reservoirs: Research and Management 8: 5–13.

Mwamburi, J and Fredrick, NO (1996/97) The distribution and concentration levels of trace metals in water and sediments of Lake Victoria (Kenya). Afri. J. Trop. Hydrobiol. Fish. (1996/1997) 7, 37 – 48.

Mutuku C, Okemo P and Boga H, (2014) Metal pollutants distribution within Lake Victoria basin and their influence on the native and transient microbial flora, ARPN Journal of Agricultural and Biological Science vol. 9, no. 4 issn 1990-6145.

Neal C, Williams RJ, Neal M, Bhardwaj LC, Harrow M and Hill LK (2000) The water quality of the Thames river at a rural site downstream of Oxford. Sci Total Environ 251/2:441–457.

Nriagu JO (1989) A global assessment of natural sources of atmospheric trace metals. Nature 338:47–49.

NRBMI, A Public Private Partnership between Civil Society, Learning Institutions and Communities (2006- 2011).

Okonkwo JO, Mothiba M, Awofolu OR and Busari O (2005) Levels and speciation of heavy metals in some rivers in South Africa. Bull Environ Contam Toxicol 75:1123–1130.

Olajire AA, Ayodele ET, Oyediran GO and Oluyemi EA, (2007) Level of speciation of heavy metals in soils of industrial Southern Nigeria. Environmental Monitoring and Assessment. 85: 135 - 155.

Oliver DC (2004) Environmental impacts of sugar production. CABI Publishers, United Kingdom.

Olivares-Rieumont S, Rosa DL, Graham L, Alessandro DW, Borroto KD, Martinez JF and Sanchez J (2005) Assessment of heavy metal levels in Almendares River sediments—Havana City, Cuba. Water Res 39:3945–3953.

Omwoma S, Lalah JO, Ongeri DMK, and Wanyonyi MB(2010) Impact of Fertilizers on Heavy Metal Loads in Surface Soils in Nzoia Nucleus Estate Sugarcane Farms in Western Kenya, Bull Environ Contam Toxicol.

Onyari JM (1985). The concentration of Mn, Pb, Fe, Cu, Zn, Cd in sediments and fish from Winam gulf of Lake Victoria and fish bought in Mombasa town markets. M.Sc. Thesis, University of Nairobi. 282.

Onyari JM and Wandiga SO (1989) Distribution of Cr, Pb, Cd, Zn, Fe and Mn in Lake Victoria sediments. Bull.Contam. Toxicol. 42, 807–13.

Opaluwa, O., Aremu, M., Ogbo, L., Abiola, K., Odiba, I., Abubakar, M. and Nweze, N. (2012). Heavy metal concentrations in soils, plant leaves and crops grown around dump sites in Lafia Metropolis, Nasarawa State, Nigeria. Advances in Applied Science Research, 3 (2):780-784.

Orata Francis (2003), Determination of heavy metals in sediments, fish and auatic plants from Lake Victoria, MSc. Thesis University of Nairobi.

Öztürk, M., Özözen, G., Minareci, O. and Minareci, E. (2009) Determination of heavy metals in fish, water and sediments of Avsar Dam Lake in turkey. Iran. Journal of Environment, Health. Science and Engineering 6 (2): 73-80.

Oyekunle JAO, Ogunfowokan AO, Olutona GO, Atoyebi AO, and Lawal A(2013) Speciation Study of Heavy Metals in Water and Sediments from Asunle River of the Obafemi Awolowo University, Ile-Ife, Nigeria International Journal of Environmental Protection Vol. 3 Iss. 3, pg. 6-16.

Patients Medical, (2013) Heavy Metal Toxicity Patients Medical eNewsletter

Pekey H, Karakas D, Bakacoglu M (2004) Source apportionment o ftrace metals in surface waters of polluted stream using multivariate statistical analysis. Mar Pollut Bull 49:809–818.

Pembere AM, Oduor FDO, Kariuki DK and Jumba I (2015) Determination of selected heavy metals in agricultural soils in Bungoma and Kakamega Counties, Western Kenya. Africa Journal of Physical Sciences 2 (1)11-17

Radojevic M, Bashkin VN (1999). Practical Environmental Analysis. The Royal Society of Chemistry, Cambridge, p. 466.

Rana, P. K., Lokhande, R. S., Pitale, S. M., Janwadkar, S. P., Navarkar, P. S. and Yadav, D. K., (2012) Extractive spectrophotometric studies of acetophenone 2', 4'-dihydroxy thiosemicarbazone with iron. Journal of Pharmaceutical & Scientific Innovation, 1 (5).

Redus R (2008) Amptek Application Note XRF-1: XRF Spectra and Spectra Analysis Software.

Ridgway J, Breward N, Langston WJ, Lister R, Rees JG, et al. (2003) Distinguishing between natural and anthropogenic sources of metals entering the Irish Sea. Applied Geochemistry.18:283–309.

Romic M and Romic D (2003) Heavy metals distribution in agricultural top soils in urban area. Environ Geol 43:795–805.

Ross SM (1994) Toxic metals in soil–plant systems. Wiley, Chichester, p 469.

Sadiq R, Husain T, Bose N, Veitch B, (2003) Distribution of heavy metals in sediment pore water due to offshore discharges: An ecological risk assessment, Environ. Modell. Software 18: 451–461.

Saeed S, Marzieh VD, Akbar H and Toba K (2014) Heavy Metals in Water and Sediment: A Case Study of Tembi River, Journal of Environmental and Public Health

Saha P and Hossain M (2010) Assessment of heavy metal concentration and sediment quality in the Buriganga River, Bangladesh. In: International proceedings of chemical, biological and environmental engineering, Singapore City, pp 384–387.

Salah EAM, Zaidan TA and Al-Rawi AS (2012) Assessment of heavy metals pollution in the sediments of Euphrates River, Iraq. J Water Res Prot 4:1009–1023.

Santos IR, EV Silva-Filho, CE Schaefer, MR Albuquerque-Filho and LS Campos. (2005) Heavy metals contamination in coastal sediments and soils near the Brazilian Antarctic Station, King George Island. Mar. Poll. Bull, 50: 85-194.

Seaward MRD and Richardson DHS (1990) Atmospheric sources of metal pollution and effects on vegetation. In: Shaw AJ (ed) Heavy metal tolerance in plants evolutionary aspects. CRC Press, Boca Raton, pp 75–94.

Sirengo, J. (2001). Uptake characteristics of trace elements: lead, zinc, cadmium, and mercury by selected food crops grown along Nairobi River (Master’s thesis). University of Nairobi.

Shuhaimi MO (2008) Metals concentration in the sediments of Richard Lake, Sudbury, Canada and sediment Toxicity in an Ampipod *Hyalella azteca.* J. Environ. Sci. Technol.,vol 1: pg. 34-41.

Skeat WO (1969) Manual of British water engineering practice. Vol. b: water quality and treatment, the institution of water engineers, London, England.

