

**ASSESSMENT OF SELECTED PHYSICO-CHEMICAL
PARAMETERS OF WATER AND SEDIMENT IN RIVER
SIO, BUSIA COUNTY, KENYA**

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**Assessment of Selected Physico-Chemical Parameters of Water and
Sediment in River Sio, Busia County, Kenya**

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DECLARATION

This thesis is my original work and has not been presented for a degree in any other university.

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DEDICATION

This work is dedicated to my late mother, Betty Odalo Agutu and my son Kevin Omondi Ondoo Jr.

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ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectroscopy
ANOVA	Analysis of Variance
APHA	American Public Health Association
AWWA	American Water Works Association
BDL	Below Detection Limit
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DAP	Diammonium Phosphate
DL	Detection Limit
DNA	Deoxyribonucleic Acid
DO	Dissolved Oxygen
EC	Electrical Conductivity
EPA	Environmental Protection Agency, US
FAAS	Flame Atomic Absorption Spectroscopy
GoK	Government of Kenya
IPCC	Intergovernmental Panel on Climate Change
KEBS	Kenya Bureau of Standards
NEMA	National Environmental Management Authority, Kenya
NTU	Nephelometric Turbidity Unit
PC	Personal Computer
pH	Power of Hydrogen ion

PLI	Pollution Load Index
PMT	Photon Multiplier Tube
TDS	Total Dissolved Solids
TDS	Total Dissolved Solids
UNDP	United Nations Development Program
UNEP	United Nations Environmental Program
UV	Ultra Violet
WHO	World Health Organization
WSC	Water and Sewerage Company, Kenya
WWSC	Western Water and Sewerage Company

ABSTRACT

Pollution of ground water sources continues to remain an area of great concern due to the fact that pollution places a restriction on water use hence leading to water scarcity; and at the same time places high treatment cost for users downstream. Pollutants such as nitrates and phosphates are known to cause eutrophication of rivers and lakes, algal bloom, blue baby syndrome in new borns and also produce unpleasant smell and taste in water due to bacterial growth. High levels of heavy metals in water lead to bioaccumulation via the food chain. Bioaccumulation of metals such as lead, chromium and manganese always lead to complications such as brain and spinal cord inflammation; liver and kidney damage, liver cirrhosis and bronchitis respectively. It is therefore crucial to determine the levels of both anions and heavy metals when determining water quality. The objective of the study was to assess the quality of water along River Sio, Busia County, Kenya. Water samples were collected in pre-washed polyethylene bottles and analyzed for both physical and chemical characteristics. The data was subjected to statistical analysis using Microsoft excel. Turbidity was the highest recorded physical parameter with a range of 12.03 ± 0.61 NTU to 44.33 ± 0.5 NTU during the dry season and 212.50 ± 0.50 NTU to 481.83 ± 0.76 NTU during the wet season. The pH of water was in the range of 7.45 ± 0.02 to 7.62 ± 0.02 during the dry season and 6.70 ± 0.04 to 7.24 ± 0.05 during the wet season. Temperature was in the range of 23.47 ± 0.15 °C to 25.43 ± 0.21 °C during the dry season and 24.03 ± 0.12 °C to 27.20 ± 0.10 °C during the wet season. In water, 53% of the parameters showed significant seasonal variation at the 95% level of significance, with the mean concentration of 56% of the parameters being higher during the wet season according to paired t-test. The parameters that exceeded the WHO limit were turbidity, phosphates, lead, iron, nickel, chromium and cobalt indicating poor quality of water in River Sio. In sediments lead, copper and nickel were the only cations that were above the WHO recommended limit while cadmium was below the limit of detection. According to geoaccumulation index, nickel showed moderate pollution during the dry season. The contamination factor for lead was very high during the dry season, while pollution load index confirmed pollution due to anthropogenic activities in sampling sites 1 – 4 during the dry season and no pollution due to anthropogenic activities during the wet season. Poor agricultural practices, domestic and industrial waste water are the main factors that contribute to pollution of water and sediments in River Sio. The study proposes proper land use, proper treatment and disposal of sewage and use of organic manure and biological control as means of preventing water and soil pollution.

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

The most abundant chemical compound on planet earth is water. Water is a prerequisite for the sustenance of life on earth by all living organisms. Planet Earth is the only planet in the solar system having over 70% liquid water on its surface (Stierwalt, 2019). But due to population growth, rapid industrialization, use of inorganic fertilizers in food production and human activities like mining, water sources are increasingly getting polluted with highly toxic chemicals. Therefore, in order to protect the human species from water related illnesses, the quality of water consumed in households should be monitored on a regular basis, since consuming contaminated water leads to a variety of water borne diseases like bilharzia, dysentery and cholera (Basavaraja *et al.*, 2011). The availability of high-quality water is key in preventing diseases and improving the quality of both animal and plant life. Different types of impurities find their way into natural water sources through leaching, dissolution of aerosol particles and also via weathering of rocks. Human activities like the use of inorganic metal-based fertilizers and mining greatly contribute to pollution of natural water sources (Adefemi and Awokunmi 2010; Adeyeye 1994; Asaolu 1997).

On a global scale, if a country's renewable fresh water supply is below 1000m³ per capita per year, then that particular country is considered to be water scarce (Davis, *et al.*, 2009). Despite Kenya being a water scarce country, toxic chemicals such as herbicides, insecticides and untreated sewage have been continuously released into water sources hence making water unsuitable for agricultural and domestic use. Poor water quality and water pollution is becoming a menace especially in third world countries and if not checked will negatively affect fresh water bodies as well as the ecosystem. Pollution of fresh water bodies has been on the rise due to industrialization rat race as countries rush to attain industrialization. Kenya's quest to attain vision 2030

has seen a further increase in pollution related cases. Vision 2030 has led to increased industrialization and this has in turn led to the discharge of toxic effluent into water bodies leading to water and sediment pollution (Kithiia, 2011).

The Sio, Malaba and Malakisi Rivers drain two adjacent catchments in the Kenya – Uganda border with Sio River discharging into Lake Victoria and the Malaba and Malakisi Rivers discharging into Lake Kyoga. These Basins are home to 1.06 million people, 80% of who practice agriculture (Barasa *et al.*, 2011). The Malaba – Malakisi catchment covers an area of 1750 Km² while Sio catchment covering 1390Km². Globally, Kenya is ranked 146th on the Human Development Index whereas Uganda is ranked 163rd out of 188 countries (UNDP, 2017). The origin of River Sio is in Kaujai and Luucho Hills in Bungoma County, Kenya at 1800M above sea level. It then flows through Bungoma County, Teso sub-county in Busia County into Berkeley Bay and drains into Lake Victoria in Uganda, at an altitude of 1134M. Sixty five percent of the upper catchment of the River is in Kenya while the remaining thirty five percent is in neighboring Uganda. The catchment is the main source of livelihood for small scale farmers engaged in crop and animal farming as well as fishing. (Kamukoso and Aniya, 2007).

Upstream of River Sio before it gets to Busia town, subsistence agriculture is practiced which constitutes 80% of land use in the area. Pollution on the River at this phase is as a result of deposition of fertilizer-based chemicals which find their way into the River as a result of surface runoff during the rainy season into the River. The presence of maize milling industries located close to the banks of the River leads to the discharge of organic pollutants leading to high biological oxygen demand (BOD) of the River water. Agriculture is practiced in large scale in Busia and Bungoma counties using water from River Sio for irrigation. The high content of organic matter from the effluents discharged into the River by industries serves to further pollute the River with organic pollutants. Owing to the high demand for residential houses in Busia town, there has been a sharp rise in population growth and this has in turn led to poorly maintained

sewage systems leading to sewage leaks which end up in River systems leading to further pollution by the introduction of heavy metals and other toxic organic pollutants in the water system. This serves to elevate water scarcity since it places restrictions on the amount of water available for both domestic, agricultural and industrial use and at the same time increases the cost of water treatment for users downstream (Krhoda, 2006).

1.2 Statement of the Problem

Water pollution is caused by both human activities and natural processes, but human activities contribute a significant percentage towards water pollution. Poor agricultural practices coupled with industrial revolution have largely contributed to a rise in cases of water and soil pollution (Basavaraja Simpi *et al.*, 2011). There are extensive anthropogenic activities along River Sio which lead to pollution of the River. There are maize, sugarcane, millet and sorghum farms located upstream of River Sio. The increase in population of Busia County with poor or no sewer systems has also led to an increase in wastes that are dumped in the River hence leading to an increase in the level of pollutants in the River.

1.3 Justification

Water from River Sio is used for domestic purposes and is likely to be polluted by anthropogenic activities. Pollution of water sources leads to water scarcity since it places restrictions on water use and at the same time increases the cost of water treatment on users downstream (Krhoda, 2006). There is need to determine the presence and concentration of phosphates, nitrates, chlorides and sulphates from fertilizers, as well as heavy metals like lead, chromium, cadmium, iron, nickel, cobalt, copper, manganese and zinc in order to determine the pollution level of water in River Sio. After the determination of pollution levels in river Sio, the findings will be used to develop pollution preventive measures that will protect the river from further pollution in the future.

1.4 Hypothesis

Water and sediments in river Sio are of high quality and are not polluted by anthropogenic activities.

1.5 Objectives

1.5.1 General Objective

To assess the physico-chemical characteristics of water and sediments along River Sio.

1.5.2 Specific Objectives

- i. To determine the physico-chemical characteristics (pH, turbidity, electrical conductivity, temperature and dissolved oxygen) of water from River Sio during wet and dry seasons.
- ii. To determine the levels of selected heavy metals (Pb, Cr, Cd, Fe, Mn, Co, Ni, Cu and Zn) in water and sediments from River Sio during wet and dry seasons.
- iii. To determine the levels of phosphates, nitrates, sulphates and chlorides in water and sediments from River Sio during wet and dry seasons.
- iv. Carry out processing of data obtained from seasonal analysis of water and sediments to determine the level of pollutants and compare the results to WHO and KEBS standards.

CHAPTER TWO

LITERATURE REVIEW

2.1 Water Pollution

The chemical, radiological, biological and physical properties of water are the major parameters used to define the quality of water. These parameters are used in setting standards for assessment of compliance to the set water quality standards by WHO and local standardization bodies such as the KEBS. Abiotic factors directly affect the role and quality of plant and animal life in an ecosystem. These factors include temperature, salinity, pH and dissolved oxygen (Diersing, 2009). The presence or absence of pollutants in a River is dependent on the terrain through which the water flows. If there is a high concentration of pollutants in a given River terrain then the level of pollutants in the River will be high. The presence of chemical industries along the path which the river flows also serves to increase the concentration of pollutants such as heavy metals and organic materials. There are two sugar processing industries located close to River Sio. These are Western sugar processing factory and Busia sugar industry. Plates 2.1 and 2.2 show both the front gate and conveyor belts of Busia sugar industry, which is located on the banks of River Sio.



Plate 2.1: Front gate of Busia sugar industry located on the banks of river Sio (Source: author)



Plate 2.2: Busia sugar industry located on the banks of river Sio (Source: author)

River systems are vital for sustenance of terrestrial and aquatic life, including smooth functioning ecosystems, communities and economies. Unfortunately, the major fresh water bodies in the world are under threat of pollution as a result of agricultural and industrial growth. The release of toxic gases such as NO_2 , SO_2 , SO_3 and CO_2 also serve to increase pollution levels as well as depleting the ozone layer (UNEP, 2010). Low water quality is a threat to ecosystem and economic growth and it also threatens the lives of animals and plants in different habitats. This negatively affects the quality of finished products and agricultural produce and this in turn leads to a decline in global economic growth. The quality of water is affected by a number of human related activities including mining, discharge of urine and fecal matter into Lakes and Rivers, as well as the use of metal based inorganic fertilizers in agriculture. The use of chemicals such as pesticides in controlling pests and weeds releases toxic chemicals into water systems and it is estimated that approximately 300 – 400 million tons of chemical waste into the waters of the world annually (UNEP, 2010).

In terms of support, water quality has been given priority as compared to water quantity even though both play a key role in the support of life in both aquatic and terrestrial habitats. If the quality of water is poor then it will have a direct negative impact on

water quantity since it limits the amount of water that is available for agriculture, domestic and industrial sectors (IPCC, 2001). By the year 2030 half of earth's population will be living in areas of low water availability, according to the projected climate change scenarios (UNEP, 2010). Therefore, it is important to preserve and protect the existing fresh water sources such as Lakes and Rivers so as to protect them from pollution, eutrophication and ultimately drying up. Most countries in Africa are facing water scarcity and Kenya is one such country, with low fresh water endowment of 526 m³ per capita per year (GoK, 2015).

Therefore, to ascertain the suitability of water for consumption, it is necessary to undertake the examination of water quality through physical, biological and chemical analysis of water (Khopkar, 1993). The assessment of water quality is crucial in controlling pollution and also in ensuring sustenance of both aquatic and terrestrial lives. High quality water is that which is free of fecal matter, color, heavy metals and suspended matter (Ali *et al.*, 2008). Environmental water quality relates to water bodies such as Rivers, lakes and Oceans. Water quality standards for surface water vary significantly due to difference in the environmental conditions, ecosystems and intended human uses. Toxic chemicals and high population of microbes' present health hazard for non-drinking water such as that used for swimming, irrigation, skiing, fishing, and industrial uses. These can in turn affect aquatic animals which depend on water as a source of food and as a habitat (Diersing, 2009).

2.2 Physical Parameters for Water Quality

Physical examination of water can be used to ascertain its quality. This is done through the study of physical parameters such as color, turbidity, pH, TDS, odor and electrical conductivity (Khoprar, 1993). Before water is used for agricultural and domestic purposes it should be tested to determine its suitability for these purposes. The parameters employed for the determination of water quality will mainly depend on the water's intended use and the desired degree of quality and purity. Since the pollutants present in water range from dissolved, floating to microbiological, it is vital to determine

the quality of water on a regular basis if water borne diseases and harmful chemical compounds are to be kept at bay (Begum *et al.*, 2005).

2.2.1 Turbidity

Turbidity is the amount of particulate matter suspended in water. It measures the scattering effect that suspended solids have on light. The higher the intensity of scattered light the higher is the turbidity. Turbidity in water is caused by various substances such as suspended particles that are low in mass and cannot settle by gravitational influence. Turbidity influences the level in which sunlight penetrates water. If the water is more turbid, less light will pass through and if it is less turbid more sunlight will penetrate it. This will in turn have a positive or negative impact on the rate at which green hydrophytes carry out photosynthesis. During the rainy season, clay, silt and other suspended particles contribute to high turbidity of water, while during the dry season silt, clay and other suspended particles will settle contributing to low turbidity (Saksena *et al.*, 2008). Water transparency is the inverse of turbidity. High turbidity in water can be prevented by limiting the number of particles that find their way into water systems and this can be done through proper land use techniques such as terracing. The particles responsible for high turbidity in water include soil particles, suspended matter from garbage and untreated sewage (Dojlido and Gerald, 1993).

2.2.2 Electrical Conductivity

Electrical conductivity is directly related to salinity levels in water, even though agricultural activities such as fertilizer addition can also lead to an increase in the level of salts in River water. Rocks rich in minerals find their way into water bodies through weathering and these dissolved minerals eventually increase water's salinity, translating to increased electrical conductivity. The salts which affect the salinity of surface and ground water include salts like sodium chloride, magnesium nitrate and potassium hydrogen carbonate. Elevated levels of electrical conductivity are directly related to total dissolved solids (Provin and Pitt, 2010).

Electrical conductivity shows strong positive correlation with other water quality parameters such as chemical oxygen demand, temperature, pH, TDS, total hardness, chloride and iron concentration in water. Electrical conductivity is determined with the help of portable electrical conductivity meter which measures the resistance offered by water between two platinized electrodes. The instrument is standardized with known values of conductance observed with standard potassium chloride solution. Dissolved chemical species that affect the conductivity of water include cations and anions such as sodium, potassium, manganese, copper and chlorides, nitrites, phosphates and sulphates respectively (Morrison *et al.*, 2001).

2.2.3 Total Dissolved Solids

Water hardness is expressed in terms of the bicarbonates of calcium and magnesium present in it. These are the compounds that cause water hardness. Hard water does not lather easily with soap and therefore makes cooking and cleaning difficult since it consumes a lot of soap and at the same time leaves black spots on cooking vessels made of aluminium, pipes and water heaters. Depending on the type of hardness present in water, hardness of water can be removed by either boiling the water or passing the water through sodium cationic exchanger (Provin and Pitt, 2010).

2.3 Chemical Characteristics of Water Quality

Chemical characteristics give specific information about water, as opposed to physical properties; hence they come in handy when determining the properties of water samples. When determining the presence of heavy metals in water, the presence of suspended sediment particles must be taken into account since these particles contain a significant number of heavy metals adsorbed on their surfaces. Even though these particles don't dissolve in water, they can bio accumulate in human tissues when this water is consumed by humans. Therefore, addition of concentrated nitric acid to water during sampling prevents adsorption of these metallic species to the walls of the container therefore making the metal analytes present in high concentration in solution form (Tebbutt, 1983).

2.3.1 Dissolved oxygen

The level of dissolved oxygen in a water body is indicative of photosynthesis levels, bacterial activity and nutrient availability. The levels of dissolved oxygen are usually high during the dry seasons due to high temperatures and this influences the solubility of respiratory gases, such as CO₂ and O₂ in water. Since there is intense sunlight during the dry season, phytoplankton and other aquatic plants carry out photosynthesis at a much higher rate using CO₂ and releasing a lot of O₂ in the process, accounting for high levels of O₂ during the dry season (Krishnamurthy, 1990).

2.3.2 Nitrates

When nitrites or nitrates are present in large amounts in drinking water, they cause complications in infants such as the blue baby syndrome. Therefore, domestic water used by pregnant women as well as infants should not have high levels of these anions. The growth of algae in water bodies can be brought about by elevated nitrate concentration and the presence of microbes which may lead to water having unpleasant smell and taste (Provin and Pitt, 2010). The continued use of nitrogen-based fertilizers coupled with oxidation of ammonia in sewage waste has significantly contributed to a sharp rise in the levels of nitrates and nitrites in Rivers and Lakes. During the nitrogen fixation process in the root nodules of leguminous plants, the oxidative conversion of nitrogen to nitrates leads to the formation of nitrites as intermediates. The nitrates present in ground water are always converted to nitrites via a reduction process by denitrifying bacteria (Morrison *et al.*, 2001).

Depending on the levels of microbiological activities in surface water, the concentration of nitrates may increase or decrease with change in seasons from dry to wet. The presence of algae in surface water may also serve to decrease the concentration of nitrates. So far, the best way to reduce the high concentration of these anions in water bodies is through protection of Rivers and Lakes from pollution since there is no known process that is capable of completely getting rid of nitrites and nitrates from water. When coming up with measures to prevent water pollution, consideration should be given to point where raw sewage and fertilizers from farms find their way into water

bodies. The most appropriate water treatment technique that can be employed in getting rid of nitrates and nitrites from surface water is reverse osmosis (Provin and Pitt, 2010).

2.3.3 Phosphates

High levels of phosphorus are found in inorganic fertilizers such as ammonium phosphate and organic/compost manure. Phosphorus may find its way into Rivers and Lakes due to leaching and weathering of rocks rich in phosphorus e.g. fluorspar, surface runoff from farms during the rainy season and the discharge of industrial effluent rich in phosphorus. Phosphates are also introduced into surface water through the use of soap and detergents in washing which leads to surfactants getting into water therefore leading to elevated levels of phosphates. The major side effect of elevated levels of phosphorus in surface water is the growth of algae, which if goes unchecked can lead to eutrophication of Rivers and Lakes. Therefore, there is a strong correlation between the levels of phosphorus in surface water and the development of algal bloom (Dojlido and Gerald, 1993). Water will develop unpleasant odor and taste due to the presence of algae in it. Presence of algae on surface water may serve to balance the O₂ and CO₂ levels. This is due to the fact that green algae have photosynthetic tissues which carry out photosynthesis during the day, producing O₂ as a byproduct, while at the same time-consuming CO₂ which is a raw material for photosynthesis (Ellis *et al.*, 1989).

2.3.4 Chlorides

NaCl is polar and hence water soluble, producing both Cl⁻ and Na⁺. The Oceans and Seas are usually salty due to the dissolution of chloride bearing rocks in water. The concentration of NaCl is usually high in Rivers located in the coastal regions due to their proximity to the oceans. Sea spray brought about by wind may also contribute to increased salinity of the coastal Rivers (Provin and Pitt, 2010). Increased surface water salinity is strongly correlated with pollution from human activities e.g. urine and fecal matter, use of salts to melt ice on roads especially during winter and effluent from water treatment plants especially sodium salts used as water softeners. Increased salinity, caused by high concentration of dissolved salts, has a negative effect on water quality

since it leads to the death of fresh water organisms through dehydration, places restrictions on water usage and at the same time imposes high water treatment cost since desalination is a complex and expensive process (Mullaney *et al.*, 2009).

2.3.5 Sulphates

Sulphate is a radical of sulphuric acid given off when the acid ionizes. They are present in nature in combined form in minerals such as calcium sulphate, ammonium sulphate and sodium sulphate. These minerals eventually find their way into ground water via dissolution. During the rainy seasons, sulphates are introduced in Rivers and Lakes courtesy of surface runoff from sulphate-based fertilizers and industrial effluents rich in sulphates. Soils and rocks rich in minerals such as gypsum and sulphur-based compounds like iron sulphide contribute to pollution by sulphates in water bodies when these compounds are introduced into water bodies and eventually converted to sulphates either through oxidation or by the action of sulphur bacteria. Calcium sulphate is one compound that is responsible for permanent hardness of water and can therefore lead to blockage of water pipes due to scale formation and also reduce the efficiency of steam boilers due to formation of scales. When sulphates are present in high concentration, water will develop bitter taste and in some instances the smell of rotten eggs due to the presence of hydrogen sulphide (Provin and Pitt, 2010).

Huge volumes of hydrogen sulphide gas are usually produced by sulphur reducing bacteria, making use of sulphur as an energy source during a process known as chemosynthesis, converting sulphates present in water to hydrogen sulphide. Low levels of sulphates in water bodies encourages the growth of algae while high sulphate levels cause pipe blockages, bitter taste in water and the unpleasant rotten egg odor of hydrogen sulphide gas. When water has high concentration of sulphates, it becomes hard due to the combination of calcium and magnesium ions with sulphate radicals forming sulphates of magnesium and calcium which are responsible for permanent hardness of water. Hard water doesn't lather easily with soap and this makes washing an uphill task due to wastage of soap (WHO, 2004). Not all of the above listed pollutants occur naturally. A big number of pollutants are introduced into the environment as a result of

human activities including mining, poor agricultural practices and disposal of raw sewer and untreated industrial effluents into soil and water bodies. Hence pollution mitigation focuses on removal of pollutants from Rivers and Lakes. For this dream to be realized, certain measures should be put in place and this include seeking alternative agricultural practices, setting up laws that govern mining activities and seeking heavy penalties for those breaking environmental laws.

2.4 Land use and Soils in Sio Catchment

Matayos sub-county in Busia County is home to the Sio catchment. The region experiences two rainy seasons; the long rains that last from March to June whereas the short rains start from September to November. The catchment has witnessed significant population growth due to the availability of fertile soil for agricultural practices. About 80% of land in the Sio catchment is used for agriculture. The parts of the catchment that receive maximum rainfall are located around Lake Victoria and on the slopes of Mt. Elgon. The annual temperatures of Sio catchment range from 16.2 °C to 28.7 °C. The major food crops grown in the catchment include maize, sorghum, sweet potatoes, millet and cassava whereas the cash crop is mainly sugarcane which is a raw material for a number of sugar processing industries located around the study area. Sugar cane plantation at the banks of river Sio is shown in Plate 2.3. The percentages of land use along the River is as follows: grassland patches account for 15.1%, subsistence farming takes 24.2%, bush land patches cover 32% of the land under use whereas wet land patches cover 40% of the land under use. Soils in the catchment are mainly volcanic ash soils while soils at the lower segment of the catchment originate from metamorphic rocks (Barasa *et al.*, 2011).



Plate 2.3: Sugarcane plantation located a few meters from river Sio (Source: author)

2.5 Water Pollution

Thanks to industrial revolution, development in technology and human activities, most naturally occurring water sources are contaminated by pollutants from both point and non-point sources. These sources include surface runoff from farms, raw sewage and untreated industrial effluent. Most of these chemical pollutants remain persistent in the environment much longer before they decay while some are completely non-biodegradable and cannot be decomposed by bacteria. Pollutants that are much denser than water e.g. halogenated solvents from pesticides tend to vertically move downwards and collect at the bottom of the River where they get adsorbed on sediment particles. Since non-point pollutants originate from different sources, they are quite hard to detect as they originate from larger areas of the catchment. It is therefore important to keep an eye on human activities, such as mining and agricultural practices, in areas around natural sources of water such as Rivers and Lakes in order to keep water and soil pollution at bay (Sliva and Williams, 2001).

2.6 Pollution Indices

The extent to which a water source has been polluted can be determined by examining the level of pollutants in sediments, since sediments are sinks and hence act as reservoirs for pollutants. The measured concentrations of heavy metals in sediments can be used to calculate the following pollution indices: geo accumulation index, enrichment factor, contamination factor and pollution load index. The background values used to determine geo accumulation index, enrichment factor and contamination factor are mostly obtained from Taylor and Mc Lennan, 1995 (Taylor and Mc Lenan, 1995).

2.6.1 Geo-accumulation Index

In order to determine the extent of pollution in sediments, geo accumulation index is calculated for each element. Defined by Muller (1979) geo accumulation index determines metal contamination in sediments by comparison of metals in samples with background concentration levels. Muller (1981) distinguished seven categories of geo accumulation index classes as shown in table 2.1 (Cardellicchio *et.al.*, 2010).

Table 2.1: Geo-accumulation Index classes by Muller (1981)

I geo value	Class	Sediment Quality
≤ 0	0	Unpolluted
0 - 1	1	Unpolluted to moderately polluted
1 to 2	2	Moderately polluted
2 to 3	3	Moderately to strongly polluted
3 to 4	4	Strongly polluted
4 to 5	5	Strongly polluted to extremely polluted
> 5	6	Extremely polluted

2.6.2 Contamination Factor

Defined by Hakanson (1980), the contamination factor is used to evaluate the contamination of sediments in a given location. Contamination factor classifies heavy metal pollutants in sediments into four categories. $C_f \leq 1$ = low, $C_f 1 - 3$ = moderate, $C_f 3 - 6$ = considerable contamination while $C_f > 6$ = very high contamination.

2.6.3 Enrichment Factor

Proposed by Simex and Helz (1981), it is used to assess the level of metals in sediments compared to the pre-industrial era. Enrichment factor normalizes the concentration of metals as a ratio to the concentration of another metal in the sediment (Mohsen and Alireza, 2014). In this study, iron was used as the reference element. The enrichment factor (E.F) is divided into several classes. $E.F < 1$ = no enrichment, $E.F 1 - 3$ = minor enrichment, $E.F 3 - 5$ = moderate enrichment, $E.F 5 - 10$ = moderately severe enrichment, $E.F 10 - 25$ = severe enrichment, $E.F 25 - 50$ = very serious enrichment while $E.F > 50$ = extremely severe enrichment.

2.6.4 Pollution Load Index

The pollution load index (PLI) is used to determine pollutants that arise as a result of anthropogenic activities. Pollution due to anthropogenic activities is indicated by a $PLI > 1$ while a $PLI < 1$ indicates no pollution by anthropogenic activities (Dimuthu, N and Wijeyarante W.M, 2016)

2.7 Sources of Water Pollution

The major source of non-point pollutants in Rivers and Lakes is agricultural activities. Elevated levels of heavy metals, pesticides and herbicides have come about mainly as a result of agricultural activities. The origin of dissolved salts, organic compounds, sulphates, phosphates and chlorides can be traced back to agriculture. Whether from point or non-point sources, elevated concentration of heavy metals in water is becoming a serious threat to organisms in both aquatic and terrestrial habitats (Humood 2013, and Naveedullah *et al.*, 2014). When heavy metal concentration in water exceeds environmental tolerance limits, use of that water in agricultural irrigation and aquaculture activities could be harmful to the aquatic ecosystem and humans via the food chain (Wright and Welbourn, 2002). Continued use of inorganic fertilizers has resulted in an increase in the levels of heavy metals in water due to surface run-off during the rainy season. Water contamination by fecal matter leads to water borne diseases like cholera, bilhazia and dysentery (Adefemi and Awokunmi, 2010).

Agriculture is the backbone of Kenya's economy and the rise in Kenya's population demands that food productivity should also be increased at the same rate. This strains the existing land resources as more land has to be put under cultivation to cater for the rising demand for food. Changes in land use together with poor agricultural practices has led to increased levels of pollution in Rivers and Lakes, hence leading to a rise in water treatment cost for users downstream (Kimani *et al.*, 2016). When untreated sewage is used for irrigation, the soil gets contaminated and the pollutants bio accumulate in plant tissues (Quinn, 1978; Hemkes, 1980). This untreated sewage contains highly toxic heavy metals like lead, mercury, selenium, arsenic and copper. Addition of these metallic species to soil renders it infertile (Adnan *et al.*, 2010). Research has proven that non-point chemical wastes from farms which are normally discharged into River systems have harmful environmental impact on aquatic organisms (Obasohan *et al.*, 2010). Sand harvesting is widely carried out downstream of river Sio. Plate 2.4 shows sand mining activity in River Sio.



Plate 2.4: Sand harvesting activity in River Sio (Source: author)

2.8 Industrial Sources of Water Pollution

The rise in industrial revolution and change in manufacturing technology has led to the generation of toxic chemicals and if these effluents are discharged into water and soil without being treated result in both water and sediment pollution (Kulkarni, 1997). Elevated levels of heavy metals such as mercury, lead, arsenic and selenium from manufacturing industries have raised an alarm as they cause pollution of water sources and at the same time endanger the life of aquatic animals (Ellis, 1989). Household wastes are rich in organic pollutants and when these pollutants find their way into water bodies lead to an increase in the levels of biological oxygen demand BOD (Kulkarni, 1997). High levels of organic matter make water unsafe for both irrigation and drinking (Hari, 1994). However, the use of urine and sewage effluent as fertilizer is gaining prominence in developing countries, especially in Africa, and is considered an excellent source of organic matter and serves as excellent compost manure (Patil *et al.*, 2012).

2.9 Heavy Metals

The major sources of surface and ground water pollution by heavy metals are natural and anthropogenic activities (Ato *et al.*, 2010; Naveedullah *et al.*, 2014). Irrespective of the source, increasing levels of heavy metals in water continues to pose a threat to humans and aquatic organisms (Humood, 2013; Naveedullah *et al.*, 2014). The heavy metals that pose serious threat to human health are arsenic, chromium, nickel, zinc, lead and cadmium (EU, 1998; TBS, 2005; WHO, 2008). The use of contaminated water for irrigation poses a threat to both plants and aquatic organisms as the heavy metals present in water are passed from one organism to the other via the food chain (Wright and Welbourn, 2002). In mineral rich countries, mining activities are on the rise and this increases heavy metal pollution of water bodies way beyond the recommended WHO limits. The situation is worsened by the absence of practices and laws to curb environmental pollution (IAEA, 2010).

In a bid to put in place measures that curb pollution during mineral extraction, African nations, Kenya included, have set up mining regulations that will see the prevention of

water and soil pollution by heavy metals (SA 1996, Akabzaa2004, MEM 2010, TAEC 2011, Kenya 2014). But if these adopted measures are to be realized, the participating parties must be ready and willing to comply with the set water and soil quality standard laws. The mining regulations require the determination of heavy metals in water and soil to be conducted prior to mining (IAEA 1998, IAEA 2005, IAEA 2009, Banzi *et al.*, 2015). Bioaccumulation of lead to high concentrations causes loss of memory and inability to concentrate in children to weakness, numbness and pain from nerve damage in adults (Kaur and Mehra, 2012). Nickel affects the central nervous system, damages the DNA causing mutation and is also carcinogenic (Idriss and Ahmad, 2013).

2.9.1 Lead

Lead is a transition metal in the periodic table characterized by +2 and +4 oxidation states with a concentration of 13 mg/kg in the earth's crust. Most lead isotopes occur as end products of radioactive decay (Baum, *et.al.*, 2002). Lead finds its way into water bodies via corrosion of water pipes, leaching of minerals rich in lead e.g. lead II sulphide and untreated industrial effluent (EPA, 2001). Salts rich in lead are also used in the manufacture of pigments, herbicides and insecticides. When these compounds are washed into Rivers and Lakes by surface runoff, it leads to elevated levels of lead in water bodies (Smoots, 2011). In order to get rid of lead-contaminated water in pipes, it is advisable to flush the water pipes, especially during the morning hours, before the water is used for domestic purposes. This is because water that has been in constant contact with lead pipes is most likely to dissolve high amounts of lead in it (EPA, 2001). Lead poisoning manifests itself through symptoms such as brain and spinal cord inflammation as well as gastrointestinal discomfort (Provin and Pitt, 2012).

2.9.2 Manganese

Manganese appears as a pinkish-grey, hard and brittle metal. The metal is found in combined form in compounds such as carbonates and silicates in ocean beds, rocks and soil. The oxidation states of manganese range from - 3 to +7 even though the most common oxidation states in aquatic habitats are +2 and +4. On average, soil contains

approximately 7 – 900 mg/kg of manganese while sea water contains about 10 mg/L of manganese (Mersey, 2001). Iron and manganese are similar, in that both metals can be introduced into the soil in reducing conditions followed by the deposition of the metal whose concentration is too high as water interacts with oxygen and gets aerated. Another similarity between the two metals is that both cause staining of clothes and other fabrics even though staining is more pronounced in cases where manganese interacts with laundry and fabrics (EPA, 2001). Manganese finds its way into the environment via human activities such as the use of inorganic fertilizers in agriculture, burning of fuels and discharge of raw sewage and untreated industrial effluents into the soil and water bodies (Mohaihs, *et.al.*, 2004). In the human body, manganese is vital in blood clotting, regulation of blood sugar and carbohydrate breakdown in cells (Jefferey *et.al.*, 1992).

The intake of high levels of manganese can lead to bioaccumulation of the element in body tissues, leading to liver cirrhosis. If manganese bio accumulates in tissues of an individual already suffering from liver cirrhosis, it will cause other equally fatal ailments such as lung embolism and bronchitis. Long term exposure to manganese by men leads to impotence. Manganese poisoning may be manifested by symptoms such as weakness of body muscles, lack of sleep, recurring headaches and dullness (Emelina, 2011). Very high levels of manganese in water causes a grayish/black coloration which in turn causes staining in clothes and plumbing equipment such as pipes (Provin and Pitt, 2010).

