EFFECT OF ANTHROPOGENIC ACTIVITIES AND SEASONS ON NUTRIENTS AND HEAVY METAL LOADS OF THE WATER AND SEDIMENTS ALONG AMALA AND NYANGORES, TRIBUTARIES OF RIVER MARA KENYA

BY

NYAIRO WILFRIDA NYANDUKO

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in environmental chemistry

DEPARTMENT OF CHEMISTRY

MASENO UNIVERSITY

ABSTRACT

The Mara River Basin accommodates natural forests at its source. The forests' encroachment for human settlement has led to extensive deforestation and farming activities which may cause pollution of the natural aquatic system resulting from soil erosion, farming inputs and household waste. Changing rainfall seasons cause variations in the amounts and rates of surface runoffs flowing downstream. The human settlements have caused changes in rainfall regimes in the Mara River Basin. It is not known how these human settlements and related anthropogenic activities have impacted on water quality at the tributaries of the River Mara that drains into Lake Victoria. The objective of this study was to establish if the nutrient loads and heavy metals in water and sediments and water quality physicochemical parameters along Rivers Amala and Nyangores, tributaries of the River Mara, have been influenced by the anthropogenic activities, and to determine their variations in different seasons. Samples were obtained in both dry and wet seasons in three replicates from 13 sites selected on the basis of varying human activities along each tributary; at streams feeding the tributary and on the main tributary. The nutrient levels and water quality parameters of springs closest to the forest, where land has not been disturbed, were used as control, to assess the effects of anthropogenic activities along the two tributaries. The pH and temperature of water were determined *in-situ* and electrical conductivity in the laboratory. Water samples were collected in pre-cleaned bottles and sediment samples in polythene bags and stored at 4°C. Spectrophotometric methods and atomic absorption spectrophotometer measured nutrient and heavy metals loads, respectively. ANOVA was done using a two factor completely randomized design with sites as main treatment and season as sub-treatment. The nutrient and heavy metals loads were significantly ($p \leq 0.05$) different among sites and with the control for both water and sediments implying the anthropogenic activities were influencing water quality. The River Amala registered relatively higher values of the dissolved nutrients and heavy metals than the River Nyangores. Most of the metals and nutrient loads registered a significant ($p \leq 0.05$) difference in different rainfall seasons. The nutrients and heavy metals levels obtained in this study, except for total phosphorous; were below the WHO water quality set limits. Control of the anthropogenic activities is recommended, as with time, they could seriously impact water quality of River Mara water negatively and by extension that of Lake Victoria.

CHAPTER 1

INTRODUCTION

1.1 Background of study

Water is one of the most vital natural resources in the support of life and despite the fact that about 70% of the earth's surface is covered with water, two billion people experience chronic clean water shortage worldwide (FAO, 2003). This water shortage is attributed to the fact that only 0.5 percent of the earth's surface water is clean, potable fresh water which mainly comes from streams and rivers. The availability of this fresh water is still limited due to pollution of water resources in the catchments (UNEP, 2002), rendering the quality of water unsuitable for downstream users. Population increase has put pressure on natural resources such as rivers and caused a rise in human activities such as agriculture and urbanization, which have negative effects on the quality of water (UN Habitat, 2003). Pollution of most water sources mainly comes from agriculture, sewage and resource exploitation activities such as logging (Carley and Spapens, 1998). Human settlement in water catchment areas and along rivers destroys natural vegetation such as forest cover, which is desirable in catchments to prevent soil erosion and sediment deposition into the water bodies (Hamilton and King, 1983). Land surface conversion such as cultivation and poor land use leads to severe sedimentation problems (Kunkle, 1974; Brooks *et al.*, 1997; FAO, 2003).

The forested Mau Escarpment is the catchment of the Mara River Basin where the two tributaries- Amala and Nyangores-originate. The 395 km long River Mara drains from Kenya's southwest Mau Hills and flows through the Maasai Mara and Serengeti ecosystems before entering Lake Victoria. The Kenya population annual growth rate of about 2.8% (KBS, 2009) is one of the highest in the world. The fast population growth has increased pressure on available cultivated land. One-tenth of Kenya's population lives within 5 km of a forest which covers over 30% of Kenya's land (UNEP, 2002). Land Sat Imagery show that the forested area in Amala and Nyangores catchments decreased from 572 km^2 in 1973 to 493 km^2 in the year 2000 (Gereta *et al.*, 2002). The effect of encroachment into this forested escarpment for human settlement at the upper reaches for agricultural activities and deforestation on the quality of the aquatic system water at the tributaries has not been quantified.

The application of nitrogenous and phosphorous fertilizers in agriculture is necessary to improve crop yields. Unfortunately, the fertilizers pollute surface water through surface runoffs and percolation. The contribution of inorganic fertilizer to surface water nitrogen contamination has increased since 1960, as widespread and intensive use of inorganic nitrogen fertilizers rapidly expands (Smil, 2001). Some of the effects of nitrogen pollution include; methemoglobinemia ("blue baby syndrome") in infants below the age of six months (Skipton and Hay, 1998) and eutrophication, which leads to excessive algae growth that ultimately reduces dissolved oxygen levels in the water (Murdoch *et al.*, 2001). On the other hand, inorganic fertilizers have been reported to contain traces of heavy metals (Mortvedt, 1995) that accumulate in soil with repeated application. Again the use of inorganic fertilizers lowers the soil pH making some metals more available (Alloway 1995).

