

**HEAVY METAL POLLUTION IN SEDIMENTS, WATER AND FLORA ALONG
THIKA RIVER**

By

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**A Thesis Submitted in partial fulfillment of the requirements for the award of Master of
Science Degree in Nuclear Science, University of Nairobi**

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DECLARATION

I declare that this thesis is my original work and has not been submitted for award of any degree or qualification at any other University or Institution of higher learning.

Ben Asiago Moywaywa- S56/61770/2013

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DEDICATION

I dedicate this research work to my Family, especially my Late loving Father and role model, Simon Onsare Moywaywa, for his continuous support and encouragement.

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My first thanks go to God Almighty for the gift of life, good health and protection during the course of this study.

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Abstract

The levels of heavy metals were determined in environmental samples; water, flora and sediments along the Thika River, specifically, to investigate their distribution and to determine the extent of pollution. Water, sediment and algae (*Cladophora*) samples were each collected from thirty-two (32) sampling sites identified along the river's profile and each analyzed for the selected heavy metal content using TXRF and EDXRF.

In general, the concentration levels of heavy metals in water samples ($\mu\text{g l}^{-1}$) were determined as follows; Mn (53.5 -605), Cu (< 10 -303), Zn (22-325), Ni(< 15 - 77), Pb (< 10 -84) while those in sediment samples (mg kg^{-1}) were; Mn (2230-8659), Cu (51 -115), Zn (153-432), Ni (67 - 172), Pb (32-177). The results of the concentration levels of heavy metals in *Cladophora* (mg kg^{-1}) ranged as follows; Mn (3719 - 21200), Cu (65-129), Zn (153-434), Ni (35 -235), Pb (17 - 72). There was a significant difference in heavy metal concentrations between the three media for all elements studied.

Based on results of enrichment factors, geoaccumulation indices, pollution load index (PLI), contamination factors and modified degree of contamination, all sampled sediments were generally contaminated with, Cu, Zn, Mn and Ni to a moderate degree, hence requires intervention to curb on the rising levels of pollutants.

Statistically significant interrelationship was observed between sediments and *Cladophora*, which supports the idea that, *Cladophora* is an appropriate bio-indicator for heavy metal pollution.

Heavy metal contamination levels in water samples, in this study, is variously impacted by; nearby industries, dust from the nearby mining activities and the chemical fertilizers used in the nearby commercial pineapple farms and combustion of fuel from the vehicles plying the nearby roads and therefore unsuitable for drinking.

The study consequently, recommends for the introduction of heavy metal bio-accumulators such as bamboo plants grown along Thika River basin and for enforcement of measures to restrict direct release of untreated waste waters and industrial effluents, into the river.

Further studies should also be carried out to determine the other sources contributing to the pollution of the river ecosystem.

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Abbreviations

AAS	Atomic Absorption Spectroscopy
ADMCA	Amplifier Detector Multichannel Analyzer
ANOVA	Analysis of Variance
AXIL	Analysis of X-ray Spectra by Interactive Least - Square fitting
BOD	Biological Oxygen Demand
CF	Contamination Factor
CRM	Certified Reference Material
DC	Direct Current
DNA	Deoxyribonucleic acid
EDTA	Ethylenediaminetetraacetic acid
EDXRF	Energy Dispersive X-Ray Fluorescence
EF	Enrichment Factor
EMCA	Environment Management and Coordination Act
EPA	Environmental Protection Agency
GPS	Global Positioning System
IAEA	International Atomic Energy Association
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
KEBS	Kenya Bureau of Standards
KNEB	Kenya Nuclear Electricity Board
NEMA	National Environmental Management Authority
PLI	Pollution Load Index
SRM	Standard Reference Material
TCM	Thika Cloth Mills
TOD	Total Oxygen Demand
TSM	Total Suspended Matter
TXRF	Total X-ray fluorescence
UNEP	United Nations Environmental Program
USB	Universal Serial Bus
UTI	United Textile Industry
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

Chemical Symbols

Ag	Silver
Al	Aluminium
Ar	Argon
As	Arsenic
Br	Bromine
Ca	Calcium
Cd	Cadmium
Cl	Chlorine
Co	Cobalt
Cr	Chromium
Cu	Copper
Fe	Iron
Ga	Galium
Hg	Mercury
HNO ₃	Nitric acid
K	Potassium
Mn	Manganese
Mo	Molybdenum
Ni	Nickel
Pb	Lead
Sc	Scandium
Se	Selenium
Si	Silicon
Sr	Strontium
Te	Tellurium
Ti	Titanium
V	Vanadium
W	Tungssten
Zn	Zinc
Zr	Zirconium

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Chapter 1

Introduction

1.1 Background

In general, recent rapid increases in population growth and in industrialization, have resulted in high demand for water, both for industrial and domestic uses in Kenya (*Kenya Open Data Survey, 2014*). Thika Town exemplifies a town that has undergone rapid industrial growth. Currently, there are more than 20 major and 100 minor manufacturing and processing firms located in Thika town and its environs; effectively opening up the town to international trade (Businesslists.co.ke). Table 1.1 lists some of these Industries.

Table 1.1: Some of the Manufacturing Industries Located in Thika Town (Business Lists.co.ke)

Category	Industry
Food & Tobacco	Thika Coffee Mills
	Delmonte (K) Ltd
	Alliance One Tobacco (Kenya) Ltd
	Centro Food Industries
	Bidco Oil Ltd
	British American Tobacco Ltd
	Chania Food Mills
	Mama Millers Limited
	Broadway Bakeries
	Oswal Bakery Ltd
	Kenblest Ltd
	Kakuzi
	The Coconut Grill
	Jetlak Food Ltd
	MC Neel Millers
	Brookside Dairy Ltd
	Jubilee Feeds Industries Ltd
Makadamia Nuts	
Pharmaceuticals	Dawaline Pharmaceuticals (K) Ltd
	Rupcco Pharma Limited

	Chebu Pharmaceutical Ltd
	Thika Pharmaceuticals Manufacturers Ltd
Textile	Thika Cloth Mills
	Salama Clothing Manufacturers
	United Textile Industries Ltd
	KenWear Garment Manufacturers
	Weaver Bird Garments Manufacturers
	Sona Industries Ltd
Metal	Technology Automation Concepts Ltd
	Popular Industries Ltd
	Booth Extractions Ltd
	Devki Steel Mills
Leather	Kenya Tanning Extracts Co Ltd
	Leather Industries of Kenya Ltd
	Bulleys Tannery
Motor Vehicle	Kenya Vehicle Manufacturers Ltd
	Auto Express
	Thika Motors Dealers (K) Ltd
	Capital One Motors
Rubber	Thika Rubber Industries Ltd
Wood and Paper	The Kenya Paper Mill Ltd
	Balozi Industries Ltd
	Michecha Ltd
Oil and Gas	Wajibu Mobil Service Station

Thika town population was estimated at 139,853, during the 1999 census, a remarkable increase from the 4,500 people reported in 1948, and has risen to approximately 165,342 people in 2009 (*Kenya Open Data Survey, 2014*). However, unlike in most developing countries, this population growth has not been accompanied by provision of sustainable quality water supplies and quality sanitation services (Rahman, 2011).

The increased use of chemical fertilizers in farmlands, emission from automobile and deposition of industrial waste in the environment are some of the potential sources of pollution.

The Thika River traverses Thika's industrial, residential and agricultural zones where these pollutants are introduced in the river waters along its profile with the possibility of heavy metal contamination- a potential threat to human health for the inhabitants. The Chania River, which joins the Thika River near the Blue-Post Hotel, has been the subject of pollution arising from anthropogenic activities such as clothes washing and direct dumping of industrial and domestic wastes by residents in the adjoining land (Gathua, 2015).

In some sections of the river, raw sewage, industrial effluents from nearby industries and municipal wastewater are directly released into the river (Gathua, 2015). Untreated effluents are released into the river without due consideration of their pollutants. For example, Figure 1.1 shows some of the industrial waste from the Leather Industries of Kenya Ltd being released directly into the Thika River, while, Figure 1.2 shows residents brewing at the river banks.



Figure 1.1: Industrial effluents from the Leather Industries of Kenya Ltd released into the Thika River (Source: Self)



Figure 1.2: Residents brewing at the river banks (Source: Self)

The river water is further polluted by industrial and household wastes; human excreta and industrial effluents. Thika town harbors several industrial establishments; textile factories, tanneries, garages and food processing factories (Odira, 1991).

Sediments act as a sink to pollutants by accumulating them over time; consequently, they provide means through which toxicity is introduced to the food chain.

Some aquatic plants such as algae, found in sediments, absorb metals to their cellular structures (Kelly and Whitton, 1995). The amount of accumulated heavy metals depends largely on the degree of contamination of the sediments. Thus the level of heavy metals in such plants is an indicator of the level of contamination in the sediments.

Over the last decade, the environment protection agency, EPA and other agencies engaged in environmental conservation worldwide have introduced methods for use in the identification and assessment of the extent of contamination in sediments and other environmental media.

This study investigated the levels of heavy metal contamination in Thika River water, sediments and algae, and their inter-relationships and determined the extent of contamination for evaluation of possible health hazards.

1.2 Description of the Study Area

Thika town is an industrial town located at 01°03'S37°05E' in Central Province, Kiambu County approximately 40 Km away from Nairobi towards the North East direction at an elevation of approximately 1,631 metres above sea-level (Berry, 2014).



Figure 1.3: Map of Kenya showing Thika Town and Thika River (Source: Kenya topographic map-de.svg)

Thika town occupies an area that harbours a population of 165,342, which generates a significant amount of domestic effluents (Kenya Open Data Survey 2014).

The climate of the study area depends on altitude and rainfall pattern. Generally, the area experiences fairly uniform temperatures with the highest temperatures occurring between

December and March, and the lowest temperatures occurring in between June and August. The area receives bimodal rainfall with short rains occurring in between October and December while the long rains occur in between March and June. Thika and the surrounding regions receive an average annual rainfall ranging between 900mm and 1,250 mm per year (Worldweather.com). This study was carried out in September 2015, just before the onset of the short rains.

The Thika River originates from the Aberdare mountains and flows for approximately 100 Km South East before it joins Thika town. The river then flows further 100 Km and empties its water to the Tana River (Kigira, 2010).

The study area is the river's profile that begins at (01.02023°S, 037.06724°E) under the bridge adjacent to the Blue Post Hotel and extends over a span of 13 Km to (01.04943°S, 037.15179°E).

As the river approaches Thika Town, it traverses through a region dominated by industrial activities; the Thika Cloth Mills, the Booth Industry, United Textile Industry, Kenya Tanning Extracts, Dan's Motors Garage, Delmonte (K) Ltd, Kenya Paper Mills and the Leather Industry Kenya Ltd in the middle section. Consequently, it receives effluents from these industries through either direct discharge or surface run-offs.

Nearby residential areas include; Kimathi, Makongeni, Salvation Army centre and Thika Landless Estate among others scattered several metres inland from the river and at regular intervals along it. Owing to poor drainage systems in these areas, raw sewage is released into the river.

The river's middle section traverses a region dominated by mining activities as evidenced by the quarries located in these sections. The land along which the Thika River flows is both privately and commercially owned for small scale farming. Small scale livestock farming is also a common activity in the study area. Commercial farms dominate the left side of the river profile downstream; pineapple farms by Delmonte(K) Ltd and coffee plantations.

The river offers various benefits to the surrounding population. It provides water for irrigation, industrial and domestic purposes, and electric power generation. Its catchment also accounts for at least 80% of water consumed in Nairobi (Municipality of Thika, 2008). Besides, it is famous for the Thika Falls, which offer magnificent sceneries for domestic and international tourism.

The river water is subjected to multiple sources of pollution; effluents from nearby industries and surface run-off. Commercial farms use chemical fertilizers, pesticides, fungicides and agrochemicals which are carried and deposited in the river through surface run-off. Raw sewage from surrounding residential areas is released directly into the river or deposited through surface run off, is also a potential pollutant. The dust from mining activities at nearby quarries and exhaust fumes from automobile are introduced in the river through atmospheric deposition and surface storm water run-offs.

1.3 Statement of the Problem and Justification

Although heavy metal pollution in various environmental media has been monitored over time, the problem has persisted due to the indestructible nature of these metals. When their concentrations exceed certain levels, their bioaccumulation introduces toxicity in living tissues (Lambert *et al.*, 2000).

Thika River traverses through an area that renders it susceptible to pollution from nearby industries, garages, untreated municipal industrial waste, and storm water run offs carrying pesticides and fertilizers used in nearby commercial farms. In general, although frameworks have been established for waste management in Kenya to minimize pollution, they have been weakly enforced hence allows for improper disposal of waste, leading to environmental pollution.

The aim of this study was to determine the extent of suspected heavy metal pollution of Thika River waters due to nearby industrial, agricultural and human activities. The previous assessment on heavy metal pollution on the Thika River water was done in the early 1990's (Odira, 1991). Therefore, it was necessary to update the status due to these increased anthropogenic activities. The results obtained from this study will enable for the formulation of policies in the management and utilization of natural resources for sustainable development.

1.4 Scope of the Study

This study focused on determining the level of selected toxic heavy metals; Mn, Ni, Cu, Zn and Pb in algae, water and sediments samples from 32 sampling points along the Thika River. The study covered the portion of the river that traverses Thika town beginning at (01.02023°S, 037.06724°E), at a location under the bridge adjacent to the Blue Post Hotel, and extending over approximately 13 Kilometres to (01.04943°S, 037.15179°E) near the Makongeni estate. This

section represents the part of the river most susceptible to heavy metal pollution due to various nearby anthropogenic activities.

The algae species chosen for this study was *Cladophora*. It is generally considered as the best bio- indicator of the extent of heavy metal contamination in aquatic bodies.

The sampled media were selected primarily due to their ease of identification, size, distribution, longevity, presence at polluted sites and capacity to accumulate heavy metals to an appreciable extent (Al-Homaidan *et al.*, 2011). In addition, water and sediment samples were also studied to help establish how the levels of heavy metals in the three media correlate to one another.

1.5 Objectives

1.5.1 General Objectives

To determine the current levels of toxic heavy metal contaminations in Thika River water, sediments and algae, for evaluation of extent of pollution in these media.

1.5.2 Specific Objectives

- a) To assess the levels of toxic heavy metals; Mn, Ni, Cu, Zn and Pb in water, flora (*Cladophora*) and sediment samples collected along the Thika River;
- b) To determine the extent of pollution from the toxic heavy metal contaminants in the selected environmental media and their inter-relationship.

Chapter 2

Literature Review

2.1 Introduction

In this section, we review the various recent studies undertaken in relation to water pollution from heavy metal contamination and discuss their effects on human health.

2.2 Sources of Heavy Metal Pollution in Water and their Effects on the Human Health

In general, sources of heavy metal pollution can be categorized into two; natural and anthropogenic (Holland and Turekian, 2005). Natural sources include natural processes; vulcanicity, acid rain and weathering, in which cases, chemical processes occur and result in the dissolution of the heavy metals.

Anthropogenic sources are responsible for the deposition of heavy metals in water bodies (Holland and Turekian, 2005). They include disposal of industrial effluents into water bodies and from agricultural uses of agrochemicals such as fertilizers and pesticides. Specifically, most untreated industrial processes emit effluents that contain harmful toxic heavy metals, which pollute water bodies, following disposal.

Owing to their non-biodegradable nature, these metals, upon ingestion, accumulate in organs and tissues of living aquatic organisms. In high concentrations, they affect the normal body functions and are toxic; for instance, mercury in high concentrations is very toxic and poisonous. However, living organisms require essential metals in micro quantities for normal functioning (Wang *et al.*, 2009). Other toxic elements include; nickel, zinc, iron, vanadium, cobalt, molybdenum, copper, chromium, tin and manganese (Sinh, 2005) when present in high concentration levels. Another category, non-essential metals, which is harmful to living cells, includes metals such as cadmium, lead, arsenic, mercury, titanium, bismuth and antimony (Sinh, 2005).

In this study, we will focus on the following toxic elements, namely; manganese (Mn), copper (Cu), iron (Fe), zinc (Zn), nickel (Ni) and lead (Pb).

Manganese is among the metals in high abundance in the earth's crust and occurs in association with iron. Manganese does not exist in its elemental or pure form (WHO, 2011). In the body, manganese aids in the functioning of cellular enzymes, for example, pyruvate carboxylase and manganese superoxide dismutase. It can also activate enzymes such as decarboxylases, kinases

and hydrolases (WHO, 2011). In general, manganese levels found in most drinking waters do not raise health concerns. However, extended exposure to concentrations above 0.05 mg/l (Table 2.1) in drinking water may cause neurological disorders (WHO, 2011).

Copper occurs in different states; chlorides, sulphides and carbonates. This metal is vital in cellular respiration, pigment formation and strengthening connective tissues. It is also a cofactor of various enzymes. Concentrations above 0.02mg/l (Table 2.1) cause radical formation, which may further lead to damage to the gastrointestinal tract, DNA breakage, mitochondrial damage and neuronal damage (WHO, 2011).

Nickel is considered as a moderately toxic heavy metal. Nickel exposure mainly occurs through oral consumption. Nickel occurs naturally in both water and food and may be increased through anthropogenic activities. For instance, from nickel-plated water taps; nickel from smelting and mining activities and from utensils made from alloys of nickel and steel (Kamerud *et al.*, 2013). Nickel exposure may also result from inhaling tobacco smoke and skin contact with detergents, jewellery, coins and shampoos. Exposure to nickel concentrations above 0.02 mg/l in drinking water causes allergy, nasal, and lung cancer (Sullivan and Klieger, 2001).

Zinc is the second most abundant metal in the human body after iron. In humans, it is essential for highly proliferating body cells, for instance immune cells. No guideline value has been set for Zn in drinking water because the levels found in drinking water are not of health concern. However, drinking water containing Zn levels above 3mg/l may not be acceptable for consumption (WHO, 2011).

Lead is a vital metal for use in the manufacture of piping, storage batteries, ammunition, building materials and chemicals. Concentrations higher than 0.01mg/l (Table 2.1) in drinking water may lead to brain damage, abnormal renal function, impaired fertility and hypertension (WHO, 2011).

Table 2.1: Maximum acceptable levels of heavy metal contamination in drinking water and water supporting aquatic life according to NEMA(2006) and WHO (2011)

Heavy Metal	Max. conc. in drinking water (WHO) (mg/l)	Max. conc. in drinking water (NEMA) (mg/l)	Max. conc. in water supporting aquatic life (mg/l)
Pb	0.010	0.05	0.0058
Cu	2	0.1	---
Fe	---	---	---
Mn	0.002	0.1	---
Zn	---	5	0.3
Ni	0.07	---	---

2.3 Environmental Water Pollution Studies in Kenya

In this section, we review recent studies that have been undertaken on pollution of water sources and other environmental media in Kenya.

Hadgu *et al.* (2014) assessed pollution due to disposal of agricultural wastewater in Ndarugu River in Juja, Kiambu County. The study established that BODs of the wastewater released into the river ranged between 300 and 600 mg/l while electrical conductivity ranged between 482 and 620 μ S/cm. In the river water sampled, BOD was 20mg/l, while the electrical conductivity ranged between 55 and 85 μ S/cm. Pollution of the river was attributed to anthropogenic activities by residents from the adjoining land. Proper waste water control and treatment of wastes before disposal were recommended.

Svengren (2002) carried out a study on environmental conditions in Lake Nakuru, Kenya, using isotope dating and heavy metal analysis of sediments. The researcher established that the levels of metals analyzed; Cd, Cu, Pb, Ni, Cr and Zn were within WHO guidelines for natural background sediment concentrations. However, high concentrations were noted in lakes with catchments whose bedrock contained high levels of heavy metals.

Muohi, *et al.* (2002) carried out a study on heavy metals; Cu, Zn, Pb, Cd pollution at the Kenyan Coast. From this study, which focused on the creek systems in Port Reitz and Makupa, the researchers noted higher metal concentrations in Makupa for Zn, 1017 \pm 840; Cu, 102 \pm 46.0; Cd, 51.0 \pm 14.3; Pb, 103 \pm 35.8 mg/kg as compared to Port Reitz Zn, 57.1 \pm 17.9; Cu,

21.6± 7.1; Cd, 1.38 ± 0.7; Pb, 103± 35.8 mg/kg. They attributed this to the close proximity of Makupa Creek to neighbouring municipal dumpsite and industrial activities.

In their study on mortalities associated with flamingos in the saline Lakes of the Kenyan Rift Valley; Bogoria, Nakuru, Elementaita, Magadi and Sonachi, Ndeti and Muhandiki (2005) established that differences in heavy metal contamination in these Lakes were insignificant. However, Lake Sonachi water had high levels of copper and mercury in comparison to the other Lakes. The researchers attributed this high concentration of heavy metals to natural sources and concluded that the Lake is located in the Rift Valley region where vulcanicity is active, and away from influential anthropogenic activities.

Budambula and Machiro, (2006) carried out a study on the Nairobi River pollution. In this study, they investigated for the presence of heavy metals in the River's water and fish samples (*LabeoCylindricus*). Although most metals; chromium, lead, manganese and iron recorded concentration levels lower than WHO limits, isolated cases of aluminium and mercury contamination were noted. Besides, high concentration levels were noted for Zn (360µg/g), Cu (45 µg/g), Cd (167 µg/g) and Hg (1000ng/g) in fish heart, scales and kidney tissue samples, respectively.

Muohi (2007) investigated on how trace elements accumulate in Biota (*Algae and Chiromids*) from two saline Lakes: Bogoria and Nakuru. The researcher recorded higher contamination in Lake Nakuru due to its geographical proximity to the demographically and commercially developing Nakuru town.

Most recently, Mwatsahu (2013) assessed the level of heavy metals in water, sediments and fauna along the Kenyan coastline. From the study, he noted that the levels of Cu, Zn and Pb exceeded USEPA limits.

In general, local studies, though limited have determined the extent of heavy metal pollution of water sources, for which most rely on for economic purposes; farming, fishing and portable water among others.

2.4 Pollution Studies of Thika River

Mwangi (1988) investigated the effect of agricultural, domestic and industrial on the quality of the Thika-Chania River system. In the study, parameters such as Total Suspended Solids (TSS), the Biological Oxygen Demand (BOD), Total Oxygen Demand (TOD) and heavy metals were analyzed. For all these parameters, the levels never exceeded the recommended value (140 mg/l), except chlorides (655.5 mg/l). The levels of all heavy metals (Cu, Fe, Cr, Ti, Zr and Zn) analyzed did not exceed 2.6 ppm. The highest Fe concentration obtained was 39.26 ppm. The river was thus said to be less polluted except for the isolated cases of chloride and iron pollution. Their study recommended that the specific points of discharge of these elements be identified and measures to reduce their levels identified and implemented.

In 1991, Odira carried out an investigative study on the pollution profile of Thika River. From the study, he noted high pollution (3200mg/l of suspended solids) in areas located close to the Thika Cotton Mills and Delmonte (K) Ltd. The study emphasized the need to ensure that the industries discharging their effluents directly into the river adhere to effluent standards.