Stephen SR, Alloway BJ, Carter JE, Parker E (2001). Towards the characterization of heavy metals in dredged canal sediments and an appreciation of availability. Environ pollt., vol 113: 395-401.

Suresh G, Sutharsan, P, Ramasamy V and Venkatatachalapathy R (2012) Assessment of spatial distribution and potential ecological risk of the heavy metals in relation to granulometric contents of Veeranam lake sediments, India. Ecotox. Environ. Sate- 84, 117 – 124.

Tam, NFY and Wong,YS (2000) Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. Environmental Pollution Vol 110, pp195-205.

Thomas F, Malick C, Endreszl EC and Davies KS (1998) Distinct responses to copper stress in the halophyte, Mesembryanthemum crystallium. Physiol Plant vol 102:360–368.

United Nations Environment Programme (2008) annual report. UNEP.

US Agency for Toxic Substances and Disease Registry (1999) Lead. Toxicological profiles**.** Atlanta: Centers for Disease Control and Prevention; PB/99/166704.

USEPA, “US Environmental Protection Agency (1999) Screening Level Ecological Risk Assessment Protocol for Hazardous Waste Combustion facilities,” Appendix E: Toxicity Reference Values, Vol. 3.

US Environmental Protection Agency, (USEPA), 2001 National recommended water quality criteria: 2002-correction: EPA-822-R-02-047, Washington DC, USA.

Verkleji JAS (1993) The effects of heavy metals stress on higher plants and their use as bio monitors. In: Markert B (ed) Plant as bioindicators: indicators of heavy metals in the terrestrial environment. VCH, New York, pp 415–424.

Wandiga SO (1981) The concentration of zinc, copper, lead, manganese, nickel and fluoride in rivers and lakes of Kenya. Sinet. Ethiopia J. Sci. **3,** 1.

Wang QB, Huang K, Tsunoda H and Akaiwa (2000) Distribution and partitioning for the use of sediment quality standard. Chinese J. Anal. Chem. 28: 759.

Warren C,Mackay D, Whelan M and Fox K (2005)Mass balance modeling of contaminants in river basins: A flexible matrix approach. Chemosphere 61:1458–1467. doi:10.1016/j.chemosphere.2005.04.118.

White HK, Xu L, Lima ANL, Egliton TI, and Reddy CM (2005) Abundance, composition and vertical transport of PAHs in marsh sediments. Environmental Science and Technology; 39:8273–8280.

WHO (1985) Guidelines for drinking water quality. Vol.13 Drinking water quality control in small community supplies. Geneva. p. 121.

WHO (1995) Lead. Environmental Health Criteria, vol. 165. Geneva: World Health Organization.

WHO (2001) Arsenic and Arsenic Compounds. Environmental Health Criteria, vol. 224. Geneva: World Health Organization.

WHO (2004). Guidelines for Drinking Water Quality. 3rd Edn. World Health Organization, ISBN: 92- 4-154638-7. p. 516.

WHO (2007) Guidelines for Drinking Water Quality, third ed., vol. 1, World Health Organization, Geneva.

Wintz H, Fox T and Vulpe C (2002) Responses of plants to iron, zinc and copper deficiencies. Biochem Soc Trans 30:766–768.

Wogu MD and Okaka CE, (2011) Pollution studies on Nigerian rivers: heavy metals in surface water of warri river, Delta State, Journal of Biodiversity and Environmental Sciences, vol. 1, no. 3, pp. 7–12.

Wuana, R and Okieimen, F (2011). Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. International Scholarly Research Network ISRN Ecology, 10:5402-5424.

Yadav S (2010). Heavy metals toxicity in plants: An overview on the role of glutathione and phytochelatins in heavy metal stress tolerance of plants. South African Journal of Botany, 76: 167–179.

Yong, TC,(1999) “Water pollution by agriculture, agro industry and mining ” Proceedings of the Regional workshop on water Quality management and control of water pollution in Asia and the pacific FAO water Reports **21**: 133-138 .

APPENDICES

Appendix A

Coordinates and elevation of sampling points

Sampling site code	Sampling site name	Elevation (M)	Longitude	Latitude
S1	Mumias Bridge	1265	00.37222˚	034.48387˚
S2	Shibale	1260	00.36101˚	034.48043˚
S3	Shitukhumi	1258	00.3515˚	034.47980˚
S4	Nyakwaka	1264	00.34815	034.46249
S5	Matawa Bridge	1236	00.31655	034.40859
S6	Dadira	1237	00.28160	034.40690
S7	Wang’nyang’	1228	00.27582	034.39313
S8	Lithehe	1236	00.27445	034.38802
S9	Masiro Bridge	1219	00.24917	034.34057
S10	Ligega	1190	00.19879	034.27663
S11	Nzoia Bridge	1180	00.17541	034.22551
S12	Kobare	1172	00.16600	034.18437
S13	Sango	1174	00.15956	034.20327
S14	Kalkada	1170	00.15150	034.15960
S15	Kabura	1156	00.14308	034.13025
S16	Nyatiti	1171	00.14293	034.14981
S17	Kabwana	1157	00.14050	034.12693
S18	Uhere	1147	00.11921	034.10899
S19	Goro	1157	00.12245	034.10270
S20	Nyadorera	1150	00.11313	034.10198
S21	Rwambwa	1150	00.11886	034.09363
S22	Bukala	1153	00.11822	034.07279
S23	Otoyi	1158	00.11724	034.06073
S24	Busagwa	1155	00.11387	034.05304

S25	Siginga	1151	00.10947	034.05190
S26	Magombe	1146	00.09835	034.04165
S27	Makunda	1156	00.09434	034.02341
S28	Burangasi	1155	00.09427	034.03439
S29	Hainga	1141	00.09418	033.99219
S30	Isigiri	1141	00.07593	033.97994

Appendix B

Concentration of heavy metals in water of lower River Nzoia

	Mn	Fe	Ni	Cu	Zn	Pb
S1	60.3±10.2	5987±98	<13	15±4	139±7	<10
S2	72.3±11.2	7234±123.	<13	14.3±3.8	98.5±5.8	<10
S3	72.5±8.75	5413±65	<13	15.3±2.8	99±5.5	11±3.5
S4	68±10.75	7040±110	13.5±3.8	20.3±4	103.8±6.3	<10
S5	44.5±7.75	4732±66	<13	15.8±2.8	125.8±5.3	<10
S6	77±10.3	6403±86	<13	<13	185.5±7.5	11±3.5
S7	77.5±9	5653±75	21±3.8	<13	1399.8±20	<10
S8	82.3 ±10	6815±93	<13	58.25±4	472.5±27.75	23.75±3
S9	61.5±10.75	7077±108.5	<13	<13	926.5±21.5	<10
S10	92.3±10.3	7176±94	<13	<13	59.5±4.3	<10
S11	<39	2472±43	<13	18.5±3.8	183.3±8	<10
S12	184±12.5	12314±145	<13	19.7±3.9	37±4.1	<10
S13	52.75±8.5	4544±67	<13	33.3±4	68±4.3	<10
S14	109.9±11.2	11622±138	<13	14±3.5	47.5±3.8	<10
S15	74.8±12.5	6100±111	14±3.8	18.8±3.8	182.3±7.8	24.25±4
S16	72.3±7.8	6138±72	13.25±2.8	<13	34.5±3	<10
S17	79.8±8.8	6767±78	<13	<13	28.6±3	<10
S18	60±9.3	3178.5±46	17.5±3.5	41.5±3.5	101.8±4.8	<10
S19	<39	3459±51	19±3.5	92.3±5	50.3±3.8	<10
S20	93±10.8	6212±83	<13	<13	46.8±4	<10
S21	72±11.5	4668±78	<13	18±4	149.3±7.8	10±3