Livestock manure and domestic waste also contribute to pollution in water resources (Joly, 1993). The discharge from livestock and domestic waste such as waste water and sewage from the urban centers situated along Amala and Nyangores rivers could be leading to an increased nutrients load and heavy metals in aquatic systems. There are various farming activities taking place in the catchments of Nyangores and Amala tributaries. There is significant tea farming on the Nyangores side and farming of various food crops at Amala side such as potatoes, cabbage and maize (Aboud *et al.*, 2002). The quantities of the nutrient loads and heavy metals in the water and sediments resulting from human settlements and agricultural activities along these tributaries have not been established.

Water quality is a measure of the status of a water body. A variety of physicochemical parameters are used to monitor and assess the condition of a stream or a river. These include nutrient loads, suspended solids, pH, electrical conductivity, temperature, chemical oxygen demand and presence of heavy metals (Chapman and Kimstach, 1996). The buildup of nutrients lead to increased growth of aquatic organisms creating a high biological oxygen demand in an aquatic system. Similarly, increase in temperature increases the metabolic activity of aquatic life hence high oxygen demand. Heavy metals discharged into water, even in small quantities easily accumulate in the environment over a long period of time hence are liable to enter the food chain and cause harm in humans and become toxic to aquatic life (Odiete, 1999). The heavy metals cause limited survival, growth inhibition, and abnormal movement patterns of aquatic plants and animals (USEPA, 1980).

These parameters also vary with rainfall variations. The effect of human settlements and related anthropogenic activities on the water quality along these tributaries and changes due to varying rainfall seasons have not been quantified. At the upper reaches of the River Amala there is small scale farming and livestock keeping. The main agricultural activities are food crop production and livestock keeping of which about 62% of the households are smallholder farmers (Aboud *et al.*, 2002). Forest cover has been cleared for cultivation of annual food crops such as potatoes and maize while some of the land lies fallow. This exposes the land surface to soil erosion. The upper reaches of the Nyangores which were formerly closed forested land have been replaced with open forests. The area under tea farming has increased by 214% between 1973 and 2000, while the agricultural area has increased by 203% as the area under closed forests has decreased by 32% as indicated in Table 1.

Table 1: Land use/land cover areas change statistics in the upper reaches of Mara River Basin between 1973 and 2000.

Land cover type	**1973 (km^2)**	**1986 (km^2)**	**2000 (km^2)**	**Change 1973-2000 (km^2)**	**(%) Change between 1973 and 2000**
Forests	1008	893	689	-319	-32
Tea/ Open forests	621	1073	1948	1327	214
Agricultural land	826	1617	2504	1678	203

(Source: Mutie *et al.* (2006a))

Tea is a perennial crop and provides the necessary cover for the land surface hence reducing the effects of surface run-offs (Othieno, 1975). However, the application of fertilizers on the tea farms at these tributaries may be contributing to nutrient loads downstream. The possible effects of these different farming activities on the quality of water draining into these tributaries have not been established.

Both rivers also flow through urban centers which have been experiencing a remarkable increase in population: River Nyangores goes through Bomet, Tenwek Hospital and Longisa, which are found in Bomet District, while River Amala traverses Mulot, in Narok District. Table 2 indicates the population increase in Narok and Bomet districts between 1999 and 2009. The increase in population in these district between the years 1999 – 2009 implies that part of these population contributed in the growth of the urban centres mentioned earlier. Apart from Tenwek Hospital, the other centers do not have waste treatment ponds and discharge waste directly into the rivers. The surface run-offs from farms, leaching and domestic waste are getting into the river and these may be sources of contamination of the water flowing downstream. The extent of deterioration in water quality of the tributaries caused by the growth of these urban centers has not been established.

Table 2: Population Statistics at the upper reaches of Mara River Basin, between 1999 and 2009.

	1999	2009	%increase per year
Bomet District	382,794	724,186	18.9 p.a
Narok District	365,750	850,920	23.2 p.a

(Source: KBS (2009))

The pattern of water quality on the entire River Mara had been reported to vary at different sites depending on the position along the river, land use and rainfall discharge (WQBAR, 2007). Although a study conducted three years later, indicated that the river was in "good health" with localized high concentrations of nitrogen along Rivers Nyangores and Amala (McCartney, 2010). The two studies could not relate these findings to the recent changes taking place in the upper reaches of the Mara River Basin. There is no documentation indicating the influence of encroachment into the natural forests in the upper reaches of Mara River Basin on the water quality flowing through the tributaries and the streams feeding these tributaries. There is need, therefore, to determine the contribution of human settlement and related activities to water quality and nutrient loads in the Amala and Nyangores tributaries by comparing with the water quality of the water from uncontaminated springs deep in the forest.