Besides, concerns have been raised in the recent past concerning pollution of the Thika River. In 2015, Gatuanyanga residents in Thika East Sub County complained about the health effects due to emissions from the nearby Asphalt factory which borders the Chania River, a confluent of the Thika River downstream. Consequently, the factory eventually closed down following public complaints (Musembi, 2015).

2.5 Significance of *Cladophora* (Green Algae) for assessment of heavy metal pollution

Cladophora refers to a genus of reticulated green algae that usually grows on rocks that are submerged in shallow rivers and lakes. They have a coarse appearance with filaments that branch regularly. *Cladophora* grows as a ball or tuft with filaments ranging up to 13 cm in length and having cross walls that separate multinucleate segments. It has many species whose appearances depend on age, habitat and environmental conditions. This alga has a life cycle that consists of two multicellular stages: diploid sporophyte and haploid gametophyte (Kelly and Whitton, 1995).

The cell walls of the algae constitute polysaccharides, which produce carboxyl, sulfate, amino and phosphate groups. These groups possess ion exchange properties and are useful sites for

binding metals. These characteristics render *Cladophora* suitable for pollution monitoring of heavy metals in water resources (Kelly and Whitton, 1995).

Lee and Chang (2011) investigated the biosorption of heavy metals by *Cladophora* and *Spirogyra* filamentous microalgae. The aim of the study was to identify suitable freshwater algae with a high capability to remove heavy metal ions (copper (II) and Pb (II) ions) in water solution. A comparison study of the analysis of Freundlich and Langmuir isotherm models revealed that the absorption of Cu (II) and Pb (II) by both biosorbents exhibited a better fit when the Langmuir isotherm model was used. When considering both biosorbents' adsorption of heavy metals in their ionic form, physical and chemical particle surface adsorption proved more significant than adsorption and diffusion between particles. Experiments on continuous adsorption-desorption revealed that both biomass types were excellent biosorbents.

Deng et al. (2006) investigated the absorption of lead (II) and copper (II) ions from aqueous solutions by dead green algae, *Cladophora fascicularis*. The study was carried out through the examination of kinetics, environmental and equilibrium effects. In the study, the biosorption of lead (II) and copper (II) ions by *Cladophora fascicularis* was examined as a function of temperature, initial concentration of heavy metals initial pH and other ions. The Freundlich and Langmuir isotherm models were used to describe the adsorption equilibria. The greatest possible adsorption capabilities were obtained at 0.96 mmol/g for Pb (II) ions and 1.61 mmol/g for Cu (II) ions at pH 5.0 and 298 K. The results revealed that *Cladophora fascicularis* was effective for removal and recovery of toxic heavy metals from waste waters.

Whitton et al., 1989 investigated the use of green algae, *Cladophora glomerata*, to monitor the levels of heavy metals in rivers. Sixty water and algal samples from northern England were analyzed for Pb, Zn, Fe, Cd and Cu. Additional environmental variables were also evaluated to assess their influence on metal accumulation. Extremely high correlations were established for each heavy metal in water and alga. Regression analyses were conducted to show the environmental factors that may favour metal accumulation. For example, iron seems to have a positive effect on the accumulation of Cu. Generally, capacity of *Cladophora* to accumulate heavy metals is less than that of bryophytes. However, the slope that relates metal accumulation in alga to metal accumulation in water is steeper, especially for Pb. This study revealed the effectiveness of *Cladophora* as a sensitive bio-indicator.

Aulio, (1983) investigated the level of heavy metals in green alga (*Cladophora glomerata*) in relation to the types of shores of the Archipelago Sea of South West Finland. In this study, the levels of iron, copper, manganese and zinc were determined in samples of *Cladophora glomerata* obtained from the northern Baltic Sea in the Archipelago Sea of South West Finland. From the results obtained, the researcher concluded that there were no observable trends for Mn, Cu, and Zn based on the plants' habitats. In contrast, the levels of iron obtained for algae samples collected from soft-bottom habitats were extremely higher than the levels recorded for stony and rocky shore habitats.

Özer et al. (2008) carried out an investigative study on the adsorption of heavy metal ions (chromium (VI) and lead (II)) on green algae (*Cladophora crispata*) with respect to temperature and pH in order to establish the conditions for chromium (VI) and lead (II) removal. The optimal conditions were established at 25°C, pH 5.0 and 25°C, pH 1.0 for lead (II) and chromium (VI), respectively. From the adsorption isotherms developed, it was evident that the adsorption equilibrium data matched both Langmuir and Freundlich isotherms for the metal ions studied. Besides, lead yielded higher adsorption properties as compared to chromium for both models.

Kupeet al. (2005) carried out an investigative study to determine the bioaccumulation of heavy metals; Zn, Fe, Mn, Cu, Cd, Cr, Pb and Ni in biota (*Cladophora glomerata*), water and sediments along some Albanian rivers. High concentration levels of Cd, observed in Osumi River, were attributed to effluent discharges. Similarly, high concentrations of Pb were observed in Ishmi, Gjanica and Lana.

In this study, *Cladophora* was selected for study on the basis of its effectiveness as a sensitive bio-indicator of potential heavy metal pollution in river water samples.

2.6 Regulatory Framework for Environmental Management in Kenya

Regulatory frameworks have been established by the Environmental Management Authority (NEMA) in Kenya to control waste disposal and minimize environmental pollution. For example, solid waste management in Kenya is governed by the Public Health Act, 1986 (National Council of Law Reporting, 1986), the Environmental Management Regulations, 2006 and the Environmental Management and Coordination Act, 1999 (EMCA). These Acts provide for proper waste management methods such as incineration, re-use, dumping recycling and landfills. For example, section 87 of EMCA outlaws indiscriminate waste disposal methods that

can pollute the environment or cause sickness to a person. Under section 87(4), any person who engages in activities that produce waste is required to establish necessary measures to minimize wastes through recycling, reclamation and treatment. The EMCA also provides water quality regulations which minimize pollution in aquatic environments. For instance, it prohibits the discharge of any effluent from industry, sewage treatment works or other point sources without a valid effluent discharge license (National Council of Law Reporting, 1999). The EMCA 2015, CAP 387 provides for regulations and guidelines for environmental assessment and environmental audits in principle to ensure that all project activities have minimal negative impact to the environment (National Council of Law Reporting, 2015).

2.7 Principles of Quantitative EDXRF and TXRF Analyses

X-ray fluorescence analysis is the chemical analytical tool of choice used for this study. It refers to an analytical technique, used to characterize all types of materials in their liquid, filtered, powder, solid or other form in terms of elemental content. When sufficient photon energy is absorbed by an atom, an electron is ejected from its atomic orbital if the photon energy exceeds the energy that binds it to the atom's nucleus. When an electron in the inner orbital is dislodged from the nucleus of an atom, an electron is transferred from an orbital at a higher energy level to fill up the vacancy created. When this transition takes place, the atom may emit a photon or fluorescent radiation known as a characteristic X-ray whose magnitude is equal to the energy difference between the two energy levels of the transiting electron. Since any given element always possesses the same energy between two specific orbitals' transitions, the photon it emits when an electron transits between these two orbitals is always the same.

Consequently, it is possible for one to identify an element by determining the wavelength or energy of the photon that it emits (Brouwer, 2010; Beauchaine, 2012; Antoaneta *et al.*, 2015).

For a specific wavelength or energy of fluorescent light that an element emits, the magnitude of photons in a unit time (count rate) is dependent on the sample analyte. For every detectable element in a sample, the associated count rate can be determined by counting, for a set time duration, the number of photons detected for characteristic X-ray energy lines for different analytes. Thus one can qualitatively determine the elements contained in samples by determining the energy associated with the X-ray photo peaks in the spectral data. Consequently, it is possible to quantitatively determine elemental concentrations by counting the count rate associated with various elemental photo peaks in spectral data (Brouwer, 2010; Beauchaine, 2012).

2.7.1 Quantitative Energy Dispersive X-Ray Fluorescence (EDXRF) using Fundamental Parameters

EDXRF is a relatively simple technique that basically utilizes an EDXRF Spectrometer which constitutes an x-ray tube (50-60kV, 50-300W) and a detector designed to generate electrical pulses that change according to the emitted x-rays' energies. Most EDXRF instruments used in laboratories use Si (Li) detectors that are cooled by liquid nitrogen. Benchtop instruments use proportional counters while handheld devices use detectors such as CdTe and mercuric Iodide (Antoaneta, 2015).

Sample analysis using EDXRF method takes place in two steps: qualitative analysis and quantitative analysis. In practice, the process entails measurement of spectral data to determine the elements that are present in the sample and their respective net intensities. The net intensities so obtained are used in quantitative analysis, where the concentrations of elements identified are calculated (Brouwer, 2010). The concentrations of elements of interest in the sample were calculated using the Fundamental Parameters Method, whereby the intensity of X-rays is used to determine the elemental concentrations in a given sample (Rousseau, 2006). This method has been used in various studies (Simabuco, 1994; Balasubramanian, 2016).

2.7.2 Total X-ray Fluorescence (TXRF)

The other analytical method used in this study is the TXRF Spectrometer, which uses the principle of total internal reflection for the sample irradiation. In this technique, the X-ray tube produces a monochromatic x-ray beam which passes through a sample mounted on a sample holder substrate held at a tiny angle ($0.3-0.6^\circ$) hence making the beam to be totally internally reflected. The beam interacts with the atoms of elements in the sample substrate causing it to emit a characteristic radiation, whose intensities are measured from spectral data.

The difference between a TXRF spectrometer and the conventional EDXRF spectrometers is that, the later uses monochromatic radiation and is based on the principle of total internal reflection. Using a totally internally reflected beam to illuminate the sample decreases the scattering and absorption of the beam sample matrix and the sample itself. The benefits associated with this technique include: low background noise, greater sensitivity and reduced matrix effects (Klockenkämper, 1997).

For infinitely thin samples, the intensities of the analytes are proportional to mass fractions, c_i . Therefore, for an element x , the corresponding relative mass fraction c_x can be determined by reference to the sum of all elements i identified in the spectrum (Klockenkamper and Bohlen, 1992; Klockenkamper and Bohlen, 1989).

$$C_x = \frac{I_x/S_x}{\sum I_i/S_i} \times 100\% \dots\dots\dots 2.1$$

This quantification method yields only relative mass fractions associated with the detected elements and its application is limited to extremely small volume samples such as tissues. An absolute quantification requires two extra quantities: the mass of the sample and a known quantity of an element absent to the sample. It is necessary to add this element to the sample as an internal standard solution. Then, the absolute mass fractions associated with the elements can be determined as follows (Klockenkamper and Bohlen, 1992; Klockenkamper and Bohlen, 1989).

$$C_x = \frac{I_x/S_x}{\sum I_{int}/S_{int}} \times \frac{M_{int}}{M_{sample}} \dots\dots\dots 2.2$$

Where,

C_x =mass fraction of the analyte; I_x =intensity of the analyte; S_x = sensitivity of the analyte; I_{int} = intensity of the internal standard; S_{int} = sensitivity of the internal standard; M_{int} = mass of the internal standard; M_{sample} = mass of the sample.

In a micro-sampling approach, the masses provided are too small for their weight to be measured reliably. As a result, only equation (2.1) above is used for quantification and for relative mass fractions of the elements of interest in the sample. However, this method is appropriate in the characterization of the elemental content of substances such as pigments (Von Bohlen, 2004).

In this study, the water samples were irradiated under fixed conditions of time, voltage and current and the resulting spectral data analyzed for elemental content, using appropriate software.

2.8 EDXRF and TXRF Trace Heavy Metal Analyses of Water, Sediments and Algae

Several studies have used EDXRF and TXRF to analyze the levels of heavy metals in water, sediments and algae. Some of these studies are highlighted herein.

Mwatsahu (2013) used EDXRF to investigate the level of heavy metals (Mn, Fe, Cu, Cr and Cd) in water, sediments and fauna along the Kenyan coastline. From the study, he noted that the levels of Cu, Zn and Pb exceeded values set under USEPA guidelines.

Muohi, *et al.* (2002) investigated the level of heavy metals (Cu, Zn, Pb and Cd) in sediments along the Kenyan Coastline using Atomic Absorption Spectrophotometer (AAS). The sediments were also analyzed using EDXRF for comparison. The results showed good agreement between the two methods.

Odumoet *al.* (2011) assessed the impact of toxic heavy metals on the environment and the exposure of miners to these metals in Migori, Southwest Kenya using EDXRF. Heavy metals such as Pb, Ti, As and Zn were found to have exceeded the minimum level recommended by WHO (50 mg/kg).

Makundi (2001) used EDXRF to investigate the extent of heavy metal pollution in sediments sampled from various locations in Mwanza Municipality in Tanzania. The study concluded that heavy metal contamination of Lake Victoria is largely due to direct discharge of sewage and industrial waste into the lake.

Naziriwo *et al.* (2010) used EDXRF and TXRF to assess the concentration of trace metals; Mn, Fe, Co, Cu, Zn and Pb in Lake Victoria and Nakivubo Channel waters. In general, most trace metals were found to exceed acceptable limits hence recommended the need to establish control measures.

Kilavi *et al.* (2015) carried out a study on the application of TXRF in assessing trace elements; Mn, Fe, Cu and Zn levels in infant flour from Kenya. The results revealed that the investigated samples could meet recommended daily intake requirements for Cu, Fe, Zn and Mn if the selection and combinations of individual ingredients from the study area was done following careful preparations.

In other studies, Mangala (2003) used TXRF to analyze tap and local mineral waters for heavy metal content while Gatari *et al.* (2008) used TXRF to determine the level of trace metals in commercially produced bottled drinking water in Nairobi, Kenya.

2.9 Statistical Data Analyses for Assessment of Heavy Metal Pollution Levels

In this study, the elemental concentrations results obtained was subjected to analysis of Variance (ANOVA) to establish whether there was a significant difference in the distribution of heavy metals between samples of algae, water and surface sediment along the river. The interrelationships of heavy metal contamination among the three media were determined using the Pearson correlation coefficients.

The degree of contamination and heavy metal enrichment in sediment samples were assessed through pollution factors such as the enrichment factors, geoaccumulation indices, contamination factors, modified degree of contamination factors and pollution load indices.

2.9.1 Enrichment Factors

In this method, measured heavy metal contents are normalized against a chosen reference metal (Ravichadran *et al.*, 1995). According to Buat-Menard and Chesselet, (1979), the enrichment factors are calculated using the following relation:

$$EF = \frac{C_n}{C_{ref}} \dots\dots\dots \frac{B_n}{B_{ref}} \dots\dots\dots 2.3$$

Where C_n is the content of the examined element in the examined environment; C_{ref} is the content of the examined element in the reference environment; B_n is the content of the reference element in the examined environment; B_{ref} is the content of the reference element in the reference environment.

A reference element is one whose natural occurrence within the environment is high. Common reference elements include Sc, Mn, Al and Fe (Ravichadran *et al.*, 1995). Iron (Fe) was used as the reference element in this study. According to Deely and Fergusson (1994), when calculating enrichment factors, Fe is widely accepted as a normalization element because its distribution is not dependent on other heavy metals. The natural concentration of this metal is relatively high. Consequently, one would not expect the metal to be significantly enriched through anthropogenic sources in river water, sediments or plants. In this study, the background level suggested by Taylor and McLennan (2001) for Fe (40000mg kg^{-1}) was used.

There are five possible degree of contamination categories that can be obtained based on the use of enrichment factor. These are summarized in Table 2.2.

Table 2.2: Table of contamination categories that can be obtained based on enrichment factors

Range of Enrichment Factor	Category of Contamination
EF<2	Deficiency to minimal enrichment
2<EF<5	Moderate enrichment
5 <EF< 20	Significant enrichment
20 <EF< 40	Very high enrichment
EF>40	Extremely high enrichment

The enrichment factors method is relatively simple and easy in the assessment of enrichment factors and comparison of contamination of various environmental media. These characteristics have rendered it a popular method that most studies have used to assess the extent of heavy metal contamination in sediments.

Karageorgis (2009) used enrichment factors method to assess the extent of heavy metal contamination of Koumoundourou Lake in Greece. The study revealed that the sediments were enriched in Cu, V, Pb and Ni.

Abraham and Parker (2008) assessed the heavy metal enrichment factors and the extent of contamination of sediments obtained from Tamaki estuary in New Zealand. The study revealed that the sediments in the estuary were significantly enriched in heavy metals due to urbanization in the surrounding area.

Bentumet *al.* (2011) assessed the extent of heavy metal contamination of sediments obtained from Fosu lagoon in Ghana by enrichment factors. The study established that the sediments were significantly enriched in Zn and Cu. The sediments also showed high to extremely high enrichment in Pb.

Varol (2011) used enrichment factors to assess the extent of heavy metal (Co, Zn, Pb and Cu) pollution in sediments obtained from the Tigris River in Turkey. The enrichment factors determined from the study revealed that the sediments were minimally enriched in all elements.

2.9.2 Geo-accumulation Index, I_{geo}^m

The geoaccumulation index helps to assess heavy metal contamination in sediments by comparing the current heavy metal concentrations and the original pre-industrial levels in the sediments. According to Müller (1969), the geoaccumulation index is given by:

$$I_{geo}^m = \ln \frac{C_m^s}{1.5 \times C_m^b} \dots\dots\dots 2.4$$

Where C_m^s is the heavy metal concentration of each element, m, in the sample while the factor 1.5 minimizes the impact of possible changes in background values, C_m^b which may arise from lithogenic changes in soils. The world rock averages as proposed by Taylor and McLennan (2001) were used as background concentrations. These values are summarized in Table 2.3 below.

Table 2.3: World surface rock averages as proposed by Taylor and McLennan (2001)

Element	Average sediment (ppm)
Fe	40000
Mn	680
Ni	40
Cu	40
Zn	65
Pb	17

Based on equation (2.4), the geoaccumulation indices are assessed on the basis of seven descriptive categories as given below:

Table 2.4: Categories of Geoaccumulation Indices and Their Descriptions

Value	Category	Description
$I_{geo}^m > 5$	6	Extremely contaminated
$4 < I_{geo}^m > 5$	5	Strongly to extremely contaminated
$3 < I_{geo}^m > 4$	4	Strongly contaminated
$2 < I_{geo}^m > 3$	3	Moderately to strongly contaminated
$1 < I_{geo}^m > 2$	2	Moderately contaminated
$0 < I_{geo}^m > 1$	1	Uncontaminated to moderately contaminated
$I_{geo}^m = 0$	0	Uncontaminated

Several studies have employed the geoaccumulation index to determine the extent of contamination in environmental media. In a study by Rahman, (2011), geoaccumulation indices were used to assess heavy metal (Pb, Cr, Zn, Cu and Cd) contamination in Sitalakhyia, Buriganga and Turag rivers in India. Based on the geoaccumulation indices obtained, Turag River was found to be unpolluted for Zn and Cr. All locations in Buriganga River were unpolluted for Cr and moderately polluted for Pb. In the Sitalakhya River, all locations were unpolluted for Zn, Cr and Cd.

In a study by Bentum *et al.* (2011), geoaccumulation indices were used to determine the extent of heavy metal contamination in the selected sites around the Fosu lagoon located in Ghana. The calculated geoaccumulation indices revealed that the lagoon was moderately polluted with Pb, but unpolluted with Fe, Zn, and Cu.

Rabeeet *al.* (2011) used geoaccumulation indices to assess heavy metal contamination in sediments collected from Tigris River in Baghdad. The geoaccumulation indices determined from the study showed that the sediments were slightly polluted for Cd and Pb and unpolluted for Ni, Cu and Mn.

Varol (2011) used geoaccumulation indices to assess the extent of heavy metal (Co, Zn, Pb and Cu) pollution in sediments obtained from the Tigris River in Turkey. The geoaccumulation indices obtained revealed that the sediments were strongly polluted at the first site.

Chakravarty and Patgiri (2009) used geoaccumulation indices to assess heavy metal (Ti, Fe, Pb, Cr, Cu and Ni) pollution in sediments collected from Dikrong River in India. Based on the calculated geoaccumulation indices, the sediments were found to be unpolluted for Fe, Al, Mn, Ni, Ti and Zn. However, the sediments were unpolluted to moderately polluted in Pb and moderately polluted for Cu.

Bucollieri, *et al.* (2006) used geoaccumulation indices to assess heavy metal (Zn, Ti, Cu, Cr, Al, Fe, Pb, Ni, Hg and Mn) contamination in marine sediments obtained from the Taranto Gulf in the Ionian Sea of Italy. Based on the geoaccumulation indices calculated, the sediments were reported to have heavy metal concentration levels close to background levels in the Mediterranean Sea.

2.9.3 Contamination Factors and Modified Degree of Contamination

The modified degree of contamination (mC_d) and contamination factor (CF) as proposed by Tomlinson *et al.* (1980) were used to determine the degree of contamination of the sediments in the current study. The contamination factor, according to Tomlinson *et al.* is given below:

$$CF = \frac{C_{metal}}{C_{background}} \dots\dots\dots 2.5$$

Where C_{metal} is the heavy metal concentration of each element while $C_{background}$ is the background concentration of the heavy metal. The world surface rock average as proposed by Taylor and McLennan (2001) were used as background concentrations.

The modified degree of heavy metal contamination in sediments was calculated by the method proposed by Abraham (2005) shown in equation 2.6 below.

$$mC_d = \frac{1}{N} \sum_{i=1}^N CF_i \dots\dots\dots 2.6$$

Where N represents the total number of elements analyzed.

Equation 2.4 is obtained by modifying and generalizing the degree of contamination (C_d) equation 2.5 as presented by Hakanson (1980). The degree of contamination is the algebraic sum of all contamination factors.

$$C_d = \sum_{i=1}^N CF_i \dots\dots\dots 2.7$$

The contamination factor is determined to provide the magnitude of the degree of contamination in the sediment samples. Based on formulae (2.5) and (2.7), the contamination factor and degree of contamination values are assessed on the basis of four descriptive categories as given below:

Table 2.5: Categories of contamination factors and degree of contamination categories and their descriptions

CF	C_d	Description
CF < 1	$C_d < 6$	Low degree of contamination
1 < CF < 3	$6 < C_d < 12$	Moderate degree of contamination
3 < CF < 6	$12 < C_d < 24$	Considerable degree of contamination
CF > 6	CF ≥ 24	Very high degree of contamination

The modified degree of contamination values are assessed on the basis of seven descriptive categories as given below:

Table 2.6: Categories of modified contamination factors and their descriptions

mC_d categories	Description
$mC_d < 1.5$	Nil to very low degree of contamination
1.5 $mC_d < 2$	Low degree of contamination
2 $mC_d < 4$	Moderate degree of contamination
4 $mC_d < 8$	High degree of contamination
8 $mC_d < 16$	Very high degree of contamination
16 $mC_d < 32$	Extremely high degree of contamination
$mC_d \geq 32$	Ultra high degree of contamination

The contamination factors approach has been widely used to assess the extent of heavy metal pollution in sediments. Varol (2011) used contamination factors to assess the extent of heavy metals (Co, Zn, Pb and Cu) pollution in sediments obtained from the Tigris River in Turkey. The contamination determined from the study revealed that the sediments collected from the first site were highly contaminated in Zn, Cu and Co.

