LEVELS AND DISTRIBUTIONS OF HEAVY METALS IN WATER AND SEDIMENTS OF RIVER AMBA, LAFIA, NASARAWA STATE, NIGERIA

BY

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NSU/NAS/M.Sc/CHM/722/12/13

A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, NASARAWA STATE UNIVERSITY KEFFI, IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF DEGREE OF MASTER OF SCIENCE IN INDUSTRIAL CHEMISTRY.

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DECLARATION

I hereby declare that this dissertation has been written by me and it is a report of my research work. It has not been presented in any previous publication for the award of Master of Science (Industrial Chemistry). All quotations are indicated and sources of information specifically acknowledged by means of references.

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CERTIFICATION

The dissertation titled, (Levels and Distribution of Heavy Metals in Water and Sediments of River Amba Lafia, Nasarawa State, Nigeria) meets the regulations governing the award of M.Sc. Industrial Chemistry, of the School of Postgraduate Studies, Nasarawa State University, Keffi, and is approved for its contribution to knowledge.

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DEDICATION

This research work is dedicated to the Lord God Almighty and to my beloved family.

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ABSTRACT

The research was carried out to assess seasonal variations in the levels of physicochemical parameters and heavy metals (Cd, Cr, Cu, Fe, Mn, Zn and Pb) concentration in water and bed sediment of Amba River. The water and sediment samples were collected during rainy and dry seasons. Metal concentrations were quantified using Graphite Atomic Absorption Spectrometer (GAAS). Results obtained indicated that water and sediment pH (6.70 - 6.80) were slightly acidic. Total dissolved solids (TDS), electrical conductivity (EC) and alkalinity values of water decreased during the rainy season. Metal levels in water were higher during the rainy season, except for the decrease in Cr (0.80±1.69 mg/L) and Zn (0.04±0.08 mg/L) concentrations. Fe and Cu levels were highest amongst metals. Cd, Cr, Cu, and Zn concentrations in water during rainy and dry seasons were significantly different ($P \leq 0.05$). Metal levels in sediment decreased during the dry season, however, concentrations of Cr (3.61±0.67mg/Kg) and Fe (4.25±1.83mg/Kg)increased during the same period. Metal levels were higher in water and sediment during dry and rainy seasons respectively. Sediment generally contained higher metal concentrations compared to water. Cr, Cu, and Mn levels in water and sediment were significantly different ($P \leq 0.05$) for both seasons. Correlations among metal concentrations during the rainy season were positively strong for Cd-Fe (0.786) and Fe-Pb (0.834), while Fe-Pb (0.886) correlation was strongly positive in dry season. During the rainy season, there were excellent correlations between Cd-Mn (0.974), Mn-Pb (0.932), Cd-Pb (0.854) Cr-Zn (0.786), and Fe-Zn (0.720), while in dry season, Cr-Pb (0.670), Cu-Mn (0.791), Cu-Pb (0.776) and Fe-Zn (0.689) show strong associations. Correlations between metal concentrations in sediment and water were positively strong for Cu (0.960) and Zn (0.951) during rainy season and excellent for Mn (0.920) during dry season. Partition coefficient (Kd) values for the levels of metals in sediment and water were greater than 1 except for Cu (0.00) and Zn (0.99) in rainy season and Cr (0.72) in dry season. Pollution load index (PLI) values during rainy and dry seasons were less than 1which account for the unpolluted nature of the river water. Levels of physicochemical parameters and heavy metals were within the WHO permissible limits for drinking water except for the metals Fe, Cd and Cr.

CHAPTER ONE

INTRODUCTION

1.1. Background of the Study

Contamination of aquatic environment by heavy metals has attracted global attention owing to its abundance, persistence and environmental toxicity (Islam *et al*., 2015).Studies on heavy metals in rivers, lakes and sediments have been a major environmental focus especially during the last decade (Ozmen *et al*., 2004; Fernandes *et al*., 2008; Ozturk *etal*., 2008; Pote *et al*., 2008 and Praveena *et al*., 2008). Contamination of river water by heavy metals is one of the major quality issues in fast growing cities because maintenance of water quality and sanitation infrastructure do not increase along with population and urbanization growth especially in developing countries(Akoto *et al*., 2008 & Ahmad *et al*., 2010).

Heavy metals are released into the environment by both natural and anthropogenic sources (Khan *et al.*, 2008). Anthropogenic inputs are associated with industrialization and agricultural activates deposition, such as atmospheric deposition, waste disposal, waste incineration, urban effluent, traffic emissions, fertilizer application and long-term application of wastewater in agricultural land (Martin *et al*., 2015).

Organic matter and pH are the most important parameters that control the accumulation and the availability of heavy metals in sediment (Ramesh *et al*., 2010; Eneje & Lemoha, 2012). Change in pH alters the adsorption capacity of minerals and organic colloids. Positive charge prevails at low pH conditions under which anion exchange capacity is dominant, while at high, pH negative charge prevails and cation exchange capacity predominates (Tukura *et al*., 2013).

Heavy metals discharged into aquatic ecosystems are likely to be scavenged by particles leading to their accumulation in sediments (Luoma, 1989). Sediments are important sinks for various pollutants such as pesticides and heavy metals and play a significant role in the remobilization of contaminants in aquatic systems under favorable conditions (Ozturk *et al*., 2009). However, the

extent of the risks is difficult to accurately assess because of the complexity of biological and chemical interactions that alter the bioavailability of metals. Release from sediments may not only result from re-suspension of particulates, but also through the activities of microorganisms within the sediments and at the sediment-water interface, resulting in bio-transformation to more volatile/soluble forms (Gilmour *et al*., 1985).

Among environmental pollutants, metals are of particular concern due to their potential toxic effect and ability to bioaccumulate in aquatic ecosystems (Censi *et al*., 2006).

1.2 Statement of the Problem

The runoff from household waste and agricultural activities along the river may introduce heavy metals into the water and sediments and thereby affect their quality. The presence of heavy metals in aquatic systems originates from the natural interactions between the water, sediments and atmospheres. The concentrations fluctuate as a result of continuous chemical and biological forces. Man, through industrialization and technology, has developed the capacity to alter these natural interactions to the extent that the very water and the aquatic life therein have been threatened to a devastating point.

1.3 Aim and Objectives of the Study

The aim of the research is to assess the levels and seasonal distribution of heavy metals (lead, copper, zinc, cadmium, chromium, manganese and iron) in water and sediment from Amba River in Lafia Local Government Area of Nasarawa State, Nigeria.

The objectives of the study are to:

i. Determine the physicochemical characteristics of water and sediment from Amba River.
ii. Determine the levels of lead, zinc, cadmium, chromium, manganese and iron in water and sediment of the Amba River.
iii. Determine the spatial and temporal variations of heavy metals in water and sediment of Amba river.
iv. Determine heavy metals partition coefficients in water and sediment

v. determine the Pollution Load Index (PLI) of heavy metals in water and sediment of river Amba.

1.4 Significance of the Study

This research work attempts to present a practical baseline data of the concentrations of heavy metals pollution occurring in the river water and sediment and to identify the sources of the pollution in order to create awareness to the settlers on the adverse effect of drinking water directly from the Amba River. Water is a valuable natural resources that should be guided with keen interest and pollutants or heavy metals levels should be constantly checked in order to control water quality and minimize the effects on the aquatic organisms.

1.5 Scope of the Study

The scope of this study is limited to study of some heavy metals levels and distribution in water and sediment of Amba River. The research will also cover seven selected heavy metals: cadmium, chromium, copper, iron, manganese, zinc and lead which persist in the aquatic environment and alter the quality of water and that of sediment. The effects of some physicochemical parameters on the accumulation of these heavy metals will be studied along in the river. The research samplings covered a section of a river within Lafia axes and a period of rainy and dry seasons (September, 2015 and March, 2016).

CHAPTER TWO

LITERATURE REVIEW

In view of the objective of the present research, a critical survey of literature was carried out to gather information on various relevant aspects such as physicochemical features, heavy metals concentrations and their bioaccumulation.

Heavy metals refer to any metallic chemical element that has relatively high density with specific gravity that is at least 5 times the specific gravity of water Lars, (2003). Aquatic environments are receiving continuously increasing levels of heavy metals with anthropogenic sources having been identified as the major sources of heavy metal pollutants in aquatic systems Linnik, (2000). Sediments are important sinks for various pollutants such as pesticides and herbicides while, heavy metals in surface water may exist as simple hydrated ions as well as inorganic and organic complexes Linnila, (2000).

2.1 Metals in Water

Heavy metals are considered to be major toxicant in contaminated water worldwide Li *et al*., (2012). Several studies have attempted assessing heavy metal pollution according to the distribution of particle size and to relationship of its organic content Jerry & Terry, (2005). Heavy metal levels in many natural water bodies across the world have been investigated for instance, Obasohan, (2008), analyzed water quality of the river Tean Staff and found increase in cadmium levels (0.83±0.02 mg/L). Ong Che, (1999), analyzed heavy metal levels in water of the Chao Phraya river estuary; Thailand and discussed their long term impact on the aquatic environment. Tuzen, (2002), determined heavy metal levels in the eastern Arctic Ocean while Fernandes, (2007), determined heavy metals in Shatt Al-Arab River, Iraq and indicated metal levels to be within the recommended limits. Abdel-Baki *et al.*, (2011), analyzed cadmium and zinc concentrations in drinking water supplies of Dhaka city, Bangladesh and highlighted the impact of addition of bleaching powder and pumping on zinc concentration. Ramesh *et al*., (2010), analyzed concentrations of trace metals in the Qiantang-Jiang river and its estuary Southern China and

found higher levels of metals with addition of industrial wastes. Ozmen *et al.,* (2004), conducted a preliminary study on heavy metal (Zn, Mn, Ni, Cu, Cr, Co and Pb) concentrations in surface water of Hazar lake and discussed the heavy metal pollution status of the lake. Gonzalez *et al.*, (2005), evaluated heavy metals loading of river Ijana, Nigeria and results indicated higher metal contents in winter season. Reilly, (2002), in a multivariate analysis of heavy metal concentration in soil, sediment and water in the region of Meknes (Central Morocco), compared the metal contents in water and sediment to suggest correlations between them. Ahmad *et al.,* (2010), analyzed Fe, Cr, Cd, As, Ni, Co and Zn in drinking water samples in Akure, Nigeria. Adefemi *et al.,* (2008), determined heavy metal (Zn, Pb, Mn, Fe, Cu, Co, Cr, Cd and Ni) contents in water from Ureje dam in South-Western Nigeria to assess the water quality as Pb (0.013mg/L), Cd (0.001mg/L) Cu (0.350mg/L), Cr (0.040mg/L), Ni (0.527mg/L), Fe (2.493mg/L), Mn (0.370mg/L) and Zn (0.043mg/L). Also the impact of heavy metal inputs from various industries has been investigated in several studies. Pote *et al.,* (2008), determined cadmium levels in the Rhone River polluted by industrial wastes. Praveena *et al.,* (2008), studied distribution of heavy metals in Gove harbor, northern territory, Australia to find the impact of a bauxite treatment plant on the heavy metal status of water. Kar *et al.,* (2008), investigated heavy metals to study effects of industrial lead inputs into the San Andres lagoon, Tamaulipas, Maxico. They carried out a comparative study of several metals (Cd, Co, Cu, Fe, Mn, Ni, and Zn). Linnik *et al.*, (2000), conducted a study on assessment of heavy metal pollution of water in the Narayani River, Nepal contaminated by paper industry effluents. Gupta *et al.,* (2009), analyzed heavy metal levels in Zayandeh Rood River, Isfahan-Iran at seven sites to observe the influence of the industrial activities and dump of municipal waste on heavy metal concentrations in this region as Pb (45.04±0.79mg/L), Ni (0.74±0.24mg/L), Zn (36.37±0.12mg/L), Cd (1.81±0.19mg/L), Cr (3.33±0.08mg/L) and Mn (30.88±0.05mg/L).

2.2 Metals in Sediment

Natural background levels of heavy metals exist in the majority of sediments due to mineral weathering and natural soil erosion. It is when man's activities accelerate or antagonize these processes that the background levels are increased, by pollution, to levels that have detrimental effects on the environment. Sediments with low heavy metal concentrations are not necessarily "natural" just because the levels are indeed low. They may represent a mixture of small quantity of pollutants diluted by a large amount of natural sediment with low heavy metal content (Herut *et al.*, 1993).

In the past sediments and particulate matter have been considered as purely abiotic material. This is obviously not the case and it is now well known that sediments contain large bacterial populations Özturk et al., (2009). Sediments are also complex mixtures of a number of solid phases that may include clays, silica, organic matter, carbonates and large bacterial populations. Mechanisms by which heavy metals may be taken up by sediments and suspended matter include physicochemical adsorption from the water column, biological uptake by organic matter or organisms and .physical accumulation of metal enriched particulate matter by sedimentation or entrainment Akan *et al*., (2009).

Physicochemical adsorption direct from the water column happens in many different ways. Physical adsorption usually occurs when particulate matter directly adsorbs heavy metals straight from the water. Chemical and biological adsorption is more complicated as they are controlled by many factors such as pH and oxidation.

Natural organic matter has a very important influence on the distribution of heavy metals in aquatic systems. Metal ions are strongly adsorbed by solid organic matter. The structure and composition of humic matter can vary considerably depending upon its origin and can be expected to influence the results of sorption experiments. In addition uptake may be actively completed by bacteria and algae. This results in sediment enrichment. Sedimentation of enriched particulate

matter is the other potentially important mechanism by which sediments may concentrate heavy metals (Hart, 1982).