1.2 Problem Statement.

There has been encroachment into the Mau Forest catchment area of the Amala and Nyangores tributaries arising from the need for fertile agricultural and settlement land due to population increase (Table 1 and 2). Anthropogenic activities associated with human settlements may be contributing to buildup of nutrient loads and other pollutants in the water through surface run-offs and leaching leading to deterioration of the water quality of River Mara and hence Lake Victoria. Accumulation of nitrogen and phosphorous, from the activities can seriously affect aquatic systems and water quality downstream. The accumulation may lead to eutrophication, water contamination and death of aquatic life downstream. However, levels of these nutrients have not been quantified in Rivers Amala and Nyangores and the variations of water quality parameters between the tributaries have not been quantified. Through bioaccumulation and bioconcentration these pollutants can reach higher order animals in the food chain causing damage to some body functions. It is also not known if the levels of heavy metals and nutrients are within acceptable water quality limits. The physicochemical parameters, nutrient levels and heavy metal concentration vary with changes in the rainfall discharge. It is not known whether these nutrients and physicochemical parameters along Rivers Amala and Nyangores vary due to changes in seasons.

1.3 Main objective

To determine the effects of anthropogenic activities along the Rivers Amala and Nyangores, tributaries of River Mara, on the quality of water flowing downstream.

1.4 Specific objectives

1. To determine if the levels of selected water quality parameters namely; pH, temperature and electrical conductivity in the water samples of Rivers Amala and Nyangores tributaries of the River Mara are influenced by anthropogenic activities.
2. To determine whether variations in the levels of NO_3^--N, NO_2^--N, NH_4^+- N, TN, SRP, TP, Fe, Mn, Cd, Pb, Cu, Zn, Se and Cr in the water and sediment samples of Rivers Amala and Nyangores tributaries of the River Mara are due to anthropogenic activities.
3. To determine seasonal variations in the levels of selected water quality parameters, NO_3^--N, NO_2^--N, NH_4^+- N, TN, SRP, TP, Fe, Mn, Cd, Pb, Cu, Zn, Se and Cr in the water and sediment samples of Amala and Nyangores rivers tributaries of the Mara River.

1.5 Research hypothesis

Null hypothesis, H_0

1. Anthropogenic activities have no effect on the selected water quality parameters namely; temperature, pH, electrical conductivity in the water samples of Rivers Amala and Nyangores, tributaries of the River Mara.
2. Anthropogenic activities have no effect on the levels of NO_3^--N, NO_2^--N, NH_4^+-N, TN, SRP, TP, Fe, Mn, Cd, Pb, Cu, Zn, Se and Cr in the water and sediment samples of Rivers Amala and Nyangores.
3. There are no seasonal variations in the levels of selected water quality parameters, nutrients and heavy metals in water and sediments in the two tributaries

Alternative hypothesis, H_1

If the null hypotheses does not hold, the alternative hypotheses will be accepted.

1.6 Justification

There is human encroachment into the upper reaches of Mara River Basin for settlement and agricultural activities. With an annual population increase of 7% within the basin, and an increase in acreage of agricultural land at the rate of 55% over the last 14 years, the basin is under constant pressure (Mati *et al.*, 2005). Improper agricultural practices and absence of buffer zones along the river banks indicate that soil erosion and surface run-offs wash nutrients downstream and this may be gradually deteriorating the water quality. It is therefore necessary to quantify possible water problems that may arise due to human activities along Rivers Amala and Nyangores. The results will provide data leading to development of sustainable policy to control water quality deterioration that may negatively affect life downstream. The generated data will also be used to formulate policies guiding settlements in water catchment areas.

1.7 The Significance of the Study

The Mara River Basin is a trans-boundary resource which providing a livelihood to many people and animals. It drains into Lake Victoria, which is also the upper catchment for River Nile that traverses many countries. The study will help stakeholders, policy makers, researchers and the governments to institute appropriate measures towards the conservation and management of the Mara River Basin.

CHAPTER 2

LITERATURE REVIEW

2.1 Human settlement and related activities on water catchment areas

Forest covers are desirable in catchments and are almost the best natural protection for streams (Kunkle, 1974). The forests in watersheds contribute to higher quality water than land uses such as agriculture and settlement, which usually increase pollutants entering river waters. Indeed forests to some extent help to regulate soil erosion and reduce sediment deposition (Hamilton and King, 1983). Forests have positive significant impacts in water quality (USEPA, 1994a). Deforestation in the catchment increases sediments in the water bodies due to land surface degradation. Human population growth, deforestation, poor agricultural practices, and agricultural expansion at the upper reaches of Mara River Basin are putting pressure on the natural resources.

There is accelerated loss of vegetation cover in the upper catchments and associated land degradation, which consequently pose a threat to the river flows and the ecosystem (IUCN, 2000; Aboud *et al.*, 2002; Dwasi, 2002; Machiwa, 2002; Mati *et al.*, 2005). These may be causing a buildup of nutrient loads in the River Mara and its tributaries through soil erosion, leaching and surface runoffs thus impairing the quality of water flowing into Lake Victoria. Unfortunately, for the users of the Mara River Basin, water shortage, poor water quality and environmental degradation are their main problems (LVBC and WWF-EARPO, 2010). Although there are some local community efforts to plant more trees to reduce the effect of deforestation, this may not be adequate in countering the gradual land surface degradation and destruction of the catchment area.