Rahman, (2011) used contamination factors and modified contamination factors to assess heavy metal contamination in Sitalakhyia, Buriganga and Turag rivers in India. Based on degree of contamination factors, three sampling sites along Turag River were contaminated to a low degree while two were contaminated to a moderate degree. In Buriganga River, the first site was contaminated to a considerable degree while the next two sites were polluted to a moderate degree. Two sites were contaminated to a very high degree. In the Sitalakhya River, all sites were contaminated to a low degree except the first site, which was moderately contaminated.

Pekeyet *al.* (2004) used the degree of contamination indices to carry out a trace element ecological risk assessment on surface sediments obtained from Izmit Bay in Turkey. The degree of contamination factors determined from the study revealed a very high degree of contamination.

Loskaet *al.* (1997) used contamination factors to the extent of heavy metal (Ni, Pb, Cd and Cu) contamination in Rybnik water reservoir, Poland. The contamination factors obtained from the study revealed that the sediments were contaminated to a considerable degree for Ni and a very high degree for Cu, Cd and Pb.

2.9.4 Pollution Load Index (PLI)

According to Tomlinson *et al.* (1980), the pollution load index (PLI) is given by the equation 2.8 below.

$$PLI = CF_1 \times CF_2 \times CF_3 \times \dots \times CF_N^{1/N} \dots \dots \dots 2.8$$

Where N refers to the number of metals under study while CF is a contamination factors determined as shown in equation 2.6 above.

When $PLI < 1$, the sediment is not polluted while $PLI = 1$ indicates presence of heavy metals at only their baseline levels. When $PLI > 1$, the sediment is polluted, hence the need for intervention to curb it.

The pollution load index has been widely applied in studies assessing heavy metal pollution in environmental media. In the study by Rahman (2011), pollution load indices (PLI) were used to assess heavy metal contamination in Sitalakhyia, Buriganga and Turag rivers in India. According to the PLI values obtained, three sampling sites along Turag River were unpolluted while two were polluted. All locations in Buriganga River were polluted for all elements. In the Sitalakhyia River, all locations were polluted.

Rabeeet *al.* (2011) used pollution load index to assess heavy metal contamination in sediments collected from Tigris River in Baghdad. The pollution load index values obtained from the study showed that the sediments were not polluted.

Varol (2011) used pollution load indices to assess the extent of heavy metals (Co, Zn, Pb and Cu) pollution in sediments obtained from the Tigris River in Turkey. The pollution load indices determined from the study revealed that the sediments were moderately polluted in all sampling sites except the first site.

Chakravarty and Patgiri (2009) used pollution load indices to assess heavy metal (Ti, Fe, Pb, Cr, Cu and Ni) pollution in sediments collected from Dikrong River in India. Based on the calculated pollution load indices, the sediments were found to be contaminated in Pb and Cu.

2.9.5 Analysis of variance (ANOVA)

In this study, ANOVA has been used as a statistical analysis tool to determine the extent to which at least two groups differ or vary in an experiment. In most experiments, a big difference or variance implies that the finding is significant. Most experiments need the researcher to formulate null and alternative hypotheses. The null hypothesis assumes that differences do not exist between the groups tested hence the study will not reveal significant results. In contrast, the

alternative hypothesis assumes the existence of a difference between the groups tested as evidenced by ANOVA done on the data collected (Cardinal and Aitken, 2006). ANOVA has been used in various studies to establish the existence of differences in mean values between groups. For example Viard *et al.* (2004), Atli and Canli (2003), Yilmaza *et al.* (2007) and Clements *et al.* (2000) among others. ANOVA was used in this study to establish whether a difference exists in the mean heavy metal concentrations between the three media.

2.9.6 Pearson Correlation Analysis

Pearson correlation is an analysis that determines the degree to which two variables associate and the direction that their relationship takes. The strength of a relationship assumes a Pearson correlation coefficient whose value lies between -1 and +1. The strength of the correlation can be described using a guide developed by Evans (1996) as shown in Table 2.7 below.

Table 2.7: Classification of Pearson Correlation Coefficients

Pearson Correlation Coefficient	Strength of Correlation
0.00 - ± 0.19	Very weak
0.20 - ± 0.39	weak
0.40 - ± 0.59	moderate
0.60 - ± 0.79	strong
0.80 - ± 1.00	Very strong

When the correlation coefficient is valued around ± 1 , then there is a perfect/significant correlation between the two variables. As the value of the correlation coefficient approaches 0, the correlation between the two variables weakens. A correlation coefficient of 0 implies that there is no correlation between the two variables. The direction of association between variables is denoted by “-” and “+” signs which imply negative and positive directions respectively (Cohen *et al.*, 2014).

Several studies have used correlation analysis to establish the relationship between different variables obtained from the studies. They include Maeset *al.* (2005), Nottenet *al.* (2005), Penget *al.* (2008), Zbikowskyet *al.* (2007) and Muohiet *al.* (2002). Pearson correlation analysis was used to determine the relationship of heavy metal concentration levels between the three media in this study.

Chapter 3

Materials and Methods

3.1 Introduction

In this section, the various methodologies used for the analysis of heavy metal content and the various procedures used in sampling, sample preservation, sample preparation and analysis with EDXRF and TXRF methods are described.

3.2 Sampling and Sample Preservation

In this study, thirty two (32) sampling points were identified along the Thika River ecosystem (Figure 3.1). The criteria used were; presence of all pollution media (water, sediments and *Cladophora*), inflow regions along the river, proximity of industries to the river, drainage patterns, accessibility to the river and proximity of residential units to the river.

Sample collection was done during the first two weeks of September 2015, considered a dry period just before the commencement of the short October-December rains. Selected plant species (*Cladophora*), water and surface river sediments samples were collected at every sampling point identified and labeled W01 - W32, A01 - A32 and S01 - S32 for the water, *Cladophora* and sediment samples, respectively. The elevation and geographical coordinates of each sampling point was determined using hand held global positioning system (GPS) of model Garmin Etrex 10. A brief description of the area around each sampling point was also recorded (Appendix A).

Prior to sampling, sampling equipment and sample containers were thoroughly cleaned to minimize contamination. The Polyethylene (PE) bottles used for water sampling and storage were acid cleaned and soaked overnight in a plastic bucket containing soapy water. Thereafter, they were rinsed in tap water followed by further cleaning with distilled de-ionized (ultrapure) water. The rinsed bottles were immersed in 10% (v/v) concentrated nitric acid (HNO_3) solution and left to stand for three days after which they were rinsed with distilled de-ionized water. This was repeated. After the final rinsing, the bottles were dried in air and stored in plastic polythene bags (IAEA TECH-DOC-950, 1997).

Water samples were directly collected from the water surface using Polyethylene (PE) bottles. At each sampling point, approximately a half litre of water was collected midway across the river by

submerging the PE bottles just below the water surface. The temperature and pH of the water samples collected were measured using pH meter of model HI98127 and acidified immediately with a drop of concentrated nitric acid (HNO₃).

Surface sediments, each weighing 0.3-0.5 kg, were collected at every sampling point identified along the river's profile in this study. The sediments were scooped using an auger, placed in plastic containers and labeled. The sediment samples were dried to constant weight then stored, prior to sample preparation for heavy metal analysis.

In addition, thirty two (32) algae samples of selected species (*Cladophora*), each weighing approximately 0.3-0.5 kg, were collected at every sampling point identified along the river; from hard rock surfaces in the river water where applicable. The algae found in hard substrates were sampled by scraping them off their respective rock surfaces using plastic scrapers. The samples obtained were put in plastic bags and labeled for further laboratory sample preparations.

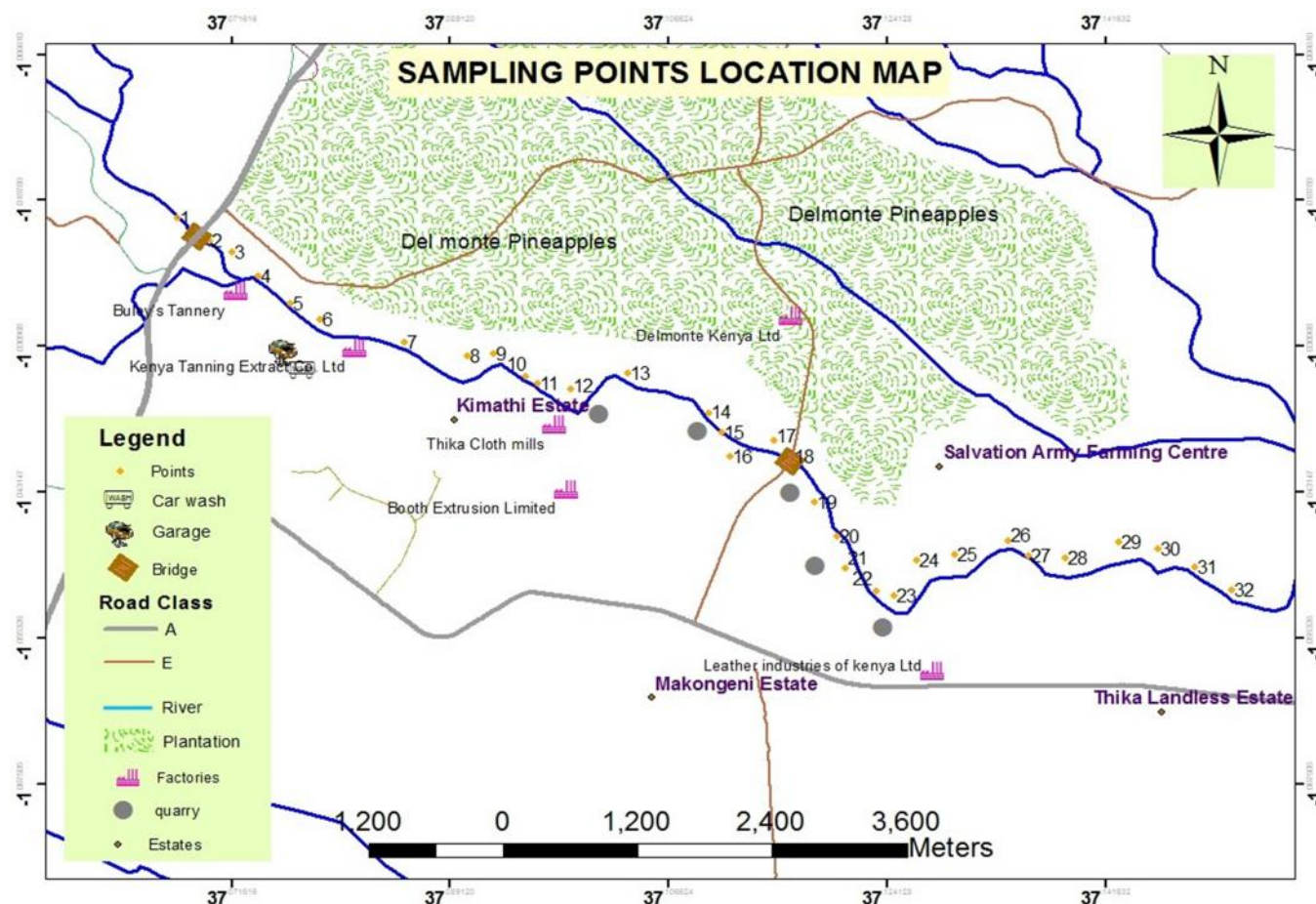


Figure 3.1: Location of the study area and sampling locations along the Thika River

3.3 Sample Preparation and Analyses with TXRF and EDXRF

3.3.1 Procedure for Cleaning of Sample Carriers for TXRF

Prior to sample preparation for TXRF analyses the sample carriers, thick glass substrate of 3 cm diameter, were first cleaned using the following procedure.

The carriers were soaked in soapy water overnight, thereafter wiped with clean tissue, carefully rinsed in distilled water thrice then immersed in Ethylenediaminetetraacetic acid (EDTA) after which they were placed on a hot oven at 150°C in a fume chamber for one hour. The carriers were rinsed three times in distilled water and immersed in a 1000ml beaker containing 0.1% vol/vol nitric acid. The beaker was heated on a hot plate at 150°C in a fume chamber for a further one hour. The carriers were rinsed in distilled water thrice and placed on a hot plate at 50°C until they were dry. The dry carriers were wiped using a soft tissue soaked in annular grade ethanol and placed in clean petri dishes. The carriers were scanned for 100 seconds in the S2 PICOFOX TXRF machine to ensure that they were not contaminated in any way, except for the identification of argon and silicon spectral lines (Figure 3.2). Carriers considered contaminated were cleaned again and rescanned for contamination checks. The clean carriers were stored in clean petri dishes awaiting sample spiking (IAEA TECH-DOC-950, 1997).

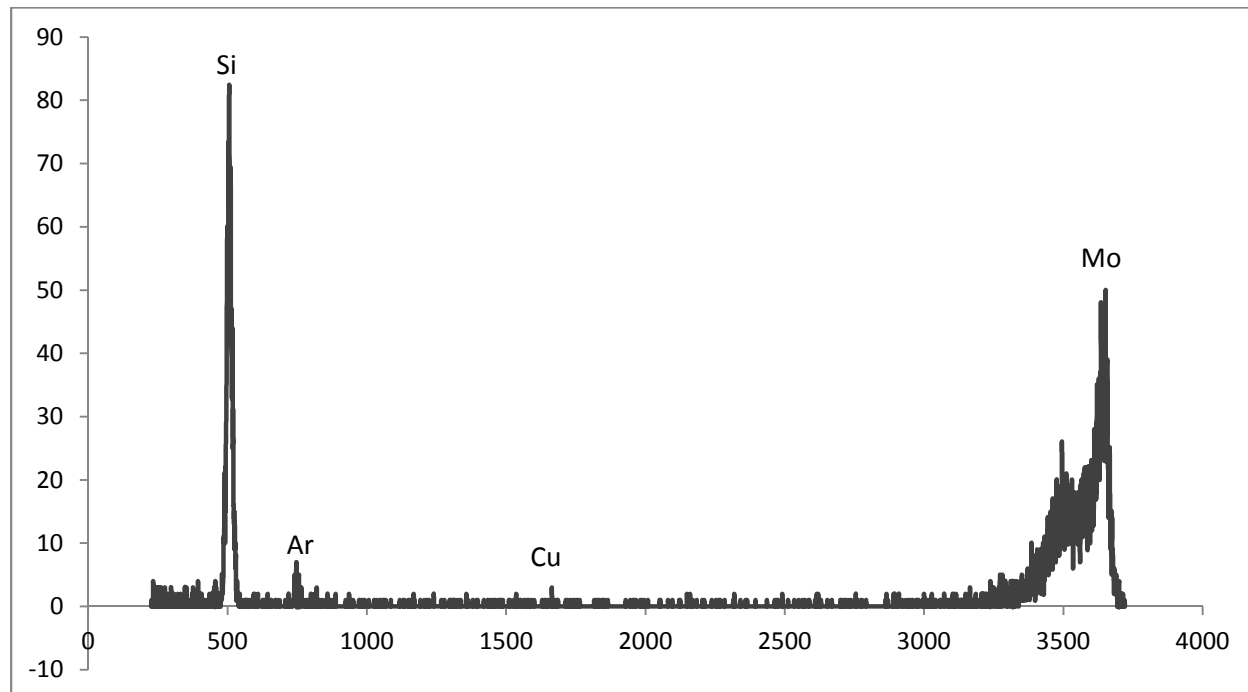


Figure 3.2: Spectrum acquired from the analysis of a clean carrier showing Si peaks

3.3.2 Water samples for TXRF Analysis

Approximately half litre of each water sample was filtered using WHATMAN number 42 filter papers to remove suspended solids. For each sample, three sub samples were prepared by pipetting aliquots of 20 ml of the sample into three separate vials and 10 μ l of Gasolution added as an internal standard solution (1000 ppm). The mixture was then shaken to achieve homogeneity and an aliquot of 10 μ l of each standardized sub sample transferred to a clean carrier, dried at 50°C, and analyzed with TXRF for heavy metal content.

3.3.3 Algae Samples for EDXRF Analysis

The samples were dried to constant weight and crushed in a mortar and pestle to fine powder (~ 100 μ m) after sieving. Approximately 0.3 - 0.5g of the homogenized mixture was then transferred to a die assembly, carefully positioned on a hydraulic press (Figure 3.3) and pressure applied at between 5-8 tons for 3-5 minutes to ensure the powder was fully compressed into a pellet of 2.5 cm diameter. Pressure on the hydraulic press was then released slowly and the die assembly removed and subsequently disassembled to remove the pellet. The mass of the pellet was determined using an electronic balance and recorded. Triplicates of sample aliquots in form of pellets were prepared for EDXRF analyses for heavy metal content (IAEA TECH-DOC-950, 1997).

3.3.4 Sediment Samples for EDXRF Analysis

The samples were dried to constant weight and crushed in a mortar and pestle to fine powder (~ 100 μ m) after sieving. Approximately 1.6g of the fine sediment powder was mixed with approximately 0.4g of starch binder and the mixture thoroughly mixed to achieve homogeneity. Approximately 0.3 - 0.5g of the homogenized mixture was then transferred to a die assembly, carefully positioned on a hydraulic press (Figure 3.3) and pressure applied at between 5 - 8 tons for 3 -5 minutes to ensure the powder was fully compressed into a pellet of 2.5 cm diameter. Pressure on the hydraulic press was then released slowly and the die assembly removed and subsequently disassembled to remove the pellet. The mass of the pellet was determined using an electronic balance and recorded. Triplicates of sample aliquots in form of pellets were prepared for EDXRF analyses for heavy metal content (IAEA TECH-DOC-950, 1997).



Figure 3.3: Hydraulic press and die assembly used for pelletized solid samples (Source: Self)

3.3.5 Instrumentation for the EDXRF Spectrometer

The AMPTEK EXP-1 EDXRF Spectrometer was used for analyzing sediment and algae samples for the heavy metal content. It constitutes of an XR100SiLi detector system, the PX4, the Mini-X, baseplate and sample analysis software.

The X100 constitutes the X-ray Si (Li) detector and its preamplifier. The PX4 constitutes three main parts: shaping amplifier, multichannel analyzer and power supply. The Mini-X is an X-ray tube system that constitutes a 40kV/100 μ A power supply, X-ray Mo tube, USB provision for communication between computer and electronics. The base plate holds the sample, detector, and radiation source to a well-known fixed geometry. The source and detector are positioned at an angle of 45° relative to each other for scatter and incident angles of 67.5°. The distance between the detector and the sample is 1.6 cm. The software used in this system constitutes the ADMCA tube control and data acquisition software and XRS-FP spectrum analysis software (Deangelo and Bedford, 2016). The AMPTEK EXP-1 EDXRF Spectrometer system used in this study is available at the Institute of Nuclear Science and Technology, Nairobi University (Figure 3.4).

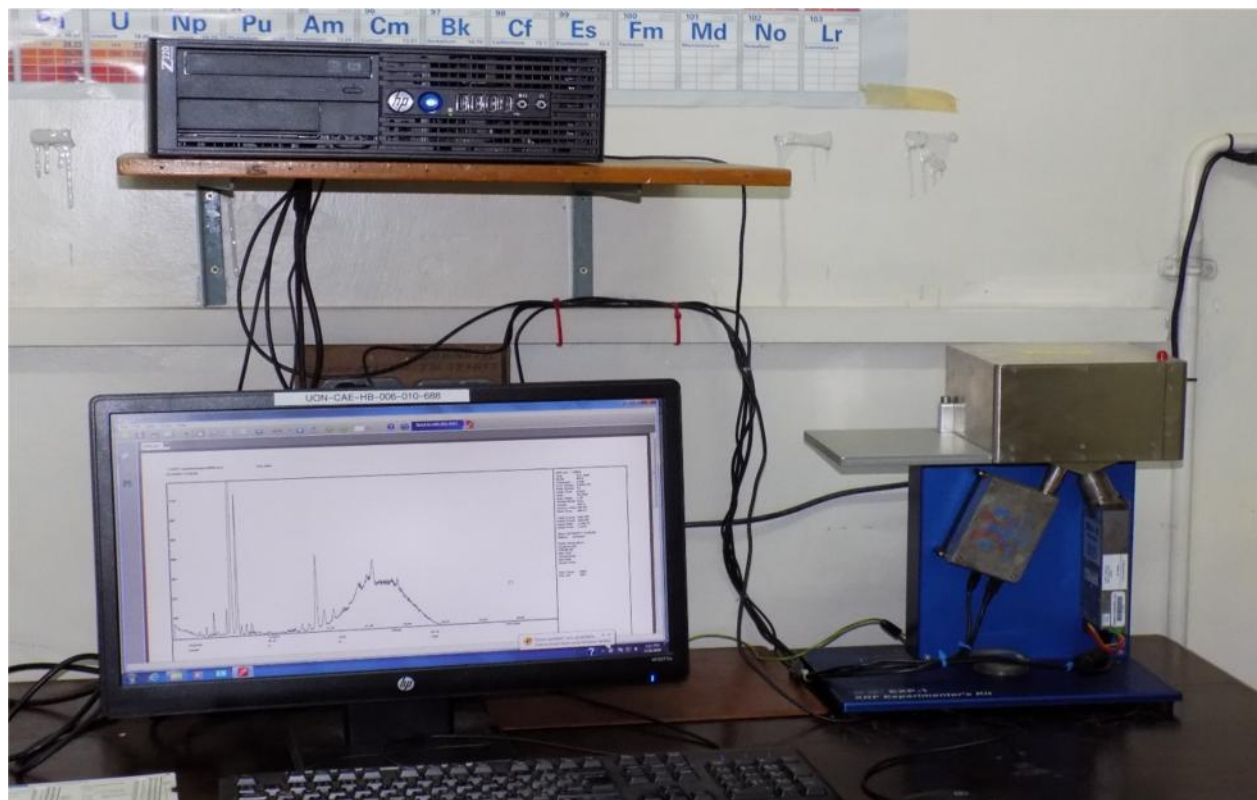


Figure 3.4: The AMPTEK EXP-1 EDXRF Spectrometer system (Source: Self)

3.3.6 Instrumentation for the TXRF Spectrometer

The S2 PICOFOX TXRF system used for analysis of water sample in this study consists of an x-ray spectrometer, spectral acquisition and quantification software (Bruker AXS Inc., 2015).