There is no evidence to suggest that trace metal binding to solid natural organic matter should be any different to that by soluble natural organic matter. The difference between these surface types is not well understood particularly with respect to trace metal uptake. Gardner (1974), found that adsorption of cadmium by river mud samples was very rapid (in the order of minutes) and that some additional adsorption occurred over a further 24 hour period. Within the soil, trace metals can be either transformed to less soluble forms or they can move to living biota. There is also the possibility that they may be eluted into the watershed and contribute to diffuse pollution in that area.

Elevated levels are helped also by the oxidation of surface sediments due to periodic drying between tides. This, incorporated with some biological processes such as bioturbiation or O_2 release from mangrove roots, can enhance uptake rates. This exposure to O_2 results in the oxidation of sulphides in the sediment. A reduction in sediment pore water pH due to production of sulphuric acid, allow the mobilization of metals (Clark *et al*., 1998).

Many authors, Fernandes *et al.,* (2007), and Gupta *et al.,* (2009), proposed that the interface between water and sediment plays many important roles in the chemistry of trace metals. Firstly, the upper layer of sediment is usually oxidised (as previously stated) and therefore, acts as a diffusion barrier for mobilized solutes travelling upward from reducing zones of sediment.

Secondly, the surface sediments on the bed of many estuaries exchange readily with suspended solids in the water column and therefore easily adsorb any passing material. Ultimately, Szefer & Geldon (1998), suggested that the sediments at the water interface (i.e. the topsoil) are more important to biological fauna than when compared with subsurface meiofauna. They, therefore, offer a higher opportunity for uptake by benthic organisms.

Long (1992), suggested that the oxidation-reduction potential and the concentration of sulphides in the sediments can strongly influence the concentration of trace metals and their availability. Clark

et al., (1998), explain that the redox potential of the sediment can affect metal trapping directly through change in the oxidation state of the metal itself, or indirectly through a change in the oxidation state of the ions that can form complexes with the metal.

There is a small variation between the mobility of particulate in river waters and seawater. This is very supervising due to a wide expected variation in particle types. Therefore, metals and the subsequent pollution Depending upon the environment the sediment particle size distribution may range from very small colloidal particles (of < 0.1um in diameter) to large sand and gravel will progress equally in both rivers and the ocean. Harbison (1986), has reported that tidal mudflats and particularly mangrove substrates contain a much greater load of trace metals than other shoreline sediments. This is where the sediments are most vulnerable to the environmental parameters that might influence the migration of these metals.

Cadmium and manganese ions may also influence the sorption of other trace metals ions. This happens, on oxide surfaces, in either of three ways: Firstly Cd and Mn are normally present at concentrations many orders of magnitude higher than the other trace metals Mwangi, (2009). They may, therefore, occupy most of the surface binding sites and leave little opportunity for binding of other metals even though they form less stable surface complexes. Benjamin (1980), however, suggested that oxide surfaces may consist of many groups of binding sites. The strength of binding between a given metal ion and the surface may vary by an order of magnitude, from one site to another. At small sorption densities all types of sites are available in excess. Hart (1982), supports this statement by reporting that at higher adsorption densities the availability of the strongest binding sites decreases in the apparent adsorption equilibrium constant. This seems to occur only when a few percent of all surface sites are occupied.

Many studies indicated that levels of metals were higher in sediment than in water. Islam. (2015), suggested the heavy metal concentration increases in the sediment due to the adsorption of cations by organic matter present in the sediment layers. Similarly, Li *et al*., (2014), suggested that metals interact with organic matter in aqueous phase and settle down resulting in high concentrations in

sediments. The role of sediments in adsorption of cations has been demonstrated in a study on rivers as contained in APHA, (2005).

Many studies conducted on metal accumulation in sediment Martin *et al.*, (2015), showed increase in metal levels in sediment with addition of sewage, industrial effluents and agricultural wastes. Yin *et al.*, (2008), in a study of Coeur D' Alene river delta, found bottom of the lake to be covered with metal polluted sediments. Similarly, Akan *et al.*, (2009), analyzed estuarine sediments in Florida for heavy metal deposits. Hingston, (2001), analyzed heavy metal residues in the sediments of lakes in the Atchafalaya river basin (Louisiana). Forstner, (1983), analyzed heavy metal concentrations in sediments of coastal South Carolina Marinas and discussed seasonal variations in metal accumulation.

An exploratory study of the heavy metals Cd, Cu, Mn, Pb and Zn in sediments of Lake Valencia (Venezuela) was undertaken by Miller *et al*., (2002). Gardiner, (1974), determined heavy metal contents in river sediments of Carinthia (Austria). Dayan & paine, (2001), observed the distributions of Fe, Mn, Pb, Cu, Ni, Cr, Zn and Hg in the surface sediment of the Erdek bay, sea of Marmara in Turkey while Karen, (2004), analyzed metals in an urban watershed in Southeastern Michigan.

2.3 Environmental Effects of Heavy Metals

Some heavy metals such as copper (Cu), zinc (Zn), iron (Fe), chromium (Cr), manganese (Mn) and nickel (Ni) though essential to human body, are toxic at elevated levels, whereas cadmium (Cd) and lead (Pb) are non-essential metals and are toxic even in trace amounts. Toxicity is highly aggravated by their non-degradability and tendency to bio-accumulate to toxic levels (Tuzen, 2003).Heavy metal toxicity can result in lower energy levels and damage blood composition, lungs, liver, kidneys and other vital organs, damaged or reduced mental and central nervous function or even cause cancer (Canlý & Atly, 2003; Tuzen, 2003;Fernandes *et al.,* 2008). Heavy metal poisoning is more likely to result from inhalation, ingestion, skin contact with the metals or

compounds from dust, fumes or materials from work place, or in residential settings, especially homes with lead paints or old plumbing (Mtanga & Machiwa, 2007).

2.3.1 Zinc

Zinc makes up about 75 ppm of the Earth's crust, making it the 24th most abundant element with a density of 7.14g/cm^3. Zn is normally found in association with other base metals such as Cu and Pb in ores and has a low affinity for oxygen and prefers to bond with sulphur and occurs as ores such as sphalerite (ZnS), calamite ($ZnCO_3$) and zincite (ZnO). Zn forms alloys such as brass and bronze and has been used in construction of buildings, roofing and cladding (Emsley, 2001). Other uses of Zn include making circuit boards, photocopiers, dry cell batteries and its compounds are used in chemical and pharmaceutical industries such as paints, medicines and nutritional supplements (Reilly, 2002).

The toxicity of Zn is as a result of excessive absorption which suppresses copper and iron absorption while free Zn^{2+}^{ion} in solution is highly toxic to plants, invertebrates, and even fish (FAO/WHO, 2011). Zinc salts are intestinal irritants and can cause nausea, and abdominal pain (ATSDR, 2002). Prolonged exposure to high intakes of Zn results in copper deficiency and subsequent anemia (Reilly, 2002). There is also a condition called the zinc shakes or "zinc chills" that can be induced by the inhalation of freshly formed Zn oxide formed during the welding of galvanized materials. It has been reported that zinc is able to damage nerve receptors in the nose, which can cause anosmia and recommended that consumers should stop using zinc-based intranasal cold products and ordered their removal from store shelves (Johnson *et al*., 2007; Safty *et al*., 2008).

River sediments have been found to have levels of Zn in a number of rivers with values that vary from the recommended limit of 123 mg/kg (Kage, 2003; WHO, 2003; Alaa & Osman, 2010; and Agatha, 2010). Zinc concentrations of 91.5 to 307 mg/kg have been recorded in sediments from Nile River during the dry season. 34.61mg/kg from Forcados River’s sediments and 126.33-307.00

mg/kg from Nairobi River's sediments were obtained where some did not constitute immediate hazard to aquatic fauna and human consumers (Kage, 2003; Alaa & Osman, 2010; Agatha, 2010). A concentration of 0.60 mg/kg from Nairobi River was found to be below the recommended limit of 123 mg/kg for Zn in sediment (Wachira, 2007). Constant monitoring of levels of contamination to assess the impact of heavy metals in the aquatic system was, however, recommended (Wachira 2007 and Agatha, 2010).

Levels of Zn in rivers flowing through industrial or mining areas can be as high as 20 mg/l while soils contaminated with Zn through the mining of zinc-containing ores, refining, or where zinc-containing sludge is used as fertilizer, can contain several grams of zinc per kilogram of dry soil (Emsley, 2001). A higher Zn mean level of 76.25 mg/l than the 3 mg/l recommended limits was recorded from Forcados River while lower mean levels of 0.085 mg/l during dry season and 0.716 mg/l during wet season from River Ganga's water and 1.0 mg/l from Nairobi River's water were recorded (WHO, 2003; Kithiia, 2006; Kar *et al.*, 2008;Agatha, 2010). This level was attributed to land use activities such as agriculture system and effluent from residential and industrial area. Downstream decrease in water pollutants was observed and was attributed to the dilution effect and self-purification. Constant monitoring of the levels of contamination to assess the impact of the heavy metal in the aquatic system and use of riverine vegetation was recommended as useful in absorbing heavy metals as a means of purification (Kithiia, 2006; Agatha, 2010)

2.3.2 Chromium

Chromium has density of 7.2g/cm^3 and is the 21st most abundant element in Earth's crust with an average concentration of 100 ppm (Emsley, 2001). Chromium compounds are found in the environment, due to erosion of Cr -containing rocks, animals, plants, soil and can be a liquid, solid or gas. Cr can exist in valences of +3and +6 with oxidation state in Cr (III) being stable and give series of chromic compounds, like oxides (Cr_2O_3), chlorides ($CrCl_3$) and sulphates ($Cr_2(SO_4)_3$) (Emsley, 2001; Gonzalez *et al*., 2005). Cr is used in metal alloys such as stainless steel, protective

coatings of metal (electroplating), magnetic tapes, and pigments for paints, cement, paper, rubber and its soluble form is used in wood preservatives as well as additive in water to prevent corrosion in industrial and other cooling system (Hingston, 2001; WHO, 2003). Hexavalent Cr is very toxic and mutagenic when inhaled and is a known human carcinogen. Breathing high levels of the element in this form can cause irritation to the lining of the nose and breathing problems such as asthma, cough, shortness of breath, or wheezing where long term exposure can cause damage to liver, kidney circulatory and nerve tissues, as well as skin irritation (Dayan & Paine, 2001).

Sediments act as the most important reservoir or sink of metals and other pollutants in the aquatic environment (Gupta *et al*., 2009). Heavy metal contamination in sediment can affect the water quality and bioaccumulation of metals in aquatic organisms, resulting in potential long-term implication on human health and ecosystem (Fernandes *et al*., 2007). Increased levels of Cr in agricultural soils and thus potentially in crops, can occur through the application of sewage sludge and by atmospheric deposition of fumes produced by industry (Reilly, 2002). In the Wadi Hanifah River's sediment samples, the average concentration of Cr was 9500 μg/kg (Abdel-Baki *et al*., 2011).

Chromium has been found to vary from the recommended level of 0.05 mg/l for domestic water (WHO, 2008; Abdel-Baki *et al*., 2011). Higher Cr concentrations than the recommended limit in the Wadi Hanifah River's water samples was 6.4 ppb while Cr mean concentrations from Msimbazi River water ranged from 1.414 to 0.01 mg/l. These were from points of the rivers that receive effluents loaded with pollutants from various industries including textile, which are known to contain Cr (Mwegoha & Kihampa, 2010; Abdel-Baki *et al*., 2011). Wachira (2007) recorded Cr mean levels of 0.02 mg/l in water from Nairobi River which was not higher than 0.05mg/l recommended limit for drinking water. Thus, Nairobi river water was suitable for domestic use as far as Cr is concerned (WHO, 2003; Wachira, 2007).

2.3.3 Lead

Lead has a density of 11.3g/cm^3 atomic number 82 and is obtained from its sulphide mineral galena (PbS), carbonate cerussite ($PbCO_3$) and sulphate anglesite ($PbSO_4$). The ores are frequently found in combination with other recoverable metals such as Cu, Zn and Cd. Lead exists in various oxidation states (O, I, II and IV), which are of environmental importance with oxidation +2, the form in which most Pb is bio-accumulated by aquatic organisms (Akan *et al*., 2009). Lead was placed position 2 on the Agency for Toxic Substances and Disease Registry's (ATSDR) top 20 list of most dangerous heavy metals and it accounts for most of the cases of paediatric heavy metal poisoning (ATSDR, 2002). Lead has been used in pipe making, drains and soldering materials as well as battery manufacture, plumbing, ammunition, fuel additives, paint pigments and pesticides (ATSDR, 2005).

Lead has been of particular concern due to its toxicity and ability to bioaccumulate in aquatic ecosystems, as well as persistence in the natural environment (Miller *et al*., 2002; Anim *et al*., 2010). Some effects of Pb poisoning include deficiency in cognitive function due to destruction of the central nervous system, abdominal pain and discomfort, formation of weak bones as Pb replaces calcium and causes anaemia due to reduction of enzymes concerned with synthesis of red blood cells (Lars, 2003).

Lead also leads to decreased fertility, causes cancer and other minor effects like vomiting, nausea, and headache (Lars, 2003; WHO, 2008). Exposure to high Pb levels can severely damage the brain and kidneys, cause miscarriage in pregnant women, damage the organs responsible for sperm production in men and it may ultimately cause death (ATSDR, 2002).