S22	103.8±12	7741±120	<13	<13	165.8±7.3	<10
S23	<39	1574±29	<13	38.5±3.8	84.5±4.3	10.5±3
S24	68.3±10	7503±109	13.25±4.5	30.8±4.3	468±13.3	<10
S25	73.8±7.5	5026±57	<13	18.25±3	102.8±4.8	<10
S26	78.5±10	8615±111	<13	<13	44.3±4	<10
S27	57.3±8	4768±60	<13	<13	198.3±6.5	<10
S28	122.8±13	11247±158	14.5±3.8	19.8±3.3	46±3.8	10.8±2.5
S29	150±15	8682±148	<13	35.5±4.8	583±16.8	<10
S30	217.5±20.3	12060±163	<13	15.8±3.5	129.8±7.8	13.3±3.3
Mean	78	6607	15.74	27.67	212.05	14.94
Medium	73.8	6307.5	14.25	19.25	103.3	11
Maximum	217.5	12314	21	92.3	1399.8	24.2
Minimum	44.5	1574	13.2	14	28.6	10.5
Std Deviation	40.17	2662	3.01	19.21	297.94	6.24

Appendix C

Concentrations of Manganese in sediments

Sample point	D30	D50	D100
S1	938.8±78.6	767.5±66.8	731.6±80.4
S2	746.2±63.4	835±65.6	940.5±70.2
S3	708.9±65.9	1067.2±86.8	1034.4±78
S4	973.8±87.4	1109.2±85.8	946.6±76.9
S5	1513.3±118.6	798.3±67.3	767.4±65.6
S6	1193.1±80.9	667.9±66.7	977.±91
S7	974.1±408.6	1000.8±70.4	1120.1±81.8
S8	1592.1±91.5	1426.9±90.1	1844.3±142.2
S9	1028.1±82.8	976.1±73.8	905.1±68.7
S10	1020.8±88.7	1016.9±80.3	1224.1±87.3
S11	1013.3±72.2	935.2±71.4	856.6±73.2
S12	1577.4±121.1	1367.6±106.4	1230.9±98.8
S13	1227.1±93.9	1140.1±80.1	1274.1±97.8
S14	1307.6±98.9	899.2±67.1	953.3±78.5
S15	1042.7±82.1	938.2±74.5	1019.7±76.3
S16	1336.2±62.1	1384.5±84.1	1843.1±106.5
S17	1033±79.0	1184.2±89.6	1381.6±104.1
S18	1373.8±77.2	1024.8±70.1	1072.7±86.5
S19	814.2±69.3	1395.5±96.5	1140.6±91.3
S20	1422.2±103.2	1231.4±101	1132.7±91

S21	877.8±79.3	1726.4±104	2064.8±118.1
S22	1186.2±81.9	1081.65±76.9	1650.2±105.0
S23	1840.5±111.1	1266.0±80.3	879.6±69.8
S24	1053.2±76.9	1442.3±98.5	1157.1±84.9
S25	1486.3±88.7	1643.3±88.9	939.2±72.3
S2	1738.3±128.6	1390.8±84.4	1580.9±89.8
S27	1041.9±82.5	973.3±71.0	930.9±77.6
S28	1292.5±89.2	1330.6±93.5	519.1±54.0
S29	1205±77.2	1010±84.9	1448±84.4
S30	1413.9±90.5	1236.9±100.5	902.7±80.7

Appendix D

Concentrations of iron in sediments

Sampling site	D30	D50	D100
S1	3.5±0.1	3.7±0.1	4.0±0.1
S2	2.7±0.1	3.7±0.2	5.1±0.2
S3	3.4±0.1	4.4±0.1	4.6±0.2
S4	3.4±0.1	4.4±0.2	5.6±0.2
S5	3.4±0.1	4.1±0.1	4.5±0.1
S6	3.4±0.1	3.7±0.1	3.8±0.1
S7	3.7±1.2	5.2±0.2	5.4±0.2
S8	3.8±0.2	5.2±0.2	5.5±0.2
S9	3.8±0.1	4.2±0.2	4.3±0.1
S10	3.5±0.1	4.2±0.1	4.6±0.2
S11	3.4±0.1	3.9±0.1	4.0±0.1
S12	3.9±0.2	4.6±0.2	5.4±0.2
S13	4.6±0.2	5.4±0.2	5.3±0.2
S14	3.9±0.1	4.9±0.2	5.1±0.1
S15	3.8±0.2	3.9±0.1	4.0±0.1
S16	4.9±6.8	5.3±0.2	5.8±0.2
S17	3.9±0.2	4.3±0.2	5.2±0.2
S18	3.0±0.1	4.3±0.1	3.9±0.1
S19	3.9±0.2	5.4±0.2	4.8±0.2

S20	4.6±0.2	5.0±0.2	4.5±0.2
S21	4.4±0.1	5.2±0.2	6.5±0.2
S22	4.1±0.1	4.5±0.1	5.9±0.2
S23	3.6±0.1	4.7±0.1	6.6±0.2
S24	4.1±0.1	5.2±0.2	5.9±0.2
S25	4.0±0.1	5.1±0.1	5.6±0.1
S26	4.7±0.1	5.4±0.2	5.9±0.3
S27	4.5±0.2	5.1±0.2	4.9±0.2
S28	4.4±0.2	4.7±0.1	6.3±0.2
S29	4.5±0.2	4.8±0.1	4.9±0.2
S30	4.8±0.1	5.3±0.2	8.3±0.2

Appendix E

Concentrations of copper in sediments

Sampling Site	D30	D50	D100
S1	310.1±18.6	320.4±18.9	371.5±20.8
S2	357.8±22.8	352.7±20.7	359.7±22.9
S3	319.4±19	345.7±21.5345.7±21.5	346.8±20.4
S4	291.2±19.1	331.7±18.9	349.6±19.5
S5	301.4±17.1	362.6±18.9	361.8±20.0
S6	309.6±18.5	305.9±18.9	321.9±17.1
S7	322.2±21.5	312.3±17.3	332.9±19.1
S8	324.5±20.9	362.5±20.1	386.7±20.9
S9	332.8±19.1	335.1±18.3	329.3±18.7
S10	324.8±18.3	361.1±20.0	371.2±20.0
S11	334.2±18.9	350.1±21.1	331.7±19.8
S12	365.7±20.7	373.4±23.6	390.8±21.8
S13	366.9±23.7	388.9±21.1	398.1±22.9
S14	353.8±19.9	371±23.2	366.7±21.7
S15	332.6±95.6	359.0±22.0	368.4±20.2
S16	352.3±15.9	351.6±20.8	384±21.5
S17	367.3±23.2	345.4±22.5	397.4±22.6
S18	312.3±18.6	315.4±21.7	378.8±19.1
S19	299.0±18.3	332.5±19.9	316.2±20.9
S20	352.4±21.6	335.4±22.8	419.6±23.9
S21	347.1±21.5	379.1±21.6	373.8±21.4
S22	336.2±17.8	335.5±20.2	362.0±21.3