2.9.3 Cadmium

Cadmium is a d-block element with a soft silver-white appearance. It doesn't naturally occur in its pure state. Cadmium occurs in combined states in form of carbonates, sulphides as well as oxides of lead, copper and zinc. Cadmium may find its way into the environment through mining and metal refinery, especially during the purification of zinc hence there is a strong correlation between zinc refinery and cadmium production. The rate at which cadmium has been produced annually since 1990 has been about twenty tons. The rate at which cadmium has been released into the environment has decreased thanks to new metal smelting and refining technologies. About 18% of the

cadmium that is produced globally is as a result of recycling. About 81% of the cadmium that is produced globally goes into battery manufacture, especially in the manufacturing of nickel-cadmium batteries. Cadmium also finds use in pigments used in the manufacture of plastics, steel and iron plating, and also in the manufacture of alloys of cadmium with metals such as copper, tin and lead (Greenfacts, 2018). Compounds of cadmium also find use in industries such as photography, lasers, pesticides, fertilizers (especially superphosphate fertilizers), solar cells, semi-conductors and printing industries. In order to curb cadmium pollution in both terrestrial and aquatic ecosystems, measures such as the use of pesticides and fertilizers with very low cadmium levels should be embraced. Proper disposal of industrial effluent should also be considered as effluents from industries like battery manufacturing and printing industries are high in cadmium and should therefore not be disposed in soil and water. (Baum, 2002; Schute *et al.*; 2008 Walakira, 2011). Volcanic eruptions and the weathering of rocks are responsible for the natural release of cadmium from the earth's crust into the environment.

The high toxicity of cadmium to living organisms arises from the fact that elemental cadmium cannot be broken down into harmless products hence it remains persistent in the environment as it gets carried from one ecosystem to the other by surface runoff, especially during the rainy seasons (Greenfacts, 2018). Cadmium poisoning in humans manifests itself through symptoms like retarded growth, hypertension and anemia (Provin and Pitt, 2010). Bio accumulation of cadmium in animal tissues is elevated by feeding on foods that have low levels of iron. Cadmium destroys body organs by hardening tissues and if not controlled it may lead to death. Cadmium affects human fertility by lowering sperm count in men and reducing fertility in women (Johannes *et al.*, 2006).

2.9.4 Copper

Copper is a transition metal with reddish-brown appearance whose structure is face-centered cubic. It is a very good conductor of heat and electricity due to the presence of delocalized electrons, ductile and malleable. The oxidation states of copper are the +1

and +2 oxidation states but the most abundant oxidation state is the +2 oxidation state. Copper has got three ores that are abundant in nature. These are the sulphides, halides and oxides of copper (Provin and Pitt, 2010). In nature, copper is found in water, sediments and rocks and at low concentrations in the air. The level of copper metal in the earth's crust is 50 mg/kg. Environmental pollution by copper occurs via mining activities, especially in copper belt regions, fossil fuel combustion, and fertilizer production and also from natural sources such as volcanic eruptions, forest fires, wind-blown dust and sea sprays. When copper interacts with the soil, it doesn't move away from the source of introduction due to the fact that it strongly bonds to humus and other particles in the soil. Most compounds of copper are water soluble and are usually transported from the source as copper ions bound to water particles. Copper also interacts strongly with sediments and this explains why the concentration of the metal is usually high in sediments as compared to water from the same source. Metallurgical dusts from metal processing plants are mainly responsible for the presence of copper in the atmosphere. Combustion of fuels like kerosene (used in cooking and lighting houses in most third world countries) is to blame for the high levels of copper metal indoors (ATSDR, 2004). Copper is vital in human nutrition since it forms a major part of a group of enzymes known as metalloenzymes which are responsible for speeding up the rate of biochemical reactions in the body. The role of copper in metalloenzymes is that it donates or accepts electrons during the enzymatic action of metalloenzymes.

High concentration of copper in mammalian system has its side effects which may range from Alzheimer's disease to other neurological diseases like Prion disease. Humans get exposed to copper through taking water and food that is contaminated with copper. When this exposure is high, complications such as anemia may result due to the fact that high levels of copper in the bloodstream interferes with the metabolism and transport of iron hence leading to iron deficiency in the body. This in turn leads to the formation of fewer red blood cells since iron is a major component of hemoglobin in the red blood cells. However, ingesting 20 – 70 g of copper may result to symptoms such as nausea,

gastrointestinal bleeding, organ failure (mainly the kidney and liver) and finally death occurs if one doesn't seek immediate medical attention (ATSDR, 2004).

2.9.5 Nickel

The 24th metal in the earth's crust in terms of percentage abundance is nickel. It is a hard metal with a silvery-white appearance. Owing to nickel's reactivity, the element doesn't naturally occur in its free state but rather occurs in combined form with other elements such as chlorine, oxygen and sulphur. It also occurs naturally in outer space, in meteorites, and on the floor of oceans as sea floor nodules. In metallurgical industries, nickel is usually combined with chromium, copper, zinc and iron to give alloys which are in turn used in minting coins, jewelry making and also in making parts of machines used in manufacturing processes such as heat exchangers. The most notable alloy of nickel which has found wide applications in equipment manufacture due to its corrosion resistant nature is stainless steel. Most compounds of nickel are polar and therefore soluble in water and are green in color (ATSDR, 2005). Nickel finds wide applications in electronics manufacture and in nickel-cadmium batteries. Nickel gets adsorbed on soil and sediment surfaces when it interacts with soil and this explains why the levels of nickel in soils and sediments are usually much higher as compared to the concentration of nickel in water.

Nickel is usually absorbed into the body as soluble nickel ions. The amount that is absorbed through the skin will mainly depend on the charge, shape and size of the particles. Even though there is poor absorption of nickel via the gastrointestinal tract, nickel poisoning mainly occurs through intake of contaminated food and water. Exposure to very high concentrations of nickel leads to development of symptoms ranging from severe abdominal pain, diarrhea, breathing difficulties to nausea and vomiting. Exposure to extremely high levels of nickel leads to death through cardiac arrest (Young, 1995). Nickel poisoning lowers the ability of the body to fight infections by lowering body immunity. It also leads to the formation of free radicals in the body, leading to mutation which can be cancerous to the body (Das, *et.al.*, 2008).

2.9.6 Chromium

Chromium occurs naturally in rocks, animal and plant tissues and also in the soil. It occurs in combination with other elements such as oxygen, sulphur and chlorine. Compounds of chromium occur in different oxidation states. These include chromium (0), chromium (III) and chromium (VI). Although chromium is toxic, chromium (III) is needed in very small concentrations for human health development (ATSDR, 2012). Chromium may be introduced into the environment through surface runoff from agricultural farms during the rainy season and leaching of rocks rich in ores of chromium e.g. chromites. Volcanic eruptions also account for the distribution of chromium rich rocks. The average level of chromium in soil is between 1-300 mg/kg that in oceans is between 5-8 mg/kg while the concentration of the metal in ground water is 0.026 mg/L (Gonzalez and Flegal, 2005). Chromium finds use in industries like electroplating, where it is used in surface coating as well as in decorative coatings of vehicles and water pipes. Salts of chromium (VI) are used in preserving timber to keep termites and other wood eating insects at bay. These salts contain compounds such as chromate-copper-arsenate (Ilhan *et.al.*, 2004). Chromium is not persistent in the atmosphere as it changes form from one oxidation state to the other, especially when it is present in soil or water (ATSDR, 2012). Chromium exposure occurs through different routes. It can occur via breathing contaminated air which has got high amounts of chromium in it. Cigarette smoke contains high levels of chromium and this accounts for huge percentages of chromium in air when combined with industrial smoke. Cigarette smoke accounts indoor chromium levels as it contains 10-400 times chromium levels as compared to air that is outdoors.

Exposure to chromium usually occurs in industries such as metallurgy and hide and skin industries where tanning is carried out. Bio-accumulation of chromium in animal tissues occurs when one feeds on food that has got high levels of chromium in it. A number of foods contain low levels of chromium. Such foods include vegetables, fruits, meat and nuts (ATSDR, 2012). Chromium (III) is vital in controlling the level of sugar in the

blood hence it helps in controlling diabetes. However high levels of chromium (VI) lead to liver and kidney damage (Dyan and Paine, 2001).

2.9.7 Zinc

Zinc is a transition metal with a bluish-white appearance but has a shiny appearance when pure. In nature, the element is found in combined form with oxygen, sulphur and chlorine. The metal is too reactive to occur in nature as a free element. The most abundant ore of zinc in the earth's crust is zinc II sulphide. All sulphides are black except zinc II sulphide and it is for this reason that zinc II sulphide, together with zinc II oxide, is used in the manufacture of white paints. These compounds of zinc are also used in the manufacture of ceramics and also in rubber production. Other compounds of zinc find application in the dyeing industry, especially in dyeing fabrics, and in wood preservation. They include zinc chloride, zinc sulphate and zinc acetate. The pharmaceutical industry makes use of compounds of zinc in the manufacture of several pharmaceutical products such as deodorants, antidandruff shampoo, sun screens and rash ointments. Zinc may find its way into the environment via human activities such as mining, metal processing and purification of zinc ores. Zinc may be introduced into water bodies through surface run-off carrying domestic waste water rich in zinc and also from discharge of untreated industrial effluent with high concentrations of zinc into Lakes and Rivers. The use of inorganic fertilizers, which contain high concentrations of heavy metals, has led to elevated levels of zinc in soil. High levels of zinc in both soil and water are mainly due to the presence of fine zinc particles in the air. When these particles settle on water and soil, it leads to increased levels of the metal in the environment. Zinc can be removed from the air by the help of rain and snow since rain and snow transports zinc from the air and deposits it in water bodies whenever it rains. Since zinc is denser than water, the metal particles usually settle at the bottom of Rivers and Lakes therefore leading to an increase in zinc levels in sediments. But small amounts of the metal can dissolve in water and remain in solution form, while the insoluble salts of zinc remain suspended on the surface of water as fine particles

(ATSDR, 2005). In living organisms, zinc plays an important role in both physiological and metabolic processes including protein synthesis (Nogawa, *et.al.*, 2004). Acidic conditions such as low pH in water leads to an increase in the levels of zinc in water since the acidic conditions result in the corrosion of the zinc-copper alloys used in making water pipes.

High concentration of zinc in water gives water a white chalky appearance and an unpleasant taste (Provin and Pitt, 2010). Short term sickness (fume fever) can be caused by inhaling huge amounts of zinc. The symptoms are reversible if one is no longer exposed to zinc. Ingesting large amounts of zinc may lead to symptoms like nausea, vomiting and stomach cramps. The pancrease may be damaged by ingesting large amounts of zinc over a long period of time. Low levels of zinc in the body may lead to low appetite, low immunity which leads to skin rashes and poor sense of smell and taste. Consuming food with very little zinc may also lead to poor sex organ development, retarded growth in children and birth defects in new borns (ATSDR, 2005).

2.9.8 Cobalt

The appearance of cobalt is silvery grey. Cobalt has similar properties to nickel and iron. Cobalt 59 is the only isotope of cobalt that is stable; all the other isotopes of cobalt are radioactive. Cobalt is found in little concentrations in water, soil, rocks, plants and animals. It also exists in outer space in meteorites. Due to the metal's reactivity, it is not found as a free element in nature, but in combined form with other elements such as arsenic, oxygen and sulphur. It may also occur in very small amounts in dissolved form in medium such as water. Cobalt is vital in growth and development in humans since it is a constituent of vitamin B₁₂. Cobalt forms alloys when combined with other metals. The metal finds wide applications in the pigment industry where it is used in the manufacturing of paints and driers and also in the manufacturing of coloured glass. Cobalt-60 is used in the treatment of cancer and also in the sterilization of surgical equipment since cobalt-60 is a source of gamma rays. Sources of cobalt in the environment may come from volcanic eruptions, windblown dust and sea water spray. It

may also be introduced into surface water from runoff from farms during the wet season when running water carries pollutants rich in cobalt into water bodies. Cobalt cannot penetrate deep into the soil since it gets strongly bonded to soil particles.

Exposure to high levels of cobalt-60 causes mutation since it destroys the DNA leading to development of cancer. However, when pregnant women are exposed to non-radioactive cobalt in high concentrations, the health of the fetus is affected, as cobalt damages body organs such as the kidney, heart and the liver (ATSDR, 2004).

2.9.9 Iron

The sixth most abundant element in the earth's crust is iron. Iron is formed during stellar evolution when a main sequence star runs out of hydrogen and starts fusing heavier elements like silicon during stellar nucleosynthesis (Mc Donald *et.al.*, 2010). Due to its reactivity, the metal does not occur freely in nature, but occurs in combined form with other elements such as oxygen, sulphur and chlorine. The most common ores of iron found in the earth's crust are hematite (Fe_2O_3) and magnetite (Fe_3O_4) (Morgan and Anders, 2008). The most common oxidation states of iron are the +2 and +3 oxidation states. In other iron-containing minerals such as ferate (K_2FeO_4), iron may exist in higher oxidation states. Ferate is purple in colour and the oxidation state of iron in ferate is +6. However, there are other organometallic compounds in which the oxidation state of iron is much lower e.g. +1, 0, - 1 and - 2 oxidation states. Double salts like Prussian blue [$\text{Fe}_4(\text{Fe}[\text{CN}]_6)_3$] have iron in more than one oxidation state. One special property of iron is that it doesn't form amalgam with mercury (Klingelhofer *et.al.*, 2007). When iron oxide is mixed with aluminium, it forms a substance called thermite which is capable of burning at very high temperatures hence it finds useful application in ore purification and joining of metals. In the red blood cells, the major constituent is hemoglobin which contains iron in it. Hemoglobin combines with oxygen in the red blood cells of mammals and transports oxygen as oxyhaemoglobin to muscle tissues. Carbon (IV) oxide also combines with hemoglobin in red blood cells and is transported as carboxyhaemoglobin. Iron is an important constituent of the active site in most respiratory enzymes and its deficiency in the body causes anemia.

When water gets highly polluted with iron, it stains laundry as well as water pipes and at the same time produces a bitter taste in water (Sandhu and Mc Pherson, 2001). Water gets polluted by iron through discharge of untreated industrial wastes into Rivers and Lakes, dissolution of soluble salts of iron from rocks into water systems and from domestic wastes that are carried by surface run-off into water systems. Intake of iron in excess of 10 mg/kg leads to rapid heartbeat, blood coagulation in vessels and dizziness (Nazir. *et.al.*, 2015).

2.10 Review of Analytical Techniques

Atomic spectroscopy is an analytical technique that is used to measure the concentration of heavy metals in different samples such as water, sediments, plants and animal tissues. It is based on the absorption or emission of radiation by ground state or excited state atoms. The radiation that is emitted is equal to the energy difference between the excited and ground states. The amount of radiation absorbed or emitted is proportional to the concentration of the analyte in the sample. There are different pathways through which samples can be converted into atomic vapor. This will determine the analytical technique employed in the analysis of heavy metals. The different techniques include flame atomic absorption spectrometry, graphite furnace atomic absorption spectrometry and inductively coupled plasma – optical emission spectrometry (Gillian Mc Mahon, 2007).

Atomic absorption spectrometry makes use of line sources of radiation such as hollow cathode lamps to provide sufficiently narrow wavelength of radiation in the region of 10^{-3} to 10^{-4} nm. FAAS is mostly used when analyzing liquid samples. The nebulizer converts the sample into aerosol followed by evaporation, volatilization and atomization. The fuel – oxidant used is air – acetylene which provides a temperature of about 2600°C. For refractory elements a much hotter nitrous oxide – acetylene flame is used at a temperature of 3100°C. In graphite furnace atomic absorption spectrometry, the sample is placed on a cylindrical tube made of graphite. The analyte is vaporized and atomized at 3000°C. The graphite furnace is programmed to evaporate the solvent in the

sample, ashing to decompose organic matter and atomization to convert the analyte of interest to free gaseous atoms. GFAAS is mostly preferred to FAAS since almost 100% of sample is atomized as compared to a mere 0.1% of sample that gets atomized in FAAS. GFAAS gives about 2 – 3 times better sensitivity as compared to FAAS. In FAAS, only samples in solution form can be analyzed but in GFAAS, solids can be analyzed directly without sample preparation (Gillian Mc Mahon, 2007).

Some metals cannot be analyzed directly and therefore have to be converted into hydride gas by sodium tetrahydroborate as a reducing agent. Such metals include arsenic, germanium, lead and tin. This technique is known as hydride generation atomic absorption spectrometry (HGAAS). Quartz tube and graphite tube atomizers are two of the most commonly used atomizers used to convert the sample into gaseous atoms in HGAAS (Gillian Mc Mahon, 2007).

For analysis that requires higher sensitivity, inductively coupled plasma – optical emission spectrometry ICP – OES is used. ICP – OES makes use of plasma (a conducting gaseous mixture with a high concentration of cations and electrons) to achieve atomization. Plasma is used for emission and not absorption as the high temperatures and relative stability ensures that the electrons in atoms are always in excited states. In ICP – OES, argon gas is ionized by a spark from a tesla coil producing cations and electrons. The cations and electrons cause further ionization of the argon gas producing a conducting gaseous mixture with significant concentration of cations and electrons (plasma). ICP – OES is more sensitive than the other AAS techniques with a 4 – 9 order of magnitude linear range and is suitable for multielement analysis (Gillian Mc Mahon, 2007).

Anions such as phosphates, nitrates and sulphates are best determined using Uv/Vis spectroscopy. Uv radiation has a wavelength range of 190 – 350 nm whereas the visible radiation has a wavelength range of 350 – 800 nm. Molecules that absorb uv/vis radiation contain certain functional groups known as chromophores. The chromophores contain electrons of low excitation energy. When a sample molecule absorbs Uv/vis radiation, the electrons in the molecule undergo excitation and de excitation. The

radiation is passed through a quartz cuvette containing the liquid sample. The radiation emerges on the other side of the cuvette with its intensity reduced as a result of absorption, reflection and scattering. The intensity of the emerging is proportional to concentration of analyte in the sample on the basis of Beer – Lambert’s law (Gillian Mc Mahon, 2007).

Apart from the uv/vis technique, anions in water and sediments can also be determined via gravimetric methods. In gravimetric analysis, the knowledge of the mass of the final products in a chemical reaction is used to determine the quantity of analyte present in the original sample. Precipitation titration is an example of gravimetric analysis where the amount of analyte present in a sample is determined by the quantity of titrant needed for complete precipitation of the analyte. Despite the fact that gravimetric analysis is a tedious analytical procedure, it is among the most accurate analytical techniques. Commercial standards used in the calibration of most analytical instruments are usually derived from gravimetric and titrimetric processes. In the analysis of water and sediments, FAAS and Uv/vis spectrophotometers are the ideal instruments of choice since they offer great accuracy, precision, sensitivity, selectivity, linearity, a wide dynamic range, stability, short analysis time and a high sample throughput.

2.10.1 Flame Atomic Absorption Spectroscopy (FAAS)

Principle

The working principle behind AAS is on the basis of the Beer-Lambert law in which there is direct proportionality between absorption of radiation by a sample and the concentration of the analyte in a sample. In flame atomic absorption spectrometry, the sample, usually in liquid form, is first aspirated into the flame followed by processes of sample evaporation, vaporization and eventually sample atomization. Application of energy to an atom will see the promotion of an electron from the lower ground state to an excited state. Promotion of an electron to the excited state is only temporary as the excited state is unstable, hence the electron immediately returns to the ground state, releasing light energy that corresponds to the energy gap between the ground and excited states. In flame AAS, the nebulizer converts the liquid sample into aerosol and

the metallic species in the aerosol are atomized. The atomized metallic species absorb light from the hollow cathode lamp, which emits radiation specific to the element of which it constitutes. This radiation is then passed through a sample cell into a monochromator. The monochromator isolates the wavelength of choice, which is then sent to the detector. In most cases, the detector is made of a photomultiplier tube in which the electric current produced is proportional to the intensity of light that passes through it. The readout device, usually a PC, measures the amount of light attenuation in the analyte and this then gets converted to the sample concentration and displayed on the readout device.

Flame atomic absorption spectroscopy (FAAS), makes use of a line source hollow cathode lamp as the radiation source. The hollow cathode lamps come in various designs e.g. single element lamp capable of only analyzing a single element at a time, or the multi-element lamp capable of carrying out the analysis of several elements all at once. But the single-element lamp has an advantage over the multi-element lamp in that it gives a higher energy output. Electrode discharge lamps and continuum radiation sources, such as deuterium lamp or high-pressure xenon arc lamp can also be employed when considering high resolution work since they give much higher radiant power as compared to line sources of radiation. The radiation specific to the element of interest is obtained from the monochromator, which is capable of separating the wavelength of choice from other radiations which are emitted by the source. The most common types of monochromator available in most instruments diffraction grating monochromator. Atomic absorption spectrometry can have a single or double beam spectrometer. In a single beam spectrometer, the radiation that passes through the atomized sample is scattered in all directions thereby leading to reduction in loss of intensity. In the double beam design, the radiation is split into two i.e. the radiation is split into sample beam as it passes through the flame (or a furnace in the case of graphite furnace AAS) and a reference beam which doesn't pass through the flame or the furnace. The two beams are then recombined before they pass through the monochromator. In the case of the double beam monochromator, splitting of the beam takes into consideration variations in

intensity of the radiation source and detector sensitivity. In order to avoid multiple calibrations when using flame AAS, it is advisable to consider a double-beam instrument whereas the single-beam instrument is considered when using graphite furnace as the atomizer and in this case the baseline needs to be reset prior to running every sample. In the case of flame AAS, the most commonly used gases are nitrous oxide-acetylene and air-acetylene. Air/oxygen serves as oxidizers while nitrous oxide/acetylene serves as fuel for the flame. Temperatures can go as high as 2600°C and this is high enough to atomize samples. Prior to atomization, the nebulizer converts liquid samples into aerosol. The path length is increased by the presence of a long burner. Most AAS instruments worldwide make use of the photomultiplier tube (PMT) as the detector. Radiation transmittance is represented as the ratio of incident radiation to that of exiting radiation. The amplifier then picks up this transmittance signal and converts it into absorbance. This information is usually obtained by interpolation from the calibration curve of standards (Gillian Mc Mahon, 2007). A block diagram of a flame atomic absorption spectrometer is displayed in Figure 2.1.

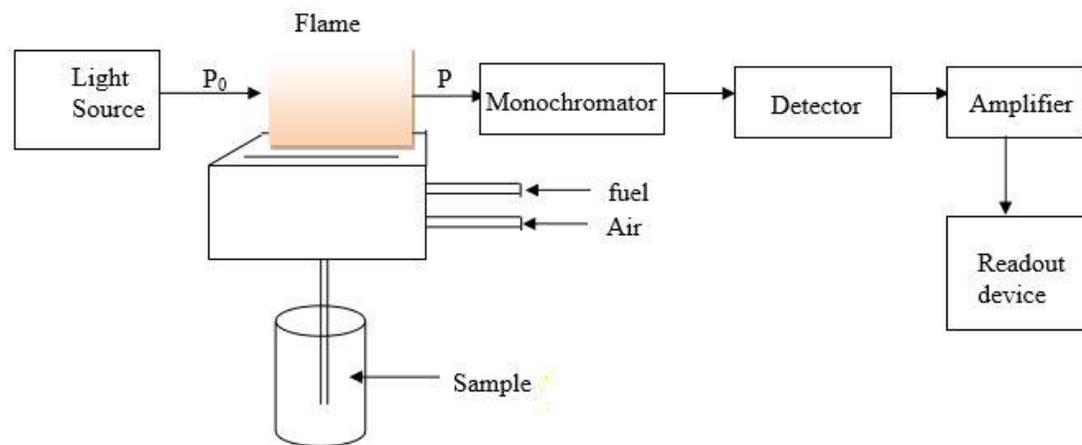


Figure 2.1: Block diagram of a flame atomic absorption spectrometer (Kosgei, 2017)

Applications

Atomic absorption spectroscopy finds a wide range of applications in different fields. It can be used to determine the concentration of metallic species in the environment in either trace or major concentrations, depending on the sensitivity of the instrument in use. FAAS has been used in the determination of highly toxic heavy metals like arsenic, mercury, selenium, lead and cadmium in soil, water, blood and urine samples. The instrument is also used in pharmaceutical industries to determine the concentration of heavy metals (concentrations as low as 2 $\mu\text{g/mL}$) in drugs such as bromhexine and flunarizine (Gillian Mc Mahon, 2007).

2.10.2 UV/Visible Spectroscopy

Principle

When electrons absorb radiation in the ultraviolet and visible regions of the electromagnetic spectrum, they become excited and are elevated to higher energy levels. The ultraviolet region is from 190nm to 350nm. The amount of energy that a photon of light possesses in these regions is equivalent to the energy necessary to excite the electron from one energy level to the other since the total energy of an electron is quantized according to quantum mechanics. When molecules in a sample absorb UV/visible radiation, the electrons in the molecule are excited to higher energy states, if the energy absorbed by the electron is equivalent to the difference in energy between the ground and the excited states. The elevation to the excited state is temporary, as the excited electron immediately loses energy and goes back to the ground state, releasing energy in the form of radiation. Since the electron's energy is quantized, the excitation and de-excitation results in lines in the absorption spectrum. If the energy of the electron is not enough for transition to a higher state then the electron cannot move to that state and that kind of transition is referred to as forbidden transition. UV/visible spectroscopy gives a measure of transmitted light that passes through the sample all the way to the detector, which in turn relates the transmitted light to the concentration of the analyte in the sample and this is done on the basis of Beer-Lambert law. When sample analysis is

carried out in the ultraviolet region then the cuvettes used should be made of quartz. Glass cannot be used when analyzing samples which absorb radiation in the ultraviolet region, such as nitrates, since glass absorbs ultraviolet radiation (Skoog *et al.*, 2004). This analytical technique makes use of deuterium and tungsten lamps as radiation sources. The tungsten lamp is in most cases made of glass instead of quartz since it is only employed in the visible region of the electromagnetic spectrum and this is due to the fact that the lamp generates continuum spectrum. The deuterium lamp on the other hand is made of quartz since it is mainly used in the ultraviolet region of the electromagnetic spectrum. It cannot be made from glass since glass absorbs ultraviolet radiation. This lamp consists of a quartz bulb filled with deuterium through which an electrical discharge is passed to excite the deuterium molecules leading to the dissociation of the molecules upon which they emit ultraviolet radiation in the range of 160-400nm. The monochromator will then select the wavelength of choice which passes through the sample (Robson, *et.al.*, 2005). UV/visible instruments are of two types, single beam spectrophotometers and double beam spectrophotometers. When using a single beam spectrophotometer, the sample is usually replaced by a blank sample in order to eliminate the matrix effect, since all the light passes through the cuvette. The double beam spectrophotometer on the other hand splits radiation into two beams before it gets to the sample. One beam passes through the sample in a cuvette whereas the other beam is the reference beam hence the sample doesn't have to be replaced by the blank from time to time. Other double beam spectrophotometers are capable of measuring the sample and reference beam at the same time due to the presence of two detectors (Gillian Mc Mahon, 2007). The instrument detectors, photoelectric transducers, absorb radiant energy where the detector's surface undergoes photoelectric effect, emitting electrons in the process leading to the conversion of radiation to electrical signal. Examples of photoelectric transducers are photomultiplier tubes and barrier layer cells (Robson, *et.al.*, 2005). A schematic diagram of a double beam UV/Visible spectrophotometer is shown in Figure 2.2.

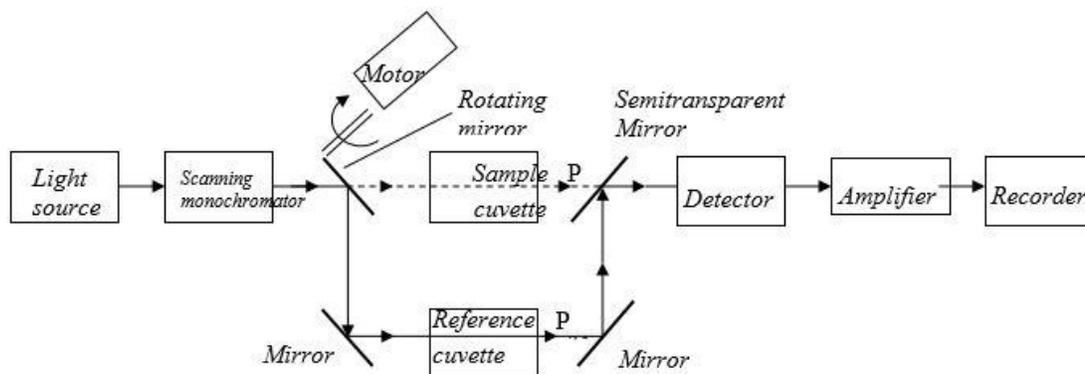


Figure 2.2: Block diagram of a double beam UV/Vis spectrophotometer (Kosgei, 2017)

Applications

UV/Visible spectroscopy finds a wide range of applications in analytical chemistry in the analysis of samples such as organic compounds with alternating double bonds, biological samples and the ionic species of transition metals. UV/Visible spectroscopy has been used in the determination of anions such as nitrates, sulphates, fluorides, phosphates and chlorides in water, soil and fertilizers. Most samples analyzed by UV/Visible spectroscopy have to be prepared in solution form, though there are some advanced instruments capable of analyzing samples in solid and gaseous form (Daniel, 2010).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

The Sio River shown in Plate 3.1 is a River in the Malaba-Malakisi catchment located in western Kenya. It originates from Kaujai and Lucho Hills in Bungoma County at an altitude of 1800 m and flows through several counties like Busia and Bungoma and finally drains into Lake Victoria in Uganda at 1134 m above sea level. It flows through forests, maize and sugarcane plantations into the highly populated and agricultural section. River Sio flows through Busibwabo (sampling point 3) where Busia sugar industry abstracts water for washing sugarcane, cooling and cleaning of the machines. Plate 3.2 shows the water abstraction station used by Busia sugar industry to abstract water from River Sio. The River then flows through Mundika in Busia town where Western Water and Sewerage Company (WWSC) has set up a water treatment plant that supplies tap water to the residents of Busia County. The part of the River which is under study will be from Nambale through to Busia town to capture pollution from both agricultural farms and urban activities. From Nambale, the River flows through Mundika estate which is densely populated and crosses the Busia-Kisumu highway as it flows through Samia sub-county where over 75% of the residents practice agriculture and rely on water from River Sio for irrigation during the dry season (Barasa *et al.*, 2011).

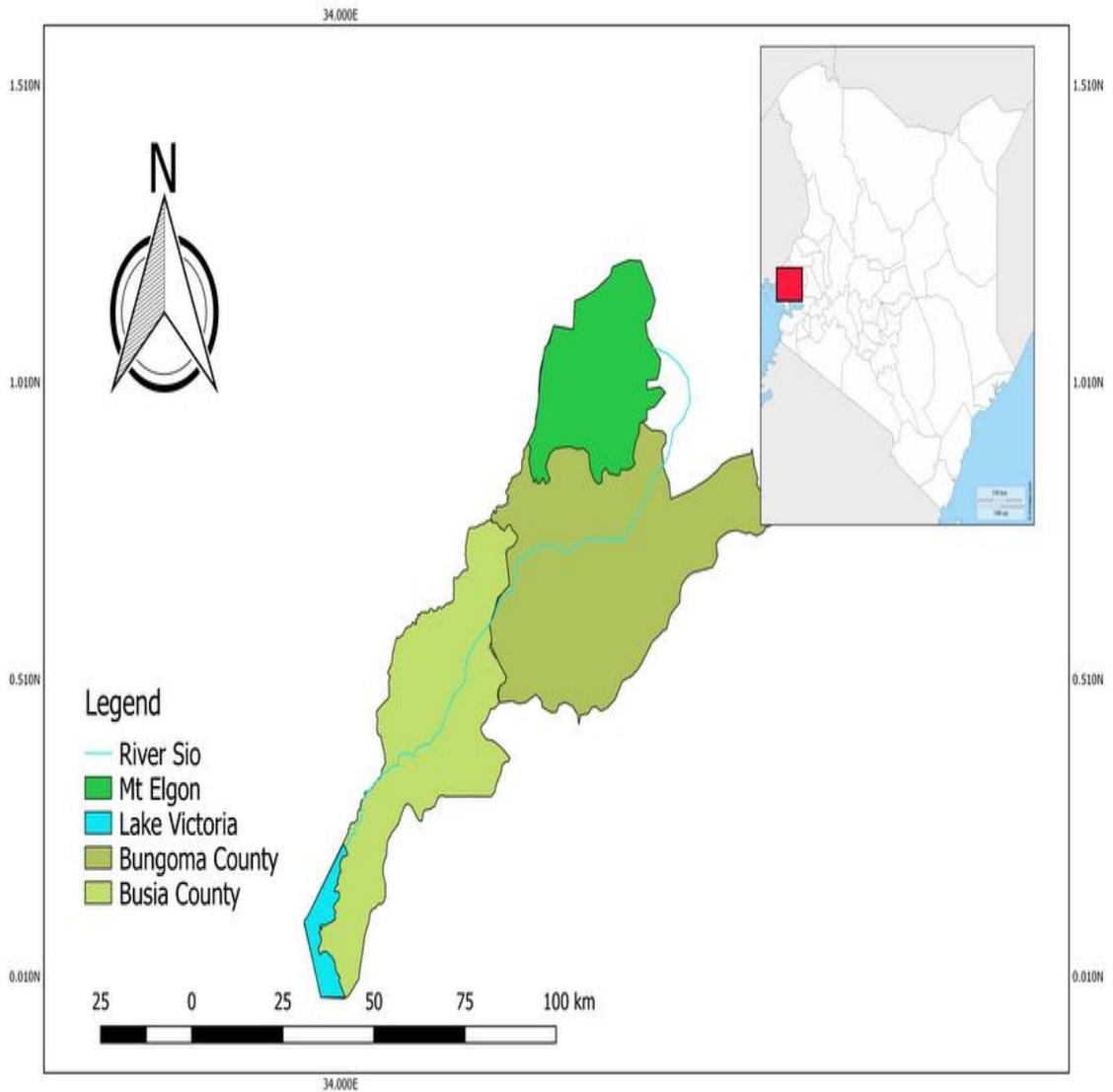


Plate 3.1: Source of river Sio and counties through which the river traverses (Source: author)



Plate 3.2: Water abstraction station used by Busia sugar industry at the banks of River Sio (Source: author)

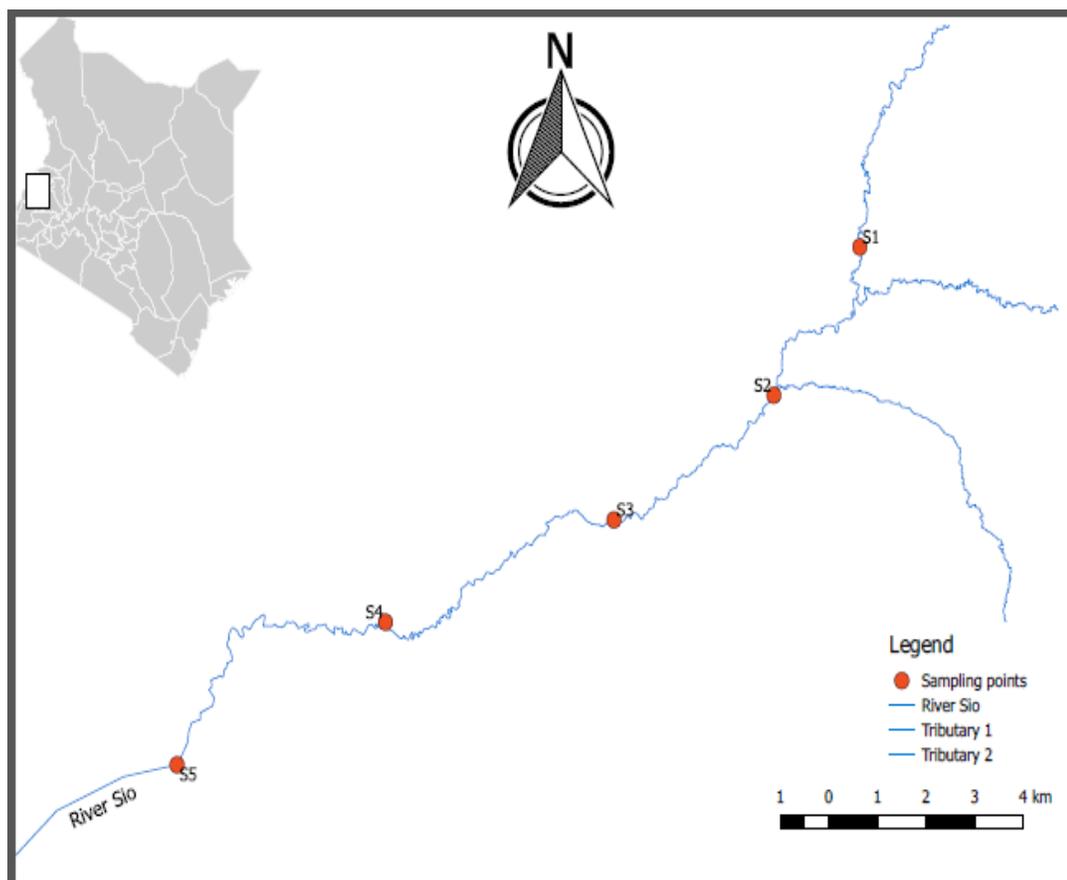


Plate 3.3: Sampling points along river Sio (Source: author)

3.2 Sample Collection

Sampling point identification to gather information on the possible sources of pollutants was done before sampling. Determination of sampling points shown in Plate 3.3 was on the basis of significant land change use (Akoto and Adiyiah 2007). GPS coordinates of the sampling sites were taken to ensure both water and sediment samples are collected at the exact same location during both the dry and wet seasons. Upstream river Sio (sampling points 1 – 3) is sugarcane and maize plantations which contribute high levels of turbidity, anions and heavy metals due to the use of inorganic fertilizers and

pesticides for farming. Downstream river Sio (sampling points 4 and 5) are extensive anthropogenic activities that lead to pollution of the river via the introduction of heavy metals from garages and workshops, discharge of raw sewage and dumping of domestic waste due to the population rise in Busia town.