Mean levels of Pb in sediments from Tyume River, were reported to range between 0.040 ± 0.005 and 0.067 ± 0.003 mg/kg, and Pb in sediments from River Nile exhibited a wide range of variation ranging from 3.1 to 76.9 mg/kg that was higher than the permissible limit of 35 mg/kg, meaning that, Nile river was polluted and needed constant control and assessment (Awofolu *et al.*, 2005; WHO, 2008; Alaa & Osman, 2010). Elevated levels of Pb could be directly detrimental to the

health of the aquatic ecosystem and indirectly to man. The sediments could be a contributing source of these heavy metals in water, hence continual assessment was highly essential (Awofolu *et al.*, 2005). Also, Agatha (2010) recorded Pb mean levels of 9.43 mg/kg from Forcados River in sediment samples that were lower than the WHO recommended limit of 35mg/kg. Decreasing concentrations of Pb metal away from pollution point has been recorded which was attributed to dilution effect as a result of runoff or rain water with a big part of heavy metals in sediments being released back to water compartment in the process of remobilization (Kar *et al*., 2008; Ozturk *el al*., 2009; Agatha, 2010). Studies from Ikpoba River recorded Pb mean concentration of 0.035mg/l in water and also Pb mean levels of 0.1 mg/l was obtained from Nairobi river which surpassed the recommended limit of 0.01mg/l for drinking water set by WHO (WHO, 2003; Kithiia, 2006; Oguzie & Izevbigie, 2009). Oguzie & Izevbigie, (2009) reported that the level of Pb in the water though lower than <1 mg/l value recommended for portable drinking water by the Federal Ministry of Environment and the World Health Organization requires that caution be taken in the discharge of effluents without treatment into Nigeria's in-land water bodies. This was because anthropogenic sources have been implicated as the major cause of pollution in aquatic environment (Kithiia, 2006; Oguzie & Izevbigie, 2009). Kithiia. (2006), recommended use of riverine vegetation as useful in absorbing heavy metals as a means of purification.

2.3.4 Cadmium

Cadmium has oxidation state of +2 and forms a number of inorganic compounds such as sulphates ($CdSO_4$), chlorides ($CdCl_2$) and acetates ($Cd[CH_3COO]_2.H_2O$ most of which are water soluble. Cd is a by-product of mining and smelting of Pb and Zn and is used in nickel-cadmium batteries and paint pigments. Cd can be found in soils under agriculture from insecticides, fungicides, sludge and commercial fertilizers. Ingestion of Cd can rapidly cause feelings of nausea, vomiting, abdominal cramp and headache, as well as diarrhoea and shock. *Itai-itai* disease in Japan was identified among people living in Cadmium-polluted areas where rice was irrigated and their

characteristics are softening of the bones, Kidney failure and Renal tubular dysfunction. Target organs include liver, placenta, kidneys, lungs, brain and bones (Reilly, 2002).

Cadmium in sediment from River Nile exhibited narrow range of variation ranging from 0.4 to 0.7 mg/kg that were higher than the permissible limit of 0.6 mg/kg (WHO, 2008; Alaa and Osman, 2010). The levels of Cd obtained in sediment samples from Tyume River varied between trace and 0.005 ± 0.003 mg/kg and were within the South African Target Water Quality Range (TWQR) for both domestic and irrigation purposes (Awofolu *et al.,* 2005). In the Wadi Hanifah River's sediment samples, the mean concentration of Cd was 71.7 ppb (Abdel-Baki *et al*., 2011). Heavy metal contamination in sediment can affect the water quality and bioaccumulation of metals in aquatic organisms, resulting in potential long-term implication on human health and ecosystem (Fernandes *et al*., 2007; Abdel-Baki *et al*., 2011).

Studies on Cd in various river water have recorded concentrations that are higher than the WHO recommended limit of 0.003 mg/l. Cd concentrations in water from River Nile ranged between 0.002 and 0.02 ppm while Cd mean levels of 0.02 mg/l in water from Nairobi River were all higher than the recommended limit making the water unsuitable for human consumption (Wachira, 2007; WHO, 2008**;**Alaa& Osman, 2010;). Also the mean concentrations of Cd from Tyume River water ranged from 0.030±0.002 to 0.044±0.003 mg/l that was higher than the tentative TWQR guideline of 0 to 0.005 mg/l in river water for domestic use (Awofolu *et al*., 2005). Sources such as agricultural runoff where fertilizers are used, possible release of sediment bound-metals, industrial wastes and atmospheric inflow of dust could have resulted in these levels (Awofolu *et al*., 2005; Alaa & Osman, 2010). It was concluded that water from Tyume River was unsuitable for domestic use and could have chronic health effects on users, hence continual assessment was highly essential (Awofolu *et al*., 2005).

2.3.5 Manganese

Manganese makes up about 1000 ppm (0.1%) of the Earth's crust, thus making it the 12th most abundant element (Emsley, 2001). Mn occurs principally as pyrolusite (MnO_2), psilomelane

$(BaH_2O)_2$ Mn_5O_{10}, and to a lesser extent as rhodochrosite ($MnCO_3$). Manganese compounds are powerful oxidizing agents with various oxidation states (+4, and +7,) and can directly combine with boron, carbon, sulphur, silicon and phosphorous (Emsley, 2001). Among the several oxidation states, the +2 oxidation state is the most stable state and the one used in living organisms for essential functions while other states are toxic for the human body. Depending on their oxidation state, Mn ions have various colours and are used industrially as pigments while MnO_2 is used as the cathode material in standard and alkaline disposable dry cells and batteries. As a free element, it is a metal with important industrial metal alloy uses, particularly in stainless steels and Mn phosphating used as a treatment for rust and corrosion prevention on steel(Zhang & Cheng, 2007). Though it is a required trace mineral for all known living organisms, in larger amounts, and apparently with far greater activity by inhalation, Mn can cause a poisoning syndrome in mammals, with neurological damage which is sometimes irreversible (ATSDR, 2002). Mn-related complications also include psychiatric and motor disturbances, termed manganism which has occurred in people employed in the production and processing of Mn alloys (Nussey *et al.*, 2000). People exposed to high levels of environmental pollution by Mn suffer from cerebella dysfunctions, neurological damage as was once observed in inhabitants of Groote Eylandt off the North coast of Australia (Reilly, 2002).

Studies of Mn in sediments from Nairobi River recorded levels that ranged from 1598.33 to 4322.83 mg/kg (Kage, 2003). Mn concentration in sediments from River Nile ranged from 139.8 to 351.8 mg/kg (WHO, 2003; Alaa & Osman, 2010).

Various levels of Mn in river water that have fluctuated from the WHO recommended limit of 0.4 mg/l have been reported (WHO, 2003; Wachira, 2007;Alaa& Osman, 2010). Mn levels from River Nile that was within the recommended limits fluctuated between 0.033 and 0.14mg/l while higher levels of 2.5 mg/l and 0.423 mg/l were recorded from Nairobi River and River Ganga respectively (WHO, 2003;Wachira, 2007; Kar *et al.*,2008;Alaa & Osman, 2010). The higher levels than the recommended limit of 0.4 mg/l was attributed to a sudden rainfall followed by high river discharge

from upstream environment, industrial effluents and municipal wastes, geology of river bed and catchment area (Wachira, 2007; Kar *et al.*,2008).Adoption of adequate measures to remove the heavy metal load from the industrial waste water and renovation of sewage treatment plants are suggested to avoid further deterioration of the river water quality (Kar *et al.*, 2008).

2.3.6 Copper

Copper is an essential micro-nutrient required in the growth of both plants and animals. In humans, it helps in the production of blood haemoglobin. In plants, copper is especially important in seed production, disease resistance and regulation of water. Copper is indeed essential, but in high doses it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation. Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth. While copper's interaction with the environment is complex, research shows that most copper introduced into the environment is, or rapidly becomes, stable and results in a form which does not pose a risk to the environment. In fact, unlike some man-made materials, copper is not magnified in the body nor bio-accumulated in the food chain (Karen, 2005).

2.3.7 Iron

Iron is the most abundant metal, and is believed to be the tenth most abundant element in the universe. Iron is a metal extracted from iron ore, and is hardly ever found in the free (elemental) state. Iron is the most used of all the metals, comprising 95 percent of all the metal tonnage produced worldwide. Its combination of low cost and high strength make it indispensable, especially in applications like automobiles, the hulls of large ships, and structural components for buildings. Steel is the best known alloy of iron with chemical combination of: 84%Fe, 0.7%C, 4%Cr, 10%W and 1%Mo. Iron is essential to all organisms, except for a few bacteria. It is mostly stably incorporated in the inside of metalloproteins, because in exposed or in free form it causes production of free radicals that are generally toxic to cells. Iron binds vividly to virtually all biomolecules so it will adhere nonspecifically to cell membranes, nucleic acids and proteins. Iron distribution is heavily regulated in mammals. The iron absorbed from the duodenum binds to

transferring, and carried by blood it reaches different cells. It is strongly advised not to let the chemical enter into the environment because it persists in the environment. Excess iron in the body causes liver and kidney damage (haemochromatosis). Some iron compounds are suspected carcinogens (Karen, 2005).

CHAPTER THREE

MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 Equipment/Apparatus

Refrigerator, pH meter, Thermometer, Hana multipurpose parameter model Hi83200, 125cm^3 Conical flask, 200cm^3 beak, Hot plate, Graphite Atomic Absorption Spectrometer, (GAAS model AA990), Measuring cylinder, Whatman filter paper, PVC pipe, 2mm Sieve, Oven, Porcelain crucible, Electronic weighing balance, Steam bath , Plastic bottles, Pestle, Mortar and spatula

3.1.2 Reagents

Nitric acid (HNO_3), Hydrochloric acid (HCl) and deionized distilled Water.

3.2 METHODS

3.2.1 Study Area

Amba River is located along Doma Road in Lafia, Nasarawa State (Fig 3.1). Agricultural activities and human settlements are found on both sides of the river. The water from the river is constantly being used to wash cars, bathing, and laundry, washing of household and domestic utensils. However, this same water is damned at some point, treated and distributed to serve the domestic needs of the people of Lafia town.

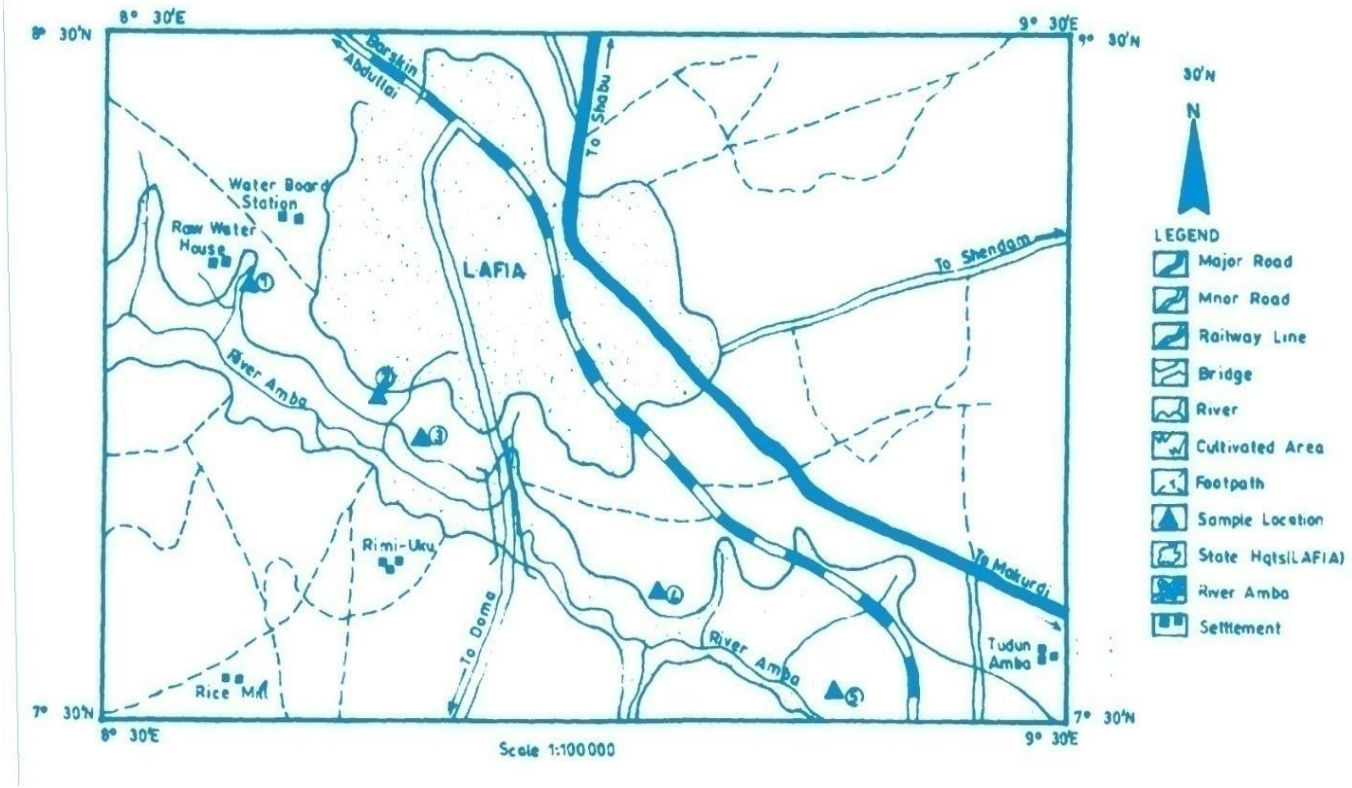

Figure 3.1: Amba River showing sampling locations.