S23	351.5±18.1	348.2±20.4	405.2±20.8
S24	366.2±23.8	356.2±20.6	352.7±20.9
S25	329.0±18.6	345.7±18.9	343.4±17.5
S26	383.9±22.3	351.5±22.5	387.5±22.2
S27	375.8±21.2	356.3±20.7	388.8±20.8
S28	344.8±21.2	360.8±19.5	408.3±25.4\
S29	343.2±20.4	348.4±21.2	384±21.5
S30	350.9±22.3	392.9±24.4	392.1±21.2

Appendix F

Concentrations of zinc in sediments

Sampling Site	D30	D50	D100
S1	59.0±8.9	50.6±7.7	53.6±8.4
S2	60.3±8.1	55.4±9.0	52.1±7.7
S3	69.3±9.2	64.8±7.5	72.8±10.2
S4	57.6±7.5	57.0±9.2	78.4±9.1
S5	61.8±10	59.2±7.8	56.3±8.2
S6	56.5±8.4	69.5±6.9	61.8±6.9
S7	56.9±22.7	77.9±8.7	77.4±8.1
S8	74.3±9.7	72.6±8.6	83±11.2
S9	80.4±9.0	68.5±8.5	67.5±8.6
S10	70.7±8.9	61.5±8.8	57.1±8.0
S11	58.7±9.6	57.1±7.1	55.2±7.1
S12	77.3±9.8	77.3±9.2	75.8±8.6\
S13	65.5±8.7	81.4±9.6	70.4±9.4
S14	82.1±9.4	52.7±6.9	78.3±10.2
S15	58.8±9.3	55.8±7.6	59.9±8.6
S16	67.5±9.2	71.2±8.6	99.8±11.6
S17	75.1±9.6	68.3±8.6	79.0±8.8
S18	83.9±7.7	54.1±7.3	66.5±8.6
S19	52.2±7.6	77.1±9.3	68.4±8.1
S20	77.8±8.7	71.2±8.8	61±8.4
S21	67.5±9.0	82.8±10.2	84.6±8.6
S22	75.5±8.1	60.1±9.1	75.5±8.5

S23	79.3±8.7	70.9±9.1	46.5±8.7
S24	63.6±9.8	81.1±9.6	68.7±8.4
S25	70.1±7.5	83.1±9.1	61.1±8.7
S26	77.6±9.3	68.1±8.3	78.9±7.9
S27	72.5±8.6	70.4±9.5	80.4±10.6
S28	66.6±7.5	79.1±9.2	42.7±7.9
S29	77.6±9.5	75.5±8.5	72.6±8.6
S30	84.5±8.5	87.2±10.8	81.9±9.4

Appendix G

Concentrations of lead in sediments

Sampling Site	D30	D50	D100
S1	11.3±7.2	10.4±7.3	7.9±6.1
S2	10.3±8.6	19.5±8.2	12.7±8.6
S3	10.5±7.9	14.1±8.5	15.6±7.7
S4	9.1±7.0	16.2±7.6	12.1±9.4
S5	22.2±8.3	19.9±9.1	8.8±8.1
S6	13.8±7.5	14.9±7.3	9.1±8.9
S7	18.1±10	11.7±7.9	10.2±6.8
S8	13.5±8.3	12.4±7.2	13.9±9.7
S9	13.1±9.1	8.5±5.9	15.7±8.6
S10	13.7±8.9	15.4±8.1	8.5±10.3
S11	8.1±6.2	9.7±6.4	19.2±6.6
S12	7.3±8.4	14.4±7.9	17±9.9
S13	10.5±6.8	14.5±7.9	13.2±7.9
S14	7.8±6.8	9.8±8.1	10.8±9.2
S15	11.5±6.9	16.2±9.7	19.3±9
S16	14.8±10.9	25.6±8.8	11.7±8.5
S17	10.6±8.5	14±9.2	21.4±7.6
S18	18.1±5.4	9±7	10.6±6.3
S19	13.9±6.9	12.0±8.3	7.2±7.2
S20	17.8±7.7	19.4±7.3	12.6±7.9
S21	14.8±7.4	12.4±7.3	26±9.3
S22	13.2±6.6	17.8±7.8	7.6±7.9

S23	12.2±8.4	15.6±7.1	16.1±9.1
S24	16.4±7.7	6.7±7.2	9.8±8.6
S25	12.3±8.6	14.3±7.6	10.4±6.8
S26	11.3±8.8	17.4±7.4	10.3±6.6
S27	18.4±7.7	16.4±7.5	15.8±8.4
S28	13±6.2	10.8±6.5	12.2±6.0
S29	13.2±6.2	13.3±6.5	14.4±7.9
S30	10.4±7.8	11.4±8.7	15.6±7.3

Appendix H

Concentrations of nickel in sediments

Sampling Site	S30	S50	S100
S1	408.2±23.1	438.5±26.4	386.1±25.1
S2	421.3±28.4	386.9±26.1	448.6±27.8
S3	404.4±29.6	423.1±24.9	396.2±25.4
S4	406.6±27.9	454.4±27.7	494.7±27.5
S5	426.4±22.8	423.9±22.9	497.9±33.1
S6	354.7±22.2	394.4±24.2	383.5±22.7
S7	435.3±26.1	422.3±24.9	292.4±24.3
S8	469.8±27.2	453.6±26.2	454.0±27
S9	424.5±25.5	403.4±25.5	428.9±23.8
S10	433.9±26.3	430.5±30.1	410.4±27.7
S11	394.4±26.3	375±24.0	423±24.8
S12	410.3±25.2	450.6±33.6	435.6±30.8
S13	430.7±28.9	483.5±33.5	457.2±30.8
S14	385.2±26.6	421.4±24.9	410.5±24.4
S15	432.4±31.4	404.8±25.3	405.6±23.8
S16	377.9±27.6	451.8±29.3	405.2±27
S17	421.1±30.8125	394.3±24.6	434.7±29.2
S18	420.3±28.1	383.8±33.2	415.9±27.5
S19	403.3±24.8	420.1±27.9	375.5±25.4
S20	400.3±25.4	417.4±29.9	401.1±27.2
S21	443.2±26.9	432.9±28.5	454.3±26.6
S22	457.5±28.7	385.5±24.5	393.5±28.6