1000 mL grab samples of water were collected using simple random sampling methods during both dry and the wet seasons. The grab water samples were collected in polyethylene bottles prewashed with detergents, 10% nitric acid and de-ionized distilled water. Total dissolved solids, pH, temperature, turbidity, dissolved oxygen and electrical conductivity of the samples were measured on site during sampling. Water samples for metal analysis were collected in clean polyethylene bottles and acidified with 5 mL 65% nitric acid per litre in order to minimize precipitation and adsorption on container walls (APHA, 2005). After transportation to the laboratory, the samples were stored at 4°C for 24 hours so as to minimize physicochemical changes. Sediment samples were collected at the same location as the water samples. The sediments were collected using a grab sampler (scoop and trowel) (EPA, 1989). Sediments were collected in containers made of Teflon in order to avoid contamination. Parts of the sediment which were in direct contact with the sampler were scrapped off in order to minimize contamination (Bodger, 2003).

Table 3.1: GPS coordinates of sampling points along river Sio

Sampling point	Location	Coordinates
1	Malomba	[0.436167] [34.263310]
2	Musoma	[0.431789] [34.255600]
3	Busibwabo	[0.395612] [34.197363]
4	Mundika	[0.383144] [34.145905]
5	Nang'oma	[0.360206] [34.131693]

3.3 Apparatus and Instrumentation

The pH, temperature, TDS and electrical conductivity were determined using an ISOLAB Laborgerate GmbH portable meter. Dissolved oxygen was determined using

the 900-Multiparameter meter, turbidity was determined using the SGZ-B portable turbidimeter while Shimadzu AA 6200 Atomic Absorption Spectrometer and Shimadzu 1800 UV/Vis Spectrophotometer were used for the determination of heavy metals and anions in both water and sediments respectively.

3.4 Reagents

3.4.1 Phosphate Reagent

Vanadate-molybdate reagent was prepared by mixing 25 g of ammonium molybdate in 300 mL of distilled water and ammonium metavanadate in 300 mL distilled water and 330 mL of concentrated hydrochloric acid. The two solutions were then mixed and made to 1 L with distilled water (APHA, 2005). In determination of phosphates, an acid hydrolysis step was done to convert polyphosphates to orthophosphates. A nitric acid-sulfuric acid digestion method was used to digest 100 mL of water sample. Nitric acid (1 mL) and sulphuric acid (5 mL) were added to 100 mL of sample and heated for 90 minutes until the volume reduced to 10 mL. This volume was then topped to 100 mL mark with distilled deionized water (APHA, 2005).

3.4.2 Nitrate Reagent

During determination of nitrates, a nitrate digesting agent was prepared by taking 3 g potassium thiosulphate and 4 g of sodium hydroxide and diluted to 100 mL. About 10 mL of water sample was taken and filled to the 50 mL mark. The nitrate digesting solution (10 mL) was added and the mixture autoclaved for 30 minutes at 120°C. After that, 5 mL of hydrochloric acid was added after cooling the samples (APHA, 2005).

3.4.3 Sulphate Reagent

Sulphate reagent was prepared by dissolving 30 g of hydrated magnesium chloride 5.0 g of hydrated sodium acetate, 1.0 g of potassium nitrate and 20 mL of 99% acetic acid in 500 mL distilled water and topped to the 1000 mL mark with distilled water (APHA, 2005).

3.4.4 Chloride Reagent

To prepare chloride reagent, 0.3 g of mercuric thiocyanate was dissolved in 100 mL of ethanol. To prepare ferric alum, 6 g of ferric ammonium sulphate was dissolved in 100 mL of 6 N nitric acid (APHA, 2005).

3.5 Standards

3.5.1 Preparation of Phosphate Standards

A 1000 ppm phosphate standard was prepared by dissolving 1.4316 g of anhydrous potassium dihydrogen phosphate in 1000 mL then topped to the mark with distilled water. An intermediate 50 ppm standard was prepared and from this phosphate standards of 0.10, 0.20, 0.40, 0.80, 1.60, 3.20 and 6.40 ppm were prepared (APHA, 2005).

3.5.2 Preparation of Nitrate Standards

A 1000 ppm nitrate stock solution was prepared by dissolving 1.629 g of potassium nitrate in 1000 mL distilled water. An intermediate 50 ppm nitrate solution was prepared and from this standards of 0.20, 0.40, 0.80, 1.60, 3.20 and 6.40 ppm were prepared via serial dilution (APHA, 2005).

3.5.3 Preparation of Sulphate Standards

A 1000 ppm standard solution was prepared by dissolving 1.4792 g of anhydrous sodium sulphate in 1000 mL volumetric flask then topped up with distilled water. Serial dilution was used to prepare 0.2, 0.4, 0.8, 1.6, 3.2 and 6.4 ppm working standards (APHA, 2005).

3.5.4 Preparation of Chloride Standards

A 1000 ppm stock solution was prepared by dissolving 1.6482 g of dried sodium chloride in 1000 mL volumetric flask then filled to the mark with distilled deionized water. An intermediate 50 ppm standard was used to prepare 0.2, 0.4, 0.8, 1.6, 3.2 and 6.4 ppm working standards (APHA, 2005).

3.6 Analytical Procedures

3.6.1 Determination of Physical Parameters

The physical parameters such as temperature, pH, turbidity, electrical conductivity and total dissolved solids were determined on site during sampling. Temperature, pH, electrical conductivity and turbidity were determined using the ISOLAB laborgerate GmbH portable meter while turbidity was determined using the SGZ-B portable turbidimeter (APHA, 2005).

3.6.2 Determination of Heavy Metals

The metals that were determined include; chromium, cadmium, lead, Iron, cobalt, nickel, manganese, copper and zinc. Determination of heavy metals was carried out using Flame Atomic Absorption Spectrometry. The reagents used for preparation of both samples and standards were analytical grade (99.999% pure) and the instrument used was Shimadzu AA 6200 Atomic Absorption Spectrophotometer (APHA, 2005).

Water sample was digested using nitric acid digestion, whereby 5 mL of concentrated nitric acid was added to 100 mL of the water sample and heated on a hot plate until the volume reduced to 20 mL. The digestate was then filtered using Whatman number 42 filter paper and filled to the mark in a 100 mL volumetric flask (APHA, 2005).

For sediments, 1 g of sample was placed in 250 mL flask for digestion. The sediment sample was then heated to 95°C with 10 mL of 50% nitric acid. The sample was then refluxed with repeated additions of 65% nitric acid until no brown fumes of NO₂ were produced. The solution was then evaporated to reduce the volume to 5 mL. After cooling the sample solution, 10% of 30 mL hydrogen peroxide was added. The mixture was then refluxed with 10 mL of 37% hydrochloric acid at 95°C for 15 minutes. The digestate was then filtered using Whatman number 42 filter paper and topped to the mark in a 100 mL volumetric flask using distilled-deionized water. The metals in both water and sediments were determined using FAAS at their respective analytical lines (Marc and Jaques, 2003). The FAAS instrumental conditions were different for each of the selected heavy metals.

3.6.3 Determination of Anions

3.6.3.1 Determination of Phosphates

A nitric acid-sulfuric acid digestion process was used to digest 100 mL of the water sample. Exactly 5 mL of sulphuric acid and 1 mL of nitric acid were mixed with 100 mL of the sample and heated for 90 minutes until the volume reduced to 10 mL. The 10 mL volume was then topped to the mark in a 100 mL volumetric flask using distilled water. A 35 mL aliquot of sample was then taken and 10 mL of vanadate-molybdate reagent added and topped to the mark in a 50 mL volumetric flask using distilled-deionized water. The absorbance for both samples and standards were measured at 460 nm using Shimadzu 1800 UV/Vis spectrophotometer. The concentration of phosphates in the sample was determined from the calibration curve (APHA, 2005).

In the determination of phosphates in sediments, 1 g of sample was mixed with 50 mL of aqua regia and transferred to a mechanical shaker for 30 minutes then left to stand for 6 hours for digestion to take place. Sample filtration was then carried out using Whatman number 42 filter paper. 3 mL of 4-nitrophenol indicator was added to 10 mL of the filtrate, followed by 6 N ammonia solution. Sample decolorization was achieved by the use of 1 N nitric acid and 5 mL vanadomolybdate reagent and the whole sample volume made up to the 50 mL mark in a volumetric flask. The concentration of phosphates in the sample was measured after 30 minutes at a wavelength of 400 nm by the use of Shimadzu 1800 UV/Vis spectrophotometer (Mesopir, *et.al.*, 2015).

3.6.3.2 Determination of Nitrates

10 mL of the sample was taken and filled to the 50 mL mark. 10 mL of the nitrate digesting solution was added and the mixture autoclaved for 30 minutes at 120°C. After cooling the sample, 5 mL of hydrochloric acid was added after. Nitrate standards were measured at 220 nm and at 275 nm in 1cm path length quartz cuvettes using a Shimadzu 1800 UV/Visible spectrophotometer. The 275 nm absorbance was used to correct the nitrate value at 220 nm. The absorbance measurements were used to prepare a calibration curve for nitrates. The samples were treated the same way as the standards in order to minimize matrix effect. (APHA, 2005).

During the analysis of sediments, a digestion mixture consisting of 25 g phenol in 250 mL of concentrated sulphuric acid was prepared, after which 50 mL of the digestion mixture was added to 1 g of the sediment sample and left to digest for six hours. 25 mL of the digestate was evaporated to dryness in a crucible after which 3 mL of phenol disulphonic acid was added while gently swirling the mixture and left to digest for about 10 minutes. This was followed by the addition of 15 mL distilled water and the mixture stirred and upon cooling 3 drops of 4-nitrophenol indicator was added followed by ammonia solution until an intense yellow colour developed. The mixture was then topped up to the 100 mL mark of a volumetric flask and concentration measured at 420 nm after 30 minutes by the use of Shimadzu 1800 UV/Vis spectrophotometer (Mesopir, *et.al.*, 2015).

3.6.3.3 Determination of Sulphates

After filtering 50 mL of water sample using Whatman number 42 filter paper, a volume of 20 mL buffer solution was added together with 0.15 g of barium chloride and the mixture stirred using a magnetic stirrer. The sulphate standards were treated in a similar manner to the samples in order to eliminate matrix effect. Both the standards and the samples were read at 420 nm using Shimadzu 1800 UV/Vis spectrophotometer. The concentration of sulphates in the samples was determined by interpolation from the calibration curve (APHA, 2005). In determination of sulphates in sediments, 1 g of sample was added to 100 mL of distilled water in a polyethylene bottle and the mixture shaken by the use of a mechanical shaker for an hour. A 50 mL sample volume was transferred to a 250 mL conical flask then 5 mL of conditioning agent, comprising of 75 g sodium chloride, 30 mL hydrochloric acid, 50 mL glycerol and 100 mL ethanol added to the sample mixture together with 5 mL barium chloride solution. Sample measurement was determined at 420 nm wavelength by the use of Shimadzu 1800 UV/Vis spectrophotometer (Mesopir, *et.al.*, 2015).

3.6.3.4 Determination of Chlorides

A 10 mL aliquot of water samples and standards were treated with 1 mL of mercuric thiocyanate and 2 mL of ferric alum and left to stand for about ten minutes, after which

absorbances were measured at 460 nm wavelength using Shimadzu UV/Visible spectrophotometer. The concentration of chlorides in the samples was determined by interpolation from the calibration curve (APHA, 2005). The level of chlorides in sediment samples was determined using precipitation method. Exactly 1 g of sample was dissolved in 25 mL of distilled water in a 50 mL polyethylene bottle. The sample mixture was then transferred to a mechanical shaker for about an hour, after which filtration was achieved by the use of Whatman number 42 filter paper. The reagent used in chloride determination was silver nitrate. The silver ions reacted with chromate ions and chloride ions present in the sediments to form red and white precipitates of silver chromate and silver chloride respectively. Titration was then carried out where 3 drops of potassium chromate solution was added to 25 mL of the extracted sediment sample. From the burette, a standard solution of silver nitrate was added to the sediment solution in a conical flask. The development of yellow colour which changed to a persistent red colour signaled the end point of the titration. The titration was repeated three times to obtain three replicate measurements (Gupta, 1999).

3.7 Determination of Pollution Indices

The pollution indices under study are: geo accumulation index, enrichment factor, contamination factor and pollution load index. The background values used to determine geo accumulation index, enrichment factor and contamination factor were from Taylor and Mc Lennan, 1995 (Taylor and Mc Lenan, 1995). The geo accumulation index (I_{geo}) is calculated as shown:

$$I_{geo} = \log_2 \frac{C_i}{1.5 C_b}$$

Where: C_i is the concentration of the metal of interest in sediments, C_b is the geo chemical background concentration of the element of interest while 1.5 is introduced into the equation to account for environmental variations in the background values (Cardellicchio *et.al.*, 2010).

The contamination factor is calculated as shown below:

$$C_f^i = \frac{C_{o-n}^i}{C_b^i}$$

Where: C_{o-n}^i is the mean concentration of the element of interest while C_b^i is the background concentration of the element of interest (Dimuthu, 2016).

The enrichment factor is expressed as:

$$EF = (C_x/C_{Fe})_{\text{sample}} / (C_x/C_{Fe})_{\text{background}}$$

Where: $(C_x/C_{Fe})_{\text{sample}}$ is the concentration of the metal and iron in the sample, while $(C_x$ and $C_{Fe})_{\text{background}}$ is the concentration of the metal under study and iron in the background respectively.

Pollution load index is defined by the formula:

$$PLI = (C_{f1} \times C_{f2} \times \dots \times C_{fn})^{1/n}$$

Where: C_{f1} , C_{f2} and C_{fn} is the contamination factor of element 1, 2 and the n^{th} element respectively and n is the total number of elements. Pollution load index measures the level of pollution in sediments (Dimuthu, 2016).

CHAPTER FOUR

RESULTS AND DISCUSSION

The physico-chemical parameters analyzed were pH, temperature, turbidity, electrical; conductivity, dissolved oxygen and total dissolved solids. The anions that were measured in both water and sediments include phosphates, nitrates, sulphates and chlorides. The selected heavy metals that were measured in both water and sediments were lead, cadmium, manganese, copper, chromium, zinc, cobalt, nickel and iron. The parameters that were above the recommended WHO levels in water were turbidity, phosphates, lead, nickel, chromium and iron. In sediments, only three metals were above the WHO recommended limits and these were lead, copper and nickel. All the anions registered high concentrations in both water and sediments during the wet season except sulphates. In water, all the metals registered high concentrations during the dry season except chromium, zinc and iron.

4.1 Physico-Chemical Parameters

4.1.1 pH

The pH range was between 7.45 ± 0.02 to 7.62 ± 0.02 during the dry season and 6.70 ± 0.04 to 7.24 ± 0.05 during the wet season as displayed in table 4.1 and figure 4.1. There was a significant difference in seasonal variation with a $T_{\text{calculated}}$ value of 5.89 against a T_{critical} value of 2.78 at $p = 0.05$ level of significance for paired t-test (appendix III). Since $T_{\text{calculated}} > T_{\text{critical}}$ there was a significant difference in pH between the dry and wet seasons. Spatial variations were significantly different during the dry and wet seasons showing slight alkalinity in all the five sampling stations during the dry season. All the five sampling points were within the 6.5 – 8.5 pH range allowed by the WHO. Pollution from domestic and industrial waste water is the cause for the slight alkalinity in the River water during the dry season (Rizvi *et.al.*, 2016). Similar findings were also reported during the study of seasonal variations of pH in Lake Chandlodia, India (Qureshimatva, *et.al.*, 2015).

Table 4.1: Physical parameters concentration in water

Parameter	Season	S1	S2	S3	S4	S5	WHO	KEBS
Temperature (°C)	Wet	24.03±0.12	24.83±0.15	25.13±0.06	26.53±0.06	27.20±0.10	–	–
	Dry	23.83±0.31	23.47±0.15	25.20±0.1	24.5±0.36	25.43±0.21		
Conductivity (µS/cm)	Wet	346.67±5.51	219.33±2.52	136.67±6.66	386.33±9.07	450.33±1.53	500-5000	1000
	Dry	108.00±2.65	105.00±7.21	152.33±10.12	148.33±1.53	181.67±2.89		
TDS (mg/l)	Wet	63.33±1.5	76.33±4.5	101.00±2.0	91.33±3.1	107.33±1.5	1000	1500
	Dry	69.00±3.61	70.33±2.08	108.67±1.53	96.67±4.16	115.67±0.58		
Turbidity (NTU)	Wet	481.83±0.76	411.67±0.76	263.00±0.50	212.50±0.50	244.00±0.50	5	5
	Dry	44.33±0.5	37.77±0.81	43.70±0.46	12.03±0.61	30.37±0.80		
pH	Wet	6.70±0.04	7.24±0.05	7.22±0.02	7.10±0.02	6.91±0.02	6.5 - 8.5	6.5 - 8.5
	Dry	7.54±0.02	7.57±0.03	7.45±0.02	7.62±0.02	7.57±0.02		
DO (mg/l)	Wet	3.42±0.02	3.45±0.01	3.46±0.01	3.66±0.02	3.71±0.03	5	5
	Dry	3.16±0.07	3.36±0.01	3.50±0.02	3.60±0.03	3.12±0.01		

* Bolded values are those values that are above the recommended WHO limit

S1: sampling point 1 at Malomba bridge

S2: sampling point 2 at Musoma bridge

S3: sampling point 3 at Busibwabo

S4: sampling point 4 at Mundika bridge

S5: sampling point 5 at Nangoma

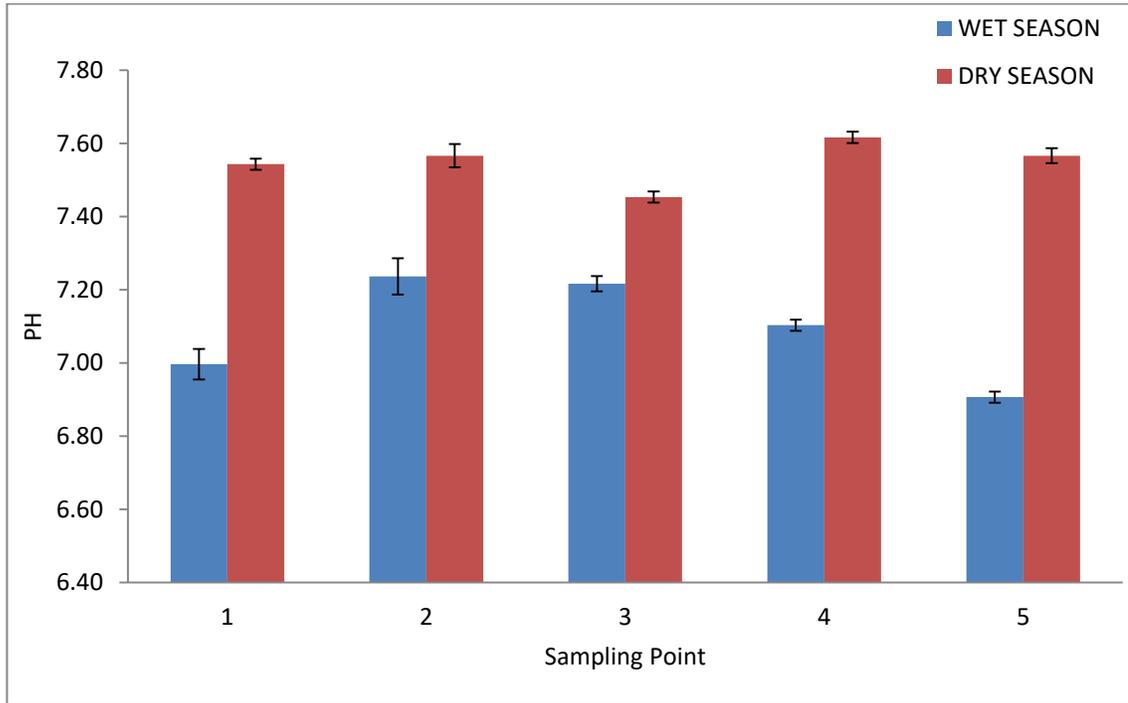


Figure 4.1: Graph of pH of water at various sampling points

4.1.2 Temperature

The temperature range for water was 23.47 ± 0.15 °C to 25.43 ± 0.21 °C during the dry season and 24.03 ± 0.12 °C to 27.20 ± 0.10 °C during the wet season as shown in table 4.1 and figure 4.2. According to paired t-test, the dry and wet seasons were not significantly different while as per one way ANOVA, the spatial variations of temperature were statistically significant. The $T_{\text{calculated}}$ value was 2.51 while the T_{critical} value was 2.78 at $p = 0.05$ level of significance as per the paired t-test (appendix III). Since the $T_{\text{calculated}} < T_{\text{critical}}$ there was no significant difference in temperature between the dry and the wet season. According to one way ANOVA, $F_{\text{calculated}}$ was 35.91 during the dry season and 469.45 during the wet season, while F_{critical} was 4.76 at $p = 0.05$ level of significance (appendix IV). Since $F_{\text{calculated}} > F_{\text{critical}}$ the spatial variations in temperature were statistically significant and this was attributed to the altitude at which sampling was done, weather conditions and the time of the day when sampling was done. The high temperatures during the wet season can be attributed to an increase in suspended

particles which absorb sunlight, leading to an increase in water temperature during the wet season.

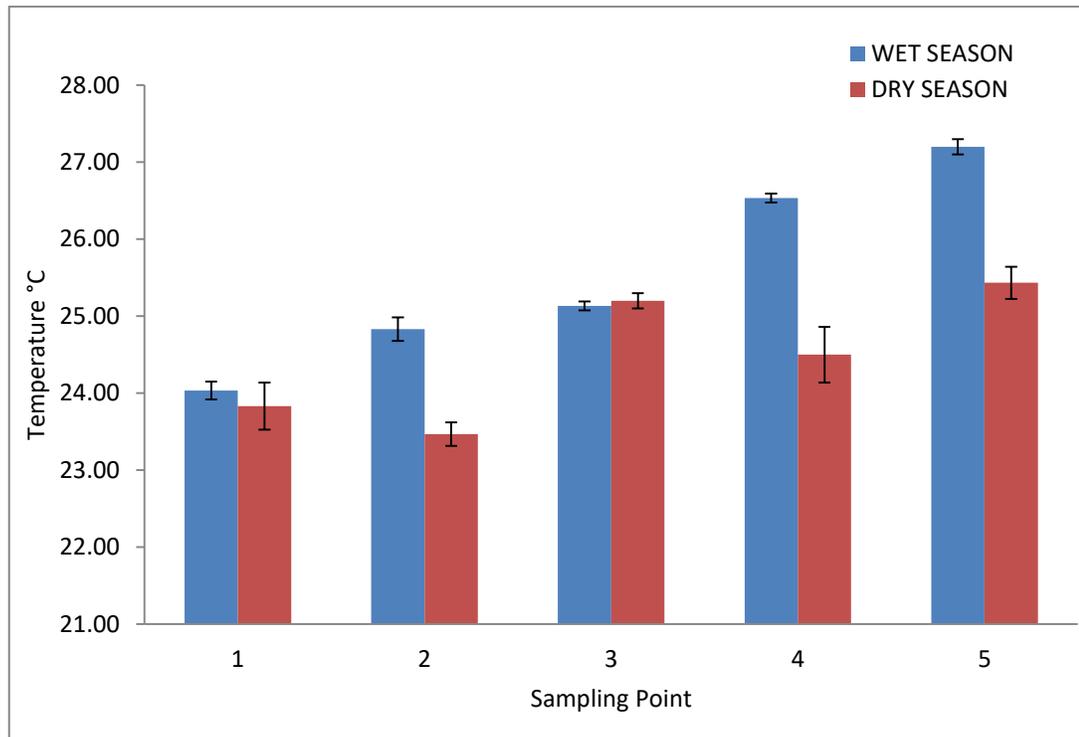


Figure 4.2: Graph of temperature of water at various sampling points

4.1.3 Electrical Conductivity

Electrical conductivity ranged from 105.00 ± 7.21 to 181.67 ± 2.89 $\mu\text{S}/\text{cm}$ during the dry season and 136.67 ± 6.66 to 450.33 ± 1.53 $\mu\text{S}/\text{cm}$ during the wet season as shown in table 4.1 and figure 4.3. Paired t-test revealed significant difference in electrical conductivity during both the wet and dry seasons. $T_{\text{calculated}} = 3.17 > T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance (appendix III). Spatial variations were statistically significant during both the wet and dry seasons as per one way ANOVA. During the dry season, $F_{\text{calculated}} = 91.62$ and during the wet season, $F_{\text{calculated}} = 1473.75$, while $F_{\text{critical}} = 3.48$ at $p = 0.05$ level of significance (appendix IV). Since $F_{\text{calculated}} > F_{\text{critical}}$ for both the dry and wet seasons, the spatial variations in electrical conductivity were statistically significant at $p = 0.05$ level of significance. The rise in electrical conductivity during the wet season can be attributed to surface run-off which carries dissolved minerals from the farms into the

river. The high values of electrical conductivity downstream can be attributed to increased anthropogenic activities such as sand mining, cultivation and laundry along the river. Electrical conductivity was within the WHO guideline limits. Similar range of electrical conductivity during the dry season was reported in the assessment of water quality in Goro Dong Adamawa state Nigeria (Yonnana *et al.*, 2017).

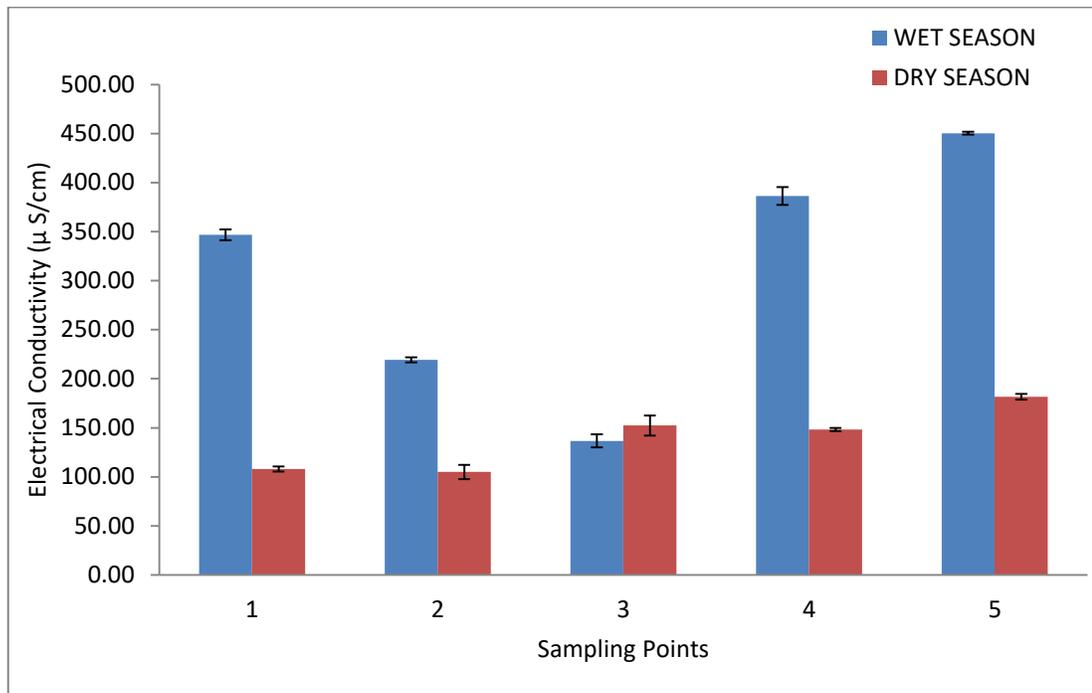


Figure 4.3: Graph of electrical conductivity of water at various sampling points

4.1.4 Total Dissolved Solids

TDS values varied from 69.00 ± 3.61 mg/L to 115.67 ± 0.58 mg/L during the dry season and 63.33 ± 1.5 mg/L to 107.33 ± 1.5 mg/L during the wet season (table 4.1 and figure 4.4). Paired t-test established no significant difference in TDS between the dry and wet seasons. $T_{\text{calculated}} = 1.61 < T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance (appendix III). One way ANOVA established a significant difference in spatial variations during both the dry and wet seasons. $F_{\text{calculated}} = 186.64$ and 127.01 during the dry and wet seasons respectively, while $F_{\text{critical}} = 3.49$ at $p = 0.05$ level of significance (appendix IV). Since $F_{\text{calculated}} > F_{\text{critical}}$ for both seasons, the spatial variations in TDS were statistically significant at $p = 0.05$ level of significance. The slight increase in TDS during the dry

season can be attributed to evaporation of water during the dry season, leading to a low water volume in the river hence a rise in TDS. The high values of TDS downstream can be attributed to increased anthropogenic activities such as cultivation, bathing and laundry along the river. The TDS values during both the dry and wet seasons were found to be below the WHO recommended standards for drinking water. A similar pattern in total dissolved solids was recorded during the determination of physico-chemical parameters of water quality in Chania catchment, Kenya (Kimani, *et.al.*, 2016).

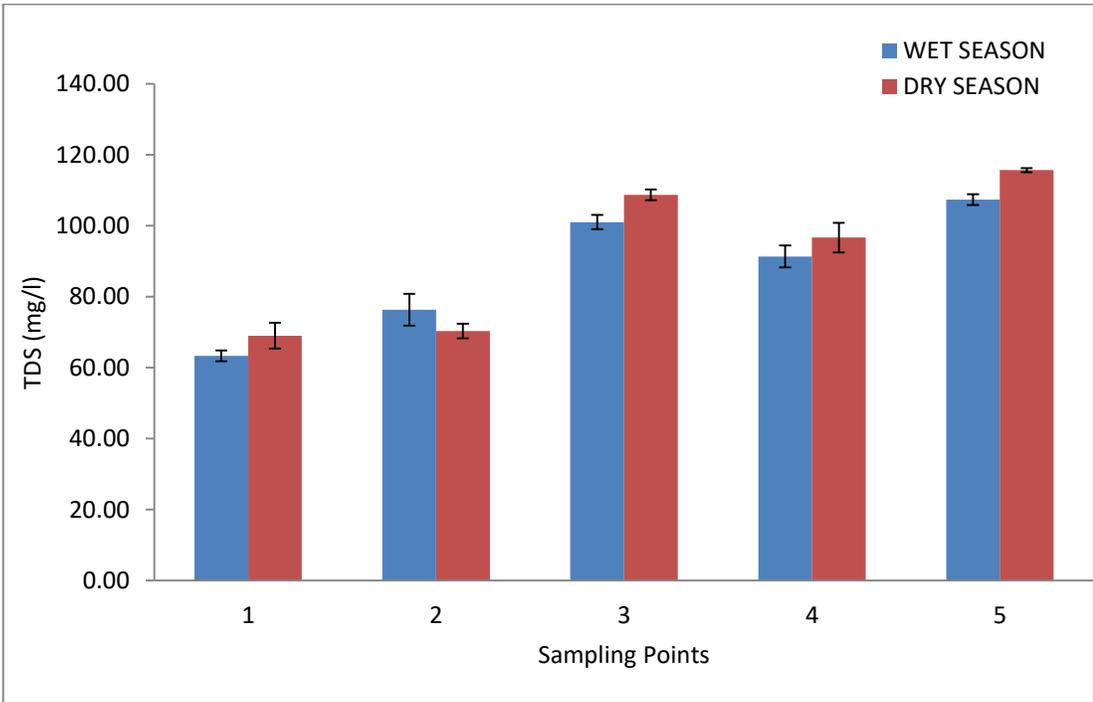


Figure 4.4: Graph of total dissolved solids in water at various sampling points

4.1.5 Turbidity

Turbidity values ranged from 12.03±0.61 NTU to 44.33±0.5 NTU during the dry season and 212.50±0.50 NTU to 481.83±0.76 NTU during the wet season as displayed in table 4.1 and figure 4.5. Paired t-test revealed a significant difference in turbidity during both the dry and wet seasons, with $T_{calculated} = 5.92 > T_{critical} = 2.78$ at $p = 0.05$ level of significance (appendix III). One way ANOVA revealed spatial variations of turbidity to

be significant since $F_{\text{calculated}} > F_{\text{critical}}$, with $F_{\text{calculated}} = 1,242.47$ and $107,883.10$ for dry and wet season respectively, while $F_{\text{critical}} = 3.48$ at $p = 0.05$ level of significance (appendix IV). The high levels of turbidity during the wet season can be attributed to suspended particles that find their way into the river via surface run-off due to poor agricultural practices upstream. If the mean turbidity value is above 0.1 NTU, it masks microorganisms from disinfection during water treatment and stimulates microbial growth. This is due to the fact that nutrients are adsorbed onto particulate surfaces thereby enabling the attached bacteria to grow more rapidly than those in free suspension. Turbidity was above the WHO recommended limit of 5 NTU during both the dry and wet seasons, with sampling station 1 recording the highest turbidity values during both seasons. High turbidity levels during the wet season was also reported during the determination of spatial and seasonal variation of selected water quality parameters in Chania River catchment, Kenya (Kimani, *et.al.*, 2016).