3.2.2 Sampling

Plastic containers were used to collect surface water samples at a depth of 0 - 27 cm from five sites along the river during the rainy season (September, 2015) and dry season (March, 2016). Similarly sediment samples from the selected sites were collected using PVC pipe of 5 cm in diameter which is pushed with pressure through the water to obtain sediment layer at a depth of approximately 0 – 15 cm during the same period as for the water samples. The sampling sites were chosen based on accessibility and intensive agricultural activities that take place at the points.

3.2.3 Sample Preparations

The samples were preserved with 5 cm^3 concentrated HNO_3 and refrigerated to 4^oC pending digestion APHA, (2005). Heavy metals in water were extracted using nitric acid, which is assumed to represent the amount that has been acquired through contamination Arnold and Lenores, (1989). In this method, 5 cm^3 concentrated HNO_3 was added to 100 cm^3 of well-mixed water sample in 125 cm^3 conical flask. The solution was evaporated to about 20 cm^3 on hot plate. Another 5 cm^3concentrated HNO_3 was added and the mixture heated until digestion was completed. Additional 10 $cm^3$of the acid was added and the content filtered and made up to 100 cm^3 with deionized distilled water.

The sediment samples were dried in an oven at 50^oC for two days, then ground and sieved using a 2 mm sieve. Ten grams (10 g) of the sieved sediment sample was weighed into porcelain crucible. Deionized distilled water 25 cm^3 was added followed by 1 cm^3 of concentrated nitric acid (HNO_3) and 3 cm^3 of concentrated hydrochloric acid (HCl). The sample was heated on a steam bath for 1 hour and cooled. The digested sample is filtered and made up to 50 cm^3 with distilled water. The filtrate was stored in plastic bottles for heavy metal analysis. All sediment samples were treated similarly.

3.2.4 Sample Measurement

Some water and sediment physicochemical parameters like pH, temperature, alkalinity, total dissolved solids and electric conductivity were immediately determined before preservation using pH meter, thermometer and Hanna multipurpose parameter model Hi 83200 respectively. Heavy metal concentrations were determined using Graphite Atomic Absorption Spectrophotometry (GAAS model AA990).

3.3 Principle of Atomic Absorption Spectrophotometry

The technique makes use of Absorption Spectrometry to assess the concentration of an analyte in a sample. It requires a standard with known analyte content to establish the relation between the measured and the analyte concentrations and relies on Beer Lambert's law (Christian, 2005; Skoog *et al.*, 2005). Beer Lambert's law states that absorbance is proportional to the concentrations of the attenuating species in the material sample. Mathematically represented as: A =£CL, where A is Absorbance, £ = Molar Absorptivity, C = Concentrations of attenuating species and L = path length. The sample is converted into atomic vapors by a process known as atomization. The precision and accuracy of this method depends on the atomization step and therefore a good choice of the atomization method is required. The two types of atomizers are continuous and discrete atomizers. In continuous atomizers the sample is fed into the atomizer continuously at a constant rate giving a spectral signal which is constant with time. Atomization methods that are of continuous type are flame, inductively coupled argon plasma and direct current argon plasma. With the discrete atomizers, a measured quantity of a sample is introduced as a plug of liquid or solid. The spectral signal in this case rises to maximum and then decreases to zero. An electro thermal atomizer is one of the discrete types. The atoms then absorb radiations of characteristic wavelength from an external source. The atoms of lead, nickel, manganese, zinc, cadmium and chromium, absorb radiations of wavelength of 217.0nm, 232.0nm, 279.5nm, 213.9nm, 228.8nm and 357.9nm, respectively from an external source which is usually a hollow cathode lamp (Ozmen et al., 2004). This technique has been widely employed for elemental analysis in a number of matrices such as soils water, nuts wine and wine products (Tuzen, 2003). Figure 3.2 shows a schematic diagram of the components of an AAS. The two sources of radiation are continuous source which makes use

of deuterium and mercury lamps and a hollow lamp which consists of an anode made of either tungsten wire or wink and a hollow cathode made of either the element of interest or its own salt. Flame atomization method consists mainly of a fuel and oxidant. Their temperatures are determined by flow rate and ratio of oxidant and fuel while the electro thermal atomizer is basically made of carbon rods. The free atoms are vaporized from the carbon atomizer

into the optical light path to a monochromator which presents a monochromatic radiation to the detector. The radiations from the monochromator are received by detector which converts then to electrical signals. Some commonly used detectors are photocells and photo multiplier tubes.

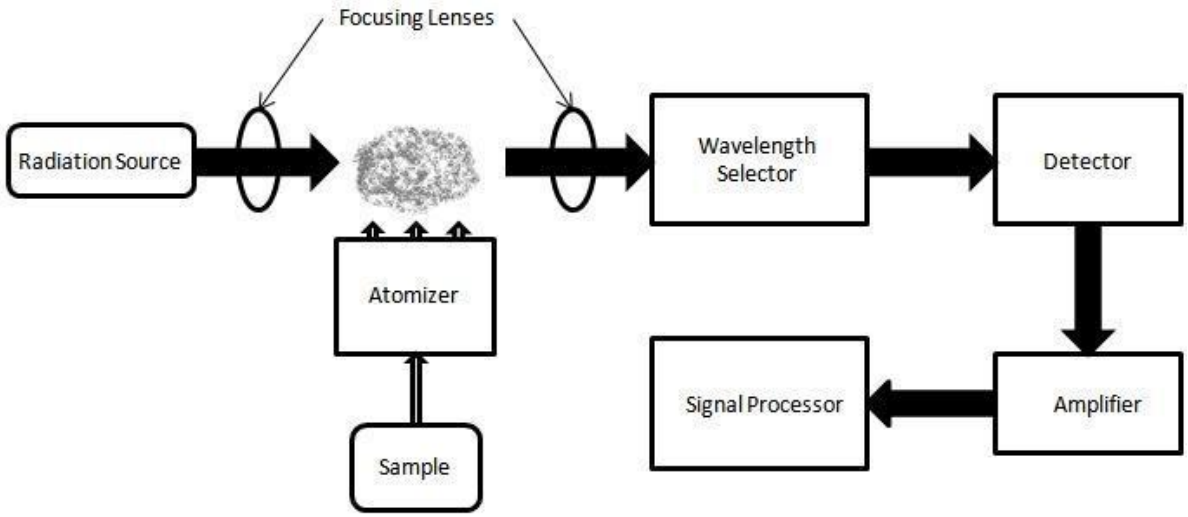

Figure 3.2: Schematic diagram of AAS equipment

3.4 Partition Coefficient

The affinity of a metal to associate with particulate matter is described by its partition coefficient (K_d). It has been shown, by that large amounts of heavy metals are bound in the fine grain fraction (< 63 µm) of the sediment; mainly because of its high surface area to grain size ratio and humic substances content (Tam & Wong, 2000).

The K_d for a metal varies in response to changes in salinity and the nature of the particulate matter present. Mercury and lead have higher coefficients than other metals. Such metals are absorbed

onto sediments have a much greater retention time and tend to remain in the dissolved phase, such as cadmium.

Solid-solution partitioning (K_d) is critical to assess metals bioavailability in sediments (Sauve *et al*., 2003). Metal partition coefficients (K_d) for sediment-water system was calculated (Jerry & Terry, 2005):

$$K_d = \frac{Metal\ concentration\ in\ sediment\ \{mg/Kg\}}{Metal\ Concentration\ in\ water\ (mg/L)} \ldots\ldots\ldots 1$$

3.5 Pollution Load Index (PLI)

The Pollution Load Index (PLI) is obtained as concentration Factors (CF). This CF is the quotient obtained by dividing the concentrations of metal in water with the concentrations of metal in sediment. The PLI of the place are calculated by obtaining the n-root from the n- CFs that was obtained for all the metal. With the PLI obtained from each place (Soares *et al*., 1999). Generally pollution load index (PLI) as developed by Tomlinson *et al.,* (1980), which is as follows:

CF = metal concentration in water / metal concentration in polluted sediment

$PLI = n\sqrt{(CF_1 \times CF_2 \times CF_3 \times \ldots \times CFn)}$……..ii

Where,

CF = contamination factor, n = number of metals

C metal = metal concentration in water

Y metal = metal concentration in polluted sediments.

The PLI value of > 1 is polluted, whereas <1 indicates no pollution (Harikumar *et al*., 2009*).*

3.6 Statistical Analysis

Significant differences ($P \leq 0.05$) in heavy metal concentrations in water and sediment during the rainy and dry seasons were determined using analysis of variance (ANOVA). Correlation analysis between metals in water and sediment were carried out to determine sources and possible contribution of metals to water from sediment. SPSS (v. 20) software was used for both analysis.

CHAPTER FOUR

RESULTS PRESENTATION AND ANALYSIS

4.1 Results Presentation

Levels of physicochemical parameters results for water during the rainy and dry seasons are presented in Tables 4.1. Table 4.2 show the results for heavy metal concentrations in water during rainy season, while results for heavy metal concentrations during dry season are presented in Table 4.3, Mean seasonal variation of heavy metal concentrations in water during rainy and dry seasons are presented in Table 4.4. Levels of physiochemical parameters in sediment during rainy and dry seasons are presented in Table 4.5, Results for heavy metal concentrations in sediment during rainy season are presented in Table 4.6, while that for dry season are shown in Table 4.7. Mean seasonal levels for heavy metal concentration in sediment during rainy and dry seasons are presented in Table 4.8. Pearson correlation coefficients results for parameters in water during rainy season, and dry seasons are presented in Tables 4.9 and 4.10 respectively. Correlation coefficients for heavy metal during rainy season are presented in Table 4.11, while that for dry season in Table 4.12. Table 4.13 show correlation coefficients between water and sediment during rainy season, while that for dry season in Table 4.14.Partition coefficients for sediment/water heavy metal concentrations during rainy season are presented in Table 4.15 and that for dry season in Table 4.16.Seasonal sediment/ water partition coefficient results are presented in Table 4.17. Pollution index for heavy metals in water and sediment are presented in Table 4.18.

Table 4.1**:** Levels of physiochemical parameters of water during rainy and dry seasons

Sampling points	Parameters				
	pH	Temp. (^{o}C)	TDS (mg/L)	EC (µs/cm)	Alkalinity (mg $CaCO_3$/L)
Rainy Season					
1	6.70±0.00	28.00±0.00	78.00±1.00	41.00±0.00	14.50±0.50
2	6.70±0.00	28.00±0.00	75.00±0.00	42.00±0.00	21.00±1.00
3	6.75±0.05	27.50±0.50	67.50±0.50	36.00±0.00	60.00±0.00
4	6.80±0.00	28.00±0.00	55.50±0.50	37.00±0.00	40.00±0.00
5	6.80±0.00	28.00±0.00	32.50±1.50	69.00±0.00	36.00±0.00
Mean±SD	6.75±0.04	27.90±0.16	69.00±7.50	45.00±9.60	34.30±13.24
Dry Season					
1	6.70±0.00	28.00±0.00	148.50±0.50	185.00±0.00	60.50±0.50
2	6.70±0.00	27.50±0.50	150.50±0.50	184.00±0.00	55.50±0.50
3	6.80±0.00	28.00±0.00	146.00±0.00	179.00±0.00	52.50±0.50
4	6.80±0.00	28.00±0.50	125.00±0.00	160.00±0.00	47.50±0.50
5	6.80±0.00	28.00±0.00	110.00±0.00	145.50±0.50	40.50±0.50
Mean±SD	6.76±0.05	27.90±0.16	136.00±14.80	170.70±14.36	51.30±5.84
NIS	6.5-8.5	NS	500	1000	50

Table 4.2: Concentrations (mg/L) of heavy metals in water during rainy season

Elements	Sampling points 1	2	3	4	5	Mean±SD	WHO(2011)
Cd	0.12±0.02[a]	0.05±0.00[a]	0.80±0.00[a]	0.18±0.00a	0.56±0.00[a]	0.34±0.27	0.003
Cr	0.01±0.01[a]	4.01±0.01[b]	ND	ND	ND	2.01±2.00	0.05
Cu	5.05±0.01[a]	7.00±0.00[a]	0.27±0.04[b]	0.31±0.00[b]	0.42±0.01[b]	2.61±2.73	2
Fe	1.62±0.06[a]	1.43±0.01[a]	9.27±0.53[b]	2.41±0.01[a]	1.62±0.01[a]	3.27±2.40	0.3
Mn	0.36±0.06[a]	ND	0.27±0.01[a]	0.30±0.00[a]	0.30±0.01[a]	0.31±0.03	0.2
Zn	ND	ND	ND	ND	0.20±0.00[a]	0.20±0.00	3
Pb	ND	ND	0.07±0.00[a]	0.01±0.00[b]	0.02±0.00[b]	0.03±0.02	0.01

ND: Below detection limit; Mean values within the same rows with different alphabets are significantly different at $P \leq 0.05$