S23	431.0±26.9	418.0±22.8	539.3±28.7
S24	420.6±26.3	426.0±25.9	411.6±25.5
S25	432.3±26.0	397.9±22.7	386.3±22.1
S26	446.3±30.1	442.7±28.2	406.9±22.2
S27	463.5±26.6	471.7±28.5	401±25.4
S28	409.2±23.5	396.9±26.0	383.0±24.9
S29	373.5±25.4	392.5±28.4	378.3±22.1
S30	432.4±25.3	438.3±28.7	393.3±25.1

Appendix I

Concentrations of vanadium in sediments

Sampling Site	D30	D50	D100
S1	97.5±114.4	15.5±112.3	153.4±131.8
S2	255.0±116.4	262.1±130.7	60.3±97.6
S3	175.9±138.5	149.1±140.1	206.6±135.1
S4	99.1±134.6	184.1±153.8	121.3±128.6
S5	68.2±123.3	70.9±140.4	374.7±210.4
S6	189.5±147	187±105.4	44.4±110.7
S7	111.6±193.4	101.9±136.2	80.1±92.8
S8	145.6±180.2	279.7±141.3	128.4±131.4
S9	215.3±121.6	284.8±122.8	111.8±117.8
S10	208.5±149	253.4±121.6	260.5±112.9
S11	207.4±109.5	125.6±120.9	241±99.6
S12	136.2±141.9	116.2±148.4	86.5±127.8
S13	296.9±122.2	131.2±140.5	195.8±115.3
S14	119.0±112.2	71.6±122.6	84.5±165.5
S15	124.8±99.4	119.1±109.6	74.8±139.3
S16	46.6±106.5	39.4±105.8	89.3±137.6
S17	143.1±114	128.4±133.4	229.6±145.8
S18	197.5±117.6	69.6±118.7	168.3±105.6
S19	25.1±149.8	120.7±139.3	112.3±130.2
S20	95.7±137	94.8±112.3	152.2±147.1
S21	72.8±139.3	131.4±139.2	102.4±152.8
S22	101.9±58.5	19.5±109.9	59.1±105.1

S23	108.6±120.9	180.4±110.5	182.875±129
S24	136.6±96.8	153.3±128.3	134.7±111.2
S25	142.3±149.2	137±141.1	130.6±139.5
S26	384.3±151	170.5±132.3	198±135.9
S27	211.3±105.9	70.8±140.6	198.7±101.2
S28	96.1±120.9	196.2±106.8	49.8±134.8
S29	121.8±117.8	138.1±114	180.7±129
S30	18.7±88.4	75.4±145.9	152.6±143.8

Appendix J

Concentrations of chromium in sediments

Sampling Site	S30	S50	S100
S1	71.9±56.4	145.7±57.8	88.3±70.3
S2	141.6±57.0	214.3±51.3	208±62.8
S3	76.3±59.1	68.6±56.4	102.2±54.0
S4	77.9±55.9	100.7±68.9	77.9±60.3
S5	117.8±59.1	111.3±81.2	301.5±96.9
S6	45.1±61.4	64.6±64.3	60.9±49.9
S7	105.7±70.2	100.5±64.1	51.1±61.6
S8	103.9±76.5	148.5±89	143.2±72.2
S9	131.1±54.7	184.5±58.7	172.6±63.3
S10	109.8±62.2	113.9±58.6	169.8±71.6
S11	94.1±50.3	123.8±60.5	142.6±67.5
S12	69.1±65.9	38±54.7	81.3±67.3
S13	216.4±61.7	135.3±60.1	165.4±66.9
S14	84.0±49.5	86.3±64	96.1±58.5
S15	168.4±68.9	134.7±58.2	67.4±57.2
S16	58.4±57.4	86.9±67.2	124.3±79.5
S17	72.5±53.4	92.7±99.0	160.2±60.3
S18	170.8±46	105.8±76.1	117.1±49.8
S19	101.1±57.2	113.8±60.2	203.1±52.7
S20	55.8±57.5	83.9±63.1	62.1±59.7
S21	96.9±66.5	145.5±58.7	131.5±57.9
S22	53.4±56.7	121.9±58.8	219.8±57.5

S23	50.3±67.7	89.5±59.2	321.7±78.5
S24	104.7±65.6	69.4±55.6	81.3±58.3
S25	120.6±77.3	57±50.7	78.2±70.8
S26	109.8±75.3	133.8±55.5	91.8±55.6
S27	127.4±62.6	80.2±59.6	145.4±60.9
S28	109±66.7	148.5±55.6	162.4±61.7
S29	108±63.7	126.7±62.6	184.5±58.7
S30	106.2±66.5	96.8±67.9	37.3±52.2

Appendix K

Concentrations of arsenic in sediments

Sampling Site	S30	S50	S100
S1	8.2±4.5	5.4±5.3	5.0±4.9
S2	5.1±5.6	2.6±5.3	8.8±5.2
S3	6.8±5.2	4.8±5.6	4.0±5.3
S4	6.1±4.9	6.1±7.6	8.8±6.2
S5	7.5±5.9	7.4±6.6	6.8±5.7
S6	8.2±4.7	2.8±3.9	5.7±6.7
S7	8.3±6.5	8.1±5.3	6.4±5.4
S8	4.9±6.9	6.8±5.2	4.1±6.6
S9	7.1±6.4	5.1±4.5	3.8±4.9
S10	15.2±6.2	7.2±5.2	14.8±4.9
S11	7.4±5.1	9.8±5	12.5±6.0
S12	9.4±5.7	10.6±5.6	8.7±7.1
S13	7.5±5	13.6±5.1	7.3±5.5
S14	4.5±4.6	11.3±6.2	12.5±7.1
S15	5.4±5	8.0±5.0	2.9±6
S16	10.0±5.7	13.6±7.2	8.7±6.5
S17	11.2±5.3	8.8±5.6	1.5±5.2
S18	1.3±3.9	6.6±4.6	3.3±4.7
S19	4.1±4.8	8.1±6.2	11.7±4.6
S20	6.5±4.5	7.2±4.3	3±5.6
S21	8.7±5.8	7.8±5.5	4.6±5.7
S22	10.2±5.4	2.1±5.4	6.8±4.9

S23	10.3±5.2	4.25±5	12.5±6
S24	12.5±6	10.7±5.3	3.7±6.5
S25	6.3±6	7.5±5.1	12.6±5.1
S26	9.1±5.7	7.8±5.1	6.3±5.8
S27	11.6±5.5	8.7±5.8	8.1±6.6
S28	4.9±4.5	7.1±4.0	6.9±4.2
S29	10.1±5.4	10.5±5.2	10.4±5.3
S30	11.5±5.7	11.8±6.4	8.6±5.1