The X-ray spectrometer constitutes a Silicon-Drift detector (area 30 mm², resolution (MnK_α 10 kcps) < 160 eV, maximum count rate > 100 kcps), a MNX 50P50/XCC high voltage generator (input 24 V, max. 2.5 A; output max. 50 kV, 2 mA, max. 50 W), a metal ceramic, air cooled x-ray source (Mo, W target, 6° target angle, 100 μm Be window, 50 kV, 1000 μA, 50 W), 17.5 KeV multilayer monochromator, an electronic unit (ADC, 4096 channels, 12 bit) and a single type sample changer (12 V, DC motor) (Bruker AXS Inc., 2015). The S2 PICOFOX TXRF system used in this study shown in Figure 3.5 is available at the Institute of Nuclear Science and Technology, Nairobi University.



Figure 3.5: The S2 PICOFOX Total X-ray Fluorescence system (Source: Indiamart.com)

3.4 Sample Analysis

3.4.1 Water Samples Analyses by TXRF

Prior to sample analysis, the TXRF spectrometer was checked for count rate, sensitivity and resolution on a daily basis during the entire period of analysis by irradiating $1\mu\text{g}$ of Ni, Mn and As for measurement of; sensitivity, resolution and count rate respectively for 1000 seconds.

A multi-elemental standard reference material (KB 10ppm) from Bernd Kraft GmbH was analyzed to validate the analytical procedure used (Figure 3.6).

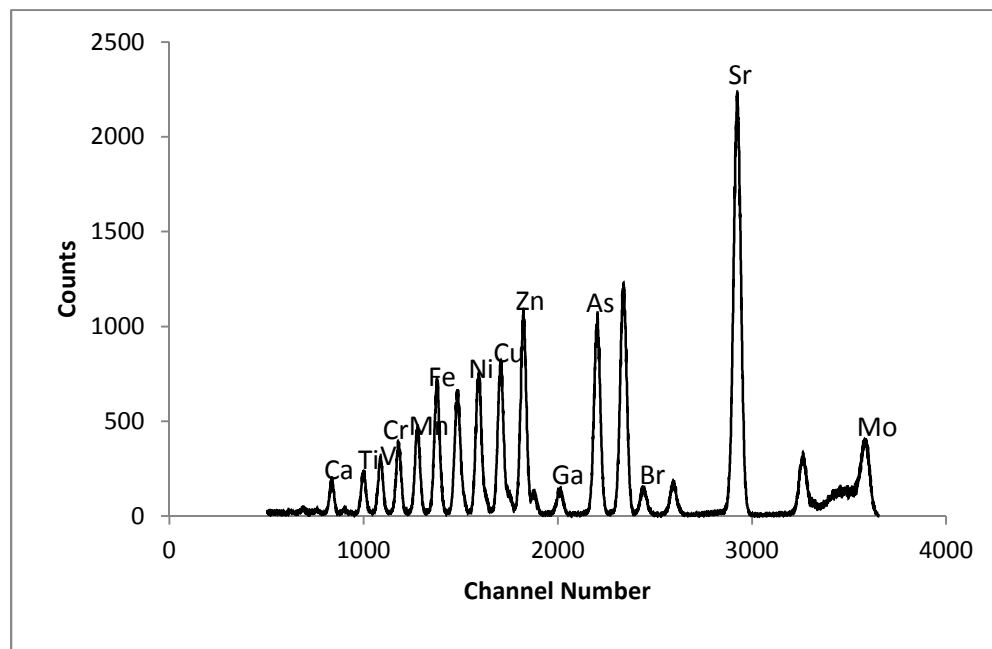


Figure 3.6: TXRF Spectral data of the KB 10ppm multielement standard

$10\mu\text{l}$ of the sample was spiked to a clean carrier and dried at 50°C to form a thin substrate residue and irradiated for 1000 seconds. The spectral data was stored and analyzed for elemental content using incorporated software according to equation 2.1 (Klockenkamper and Bohlen, 1992) and (Klockenkamper and Bohlen, 1989) (Figure 3.7). The results attained were then subjected to further statistical analyses. The lower limit of detection refers to the analyte concentration needed to produce a signal that is greater than thrice the standard deviation of noise level. The lower limits of detection of the TXRF spectrometer used for water sample analyses were determined using the inbuilt S2PICOFOX software. The limits of detection for each element were determined by averaging the detection limits obtained at every sampling point.

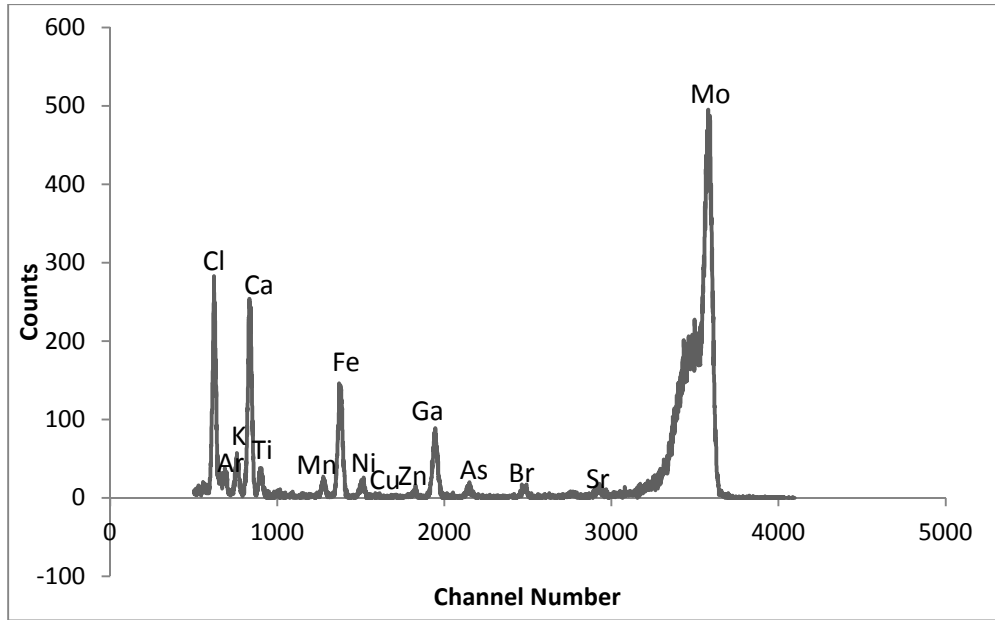


Figure 3.7: A sample spectral data of TXRF analysis of water samples

3.4.2 Sediment Samples Analyses with EDXRF

Sediment samples were analyzed for heavy metal content using the AMPTEK EXP-1 EDXRF Spectrometer. The sample aliquots in pellet form were irradiated for 200 seconds and the spectral data analyzed for elemental intensities. The samples were further irradiated for 100 seconds together with the target, a thick pure metal of Mo for purposes of absorption matrix correction, according to the fundamental parameter method used.

All the spectra obtained from the EDXRF Spectrometer were analyzed for spectral line intensities using AXIL, following conversion of spectrum file formats from MCA to SPE, and finally quantitatively analyzed to obtain concentrations. The accuracy of the results of the analytical procedure used was verified by analyses PTXRF-IAEA09 river clay certified reference material from the International Atomic Energy Agency (IAEA) for the elements of interest. For every sample, three sub-samples were prepared, analyzed and the results averaged.

The lower limit of detection refers to the analyte concentration needed to produce a signal that is greater than thrice the standard deviation of noise level. The lower limits of detection of the EDXRF spectrometer used for sediment and algae sample analyses were determined using the equation below.

$$LD = \frac{3 \times \overline{BA}}{PA} \times C_n \dots \dots \dots 3.2$$

Where LD = Limit of detection (*mg/kg*); BA=Background area; PA = Peak area; and C_n = Elemental heavy metal concentration (*mg/kg*).

3.4.3 Algae Samples Analyses with EDXRF

Algae samples were analyzed for heavy metal content using the AMPTEK EXP-1 EDXRF Spectrometer. The sample aliquots in pellet form were irradiated for 200 seconds and the spectral data obtained were analyzed for elemental intensities and contents using AXIL (Figure 3.8). The samples were further irradiated for 100 seconds together with the target, a thick pure metal of Mo for purposes of absorption matrix correction.

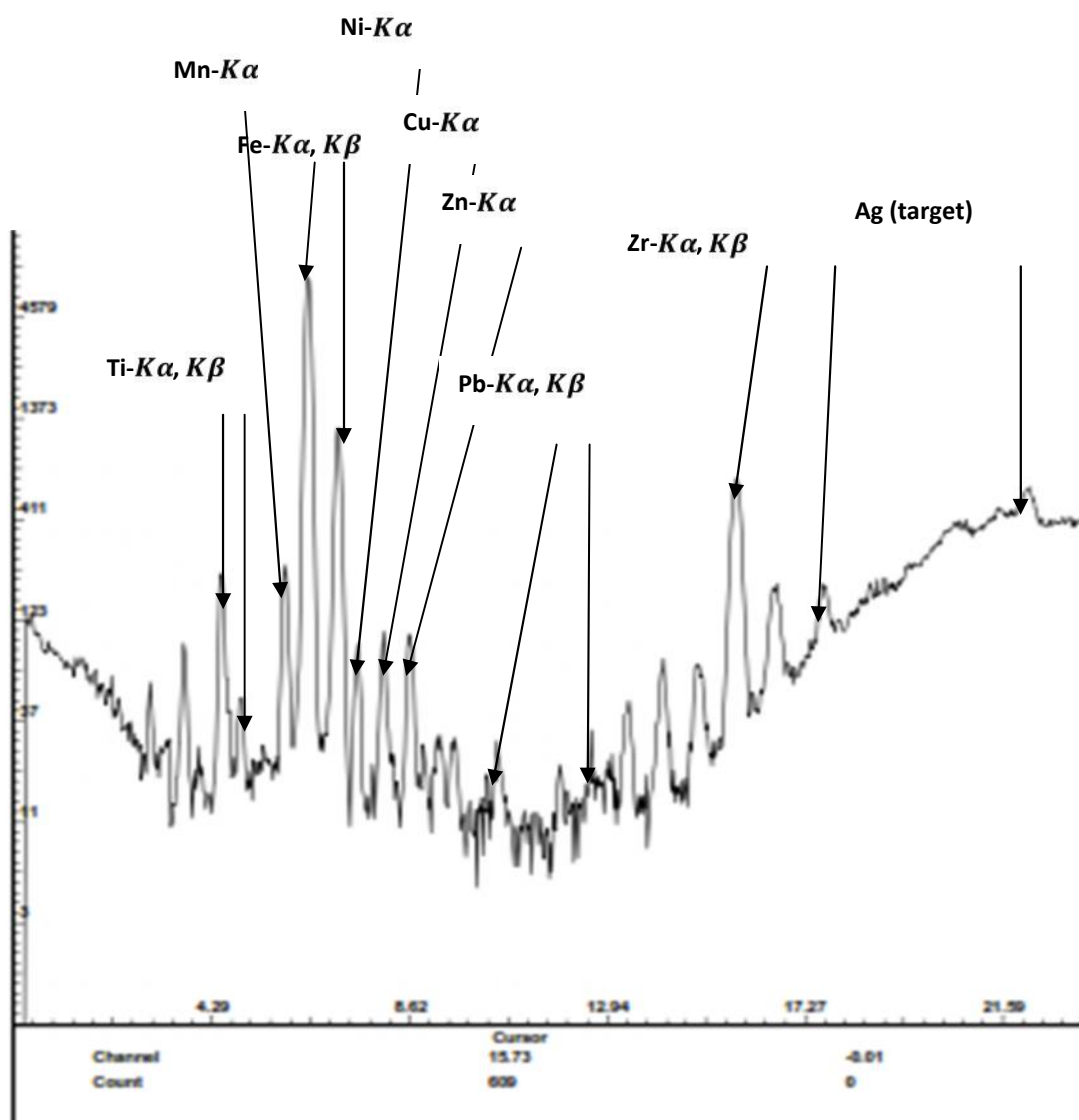


Figure 3.8: A sample spectral data of EDXRF analysis of algae sample

Chapter 4

Results and Discussions

4.1 Introduction

The procedures of the analytical methods used in this study were validated with analyses of Certified Reference Material (CRM) for the elements of interest, namely; Mn, Ni, Cu, Zn and Pb in water, *Cladophora* and sediments. The results of the levels of these elements in the three media as well as their interrelationships are also presented. The results of the extent of heavy metal pollution in these media are also discussed.

4.2 Quality Assurance of Analytical Procedures Used

4.2.1 Standard Reference Material (SRM) (IAEA09-PTXRF)

The accuracy of the EDXRF method used in this study was determined by analyzing PTXRF-IAEA09 river clay certified reference material from the International Atomic Energy Agency (IAEA) for the elements of interest. The results of analyses of the SRM using EDXRF spectroscopy are presented in Table 4.1. In general, there was no significant statistical difference between the experimental values and the certified values for all elements with estimated accuracy 10%.

Table 4.1: Results of PTXRF-IAEA09 river clay certified reference material analyses by EDXRF method (mg/Kg); n=3, X \pm SD

Element	Experimental values	Certified values	Relative standard deviation (%)
Mn	1065 \pm 80	940 - 1060	+9
Fe	29750 \pm 1550	28700 - 30700	+3
Ni	30.6 \pm 9.7	35.5 – 40.3	-10
Cu	17.8 \pm 3.8	18.1 – 22.2	-1
Zn	76 \pm 12.4	88.4 – 103.8	-10
Pb	36.6 \pm 2.8	33.47 – 40.33	+7

4.2.2 Multi Element Standard

The KB multielement standard from Bernd Kraft GmbH was analyzed for Mn, Fe, Co, Ni, C and Zn to assess the accuracy of the TXRF procedure used for analyses of water samples in this study. The standard was a mixture of different metals having a concentration of 10 ppm each. Two metals, Cu and Co, were used interchangeably as internal standards. The results of the mean

experimental values were compared with expected values to assess the accuracy of the method used in this study to analyses liquid samples. The $|t|$ values obtained in this test fell below the critical value (2.45) hence there was no there was no evidence of occurrence of systematic errors. This implies that there were no significant differences in the results of measurements ($p < 0.05$) (Miller & Miller, 2010).

Table 4.2: Results of multi-element certified reference material (KB 10ppm) analysis by TXRF, $X \pm SD$

Element	Experimental values (mg/l)	
	Cu	Co
Mn	9.84 - 0.11	9.52 - 0.34
Fe	12.74 + 1.93	12.51 + 1.77
Co	10.34 + 0.24	10.00 + 0.00
Ni	10.16 + 0.11	9.83 - 0.12
Cu	10.00 + 0.00	9.67 - 0.23
Zn	11.50 + 1.06	11.12 + 0.79
Pb	10.55 + 0.39	10.55 + 0.39
$ t $	1.83	1.14

4.3 Results of Limits of Detection for solid form samples by EDXRF and water Samples by TXRF

The lower limits of detection of the elements under study were determined after analyzing sediment and algae samples in pellet form and calculated using equation 3.1 to the results of elemental data obtained. A mean value was obtained by averaging all the values obtained for all the sampled points. Table 4.3 and Figure 4.1 show the variation of lower limits of detection with increasing atomic number for both methods used in this study. The lower limits of detection for both EDXRF and TXRF analysis decrease with increasing atomic number. For elements with atomic numbers greater than 26, TXRF analysis gives comparatively higher values of limits of detection.

Table 4.3 Lower Limits of Detection for Heavy Metal Elements during EDXRF and TXRF Analysis

Element	Atomic Number	Lower Limits of Detection	
		EDXRF(mg/kg)	TXRF ($\mu g/l$)
Lead	82	10	10
Zinc	30	15	10
Copper	29	19	10
Nickel	28	24	15
Iron	26	67	25
Manganese	25	95	30

Variation of Lower Limits of Detection for EDXRF and TXRF Analyses

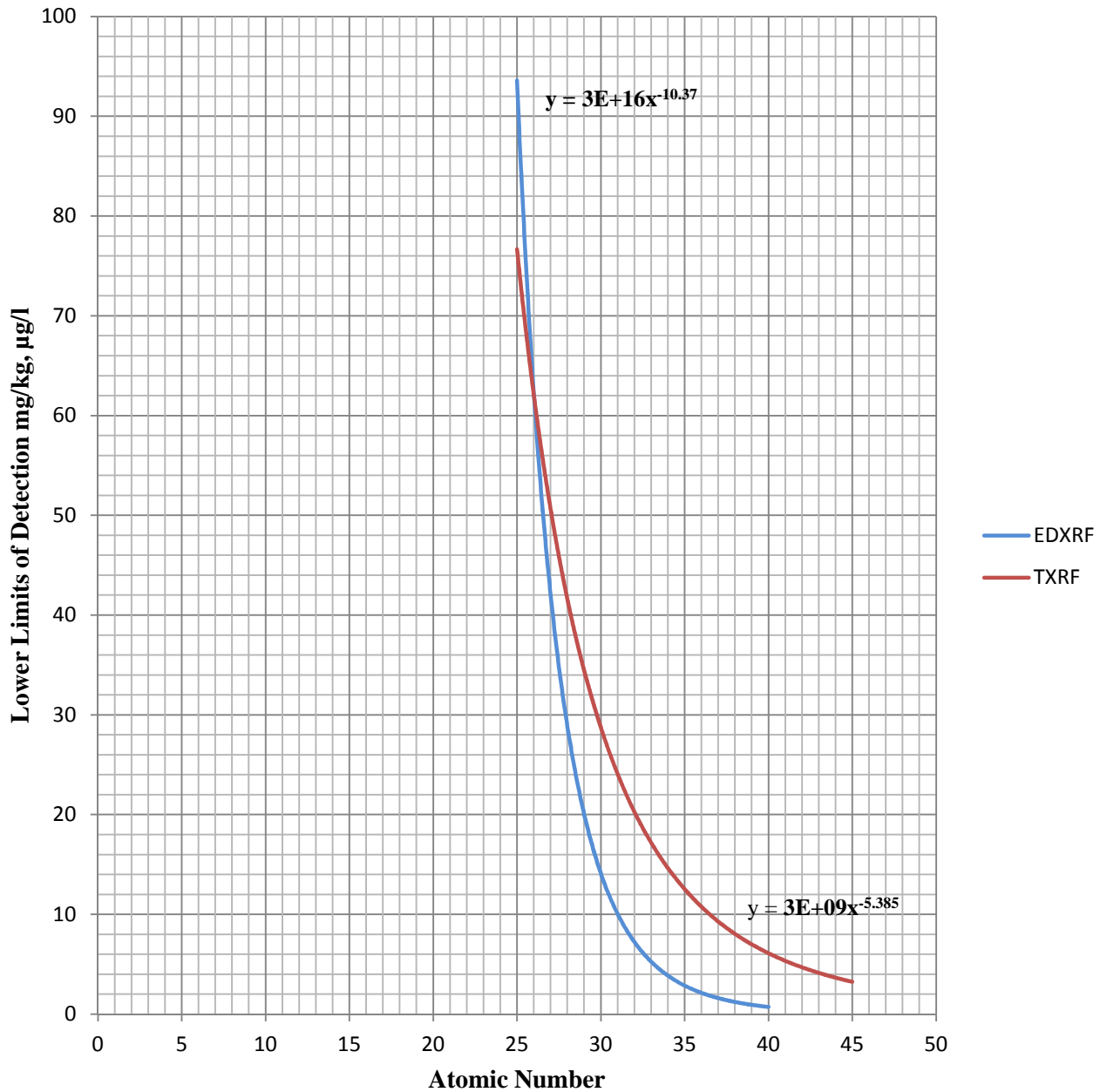


Figure 4.1 Lower limits of detection from EDXRF and TXRF analyses of sediment pellets and water samples respectively

4.4 Heavy Metal Concentration Levels

4.4.1 Water Samples

The results of TXRF analyses of water samples are presented in Table 4.4.

Table 4.4: Results of TXRF analyses of water samples ($\mu\text{g l}^{-1}$), $n=3$, $\bar{X}\pm\text{SD}$

Element	Mn	Fe	Ni	Cu	Zn	Pb
W1	53.5 ± 8.0	630± 60	< 15	12.5± 2	35.0± 2.0	< 10
W2	76.0± 2.0	962± 31	< 15	< 10	27.0± 1.0	< 10
W3	87.0± 2.0	1378± 33	24.0± 4.0	16.0± 2.0	48.0± 6.0	< 10
W4	110 ± 12	1818± 59	< 15	28.0± 4.0	47.0± 4.0	15.0± 6.0
W5	221± 19	7919± 109	< 15	24.0± 3.0	64.0± 3.0	62.0± 18
W6	203± 35	2534± 126	29.0± 4.0	< 10	69.0± 6.0	17.0± 5.0
W7	222± 4.0	2808± 323	< 15	12.5 ± 2.0	70.0± 2.0	13.0± 5.0
W8	160± 15	954± 46	21.0± 3.0	82.0± 7.0	56.0± 8.0	< 10
W9	605± 75	3309± 359	< 15	14.0± 2.0	157± 6.0	< 10
W10	201± 6.0	1547± 52	20.0± 2.0	23.0± 3.0	61.0± 9.0	< 10
W11	148± 18	2924± 464	21.0± 3.0	30.0± 5.0	45.0± 5.0	< 10
W12	213± 21	7290± 141	< 15	< 10	33.0± 3.0	< 10
W13	246± 17	1699± 289	< 15	44.0± 5.0	57.0± 6.0	< 10
W14	276± 12	1872± 63	< 15	29.0± 4.0	112± 6.0	55.0± 7.0
W15	226 ± 3	3668 ± 423	< 15	35.0± 1.0	163± 3.0	< 10
W16	429± 35	5430± 589	< 15	21.0± 3.0	75.0± 4.0	16.0± 5.0
W17	306± 35	2155± 43	< 15	17.0± 2.0	34.0± 1.0	13.0± 4.0
W18	244± 29	3171± 236	< 15	< 10	63.0± 4.0	12.0± 5.0
W19	297± 31	3152± 365	15.0± 2.0	115± 8.0	22.0± 1.0	< 10
W20	384± 9.0	9784± 1382	< 15	66.0± 7.0	38.0± 5.0	< 10
W21	450 ± 21	8072± 1079	22.0± 2.0	56.0 ± 6.0	46.0± 8.0	12.0± 4.0
W22	100 ± 16	2055± 118	< 15	303 ± 33	68.0± 20	< 10
W23	304± 40	4321± 134	< 15	12.0 ± 1.0	27.0± 3.0	< 10
W24	188± 18	5152± 750	< 15	32.0 ± 4.0	325± 30	14.0± 5.0
W25	309± 12	4119± 655	45.0± 5.0	153 ± 11	48.0± 3.0	20.0± 5.0
W26	205± 16	2852± 254	19.0± 5.0	15.0 ± 2.0	58.0± 4.0	< 10
W27	224± 29	2602± 296	20.0± 6.0	61.0± 2.0	79.0± 13	< 10
W28	144 ± 20	2261± 391	< 15	16.0± 1.0	73.0± 10	22.0± 7.0
W29	249± 23	2257± 234	22.0± 10	56.0± 11	76.0± 8.0	< 10
W30	239± 10	1426± 190	77.0± 13	13.0± 7.0	69.0± 11	84.0± 3.0
W31	140 ± 5	2097± 264	< 15	< 10	64.0± 8.0	< 10
W32	210± 8	2369± 326	57.0± 4.0	100± 4.0	300± 5.0	49.0± 16
MIN	53.5 ± 12	630 ± 21	< 15	< 10	22.0 ± 1.0	< 10
MAX	605 ± 26	9784 ± 198	77 ± 13	303 ± 33	325 ± 30	84.0 ± 3.0
MEAN	179	1499	---	---	94	---

The concentration of Mn in water samples ranged from $53.5 \pm 12 \mu\text{g l}^{-1}$ to $605 \pm 26 \mu\text{g l}^{-1}$ while the overall mean concentration was $179 \mu\text{g l}^{-1}$. In general, Mn concentration levels in all water samples analyzed were above the EPA and WHO limits ($50 \mu\text{g l}^{-1}$) for drinking water. The high concentration levels observed at site 09 may be attributed to the close proximity of the Thika Cloth Mills Factory, whose waste waters may find its way into the river ecosystem.