The water overflow and leaching from the system may be carrying excessive nutrient loads and the domestic waste polluting the water. There may be need to conserve the Mara River Basin by preventing water shortage, maintaining proper water quality and reducing land degradation. It is not quantified if the deforestation of Mau Forest is impacting on the River Mara water quality at its tributaries. Agriculture is a major cause of degradation of surface and groundwater resources through erosion and chemical runoff. This raises concerns about the global implications of agriculture on water quality

(USEPA, 1994a). Application of fertilizers without using best management practices can result in pollution (Binkley *et al.*, 1999). Surface run offs transport soil, vegetation and fertilizer from agricultural fields resulting to high nitrate and ammonia concentrations in water bodies (Romkens *et al.*, 1973).

A baseline water quality assessment conducted on River Mara reported high N concentrations (6.19 mg N/L and (TON)) at Silibwet Bridge (a station along River Nyangores), while in other sampling sites along River Nyangores had low concentrations of TON (<2 mg/L) (WQBAR, 2007). However, it is not known if the significantly high nitrogen recorded in the mentioned station is as a result of human settlements and the related activities such as agriculture. The nutrients from agricultural fields such as nitrogen and phosphorous are carried downstream and gradually buildup in the aquatic system resulting in eutrophication (Carpenter *et al.*, 1998). There is heavy use of these fertilizers on tea and small scale farming activities on cleared Mau Forest lands. It is not known how much of these nutrients are washed downstream from the farms along the two tributaries.

The forested Mau Escarpment plays an important role as the water catchment for the Mara River Basin. The forest cover regulates the river flows, helps recharge groundwater tables, improves soil fertility, reduces soil erosion and sediment loads in river water; helps regulate local climatic conditions and acts as a carbon reservoir and sink (GOK, 2009). As the Kenyan population increases, and the land resource remains constant, there is increasing demand for agricultural and settlement land hence a remarkable encroachment into the forested land. The reliable and well distributed rainfall in the highlands of the basin and fertile soils are favorable for agriculture and livestock activities hence immigrants have been attracted into the basin leading to high population growth rates, as high as 7.5% (FOC, 2000). The immigration into the catchment area is exerting pressure on the natural resources including water and the forest (Mutie *et al.*, 2006b). The extent to which the conversion of forest land to agricultural land affects water quality downstream from these tributaries has not been established.

In the mid-1980s, Kenya Nyayo Tea Zones were created to form a clear boundary and buffer between the indigenous forest and surrounding land uses to control human encroachment into the gazetted forests (NTZDC, 1986). The tea zones which are mainly at the Nyangores slopes have to a certain extent checked the encroachment, however, it has not been particularly successful in some sections as indicated in figure 1. Instead many hectares of indigenous forest have been cleared further into the forests (Birdlife International, 2008). Hence, application of fertilizer in the tea farms may be contributing nutrient loads to the river and hence altering the water quality. At the upper reaches of the Amala sub-catchment, forest land has been replaced with extensive small scale farming of annual food crops and some of the uncultivated land remains bare, making it susceptible to soil erosion. The land under cultivation in Amala sub-catchment increased from 20% in 1960 to 51% in 1991 (Mati *et al.,* 2005). The extensive deforestation has resulted in the drying up of some springs at the upper reaches of Amala. It is not known if there is a difference in the quality of the water draining from the two tributaries as a result of the different farming activities.

Figure 1: Human encroachment into a section of the forested area in the upper reaches of Mara River Basin. (Source: Fred Hoogervorst/ WWF- EARPO (2010))

2.2 Water quality parameters and their effect on the environment

The physicochemical parameters that determine water quality include temperature, pH, chemical oxygen demand, dissolved oxygen, total organic carbon, electrical conductivity, turbidity, heavy metals, nutrient loads which include NO_3^- (nitrate-nitrogen), NO_2^- (nitrite-nitrogen), ammoniacal-nitrogen and phosphorus (Kreuzinger, 2009). The description of these parameters, their sources, chemistry and aquatic impacts are given in the following sections.

2.2.1 Temperature, pH and electrical conductivity

Many aquatic organisms are sensitive to changes in water temperature. Increase in temperature leads to an increase in their metabolic rate hence increasing the uptake of dissolved oxygen (DO) (Chapman and Kimstach, 1996). At the same time, elevated temperatures decrease solubility of gases such as oxygen in water (Chapman and Kimstach, 1996). Many lakes and rivers exhibit vertical temperature gradients as the sun warms the upper water while deeper water will remain cooler.

The pH is a measurement of the acid/base activity in solution and can be altered by surface run offs. The range of natural pH in fresh waters extends from around 4.5, for acid, peaty upland waters, to over 10.0 in waters where there is intense photosynthetic activity by algae (USEPA 1997). However, the most frequently encountered range is 6.5-8.0 (IEPA, 2001). A high pH changes ionic ammonia (NH_4^+) to ammonia (NH_3) which is highly toxic to fish (Ongley, 1996). Most heavy metals in sediments such as lead become more soluble and more toxic in water as the pH decreases. At low pH, metals ionize readily thereby increasing their water solubility and mobility (Ford *et al.*, 2001).