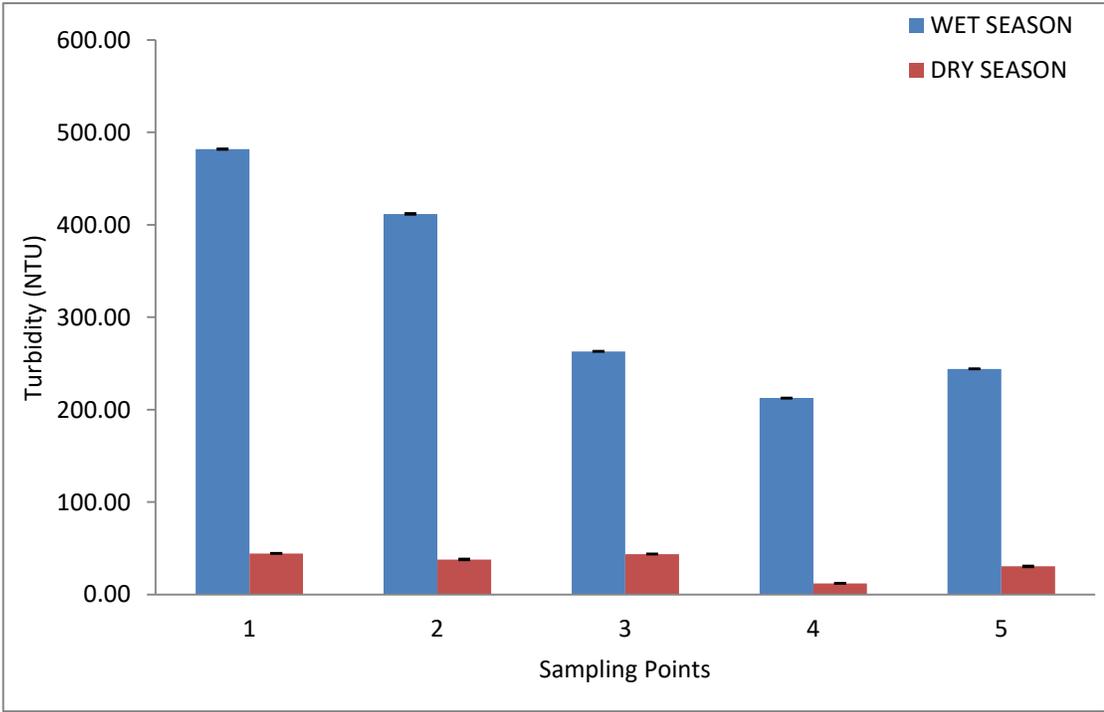


Figure 4.5: Graph of turbidity of water at various sampling points

4.1.6 Dissolved Oxygen

Dissolved oxygen ranged from 3.12 ± 0.01 mg/L to 3.60 ± 0.03 mg/L during the dry season and 3.42 ± 0.02 mg/L to 3.71 ± 0.03 mg/L during the wet season table 4.1 and figure 4.6. Paired t-test revealed no significant difference in the levels of DO between the dry and wet seasons, since $T_{\text{calculated}} < T_{\text{critical}}$ with $T_{\text{calculated}} = 1.72 < T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance (appendix III). One way ANOVA showed spatial variations to be statistically significant, since $F_{\text{calculated}} > F_{\text{critical}}$ for both seasons at $p = 0.05$ level of significance (appendix IV). $F_{\text{calculated}} = 106.13$ and 186.83 for dry and wet seasons respectively, while $F_{\text{critical}} = 3.48$ at $p = 0.05$ level of significance. Similar results for dissolved oxygen were obtained during the study of water quality parameters in the Surma basin, Bangladesh (Alam, *et.al.*, 2007).

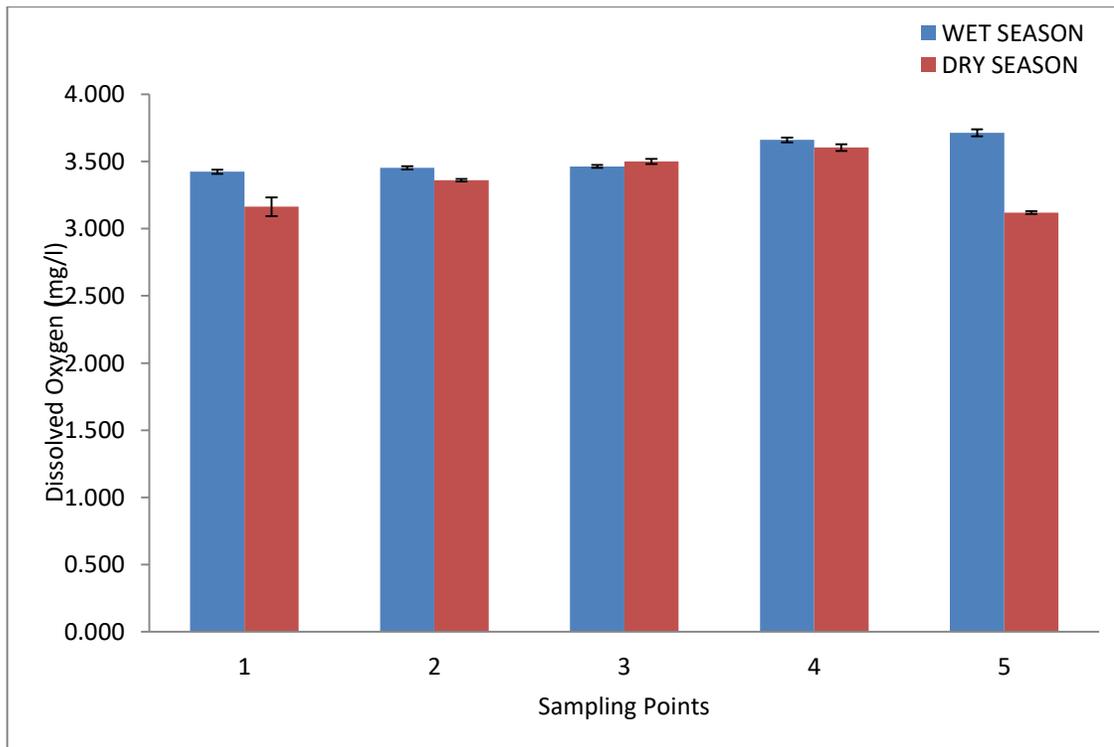


Figure 4.6: Graph of dissolved oxygen in water at various sampling points

4.2 Macro-Nutrients

4.2.1 Nitrates

Nitrates levels in water ranged from 0.74 ± 0.02 mg/L to 1.52 ± 0.12 mg/L during the dry season and 8.84 ± 0.011 mg/L to 22.61 ± 0.058 mg/L during the wet season as shown in table 4.3 and figure 4.7. Seasonal variations of nitrates were found to be statistically significant with $T_{\text{calculated}} > T_{\text{critical}}$. $T_{\text{calculated}} = 5.79 > T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance using paired t-test (appendix III). Spatial variations were also found to be statistically significant with $F_{\text{calculated}} > F_{\text{critical}}$ where $F_{\text{calculated}} = 80.01$ and $108,793.20$ during the dry and wet seasons respectively, while $F_{\text{critical}} = 3.48$ at $p = 0.05$ level of significance (appendix IV). The high concentration of nitrates during the wet season can be attributed to surface run-off carrying manure, fertilizers and domestic waste from the sugarcane and maize plantations located at the banks of the river. The high nitrate concentration downstream during the dry season can be explained by disposal of domestic sewage as the river flows through the densely populated region of Busia town. Nitrates stimulate the growth of macrophytes and phytoplankton and if left unchecked can lead to eutrophication of water bodies (Hem, 1984). Nitrate levels were below the WHO limit of 50 mg/L during both dry and wet seasons. Medudhula *et.al.*, (2012) also reported high levels of nitrates in water during the wet season in Manair reservoir, India.

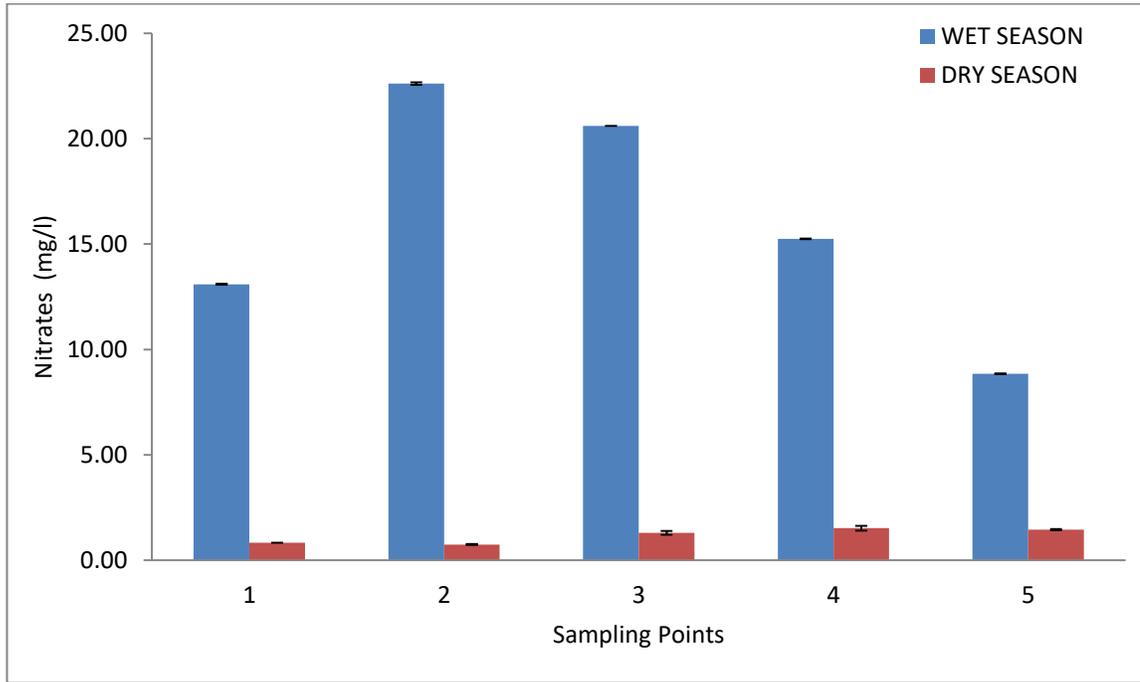


Figure 4.7: Graph of mean concentration of nitrates in water at various sampling points

The concentration of nitrates in the sediments ranged from 7.42 ± 0.72 mg/g to 27.09 ± 0.10 mg/g during the dry season and 20.80 ± 0.14 mg/g to 51.26 ± 0.80 mg/g during the wet season as shown in table 4.4 figure 4.8. Seasonal variations were found to be significantly different at 95% confidence level with $T_{\text{calculated}} = 6.13 > T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance (appendix III). Spatial variations were also found to be statistically significant at 95% confidence level ($p < 0.05$ level of significance). The high concentration of nitrates during the wet season can be attributed to surface run-off carrying manure, fertilizers and domestic waste from the sugarcane and maize plantations and residential houses located at the banks of the river. The observed increase in the concentration of nitrates downstream during the dry season can be linked to disposal of domestic waste into the river as the river flows through the densely populated region of Busia town.

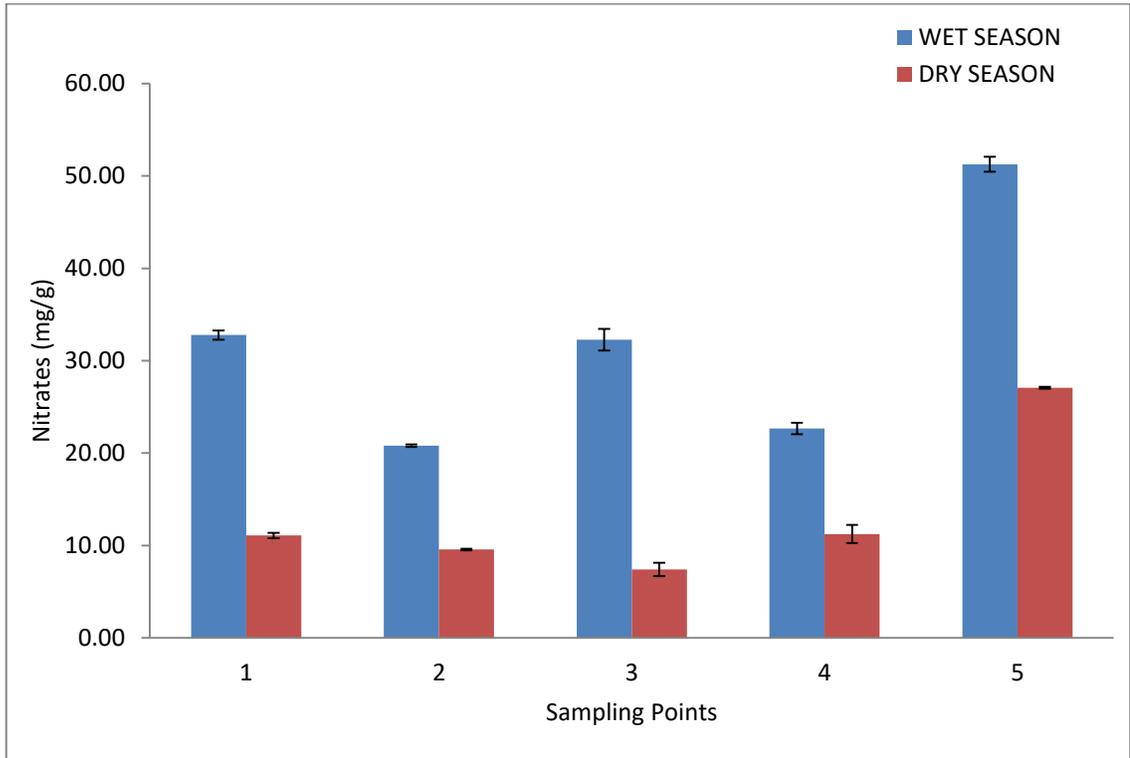


Figure 4.8: Graph of mean concentration of nitrates in sediments at various sampling points

Table 4.2: Chemical anion parameters concentration in water

Anion	Season	S1	S2	S3	S4	S5	WHO	KEBS	NEMA
NO ₃ ⁻	Wet	13.09±0.02	22.61±0.05	20.60±0.01	15.25±0.02	8.84±0.01	50	10	10
	Dry	0.83±0.00	0.74±0.02	1.30±0.09	1.52±0.12	1.45±0.03			
SO ₄ ²⁻	Wet	6.24±0.01	4.87±0.00	12.51±0.03	9.37±0.18	18.08±0.10	250	400	400
	Dry	21.87±0.38	9.89±0.03	13.54±0.05	12.17±0.16	9.19±0.04			
PO ₄ ³⁻	Wet	49.06±0.06	60.65±0.39	21.64±0.28	18.13±0.21	19.13±0.31	5	5	5
	Dry	9.71±0.04	7.38±0.16	7.77±0.10	4.70±0.10	4.61±0.05			
Cl ⁻	Wet	2.01±0.12	4.37±0.10	3.96±0.13	2.81±0.07	5.23±0.24	250	400	400
	Dry	0.56±0.01	0.48±0.02	0.03±0.01	0.76±0.02	0.51±0.01			

* Bolded values indicate parameters above the WHO limits

4.2.2 Phosphates

Phosphates concentration in water ranged from 4.61 ± 0.05 mg/L to 9.71 ± 0.04 mg/L during the dry season and 18.13 ± 0.21 mg/L to 60.65 ± 0.39 mg/L during the wet season (table 4.3 and figure 4.9). Seasonal variation was statistically significant, with $T_{\text{calculated}} = 3.27 > T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance (appendix III). Spatial variations were found to be statistically significant with $F_{\text{calculated}} = 1395.64$ and $15,480.90$ for dry and wet season respectively, while $F_{\text{critical}} = 3.48$ at $p = 0.05$ level of significance (appendix IV). The high concentration during the wet season can be attributed to leaching of phosphorus, surface runoff carrying phosphate rich fertilizers, manure, domestic waste and raw sewage into the river. The increasing trend upstream can be attributed to change in land use, as agricultural areas contribute more phosphates due to the use of phosphorus based fertilizers like ammonium phosphate. The concentration of phosphates was above the WHO recommended limit of 5 mg/L in all the sampling stations during both the wet and dry seasons, apart from sampling stations 4 and 5 whose concentrations were below the WHO recommended limit during the dry season, and this can be attributed to reduced laundry activities at these stations leading to less surfactants getting into the river.

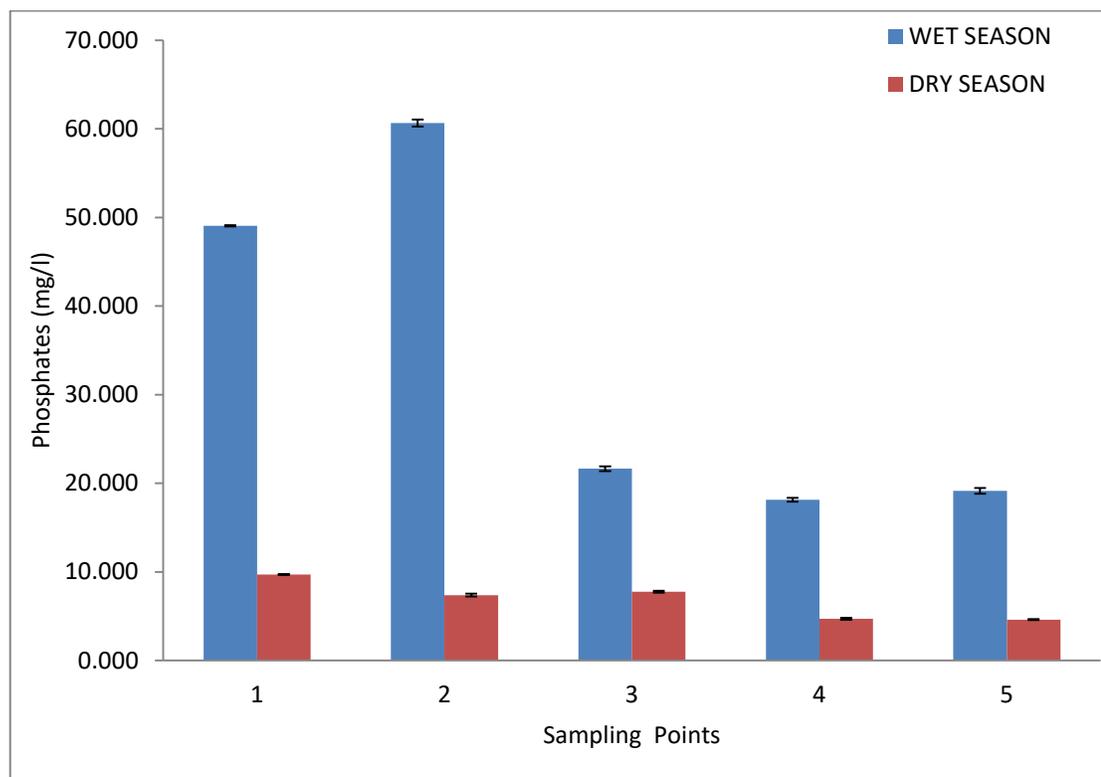


Figure 4.9: Graph of mean concentration of phosphates in water at various sampling points

In sediments, the concentration of phosphates was found to be in the range of 1.30 ± 0.00 mg/g to 4.11 ± 0.00 mg/g during the dry season and 5.48 ± 0.01 mg/g to 11.33 ± 0.04 mg/g during the wet season as shown in table 4.4 and figure 4.10. Seasonal variations were statistically different as per the paired t-test, with $T_{\text{calculated}} = 5.43 > T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance (appendix IV). One way ANOVA found the spatial variations to be statistically significant during both the wet and dry seasons at $p < 0.05$ level of significance. The high concentration of phosphates during the wet season can be attributed to surface runoff which carries phosphate based fertilizers into the river, in addition to domestic waste and raw sewage that is discharged into the river courtesy of poor sanitation and sewerage systems. The increase in the concentration of phosphates at sampling station 2 during both the wet and dry seasons and sampling station 5 during the wet season can be attributed to change in land use, since these are areas with sugarcane, millet and maize plantations hence they discharge more phosphates into the river due to

surface runoff from phosphorus based fertilizers during the wet season. There are a lot of human activities like washing of clothes and bathing which leads to more phosphates finding their way into the river due to the use of soaps and detergents during these cleaning processes.

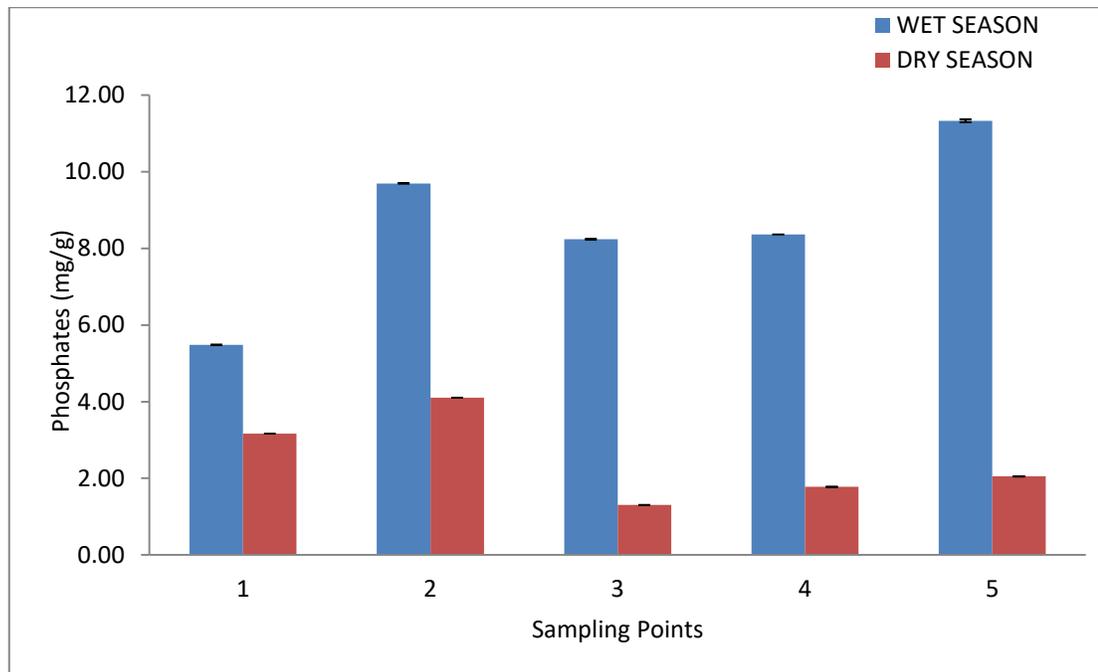


Figure 4.10: Graph of mean concentration of phosphates in sediment at various sampling points

4.2.3 Sulphates

The concentration of sulphates in water ranged from 9.19 ± 0.04 mg/L to 21.87 ± 0.38 mg/L during the dry season and 4.87 ± 0.00 mg/L to 18.08 ± 0.10 mg/L during the wet season (table 4.3 and figure 4.11). Seasonal variations were not statistically significant with $T_{\text{calculated}} = 0.79 < T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance (appendix III). Spatial variations were found to be statistically significant at $p = 0.05$, with $F_{\text{calculated}} = 2252.00$ and 9782.69 for dry and wet season respectively, while $F_{\text{critical}} = 3.48$. The high concentration of sulphates at sampling station 5 during the wet season can be linked to surface run-off containing ammonium sulphate fertilizers and domestic waste water discharges. The high concentration of sulphates at sampling point 1 – 4 during the dry

season can be attributed to dumping of domestic waste into the river and evaporation of water leading to reduced volume of water hence an increase in the concentration of sulphates. Sulphate concentration in all the five sampling stations was found to be below the WHO guideline limit of 250 mg/L.

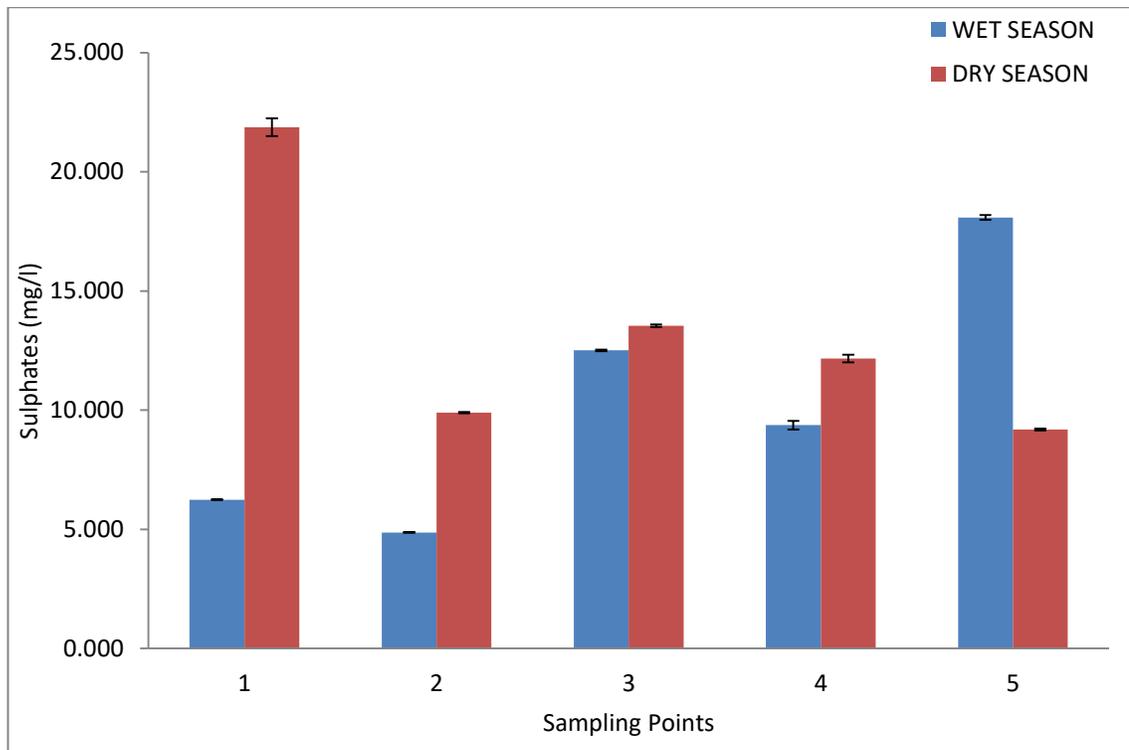


Figure 4.11: Graph of mean concentration of sulphates in water at various sampling points

Sulphate concentration in sediments ranged from 3.55 ± 0.20 mg/g to 6.66 ± 0.19 mg/g during the dry season and 1.26 ± 0.09 mg/g and 12.13 ± 0.23 mg/g during the wet season (table 4.4 and figure 4.12). There was no significant difference in seasonal variations according to paired t-test. $T_{\text{calculated}} = 0.18 < T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance. Spatial variations were found to be significantly different for both the wet and dry seasons at $p = 0.05$ level of significance as per one way ANOVA. The high concentration of sulphates at sampling points 1, 2 and 4 during the dry season can be attributed to discharge of raw sewage into the river, dumping of domestic wastes rich in sulphates as well as the evaporation of water from the river leading to reduced water

volume and hence a high concentration of sulphates. The high concentration of sulphates at sampling points 3 and 5 during the wet season can be linked to surface run off carrying manure, untreated sewage, domestic waste and sulphate rich fertilizers such as ammonium sulphate into the river.

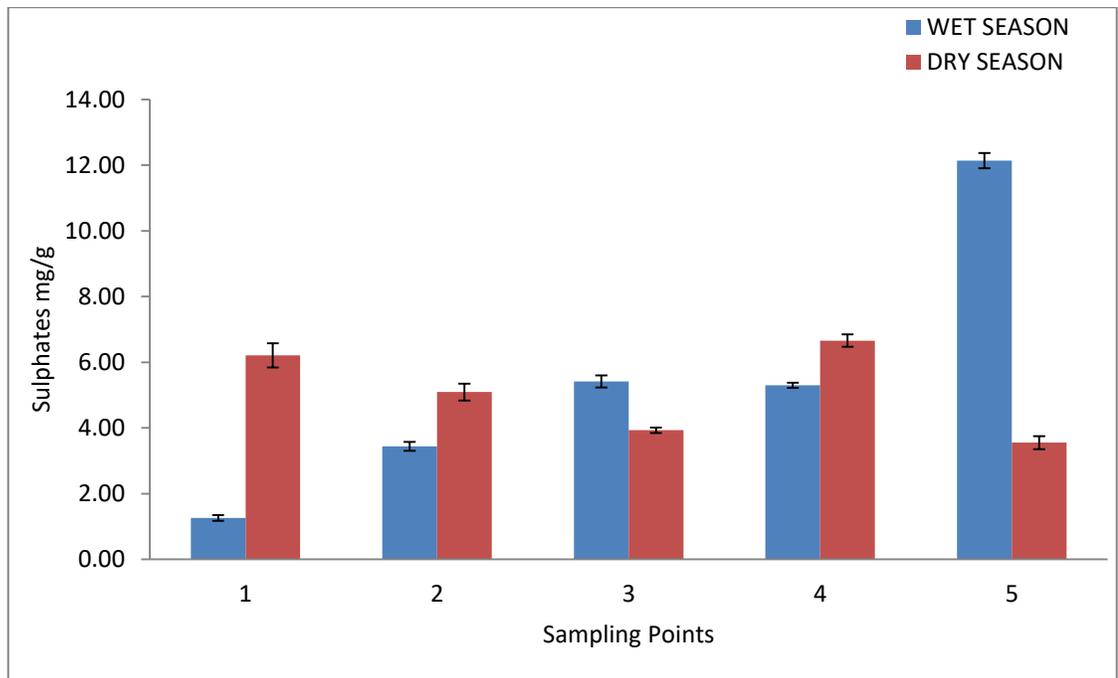


Figure 4.12: Graph of mean concentration of sulphates in sediments at various sampling points

4.2.4 Chlorides

Chloride concentration in water ranged from 0.03 ± 0.01 mg/L to 0.76 ± 0.02 mg/L during the dry season and 2.01 ± 0.12 mg/L to 5.23 ± 0.24 mg/L during the wet season as displayed in table 4.3 and figure 4.13. Both seasonal and spatial variations were found to be statistically significant at $p = 0.05$ level of significance. Paired t-test revealed $T_{\text{calculated}} = 5.17 > T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance. One way ANOVA revealed $F_{\text{calculated}} = 792.25$ and 241.08 for dry and wet season respectively $> F_{\text{critical}} = 3.48$ at $p = 0.05$ level of significance. The high chloride concentration during the wet season can be attributed to surface run-off from anthropogenic sources like raw sewage, animal waste and chloride based inorganic fertilizers like potassium chloride. However,

chloride concentrations were found to be far below the WHO recommended limit of 250 mg/L.

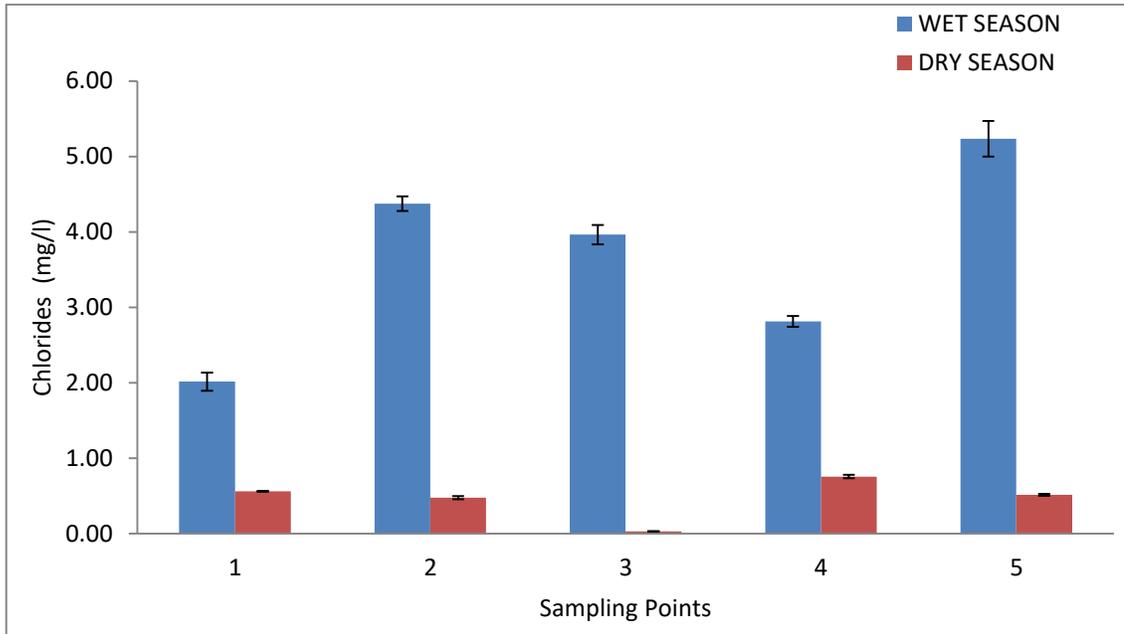


Figure 4.13: Graph of mean concentration of Chlorides in water various sampling points

The range of chloride concentration in sediments was from 5.76 ± 0.07 mg/g to 13.60 ± 0.27 during the dry season and 9.99 ± 1.13 mg/g to 20.41 ± 0.94 mg/g during the wet season (table 4.4 and figure 4.14). Paired t-test revealed significant difference in seasonal variation, with $T_{\text{calculated}} = 2.89 > T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance. One way ANOVA revealed spatial variations to be significantly different during both the wet and dry seasons at $p = 0.05$ level of significance. The rise in chloride ions concentration during the wet season can be linked to surface run-off from anthropogenic sources like raw sewage, animal waste and chloride based inorganic fertilizers such as potassium chloride and ammonium chloride.