The results of Cu concentrations in all water samples analyzed were below the WHO minimum levels ($2000 \mu\text{g l}^{-1}$). However, 13% of the samples exceeded the WHO limit ($100 \mu\text{g l}^{-1}$) and NEMA. The maximum Cu concentration ($303 \pm 33 \mu\text{g l}^{-1}$) was recorded at site 22. The potential sources of contamination impacting this site include dust from mining activities in the quarry and wear of brake pads on vehicles plying the nearby road.

The Zn concentrations ranged from $22 \pm 1.0 \mu\text{g l}^{-1}$ to $325 \pm 35 \mu\text{g l}^{-1}$ with an overall mean concentration of $94 \mu\text{g l}^{-1}$. The potential sources for a relatively high Zn concentration levels recorded at site 24 ($325 \pm 35 \mu\text{g l}^{-1}$) include; the use of fertilizers and pesticides in the cultivation of pineapples by Delmonte (K) Ltd and combustion of fuel from the nearby road (Karageorgis, 2009).

The Ni concentrations ranged from $<15 \mu\text{g l}^{-1}$ to $77 \pm 13 \mu\text{g l}^{-1}$. The Ni concentrations in three water samples (W25, W30 and W32) tested exceeded the WHO limit ($20 \mu\text{g l}^{-1}$). The potential sources of high Ni levels at site 30 include sewage from the nearby Thika Landless Estate and combustion of diesel and fuel oil from vehicles plying along the nearby road (Clayton and Clayton, 1994; Clarkson, 1988).

The Pb concentrations ranged from $< 10 \mu\text{g l}^{-1}$ to $84.0 \pm 3.0 \mu\text{g l}^{-1}$ in 44% of the samples were above the WHO limits for drinking water ($10 \mu\text{g l}^{-1}$) and water supporting aquatic life ($5.8 \mu\text{g l}^{-1}$). The concentrations were notably high at points 05, 14 and 30 where values of ($62 \pm 18 \mu\text{g l}^{-1}$), $55 \pm 7 \mu\text{g l}^{-1}$ and $84 \pm 30 \mu\text{g l}^{-1}$ respectively. The potential sources of pollution at site 05 include; municipal waste, direct dumping of solid waste from neighbouring residential areas (Kiboko, Kimathi and Thika landless Estates) and release of industrial effluents from Booth Extrusion Limited, Thika Cloth Mills, Bulley's Tannery (Mahler *et al.*, 2006).

The Fe concentrations in water ranged from $630 \pm 21 \mu\text{g l}^{-1}$ at site 01 to $9784 \pm 198 \mu\text{g l}^{-1}$ at site 20 with an overall mean concentration of $1499 \mu\text{g l}^{-1}$.

4.4.1.1 Other Water Quality Parameters

Figure 4.2 shows the results of variation of temperature and pH, respectively along the river profile waters. The temperature of river water ranged from 19.8°C to 25.6°C in general, and that temperature did not influence the rate of heavy metals dissolution in these waters.

The Thika River water samples show a narrow variation of pH values from 6.8 recorded at sampling point 15, to 8.2 recorded at sampling point 6 (Appendix B). At low pH (4-7), the rate of accumulation of heavy metals in sediments and algae increases (Li *et al.*, 2013). However, the pH variation had no significant influence on the sedimentation of heavy metals.

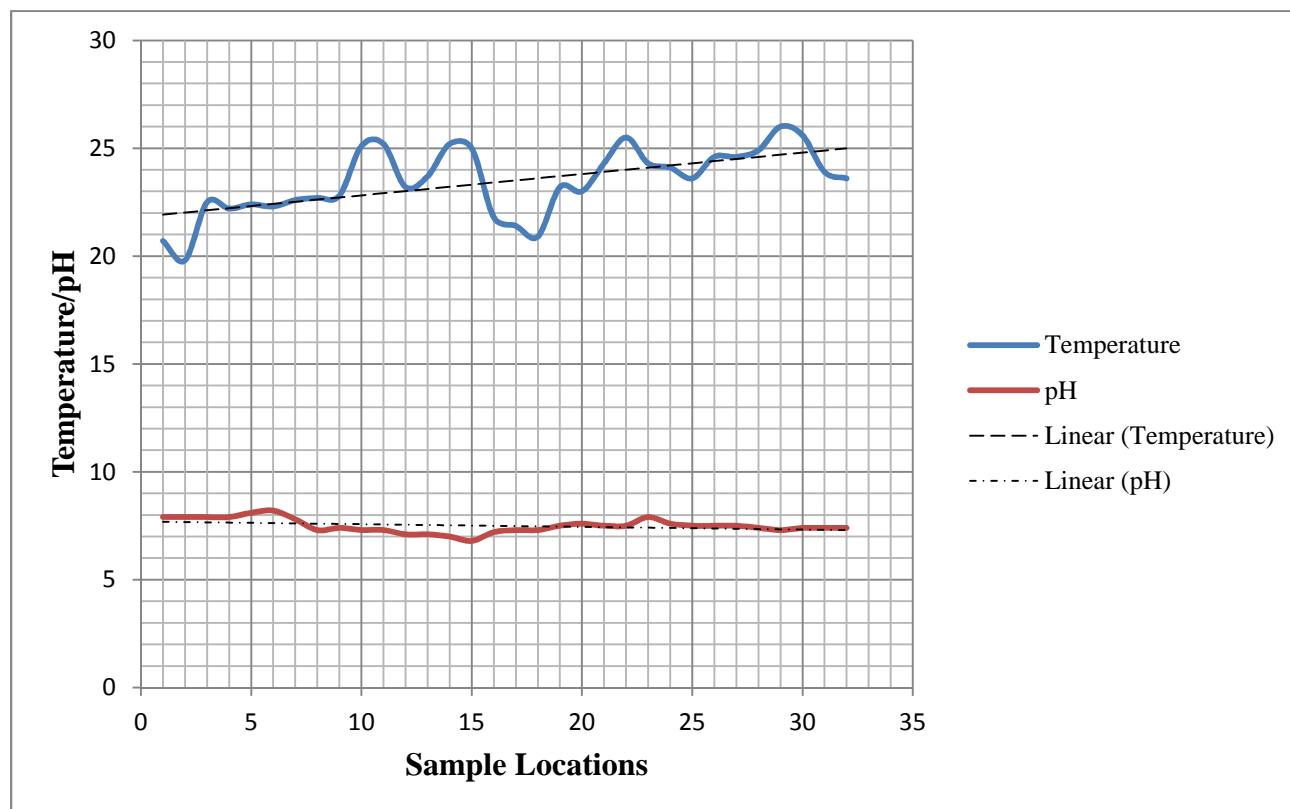


Figure 4.2: Variations of temperature and pH along the Thika River

4.4.2 Algae Samples

Table 4.5 shows the levels of heavy metal concentration in algae samples. The heavy metal concentration levels generally occurred in the order Mn > Zn > Ni > Cu > Pb.

Table 4.5: Results of EDXRF analyses of *Cladophora* samples ($mg\ kg^{-1}$), n = 3, \pm SD

Element	Mn	Fe	Ni	Cu	Zn	Pb
A01	11800± 849	112350± 5727	139± 6.0	123± 13	178±11	38.0± 5.0
A02	21200± 781	149933±5608	182±30	104±27	190± 2.0	41.0± 2.0
A03	16600± 707	144000± 6788	235±35	72.0± 12.0	153±13	48.0±9.0
A04	10965± 687	120700± 7353	136 ± 15	86.0± 10	181± 22	42.0± 8.0
A05	9628± 517	122700± 5370	134± 35	73.0± 17	183± 2.0	40.0± 3.0
A06	10333± 961	131333± 7677	215± 14	89.0± 12	197±14	46.0±7.0
A07	8179± 251	111550± 7141	92.0± 7.0	71.0± 11	238± 27	46.0± 3.0
A08	5055± 144	116267±2886	154± 25	110± 19	434± 17	72.0± 8.0
A09	5807 ± 104	124200± 3041	163± 11	80.0± 10	216± 5.0	41.0± 2.0
A10	3890± 77	114667± 3523	145± 35	65.0±12	216±14	46.0±6.0
A11	3719± 32	107000± 8773	107±37	88.0± 8.0	208± 7.0	41.0± 2.0
A12	4117± 186	112950± 9405	195± 28	79.0± 7.0	226±18	51.0± 2.0
A13	4085±239	117700± 4728	146±32	82.0±24	214±14	47.0± 4.0
A14	4799±225	138200±4504	192± 18	111± 18	178± 5.0	49.0± 6.0
A15	5550± 389	153667± 12365	198± 7.0	129±20	194± 8.0	52.0± 5.0
A16	9507±404	50033± 2307	40.0± 3.0	80.0± 2.0	163± 8.0	17.0± 2.0
A17	5832±370	80067± 2150	82.0± 10	75.0± 11	173± 13	42.0± 2.0
A18	7278± 467	74900± 4603	41.0± 7.0	78.0± 4.0	166± 5.0	33.0± 1.0
A19	4545± 101	26750± 1202	35.0± 2.0	92.0± 2.0	175±1.0	19.0± 1.0
A20	5867±261	159000± 4942	213± 6.0	109± 4.0	206±14	59.0±7.0
A21	6089± 315	106233±3859	143± 41	94.0± 5.0	257±10	39.0± 5.0
A22	11633± 379	109167± 3884	145± 6.0	74.0± 7.0	200± 3.0	34.0± 3.0
A23	9926±385	137967± 2854	225±36	119± 11	217±10	52.0 ± 2.0
A24	7875±549	143933± 11316	217±38	129± 24	203± 4.0	50.0±6.0
A25	11567± 231	138633± 987	227± 30	120± 7.0	226±16	59.0± 3.0
A26	5990± 117	134200± 2443	179±30	99.0± 7.0	200± 5.0	56.0± 2.0
A27	7875± 550	143933± 11316	216±38	129± 24	203± 4.0	50.0± 4.0
A28	12400± 152	136133± 731	184± 28	88.0± 9.0	199± 9.0	45.0± 2.0
A29	12467± 301	133967± 3050	162± 3.0	87.0 ± 6.0	206± 9.0	50.0± 1.0
A30	10267± 102	134867± 5018	176± 9.0	97.0 ± 7.0	190± 9.0	51.0± 1.0
A31	7063± 564	127833± 8328	196± 14	89.0 ± 9.0	203±18	47.0 ± 4.0
A32	9409± 255	130733± 5180	200± 5.0	105± 5.0	208±10	47.0± 4.0
MIN	3719 ± 243	26750 ± 763	35 ± 15	65.0 ± 21	153 ± 14	17.0 ± 3.0
MAX	21200 ± 781	159000 ± 5800	235 ± 34	129 ± 30	434 ± 22	72.0 ± 6.0
MEAN	8478	120174	155	95	206	45

In general, the Mn concentration levels in *Cladophora* ranged from $3719 \pm 243 \text{ mg kg}^{-1}$ at site 11 to $21200 \pm 781 \text{ mg kg}^{-1}$ at site 02, while the overall mean concentration was 8478 mg kg^{-1} . Other sampling sites with similarly high Mn concentrations include 03, 28 and 29 with $16600 \pm 350 \text{ mg kg}^{-1}$, $12400 \pm 467 \text{ mg kg}^{-1}$ and $12467 \pm 633 \text{ mg kg}^{-1}$, respectively. The high Mn levels recorded at site 02 and 03 may be attributed to atmospheric deposition of exhaust fumes from automobile using the busy Thika-Meru highway. The use of agrochemicals in the cultivation of crops may be potential causes of the relatively high Mn concentration levels in sites 28 and 29 (Agency for Toxic Substances and Disease Registry, 2012).

The Cu concentrations (mg kg^{-1}) in *Cladophora* ranged from 65 ± 21 at site 10 to 129 ± 30 at sites 24 and 27. The concentration (mg kg^{-1}) is also high in samples A15 (129 ± 28), A01 (123 ± 24), A25 (120 ± 28) and A23 (119 ± 26). The overall mean concentration for Cu in these samples was 95 mg kg^{-1} . The potential pollutants at site 24 and 27 include automobile brakes. At site 23, the potential sources of pollution include raw sewerage and effluent from leather industries (Figure 1.1). Mining activities at the quarries located approximately 50 metres inland is also a potential source of pollutants at this site (Agency for Toxic Substances and Disease Registry, 2004).

The Zn concentrations (mg kg^{-1}) in algae ranged from 153 ± 14 at point 03 to 434 ± 22 at sampling point 08 with the overall mean concentration being 206 mg kg^{-1} . The potential sources of high Zn concentration level in algae at this site include mining activities from a nearby quarry, and industrial waste from the Thika Cloth Mills (Agency for Toxic Substances and Disease Registry, 2005).

The Ni concentration levels in algae ranged from $35 \pm 15 \text{ mg kg}^{-1}$ at site 19 to $235 \pm 34 \text{ mg kg}^{-1}$ at site 03 with an overall mean concentration of 155 mg kg^{-1} . Other high concentration levels of $215 \pm 38 \text{ mg kg}^{-1}$, $213 \pm 31 \text{ mg kg}^{-1}$, $225 \pm 32 \text{ mg kg}^{-1}$, $217 \pm 32 \text{ mg kg}^{-1}$ and $227 \pm 43 \text{ mg kg}^{-1}$ were recorded at sites 06, 20, 23 and 24 and 25 respectively. Point 06 was characterized by nearby anthropogenic activities; such as farming (bananas and pineapples) and open garage situated approximately 300m from the river. Human waste, garage waste and agrochemicals from farming activities were possible causes for high Ni concentration levels in these samples (Mbuvi *et al.*, 2013). Besides, there were active mining activities in a nearby quarry; as potential point sources of heavy metal river pollution. Industrial waste (point 23) and agrochemicals from

cultivation of bananas, kales as and pineapples (point 25 and 27) are possible causes of high Nickel levels.

The Pb concentration levels in *Cladophora* ranged from $17 \pm 3 \text{ mg kg}^{-1}$ at point 16 to $72 \pm 6 \text{ mg kg}^{-1}$ at sampling point 08 with an overall mean concentration of 45 mg kg^{-1} . The potential contributors of higher Pb concentration levels include direct dumping of Pb containing wastes from nearby residential areas.

4.4.3 Sediment Samples

Table 4.6 shows the results of heavy metal concentrations in sediment samples. The heavy metal concentration levels generally occurred in the order $\text{Mn} > \text{Zn} > \text{Ni} > \text{Cu} > \text{Pb}$.

Table 4.6: Results of EDXRF analyses of sediment samples (mg kg^{-1}), $n=3$, $\bar{X} \pm \text{SD}$

Samples	Mn	Fe	Ni	Cu	Zn	Pb
S01	8659 ± 215	131966 ± 3000	154 ± 32	107 ± 30	160 ± 11	46.0 ± 4.0
S02	5341 ± 141	127800 ± 4600	145 ± 32	68.0 ± 15	161 ± 16	42.0 ± 6.0
S03	6417 ± 356	106533 ± 2887	121 ± 36	62.0 ± 10	154 ± 14	43.0 ± 1.0
S04	7001 ± 326	126733 ± 7830	137 ± 5.0	81.0 ± 17	175 ± 15	43.0 ± 3.0
S05	4399 ± 403	107667 ± 7815	156 ± 45	70.0 ± 23	171 ± 17	49.0 ± 7.0
S06	5155 ± 284	107200 ± 4828	114 ± 27	65.0 ± 19	176 ± 13	42.0 ± 2.0
S07	4136 ± 341	118267 ± 6120	116 ± 23	82.0 ± 18	330 ± 20	90.0 ± 5.0
S08	3665 ± 99	115967 ± 1501	118 ± 18	107 ± 22	432 ± 17	110 ± 7.0
S09	4380 ± 202	117667 ± 1504	144 ± 40	66.0 ± 25	167 ± 2.0	51.0 ± 5.0
S10	4815 ± 158	97367 ± 2532	84.0 ± 22	63.0 ± 16	155 ± 12	38.0 ± 4.0
S11	5119 ± 186	104767 ± 5052	149 ± 40	82.0 ± 26	182 ± 22	44.0 ± 2.0
S12	2795 ± 207	100100 ± 6483	85.0 ± 29	62.0 ± 27	153 ± 15	36.0 ± 3.0
S13	3097 ± 295	126800 ± 4279	156 ± 18	78.0 ± 24	156 ± 5.0	37.0 ± 3.0
S14	4686 ± 206	121967 ± 6390	155 ± 21	84.0 ± 6.0	174 ± 13	78.0 ± 6.0
S15	2901 ± 67	103200 ± 3061	110 ± 13	63.0 ± 31	167 ± 10	32.0 ± 1.0
S16	4433 ± 215	77635 ± 1955	101 ± 16	75.0 ± 15	225 ± 8.0	47.0 ± 3.0
S17	4025 ± 200	99100 ± 2645	81.0 ± 17	70.0 ± 6.0	155 ± 12	49.0 ± 5.0
S18	6902 ± 202	96267 ± 1150	72.0 ± 20	70.0 ± 15	161 ± 7.0	42.0 ± 3.0
S19	4977 ± 155	108500 ± 3439	107 ± 34	85.0 ± 12	162 ± 3.0	45.0 ± 1.0
S20	4263 ± 84	105800 ± 12225	93.0 ± 17	90.0 ± 21	166 ± 18	44.0 ± 3.0
S21	4540 ± 33	101167 ± 2182	123 ± 43	92.0 ± 10	155 ± 16	44.0 ± 5.0
S22	5602 ± 318	114700 ± 6601	118 ± 54	51.0 ± 40	168 ± 16	54.0 ± 5.0
S23	6403 ± 260	99700 ± 819	107 ± 18	80.0 ± 6.0	176 ± 9.0	39.0 ± 2.0
S24	3036 ± 144	110333 ± 8254	112 ± 36	100 ± 25	337 ± 10	90.0 ± 5.0
S25	4221 ± 116	109300 ± 3439	121 ± 27	115 ± 14	396 ± 31	177 ± 10
S26	4775 ± 329	113350 ± 4850	166 ± 20	81.0 ± 25	184 ± 7.0	54.0 ± 2.0
S27	2230 ± 28	130733 ± 4105	134 ± 43	64.0 ± 39	161 ± 13	52.0 ± 2.0

S28	6604 ± 234	97967 ± 4285	122 ± 22	80.0 ± 37	172 ± 6.0	53.0 ± 4.0
S29	6567 ± 400	103500 ± 5345	100 ± 29	66.0 ± 15	182 ± 14	49.0 ± 4.0
S30	4626 ± 91	107400 ± 3843	67.0 ± 20	87.0 ± 20	163 ± 4.0	47.0 ± 5.0
S31	4532 ± 90	112700 ± 1414	118 ± 21	85.0 ± 35	188 ± 13	36.0 ± 4.0
S32	5211 ± 357	130733 ± 9335	172 ± 11	75.0 ± 24	172 ± 13	53.0 ± 4.0
MIN	2230 ± 154	77635 ± 6900	67 ± 26	51.0 ± 40	153 ± 15	32.0 ± 6.0
MAX	8659 ± 436	131966 ± 6100	172 ± 34	115 ± 22	432 ± 21	177 ± 11
MEAN	4817	109198	119	78	198	56

The Mn concentration levels in sediment samples ranged from $2230 \pm 154 \text{ mg kg}^{-1}$ at site 27 to $8659 \pm 436 \text{ mg kg}^{-1}$ at site 01 while the overall mean concentration was 4817 mg kg^{-1} . Point 01 is located under a bridge nearby the Blue Post hotel along the busy Thika-Meru highway and is susceptible to atmospheric deposition of exhaust fumes from automobile using the nearby road as the potential source of high Mn concentration levels (Agency for Toxic Substances and Disease Registry, 2012).

The lowest Cu concentration was $51 \pm 26 \text{ mg kg}^{-1}$ at point 22 while the highest concentration was $115 \pm 22 \text{ mg kg}^{-1}$ at sampling point 25. Point 25 was characterized by intensive pineapple farming a few metres inland and therefore susceptible to agrochemicals carried by surface runoffs as the potential pollutants (Agency for Toxic Substances and Disease Registry, 2004).

The Zn concentration levels ranged from $153 \pm 16 \text{ mg kg}^{-1}$ at site 12 to $432 \pm 21 \text{ mg kg}^{-1}$ at point 08. The high Zn levels at site 08 indicates the possible source of pollutants from nearby Thika Cloth Mills (TCM) and mining activities from nearby quarry (Agency for Toxic Substances and Disease Registry, 2005). Heavy metal accumulation at this site is exacerbated by presence of stagnant water.

The Ni concentration levels in sediments ranged from $67 \pm 26 \text{ mg kg}^{-1}$ at site 30 to $172 \pm 34 \text{ mg kg}^{-1}$ at site 32 while the overall mean concentration was 119 mg kg^{-1} . Nickel is a common pollutant from the repeated usage of phosphate fertilizers in soil (Mortvedt, 1995). The high Nickel concentration levels noted in this study may be attributed to the use of commercial phosphate fertilizers in the nearby Delmonte pineapple farm and raw sewage from the nearby residential units in the adjoining land.

The Pb levels ranged from $39 \pm 5 \text{ mg kg}^{-1}$, at point 23, to $177 \pm 11 \text{ mg kg}^{-1}$, at point 02, while the overall mean concentration was 56 mg kg^{-1} . Major potential contributors to high Pb concentrations include mining activities at the nearby quarry and dumping of solid waste (Agency for Toxic Substances and Disease Registry, 2007).

4.5 Comparison of Variations of Heavy Metal Distributions in Water, Algae and Sediments

4.5.1 Manganese

Figure 4.3 shows the variation of Mn in the three media namely; water, algae and sediments. In general, the concentrations of Mn in *Cladophora* were highest in all sampling locations except 10 and 11.