Electrical conductivity (EC) is an indicator of the concentration of total dissolved solids (TDS) in the water. This is mostly influenced by dissolved salts such as sodium chloride and potassium chloride; therefore, it indicates the level of salinity. Conductivity of water is affected by the presence of inorganic dissolved solids such as chloride, nitrate, sulfate, and phosphate anions or sodium, magnesium, calcium, iron, and aluminum cations (Chapman and Kimstach, 1996). It is also affected by temperature: the warmer the water, the higher the conductivity. For this reason, conductivity is reported as conductivity at 25 degrees Celsius (25°C). Discharges to streams can change the conductivity depending on their make-up (Chapman and Kimstach, 1996). A failing sewage system raises the conductivity because of the presence of chloride, phosphate, and nitrate; an oil spill lowers the conductivity (APHA, 1995).

The run-offs, mineral inputs from agriculture and domestic water discharge from the human settlements along the Rivers Nyangores and Amala are flowing into the water downstream. However, data on the electrical conductivity on streams and sites specific to the tributaries is limited and it is also not known how pH, temperature and electrical conductivity levels within these tributaries are influenced by anthropogenic activities along the banks of the tributaries .

2.2.2 Nutrients

Nitrogen and phosphorous and their compounds are the most common nutrients because they are essential requirements in the growth of plants. They are normally added to the soil in form of inorganic fertilizers and manure to enhance agricultural yields. The nutrients are transported into streams and rivers through surface runoffs and leaching process. The description of the common nutrients, their sources and aquatic impacts are given in the following sections

2.2.2.1 Nitrogen

Surface water run-offs, livestock, sewage discharge, fertilizers and waste water discharges all contribute to the abundance of total nitrogen in the environment. Nitrogen exists as nitrate, nitrite, ammonia and organic nitrogen. Nitrate ion (NO_3^-) is the most common form of nitrogen in natural waters. Nitrite (NO_2^-) oxidizes into nitrate ($NO_3^{-)}$ after entering an aerobic system (Chapman and Kimstach, 1996). Nitrites normally exist in very low concentrations because it is the intermediate between ammonium and nitrates as indicated in the equation 1 and 2 below.

Equation 1: $NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^-$

Equation 2: $NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$

However, values greater than 0.03 mg/L of nitrites in water is an indication of surface water pollution (IEPA, 2001). On the other hand, the presence of nitrite in drinking water is considered to be toxic, since, it can react with organic compounds in the water to form nitrosamines that are carcinogenic (Nolan, 2005). Nitrate levels of over 5 mg/L in natural waters normally indicate anthropogenic pollution and 200 mg/L is an extreme level of pollution. Ingestion of nitrites and nitrates combined in excess of 10 mg/L in a day causes methemoglobinemia in infants of the age below six months (Skipton and Hay, 1998). At the same time high levels of oxidized nitrogen (NO_3^- and NO_2^-) lead to eutrophication, which leads to excessive algae growth that ultimately reduces dissolved oxygen levels in the water (Murdoch *et al.*, 2001).

Ammonia mainly exists in the ionized form (NH_4^+) but at high pH and temperature the ionized ammonia (NH_4^+) changes to un-ionized ammonia gas (NH_3). Ammonia gas is more harmful to freshwater aquatic life and fish, in particular (Ongley, 1996; IEPA, 2001). In aerobic systems, ammonium (NH_4^+) can easily convert to nitrite and nitrate as indicated in equation 1 above (Pg 12). According to McCartney (2010), ammonia levels recorded in the River Mara ranged from below detection to a high level of 21.92 µg/L at the Bomet Bridge and another high level of 20.73 µg/L at Ngasiat. The study indicated that the sites with high total oxidized nitrogen (TON) in the Mara River Basin were clustered in the Amala and Nyangores areas. The study focused on the general health of the Mara River Basin. However, there is no information on the relationship between these nutrients to agricultural activities and expanding urban centers due to human settlements along Rivers Amala and Nyangores.

2.2.2.2 Phosphorous

Phosphorus occurs widely in nature in plants, micro-organisms, animal wastes and domestic waste. It is an essential nutrient to living organisms and occurs naturally in water bodies, mainly in the form of phosphates (Clark and John, 1991). Sources of phosphates in the environment include domestic and industrial discharges, sewage, agricultural run-offs containing unutilized fertilizers and changes in land use in areas where phosphorous is naturally abundant in the soil (Clark and John, 1991). Phosphate pollution causes eutrophication of a stream where algae and aquatic plant growth consume the oxygen rapidly (Ongley, 1996; Kenneth and Neeltje, 2002).

Phosphorus that gains access to such water bodies, along with nitrogen as nitrate, promotes the growth of algae and other plants leading to blooms, slimes and diurnal dissolved oxygen variations of great magnitude (IEPA, 2001). The water from the Rivers Amala and Nyangores drains into the River Mara which eventually enters Lake Vitoria. The phosphorous flowing downstream may be contributing to the eutrophied waters in Lake Victoria. It is not known if the human settlements and related human activities are contributing high levels of phosphorous into these tributaries flowing into River Mara and ultimately Lake Victoria.