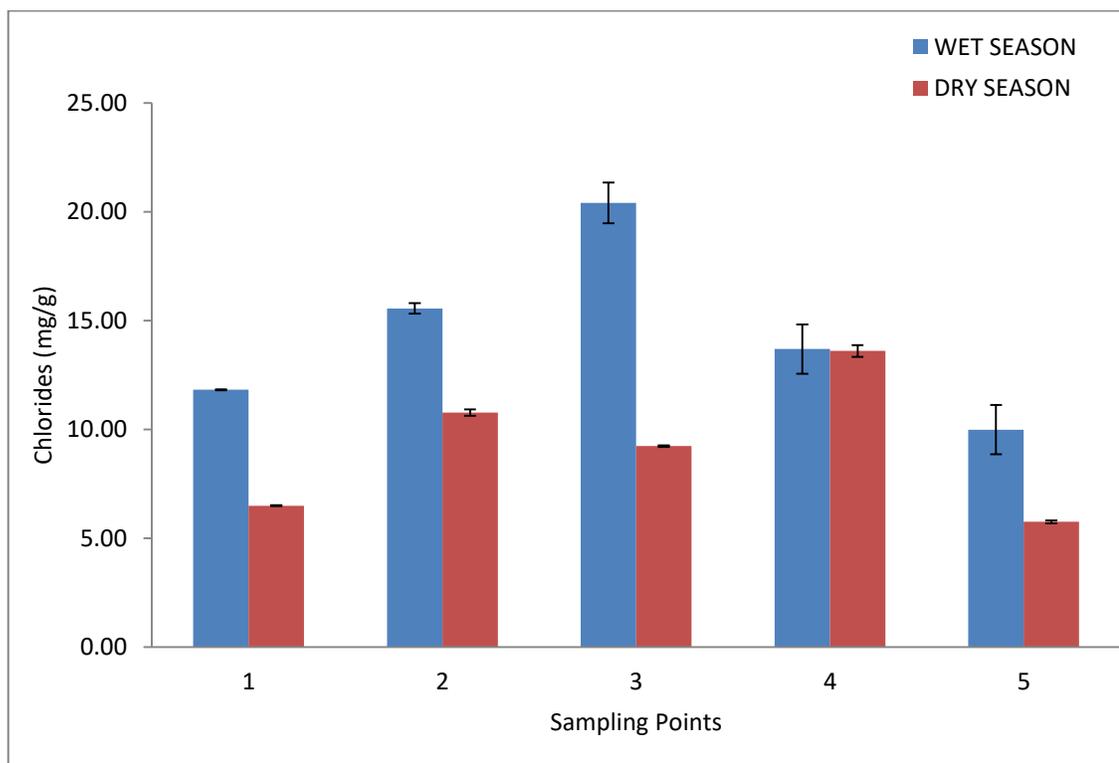


Figure 4.14: Graph of mean concentration of chlorides in sediments at various sampling points

Table 0.1: Seasonal concentration of anions in sediments

Parameter	Season	S1	S2	S3	S4	S5
Nitrates mg/g	Dry	11.09±0.30	9.57±0.09	7.42±0.72	11.24±0.98	27.09±0.10
	Wet	32.78±0.51	20.80±0.14	32.28±1.16	22.66±0.63	51.26±0.80
Sulphates mg/g	Dry	6.21±0.37	5.09±0.26	3.93±0.08	6.66±0.19	3.55±0.20
	Wet	1.26±0.09	3.44±0.14	5.41±0.18	5.30±0.08	12.13±0.23
Phosphates mg/g	Dry	3.17±0.00	4.11±0.00	1.30±0.00	1.78±0.00	2.05±0.00
	Wet	5.48±0.01	9.69±0.00	8.24±0.01	8.36±0.00	11.33±0.04
Chlorides mg/g	Dry	6.50±0.02	10.78±0.14	9.24±0.03	13.60±0.27	5.76±0.07
	Wet	11.82±0.03	15.56±0.24	20.41±0.94	13.70±1.13	9.99±1.13

4.3 Heavy Metals

4.3.1 Lead

In water, lead was only reported in four stations during the wet season, as the concentration of lead was below detection limit in all the other stations during both the

dry and wet seasons (table 4.5). During the dry season, the LOD for lead was 1.109 mg/L against a detected concentration of 0.768 mg/L hence the level of lead was reported as being BDL. The concentration range of lead in the four stations was between 0.33 ± 0.02 mg/L and 0.55 ± 0.03 mg/L as shown in table 4.4 and figure 4.15. The presence of lead in stations S2, S3, S4 and S5 during the wet season can be attributed to run-off from garages, workshops in the shopping centers and market places within the catchment, and sewage effluent washed away by run-off. The highest concentration of lead at sampling point 4 can be attributed to surface runoff carrying paints and wood preservatives from the various workshops, garages and construction sites located at this point and also from raw sewage as the river flows through the densely populated region of Busia town.

The levels of lead detected at these points were above the recommended WHO limit of 0.01 mg/L hence posing a health risk to aquatic life in the river as well as users of water from the river. Similar findings for lead were reported during the determination of selected water quality parameters in the Chania River catchment, Kenya (Kimani *et.al.*, 2016).

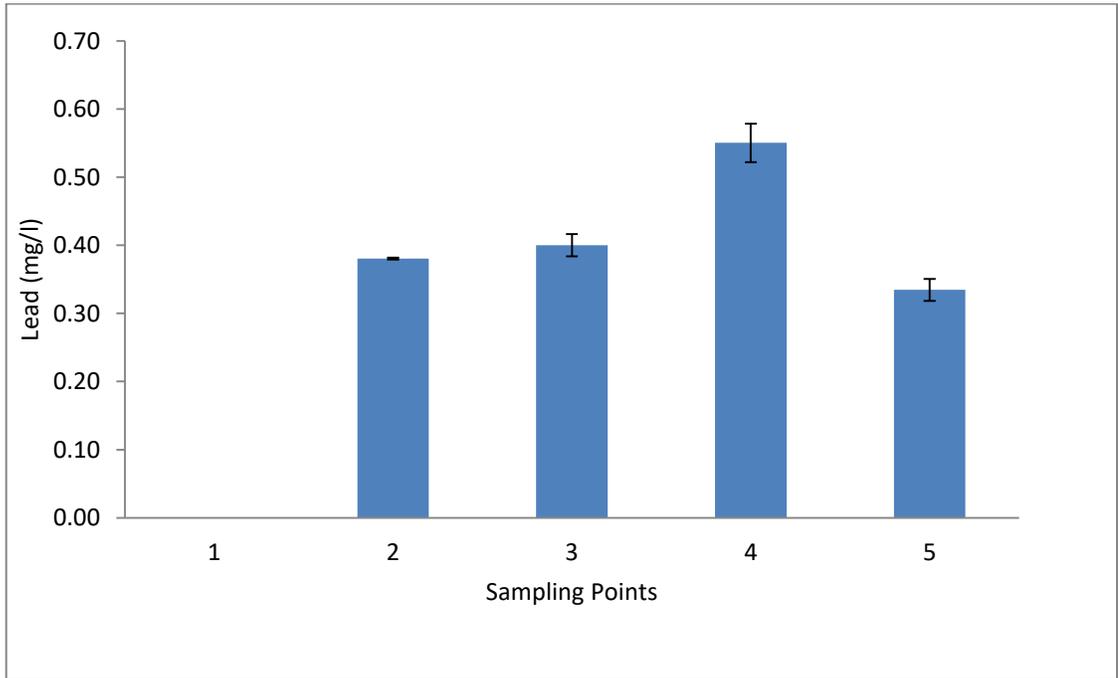


Figure 4.15: Graph of mean concentration of lead in water at various sampling point

The concentration of lead in sediments ranged from 225.50 ± 28.23 to 486.37 ± 65.25 mg/kg during the dry season to 8.00 ± 0.52 to 15.65 ± 0.90 mg/kg during the wet season (table 4.6 and figure 4.16). There was significant variation between the dry and wet season with $T_{\text{calculated}} = 6.99 > T_{\text{critical}} = 2.78$ at $P = 0.05$ level of significance using t-test. One way ANOVA revealed statistical difference in spatial variations at 95% confidence level. Water evaporation during the dry season can be linked to the high level of lead in sediments during the dry season. But this is offset by dilution during the wet season, leading to significant reduction in the concentration of lead. The level of lead was above the WHO recommended level of 100 mg/kg in all the sampling sites during the dry season but way below the WHO recommended level during the wet season.

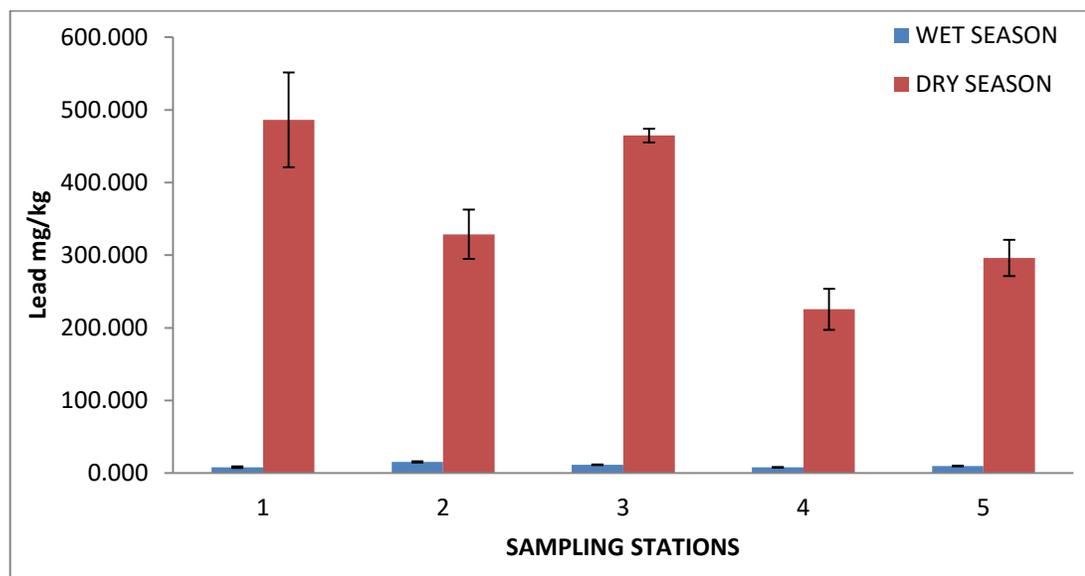


Figure 4.16: Graph of mean concentration of Lead in sediments at various sampling points

4.3.2 Cadmium

The levels of cadmium in all the stations was found to be below the limit of detection during both the dry and wet seasons in both water and sediments therefore indicating no pollution from cadmium (tables 4.5 and 4.6). The LOD for cadmium in water was 0.667 mg/L and 0.115 mg/L during the dry and wet seasons respectively; against detected concentrations of 0.043 mg/L and 0.084 mg/L during the dry and wet seasons respectively. Based on these results the level of cadmium in water was reported as BDL. The LOD for cadmium in sediments was 0.667 mg/L and 0.140 mg/L during both the dry and wet seasons respectively; against detected concentrations of 0.572 mg/L and 0.127 mg/L during the dry and wet seasons respectively. Based on these results the level of cadmium in sediments was reported as BDL.

The absence of cadmium in River water was also reported in the assessment of spatial and seasonal variation of selected water quality parameters in the Chania River catchment, Kenya (Kimani *et.al.*, 2016).

Table 4.4: Metal ion concentration in water during wet and dry seasons

Parameter	Season	S1	S2	S3	S4	S5	WHO	KEB S	NEM A
Lead	mg/L	Wet	< DL	0.38±0.00	0.40±0.02	0.55±0.03	0.33±0.02		
		Dry	< DL	0.01	0.05				
Manganese	mg/L	Wet	0.22±0.01	0.25±0.04	0.26±0.01	0.19±0.01	0.26±0.01		
		Dry	0.22±0.01	0.29±0.01	0.36±0.04	0.50±0.02	0.35±0.02	0.4	0.1
Cadmium	mg/L	Wet	< DL						
		Dry	< DL	0.003	0.005				
Copper	mg/L	Wet	0.34±0.02	0.08±0.02	0.08±0.01	0.11±0.00	0.12±0.01		
		Dry	0.52±0.03	0.58±0.00	0.58±0.01	0.60±0.02	0.59±0.01	1.0 - 2.0	0.1
Nickel	mg/L	Wet	0.35±0.01	0.24±0.03	0.13±0.01	0.24±0.05	0.14±0.03		
		Dry	0.42±0.03	0.35±0.03	0.45±0.03	0.61±0.03	0.94±0.05	0.07	0.05
Chromium	mg/L	Wet	0.04±0.00	0.10±0.01	0.18±0.01	0.24±0.01	0.29±0.01		
		Dry	0.04±0.01	0.03±0.01	0.10±0.01	0.08±0.00	0.06±0.00	0.05	0.05
Zinc	mg/L	Wet	0.10±0.01	0.13±0.01	0.10±0.01	0.21±0.02	0.33±0.01		
		Dry	0.24±0.00	0.17±0.00	0.16±0.02	0.13±0.01	0.27±0.01	3	5
Cobalt	mg/L	Wet	0.40±0.01	0.35±0.01	0.38±0.01	0.37±0.01	0.35±0.01		
		Dry	1.03±0.16	0.76±0.06	0.95±0.06	1.18±0.13	1.28±0.06	0.05	0.05
Iron	mg/L	Wet	10.57±0.5	13.73±0.1	10.00±0.2	8.93±0.10	8.78±0.13		
		Dry	8	8	8	4.29±0.09	4.22±0.14	0.3	0.3

* Bolded values are those that are above the recommended limits by WHO

Table 4.5: Metal ion concentration in sediments during the wet and dry seasons

Parameter		Season	S1	S2	S3	S4	S5	WHO
Lead	mg/kg	Wet	8.30±0.90	15.65±0.90	11.65±0.52	8.00±0.52	9.83±0.55	100
		Dry	486.37±65.25	328.73±33.93	464.57±9.41	225.50±28.23	296.13±24.90	
Manganese	mg/kg	Wet	290.33±2.84	495.00±2.65	329.67±2.52	263.33±1.26	322.50±0.87	2000
		Dry	723.83±8.02	705.33±10.68	315.50±1.73	544.17±12.11	357.17±10.02	
Cadmium	mg/kg	Wet	< DL	< DL	< DL	< DL	< DL	3
		Dry	< DL	< DL	< DL	< DL	< DL	
Copper	mg/kg	Wet	22.50±0.00	31.50±0.00	27.67±0.29	17.00±0.00	31.67±0.58	100
		Dry	106.50±7.50	360.33±14.25	120.17±9.57	61.33±2.52	77.17±6.75	
Nickel	mg/kg	Wet	81.83±5.97	95.00±1.73	97.67±3.18	95.00±3.46	115.50±7.05	50
		Dry	177.33±22.23	237.83±11.45	215.83±6.35	133.33±11.45	171.83±12.70	
Chromium	mg/kg	Wet	45.83±5.77	64.17±2.89	49.17±2.89	26.67±7.64	28.33±2.89	100
		Dry	43.83±2.02	49.00±1.73	48.83±1.53	43.83±0.76	42.50±1.32	
Zinc	mg/kg	Wet	44.67±0.76	50.50±0.00	49.33±0.76	35.83±0.29	41.67±0.76	300
		Dry	52.50±3.61	47.83±1.04	17.50±0.87	24.83±0.76	17.33±1.04	
Cobalt	mg/kg	Wet	7.83±1.26	19.00±1.32	7.17±1.61	5.67±0.58	3.00±0.87	50
		Dry	20.67±1.44	20.17±1.61	12.50±1.32	18.50±0.87	18.67±0.58	
Iron	mg/kg	Wet	2680.33±47.04	3684.00±74.2	3861.83±36.0	2881.33±24.4	2929.00±39.53	50000
				2899.67±15.7	2391.67±18.9	3298.50±37.5		
		Dry	2692.33±78.56	7	2	1	2454.50±32.08	

* Bolded values indicate parameters above the WHO recommended limit. < DL = Below detection limit

4.3.3 Manganese

Manganese levels in water ranged from 0.22 ± 0.01 mg/L to 0.50 ± 0.02 mg/L during the dry season and 0.19 ± 0.01 mg/L to 0.26 ± 0.01 mg/L during the wet season (table 4.5 and figure 4.17). There was no significant difference in seasonal variations as paired t-test revealed $T_{\text{calculated}} = 2.02 < T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance using t-test. Spatial variations were statistically significant as per one way ANOVA, with $F_{\text{calculated}} = 62.31$ and 7.52 during the dry and wet seasons respectively and this was greater than $F_{\text{critical}} = 3.49$ at $p = 0.05$ level of significance. All the stations recorded manganese concentration that was below the recommended WHO limit of 0.4 mg/L with the exception of station 4 during the dry season. The high concentration of manganese downstream from sampling point 1 – 4 is attributed to dumping of domestic waste and discharge of untreated sewage into the river as the river flows towards the densely populated region of Busia town. Concentrations of manganese in River water ranging from 0.02 – 0.68 mg/L were reported during pollution studies of heavy metals in Warri River, Delta state, Nigeria (Wogu and Okaka, 2011).

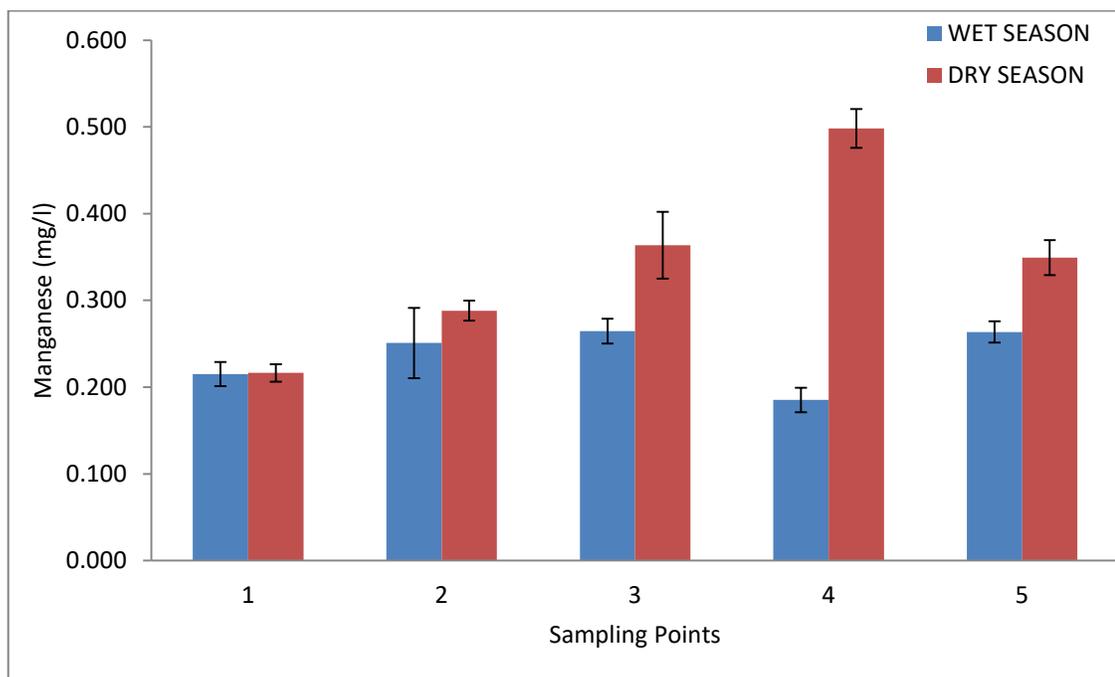


Figure 4.17: Graph of mean concentration of manganese in water in various sampling points

The level of manganese in sediments ranged from 315.50 ± 1.73 mg/kg to 723.83 ± 8.02 mg/kg during the dry season and 263.33 ± 1.26 mg/kg to 495.00 ± 2.65 mg/kg during the wet season as shown in table 4.6 and figure 4.18. There was no significant difference between the dry and wet season, since using t-test $T_{\text{calculated}} = 2.31 < T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance. Spatial variations were statistically significant at 95% confidence level. The slightly high levels during the dry season can be linked to evaporation of water from the River, leading to an increase in concentration. However, this is offset during the wet season leading to a decrease in concentration of manganese in sediments as a result of dilution from the rain water. The high concentration of manganese at sampling point 1 during the dry season can be linked to dumping of waste and discharge of raw sewage into the river.

However, the high concentration of manganese at sampling point 2 during the dry season can be attributed to the two tributaries joining the river at sampling point 2, discharging pollutants rich in manganese from other parts of the sub catchment. All the

sampling stations recorded manganese levels that were within permissible limits of 2000 mg/kg by the WHO during both the dry and the wet season.

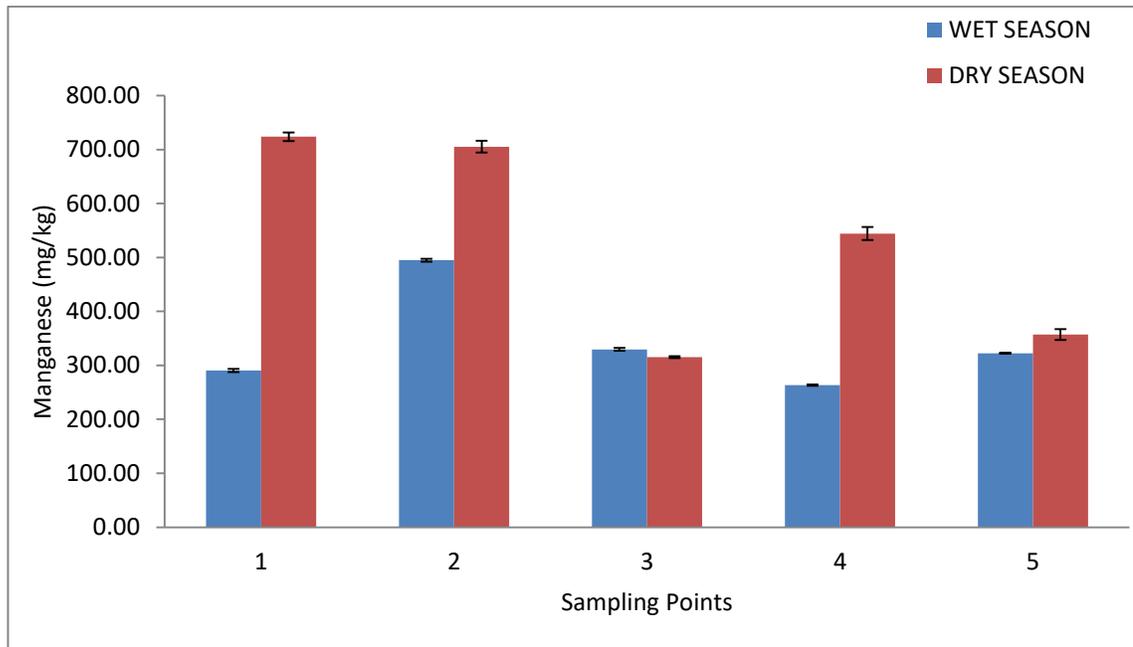


Figure 4.18: Graph of mean concentration of manganese in sediments at various sampling points

4.3.4 Copper

The concentration of copper in water ranged from 0.52 ± 0.03 mg/L to 0.60 ± 0.02 mg/L during the dry season and 0.08 ± 0.01 mg/L to 0.34 ± 0.02 mg/L during the wet season as displayed in table 4.5 and figure 4.19. Seasonal variation was statistically significant, with $T_{\text{calculated}} = 6.88 > T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance using t-test. Spatial variations were statistically significant, with $F_{\text{calculated}} = 7.10$ and 226.14 during the dry and wet seasons respectively and this was greater than $F_{\text{critical}} = 3.49$ at $p = 0.05$ level of significance. The high concentrations during the dry season can be attributed to evaporation of water from the river, leading to a lower volume of the river water as compared to dilution during the wet season. The level of copper in all the five stations was below the WHO recommended limit of 1.0 – 2.0 mg/L. Similar concentrations of copper in water were reported during the evaluation of irrigation water quality from major water sources in Ondo and Osun states, Nigeria (Olubanjo and Alando, 2018).

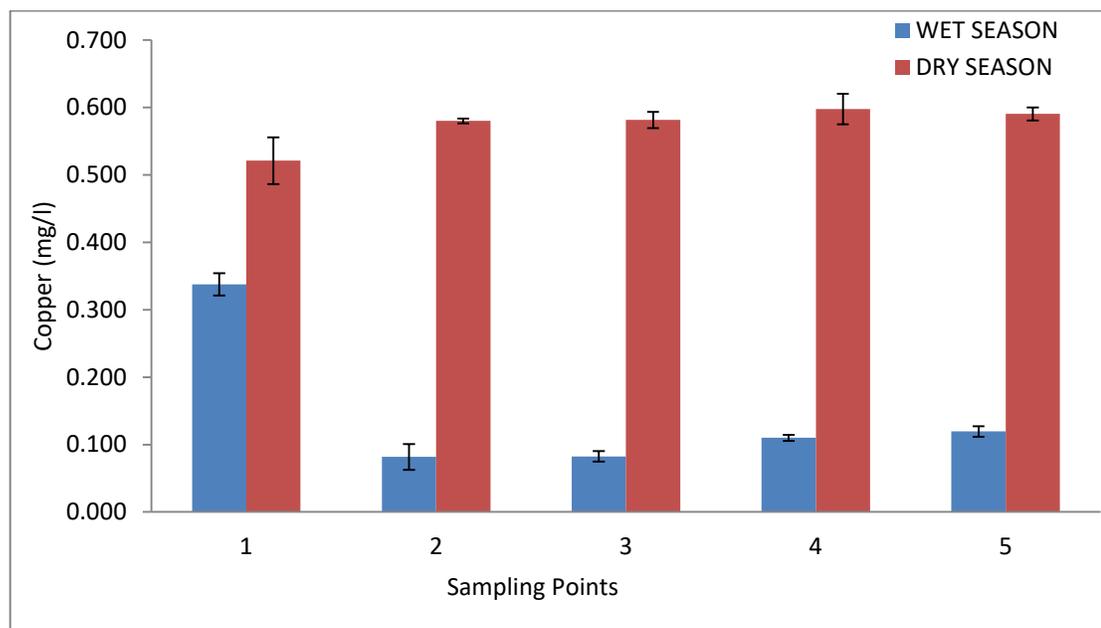


Figure 4.19: Graph of mean concentration of copper in water at various sampling points

The level of copper in sediments as shown in table 4.6 and figure 4.20 ranged from 61.33 ± 2.52 mg/kg to 360.33 ± 14.25 mg/kg during the dry season and 17.00 ± 0.00 mg/kg to 31.67 ± 0.58 mg/kg during the wet season. There was no significant difference in seasonal variations with $T_{\text{calculated}} = 2.23 < T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance. One way ANOVA revealed significant difference in spatial variation at 95% confidence level. The high concentration of copper in sediments during the dry season can be attributed to low volume of water in the river leading to a high concentration of the metal in sediments. The concentration decreases during the wet season due to dilution from the rain water, leading to a high water volume in the River which leads to low analyte concentration.

The high concentration of copper at sampling point 2 can be attributed to the two tributaries joining the river at this point, discharging into the river pollutants rich in copper from other parts of the sub catchment. Sampling stations 1, 2 and 3 recorded copper levels that were above the WHO recommended limits of 100 mg/kg during the dry season, indicating pollution by copper. The level of copper was below the WHO

recommended limit in all the sampling stations during the wet season due to dilution from rain water.

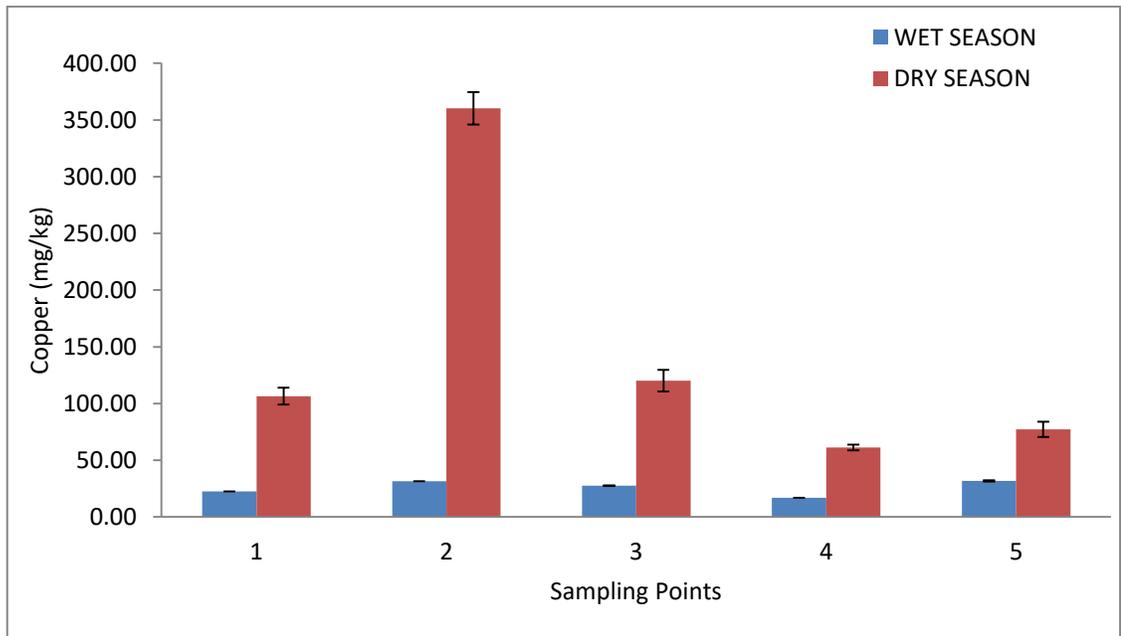


Figure 4.20: Graph of mean concentration of copper in sediments at various sampling points

4.3.5 Nickel

In this study, nickel concentration in water ranged from 0.35 ± 0.03 mg/L to 0.94 ± 0.05 mg/L during the dry season and 0.13 ± 0.01 mg/L to 0.35 ± 0.01 mg/L during the wet season as displayed in table 4.5 and figure 4.21. There was no significant difference in seasonal variation, with $T_{\text{calculated}} = 2.57 < T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance. However, spatial variations were found to be statistically significant with one way ANOVA giving values of $F_{\text{calculated}} = 121.91$ and 31.11 during the dry and wet seasons respectively and this was greater than $F_{\text{critical}} = 3.49$ at $p = 0.05$ level of significance. All the stations recorded nickel values that were above the recommended WHO limits of 0.07 mg/L during both the dry and wet seasons. These high concentrations can be linked to surface run-off from garages and workshops as well as untreated sewage since nickel can be excreted from human faeces and urine. The steady increase in the concentration of nickel downstream can be attributed to the discharge of raw sewage and dumping of

waste from garages and workshops as the river flows towards the densely populated region of Busia town with increased anthropogenic activities and poor sewerage system. Similar patterns in the concentration of nickel in River water during dry and wet seasons were reported during the assessment of physicochemical property of Okoro River estuary, south eastern Nigeria (Ukpatu *et al.*, 2018).

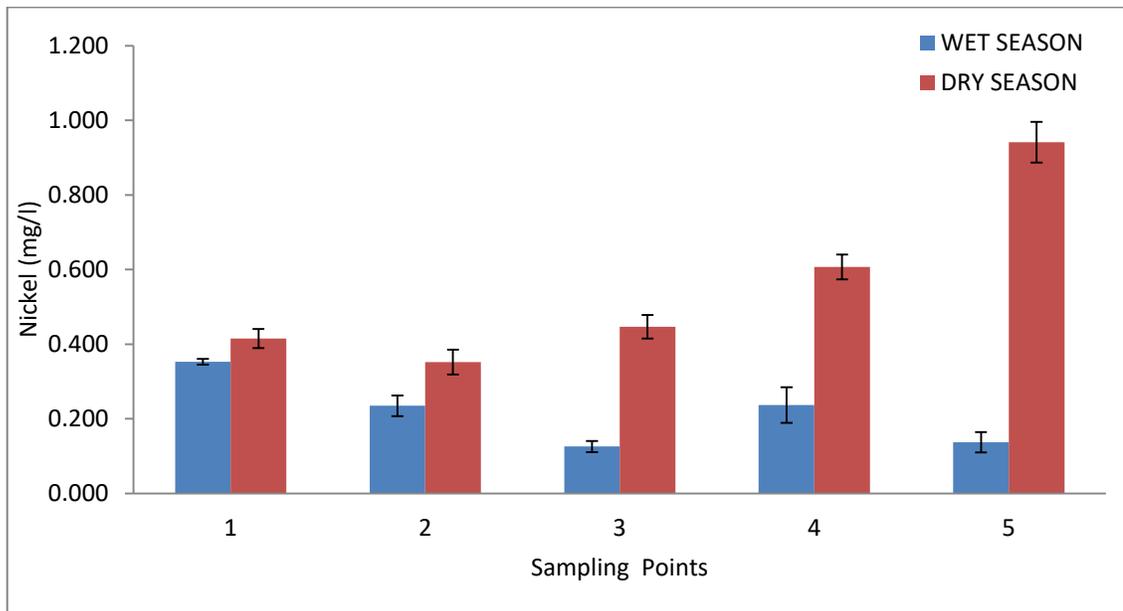


Figure 4.21: Graph of mean concentration of nickel in water at various sampling points

The concentration of nickel in sediments was between 133.33 ± 11.45 mg/kg to 237.83 ± 11.45 mg/kg during the dry season and 81.83 ± 5.97 mg/kg to 115.50 ± 7.05 mg/kg during the wet season (table 4.6 and figure 4.22). Seasonal variations were significantly different with $T_{\text{calculated}} = 4.69 > T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance. Spatial variations were also found to be statistically significant at 95% confidence level. The high concentrations of nickel during the dry season can be attributed to increased evaporation of water from the River leading to a higher concentration of the analyte. But this was quickly offset during the rainy season, as rain water caused dilution resulting to a significant decrease in the concentration of the analyte during the wet season. All the five sampling stations recorded nickel concentrations which were way above the WHO recommended level of 50 mg/kg. This

was an indication of pollution resulting from nickel and nickel related compounds from garages and workshops located on the banks of the river as well as from raw sewage that is discharged into the river due to poor sewerage services that lead to bursting of sewer pipes and overflowing of raw sewage.