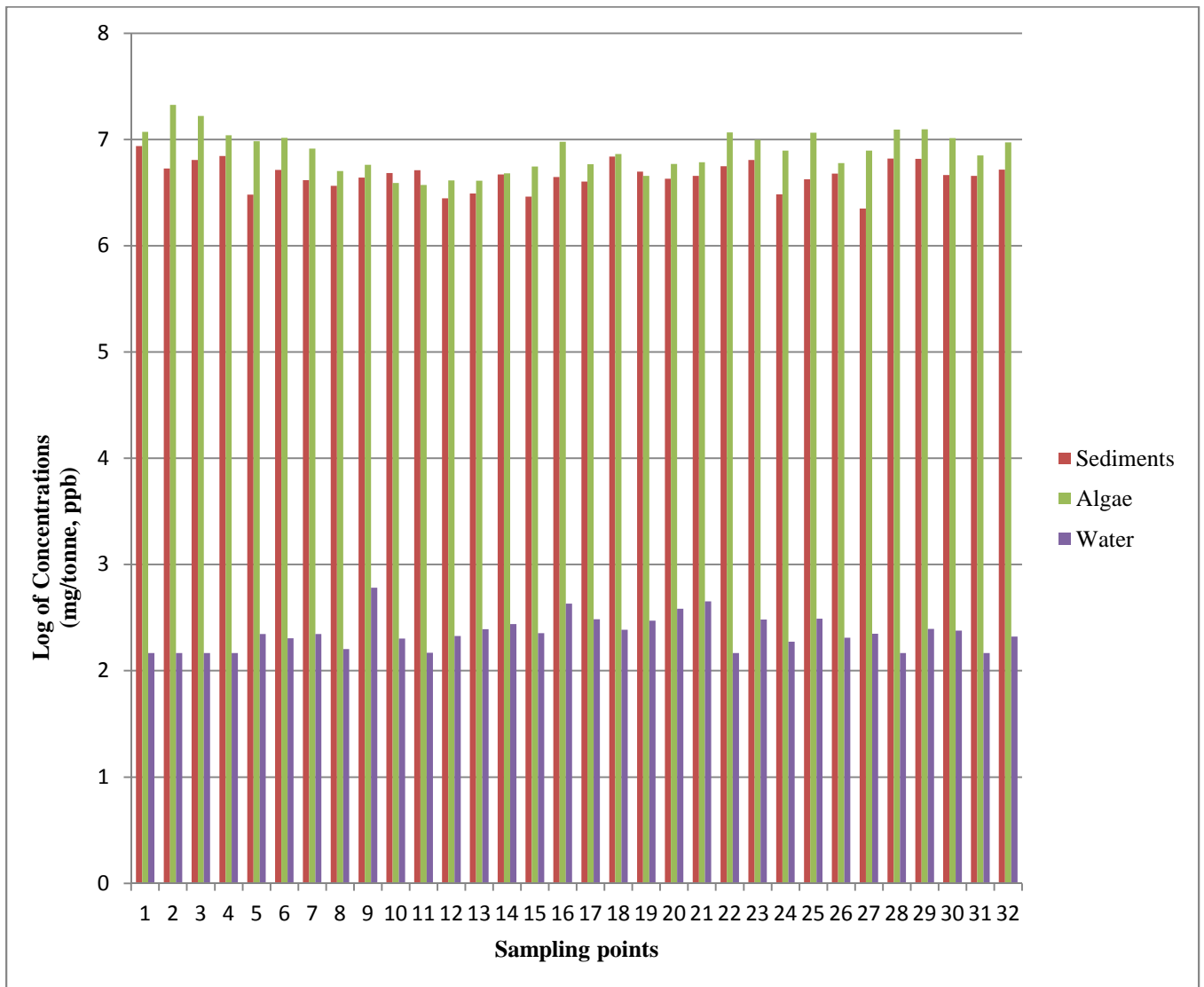


Figure 4.3: Variation of Mn in Sediments, water and *Cladophora* along the Thika River

4.5.2 Copper

Figure 4.4 shows the variation of Cu in the three media namely; water, algae and sediments. In general, the concentrations of Cu in *Cladophora* were highest in all sampling locations.

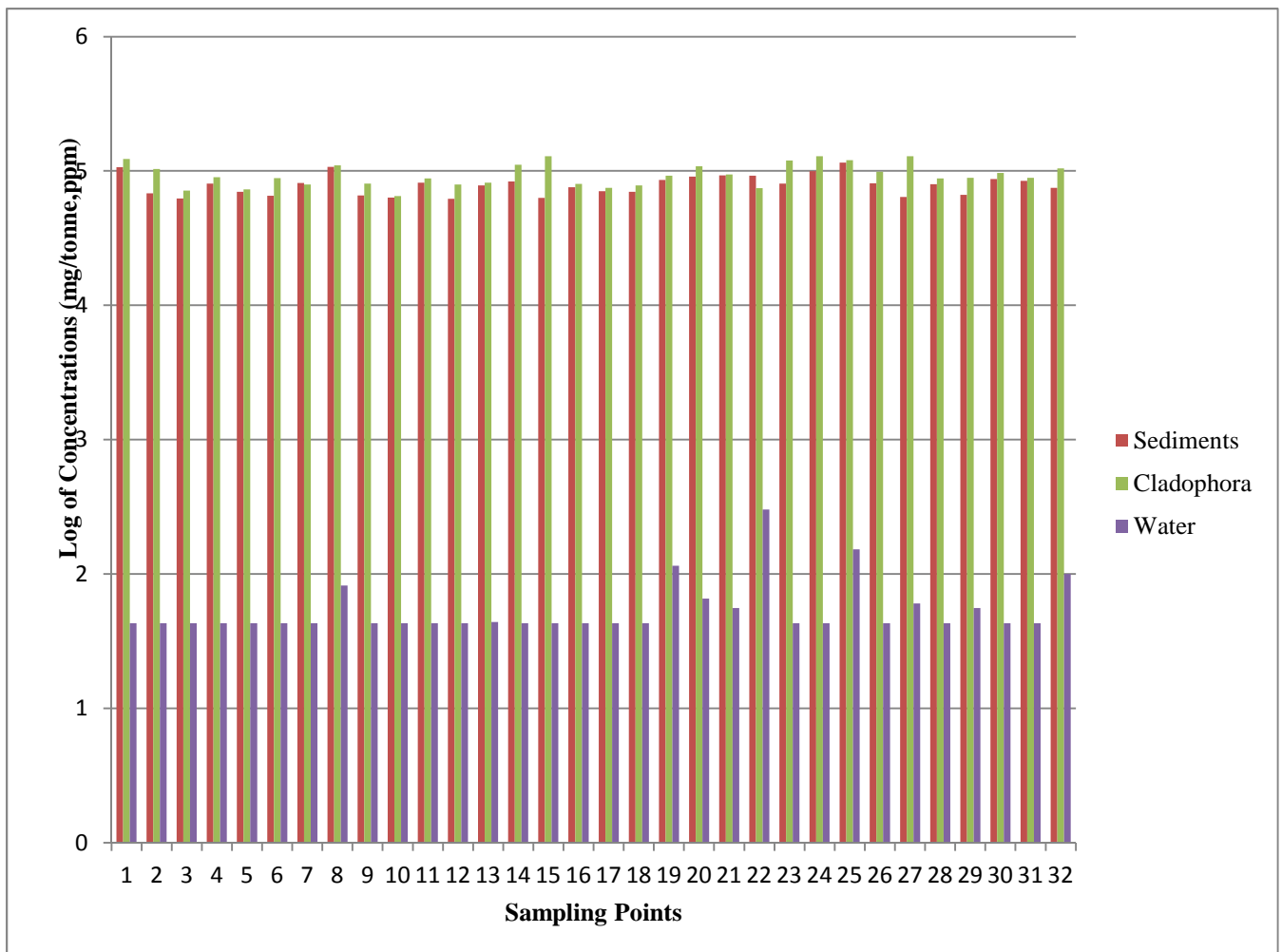


Figure 4.4: Variation of Cu in sediments, water and *Cladophora* along the Thika River

4.5.3 Zinc

Figure 4.5 shows the variation of Zn in the three media namely; water, algae and sediments. In general, the concentrations of Zn in *Cladophora* were highest in most all sampled locations except 5, 7, 8, 25 and 26. Zinc levels in the three media increases downstream.

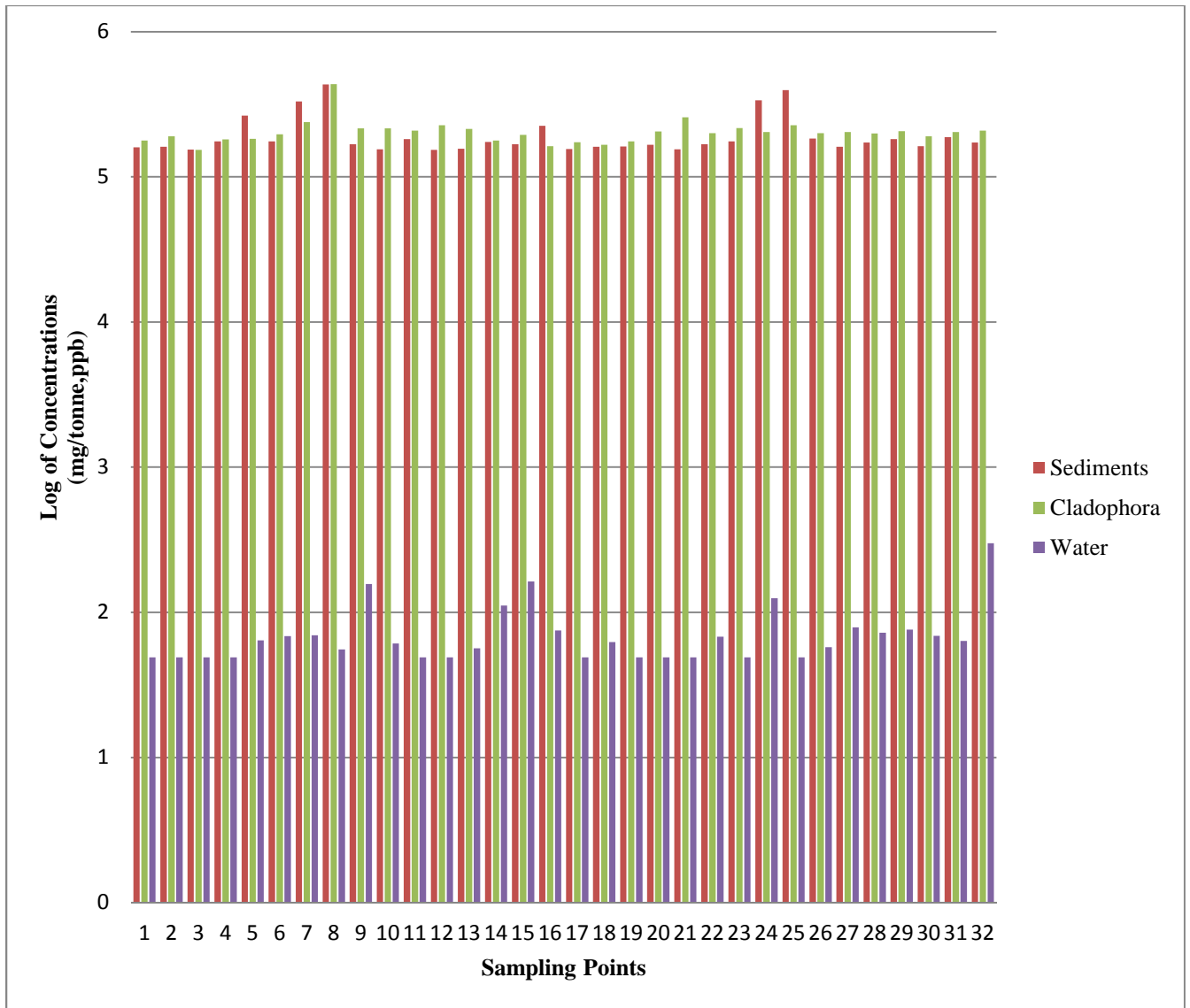


Figure 4.5: Variation of Zn in Sediments, water and *Cladophora* along the Thika River

4.5.4 Nickel

Figure 4.6 shows the variation of Ni in the three media namely; water, algae and sediments. In general, the concentrations of Ni in *Cladophora* were highest.

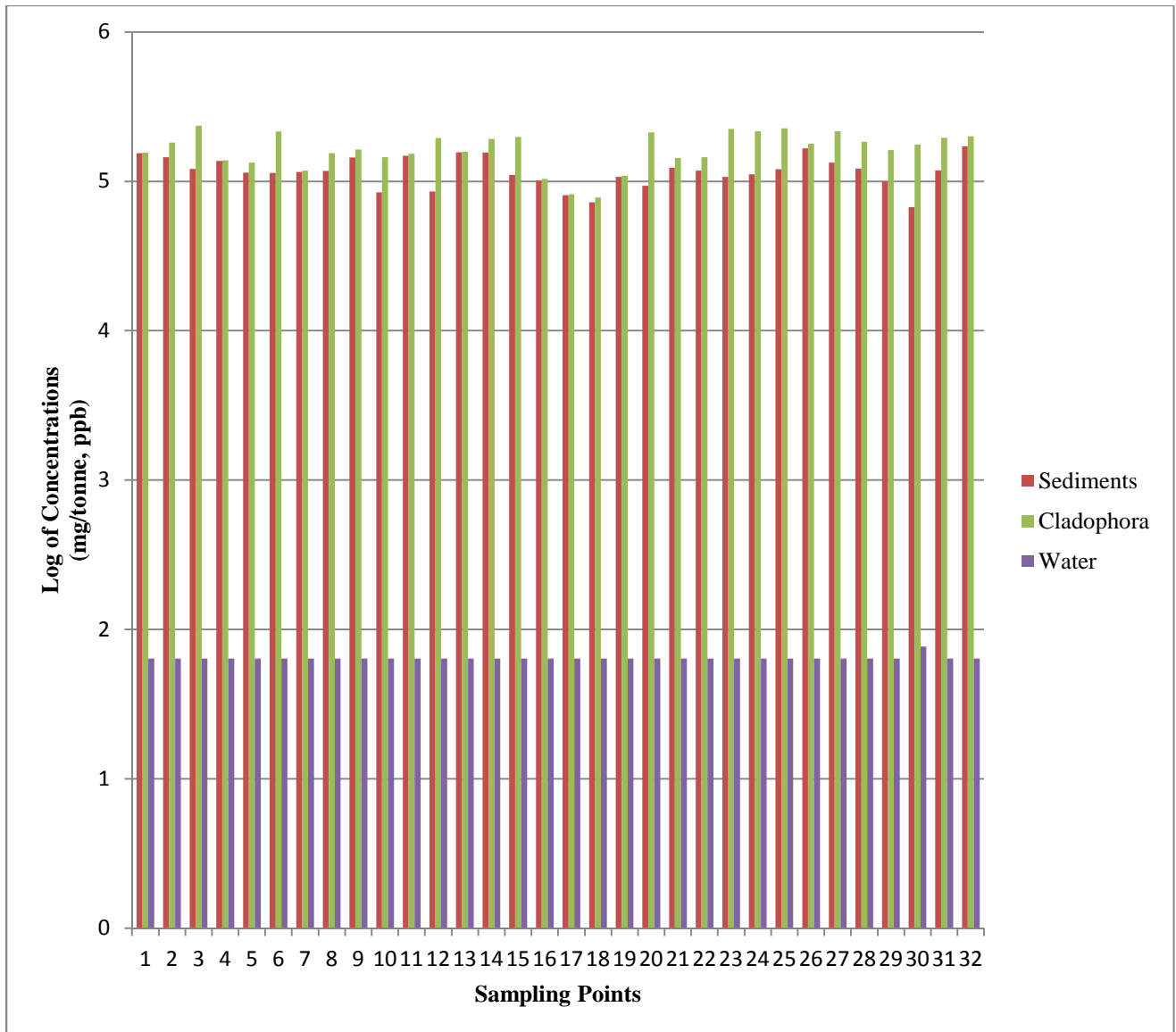


Figure 4.6: Variation of Ni in Sediments, Water and *Cladophora* along the Thika River

4.5.5 Lead

Figure 4.7 shows the variation of Pb in the three media namely; water, algae and sediments. In general, the concentrations of Pb in sediments and *Cladophora* were comparable. However, the levels in sediments were slightly higher most sampled locations. There is no significant variation in Pb levels in all water samples analyzed (< 2 mg/L).

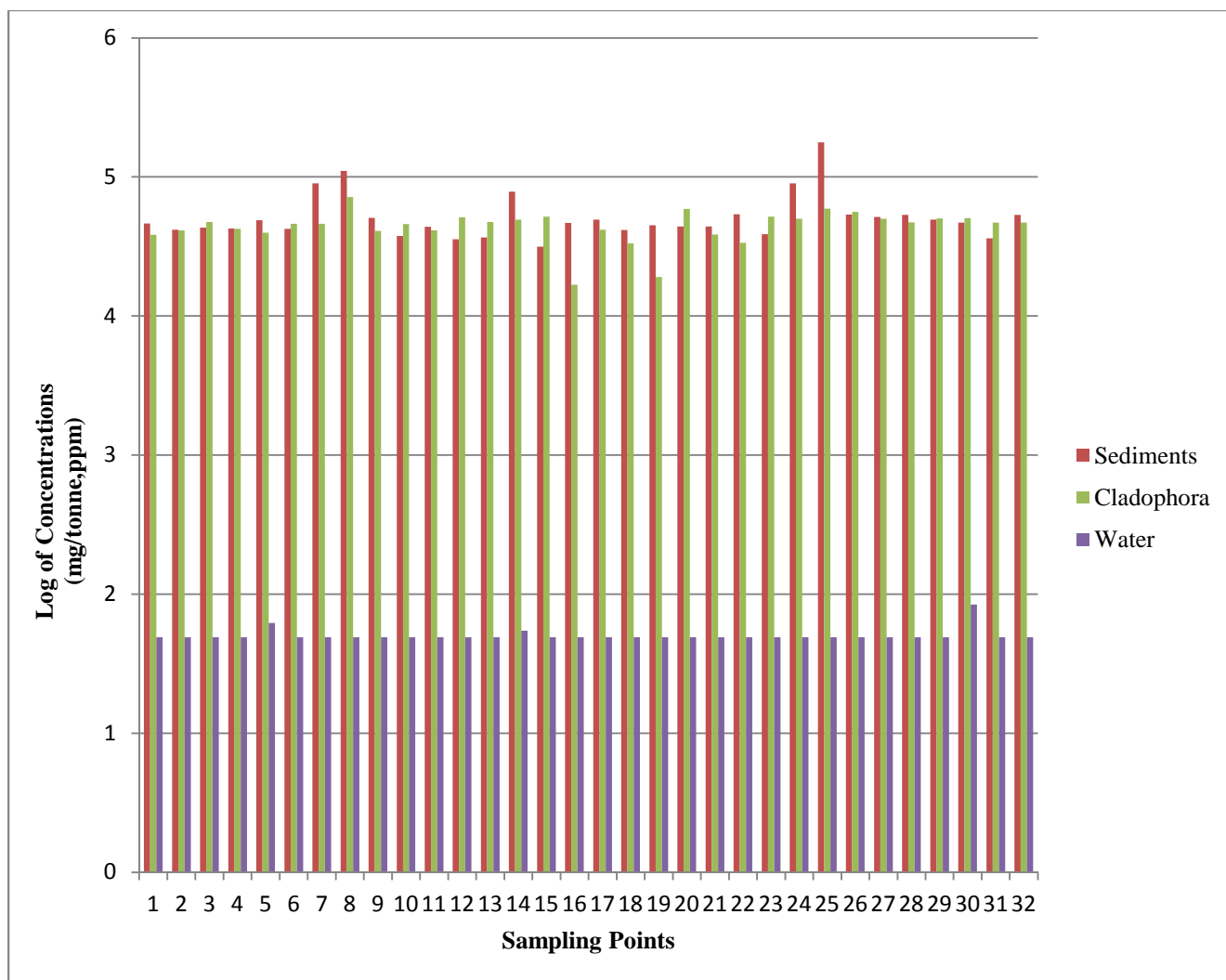


Figure 4.7: Variation of Pb in sediments, water and *Cladophora* along the Thika River

4.6 Relationship of Heavy Metal Distributions in Water, Algae and Sediments

Table 4.7 shows the results of analysis of variance (ANOVA) of heavy metal concentration levels in the three media. The mean elemental concentrations relationships between the three media significantly differ from one another; Zn ($F(175) > F_{crit}(3.09)$), Cu ($F(156) > F_{crit}(3.09)$), Mn ($F(100) > F_{crit}(3.09)$), Ni ($F(57) > F_{crit}(3.11)$), Pb ($F(50) > F_{crit}(3.11)$).

Table 4.8 shows the results of Pearson Correlation Analysis of heavy metal concentration levels in the three media, in which, it is shown that, there is a strong correlations between sediments and algae for most elements; Mn ($r = 0.4679$), Pb ($r = 0.3684$), Cu ($r = 0.7542$), and Zn ($r = 0.6142$). This supports the assertion that algae grow on sediments and are appropriate bio-indicators for heavy metal pollution (Ali *et al.*, 2011).

Table 4.7: Summary of Results of Analysis of Variance of Heavy Metal Concentrations in Water, *Cladophora* and Sediments

Element	Source of variation	SS	df	MS	F	P-Value	F Critical
Zinc	Between Groups	871235	2	435618	175	3.23E-32	3.09
	Within Groups	231963	93	2494	-	-	-
	Total	1103198	95	-	-	-	-
Copper	Between Groups	407444	2	203722	156	1.78E-30	3.09
	Within Groups	121165	93	1303	-	-	-
	Total	528609	95	-	-	-	-
Manganese	Between Groups	1.16E+09	2	5.78E+08	100	7.65E-24	3.09
	Within Groups	5.4E+08	93	5809583	-	-	-
	Total	1.7E+09	95	-	-	-	-
Nickel	Between Groups	3095384	2	1547692	57	4E-16	3.11
	Within Groups	2170263	93	27128	-	-	-
	Total	5265648	95	-	-	-	-
Lead	Between Groups	37964	2	18982	50	1.3E-14	3.11
	Within Groups	29885	78	383	-	-	-
	Total	67849	-	-	-	-	-

Table 4.8: Results of Pearson's Correlation analysis of heavy metal concentrations in water, *Cladophora* and sediment samples

Element	Media	Water	Algae	Sediments
Mn	Water	1		
	Algae	-0.2840	1	
	Sediments	-0.1579	0.4679	1
Ni	Water	1		
	Algae	0.2356	1	
	Sediments	-0.141	0.2185	1
Pb	Water	1		
	Algae	-0.0482	1	
	Sediments	0.0138	0.3684	1
Cu	Water	1		
	Algae	0.07663	1	
	Sediments	-0.0431	0.7542	1
Zn	Water	1		
	Algae	-0.0189	1	
	Sediments	0.3372	0.6142	1

4.7 Extent of Heavy Metal Pollution in Sediments

The extent of heavy metal contamination of sediments collected along the Thika River was determined using pollution indices namely; enrichment factors (EF), geo-accumulation factors (I_{geo}), pollution loading indices (PLI) and modified contamination factors.