2.2.3 Heavy Metals

Heavy metals are common surface water pollutants which enter aquatic system as trace elements through anthropogenic activities such as domestic waste water, industrial discharge, waste water treatment and usage of fertilizers. Conversely, heavy metals may enter into aquatic system naturally, through leaching of rocks, airborne dust, forest fires and vegetation (Fernandez and Olalla, 2000). The occurrence and distribution of heavy metals in the water and sediments is also a function of geochemical processes such as weathering of rocks and volcanic activities (Forstner and Wittmann, 1983; Nriagu, 1989; Veena *et al.*, 1997; Habes and Nigem, 2006). Heavy metals in surface water and sediments have been recorded in rivers. Some of the rivers empting their waters into Lake Victoria such as Sondu-Miriu, Nzoia and Nyando indicate that the presence of these trace elements was attributed to anthropogenic activities (Onyari and Wandiga, 1989; Kishe and Machiwa, 2001; Ongeri, 2008; Ogoyi *et al.*, 2011).

The communities living along the Rivers Amala and Nyangores of River Mara practice farming, discharge waste water into the tributaries and at the same time abstract the water for domestic use. Consequently, these communities may be exposed to the problems related to ingestion of these metals (Goyer and Clarkson, 2001). These trace elements also interfere with the survival and growth of aquatic life (Bryan and Langston, 1992). Heavy metals that find their way into aquatic environments, get deposited into the sediments which due to other factors like dilution, can be several orders of magnitude greater in sediments than in water (Odiete, 1999). Sediments associated with heavy metals pose a direct risk to benthic organisms, and also represent a long-term source of contamination to higher trophic organisms through the food chain (Loska and Wiechula, 2003). The River Mara also empties its water into Lake Victoria. There is inadequate documentation indicating the levels of heavy metals in water and sediments at these tributaries and their relation to the human activities taking place in the upper catchment area of Mara River Basin. The description of the heavy metals, their sources, human and aquatic impacts are given in the following sections

2.2.3.1 Cadmium

Cadmium (Cd) occurs naturally in soils, rocks and coal (Nassef *et al.*, 2006). The anthropogenic activities related to cadmium pollution are application of mineral fertilizers and industrial activities; the metal is widely used in electroplating, paints, plastics, stabilizers and battery industries (Nassef *et al.*, 2006). Cadmium is highly toxic and can cause bone damage, chronic kidney disease, cancer and hypertension in human beings (WHO, 1992; Goyer, 1996). Even at concentrations as low as 1 µg/L cadmium inhibits the growth of some species of phytoplankton (Bryan and Langston, 1992). The permissible maximum cadmium limit for domestic water is 5 µg/L USEPA (Table 4). However, cadmium levels in water can be lethal to fish from as low concentration as 0.5 µg/ L depending on the fish species (Lin and Dunson, 1993). The levels of cadmium in an aquatic system need close monitoring because it is highly toxic to aquatic life (IEPA, 2001). Fertilizers from agriculture and domestic waste from households are possible sources of cadmium along the Rivers Amala and Nyangores. The levels of cadmium at the Rivers Amala and Nyangores water and sediments in relation to the human activities taking place upstream have not been established.

2.2.3.2 Copper

Mainly, copper (Cu) is introduced to water systems through agricultural activities such as application of fungicides, sewage, vegetation, wood production and phosphate fertilizer application (Dameron and Howe, 1998; USEPA, 2007). Copper is an essential micronutrient at low concentrations in humans and other vertebrates. Copper aids in the electron transfer process which also involve iron in hemoglobin, photosynthesis in plants and the terminal step of mitochondrial respiration and hence copper influences life and supports functions like production of red blood cells and carbohydrate synthesis (USEPA, 1980). It has been used to control algal growth in water bodies and when poorly used becomes toxic to fish, invertebrates and amphibians (Horne and Dunson, 1995; IEPA, 2001). At the same time, at high concentrations copper affects root growth and morphology in plants, through the accumulation of copper in root tissue with little of it being translocated to the shoots (Marschner, 1995).

In humans, excess copper intake causes Menke's disease and Wilson's disease, generic disorders associated with accumulation of copper in vital body organs such as kidney, liver and brain (Prasad and Oberleas, 1976). The application of fertilizers and fungicides in farming and domestic waste water are possible copper pollutants at the tributaries, and the copper levels in the water and sediments of these tributaries have not been established.

2.2.3.3 Lead

Some of the sources of lead (Pb) include lead paints, water pipes and emissions from leaded fuels. Lower levels are found in fertilizers (Mortvedt, 1995; Lawrence and Brian, 2002). Continued use of these fertilizers leads to accumulation of lead in the soil which is eventually leached and transported into water bodies (Stokinger, 1981). Lead bioconcentrates and bioaccumulates in food chains resulting to a myriad of problems in living things (Stokinger, 1981). Such problems include disruption of biosynthesis of haemoglobin, a rise in blood pressure, kidney damage, miscarriages and abortions, disruption of the nervous system, brain damage and decline in fertility in men through sperm damage (Joachim and Felistas, 2000). Lead entering into the aquatic system exerts a specific toxic effect on fish blood and tissues (Mousa and Khattab, 2003; Vosyliene and Kazlauskiene, 2004). It also causes neurological problems which occur during fetal development (Goyer and Clarkson, 2001). Domestic water discharge and fertilizers may be causing lead pollution at the tributaries and there is no documentation on lead levels at these tributaries in relation to human activities at the banks of the tributaries.