Appendix A

Results of EDXRF Analysis of sediment samples for sampling site 14

```
QUANTITATIVE     ANALYSIS    REPORT
===========================
Report created on:      02-29-2016
Calibration     file:   D:\XRF\ET-CAL_2\ET-2-S~1.CAL
Created         on:     07-31-2015
Tube    excitation:     Ag      secondary      target   Operating      at:      30      KV

                  ANALYSIS-REPORT          Date:   02/29/16
                                 ===============
       Sample:          14-30A          Date    of       Measurement: 00/00/-1900
      Method:         Emission-Transmission        Mass    (g/cm2):         0.1626
          Element         Energy counts  Concentration          Error   F
         K               3.31    208     5429.2 ppm    +-       881.8   36.3229
         Ca              3.69    219     3264.2 ppm    +-       351.7   28.7316
         Ti              4.51    596     3538.5 ppm    +-       248.9   18.6241
         Cr              5.41    25      62.4   ppm    +-       37.3    12.5424
         Mn              5.89    513     880    ppm    +-       62.8    10.4228
          Fe              6.4     29650  3.26   w%     +-       0.16    8.7273
          Ni              7.47    623    333.5  ppm    +-       29.6    6.2495
          Cu              8.04    638    261.6  ppm    +-       17.8    5.3468
          Zn              8.63    146    43.5   ppm    +-       7.3     4.6123
          Ga              9.24    126    29.9   ppm    +-       5.3     4.0133
          Rb              13.38   717    54.7   ppm    +-       3.3     2.1315
          Sr              14.14   2558   173.8  ppm    +-       7.1     1.9798
          Y               14.93   384    22.5   ppm    +-       2.1     1.8528
          Zr              15.75   7444   405.2  ppm    +-       12.8    1.7458
          Nb              16.58   752    37.2   ppm    +-       3.2     1.6553
          Pb              10.54   77     19.1   ppm    +-       5.1     3.1215
```

Where F represents chi square

ANALYSIS-REPORT Date: 02/29/16

===============

Sample: 14-30B Date of Measurement: 00/00/-1900
Method: Emission-Transmission Mass (g/cm^2): 0.1626

Element	Energy	Counts	Concentration			Error	F
K	3.31	262	6150.7	ppm	+-	624.7	32.6686
Ca	3.69	226	3051.3	ppm	+-	343.7	26.0261
Ti	4.51	624	3401.3	ppm	+-	249.3	17.0984
V	4.95	39	142.2	ppm	+-	91.6	14.0575
Cr	5.41	22	51	ppm	+-	32.5	11.6568
Mn	5.89	494	792.1	ppm	+-	61.5	9.7428
Fe	6.4	29330	3.03	w%	+-	0.11	8.2036
Ni	7.47	593	301.7	ppm	+-	17.4	5.9396
Cu	8.04	580	227.3	ppm	+-	13.2	5.1099
Zn	8.63	158	45.2	ppm	+-	5.1	4.4326
Ga	9.24	147	33.8	ppm	+-	4.5	3.8783
As	10.53	38	5.5	ppm	+-	3.5	3.0533
Rb	13.38	760	57.5	ppm	+-	3.3	2.1146
Sr	14.14	2662	180	ppm	+-	6.3	1.9697
Y	14.93	340	19.9	ppm	+-	1.9	1.8477
Zr	15.75	7304	397.3	ppm	+-	10.8	1.7445
Nb	16.58	760	37.7	ppm	+-	2.7	1.6567
Pb	10.54	32	7.8	ppm	+-	4.4	3.0482

ANALYSIS-REPORT Date: 02/29/16
===============

Sample: 14-30C Date of Measurement: 00/00/-1900
Method: Emission-Transmission Mass (g/cm^2): 0.1084

Element	Energy	counts	Concentration			Error	F
K	3.31	237	4581.7	ppm	+-	446.7	17.9349
Ca	3.69	219	2449.5	ppm	+-	336.8	14.3737
Ti	4.51	568	2593.2	ppm	+-	247.7	9.5477
V	4.95	13	39.9	ppm	+-	62	7.8922
Cr	5.41	30	59	ppm	+-	36	6.5831
Mn	5.89	468	640.3	ppm	+-	45	5.5422
Fe	6.4	27630	2.46	w%	+-	0.08	4.7121
Ni	7.47	556	251.3	ppm	+-	13.6	3.5176
Cu	8.04	670	238.3	ppm	+-	13.7	3.0922
Zn	8.63	135	36	ppm	+-	6.4	2.7509
Ga	9.24	129	28.4	ppm	+-	4.8	2.4752
As	10.53	12	1.8	ppm	+-	4	2.0692
Rb	13.38	549	47.3	ppm	+-	2.7	1.6048
Sr	14.14	1769	139.5	ppm	+-	4.4	1.5315
Y	14.93	204	14.2	ppm	+-	2	1.4691
Zr	15.75	5651	374.2	ppm	+-	9.4	1.4158
Nb	16.58	524	32.2	ppm	+-	2.8	1.37
Pb	10.54	29	7.2	ppm	+-	5.7	2.0667

Appendix M

Results of TXRF analysis of water samples for sampling point 7

A

Element	Line	Energy/keV	Backgr.	Sigma	Chi	Conc./(mg/l)	SigmaC/(mg/l)	LLD/(mg/l)
Na	K12	1.04	297	25	0.82			
Mg	K12	1.254	291	24	1.79			
Al	K12	1.486	280	26	1.88	4.983	1.08	2.034
Si	K12	1.74	263	108	3.16			
P	K12	2.01	251	22	2.61			
S	K12	2.309	251	24	0.94	0.418	0.145	0.284
Cl	K12	2.622	259	32	1.4	2.029	0.134	0.183
Ar	K12	2.958	247	34	1.13			
K	K12	3.314	237	40	1.12	1.795	0.073	0.074
Ca	K12	3.692	216	91	0.84	8.979	0.151	0.05
Ti	K12	4.512	157	29	0.92	0.336	0.02	0.024
V	K12	4.953	150	18	1.49			
Cr	K12	5.415	150	19	1.29	0.026	0.008	0.014
Mn	K12	5.9	144	20	1.26	0.041	0.007	0.012
Fe	K12	6.405	134	131	1.37	4.232	0.055	0.009
Ni	K12	7.48	97	15	0.64	0.006	0.003	0.005
Cu	K12	8.046	93	15	0.8	0.007	0.002	0.004
Zn	K12	8.637	96	22	2.09	0.04	0.003	0.004
Ga	K12	9.251	93	67	1.46	0.5	0.01	0.003
Ga	L1	1.098	294	25	1.24			
As	K12	10.543	59	13	0.76	0.005	0.001	0.002
As	L1	1.282	295	24	1.74			
Br	K12	11.924	82	20	1.23	0.019	0.002	0.002
Br	L1	1.481	280	27	1.88			
Rb	K12	13.396	143	19	0.94	0.006	0.002	0.003
Rb	L1	1.692	273	48	1.9			
Sr	K12	14.165	211	31	0.97	0.044	0.003	0.003
Sr	L1	1.806	262	23	2.59			
Y	K12	14.958	290	24	2.31			
Y	L1	1.924	256	23	1.9			
Mo	K12	17.48	228	205	58.41			
Mo	L1	2.292	251	22	1.07			
Cd	L1	3.133	243	23	3.19			
Pb	L1	10.551	54	11	0.7			
Pb	M1	2.342	250	22	2.12			