Table 4.3: Concentrations (mg/L) of heavy metals in water during dry season

Elements	Sampling points					
	1	2	3	4	5	mean±SD
Cd	0.02±0.00[a]	0.25±0.00[b]	0.18±0.00[b]	0.02±0.00[a]	0.12±0.00[b]	0.12±0.08
Cr	2.80±0.00[a]	2.50±0.71[a]	3.10±0.00[a]	2.50±0.00[a]	3.00±0.00[a]	2.70±0.56
Cu	ND	ND	ND	ND	ND	ND
Fe	0.01±0.00[a]	3.16±0.00[b]	1.34±0.00[b]	2.45±0.00[b]	0.93±0.00[a]	1.59±0.98
Mn	0.01±0.01[a]	ND	ND	0.10±0.00[a]	0.65±0.07[b]	0.25±0.26
Zn	1.07±0.01[a]	1.21±0.00[a]	1.11±0.00[a]	0.02±0.00[a]	1.65±0.00[a]	1.01±0.40
Pb	ND	ND	ND	ND	ND	ND

ND: Below detection limit; Mean values within the same row with different alphabets are significantly different at $P \leq 0.05$

Table 4.4: Mean seasonal variations of heavy metals concentration (mg/L) in water

Elements	Rainy season	Dry season
Cd	0.34±0.30[a]	0.12±0.10[b]
Cr	0.80±1.69[a]	2.70±0.57[b]
Cu	2.61±3.01[a]	0.00±0.00[b]
Fe	3.27±3.19[a]	1.78±0.93[a]
Mn	0.24±0.13[a]	0.15±0.27[a]
Zn	0.04±0.08[a]	1.21±0.24[b]
Pb	0.02±0.03[a]	0.00±0.00[a]

Correlation coefficients with different alphabets within the same row are significantly different at ($P \leq 0.05$

Table 4.5: Levels of physiochemical parameters in sediment during rainy and dry seasons

Sampling points	Parameters				
	pH	Temp. (^{o}C)	TDS (mg/Kg)	EC (µs/Cm)	Alkali. (mg$CaCO_3$/L)
Raining season					
1	6.75±0.05	28.00±0.00	81.00±0.00	36.00±0.00	23.50±0.50
2	6.70±0.00	27.50±0.50	66.50±0.50	46.00±0.00	29.00±1.00
3	6.80±0.00	28.50±0.50	71.00±0.00	40.00±0.00	52.50±0.50
4	6.80±0.00	28.00±0.00	70.00±0.00	45.00±0.00	36.00±0.00
5	6.80±0.00	27.50±0.50	25.50±0.50	70.55±0.45	45.00±1.00
Mean±SD	6.77±0.04	27.90±0.32	62.80±14.92	47.51±9.22	37.20±9.24
Dry season					
1	6.80±0.00	28.00±0.00	126.00±0.00	191.00±0.00	80.00±0.00
2	6.70±0.00	28.00±0.00	128.00±0.00	176.00±0.00	37.00±0.00
3	6.80±0.00	28.00±0.00	138.00±0.00	186.00±0.00	48.00±0.00
4	6.70±0.00	27.50±0.50	116.00±0.00	155.00±0.00	46.00±0.00
5	6.80±0.00	28.00±0.00	108.50±0.50	162.00±0.00	38.00±0.00
Mean±SD	6.76±0.05	27.90±0.16	123.30±8.84	174.00±12.40	49.80±12.08

Table 4.6: Concentrations (mg/Kg) of heavy metals in sediment during rainy season

Elements	Sampling points					mean±SD	WHO(2008)
	1	2	3	4	5		
Cd	0.25±0.00[a]	0.81±0.01[b]	0.42±0.00[b]	1.60±0.00[b]	0.22±0.01[a]	0.53±0.43	0.6
Cr	ND	0.19±0.01[a]	0.37±0.02[b]	ND	0.20±0.00[a]	0.25±0.08	37.5
Cu	4.77±0.33[a]	10.91±0.03[a]	0.43±0.00[b]	0.38±0.00[b]	0.96±0.01[b]	3.49±3.48	20
Fe	5.82±0.01[a]	9.60±0.06[a]	10.01±0.01[a]	8.72±0.00[a]	4.04±0.00[a]	7.64±2.17	1.88
Mn	0.20±0.00[a]	3.28±0.00[a]	2.05±0.07[a]	11.05±0.08[b]	1.55±0.01[a]	3.63±2.97	9.30
Zn	ND	0.10±0.00[a]	0.35±0.00[a]	0.06±0.01[a]	ND	0.17±0.12	123
Pb	0.01±0.00[a]	0.12±0.01[a]	0.07±0.01[a]	0.33±0.01[a]	0.16±0.01[a]	0.14±0.09	3.70

ND: below detection limit; Mean values within the same row with different alphabets are significantly different at $P \leq 0.05$

Table 4.7: Concentrations (mg/Kg) of heavy metals in sediment during dry season

	Sampling points					
Elements	1	2	3	4	5	mean±SD
Cd	1.05±0.00[a]	0.52±0.00[a]	0.73±0.00[a]	1.01±0.00[a]	0.67±0.00[a]	0.80±0.19
Cr	2.10±0.01[a]	2.05±0.07[a]	3.70±0.00[a]	4.80±0.00[b]	4.50±0.00[b]	3.47±0.87
Cu	0.13±0.00[a]	0.17±0.00[a]	0.01±0.00[a]	0.38±0.01[a]	ND	0.17±0.10
Fe	6.31±0.00[a]	3.37±0.00[a]	6.26±0.00[a]	3.36±0.00[a]	1.96±0.00[a]	4.25±1.63
Mn	0.10±0.07[a]	0.35±0.07[a]	0.10±0.07[b]	0.35±0.07[a]	0.02±0.00[b]	0.18±0.13
Zn	1.10±0.00[a]	1.08±0.00[a]	1.04±0.00[a]	1.02±0.00[a]	0.55±0.07[b]	0.96±0.16
Pb	0.04±0.00[a]	0.02±0.00[a]	0.02±0.01[a]	0.43±0.00[a]	0.13±0.00[a]	0.13±0.15

ND: below detection limit; Mean values within the same row with different alphabets are significantly different at $P \leq 0.05$

Table 4.8: Mean seasonal variations of heavy metals concentration (mg/kg) in sediment

Elements	Raining season	Dry season
Cd	0.66±0.54[a]	0.80±0.21[a]
Cr	0.15±0.15[a]	3.47±0.87[b]
Cu	3.49±4.27[a]	0.14±0.14[b]
Fe	7.64±2.44[a]	4.25±1.83[b]
Mn	3.63±4.05[a]	0.16±0.17[b]
Zn	0.10±0.14[a]	0.96±0.22[b]
Pb	0.14±0.11[a]	0.13±0.17[a]

Correlation coefficients with different alphabets within the same row are significantly different at ($P \leq 0.05$)

Table 4.9: Pearson correlation coefficients for water parameters during rainy season

pH	TDS	Cd	Cr	Cu	Fe	Mn	Zn	Pb	
pH	1	-0.779	0.394	-0.501	-0.791	0.040	0.353	0.500	0.373
TDS		1	-0.426	0.402	0.689	0.147	-0.286	-0.882	-0.105
Cd			1	-0.504	-0.727	0.786	0.319	0.376	0.711
Cr				1	0.769	-0.304	-0.962	-0.250	-0.425
Cu					1	-0.476	-0.598	-0.383	-0.687
Fe						1	0.147	-0.273	0.834
Mn							1	0.196	0.246
Zn								1	-0.158
Pb									1

Table 4.10: Pearson correlation coefficients for water parameters during dry season

		pH	TDS	Cd	Cr	Fe	Mn	Zn	Pb
pH	1	-0.693	-0.138	0.649	-0.287	0.479	-0.188	0.028	
TDS		1	0.314	- 0.541	0.296	-0.891	-0.050	-0.024	
Cd			1	-0.292	0.402	-0.067	0.521	0.022	
Cr				1	-0.907	0.596	0.347	-0.716	
Fe					1	- 0.438	-0.436	0.886	
Mn						1	0.467	-0.347	
Zn							1	-0.760	
Pb								1	

Table 4.11: Pearson correlation coefficients for physiochemical parameters in sediment during rainy season

	pH	TDS	Cd	Cr	Cu	Fe	Mn	Zn	Pb
pH	1	-0.482	0.412	-0.592	-0.388	-0.287	0.494	-0.462	0.547
TDS		1	-0.038	0.008	0.880	0.507	-0.263	0.155	-0.490
Cd			1	-0.415	-0.049	0.515	0.974	-0.050	0.854
Cr				1	-0.090	0.317	0.398	0.786	-0.339
Cu					1	0.229	-0.256	-0.189	-0.340
Fe						1	0.389	0.720	0.125
Mn							1	0.071	0.932
Zn								1	-0.227
Pb									1

Table 4.12: Pearson correlation coefficients for sediment parameters during dry season

	pH	TDS	Cd	Cr	Cu	Fe	Mn	Zn	Pb
pH	1	0.569	-0.164	0.301	0.816	-0.335	0.698	0.258	0.700
TDS		1	-0.049	- 0.419	0.689	-0.196	0.813	0.511	0.169
Cd			1	-0.048	0.476	0.419	-0.093	0.308	0.476
Cr				1	0.124	-0.541	0.075	-0.555	0.670
Cu					1	-0.167	0.791	0.448	0.776
Fe						1	-0.345	0.689	-0.441
Mn							1	0.496	0.483
Zn								1	-0.104
Pb									1

Table 4.13: Pearson correlation coefficients between water and sediment parameters during rainy season

	pH	TDS	Cd	Cr	Cu	Fe	Mn	Zn	Pb
pH	0.408	-0.343	-0.223	-0.408	-0.314	-0.336	0.385	0.102	-0.099
TDS	-0840	0.878	-0.526	0.766	0.894	-0.075	- 0.650	-0.664	-0.361
Cd	0.297	0.020	-0.413	0.143	-0.135	-0.142	-0.182	-0.426	0.149
Cr	0.000	-0.111	0.786	0.126	-0.244	0.731	-0.296	0.181	0.518
Cu	-0.708	0.582	-0.666	0.916	0.960	-0.446	-0.788	-0.312	-0.630
Fe	-0.229	0.560	-0.011	0.423	0.122	0.531	-0.508	-0.776	0.451
Mn	0.472	-0.173	-0.271	-0.046	-0.341	-0.105	-0.018	-0.270	0.240
Zn	-0.069	0.280	0.651	-0.004	-0.273	0.951	-0.154	-0.388	0.752
Pb	0.650	-0.498	-0.165	-0.095	-0.462	-0.230	-0.011	0.090	0.176

Table 4.14: Pearson correlation coefficients between water and sediment parameters during dry season

	pH	TDS	Cd	Cr	Fe	Mn	Zn	Pb
pH	0.089	-0.096	-0.159	-0.508	0.677	-0.218	-0.726	0.851
TDS	-0.668	0.388	-0.101	-0.962	0.842	-0.461	-0.375	0.707
Cd	0.039	-0.027	-0.947	0.179	-0.327	-0.237	-0.623	0.020
Cr	0.944	-0.789	-0.101	0.434	-0.038	0.538	-0.273	0.272
Cu	-0.078	0.006	-0.439	-0.606	0.641	-0.378	-0.704	0.872
Fe	-0.275	0.741	-0.146	0.080	-0.307	-0.712	-0.094	-0.441
Mn	-0.182	0.137	0.136	-0.827	0.920	-0.369	-0.602	0.930
Zn	-0.512	0.865	-0.016	-0.621	0.443	-0.994	-0.513	0.375
Pb	0.508	-0.576	-0.578	-0.044	0.259	0.162	-0.792	0.664

Table 4.15: Sediment/water heavy metals partition coefficients (K_d) during rainy season

	Sampling points				
Elements	1	2	3	4	5
Cd	2.06	15.48	0.52	8.76	0.39
Cr	0.00	0.05	0.37	0.00	0.00
Cu	0.94	1.56	1.59	1.23	2.27
Fe	3.60	6.71	1.08	3.62	2.50
Mn	0.56	3.28	7.59	36.83	5.25
Zn	0.00	0.00	0.00	0.00	0.00
Pb	0.00	0.00	1.01	36.67	10.33

Table 4.16: Sediment/Water heavy metals partition coefficients (K_d) during dry season

	Sampling points				
Elements	1	2	3	4	5
Cd	64.86	2.08	3.97	56.08	5.45
Cr	0.43	1.03	1.19	1.85	1.36
Cu	0.00	0.00	0.00	0.00	0.00
Fe	485.04	1.06	4.69	1.37	2.11
Mn	10.00	0.00	0.00	3.50	0.04
Zn	1.04	0.89	0.94	14.61	0.33
Pb	0.00	4.70	16.00	61.57	0.00

Table 4.17 Seasonal mean Sediment /Water partition coefficients

Elements	Rainy Season	Dry Season
Cd	1.14	1.46
Cr	0.72	1.03
Cu	1.06	0.00
Fe	1.12	1.22
Mn	1.72	1.04
Zn	1.20	0.99
Pb	1.50	2.18

Table.4.18: Pollution Index values for Heavy Metals in Water and Sediment along Amba River

Elements	Raining season	Dry season
Cd	0.44	0.09
Cr	0.00	0.95
Cu	0.69	0.00
Fe	0.33	0.17
Mn	0.00	0.00
Zn	0.00	0.57
Pb	0.00	0.00

4.2 Discussion of Results

4.2.1 Physicochemical properties of water

The results for water physicochemical parameters during rainy and dry seasons are presented in Table 4.1.The water pH varied slightly according to sites and similar for both seasons. Mean water pH values during rainy season (6.75±0.04) and dry season (6.76±0.05) were slightly above the maximum permissible limit of pH= 6.5 as recommended by WHO, (2011).The measured temperature of the water depicted the changes according to the seasons. The surface water temperature varied from 27.5 to 28 ^{o}C during rainy season and 27.5 to 28.5 ^{o}C in the dry season.