2.2.3.4 Zinc

Zinc (Zn) is found in plumbing materials like water pipes and galvanized roofing materials. In water, commercial inorganic fertilizers are the main source of zinc (Mortvedt, 1995). Most enzymatic functions such as DNA, RNA and protein synthesis require zinc (USEPA, 1980). Zinc is also involved in carbohydrate metabolism, reproduction, fetal development and adrenal gland metabolism (USEPA, 1980). Water containing zinc levels above 5 ppm has an objectionable taste, causes adverse effects on growth, survival and reproduction in aquatic life (Eisler, 1993). Excessive zinc intake has also been associated with copper deficiency anemia because zinc interferes with copper and iron metabolism (USEPA, 1980). Continued use of inorganic fertilizers and domestic waste at the Amala and Nyangores regions may lead to accumulation of zinc in rivers through run offs and leaching, which eventually interfere with aquatic systems. It is not known whether the zinc levels in the upper catchment of Mara River basin are associated with anthropogenic activities around these tributaries.

2.2.3.5 Iron

Iron (Fe) is found in almost every food with higher concentrations in animal tissues than in plants (Hammond and Beliles, 1980). The major component in blood formation is iron, with an adult human body of 70kg body mass containing between 4.2 – 4.5 g of iron (Snyder *et al.*, 1975; Stokinger, 1981). Iron deficiency is the most common cause of anemia, mental disorders and reduced intellectual performance in animals and children (Prasad and Oberleas, 1976; Pollit *et al.*, 1989). Therefore, iron contributes significantly to brain development (Agarwal, 1990). However, excess iron in aquatic systems can affect fish by clogging gills and reducing respiratory potential and subsequent survival (Lehtinen and Kingstedt, 1983; Peuranen *et al.*, 1994, Dalzell and MacFarlane, 1999). Subsequently, high iron concentrations can cause reduction in species diversity of benthic invertebrates and fish. Since iron is found in virtually every food including water, plants and even aquatic animals and that as mentioned earlier it is toxic when it is in excess in aquatic systems, therefore, it is necessary to monitor the accumulation of iron getting into these tributaries through anthropogenic activities.

2.2.3.6 Chromium

The main entries of chromium (Cr) into surface water are through sewer sludge, building works and municipal waste (ARB, 1986). The most stable oxidation states of chromium are Cr^{3+} and Cr^{6+}. Chromium (VI) is a byproduct of industrial applications and textiles. A daily intake of 50 – 200 µg Cr^{3+} is essential for normal glucose, protein and fat metabolism in human beings (ATSDR, 2003). The cation Cr^{6+} has been classified by USEPA as a human carcinogen and the most toxic, though the body is able to reduce it to Cr^{3+} which is less harmful. It readily damages cell walls being a strong oxidizer. It also inhibits growth in duckweed and algae, reduces survival of benthic invertebrates and reduces growth of freshwater fingerlings (USEPA, 1994b).

The urban centers along Rivers Nyangores and Amala do not have waste treatment ponds. The possible chromium pollution sources at the tributary are sewer sludge, building sites and general municipal waste getting into the rivers at the urban centers. The levels of chromium in Rivers Amala and Nyangores are not known.

2.2.3.7 Manganese

Naturally manganese (Mn) exists in the earth's crust in form of oxides, carbonates or sulfides. It exists in several oxidation states ranging from -3 to +7, with the most common ones being Mn^{2+}, Mn^{4+} and Mn^{7+}. The Mn^{2+} ion is more soluble than Mn^{4+} and it tends to become more bioavailable with decreasing pH and redox potential (Heal, 2001). The major anthropogenic sources of environmental manganese include municipal wastewater discharges and sewage sludge (HSDB, 2001). Manganese compounds have various uses including: manganese dioxide used for dry-cell batteries, manganese chloride as a catalyst in the chlorination of organic compounds, manganese sulfate used as a fertilizer, livestock supplement and fungicide, potassium permanganate used for bleaching, as a purifier in water and waste treatment plants (USEPA, 1984; HSDB, 1998). Manganese is an essential micronutrient in the activation of numerous enzymes for plant and animal growth (Underwood, 1977; Woolhouse, 1983; Burnell, 1988). In aquatic systems, manganese of levels greater than 1.5 ppm cause growth inhibitions and total chlorophyll reduction in algae (Fargašová *et al.*, 1999). The untreated waste water discharges and run off from agricultural farms along the tributaries may be discharging manganese into the water. However, levels of manganese in the water and sediments along Rivers Nyangores and Amala have not been quantified.