B

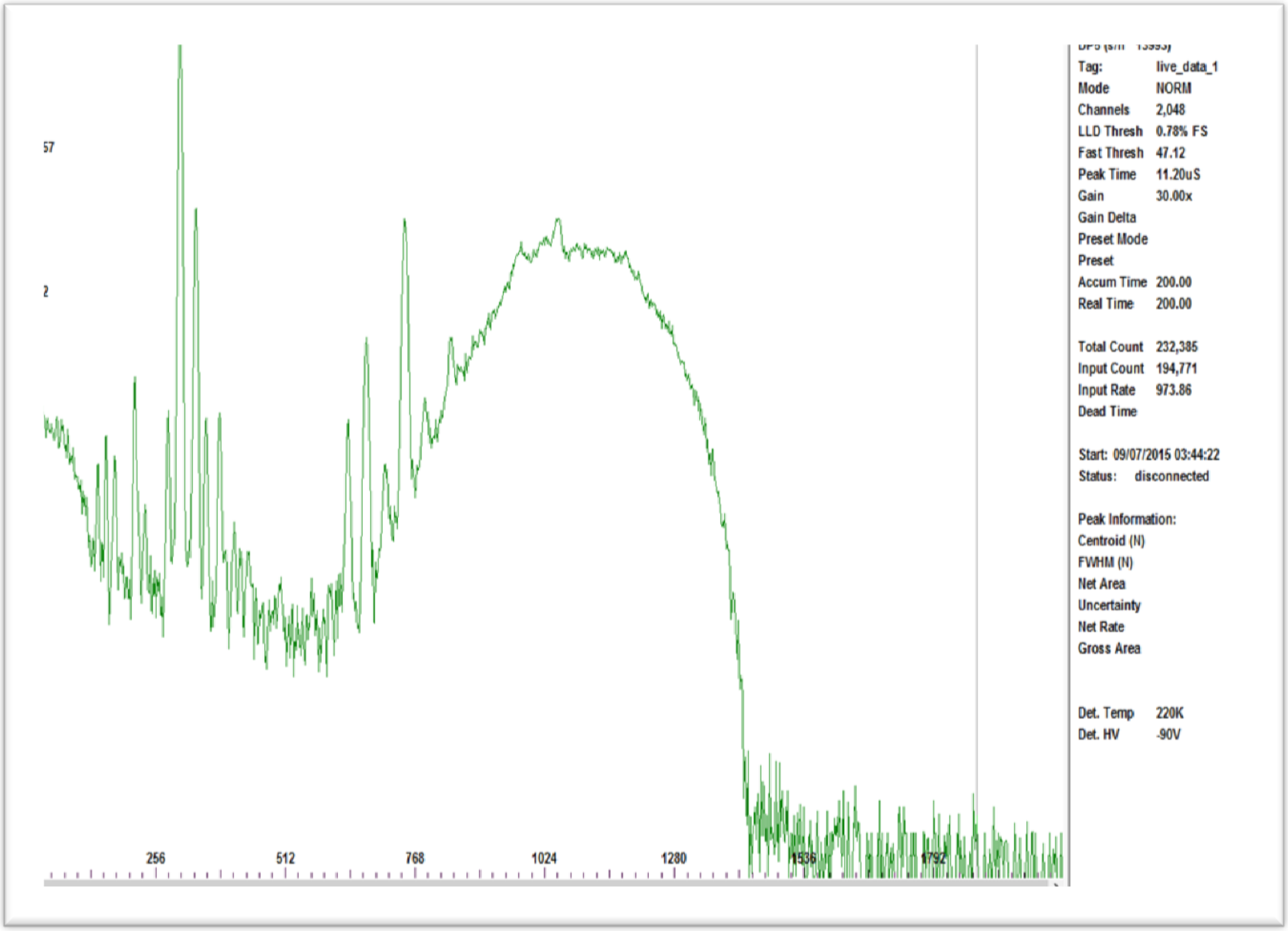
Element	Line	Energy/keV	Backgr.	Sigma	Chi	Conc./(mg/l)	SigmaC/(mg/l)	LLD/(mg/l)
Na	K12	1.04	285	24	2.21			
Mg	K12	1.254	272	23	0.8			
Al	K12	1.486	253	25	1.1	9.911	1.918	3.452
Si	K12	1.74	234	115	2.4			
P	K12	2.01	205	20	1.54			
S	K12	2.309	183	19	1.41			
Cl	K12	2.622	177	24	2.78	1.476	0.175	0.273
Ar	K12	2.958	173	32	1.13			
K	K12	3.314	162	27	0.91	1.13	0.086	0.109
Ca	K12	3.692	148	61	0.5	7.027	0.181	0.075
Ti	K12	4.512	102	18	1.13	0.14	0.022	0.034
V	K12	4.953	86	15	1.81	0.044	0.014	0.026
Cr	K12	5.415	89	14	0.83			
Mn	K12	5.9	90	15	1.04	0.021	0.009	0.016
Fe	K12	6.405	86	73	1.7	2.357	0.052	0.013
Ni	K12	7.48	74	13	0.25			
Cu	K12	8.046	80	14	0.51	0.008	0.004	0.007
Zn	K12	8.637	81	15	0.78	0.014	0.004	0.006
Ga	K12	9.251	80	51	1.13	0.5	0.015	0.006
Ga	L1	1.098	280	24	0.96			
As	K12	10.543	58	12	0.52	0.005	0.002	0.004
As	L1	1.282	269	24	0.86			
Br	K12	11.924	65	17	1.68	0.025	0.003	0.004
Br	L1	1.481	254	23	0.87			
Rb	K12	13.396	140	17	0.79			
Rb	L1	1.692	235	44	2.39			
Sr	K12	14.165	221	28	1.35	0.046	0.004	0.006
Sr	L1	1.806	226	21	1.87			
Y	K12	14.958	291	24	1.42			
Y	L1	1.924	211	21	1.57			
Mo	K12	17.48	222	197	47.84			
Mo	L1	2.292	184	19	1.65			
Cd	L1	3.133	167	19	2.12			
Pb	L1	10.551	53	11	0.45			
Pb	M1	2.342	185	19	1.58			