The levels of TDS ranged from 32.5 to 78 mg/L during rainy season and 110 to 150.5 mg/L during the dry season. The TDS level (136.00±14.36 mg/L) was higher during the dry season; which might be attributed to reduced water volume. The concentrations of total dissolved solids (TDS) were within the permissible limits of (500mg/L) set by WHO (2011).

Conductance quantitatively reflects the status of inorganic pollution and is a measured of total dissolved solids and ionized species in the water. The conductivity of water was found to have varied from 36 to 69µs/cm in dry season and 145.5 to 185 µs/cm during rainy season. The EC levels during rainy season was highest at site 5 (69.00 µs/cm) and lowest at site 3 (36.00 µs/cm); but highest at site 1 (185.00 µs/cm) and lowest at site 5 (145.00 µs/cm) during the dry season. The increase in EC during the dry season might be connected to decrease in the volume of water. All the values were found to be below the maximum permissible limits of 1000µs/cm set by WHO (2011) as indicated in Table 4.1.

Total alkalinity levels of water ranged from 14.50 to 60.00 mg$CaCO_3$/L during rainy season and 40.50 to 60.50 mg$CaCO_3$/L in dry season. The concentration of total alkalinity was highest at site 3 (60.00 mg$CaCO_3$/L) and lowest at site 1 (14.50 mg$CaCO_3$/L) during rainy season, while highest at site 1 (60.00 mg$CaCO_3$/L) and lowest at site 5 (40.00 mg$CaCO_3$/L) during the dry season which followed slightly same trend for both seasons. The mean level (51.30±5.80 mg$CaCO_3$/L) indicated

lower level of alkalinity as compared to FAO, (2011) and WHO, (2011) permissible limits of 100 mg/L. The results in this study were consistent with what was reported by Tukura *et al*., (2012).

4.2.2 Metal concentrations in water

The levels of Cd, Cr, Cu, Fe, Mn, Zn, and Pb in water during rainy and dry seasons are presented in Tables 4.2 and 4.3 respectively. Metal levels show some seasonal variations. The presence of these heavy metals in the water could be attributed to discharge of agricultural effluents and municipal wastes, geology of river bed and catchment area (Kar*et al.*, 2008; Obasohan, 2008). It was also found that most of the elements varied significantly ($P \leq 0.05$) between the sampling sites. Cadmium concentration ranged from 0.05 to 0.80 mg/L during rainy season and 0.02 to 0.25 mg/L during the dry season. Relatively higher concentrations were recorded at sites 3 (0.80 mg/L) and 5 (0.56 mg/L) respectively, while site 2 had the lowest value (0.05 mg/L) during rainy season. Cd concentration was highest at site 2 (0.25 mg/L) during the dry season. There were no significant differences ($P \leq 0.05$) in Cd concentrations along the sampling stations for both seasons. The mean concentrations of Cd (Table 4.2) during the rainy season (0.34±0.27 mg/L) and dry season (0.12±0.08 mg/L) indicated that cadmium was higher during the rainy season. The levels of Cd recorded were above the recommended limit of 0.003 mg/L in drinking water (WHO, 2011). The element is toxic even at low levels which can result to feelings of nausea, vomiting, abdominal cramp and headache, as well as diarrhea and shock. About 15 mg of cadmium has been reported to cause these effects with target organs including liver, placenta, kidneys, lungs, brain and bones (Li *et al.*, 2014).

The concentration of Cr ranged from 0.00 to 4.01 mg/L during the rainy season and from 2.50 to 3.10mg/L during the dry season. Cr concentrations were greatly higher during the dry season, especially at sites 3 (3.10 mg/L) and 5 (3.00 mg/L) compared to rainy season; however, at site 2 during the rainy season, the concentration of Cr (4.01 mg/L) was highest. The higher concentrations of Cr during the dry season may be as a result of the decrease in water volume (Martin *et al*., 2015). Cr mean levels were above recommended limit of 0.05 mg/L in drinking

water (WHO, 2011).The element is very toxic and mutagenic when inhaled and is a known human carcinogen. Breathing of Cr at high levels can cause irritation to the lining of the nose, runny nose and breathing problems (Dayan & Paine, 2001).

The concentration of Cu varied from 0.27 to 7.00 mg/L during the rainy season but below detection limit during the dry season for all sampling sites. The concentrations of Cu were highest at sites 1 (5.05 mg/L) and 2 (7.00 mg/L), but lowest at site 3 (0.27 mg/L) during rainy season. The increase in concentration upstream during the rainy season may be as a result of increased farming, rice millers' activities and waste discharged from Water Board treatment plant, whereas non detection of Cu at dry season may be attributed to reduced runoff into the water, and perhaps intake of this element by fish and plants (Akan *et al.,* 2010).

The concentration of Fe ranged from 1.43 to 9.27 mg/L during the rainy season and 0.01 to 3.16 mg/L in dry season. Concentration of Fe varied significantly ($P \leq 0.05$) at site 3 from other sites. During the dry season, concentration was highest at site 2(3.16 mg/L) and lowest at site 1 (0.01 mg/L). Fe mean concentrations of 3.27±2.40 mg/L for rainy season and 1.75±0.93 mg/L for dry season reflected higher concentration during the rainy season over dry season; and the values exceeded the recommended limit of 0.30 mg/L (WHO 2011). Variations in concentration of Fe during the rainy season show that the highest level was recorded at site 3 (9.27±0.53 mg/L) where the rice mill waste is discharged into the river.

Concentration of Mn ranged from 0.00 to 0.36 mg/L during rainy and varied from 0.00 to 0.65 mg/L at dry season. Mn concentration was highest at site 1 (0.36 mg/L) and lowest at site 3(0.27 mg/L) during the rainy season, while the highest level was recorded at site 5 (0.65 mg/L) during the dry season. The mean concentrations of Mn were0.31±0.03 mg/L and 0.25±0.26 mg/L for rainy and dry seasons respectively, and were within the recommended limit (0.4 mg/L) for drinking water(WHO, 2011).The high concentration may be attributed to runoff from rice mill and residential areas into the River (Maceda-Veiga *et al.,* 2012).

Zn concentration varied from 0.00 to 0.20 mg/L during the rainy season and ranged from 0.02 to 1.65 mg/L in dry season. The concentration of Zn was only recorded at site 5 (0.20mg/L)for rainy season and below detection limit upstream. Concentration of Zn was highest at site 5 (1.65 mg/L) and lowest at site 4 (0.02 mg/L) during the dry season. The mean levels of Zn were 0.20±0.00 mg/L for rainy season and 1.01±0.40 mg/L during the dry season. Zn levels were highest in dry season. Zn levels were within the recommended limit of 3 mg/L for drinking water (WHO, 2011). Zn metal concentrations do not follow any particular trend during the seasons.

Pb concentrations recorded during rainy season ranged from 0.00 to 0.07 mg/L and were below detection limit during dry season. Pb concentration was highest at site 3 (0.07 mg/L), but lowest at site4 (0.01 mg/L) during the rainy season. Pb mean value (0.03±0.02 mg/L) during the rainy season Table 4.2 was higher than the WHO recommended limit of 0.01 mg/L in drinking water (WHO, 2011). This indicates a high pollution of water from the river, which may pose health risk of Pb poisoning,; as the element is known to be toxic even at low levels **(**Mwegoha & Kihampa, 2010).

Seasonal mean variations in heavy metal concentrations in water Table 4.4 shows that Fe has the highest mean concentration of 3.27±3.19 mg/L followed by Cu(2.61±3.01 mg/L) and the least for Pb(0.02±0.03 mg/L) during the rainy season, while Cr has the highest mean concentration of 2.70±0.57 mg/L followed by Fe(1.78±0.93 mg/L) and Zn (1.21±0.24 mg/L), and the lowest levels for Cu and Pb during the dry season. Analysis of variance for rainy and dry seasons indicated that Cd, Cr, Cu, and Zn in water were significantly different ($P \leq 0.05$). Variation in heavy metal levels in water during the periods of analysis might be attributed to changes in physicochemical parameters to include pH and temperature.

The present study reported higher mean concentrations of heavy metals in water during the rainy season than the previous results reported by Usman *et al.*,(2010), except for Cd, Zn and Pb. Isibor and Izegaebe (2016) reported higher concentrations of Mn, Zn and Pb in Ovia River compared to the results obtained in this study.

4.2.3 Physicochemical properties of sediment

Physicochemical properties results for sediment are presented in Table 4.5. The pH varied according to sites and seasons. During the both seasons, sediment pH was slightly acidic and ranged from 6.7 to 6.8. At low pH, hydrogen ion competes with metal cations adsorbed onto sediment surface leading to their remobilization into the water column. Temperature also varied according to sites and ranged from 27.5 to 28.5^{o}Cand 27.5 to 28^{o}C during the rainy and dry seasons respectively. TDS levels ranged from 25.5 to 81 mg/Kg at rainy rainy season and 108.5 to 138 mg/Kg during the dry season. The highest and lowest concentrations were recorded at sites1 (81.00 mg/Kg) and 5 (25.5 mg/Kg) during rainy season and 5(108.50 mg/Kg) and 3 (138.00 mg/Kg) during dry season. The mean levels of TDS according to seasons indicated higher levels during the dry season.

Conductivity ranged from 36.00 to 70.55 µs/cm in rainy season and 155.00 to 191.00 µs/cm during the dry season. The lowest and highest levels during the rainy season were at sites 1 (36.00 µs/cm) and 5 (70.55 µs/cm) respectively, and at sites 4 (155.00 µs/cm) and 1 (191.00 µs/cm) during the dry season. The mean levels for rainy season (47.51±9.22 µs/cm) and dry season (174.00±12.40 µs/cm) show that conductivity during dry season was higher than rainy season, which may be as a result of the decrease in water volume during the period. The levels of alkalinity ranged from 23.50 to 52.50 mg$CaCO_3$/L during rainy season and 37.00 to 80.00 mg$CaCO_3$/L during dry season. Highest level of alkalinity was obtained at site 3(52.50 mg$CaCO_3$/L) and the lowest at site 1 (23.50 mg$CaCO_3$/L) during rainy season, and at sites 1 (80.00 mg$CaCO_3$/L) and 2 (37.00 mg$CaCO_3$/L) during the dry season. The mean levels of alkalinity were 37.20±9.24 mgCaCO3/L for the rainy season and 49.80±12.08 mg$CaCO_3$/L during the dry season, which was higher than the level recorded during the rainy season. Variations in physicochemical properties agreed with the results reported by Tukura *et al.,(*2012) for water and sediment.

4.2.4 Metal concentrations in sediment

The levels of heavy metals in sediments during the rainy season are presented in Tables 4.6.The concentrations of Cd ranged from 0.22 to 1.60mg/kg in rainy season. The highest and lowest Cd levels were recorded at sites 4 (1.60 mg/Kg) and 5 (0.22 mg/Kg) respectively during the rainy season. At sites 2 (0.81 mg/Kg) and 4 (1.60 mg/Kg), the levels were higher than the recommended limit of 0.6 mg/Kg, while the values at sites 1(0.25 mg/Kg), 3 (0.42 mg/Kg) and 5 (0.22 mg/Kg) during the rainy season were below the recommended limit WHO, (2008). The mean concentration was recorded as 0.53±0.43 mg/Kg during the rainy season. There were significant differences ($P \leq 0.05$) in the levels of Cd reported during the rainy season among the sampling points. However, the highest concentration (1.60 mg/Kg) was recorded at site 4 and the lowest (0.22 mg/Kg) at site 5. Urban waste may be attributed to these high levels at station 4 Concentrations for chromium during the rainy season ranged from 0.00 to 0.37 mg/Kg. Cr was highest at site 3 (0.37 mg/Kg) and has the lowest value at site 2 (0.19 mg/Kg) during the rainy season, whereas at sites 1and 4 the levels were below detection limit. The mean levels of Cr during the rainy season and dry season were significantly different ($P \leq 0.05$). The values were below the recommended limit of 37.5 mg/kg in sediments as recommended by WHO, (2008).

The copper concentrations ranged from 0.38 to 10.91 mg/Kg during the rainy season. The concentration of Cu was highest at site 2 (10.91 mg/Kg) and lowest at site 4 (0.38 mg/Kg) during the rainy season. Sites 1 and 2 were located at water pumping station and rice mill waste drainage respectively, which were characterized by untreated waste from these sources. The concentrations of copper were significantly different ($P \leq 0.05$) during the rainy season.

The concentration of Fe ranged from 4.04 to 10.01 mg/Kg during the rainy season. The highest concentration of Fe was observed at site 3 (10.01 mg/Kg) and lowest value at site 5 (4.04 mg/Kg) during the period. The mean concentration of Fe during the rainy season was 7.64±2.17 mg/Kg. Statistical tests showed that the metal concentrations were not significantly different ($P \leq 0.05$)

among sampling sites. The levels of Fe in all sampling points were higher than the permissible limit of 1.88 mg/Kg (WHO, 2008).