4.7.1 Enrichment Factors

Table 4.9 summarizes the percentage frequency of occurrence of each category of enrichment for each heavy metal of interest. The results of calculated enrichment factors (EFs) for sediment samples analyzed in this study are presented in Appendix C.

Table 4.9: Summary of the percentage frequency of occurrence of each enrichment category for each heavy metal of interest

Category	Description	Percentage frequency of occurrence by each heavy metal (%)				
		Mn	Cu	Ni	Zn	Pb
1	Deficiency to minimal	53	47	100	100	100
2	Moderate	47	53	0	0	0
3	Significant	0	0	0	0	0
4	Very high	0	0	0	0	0
5	Extremely high	0	0	0	0	0

In general, sediment samples are equally enriched (minimal ($EF < 2$) – moderate ($2 \leq EF < 5$)) with Mn and Cu, but minimally enriched with Ni, Zn and Pb. Similar results were reported in a study conducted by Chakravarty and Patgiri (2009) on sediment samples collected from Dikrong River in India. In a study by Bentum *et al.* (2011) extremely high enrichment in Pb was reported. This was attributed to the presence of an automobile work shop where automobile repair and other associated activities such as disposal of used batteries were frequent.

However, these findings are slightly different from a study conducted by Varol (2011), on sediments collected from Tigris River in Turkey, in which, all their samples were minimally enriched in Cu. Bentum *et al.* (2011) reported significant enrichment in Cu on sediments collected from Fosu lagoon in Ghana. The study attributed these high levels to dispersion from the upper catchment of Dikrong River basin, which is rich in Cu ore minerals. Chakravarty and Patgiri (2009) reported very high enrichment in Cu, which they attributed to wear of brakes from vehicles that ply daily along the nearby road, and from domestic effluents and sewage from nearby settlements.

4.7.2 Geo-accumulation Indices (I_{geo}^m)

Appendix D summarizes results of the geo-accumulation indices for sediments analyzed in this study. Figures 4.8 to 4.12 show the variation of geoaccumulation indices for Mn, Ni, Cu, Zn and Pb, respectively.

The geoaccumulation indices for Mn range from 0.78 at location 27 to 2.14 at location 01 (Figure 4.8) with a mean value of 1.52. Most of the samples (93%) are moderately polluted ($1 < I_{geo}^m < 2$). Only one sample (S01) was moderately to strongly polluted for Mn ($2 < I_{geo}^m < 3$). However, similar studies by Rabee *et al.* (2011), Chakravarty and Patgiri (2009) and Bucollieri, *et al.* (2006), found sediment samples to be unpolluted.

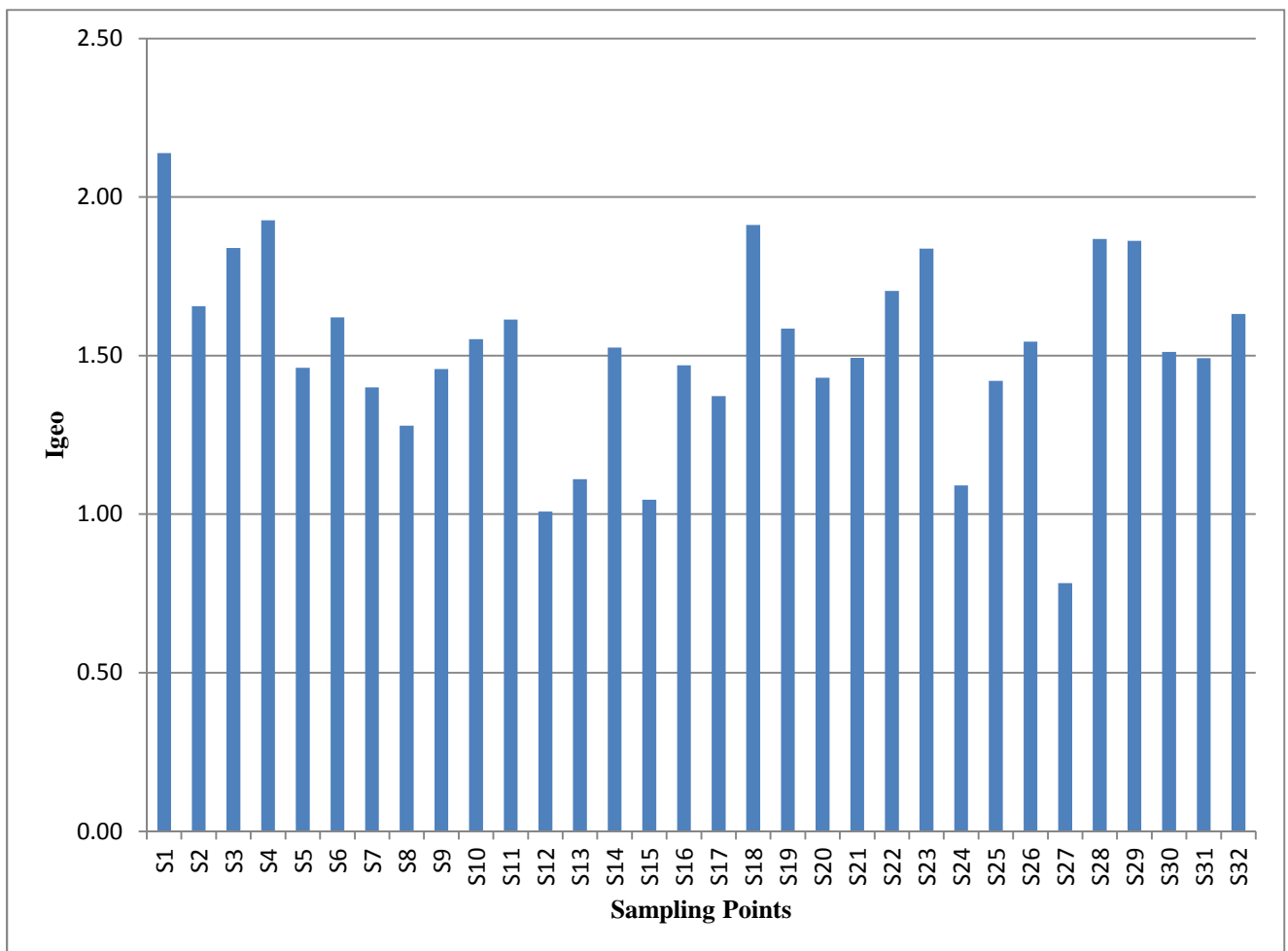


Figure 4.8: Variation of Geoaccumulation Indices for Mn in sediments collected along the Thika River

Figure 4.9 shows the variation of geoaccumulation indices for Ni to range from 0.00 at location 10 to 1.05 at location 32 with a mean value of 0.65. All sampling locations were unpolluted to moderately polluted with Ni ($0 < I_{geo}^m < 1$). These findings were generally similar to studies by Rabeet *et al.* (2011), Chakravarty and Patgiri (2009) and Bucollieri, *et al.* (2006) where the sediments analyzed were found to be unpolluted to moderately polluted.

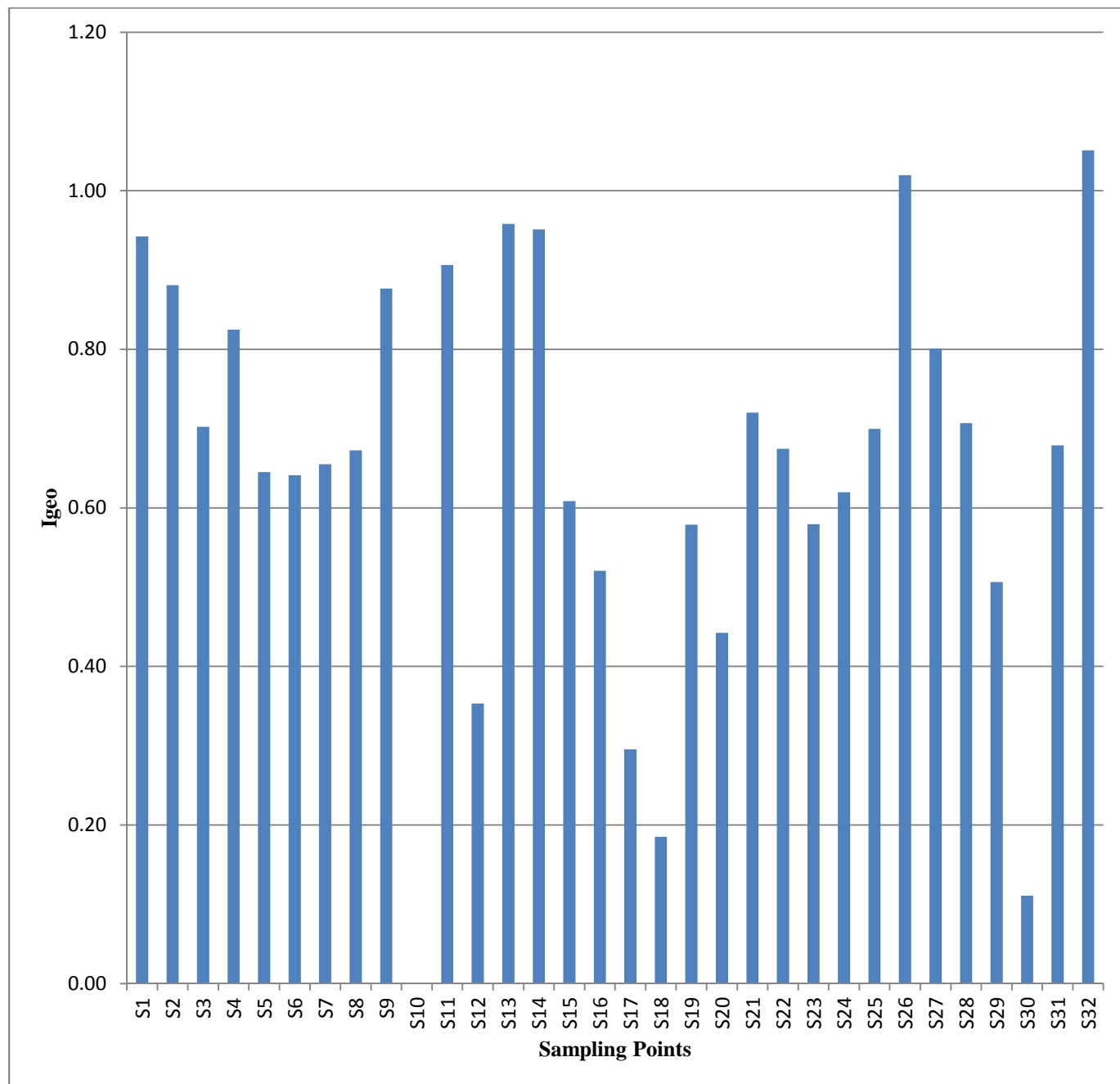


Figure 4.9: Variation of Geoaccumulation Indices for Ni in sediments collected along the Thika River

Figure 4.10 shows the variation of geoaccumulation indices for Cu to range from 0.03 at location 12 to 0.65 at location 25 with a mean value of 0.27. All sampling locations were unpolluted to moderately polluted with Cu ($0 < I_{geo}^m < 1$). In a study by Bentum *et al.* (2011), sediments obtained from on Fosu Lagoon, Ghana were found to be moderately polluted with Cu. Similar findings were reported by Chakravarty and Patgiri (2009) on their study on Dikrong River, India and Bucollieri *et al.* (2006) on sediments from Taranto Gulf in the Ionian Sea, Italy. However, sediments collected from the Tigris River were reported by Varol (2011) to be strongly polluted due to wastewater discharged from a copper mining plant. In comparison, Thika River is less polluted.

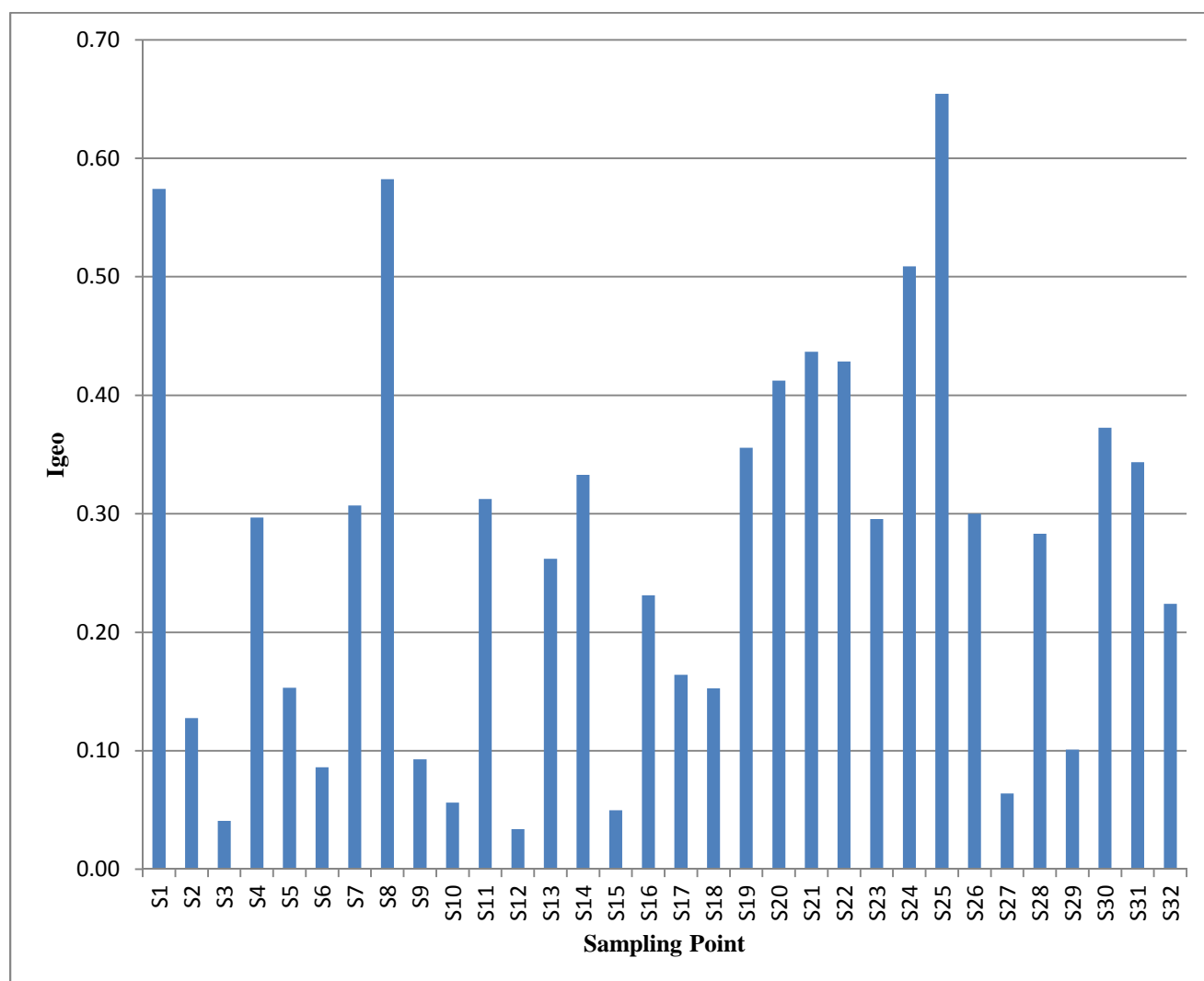


Figure 4.10: Variation of Geo-accumulation Indices for Cu in sediments collected along the Thika River

Figure 4.11 shows the variation of geo-accumulation indices for Zn to range from 0.45 at location 12 to 1.9 at location 8 with a mean value of 0.65. Most locations 1-6, 9–23, 26-32 were unpolluted to moderately polluted ($0 < I_{geo} < 1$) with Zn while locations 7, 8, 24 and 25 were moderately polluted with Zn.

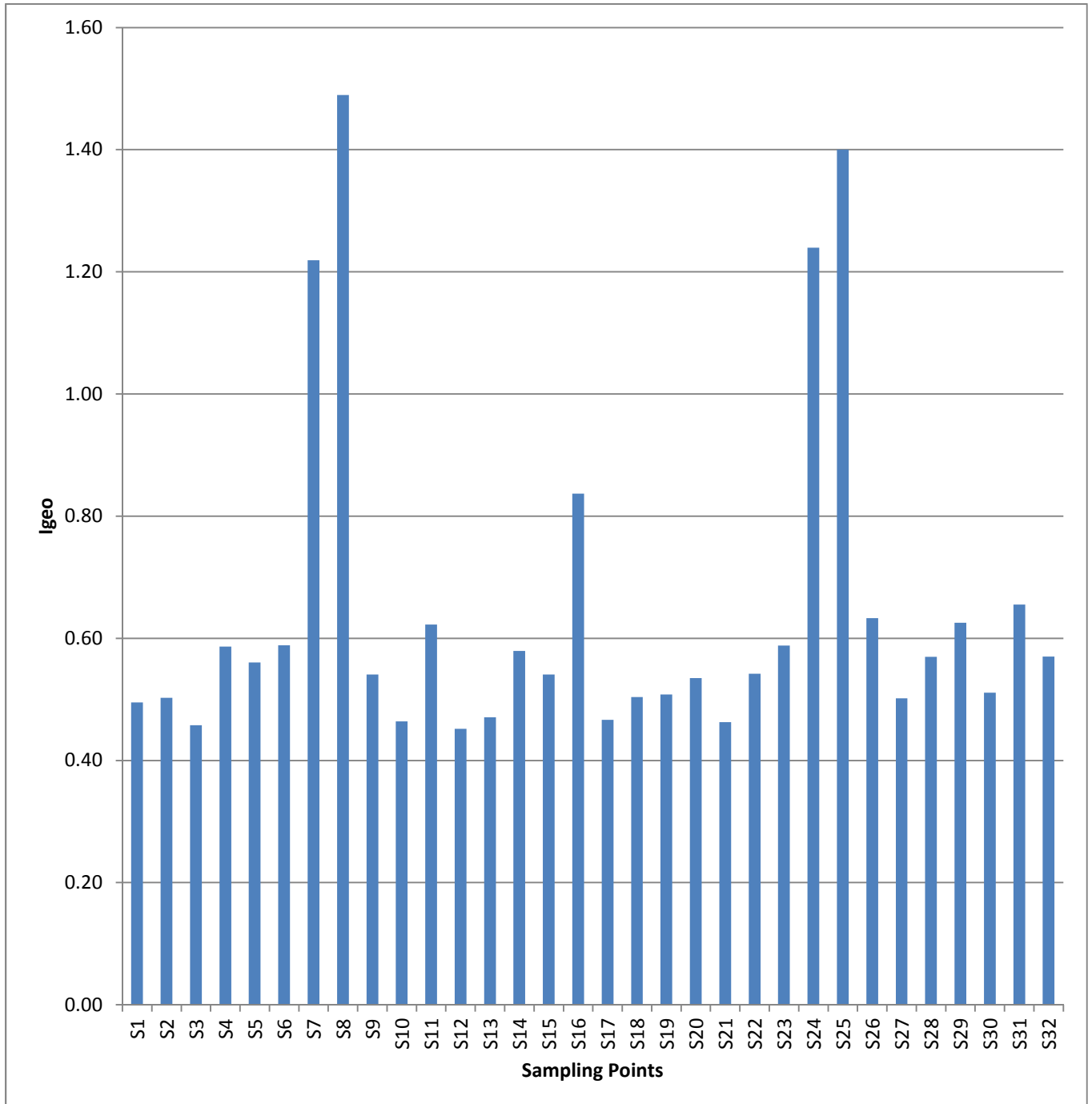


Figure 4.11: Variation of Geoaccumulation Indices for Zn in sediments collected along the Thika River

Figure 4.12 shows the variation of the geoaccumulation indices for Pb range from 0.21 at location 15 to 1.94 at location 25 with a mean value of 0.68. Locations 1- 6, 9 - 21, 23, 26 - 32 were unpolluted to moderately polluted with Pb ($0 < I_{geo}^m < 1$) while locations 7, 8, 24 and 25 were moderately polluted ($1 < I_{geo}^m < 2$). The pollution status of Thika river based on geoaccumulation indices was generally similar to that of Dikrong River (Chakravarty and Patgiri, 2009) and Buriganga River (Rahman, 2011) both in India. However, the Tigris River in Turkey was polluted in Pb to a larger extent with the geoaccumulation indices obtained indicating strong pollution (Varol, 2011).

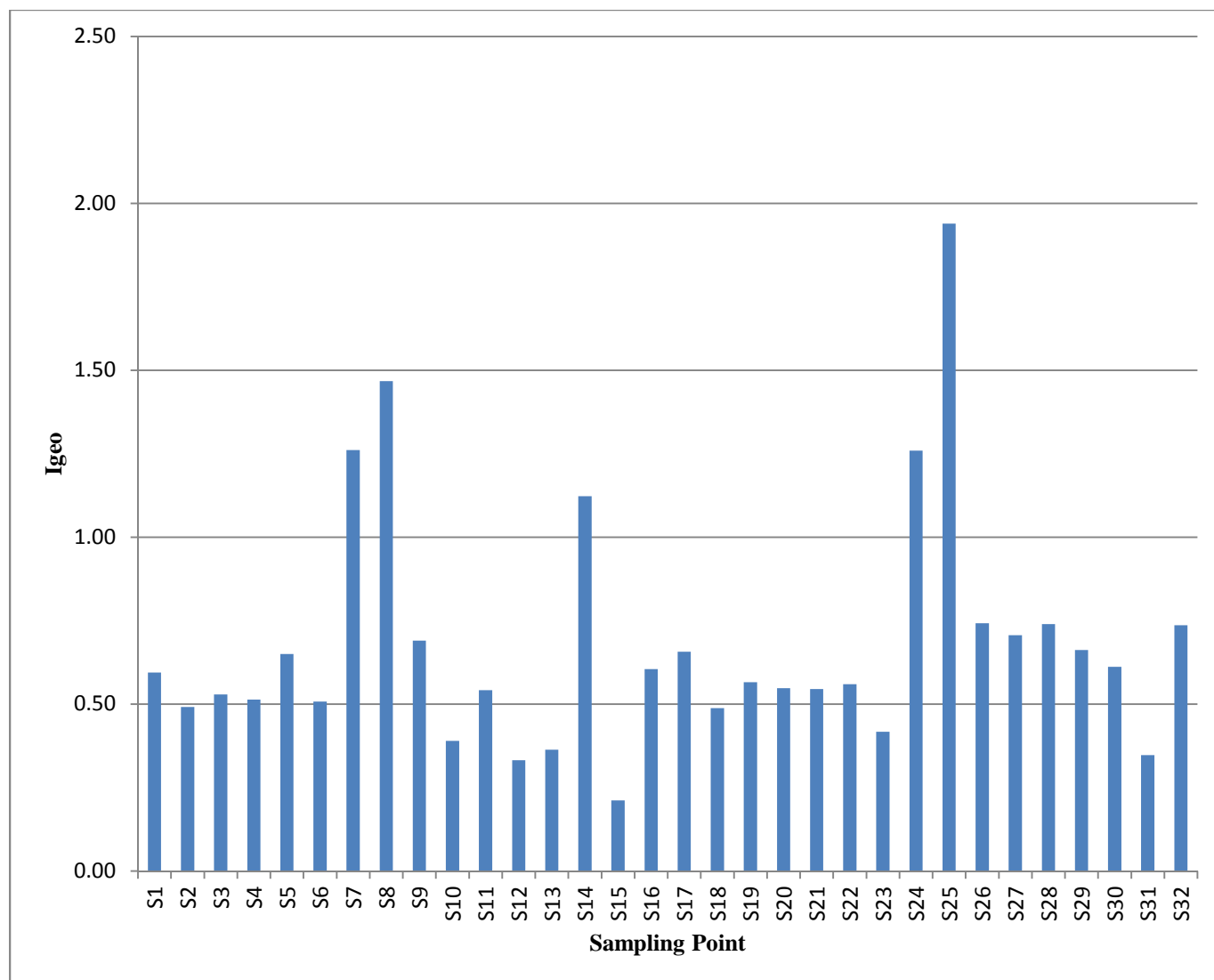


Figure 4.12: Variation of Geoaccumulation Indices for Pb in sediments collected along the Thika River

4.7.3 Contamination Factors (CF), Modified Degree of Contamination (mC_d) and Pollution Load Indices (PLI).

The degree of contamination based on contamination factor and pollution load index were also used to determine the extent of pollution of the Thika River. Appendix E summarizes the results of contamination factors (CF), modified degree of contamination (mC_d) and pollution load indices (PLI) of sediment samples analyzed in this study.