C

Element	Line	Energy/keV	Backgr.	Sigma	Chi	Conc./(mg/l)	SigmaC/(mg/l)	LLD/(mg/l)
Na	K12	1.04	190	20	1.16			
Mg	K12	1.254	188	19	1.07			
Al	K12	1.486	183	21	1.38	3.04	0.896	1.714
Si	K12	1.74	178	66	0.63			
P	K12	2.01	162	18	1.51			
S	K12	2.309	156	19	2.21			
Cl	K12	2.622	156	25	0.89	1.296	0.106	0.149
Ar	K12	2.958	155	30	0.89			
K	K12	3.314	145	34	1.05	1.453	0.063	0.06
Ca	K12	3.692	127	72	1.27	5.886	0.111	0.04
Ti	K12	4.512	100	22	1.38	0.173	0.015	0.02
V	K12	4.953	103	15	0.59			
Cr	K12	5.415	105	16	0.94	0.016	0.007	0.012
Mn	K12	5.9	100	20	1.29	0.07	0.007	0.01
Fe	K12	6.405	92	107	1.65	2.982	0.041	0.008
Ni	K12	7.48	67	12	0.42			
Cu	K12	8.046	60	12	0.41			
Zn	K12	8.637	61	21	1.26	0.043	0.003	0.003
Ga	K12	9.251	59	65	0.85	0.5	0.01	0.003
Ga	L1	1.098	188	19	0.77			
As	K12	10.543	44	10	0.15			
As	L1	1.282	187	20	1			
Br	K12	11.924	47	14	0.95	0.01	0.001	0.002
Br	L1	1.481	183	20	1.41			
Rb	K12	13.396	78	15	0.93	0.007	0.001	0.002
Rb	L1	1.692	177	30	0.93			
Sr	K12	14.165	121	29	1.83	0.049	0.003	0.003
Sr	L1	1.806	174	20	1.3			
Y	K12	14.958	175	19	1.15			
Y	L1	1.924	167	18	1.63			
Mo	K12	17.48	156	146	36.19			
Mo	L1	2.292	156	18	1.89			
Cd	L1	3.133	147	18	2.1			
Pb	L1	10.551	40	10	0.11	0.003	0.001	0.003
Pb	M1	2.342	155	18	2.45			

Appendix N

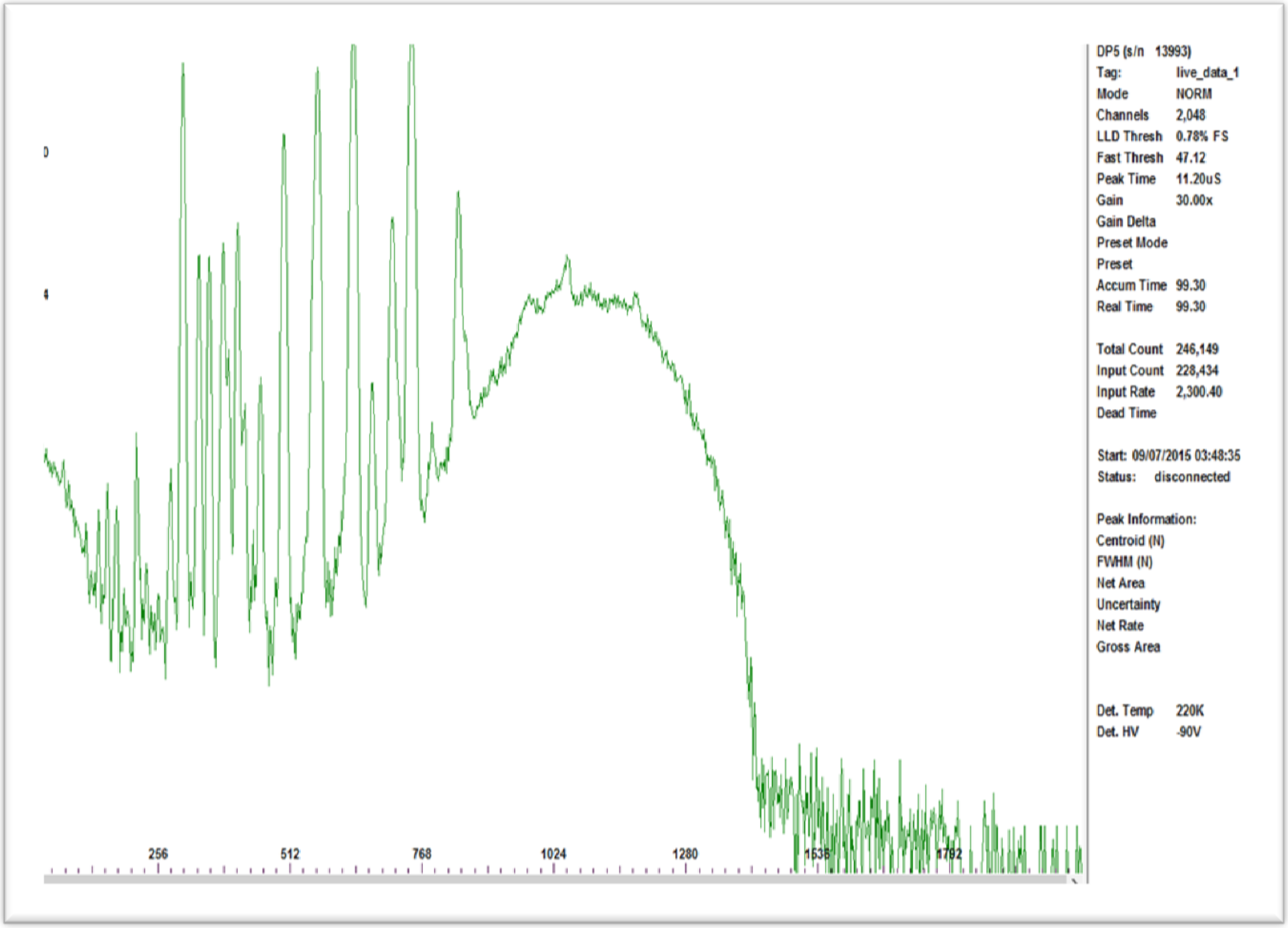
EDXRF Spectrum for sample



```
DP5 (s/n 13993)
Tag:          live_data_1
Mode          NORM
Channels      2,048
LLD Thresh    0.78% FS
Fast Thresh   47.12
Peak Time     11.20uS
Gain          30.00x
Gain Delta
Preset Mode
Preset
Accum Time    200.00
Real Time     200.00

Total Count   232,385
Input Count   194,771
Input Rate    973.86
Dead Time

Start: 09/07/2015 03:44:22
Status:    disconnected

Peak Information:
Centroid (N)
FWHM (N)
Net Area
Uncertainty
Net Rate
Gross Area


Det. Temp     220K
Det. HV       -90V
```

Appendix O

EDXRF Spectrum for sample and target



```
DP5 (s/n   13993)
Tag:           live_data_1
Mode           NORM
Channels       2,048
LLD Thresh     0.78% FS
Fast Thresh    47.12
Peak Time      11.20uS
Gain           30.00x
Gain Delta
Preset Mode
Preset
Accum Time     99.30
Real Time      99.30

Total Count    246,149
Input Count    228,434
Input Rate     2,300.40
Dead Time

Start: 09/07/2015 03:48:35
Status:    disconnected

Peak Information:
Centroid (N)
FWHM (N)
Net Area
Uncertainty
Net Rate
Gross Area


Det. Temp      220K
Det. HV        -90V
```