Concentrations of Mn recorded during the rainy season varied from 0.20 to 11.05 mg/Kg. Concentration at site 4 (11.05 mg/Kg) was the highest, and varied significantly from remaining sampling sites. The lowest level was recorded at site 1 (0.20 mg/Kg) during the rainy season. The level of Mn decreased during the dry season, and was below recommended limit of 9.30 mg/Kg in sediment (WHO, 2008). The decrease in the level of Mn may be due to decrease in the volume of water during the season. The mean seasonal levels of Mn varied significantly ($P \leq 0.05$), with higher values recorded during the rainy season. The higher values observed during rainy season could be attributed to water runoff from the garages, car wash and surface soils exposed to water (Alaa and Osman, 2010). The low concentration of Mn during dry season may be due to remobilization of heavy metals back to the water and uptake by aquatic plant (Kar *et al*., 2008). Though the limit of Mn in sediments is not documented, in larger amounts, and apparently with far greater activity by inhalation, Mn can cause a poisoning syndrome in mammals, with neurological damage which is sometimes irreversible (ATSDR, 2002).

Zinc concentrations recorded during the rainy season ranged from 0.00 to 0.35 mg/Kg. Zinc have highest and lowest values at sites 3 (0.35 mg/Kg) and 4 (0.06 mg/Kg) during the rainy respectively. The mean level was 0.17±0.12 mg/Kg below threshold limit of 123 mg/Kg in sediment (WHO, 2008).

Lead concentrations varied from 0.01 to 0.33 mg/Kg during the rainy season. Lead concentration was higher at site 4 (0.33 mg/Kg) and lower at site 1 (0.01 mg/Kg) during the rainy season and there was no significant different ($P \leq 0.05$) among the sites during the rainy season. The mean concentration of Pb was 0.14±0.09 mg/Kg below recommended limit of 3.70 mg/Kg in sediment WHO (2008). Generally, the Pb concentrations indicated a decrease downstream which might be attributed to the remobilization of sediment into the water column (Mwegoha & Kihampa, 2010). The seasonal variations in the mean levels of Pb show higher concentrations during the rainy

season. Nonetheless, the levels were not significantly different (P≤0.05).The concentrations of heavy metals in sediment during the dry season are presented in Table 4.7 and Appendix IV. The Cd levels varied from 0.52 to 1.05 mg/Kg during the dry season. Cd has the highest level at site 1 (1.05 mg/Kg) and 2 (0.52 mg/Kg) during the dry season respectively. The levels of Cd sites 1(1.05 mg/Kg), 3 (0.73 mg/Kg), 4 (1.01 mg/Kg) and 5 (0.67 mg/Kg), except site 2 (0.52 mg/Kg) were higher than the recommended limit of 0.6 mg/Kg (WHO, 2008) during the dry season. Higher mean concentration (0.80±0.19 mg/Kg) of Cd was recorded during the dry season. There was no significant difference (P≤0.05) in the concentration of Cd in the sampling sites during the dry season.

The levels of Cr during the dry season ranged from 2.10 to 4.80 mg/Kg. Cr was highest at site 4 (4.80 mg/Kg) and lowest at site 1 (2.10 mg/Kg) during dry season. The mean concentration of Cr was during the dry season. Higher concentrations of Cr (3.47±0.87 mg/Kg) during the dry season may be due to decrease in the volume of water in the river. The seasonal mean concentration of Cd was during dry season, and was not significantly different (P ≤ 0.05).

Copper levels varied from 0.00 to 0.38 mg/Kg during the dry season. The concentration of Cu was highest at site 4 (0.38 mg/Kg) and lowest at site 3 (0.01 mg/Kg) during the dry season. The levels of Cu across sites were not significantly different (P≤0.05) during the dry season. The mean level of Cu for rainy season was significantly higher than during the dry season, however, below the recommended limit of 20 mg/Kg (WHO, 2008).Low concentration of Cu during dry season may be attributed to remobilization of this metal into water and absorption of its fraction by plants (NIS, 2011).

The levels of Fe ranged from 1.96 to 6.31 mg/Kg during the dry season. The highest and lowest Fe concentrations in dry season were observed at sites 1 (6.31 mg/Kg) and 5 (1.96 mg/Kg) respectively.

The concentrations of Mn ranged from 0.02 to 0.35 mg/Kg during the dry season, and was highest at sites 2 and 3 (0.35 mg/Kg), while the lowest level was recorded at site 5 (0.02 mg/Kg) during

the dry season. The values were not significantly different (P≤0.05). The seasonal mean variations of Fe were significantly (P≤0.05) higher during the rainy season. The increased in the concentrations of iron during the rainy season may be due to the runoff of rainfall and reduction in iron concentration in dry season may be due to reduced erosion that washed waste from domestic and agricultural effluent into the River (Phiri *et al.,* 2005).

Zinc levels recorded during thedry season ranged from 0.55 to 1.10 mg/Kg. Zinc levels were highest at site 1 (1.10 mg/Kg) and lowest at site 5 (0.55 mg/Kg) during the dry season. Site 5 (0.55 mg/Kg) was significantly different (P≤0.05) from the remaining sites. The mean concentration of Zinc was 0.96±0.16 mg/Kg in the dry season and below permissible limit of 123 mg/Kg in sediment WHO, (2008).Seasonal variations of Zn during the rainy and dry seasons show that the values were significantly different (P≤0.05) higher during the dry than rainy season. Sediments are known to accumulate heavy metals and with time might be remobilized back to the water and follow the food chain (WHO, 2003; Kar *et al*., 2008).

The levels of lead varied from 0.02 to 0.43 mg/Kg during the dry season. Lead concentration was higher at site 4 (0.43 mg/Kg) and lower at sites 2 and 3 (0.02 mg/Kg) respectively during the dry season. The seasonal levels of Pb were not significant different (P≤0.05). The mean concentration of Pb (0.13±0.15 mg/Kg) during the dry season was below the threshold limit of 3.70 mg/Kg (EPA, 2008); an indication of low pollution.

The present research recorded lower concentrations of heavy metals, except for Cr and Pb which were higher compared to the results reported by Isibor and Izegaebe (2016) for the sediment in Ovia River. Metal levels generally varied in the order of Fe (7.64±2.17 mg/Kg) > Mn (3.63±2.97 mg/Kg)> Cu (3.49±3.48 mg/Kg) > Pb (0.14±0.09 mg/Kg) during the rainy season (Table 4.6), while Cr (3.47±0.87 mg/Kg)and Pb (0.13±0.15 mg/Kg)had the highest and lowest concentrations during the dry season (Table 4.7).Tukura (2015), reported higher mean concentrations of Fe (12.02±0.50 mg/Kg), Zn (0.98±0.02 mg/Kg) and Pb (5.00±0.26 mg/Kg) in sediment from Mada

River during rainy and dry seasons compared to the present study that however recorded low concentrations of Cd (0.66±0.54 mg/Kg), Cu (3.49±4.27 mg/Kg) and Mn (3.63±4.05 mg/Kg).

4.2.5 Pearson's Correlation Coefficients of Metal Levels in Water and Sediment.

Heavy metals in environment usually have complicated relationships among them (Li *et al.,* 2012). Heavy metals showing very high correlation may indicate same origin and controlling factors (Rafiei *et al.,* 2010). Correlation analysis between physicochemical and metals in water samples during rainy season (Table 4.9) showed a positively strong association between Fe-Pb (0.834) followed by a very strong relationships between Cd-Fe (0.786), Cd-Pb (0.711) and Cr-Cu (0.769) respectively. While a moderate relationship existed between TDS-Cu (0.689) and pH-Zn (0.500). There also existed positively negative relationships between TDS-Zn (-0.882) and Cr-Mn (-0.962) and a very strong negative association between pH-TDS (-0.779), pH-Cu (-0.791) and Cd-Cu (-0.727) respectively. During the dry season (Table 4.10), there was strong association between Fe-Pb(0.886), but a moderate relationship existed between Cd-Zn (0.521) and pH- Cr (0.649) and weak association between pH-Mn (0.479) and Cu-Fe (0.402). A very strong negative association existed between TDS-Mn (-0.891) and Zn-Pb (-0760) with a moderate negative relationship between pH-TDS (-0.693) and TDS-Cr (-0.541).Correlation analysis of sediment during the rainy season (Table 4.11) shows that there was positive and very strong association between Cd-Mn (0.974), Mn-Pb (0.932), Cd-Pb (0.854) Cr-Zn (0.786), Fe-Zn (0.720), and TDS-Cu (0.880).pH-Pb (0.547), TDS-Fe (0.507) and Cd-Fe (0.515) were moderately associated. During the dry season (Table 4.12),pH-Cu (0.816), pH-Mn (0.698), pH-Pb, (0.700), Cr-Pb (0.670), Cu-Mn (0.791), Cu-Pb (0.776), Fe-Zn (0.689), TDS-Cu (0.689) and TDS-Mn (0.813) show strong association. However, pH-TDS (0.569) and TDS-Zn (0.511), but Cd-Fe (0.419), Cd-Pb (0.476) and Cu-Zn (0.448) related weakly.

Correlation coefficients between heavy metal concentrations in sediment and water were determined. During the rainy season (Table 4.13), Cu-Cr (0.916), Cu-Cu (0.960) and Zn-Fe

(0.951) were excellently positive. Then TDS-Cr (0.766), TDS-Cu (0.894), Cr-Cd (0.786), Cr-Fe (0.731) and Zn-Pb (0.752) correlated strongly. Correlations for Cu-TDS (0.582), Cr-Pb (0.518), Fe-TDS (0.560), Fe-Fe (0.531), Zn-Cd (0.651) and Pb-pH (0.650) were moderate. Correlation for TDS-pH (-0.840), Cu-pH (-0.708), Cu-Mn (-0.788) and Fe-Zn (-0.776) were strongly negative, while TDS-Cd (-0.526), TDS-Mn (-0.650), TDS-Zn (-0.664), Cu-Cd (-0.666), Cu-Pb (-0.630) and Fe-Mn (-0.508) associated moderately. Results for dry season (Table 4.14) show that Cr-pH (0.944), Mn-Fe (0.920) and Mn-Pb (0.930) were excellently correlated. However pH-Pb (0.851), TDS-Fe (0.842), TDS-Pb (0.707), Cu-Pb (0.872), Fe-TDS (0.741), and Zn-TDS (0.865) correlated strongly. Relationships existed between Cr-Mn (0.538), Cu-Fe (0.641), Pb-pH (0.508) and Pb-Pb (0.664) were moderate, except for Zn-Fe (0.443) which correlated weakly. Conversely, TDS-Cr (-0.962), Cd- Cd (-0.947) and Zn-Mn (-0.994) were negatively excellent. pH-Zn (-0.726), Mn-Cr (-0.827), Cr-TDS (-0.789), Fe-Mn (-0.712), Pb-Zn (-0.792) and Cu- Zn (-0.704) were strongly negative. In conclusion, pH-Cr (-0.508), TDS-pH, (-0.668), Cd-Zn (-0.623), Cu-Cr (-0.606), Zn-pH (-0.512), Zn-Cr (-0.621), Zn-Zn (-0.513), Pb-TDS (-0.576) and Pb-Cd (-0.578) were slightly negative.

4.2.6 Heavy Metal Partition Coefficients

Partition coefficient results for sediment- water heavy metal concentrations during rainy season are presented in Table 4.15. When the value of K_d (<1), then there are more of heavy metals in water; but K_d (=1) indicates equal ratio of heavy metals between water and sediment whereas K_d (>1) represent greater concentration of heavy metal in sediment. K_d for Cd at the sites varied from 0.39 to 15.76 kg-^{1}, Cr ranged from 0.00 to 0.37 kg-^{1}and Cu from 0.94 to 2.27 kg-^{1}, while $K_d$for Fe and Mn varied from 1.08 to 6.71 kg-1 and 0.56 to 36..83 kg-^{1}, respectively. K_d for Zn was 0.00 and Pb from 0.00 to 36.67 kg-^{1}.

K_d results for sediment- water heavy metal concentrations during dry season are presented in Table 4.16. Heavy metal K_d varied according to sites for Cd and Cr ranged from 2.08 to 64.86 kg-l and 0.43 to 1.85kg-^{1}respectively. K_d for Fe varied from 1.06 to 485.04 kg-^{1}, while K_d for Mn ranged

from 0.00 to 10.00 kg-^{1}, Zn varied from 0.33 to 14.61kg-^{1} and Pb from 0.00 to 61.57 kg-^{1}.K_d for Mn and Pb were highest at Sites 4 (36.83 kg-^{1}) and (36.67 kg-^{1}) respectively, but Cr at site 2 (0.05kg-^{1}) was lowest during rainy season, while Cd (64.86kg-^{1}) and Fe (485.04kg-$^{1)}$ have the highest K_d while Mn (0.04kg-l) lowest at Site 5 during the dry season. These results agreed with the assertion that sediment is a sink for heavy metals (Öztürk *el al*., 2008).

K_d values varied according to season (Table 4.17), and K_d values were relatively higher than 1 during rainy and dry seasons, though less than 1, was observed for Cr (0.72) during rainy season and Cu (0.00) and Zn (0.99) during dry season. Lower K_d values suggest lower affinity of organic sediments to adsorb metals (Ackay, *et al*., 2003). The more the sediment becomes saturated with cations, the lower the metal affinity for the remaining sites, which would lead to decrease in adsorption with increasing total metal levels (Jerry & Terry, 2005).