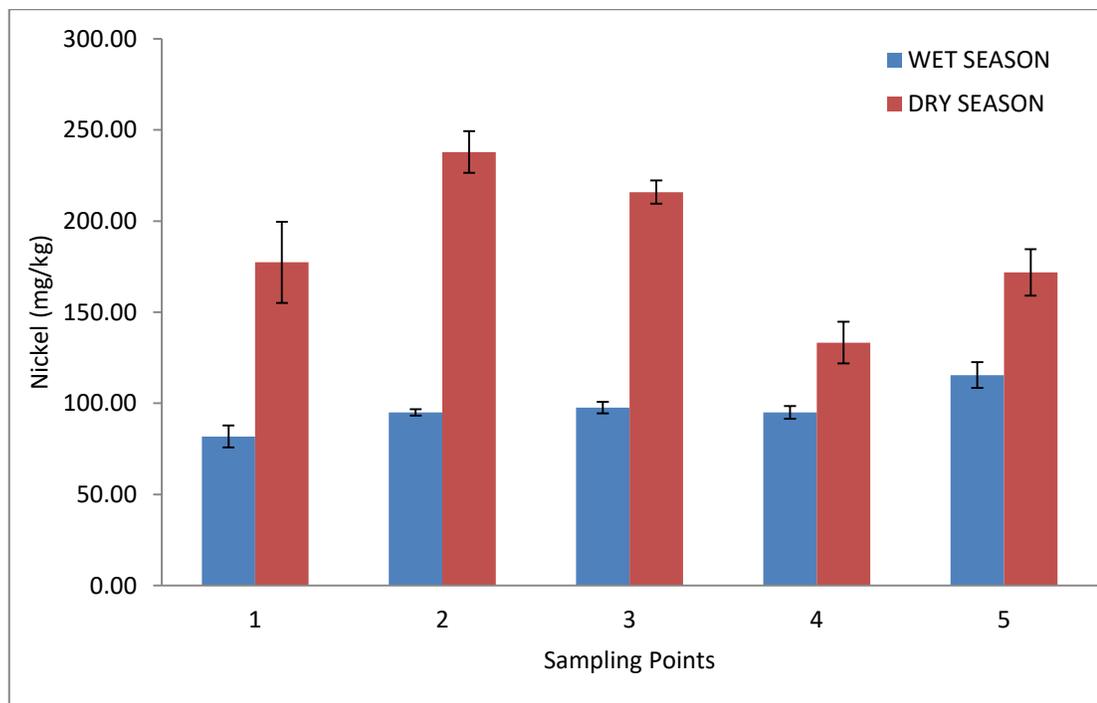


Figure 4.22: Graph of mean concentration of nickel in sediments at various sampling points

4.3.6 Chromium

In water, chromium concentration as shown in table 4.5 and figure 4.23 ranged from 0.03 ± 0.01 mg/L to 0.10 ± 0.01 mg/L during the dry season and 0.04 ± 0.00 mg/L to 0.29 ± 0.01 mg/L during the wet season. Seasonal variations showed no significant difference between the dry and wet seasons with $T_{\text{calculated}} = 2.72 < T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance (appendix III). There was a significant difference in spatial variations, with $F_{\text{calculated}} = 48.77$ and 394.89 during the dry and wet seasons respectively and this was greater than $F_{\text{critical}} = 3.49$ at $p = 0.05$ level of significance (appendix IV). Only station 1 recorded chromium concentrations below the WHO recommended limits of 0.05 mg/L during the dry and wet seasons, while station 2 recorded chromium

concentrations that were below the WHO recommended levels only during the dry season. All the remaining stations recorded chromium concentrations above the WHO recommended levels of 0.05 mg/L. The high concentration of chromium during the wet season can be attributed to surface runoff that carried paints from workshops and garages, wood preservatives from construction sites and pesticides from farms since chromium VI is used in the manufacture of pesticides. The steady increase in chromium levels downstream can be attributed to increase in anthropogenic activities such as workshops and garages, construction sites as well as discharge of raw sewage into the river, as the river flows through the densely populated region of Busia town. Similar results for chromium in water were also reported during the determination of heavy metals from some selected dams in Katsina state, Nigeria (Yaradua, *et al.*, 2018).

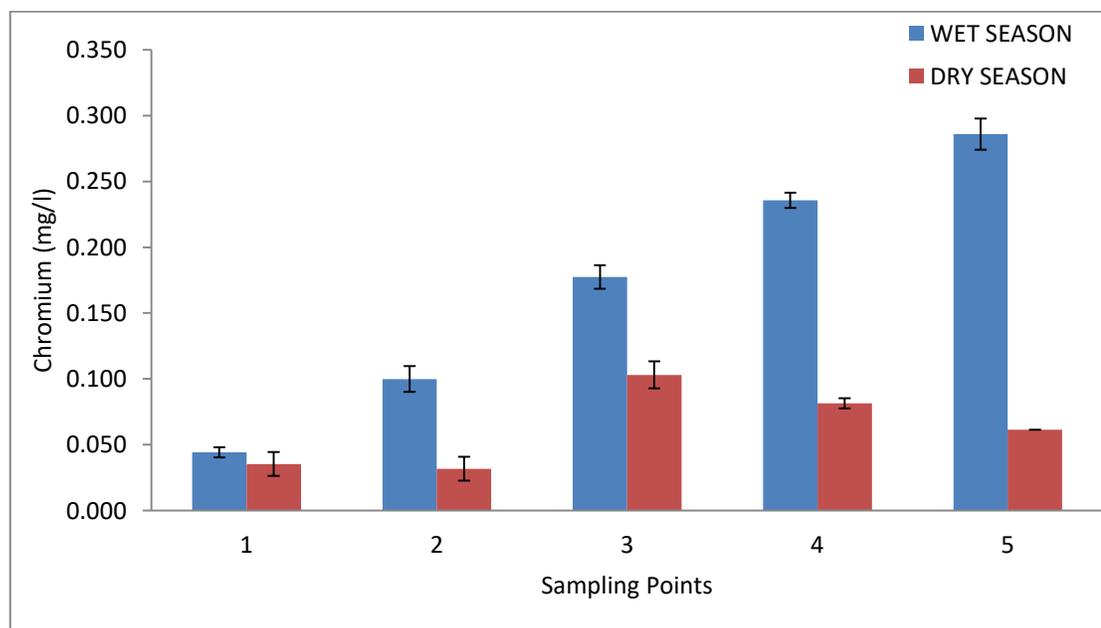


Figure 4.23: Graph of mean concentration of chromium in water at various sampling points

The concentration of chromium in sediments was between 42.50 ± 1.32 mg/kg to 49.00 ± 1.73 mg/kg during the dry season and 26.67 ± 7.64 mg/kg to 64.17 ± 2.89 mg/kg during the wet season (table 4.6 and figure 4.24). There was no significant difference between the dry and the wet season, since $T_{\text{calculated}} = 0.47 < T_{\text{critical}} = 2.78$ at $p = 0.05$

level of significance (appendix III). Spatial variations were statistically significant at 95% confidence level. The slightly high concentrations of chromium at sampling stations 1, 2 and 3 during the wet season can be linked to surface runoff that carried paints from workshops and garages, wood preservatives from construction sites, pesticides from farms and raw sewage into the river. The level of chromium in all the five sampling stations was below the WHO recommended limits of 100 mg/kg during both the dry and wet seasons, indicating no pollution from chromium compounds.

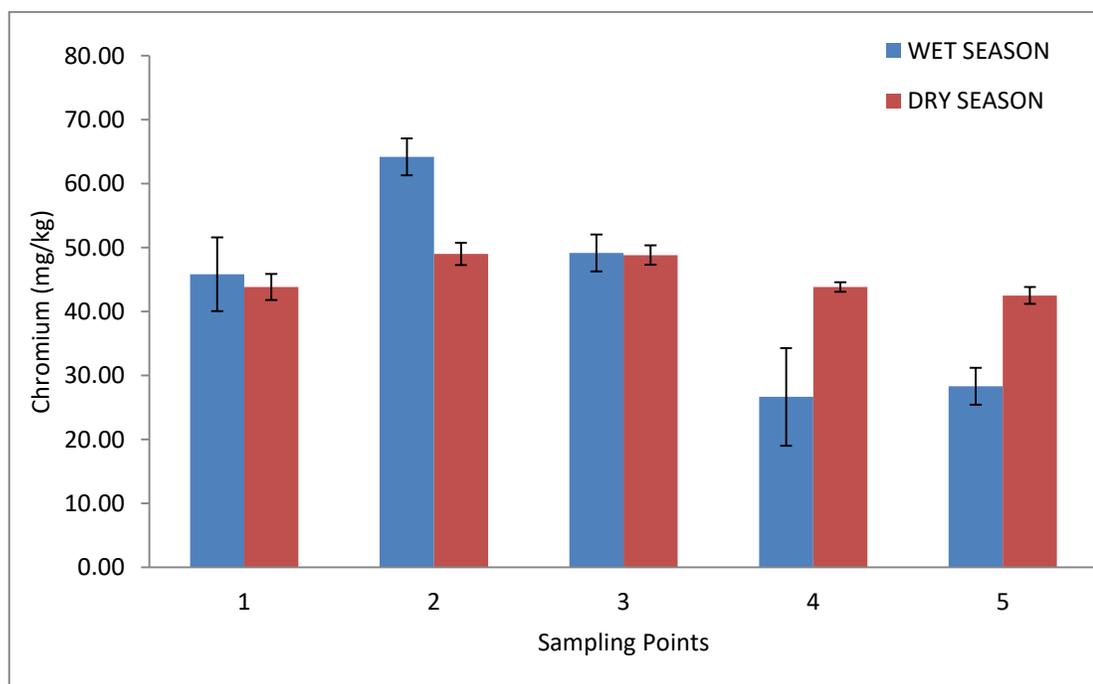


Figure 4.24: Graph of mean concentration of chromium in sediments at various sampling points

4.3.7 Zinc

Zinc levels in water ranged from 0.13 ± 0.01 mg/L to 0.27 ± 0.01 mg/L during the dry season, to 0.10 ± 0.01 mg/L to 0.33 ± 0.01 mg/L during the wet season as shown in table 4.5 and figure 4.25. There was no significant difference in seasonal variation between the dry and wet seasons. According to paired t-test, $T_{\text{calculated}} = 0.49 < T_{\text{critical}} = 2.78$ at $p = 0.05$ at level of significance (appendix III). The spatial variations were significantly

different, with $F_{\text{calculated}} = 132.23$ and 137.62 during the dry and wet seasons respectively and this was greater than $F_{\text{critical}} = 3.49$ at $p = 0.05$ level of significance (appendix IV).

The increase in the concentration of zinc downstream during the wet season can be attributed to increased anthropogenic activities such the setting up of workshops and garages, construction sites, dumping of solid waste by the river banks and discharge of raw sewage into the river as the river flows through the densely populated region of Busia town. The level of zinc in all the five stations was below the WHO recommended limit of 3.0 mg/L.

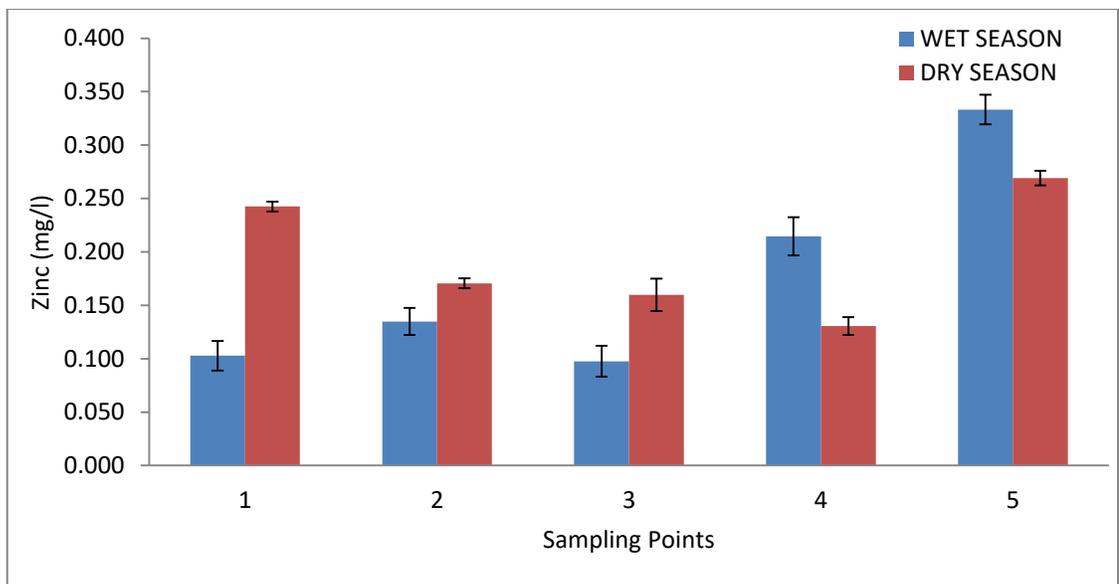


Figure 4.25: Graph of mean concentration of zinc in water at various sampling points

Zinc levels in sediments ranged from 17.33 ± 1.04 mg/kg to 52.50 ± 3.61 mg/kg for the dry season and 35.83 ± 0.29 mg/kg to 50.50 ± 0.00 mg/kg during the wet season (table 4.6 and figure 4.26). There was no significant difference between the dry season and the wet season, since $T_{\text{calculated}} = 1.73 < T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance using t-test. One way ANOVA revealed a significant difference in spatial variations. The slightly high levels of zinc during the wet season can be attributed to surface runoff carrying paints, wood preservatives, fertilizers, domestic waste and raw sewage into the river. The high concentration of zinc upstream can be attributed to increased use of zinc

based fertilizers as well as the dumping of domestic waste and discharge of raw sewage into the river. The high levels of zinc at sampling point 2 can be linked to the tributaries joining the river at this point, discharging pollutants rich in zinc from other parts of the sub catchment.

The level of zinc in all the sampling stations was below the WHO recommended levels of 300 mg/kg for both the dry and the wet season, indicating no pollution from compounds of zinc.

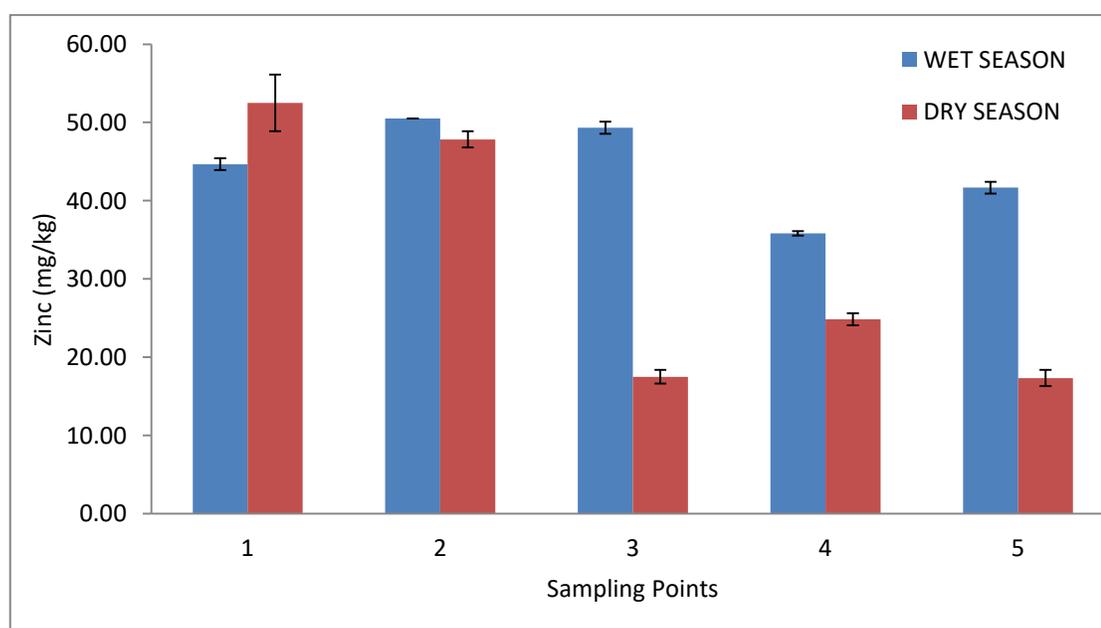


Figure 4.26: Graph of mean concentration of zinc in sediments at various sampling points

4.3.8 Cobalt

Cobalt concentration in water ranged from 0.76 ± 0.06 mg/L to 1.28 ± 0.06 mg/L during the dry season and 0.35 ± 0.01 mg/L to 0.40 ± 0.01 mg/L during the wet season as shown in table 4.5 and figure 4.27. Seasonal variations showed significant difference according to paired t-test, with $T_{\text{calculated}} = 7.35 > T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance. Spatial variations were statistically significant, with $F_{\text{calculated}} = 11.89$ and 13.53 during the dry and wet seasons respectively which was greater than $F_{\text{critical}} = 3.49$ at $p = 0.05$ level of significance. All the stations recorded cobalt concentrations above the

recommended WHO limits of 0.05 mg/L. These high concentrations of cobalt can be attributed to dumping of waste from garages, workshops and construction sites into the river as well as the discharge of raw sewage into the river. The use of cobalt sulphate heptahydrate fertilizer, which contains about 21% cobalt, has also led to the increase in the level of cobalt in water. The steady increase in the concentration of cobalt downstream during the dry season can be linked to increased anthropogenic activities as the river flows through the densely populated region of Busia town. High concentration of cobalt during dry season and low concentrations during the wet season were also reported in the study of seasonal variation of metals in water and sediments in Port Said, Egypt (Nabil *et al.*, 2018).

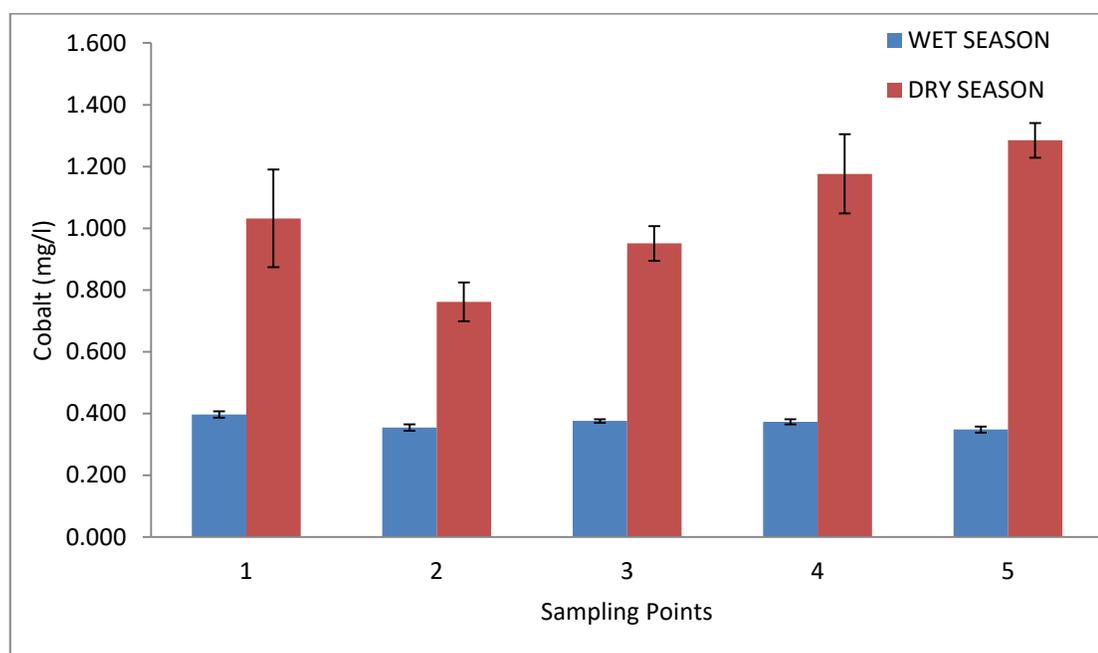


Figure 4.27: Graph of mean concentration of cobalt in water at various sampling points

The level of cobalt in sediments was between 12.50 ± 1.32 mg/kg to 20.67 ± 1.44 mg/kg during the dry season and 3.00 ± 0.87 mg/kg to 19.00 ± 1.32 mg/kg during the wet season (table 4.6 and figure 4.28). Variation between the dry and the wet season was significantly different with $T_{\text{calculated}} = 3.53 > T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance using paired t-test (appendix III). Spatial variations were found to be

significantly different as per one way ANOVA at 95% confidence level. The high levels of cobalt in the sediments during the dry season can be attributed to dumping of waste from garages, workshops and construction sites as well as the discharge of raw sewage into the river. The high levels of cobalt at sampling point 2 during both the dry and wet seasons can be attributed the tributaries joining the river at this point, discharging pollutants rich in cobalt from other parts of the sub catchment. Cobalt levels in all the five sampling stations during the dry and wet seasons were below the 50 mg/kg level recommended by WHO indicating lack of pollution by cobalt in the sediments.

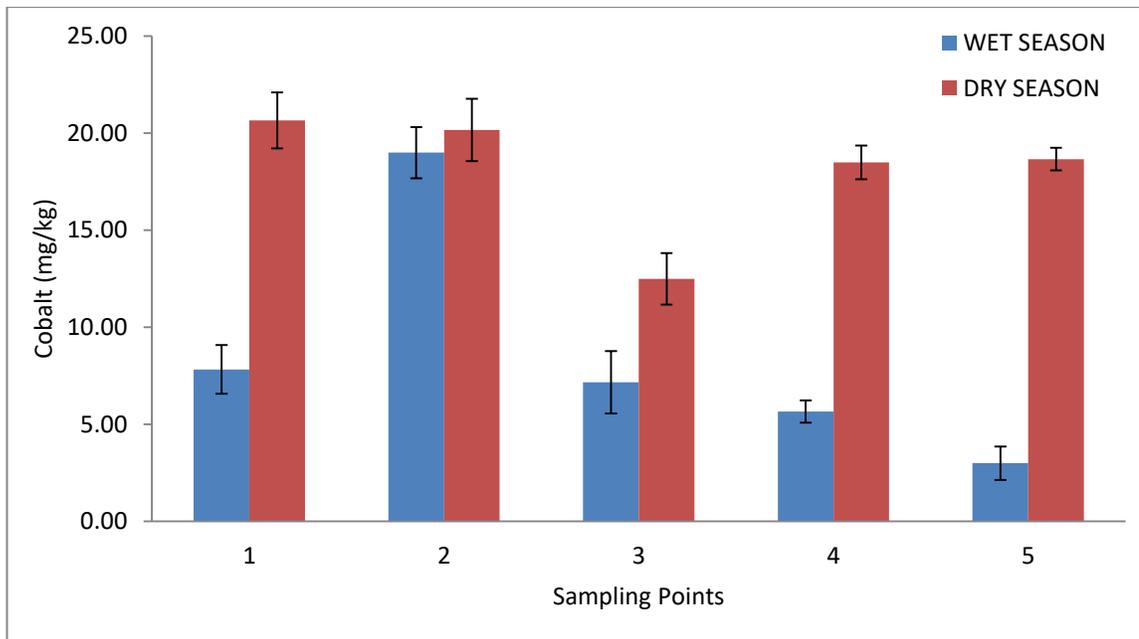


Figure 4.28: Graph of mean concentration of cobalt in sediments at various sampling points

4.3.9 Iron

The concentration of iron in water ranged from 2.93 ± 0.08 mg/L to 4.29 ± 0.09 mg/L during the dry season and 8.78 ± 0.13 mg/L to 13.73 ± 0.18 mg/L during the wet season as shown in table 4.5 and figure 4.29. The paired t-test results indicated there was significant difference between the dry and wet seasons, with $T_{\text{calculated}} = 6.79 > T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance (appendix III). One way ANOVA indicated spatial difference to be statistically significant, with $F_{\text{calculated}} = 82.99$ and 125.86 during the dry

and wet seasons respectively and this was greater than $F_{\text{critical}} = 3.49$ at $p = 0.05$ level of significance (appendix IV).

The high iron concentrations observed during the wet season can be attributed to surface runoff from farms, workshops and garages located at the banks of the river, construction sites located downstream as well as raw sewage. The high levels of iron at sampling point 2 can be linked to the tributaries joining the river at this point, discharging pollutants rich in iron from other parts of the sub catchment. The concentration of iron was above the WHO recommended limit of 0.3 mg/l during both the dry and wet seasons. High concentration of iron in water stains laundry and plumbing fixtures. Iron concentration of above 0.3 mg/L in water produces a noticeable iron taste in water (Kimani, *et.al.*, 2016). High levels of iron during the wet season was also reported during the assessment of water quality in Surma River, Bangladesh (Alam, *et.al.*, 2007).

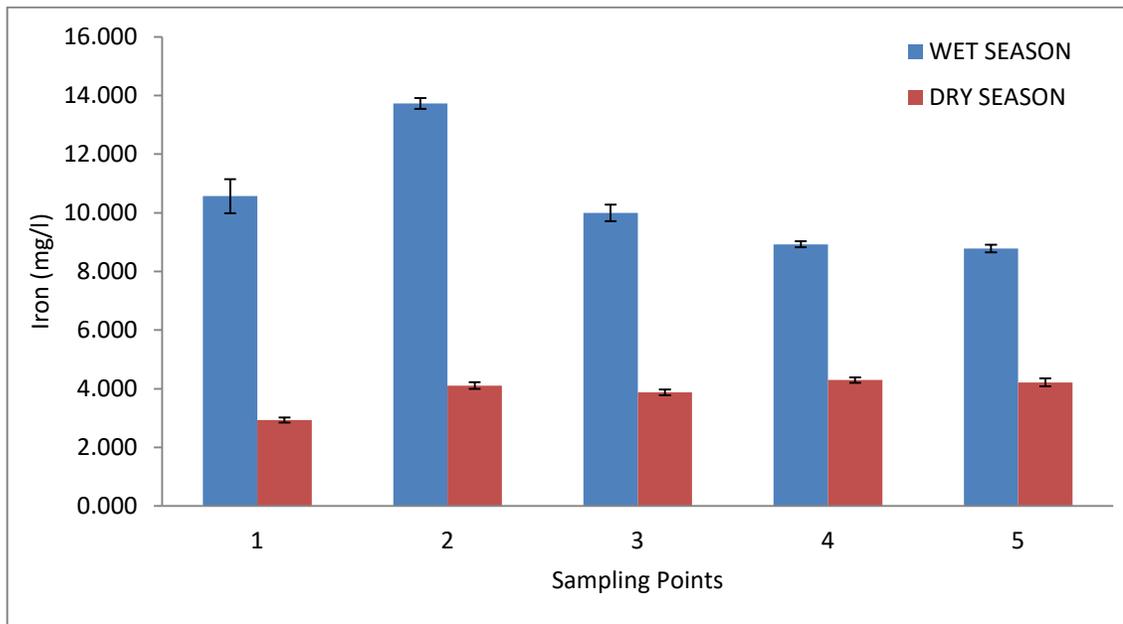


Figure 4.29: Graph of mean concentration of iron in water at various sampling points

The concentration of iron in the sediments was between 2391.67 ± 18.92 mg/kg to 3298.50 ± 37.51 mg/kg during the dry season and 2680.33 ± 47.04 mg/kg to 3861.83 ± 36.06 mg/kg during the wet season (table 4.6 and figure 4.30). There was no

significant difference between the dry and wet seasons as per the paired t-test, with $T_{\text{calculated}} = 1.41 < T_{\text{critical}} = 2.78$ at $p = 0.05$ level of significance (appendix III). However, spatial variations were statistically significant at $p = 0.05$ level of significance. The slightly high levels of iron during the wet season can be attributed to surface run off that carried compounds of iron from garages, car wash and fertilizers from the trading centers close to the River and the maize and sugarcane plantations respectively. The level of iron in the sediments was below the WHO recommended levels of 50,000 mg/kg in all the sampling stations during both the wet and dry seasons, which indicated no pollution from iron. High levels of iron in sediments was also reported during the determination of heavy metals in sediments of Avsar dam Lake in Turkey (Ozturk *et.al.*, 2009).

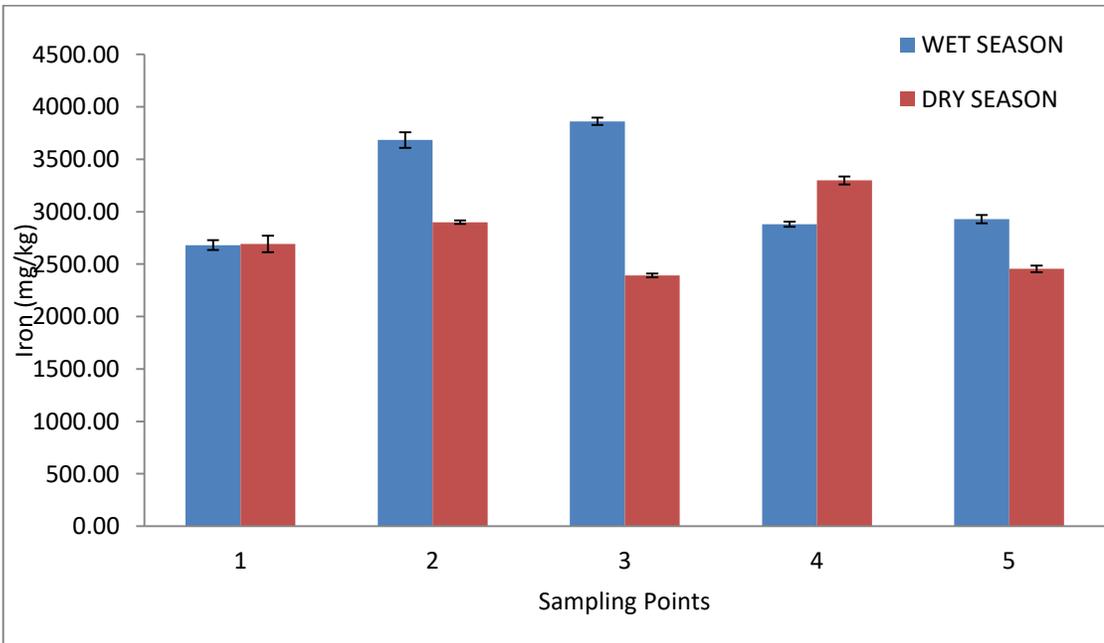


Figure 4.30: Graph of mean concentration of iron in sediments at various sampling points

4.4 Pollution Indices

4.4.1 Geoaccumulation Index

Table 4.6 shows the geoaccumulation index values for heavy metals in sediments from River Sio.

Table 4.6: Geoaccumulation values of sediments in River Sio

Sampling Site	Season	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb
S1	Dry	-1.34	-0.49	-4.48	-0.2	1.56	0.83	-0.89	4.25
	Wet	-1.28	-1.18	-4.48	-1.62	0.45	-1.42	-1.13	-1.62
S2	Dry	-1.18	-0.53	-4.37	-0.25	1.99	2.59	-1.03	3.69
	Wet	-0.79	-1.04	-4.03	-0.34	0.66	-0.93	-0.95	-0.70
S3	Dry	-1.18	-1.69	-4.65	-0.94	1.85	1.00	-2.48	4.19
	Wet	-1.17	-1.63	-3.96	-1.74	0.70	-1.12	-0.98	-1.13
S4	Dry	-1.34	-0.91	-4.19	-0.38	1.15	0.03	-1.97	3.15
	Wet	-2.06	-1.95	-4.38	-2.08	0.66	-1.82	-1.44	-1.67
S5	Dry	-1.38	-1.51	-4.61	-0.36	1.52	0.36	-2.49	3.54
	Wet	-1.97	-1.66	-4.36	-3.00	0.95	-0.92	-1.23	-1.38

Cr, Mn, Fe, Co and Zn showed negative geoaccumulation index values, showing unpolluted status (class 0). However, Ni showed moderate pollution in sediments during the dry season (class 2) and unpolluted to moderately polluted during the wet season (class 1). The shift from class 2 to class 1 in the geoaccumulation index can be attributed to dilution during the wet season. The high geoaccumulation index values for nickel can be attributed to the discharge of raw sewage into the river together with the dumping of wastes from metal workshops and garages located at the banks of the river. The high geoaccumulation index value for nickel at sampling point two can be attributed to the two tributaries joining the river at this point, bringing in pollutants rich in nickel from different parts of the sub catchment. For copper, sampling stations 1, 3, 4 and 5 were classified under class 1 in the geoaccumulation index showing that the levels of copper in sediments in these stations vary from unpolluted to moderately polluted during the dry season. However, sampling station 2 had a geoaccumulation index value of 2.59 for copper during the dry season, and is therefore classified under class 3, which ranges from moderately polluted to strongly polluted. But the geoaccumulation index values for

copper were below 0 during the wet season, showing no pollution during the wet season. This can be attributed to dilution during the wet season, leading to a decrease in the concentration of copper. Sampling sites 2, 4 and 5 were strongly polluted with lead whereas sampling sites 1 and 3 ranged from strongly to extremely polluted with lead during the dry season. The geoaccumulation index value for lead was below zero in all the sampling sites during the wet season, indicating no pollution due to lead during the wet season. Similar patterns of geoaccumulation index were reported by Cardellicho *et.al*; 2010 in a study involving seasonal variations of heavy metals in river sediments (Cardellicho *et.al*; 2010).

4.4.2 Contamination Factor

Using contamination factor, heavy metal pollution in sediments can be classified into four categories. $C_f \leq 1$ = low, C_f 1 – 3 = moderate, C_f 3 – 6 = considerable contamination while $C_f > 6$ = very high contamination. Table 4.7 shows the contamination factor for the heavy metals in River Sio.

Table 4.7: Contamination Factor values for sediments in River Sio

Sampling Site	Season	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb	PLI
S1	Dry	0.59	1.07	0.07	1.29	4.43	2.66	0.81	28.61	1.41
	Wet	0.62	0.43	0.07	0.49	2.05	0.56	0.69	0.49	0.49
S2	Dry	0.66	1.04	0.07	1.26	5.95	9.01	0.74	19.34	1.62
	Wet	0.87	0.73	0.09	1.19	2.38	0.79	0.78	0.92	0.74
S3	Dry	0.66	0.46	0.06	0.78	5.40	3.00	0.27	27.33	1.07
	Wet	0.67	0.49	0.10	0.45	2.44	0.69	0.76	0.69	0.58
S4	Dry	0.59	0.80	0.08	1.16	3.33	1.53	0.38	13.27	1.02
	Wet	0.36	0.39	0.07	0.35	2.38	0.43	0.55	0.47	0.42
S5	Dry	0.57	0.53	0.06	1.17	4.30	1.93	0.27	17.42	0.98
	Wet	0.38	0.47	0.07	0.19	2.89	0.79	0.64	0.58	0.46

PLI = Pollution Load Index

The contamination factor for Cr, Fe and Zn were low ($C_f < 1$) during both the dry and wet seasons. The contamination factor for manganese was low for both the dry and wet seasons, except for sampling sites 1 and 2 in which the contamination factor was >

During the dry season, indicating moderate contamination by manganese. The contamination factor for cobalt was moderate during the dry season, ($C_f > 1$) and low during the wet season ($C_f < 1$) and this can be attributed to dilution of the metals in the river water during the wet season. Copper showed moderate contamination in sampling sites 1, 3, 4 and 5 while sampling site 2 showed very high contamination ($C_f > 6$) of copper during the dry season. However, copper showed low contamination in all the sampling sites during the wet season and this is due to dilution during the wet season, leading to low concentration of copper in sediments during the wet season. Nickel had the highest contamination factor during both the dry and wet seasons. During the dry season, there was considerable contamination by nickel ($C_f < 6$) but showed moderate contamination during the wet season ($C_f < 3$) due to dilution during the wet season. The high contamination factor values for nickel can be attributed to the discharge of raw sewage into the river together with the dumping of wastes from metal workshops and garages located at the banks of the river. The high contamination factor value for nickel at sampling point two can be attributed to the two tributaries joining the river at this point, bringing in pollutants rich in nickel from different parts of the sub catchment. The contamination factor for lead was very high in all the sampling sites during the dry season ($C_f > 6$) while it was moderate during the wet season ($C_f 0.42 - 0.74$). The reduction in contamination factor values witnessed during the rainy season can be linked to dilution by rain water, leading to a decrease in the concentration of the analyte.