Based on results of enrichment factors, geoaccumulation indices, pollution load index (PLI), contamination factors and modified degree of contamination, all sampled sediments were generally contaminated with Pb, Cu, Zn, Mn and Ni to a moderate degree.

In a similar study, Likuku *et al.* (2013), Shakeri *et al.* (2014), found the samples collected from the Phikwe region in Eastern Botswana to be contaminated in Mn, Zn and Pb to a moderate degree.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

- The variation of heavy metal levels in water samples ($\mu\text{g l}^{-1}$) were as follows: Mn (53.5 - 605), Cu (< 10 - 303), Zn (22 - 325), Ni (<15-77), Pb (< 10 - 84) with mean concentrations ($\mu\text{g l}^{-1}$) of 179 and 94, for Mn and Zn, respectively. Heavy metal contamination levels in water samples, in this study, is variously impacted by; nearby industries, dust from the nearby mining activities and the chemical fertilizers used in the nearby commercial pineapple farms and combustion of fuel from the vehicles plying the nearby roads and therefore unsuitable for drinking.
- The variation of heavy metal concentration levels in sediment samples (mg kg^{-1}) were as follows: Mn (2230 - 8659), Cu (51 -115), Zn (153 - 432), Ni (67 - 172), Pb (32 - 177) with mean concentrations of 4817, 119, 78, 198 and 56 for Mn, Ni, Cu, Zn and Pb respectively.
- The heavy metal variations in *Cladophora* samples (mg kg^{-1}) were as follows: Mn (3719 - 21200), Cu (65-129), Zn (153 - 434), Ni (35 - 235), Pb (17 - 72). The mean concentrations (mg kg^{-1}) of Mn, Zn, Ni, Cu, and Pb were 8478, 206, 155, 95 and 45 respectively.
- There is a significant difference in heavy metal concentration among the three media, following the ANOVA analyses. The levels of heavy metal concentration in sediments and algae generally occurred in the order Mn > Zn > Ni > Cu > Pb but slightly higher in algae in comparison. However, water samples showed a slightly different order in concentration levels (Mn > Zn > Cu > Ni > Pb).
- There is strong correlation between sediments and algae for most elements; Mn ($r = 0.4679$), Pb ($r = 0.3684$), Cu ($r = 0.7542$), and Zn ($r = 0.6142$). This supports the assertion that algae grow on sediments and are appropriate bio-indicators for heavy metal pollution monitoring.
- Based on results of enrichment factors, geoaccumulation indices, pollution load index (PLI), contamination factors and modified degree of contamination, all sampled sediments were generally contaminated with Pb, Cu, Zn, Mn and Ni to a moderate degree, hence requires intervention to curb on the rising levels of pollutants.

5.2 Recommendations

In summary, the study recommends the following measures for mitigation of pollutants in these environmental media:

- a) There is need to create public awareness to the residents using the river water for domestic purposes on the status of pollution levels;
- b) There is need for environmental protection agencies such as NEMA to establish necessary intervention measures to curb the rising levels of pollutants in the river; For instance, introduce bamboo plants along the banks of this river to help in its detoxification;
- c) There is need to critically evaluate the actual components of industrial and municipal waste discharges into the Thika River;
- d) Further studies should be carried out to determine the other sources; organic and inorganic, that contribute to the pollution of the river ecosystem.

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APPENDICES

APPENDIX A: Geographical Coordinates and Descriptions of Sampling Locations

Sampling Point	Elevation (m)	Longitude	Latitude	Description
01	1488	01.02023°S	037.06724°E	Point located under a bridge built across the busy Thika-Meru highway and near the Blue Post hotel. A thin forest cover was spotted nearby and bathing spots identified in areas adjacent to the sampling point.
02	1478	01.02216°S	037.06985°E	The location was surrounded by thick forest with bathing spots nearby. The river was shallow and its bed rocky.
03	1460	01.02316°S	037.07163°E	This sampling point was located at the confluence between the Thika and Chania rivers. Nearby area was covered with a thick forest.
04	1456	01.02512°S	037.07373°E	This point was nearby a residential area with sugarcane, maize, napier grass, bananas, Delmonte pineapple farms noted nearby It was also surrounded by a thick forest.
05	1456	01.02738°S	037.07626°E	The location was adjacent to banana and pineapple farms with a thick forest nearby. Residential units were spotted approximately 200m inland.
06	1456	01.02871°S	037.07870°E	The sampling point was near banana and pineapple plantations. The immediate surrounding area was dominated by thin forest cover with bathing spots located in both upstream and downstream directions.
07	1455	01.03069°S	037.08546°E	The sampling site was located in an area dominated by thin forest cover. A bridge was also spotted a few metres ahead.
08	1454	01.03176°S	037.09047°E	This point was located close to a residential area with raw sewage spotted joining the river directly. The Thika Cloth Mills company is located nearby.

09	1452	01.03164°S	037.09259°E	Point located near the Thika Cloth Mills. Forest cover and napier grass grown on the adjacent land. Pig sty few located few metres upstream with the river water almost stagnant.
10	1449	01.03354°S	037.09520°E	Sampling point located near the Thika Cloth Mills. Banana plantations were spotted a few metres inland.
11	1449	01.03406°S	037.09606°E	Sampling point located near the Thika Cloth Mills. Subsistence farming on nearby land. Thin forest nearby with raw sewage finding its way to the river channel.
12	1448	01.03456°S	037.09877°E	A quarry is located approximately 100m inland with an open bathing spot a few metres upstream. Sampling point located near the Thika Cloth Mills. Pineapple farm located approximately 200m inland.
13	1448	01.033185°S	037.10332°E	Pineapples and sugarcane farms located a few metres inland. Raw sewage from neighbouring residential area released into the river. The Booth industry and United Textile Industry (UTI) located a few metres further inland.
14	1446	01.03656°S	037.10983°E	Point located where river water is almost stagnant. Sugarcane farming done in the surrounding land by residents from the nearby Kiboko estate.
15	1444	01.03817°S	037.11088°E	Pineapples farming done on land nearby. Industries such as Kenya Paper Mills and Delmonte (K) Limited located in the nearby land. An open spot was spotted a few metres upstream.
16	1450	01.04022°S	037.11152°E	Pineapple farming practiced on land nearby. Point located near a busy highway.
17	1446	01.03883°S	037.11509°E	Thin forest cover and pineapple farming

				practiced on nearby land. An open bathing spot and animal watering point were noted. A quarry was located at a point approximately 50 metres inland.
18	1441	01.04014°S	037.11651°E	Thin forest cover and pineapple farming carried out on nearby land. Sample location located adjacent to a residential area.
19	1441	01.04402°S	037.11834°E	Mining activity was spotted as evident in a quarry located approximately 100m inland with an open bathing spot and an animal watering point a few metres upstream.
20	1440	01.04687°S	037.12008°E	Sampling point located at a location adjacent to a salvation army church and a residential area (Umoja Estate). Pineapple farming by Delmonte (K) Ltd taking place on adjacent land with a cloth washing spot located nearby.
21	1437	01.04950°S	037.12079°E	Banana plantation and pineapples by Delmonte (K) Ltd grown on nearby land. An open bathing spot was located nearby.
22	1437	01.05146°S	037.12322°E	Sampling point located at a point surrounded by a thin forest with a quarry and the salvation Army residence approximately 200m further inland. A watering point for domestic animals was located a few metres upstream.
23	1435	01.05182°S	037.12471°E	Raw sewerage from surrounding residential area and a dark smelly discharge from the Leather Industries of Kenya Ltd were released directly into the river channel. A quarry nearby was located approximately 50 metres inland.
24	1435	01.04887°S	037.12653°E	Sampling point located adjacent to the Delmonte (K) Ltd pineapple plantation. Some local inhabitants were spotted brewing chang'aa within the river channel (Figure 1.2). Two other brewing spots were

				spotted on the river shore.
25	1435	01.04841°S	037.12959°E	Surrounding area was characterized by residential units with thin forest cover growing adjacent to the river. Large-scale farming of pineapples was carried out further inland.
26	1434	01.04725°S	037.13388°E	Banana and pineapple plantations were grown on land adjacent to the sampling point. Napier grass and kales were also grown on small scale.
27	1432	01.04849°S	037.13547°E	Pineapple plantations were grown on land adjacent to the sampling point. Napier grass was also grown on small scale. A water pump was spotted nearby.
28	1432	01.04864°S	037.13840°E	Banana plantations were grown on land adjacent to the sampling point. Napier grass was also grown on small scale.
29	1431	01.04733°S	037.14271°E	Surrounding area was characterized by residential units with thin forest cover growing adjacent to the river. Onions, kales and tomatoes were grown on small scale on nearby land.
30	1430	01.04788°S	037.14582°E	Large-scale farming of pineapples was carried out on adjacent land. Residential units were also spotted nearby. Thick forest cover with an open bathing spot was identified near the sampling site.
31	1430	01.04943°S	037.14880°E	Residential units were spotted near the sampling point. The surrounding area was dominated by banana and pineapple plantations as well as napier grass.
32	1428	01.05136°S	037.15179°E	The area surrounding the sampling point had thin forest cover. Banana plantations and napier grass were also spotted.

APPENDIX B: Temperature and pH Variations along the Thika River

Sample Location	Temp (°C)	pH
1	20.7	7.9
2	19.8	7.9
3	22.5	7.9
4	22.2	7.9
5	22.4	8.1
6	22.3	8.2
7	22.6	7.8
8	22.7	7.3
9	22.8	7.4
10	25.1	7.3
11	25.2	7.3
12	23.2	7.1
13	23.7	7.1
14	25.2	7.0
15	25.0	6.8
16	21.8	7.2
17	21.4	7.3
18	20.9	7.3
19	23.2	7.5
20	23.0	7.6
21	24.3	7.5
22	25.5	7.5
23	24.3	7.9
24	24.1	7.6
25	23.6	7.5
26	24.6	7.5
27	24.6	7.5
28	24.9	7.4
29	26.0	7.3
30	25.6	7.4
31	23.9	7.4
32	23.6	7.4

APPENDIX C: Enrichment factors for heavy metal concentrations in sediments

Sample	Mn	Cu	Ni	Zn	Pb
S1	3.00 (2)	1.07 (1)	1.55 (1)	0.21 (1)	0.02 (1)
S2	1.93 (1)	0.71 (1)	1.50 (1)	0.22 (1)	0.02 (1)
S3	2.78 (2)	0.78 (1)	1.51 (1)	0.26 (1)	0.02 (1)
S4	2.55 (2)	0.84 (1)	1.43 (1)	0.24 (1)	0.02 (1)
S5	2.02 (2)	0.86 (1)	1.91 (1)	0.68 (1)	0.07 (1)
S6	2.22 (2)	0.81 (1)	1.41 (1)	0.29 (1)	0.02 (1)
S7	1.61 (1)	0.91 (1)	1.29 (1)	0.49 (1)	0.04 (1)
S8	1.46 (1)	1.23 (1)	1.34 (1)(1)	0.66 (1)	0.05 (1)
S9	1.72 (1)	0.74 (1)	1.62 (1)	0.25 (1)	0.02 (1)
S10	2.28 (2)	0.86 (1)	1.15 (1)	0.28 (1)	0.02 (1)
S11	2.25 (2)	1.04 (1)	1.88 (1)	0.31 (1)	0.02 (1)
S12	1.29 (1)	0.82 (1)	1.13 (1)	0.27 (1)	0.02 (1)
S13	1.13 (1)	0.81 (1)	1.63 (1)	0.22 (1)	0.01 (1)
S14	1.78 (1)	0.91 (1)	1.69 (1)	0.25 (1)	0.03 (1)
S15	1.30 (1)	0.81 (1)	1.42 (1)	0.29 (1)	0.01 (1)
S16	2.63 (2)	1.29 (1)	1.72 (1)	0.51 (1)	0.03 (1)
S17	1.87 (1)	0.95 (1)	1.08 (1)	0.28 (1)	0.03 (1)
S18	3.30 (2)	0.96 (1)	0.99 (1)	0.30 (1)	0.02 (1)
S19	2.11 (2)	1.05 (1)	1.31 (1)	0.26 (1)	0.02 (1)
S20	1.86 (1)	1.14 (1)	1.71 (1)	0.28 (1)	0.02 (1)

S21	2.07 (2)	1.22 (1)	1.61 (1)	0.27 (1)	0.02 (1)
S22	2.25 (2)	1.06 (1)	1.36 (1)	0.26 (1)	0.00 (1)
S23	2.96 (2)	1.07 (1)	1.42 (1)	0.3 (1)	0.02 (1)
S24	1.27 (1)	1.20 (1)	1.34 (1)	0.54 (1)	0.04 (1)
S25	1.78 (1)	1.40 (1)	1.46 (1)	0.64 (1)	0.08 (1)
S26	1.94 (1)	0.95 (1)	1.94 (1)	0.29 (1)	0.02 (1)
S27	0.79 (1)	0.65 (1)	1.35 (1)	0.22 (1)	0.02 (1)
S28	3.11 (2)	1.08 (1)	1.65 (1)	0.31 (1)	0.03 (1)
S29	2.92 (2)	0.85 (1)	1.27 (1)	0.3 (1)	0.02 (1)
S30	1.99 (1)	1.07 (1)	0.83 (1)	0.27 (1)	0.02 (1)
S31	1.85 (1)	0.99 (1)	1.39 (1)	0.29 (1)	0.01 (1)
S32	1.84 (1)	0.76 (1)	1.74 (1)	0.23 (1)	0.02 (1)
Mean	2.06	1.98	1.44	0.33	0.03

KEY

Category	Description	Description
1	Deficiency to minimal	(EF < 2)
2	Moderate enrichment	(2 < EF < 5)
3	Significant enrichment	(5 < EF < 20)
4	Very high enrichment	(20 < EF < 40)
5	Extremely high enrichment	(> 40)

Note: Figures enclosed in brackets represent the enrichment category

APPENDIX D: Summary of Geo-accumulation indices(I_{geo}^m) at different sampling locations along Thika River

Sample Location	Mn	Ni	Cu	Zn	Pb
Geoaccumulation Indices/Category					
1	2.14	0.94	0.57	0.49	0.60
	3	(1)	(1)	(1)	(1)
2	1.66	0.88	0.13	0.50	0.49
	(2)	(1)	(1)	(1)	(1)
3	1.84	0.70	0.04	0.46	0.53
	(2)	(1)	(1)	(1)	(1)
4	1.93	0.82	0.30	0.59	0.51
	(2)	(1)	(1)	(1)	(1)
5	1.46	0.65	0.15	0.56	0.65
	(2)	(1)	(1)	(1)	(1)
6	1.62	0.64	0.09	0.59	0.51
	(2)	(1)	(1)	(1)	(1)
7	1.40	0.65	0.31	1.22	1.26
	(2)	(1)	(1)	(2)	(2)
8	1.28	0.67	0.58	1.49	1.47
	(2)	(1)	(1)	(2)	(2)
9	1.46	0.88	0.09	0.54	0.69
	(2)	(1)	(1)	(1)	(1)
10	1.55	0.00	0.06	0.46	0.39
	(2)	(0)	(1)	(1)	(1)
11	1.61	0.91	0.31	0.62	0.54
	(2)	(1)	(1)	(1)	(1)
12	1.01	0.35	0.06	0.45	0.33
	(2)	(1)	(1)	(1)	(1)
13	1.11	0.96	0.26	0.47	0.36
	(2)	(1)	(1)	(1)	(1)
14	1.52	0.95	0.33	0.58	1.12
	(2)	(1)	(1)	(1)	(2)
15	1.05	0.61	0.05	0.54	0.21
	(2)	(1)	(1)	(1)	(1)
16	1.47	0.52	0.23	0.84	0.61
	(2)	(1)	(1)	(1)	(1)
17	1.37	0.30	0.16	0.47	0.66
	(2)	(1)	(1)	(1)	(1)
18	1.91	0.19	0.15	0.50	0.49
	(2)	(1)	(1)	(1)	(1)
19	1.59	0.58	0.36	0.51	0.57
	(2)	(1)	(1)	(1)	(1)
20	1.43	0.44	0.41	0.53	0.55

	(2)	(1)	(1)	(1)	(1)
21	1.49	0.72	0.44	0.46	0.54
	(2)	(1)	(1)	(1)	(1)
22	1.70	0.67	0.43	0.54	---
	(2)	(1)	(1)	(1)	
23	1.84	0.58	0.30	0.59	0.42
	(2)	(1)	(1)	(1)	(1)
24	1.09	0.62	0.51	1.24	1.26
	(2)	(1)	(1)	(2)	(2)
25	1.42	0.70	0.65	1.40	1.94
	(2)	(1)	(1)	(2)	(2)
26	1.54	1.02	0.30	0.63	0.74
	(2)	(2)	(1)	(1)	(1)
27	0.78	0.80	0.06	0.50	0.71
	(1)	(1)	(1)	(1)	(1)
28	1.87	0.71	0.28	0.57	0.74
	(2)	(1)	(1)	(1)	(1)
29	1.86	0.51	0.10	0.63	0.66
	(2)	(1)	(1)	(1)	(1)
30	1.51	0.11	0.37	0.51	0.61
	(2)	(1)	(1)	(1)	(1)
31	1.49	0.68	0.34	0.66	0.35
	(2)	(1)	(1)	(1)	(1)
32	1.63	1.05	0.22	0.57	0.74
	(2)	(1)	(1)	(1)	(1)
Mean	1.52	0.65	0.27	0.65	0.68

KEY

Category	Description
6	Extremely contaminated
5	Strongly to extremely contaminated
4	Strongly contaminated
3	Moderately to strongly contaminated
2	Moderately contaminated
1	Uncontaminated to moderately contaminated
0	Uncontaminated

Note: Figures enclosed in brackets represent the enrichment category

APPENDIX E: Summary of contamination factor, modified contamination factor and pollution load index of Thika River sediment samples

Sample Location	Contamination factor of single metal					PLI		Modified degree of Contamination Factors	Remarks
	Mn	Ni	Cu	Zn	Pb				
1	12.73	3.85	2.66	2.46	2.72	3.87	Polluted	3.49	Moderate
2	7.85	3.62	1.70	2.48	2.45	3.12	Polluted	2.59	Moderate
3	9.44	3.03	0.51	2.37	2.55	2.45	Polluted	2.56	Moderate
4	10.30	3.42	2.02	2.70	2.51	3.44	Polluted	2.99	Moderate
5	6.47	2.86	0.90	2.63	2.87	2.63	Polluted	2.25	Moderate
6	7.58	2.85	0.84	2.70	2.49	2.61	Polluted	2.35	Moderate
7	6.08	2.89	2.04	5.08	5.29	3.95	Polluted	3.05	Moderate
8	5.39	2.94	2.69	6.65	6.51	4.50	Polluted	3.45	Moderate
9	6.44	3.60	1.65	2.58	2.99	3.12	Polluted	2.47	Moderate
10	7.08	2.11	0.56	2.39	2.22	2.13	Polluted	2.05	Moderate
11	7.53	3.71	2.05	2.80	2.58	3.34	Polluted	2.67	Moderate
12	4.11	2.14	0.53	2.36	2.09	1.87	Polluted	1.60	Low
13	4.55	3.91	1.95	2.40	2.16	2.82	Polluted	2.14	Moderate
14	6.89	3.88	2.09	2.68	4.61	3.70	Polluted	2.88	Moderate
15	4.27	2.76	1.58	2.58	1.85	2.45	Polluted	1.86	Low
16	6.52	2.53	1.17	3.46	2.75	2.83	Polluted	2.35	Moderate
17	5.92	2.02	0.94	2.39	2.89	2.39	Polluted	2.02	Moderate
18	10.15	1.81	0.80	2.48	2.44	2.45	Polluted	2.53	Moderate
19	7.32	2.68	1.22	2.49	2.64	2.75	Polluted	2.34	Moderate
20	6.27	2.34	1.24	2.56	2.59	2.61	Polluted	2.14	Moderate

21	6.68	3.08	1.30	2.38	2.59	2.77	Polluted	2.29	Moderate
22	8.24	2.94	1.28	2.58	3.17	3.03	Polluted	2.6	Moderate
23	9.42	2.68	1.12	2.70	2.28	2.80	Polluted	2.60	Moderate
24	4.46	2.79	2.50	5.18	5.28	3.85	Polluted	2.89	Moderate
25	6.21	3.02	2.89	6.08	10.43	5.09	Polluted	4.09	High
26	7.02	4.16	2.03	2.82	3.15	3.50	Polluted	2.74	Moderate
27	3.28	3.34	1.60	2.48	3.04	2.66	Polluted	1.96	Low
28	9.71	3.04	1.99	2.65	3.14	3.45	Polluted	2.93	Moderate
29	9.66	2.49	1.66	2.80	2.91	3.18	Polluted	2.79	Moderate
30	6.80	1.68	1.15	2.50	2.76	2.46	Polluted	2.13	Moderate
31	6.67	2.96	2.12	2.89	2.12	3.03	Polluted	2.39	Moderate
32	7.66	4.29	1.88	2.65	3.13	3.48	Polluted	2.80	Moderate