4.2.7 Pollution Load index (PLI)

Pollution load index is an effective instrument for assessing and comparing the sediment quality. According to Mohiuddin *et al.*,(2010), PLI = 0: indicates perfection; PLI = 1: points to permissible levels of pollutants present and PLI values > 1 represent progressive deterioration of sites. Pollution load index values for metals were PLI $\geq 0 \leq 1$. However, pollution load index for cadmium, copper and iron during the rainy season and chromium and zinc during the dry season that shows relativity toward one reflecting unpolluted nature of the sediments (Table 4.19).

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 Summary

The main purpose of this study to assessed the seasonal variations in the levels of physiochemical parameters and heavy metal concentrations in water and sediments of Amba River Lafia. Results obtained indicated that water and sediment pH (6.70-6.80) were slightly acidic. Total dissolved solids (TDS), electrical conductivity (EC) and alkalinity values of water decreased during the rainy season. Metal levels in water were higher during the rainy season, except for the decrease in Cr (0.80±1.69 mg/L) and Zn (0.04±0.08 mg/L) concentrations. Fe and Cu levels were highest amongst metals. Cd, Cr, Cu, and Zn concentrations in water during rainy and dry seasons were significantly different ($P \leq 0.05$). Metal levels in sediment decreased during the dry season, however, concentrations of Cr (3.61±0.67 mg/Kg) and Fe (4.25±1.83 mg/Kg) increased during the same period. Metal levels were higher in water and sediment during dry and rainy seasons respectively. Sediment generally contained higher metal concentrations compared to water. Cr, Cu, and Mn levels in water and sediment were significantly different ($P \leq 0.05$) for both seasons. Correlations among metal concentrations during the rainy season were positively strong for Cd-Fe (0.786) and Fe-Pb (0.834), while Fe-Pb (0.886) correlation was strongly positive in dry season. During the rainy season, there were excellent correlations between Cd-Mn (0.974), Mn-Pb (0.932), Cd-Pb (0.854) Cr-Zn (0.786), and Fe-Zn (0.720), while in dry season, Cr-Pb (0.670), Cu-Mn (0.791), Cu-Pb (0.776) and Fe-Zn (0.689) show strong associations. Correlations between metal concentrations in sediment and water were positively strong for Cu (0.960) and Zn (0.951) during rainy season and excellent for Mn (0.920) during dry season. Partition coefficient (Kd) values for the levels of metals in sediment and water were greater than 1 except for Cu (0.00) and Zn (0.99)

in rainy season and Cr (0.72) in dry season. Pollution load index (PLI) values during rainy and dry seasons were less than 1which account for the unpolluted nature of the river water.

5.2 Conclusion

Levels of physicochemical properties of water and sediment during rainy and dry season show that the values f.or TDS, EC and alkalinity were higher in rainy season. pH and temperature were similar for both seasons. Variations according to sampling points indicated that the levels of Cr and Zn in water were not significantly different ($P \leq 0.05$) during the rainy season. Cu and Pb levels were below detectable limits in dry season. Metal levels in water were significantly higher during the rainy season, except for Fe and Pb. Metal concentrations in sediment show that Fe and Pb in dry season, and all other metals in dry season, except Mn and Cr, did not vary significantly according to sites. Cu, Fe and Mn concentrations in sediment significantly increased in rainy season. Concentrations of Fe and Cu in water and sediment were relatively the highest. Levels of physicochemical parameters and heavy metals in water were within the WHO permissible limits for drinking, except for Fe, Cd and Cr. Correlations between Fe and Pb in water for both seasons were positively strong. pH correlated moderately with Zn (0.500) in rainy season and with Cr (0.649) in dry season. In sediment, Cd correlated strongly with Mn and Pb, while in dry season, Zn correlated with all metals except with Cr. Relationship between metal concentrations in water and sediment show that there were excellent correlations for Cr/Cr and Cu/Cu in rainy season, and positive correlations of Pb with all metals in dry season. K_d values show that metal levels were higher in sediment than in water, except for Cr in rainy season, and Cu and Zn in dry season. Cd (0.44 & 0.09), Cr (0.00 & 0.95), Cu (0.69 & 0.00), Fe (0.33 & 0.17), Mn (0.00 & 0.00), Zn (0.00 & 0.57) and Pb (0.00 & 0.00) for both rainy and dry seasons have pollution load index below 1 which indicated that sediment from the river is not polluted.

5.3 Recommendation

i) There is need for constant monitoring of the heavy metal concentrations in Amba River since the river serves as source of drinking water, irrigation and fish for the local inhabitants in the study area.

ii) The results of the present investigation point out the need to implement common objectives, compatible policies and programmes for improvement in the discharge of waste into River body.

iii) Pollution load index values are easy to understand and can be use to educate the public and the policy makers to ascertain the pollution load of an area to take necessary remedial measures.

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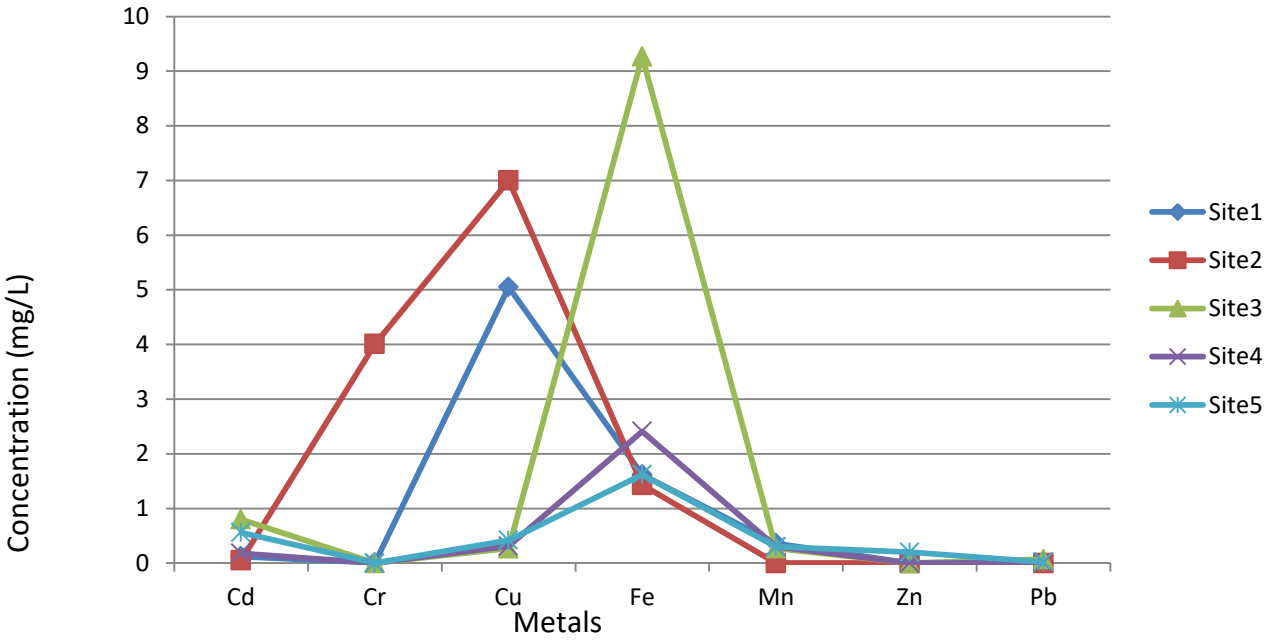
APPENDICES

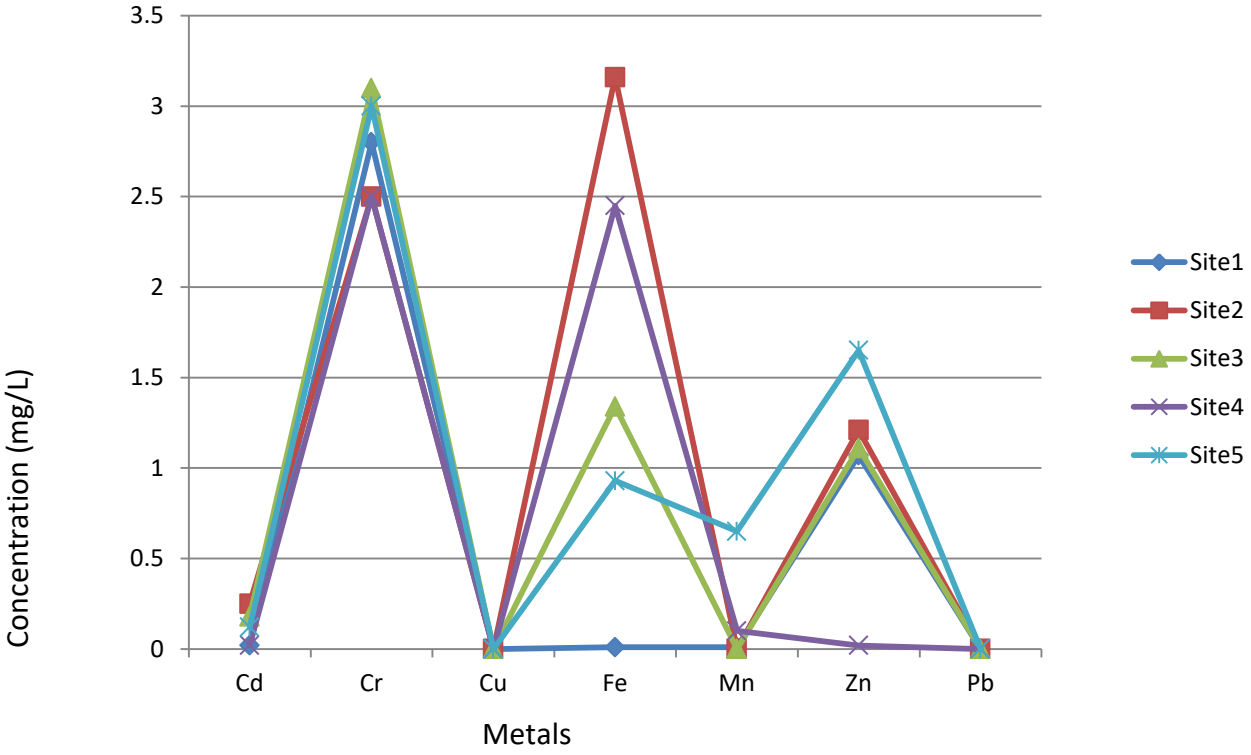
Appendix I

Rainy season variations in heavy metal concentrations (mg/L) in water



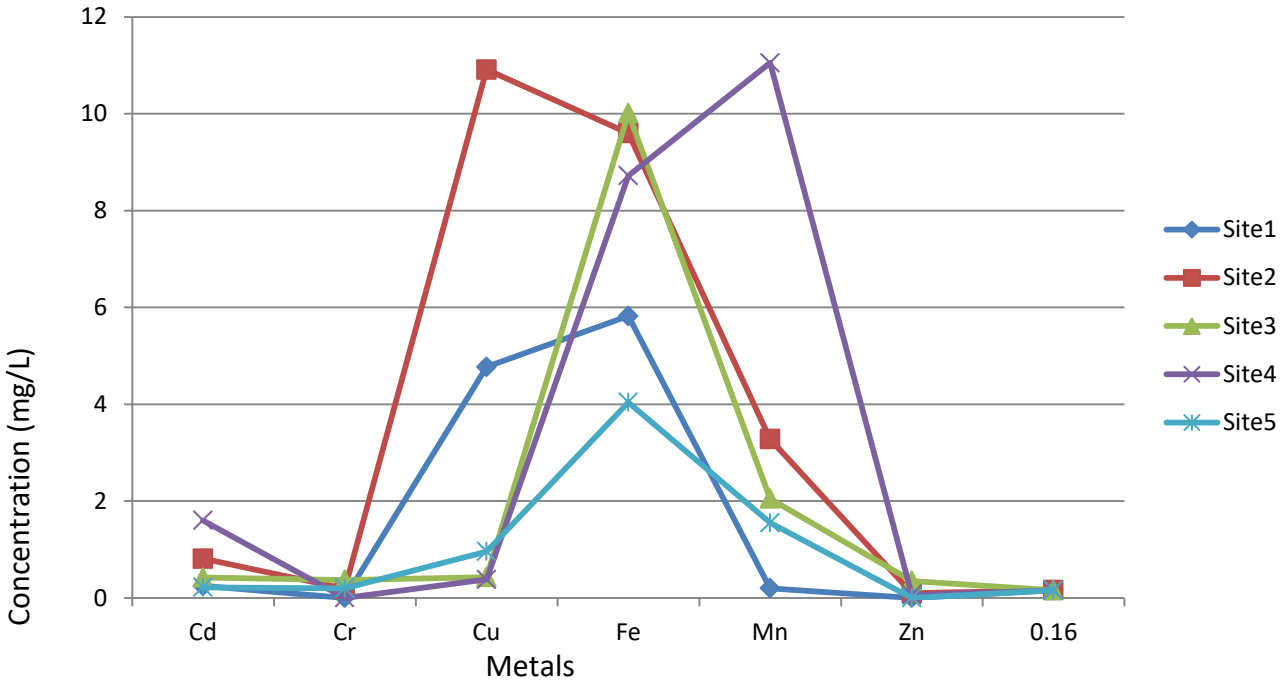
Appendix II

Dry season variations in heavy metal concentrations (mg/L) in water



Appendix III

Rainy season variations in heavy metal concentrations (mg/Kg) in sediment



Appendix IV

Dry season variations in heavy metal concentrations (mg/Kg) in sediment