4.4.3 Pollution Load Index

Pollution due to anthropogenic activities is indicated by a $PLI > 1$ while a $PLI < 1$ indicates no pollution from heavy metals due to anthropogenic activities (Dimuthu, N and Wijeyarante W.M, 2016). Sampling site 5 showed no pollution from heavy metals due to human related activities during the dry season ($PLI < 1$). However, all the remaining sampling sites showed pollution due to anthropogenic activities during the dry season ($PLI > 1$) while during the wet season there was no pollution by heavy metals from anthropogenic activities ($PLI < 1$).

4.4.4 Enrichment Factor

The enrichment factor (E.F) is divided into several classes. E.F < 1 = no enrichment, E.F 1 – 3 = minor enrichment, E.F 3 – 5 = moderate enrichment, E.F 5 – 10 = moderately severe enrichment, E.F 10 – 25 = severe enrichment, E.F 25 – 50 = very serious enrichment while E.F > 50 = extremely severe enrichment. In this study, iron was used as the reference metal in calculating the enrichment factor. The enrichment factor for the different heavy metals under study is given in table 4.8.

Table 4.8: Enrichment Factor for heavy metals in sediments during dry and wet season.

Sampling Site	Season	Cr	Mn	Co	Ni	Cu	Zn	Pb
S1	Dry	8.90	15.82	19.19	65.87	39.56	12.00	425.06
	Wet	9.24	6.37	7.30	30.53	8.39	10.26	7.29
S2	Dry	9.13	14.31	17.39	82.02	97.81	10.15	266.75
	Wet	9.42	7.90	12.89	25.79	8.55	8.44	9.99
S3	Dry	11.04	7.76	13.07	90.24	50.25	4.50	457.05
	Wet	6.88	5.02	4.64	25.29	7.17	7.86	7.10
S4	Dry	7.18	9.70	14.02	40.42	18.59	4.63	160.86
	Wet	5.00	5.38	4.92	32.97	5.90	7.65	6.53
S5	Dry	9.36	8.56	19.02	70.01	31.44	4.35	287.39
	Wet	5.23	6.48	2.56	39.43	10.81	8.76	7.90

Cr recorded moderately severe enrichment in all the sampling sites during both the dry and wet season, except for sampling site 3 which recorded severe enrichment during the dry season. There was moderately severe enrichment of manganese in all the sampling sites during both seasons except in sampling sites 1 and 2 which recorded severe enrichment during the dry season. The enrichment factor for cobalt was moderately severe during the wet season and severe during the dry season except for sampling site 2 which recorded severe enrichment during the wet season. Elevated enrichment was observed in nickel as all the sampling sites recorded extremely severe enrichment during the dry season and very severe enrichment during the wet season. The high enrichment

factor values for nickel can be attributed to the discharge of raw sewage into the river together with the dumping of wastes from metal workshops and garages located at the banks of the river. Similar levels of enrichment was observed in copper, which recorded extremely severe enrichment in sampling sites 2 and 3 during the dry season, very severe enrichment in sampling sites 1 and 5 during the dry season and severe enrichment in sampling site 4 during the dry season. During the wet season, sampling sites 1, 2, 3 and 4 recorded moderately severe enrichment during the wet season, whereas sampling site 5 recorded severe enrichment in copper during the same season. All the sampling sites were moderately enriched with zinc except sampling site 1 during both the dry and wet season and sampling site 2 during the dry season. These sampling sites recorded moderately severe enrichment. The high levels of enrichment during the dry season can be attributed to dumping of domestic waste rich in zinc as well as the discharge of raw sewage at these sampling points. The high levels of zinc at sampling point 2 can be linked to the tributaries joining the river at this point, discharging pollutants rich in zinc from other parts of the sub catchment. The enrichment factor for lead was extremely severe in all the sampling sites during the dry season ($E.F > 50$) while the wet season witnessed moderately severe enrichment ($E.F 5 - 10$). The low enrichment levels during the wet season can be linked to dilution leading to low concentration of metals in sediments.

4.5 Correlation between Physical and Chemical Parameters

Correlation coefficient (r) measures the joint variation between two variables, x and y . It measures the strength and direction of a linear relationship between the two variables on a scatter plot. The correlation coefficient r can only take values in the range $-1 \leq r \leq +1$. An r value of -1 describes a perfect negative correlation and an r value of $+1$ indicates a perfect positive correlation while an r value of 0 indicates no linear correlation between the values of x and y (Miller, J. N. and Miller, 2010). Appendix 5 and 6 shows correlation in water between physical and chemical parameters for dry and wet seasons respectively. During the dry season, chloride was strongly correlated to pH

($r = 0.96$). Chloride is introduced into the river via raw sewage that is either acidic or alkaline, depending on the nature of the pollutants hence the strong correlation between chlorides and pH. Electrical conductivity was strongly correlated to total dissolved solids, temperature, nitrates, copper, nickel, chromium and cobalt, with medium correlation to manganese and iron. The strong correlation between electrical conductivity and total dissolved solids is attributed to dissolved salts that dissociate into their respective ions in solution. The strong correlation between electrical conductivity and temperature is due to the fact that as temperature rises, the solubility of most salts in water increases leading to an increase in electrical conductivity. The strong correlation between electrical conductivity and nitrates, copper, nickel, chromium and cobalt are due to the fact that the salts of these anions/metals dissolve in water and dissociate into their respective ions leading to a rise in electrical conductivity. Total dissolved solids were strongly correlated to temperature, nitrates, nickel, cobalt and chromium, with medium correlation to iron and manganese. This is because the nitrate salts and the salts of these metals are soluble in water leading to a rise in the total dissolved solids.

Nitrate was strongly correlated to manganese, copper, chromium, nickel and cobalt with medium correlation to iron, meaning that these metal compounds mostly occur in nitrate form. Copper showed strong correlation to iron ($r = 0.99$) with medium correlation to chromium ($r = 0.53$) while nickel showed strong correlation to cobalt ($r = 0.88$). This strong correlation between the metals points to the existence of metal – metal complexes in solution form. During the wet season, pH showed strong correlation with nitrate ($r = 0.99$) indicating a high concentration of nitrate ions from farms as a result of surface run-off during the wet season. There was a strong correlation between temperature and dissolved oxygen ($r = 0.98$), sulphate, chromium and zinc. The strong correlation between temperature and dissolved oxygen is due to the fact that an increase in temperature leads to an increase in the rate at which oxygen dissolves in water. The strong correlation between temperature and sulphates, chromium and zinc is because as temperature rises, the solubility of sulphates, chromium and zinc salts also increases. The correlation between turbidity and phosphates was high ($r = 0.91$) indicating high

concentrations of phosphates being carried into the River during the wet season as a result of surface run-off. Several metals showed a high correlation with turbidity and they include copper, nickel and iron. This is an indication of copper, nickel and iron adsorbed on the surfaces of particulate matter that contributes to high water turbidity. Phosphate showed a strong correlation with nickel and iron, whereas sulphate showed strong correlation to chromium and zinc, which is a strong indication that these metals exist in the form of phosphates and sulphates respectively.

Appendix 9 and 10 shows the correlation between different parameters in sediments for both the dry and wet seasons respectively. During the dry season, there was a strong correlation between manganese, copper, zinc and cobalt to the phosphate anion ($r = 0.85, 0.79, 0.89$ and 0.75 respectively) indicating that these metals in sediments exist in phosphate form. Sulphate showed strong correlation to manganese and iron ($r = 0.73$ and 0.83 respectively) and medium correlation to zinc and copper ($r = 0.55$ and 0.51 respectively) indicating that manganese and iron are most likely to exist in sulphate form. Chloride showed a strong correlation to iron ($r = 0.81$) indicating high levels of iron (II) chloride in the sediments. Manganese showed strong correlation to zinc and cobalt ($r = 0.95$ and 0.79 respectively) indicating the presence of zinc – cobalt metal complexes adsorbed on the surface of sediments. The strong correlation of copper to nickel and chromium ($r = 0.81$ and 0.71) indicates the presence of these metal – metal complexes bonded to humus in sediments. Nickel strongly correlated to chromium ($r = 0.85$) and zinc to cobalt ($r = 0.70$) providing a strong evidence of the existence of metal – metal complexes bound to sediment particles and also the presence of metal workshops and garages along the river banks. During the wet season, nickel was strongly correlated to nitrates, phosphates and sulphates ($r = 0.66, 0.92$ and 0.98 respectively) indicating the presence of nitrates, phosphates and sulphates of nickel in sediments. Manganese showed strong correlation to copper, chromium, zinc, cobalt and iron providing further evidence of the existence of metal – metal complexes that are strongly bound to sediment particles. Strong correlation of chromium to zinc and cobalt ($r = 0.91, 0.88$ respectively) and lead to manganese, copper, chromium, zinc, iron and

cobalt ($r = 0.97, 0.72, 0.82, 0.80, 0.81$ and 0.84 respectively) provides further evidence for the existence of metal – metal complexes as well as metal workshops and garages along the river banks. The strong correlation of nitrates to pH points to the fact that ammonia in sewage water gets oxidized to nitrates leading to a rise in pH to alkaline. Hence the nitrogen cycle which leads to formation of ammonia as precursor to the formation of nitrates leads to a rise in pH of water.

During the wet season, the strong correlation between sulphates and nitrates points to the fact that a high concentration of nitrates in sediments promotes the adsorption and dissolution of sulphates. The strong correlation between sulphates and phosphates is due to the fact that high concentration of sulphates increases the amount of phosphates that is released from sediments. The strong correlation between copper and chromium with manganese, zinc and chromium, cobalt with manganese and chromium, lead with manganese, chromium, zinc, cobalt and iron points to the existence of these metal – metal complexes adsorbed on the surface of sediments.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Temperature, electrical conductivity and turbidity were high during the wet season but low during the dry season. The pH of water was slightly alkaline during the dry season but dropped during the wet season. There was no significance difference in seasonal variations for total dissolved solids and dissolved oxygen. Phosphates, nitrates and chlorides recorded high concentrations during the wet season but low concentrations during the dry season whereas sulphates recorded high concentrations during the dry season but low concentration during the wet season. Lead was BDL in water during the dry season while cadmium was BDL in both water and sediments during both the dry and wet seasons. Most of the selected heavy metals recorded high concentrations during the dry season but low concentration during the wet season in both water and sediments. These include: manganese, copper, nickel and cobalt. Chromium, iron and zinc registered high concentration during the wet season but low concentrations during the dry season in most of the sampling points. The geoaccumulation index, contamination factor and enrichment factor for nickel and lead were high during the dry season but during the wet season, the metals recorded low values for these pollution indices.

In water, turbidity, phosphates, lead, nickel, chromium, cobalt and iron were the parameters that were above the WHO recommended levels, mainly as a result of surface run-off during the wet season. High turbidity levels is as a result of surface run off carrying suspended particles from garages, workshops, construction sites, untreated sewage as well as farms and dumping them into the river. The rise in the concentration of phosphates points to the use of manure and fertilizers such as DAP and the discharge of untreated sewage into the river via surface runoff during the wet season. The high concentrations of heavy metals is mainly as a result of dumping of waste from workshops, garages and construction sites as well as the discharge of raw sewage

especially downstream as the river flows through the densely populated regions of Busia town. These high levels pose a threat to both terrestrial and aquatic life that depend on the water from the river and imposes high water treatment cost to downstream users as well.

In sediments lead, copper and nickel were the only cations that were above the WHO recommended limits during both the dry and wet seasons. However, the level of lead was above the WHO recommended limit only during the dry season. The concentration of cadmium in both water and sediments was found to be BDL, while all the remaining cations were below the WHO recommended limits. The high concentration of phosphates, nitrates and chlorides during the wet season is as a result of surface runoff carrying fertilizers, organic manure and raw sewage into the river. The high concentration of sulphates during the dry season can be attributed to dumping of domestic waste and discharge of untreated waste into the river. High levels of lead, copper and nickel in the sediments points to the presence of metal workshops, garages and construction sites along river Sio as well as the discharge of raw sewage into the river as it flows downstream into Busia town which has got high levels of anthropogenic activities owing to population increase. The release of these metals into the River poses a threat to aquatic and terrestrial forms of life that depend on the River due to their high toxicity. This situation is further worsened by skyrocketing levels of anions which are most likely to cause the eutrophication of river Sio, in addition to affecting the physico-chemical characteristics of water from the River. According to geoaccumulation index, nickel showed moderate pollution during the dry season. The contamination factor for lead was very high during the dry season, while pollution load index confirmed pollution due to anthropogenic activities in sampling sites 1 – 4 during the dry season and no pollution due to anthropogenic activities during the wet season.

5.2 Recommendations

5.2.1 Recommendations for this Work

In view of the above, this study recommends the following measures to be adopted in order to curb water and soil pollution:

- i. Broken sewer lines should be repaired in a timely manner so as to prevent the discharge of untreated sewage into the river
- ii. Waste from workshops, garages and construction sites should be properly disposed of instead of dumping it by the river side where it ends up into the river.
- iii. Scrap metals should be recycled instead of dumping them in soil where heavy metals find their way into the water during the rainy season, leading to elevated levels of heavy metals in sediments.
- iv. Biodegradable household wastes should be disposed in a compost pit to form compost manure for organic farming instead of dumping them into the farms where they contribute to increasing of heavy metals in the River.
- v. Environmentally friendly trees such as bamboos should be planted by the river banks. These trees have been shown to clean the river by absorbing pollutants from both anions and heavy metals.
- vi. Community sensitization on pollution should be carried out so as to enlighten the community on the importance of conserving water sources like rivers.

5.2.2 Recommendations for Further Work

- i. Pesticide leaching and microbiological quality of water, soil and sediments should be considered for further research.
- ii. Both the county and national governments should enforce appropriate legislations on environment conservation.
- iii. International treaties on environmental conservation, that try to curb water and soil pollution, should strictly be adhered to.
- iv. Environmental management players like National Environment Management Authority (NEMA) should also come in and act accordingly by enforcing laws

that will see the reduction of land and water pollution. This can be done by monitoring of soil and water quality on regular intervals, prosecuting those who violate environmental laws by imposing heavy penalties and ensuring proper treatment and disposal of sewage and industrial effluent before discharging it into water bodies.

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APPENDICES

Appendix I: Sampling stations descriptions and codes

Station	Description
S1	River Sio at Malomba bridge, next to sugarcane and maize plantations
S2	River Sio at Musoma bridge, where Western sugar company abstracts water for cooling engines
S3	River Sio at Busibwabo, next to Busia sugar company
S4	River Sio at Mundika bridge, where the River crosses Busia town next to Busia water company treating plant
S5	River Sio few kilometers from Busia town, downstream next to maize plantations

Appendix II: Water quality parameters, units and analytical methods of estimation

Parameter	Abbreviation	Units	Analytical method
H ⁺ ion concentration ¹	pH	-	pH meter
Electrical Conductivity ¹	E.C	μS/cm	Electrical conductivity meter
Total Dissolved Solids ¹	TDS	Mg/l	TDS meter
Temperature ¹	T	°C	Thermometer
Dissolved Oxygen ¹	DO	Mg/l	DO meter
Turbidity ¹	Turbidity	NTU	Turbidity meter
Nitrates ²	NO ₃ ⁻	Mg/l	Screening method
Phosphates ²	PO ₄ ³⁻	Mg/l	Ascorbic acid method
Sulphates ²	SO ₄ ²⁻	Mg/l	Turbidimetric method
Chlorides ²	Cl ⁻	Mg/l	Mercuric Thiocyanate method
Heavy Metals ³	Pb, Mn, Cd, Cu, Ni, Cr, Zn, Co, Fe	Mg/l	Atomic Absorption Spectroscopy

*μ = micro, *NTU = Nephlo Turbidimetric Units, *S = Siemens * 1 = Physical Parameter, *2 = Anions, *3 = Cations

Appendix III: Paired t-test showing seasonal variations in water (P = 0.05)

Parameter	Seasonal variation (T critical = 2.78, P = 0.05, df = 4)	
	T calculated	Significance
pH	5.89	0.004
EC	3.17	0.034
Temperature	2.51	0.066
Dissolved Oxygen	1.72	0.160
Turbidity	5.92	0.004
TDS	1.61	0.183
Nitrates	5.79	0.004
Phosphates	3.27	0.031
Sulphates	0.79	0.472
Chlorides	5.17	0.007
Manganese	2.02	0.114
Lead	-	-
Copper	6.88	0.002
Nickel	2.57	0.062
Chromium	2.72	0.053
Cobalt	7.35	0.002
Zinc	0.49	0.647
Iron	6.79	0.003

* Bolded values show significant variation, *df = degrees of freedom

Appendix IV: One - way ANOVA showing spatial variation of physico – chemical parameters in water (P = 0.05)

Parameter	Spatial Variation (df = 4, F critical= 4.76, P = 0.05)			
	Wet Season		Dry Season	
	F calculated	Sig.	F calculated	Sig.
pH	59.24	0.000	24.9	0.000
EC	1473.75	0.000	91.62	0.000
Temperature	469.45	0.000	35.91	0.000
Dissolved oxygen	186.83	0.000	106.13	0.000
Turbidity	107883.1	0.000	1242.47	0.000
TDS	127.01	0.000	186.63	0.000
Nitrates	108793.2	0.000	80.01	0.000
Phosphates	15480.9	0.000	1395.64	0.000
Sulphates	9782.69	0.000	2251.99	0.000
Chlorides	241.08	0.000	792.25	0.000
Lead	93.13	0.000	-	-
Manganese	7.52	0.005	62.31	0.000
Copper	226.14	0.000	7.1	0.006
Nickel	31.11	0.000	121.91	0.000
Chromium	394.89	0.000	48.77	0.000
Zinc	137.62	0.000	132.23	0.000
Cobalt	13.53	0.001	11.89	0.001
Iron	125.86	0.000	2251.99	0.000

Appendix V: Correlation coefficient matrix for water - dry season

	pH	EC	TDS	°C	DO	TURB	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻	Mn	Cu	Ni	Cr	Zn	Co	Fe
pH	1.00																
EC	-0.04	1.00															
TDS	-0.22	0.98	1.00														
°C	-0.32	0.96	0.98	1.00													
DO	0.00	0.00	0.13	0.01	1.00												
TURB	-0.77	-0.39	-0.30	-0.16	-0.46	1.00											
NO ₃ ⁻	0.13	0.90	0.89	0.84	0.34	-0.66	1.00										
PO ₄ ³⁻	-0.54	-0.74	-0.67	-0.53	-0.23	0.83	-0.79	1.00									
SO ₄ ²⁻	-0.23	-0.50	-0.51	-0.34	-0.22	0.43	-0.41	0.78	1.00								
Cl ⁻	0.96	-0.13	-0.31	-0.37	-0.09	-0.69	0.06	-0.37	0.03	1.00							
Mn	0.34	0.57	0.59	0.46	0.73	-0.85	0.83	-0.79	-0.52	0.21	1.00						
Cu	0.22	0.62	0.65	0.48	0.52	-0.63	0.67	-0.86	-0.91	-0.02	0.81	1.00					
Ni	0.32	0.87	0.74	0.73	-0.34	-0.46	0.73	-0.77	-0.45	0.26	0.37	0.45	1.00				
Cr	-0.41	0.65	0.78	0.75	0.63	-0.26	0.77	-0.36	-0.22	-0.47	0.70	0.53	0.22	1.00			
Zn	-0.03	0.19	0.06	0.19	-0.98	0.39	-0.14	0.12	0.21	0.07	-0.61	-0.45	0.49	-0.46	1.00		
Co	0.35	0.77	0.64	0.67	-0.21	-0.54	0.78	-0.62	-0.07	0.40	0.44	0.22	0.88	0.30	0.40	1.00	
Fe	0.33	0.55	0.56	0.38	0.45	-0.65	0.58	-0.88	-0.95	0.08	0.75	0.99	0.45	0.39	-0.40	0.18	1.00

Bolded values show significant correlation

Appendix VI: Correlation coefficient matrix for water - wet season

	pH	EC	TDS	°C	DO	TURB	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻	Mn	Cu	Ni	Cr	Zn	Co	Fe	Pb
pH	1																	
EC	-0.88	1																
TDS	-0.12	0.09	1															
°C	-0.42	0.59	0.81	1														
DO	-0.55	0.74	0.69	0.98	1													
NO ₃ ⁻	0.99	-0.9	-0.21	-0.51	-0.64	0.19	1											
PO ₄ ³⁻	0.31	-0.3	-0.83	-0.75	-0.72	0.91	0.44	1										
SO ₄ ²⁻	-0.53	0.36	0.89	0.77	0.71	-0.71	-0.58	-0.8	1									
Cl ⁻	0	-0.03	0.69	0.55	0.41	-0.41	0.01	-0.19	0.61	1								
Mn	0.1	-0.4	0.43	0.03	-0.13	-0.02	0.17	0.04	0.45	0.79	1							
Cu	-0.51	0.32	-0.7	-0.53	-0.36	0.68	-0.44	0.34	-0.32	-0.71	-0.38	1						
Ni	-0.13	0.2	-0.94	-0.62	-0.44	0.76	-0.07	0.62	-0.76	-0.81	-0.66	0.8	1					
Cr	-0.32	0.43	0.92	0.97	0.92	-0.93	-0.43	-0.85	0.84	0.57	0.12	-0.6	-0.75	1				
Zn	-0.67	0.78	0.62	0.92	0.94	-0.58	-0.71	-0.53	0.73	0.56	0.08	-0.28	-0.42	0.83	1			
Co	0	-0.15	-0.59	-0.66	-0.55	0.44	0	0.13	-0.46	-0.92	-0.52	0.75	0.66	-0.61	-0.67	1		
Fe	0.62	-0.55	-0.58	-0.64	-0.69	0.68	0.72	0.91	-0.73	0.07	0.23	-0.07	0.3	-0.69	-0.54	-0.12	1	
Pb	0.43	-0.12	0.63	0.62	0.51	-0.8	0.32	-0.5	0.24	0.4	-0.05	-0.9	-0.62	0.66	0.31	-0.55	-0.15	1

Bolded values show significant correlation

Appendix VII: Paired t-test showing seasonal variations in sediments (P = 0.05)

Parameter	Seasonal variation (T critical = 2.78, P = 0.05, df = 4)	
	T calculated	Significance
Nitrates	6.13	0.004
Phosphates	5.43	0.006
Sulphates	0.18	0.863
Chlorides	2.89	0.045
Manganese	2.31	0.082
Lead	6.99	0.002
Copper	2.23	0.089
Nickel	4.69	0.009
Chromium	0.47	0.663
Cobalt	3.53	0.024
Zinc	1.73	0.158
Iron	1.41	0.23

* Bolded values show significant variation, *df = degrees of freedom

Appendix VIII: One - way ANOVA showing spatial variations of chemical parameters in sediments (P = 0.05)

Parameter	Spatial Variation (df = 4, F critical= 4.76, P = 0.05)			
	Wet Season		Dry Season	
	F calculated	Sig.	F calculated	Sig.
Nitrates	824.92	0.000	584.53	0.000
Phosphates	45458.13	0.000	702343.1	0.000
Sulphates	2075.11	0.000	97.49	0.000
Chlorides	68.57	0.000	1577.05	0.000
Manganese	5176.18	0.000	1264.13	0.000
Lead	59.74	0.000	27.14	0.000
Copper	1425.3	0.000	559.18	0.000
Nickel	19.72	0.000	25.91	0.000
Chromium	31.37	0.000	12.09	0.001
Zinc	291.43	0.000	260.83	0.000
Cobalt	80.76	0.000	21.35	0.000
Iron	374.56	0.000	220.69	0.000

*df = degrees of freedom * Bolded values shows spatial significance

Appendix IX: Correlation coefficient matrix for sediment parameters during the dry season.

	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻	Mn	Cu	Ni	Cr	Zn	Co	Fe	Pb
NO ₃ ⁻	1.00											
PO ₄ ³⁻	-0.14	1.00										
SO ₄ ²⁻	-0.47	0.27	1.00									
Cl ⁻	-0.56	-0.07	0.52	1.00								
Mn	-0.37	0.85	0.73	0.16	1.00							
Cu	-0.35	0.79	-0.06	0.20	0.50	1.00						
Ni	-0.34	0.47	-0.47	-0.15	0.09	0.81	1.00					
Cr	-0.69	0.22	-0.22	0.33	0.03	0.71	0.85	1.00				
Zn	-0.39	0.89	0.55	-0.06	0.95	0.55	0.29	0.14	1.00			
Co	0.26	0.75	0.51	-0.10	0.79	0.26	-0.21	-0.45	0.70	1.00		
Fe	-0.30	0.22	0.83	0.81	0.54	0.10	-0.45	-0.13	0.27	0.46	1.00	
Pb	-0.39	0.07	-0.15	-0.53	0.07	0.03	0.46	0.32	0.33	-0.28	-0.63	1.00

Bolded values show significant correlation

Appendix X: Correlation coefficient matrix for sediment parameters during the wet season.

	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻	Mn	Cu	Ni	Cr	Zn	Co	Fe	Pb
NO ₃ ⁻	1.00											
PO ₄ ³⁻	0.38	1.00										
SO ₄ ²⁻	0.76	0.83	1.00									
Cl ⁻	-0.47	-0.14	-0.32	1.00								
Mn	-0.32	0.38	-0.14	0.26	1.00							
Cu	0.43	0.63	0.42	0.07	0.70	1.00						
Ni	0.66	0.92	0.98	-0.20	0.06	0.55	1.00					
Cr	-0.48	-0.18	-0.59	0.52	0.81	0.46	-0.42	1.00				
Zn	-0.14	-0.03	-0.31	0.57	0.73	0.68	-0.16	0.91	1.00			
Co	-0.67	-0.01	-0.55	0.33	0.89	0.34	-0.36	0.88	0.66	1.00		
Fe	-0.31	0.27	-0.07	0.86	0.64	0.52	0.12	0.67	0.76	0.53	1.00	
Pb	-0.32	0.40	-0.10	0.47	0.97	0.72	0.11	0.82	0.80	0.84	0.81	1.00

Bolded values show significant correlation

Appendix XI: Published research paper



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Determination of Selected Water Quality Parameters in River Sio, Busia County, Kenya

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Authors' contributions

This work was carried out in collaboration among all authors. Author KOO designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors JKK and AOO supervised the research while authors SMS, BEO and JKO managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

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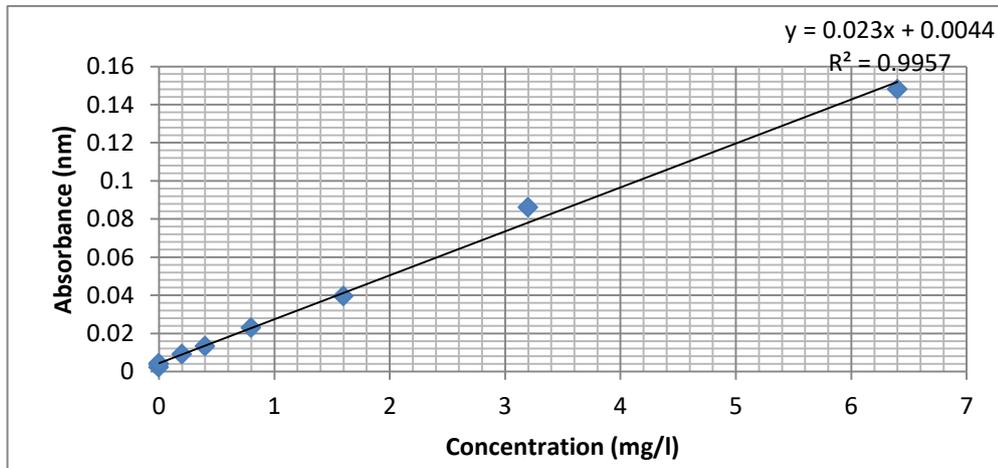
Original Research Article

ABSTRACT

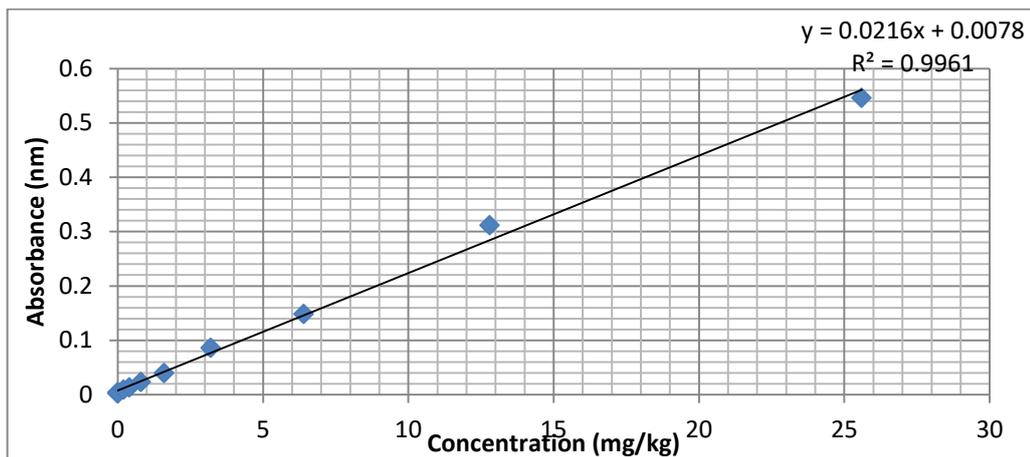
Water samples were taken from five sampling points and their quality assessed through analysis of physical and chemical characteristics. Turbidity, temperature, conductivity, pH, dissolved oxygen and total suspended solids were determined on site during sample collection, using portable meters. Anions were determined using UV/Visible spectroscopy while heavy metals were determined using flame Atomic Absorption Spectroscopy (AAS) in accordance with AWWA standard methods. Turbidity was the highest recorded parameter during the wet season with a mean of 481.83 NTU. 53% of the parameters showed significant seasonal variation ($P < 0.5$) with the mean concentration of 56 % of the parameters being higher during the wet season. The parameters that exceeded the WHO limit were turbidity, phosphates, lead, iron, nickel, chromium and cobalt indicating poor quality of water in River Sio. Poor agricultural practices, domestic and industrial wastewater are the main factors that contribute to pollution of the River. The study proposes proper land use, proper treatment and disposal of sewage and use of organic manure and biological control as means of preventing water and soil pollution.

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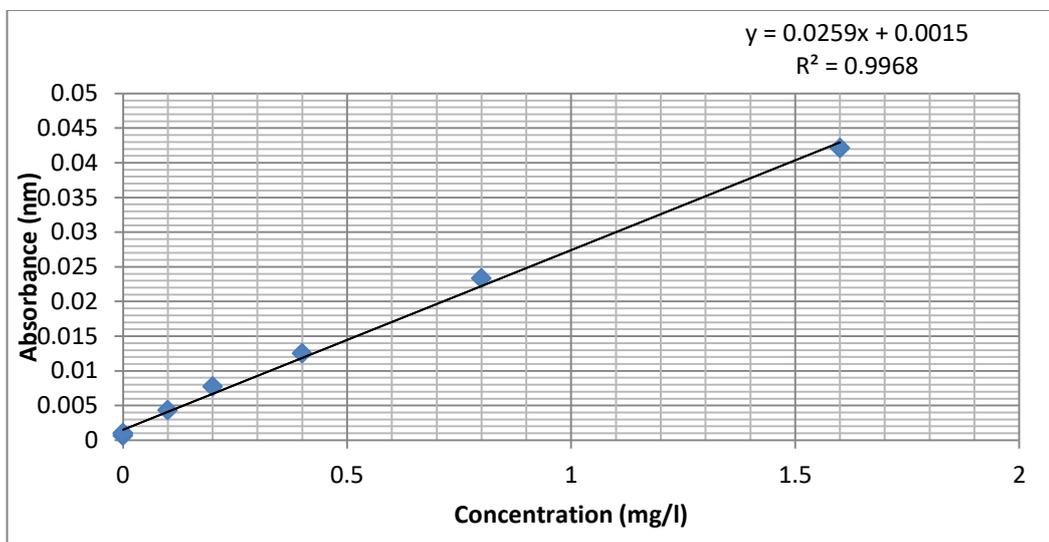
Appendix XII: Calibration curve of concentration of iron in water



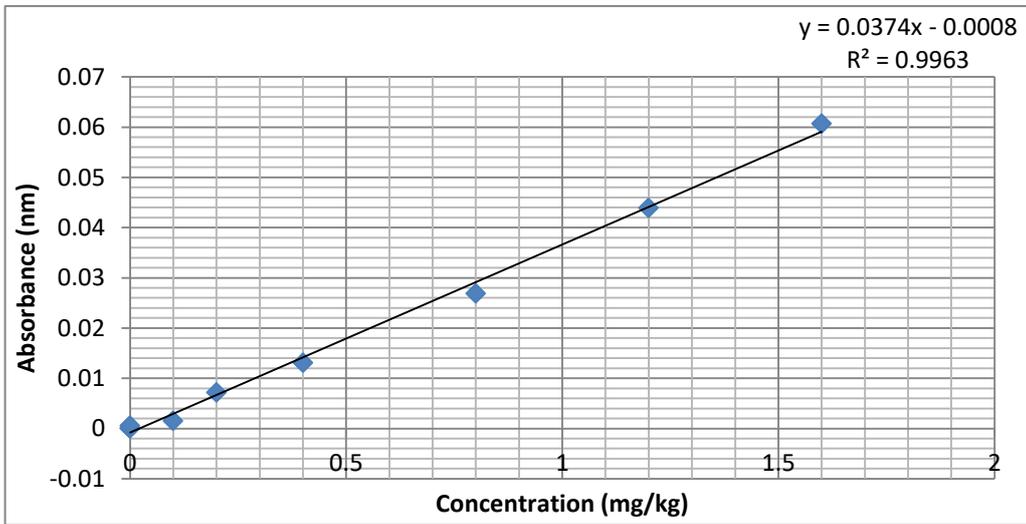
Appendix XIII: Calibration curve of concentration of iron in sediments



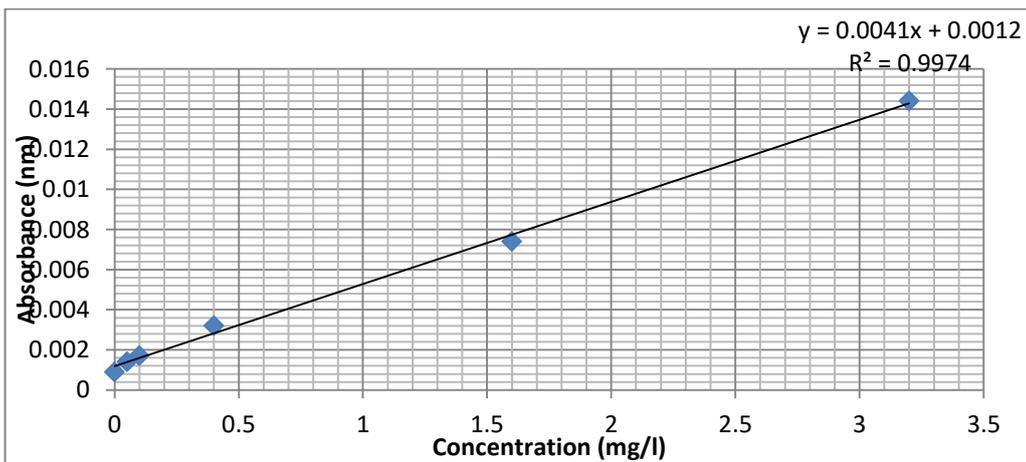
Appendix XIV: Calibration curve of concentration of zinc in water



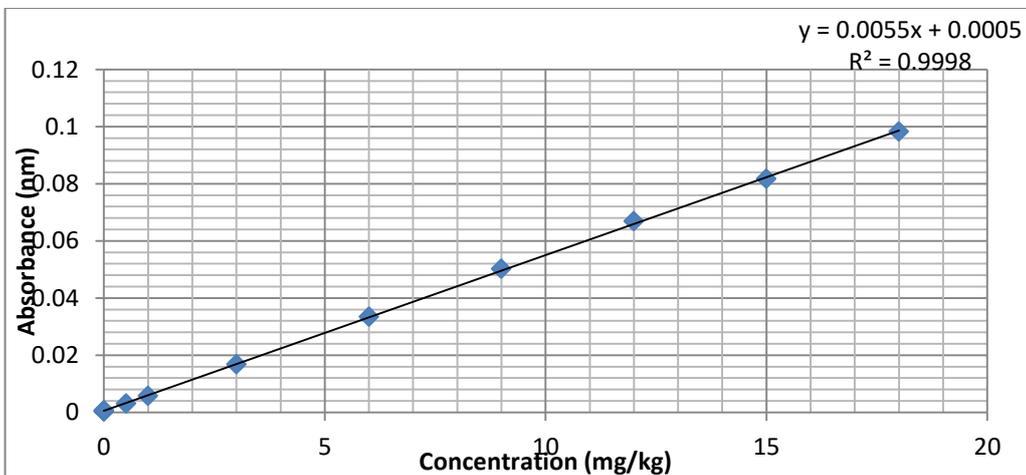
Appendix XV: Calibration curve of concentration of zinc in sediments



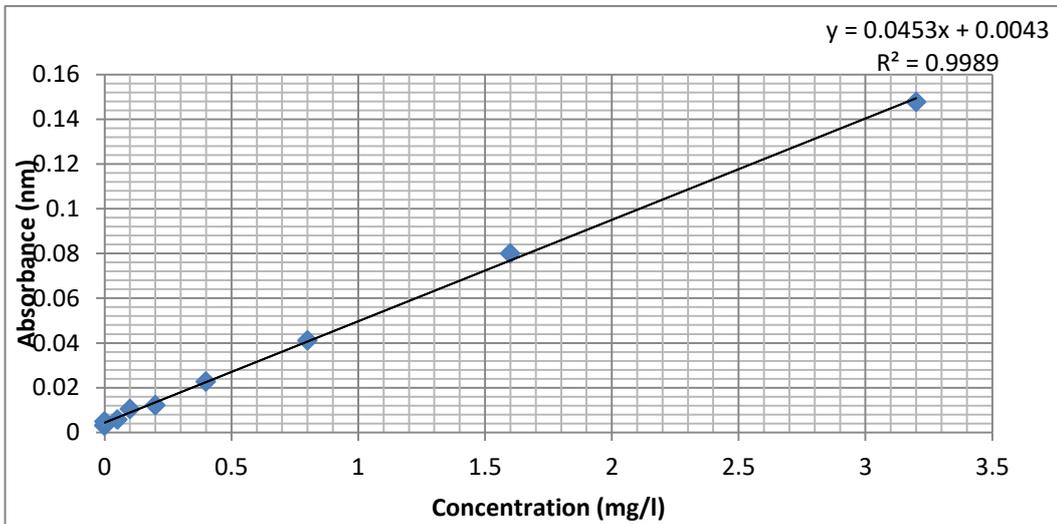
Appendix XVI: Calibration curve of concentration of lead in water



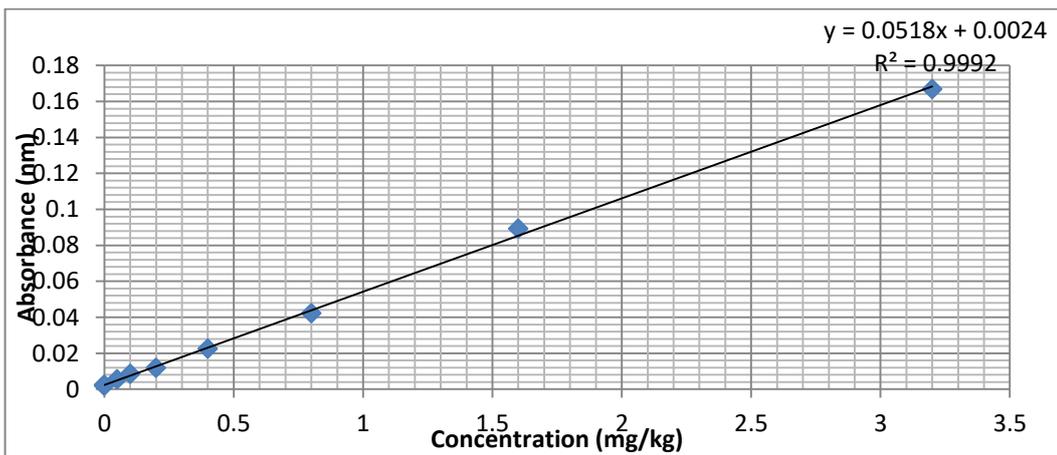
Appendix XVII: Calibration curve of concentration of lead in sediments



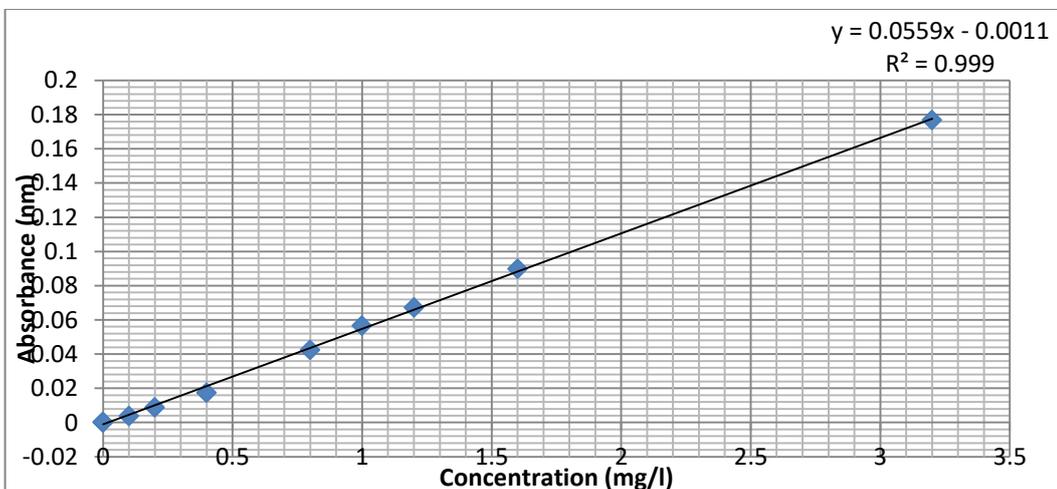
Appendix XVIII: Calibration curve of concentration of chromium in water



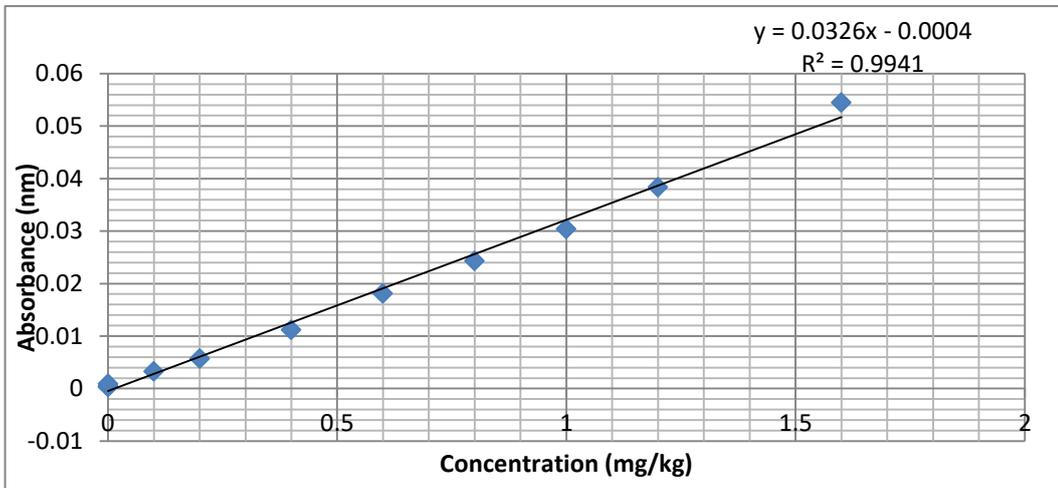
Appendix XIX: Calibration curve of concentration of chromium in sediments



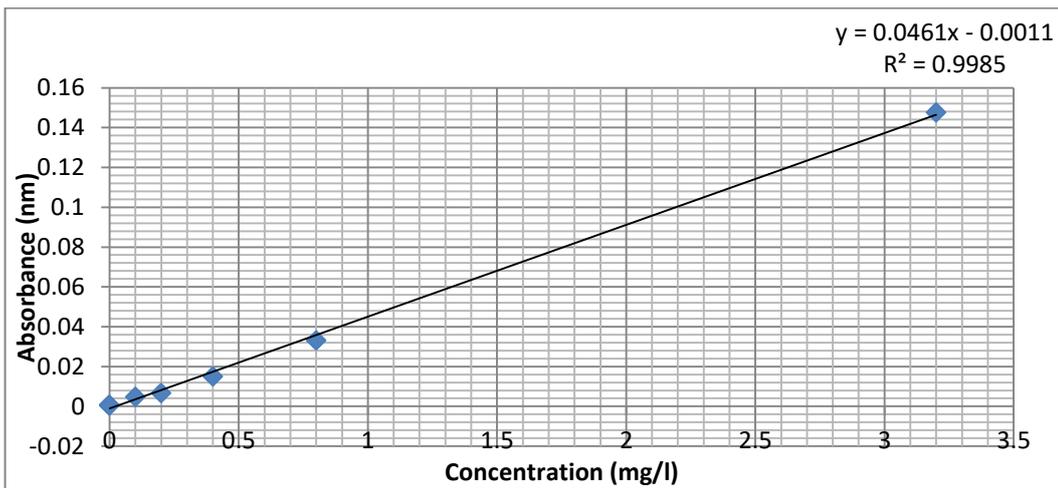
Appendix XX: Calibration curve of concentration of cadmium in water



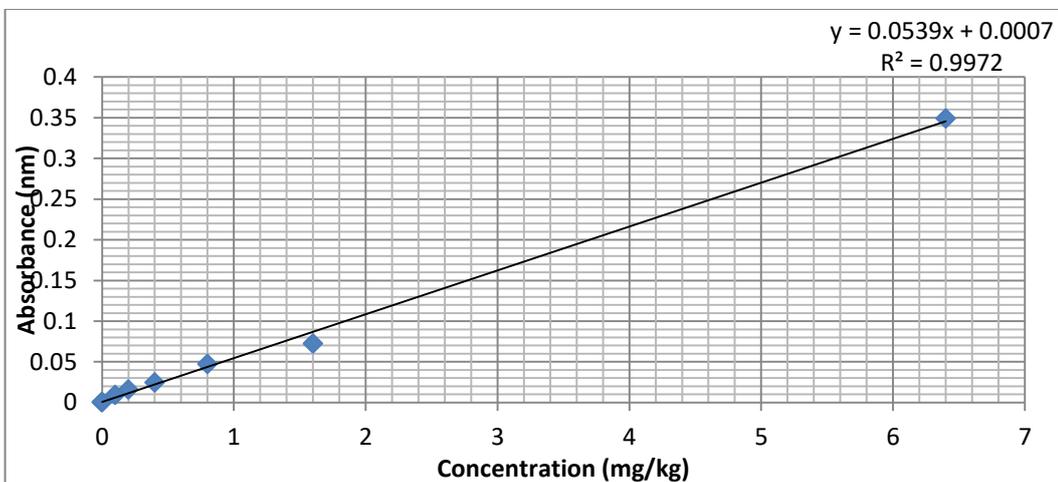
Appendix XXI: Calibration curve of concentration of cadmium in sediments



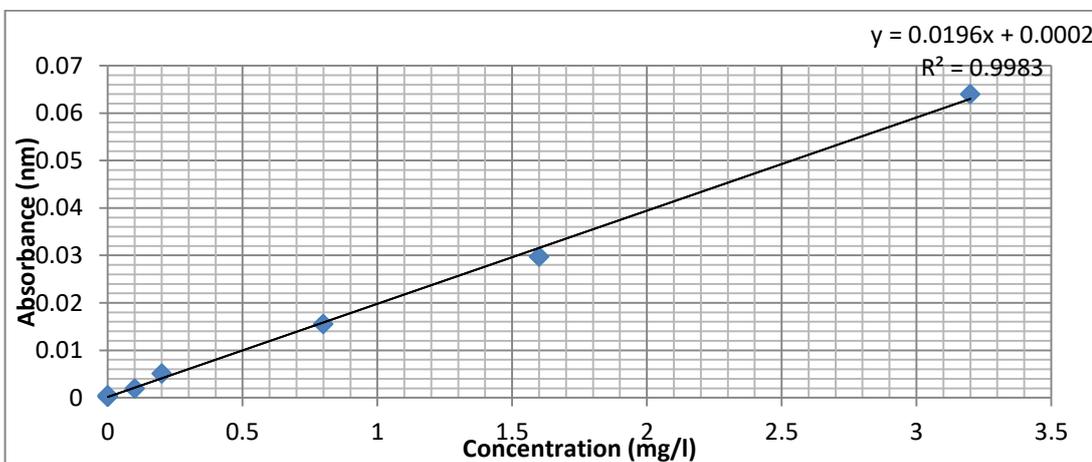
Appendix XXII: Calibration curve of concentration of copper in water



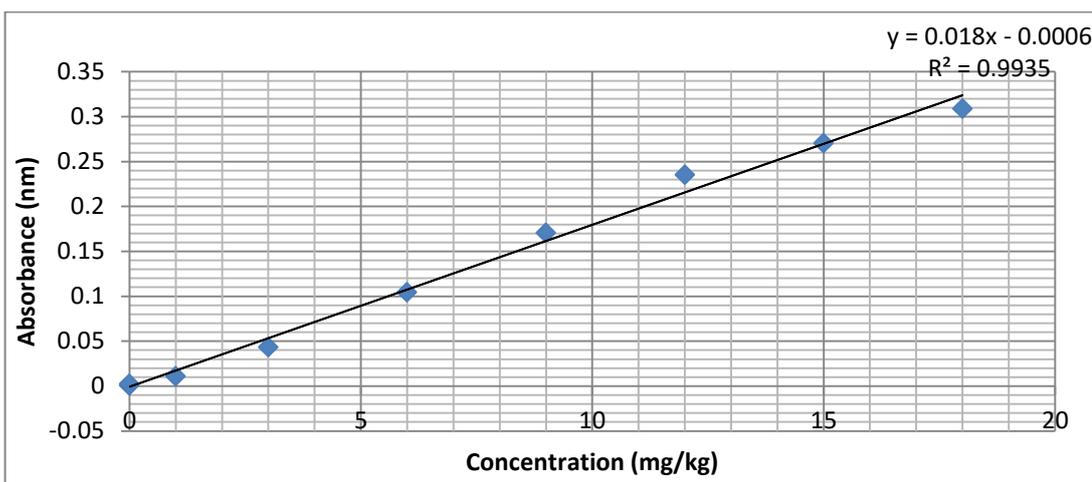
Appendix XXIII: Calibration curve of concentration of copper in sediments



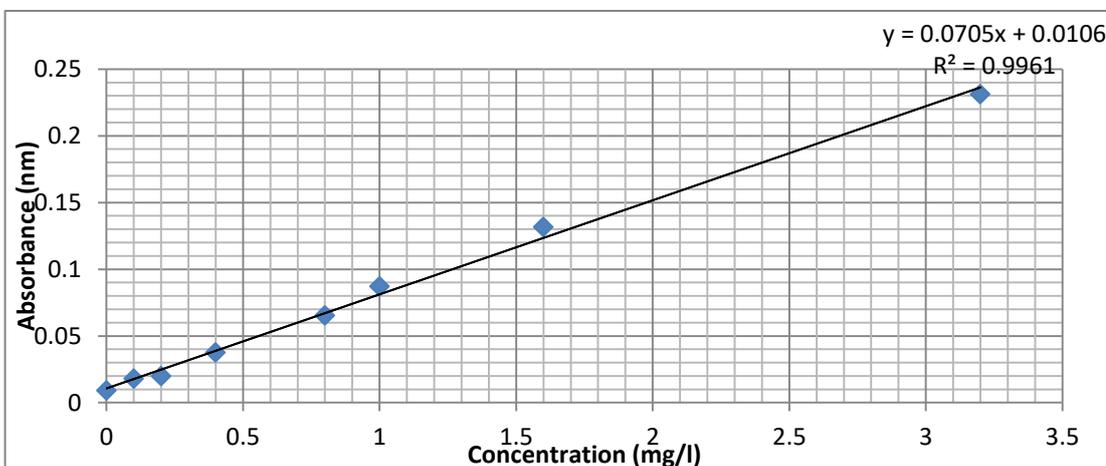
Appendix XXIV: Calibration curve of concentration of nickel in water



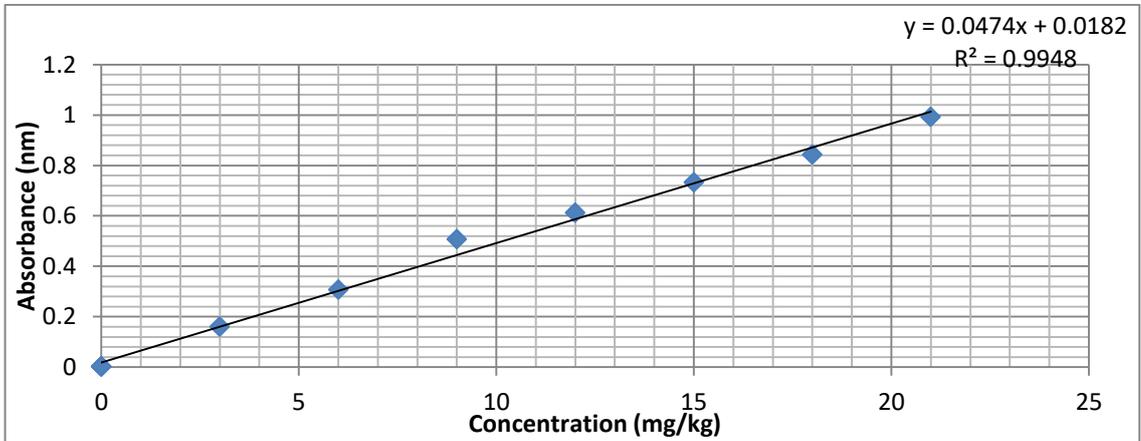
Appendix XXV: Calibration curve of concentration of nickel in sediments



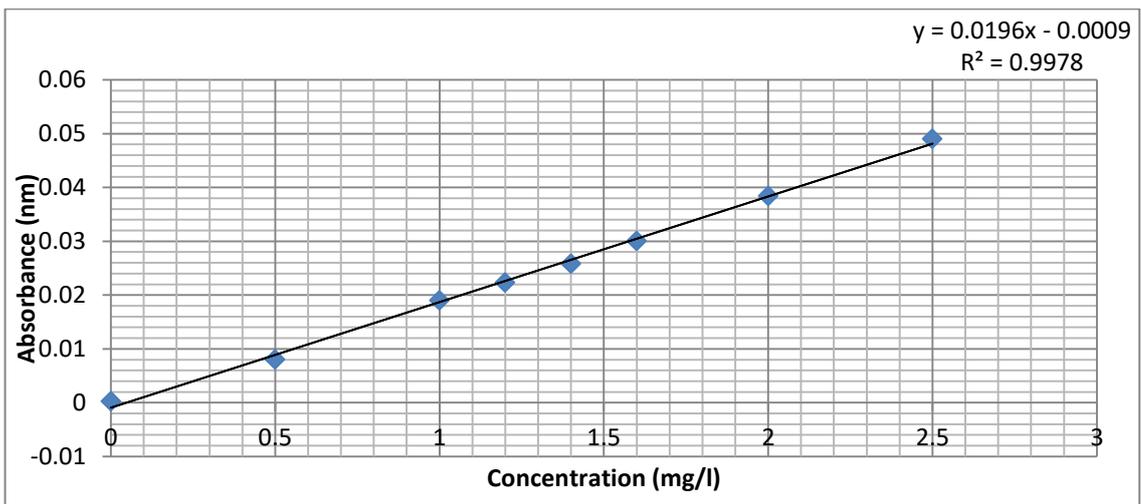
Appendix XXVI: Calibration curve of concentration of manganese in water



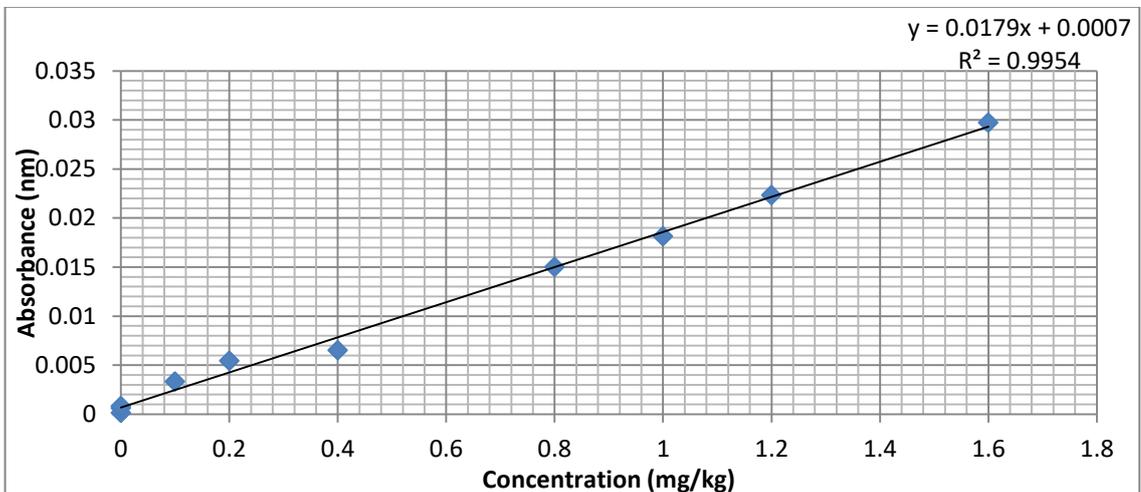
Appendix XXVII: Calibration curve of concentration of manganese in sediments



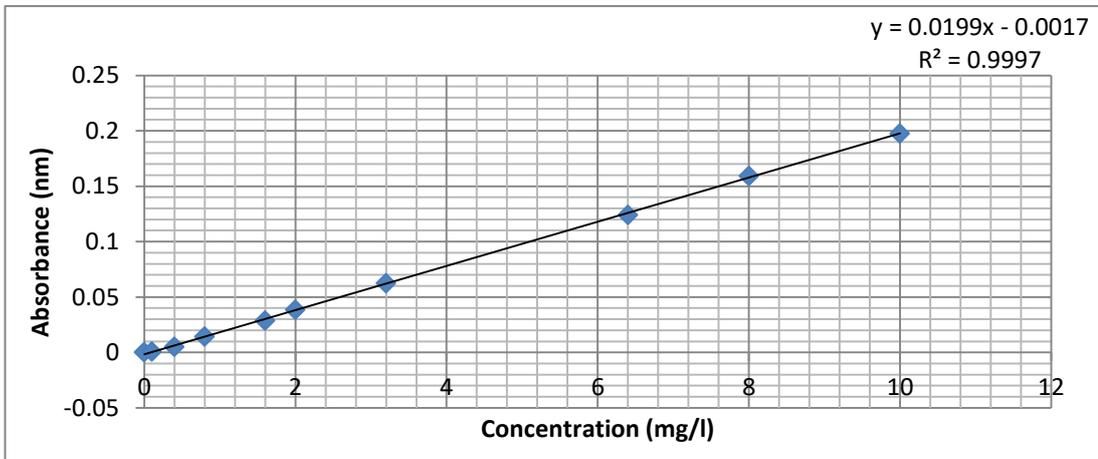
Appendix XXVIII: Calibration curve of concentration of cobalt in water



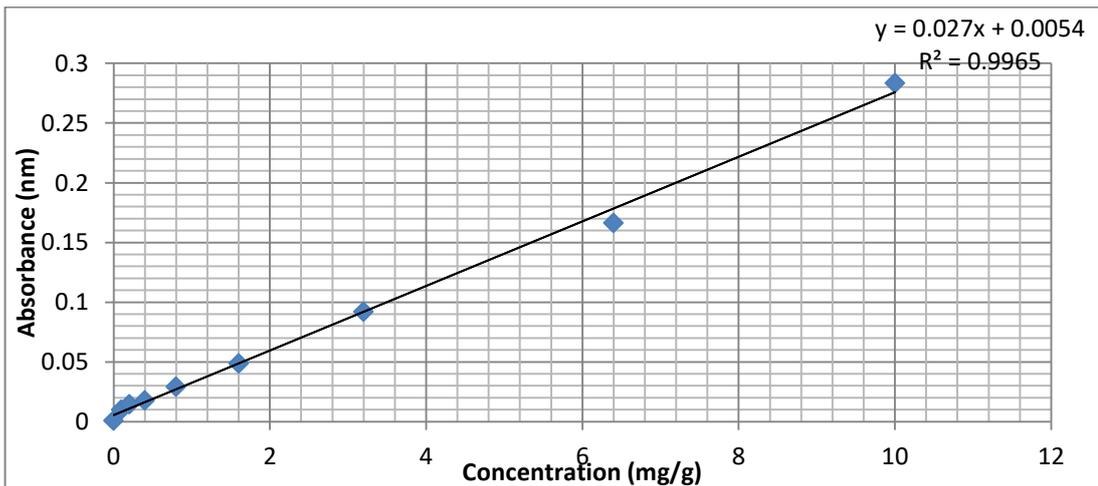
Appendix XXIX: Calibration curve of concentration of cobalt in sediments



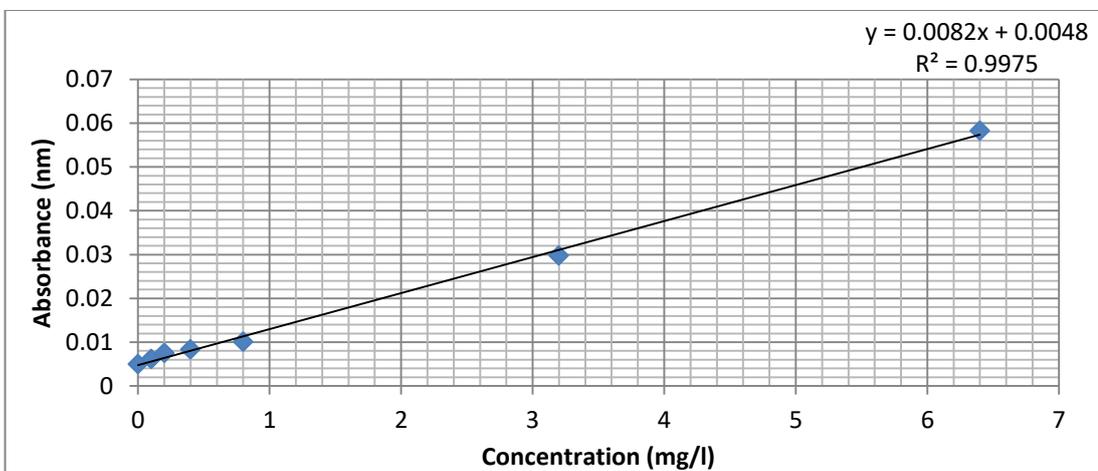
Appendix XXX: Calibration curve of concentration of phosphates in water



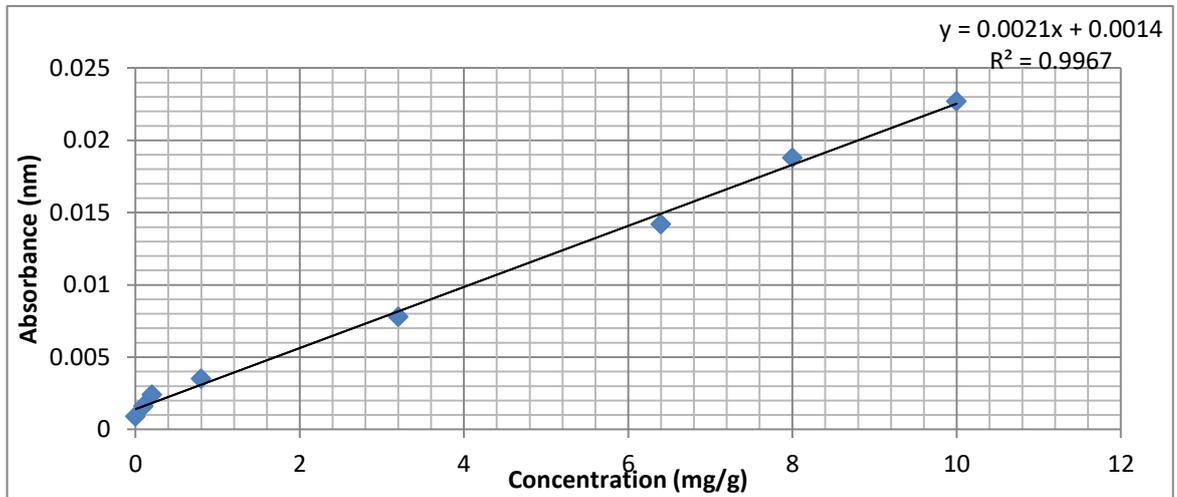
Appendix XXXI: Calibration curve of concentration of phosphates in sediments



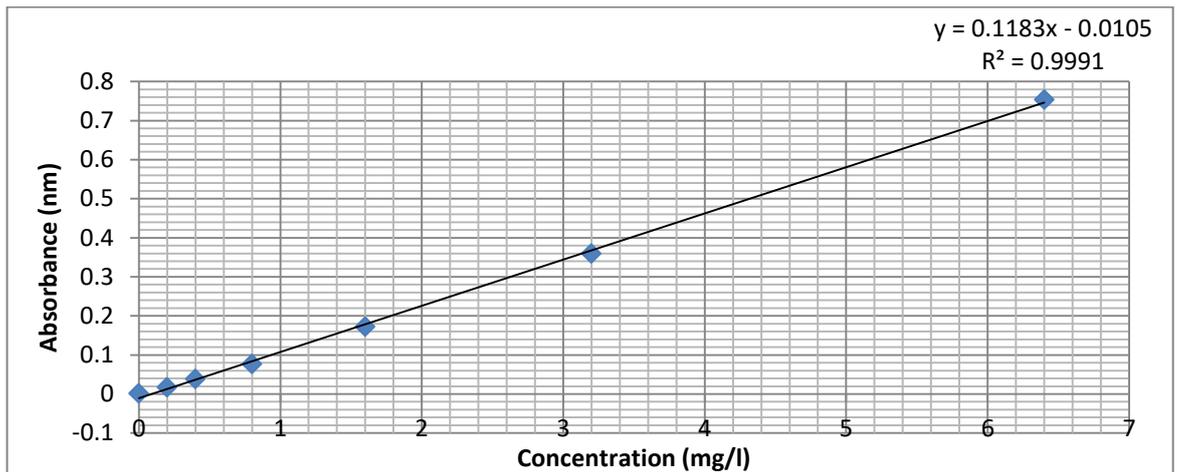
Appendix XXXII: Calibration curve of concentration of sulphates in water



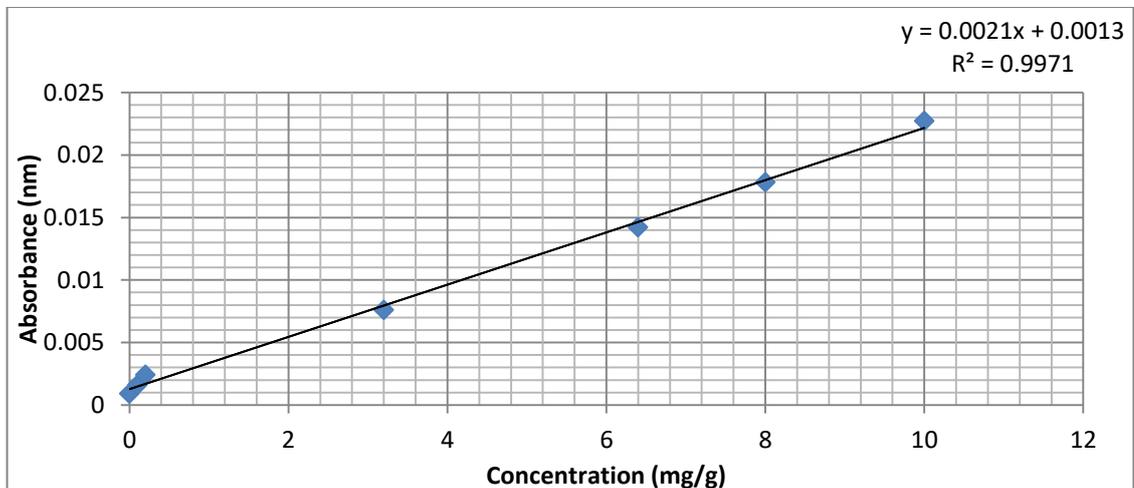
Appendix XXXIII: Calibration curve of concentration of sulphates in sediments



Appendix XXXIV: Calibration curve of concentration of nitrates in water



Appendix XXXV: Calibration curve of concentration of nitrates in sediments



Appendix XXXVI: Calibration curve of concentration of chlorides in water