2.2.3.8 Selenium

Selenium (Se) is a metalloid found in soils and can get into aquatic systems in dissolved inorganic forms of selenate or selenite and the organic selenides. Selenium is both essential for phytoplankton growth at low levels and toxic at levels greater than 0.005 ppm in water (Ishimaru *et al.*, 1989: Kiffney and Knight, 1990) and cases of reproductive failure in fishes has been cited (Lemly,1999). The micronutrient is known for its cancer preventive capacity (Clark *et al.*, 1996; Yu *et al.*, 1997), an anti-viral effect (Beck *et al.*, 1995; Baum *et al.*, 1997; Yu *et al.*, 1997, 1999) and ability to contain cardiovascular diseases in animals (Yu *et al.*, 1999). It is available to human beings through plants and animals. The levels of selenium in surface water and sediments at the Rivers Amala and Nyangores have not been quantified to establish whether they are within environmentally acceptable levels.

2.3 National and international permissible levels of various parameters in the current study

National and international permissible levels or standards of various water quality parameters are important in any environmental study. The standards enable the researcher to gauge the extent of pollution in a study area. The local standard organization is National Environmental Management Authority (NEMA) while there are a number of international organizations like USEPA, WHO, EU among others. The local and international standards for some selected parameters in domestic water, surface water and dry sediments are presented in tables 3,4 and 5 respectively.

Table 3: The national and international standards for some selected parameters in domestic water

Parameter	NEMA	USEPA	WHO
pH	6.5-8.5		6.5-8.5
Conductivity		150-500(µS/cm) for fish	
Temperature	Maximum of 30°C		
Ammonium	0.5 mg/L		0.5 mg/L
Nitrate	10 mg/L		10 mg/L
Nitrite	3 mg/L		
Total nitrogen		2-6 mg/L	
SRP		0.01 mg/L rivers	
Total phosphorous		0.10 mg/L	

(USEPA,1997; WHO, 1998; NEMA, 2006)

Table 4: USEPA Standards limits for heavy metals in surface water in ppm

Dissolved Metal	Domestic	Livestock
Copper	0.05	0.2
Cadmium	0.005	0.01
Zinc	5.0	2.0
Iron	0.3	5.0
Chromium	0.1	0.1
Manganese	0.05	0.2
Lead	0.005	5.0
Selenium	0.005	------

(USEPA, 1997)

Table 5: Threshold limit concentrations of metals in dry sediments (in µg/g) that have effect on surface water

	Cu	Cd	Fe	Zn	Cr	Mn	Pb	Se
Canada	36	0.6		123	37		35	
USEPA	31.6	0.99		121	43.3		35.8	

2.4 Relationship between sediments and water.

Sediments in water bodies form an important habitat for aquatic organisms. At the same time sediments act as natural source and sink for various substances including nutrients and heavy metals (Biney *et al.*, 1994). Therefore, sediments have an impact on ecological quality depending on their quality and quantity (Stronkhorst *et al*., 2004). The sediments, both suspended and precipitated substances stored on the water bottom, form a reservoir for many pollutants and trace substances (Biney *et al.*, 1994; Barbour *et al.*, 1998, 1999). These pollutants are slowly released into overlying surface water hence altering water quality downstream. The levels of both nutrient and heavy metals in the sediment at Rivers Amala and Nyangores have not been quantified to establish their relationship with anthropogenic activities in the area.

2.5 Relationship of water quality and rainfall variations

Rivers are subjected to various natural processes taking place in the environment, such as the hydrological cycle. Rainfall variations affect the flow rate of water downstream, substance input and transport, and sedimentation leading to changes in physicochemical parameters. Nutrient concentrations and distributions have therefore been documented as having seasonal patterns (Baird and Ulanowicz, 1989; Morris, 2000). For instance, nitrates tend to buildup during dry seasons and high levels of nitrates are only observed during early rainy seasons. This is because initial rains flush out deposited nitrate from near-surface soils and nitrate level reduces drastically as rainy season progresses (Wolfhard and Reinhard, 1998). This aspect is considered as the "solution" effect, through which the salts contained in dry lands because of the dead vegetation and animals penetrate into the waters during the heavy down pour (Welcome, 1992). This also causes an increase in mineral content and electrical conductivity of the water in a river. However, there is also the "dilution" effect in which the concentrations of the different materials, present in the water, decrease during the wet season (Kunkle, 1974).

Similarly, water temperature decreases during the wet season due to a decrease in air temperature (Welcome, 1992). Rainy seasons in the Mara River Basin are variable, but generally there is a long wet season between the months of March and June and a shorter wet season that runs from September to December. Though the amounts vary from year to year, the Mau region receives roughly 1,000 to 1,750 mm of annual precipitation (Mati *et al*, 2005). The quantities of agriculturally related materials such as unutilized fertilizers and livestock waste, and domestic waste from households getting their way into the water downstream may be subject to seasonal cycles. There is limited documentation indicating the variations in physicochemical parameters of water and sediments with the different rainfall season along Rivers Amala and Nyangores of River Mara.

CHAPTER 3

MATERIALS AND METHODS

3.1 Study Area

The study area was along Rivers Nyangores and Amala tributaries of the River Mara, found in East Africa, that originate from the forested Mau Complex (Figure 2). The area is located between longitudes 35°00'E and 35°47' E and latitudes 0°28' S and 1°02' S.

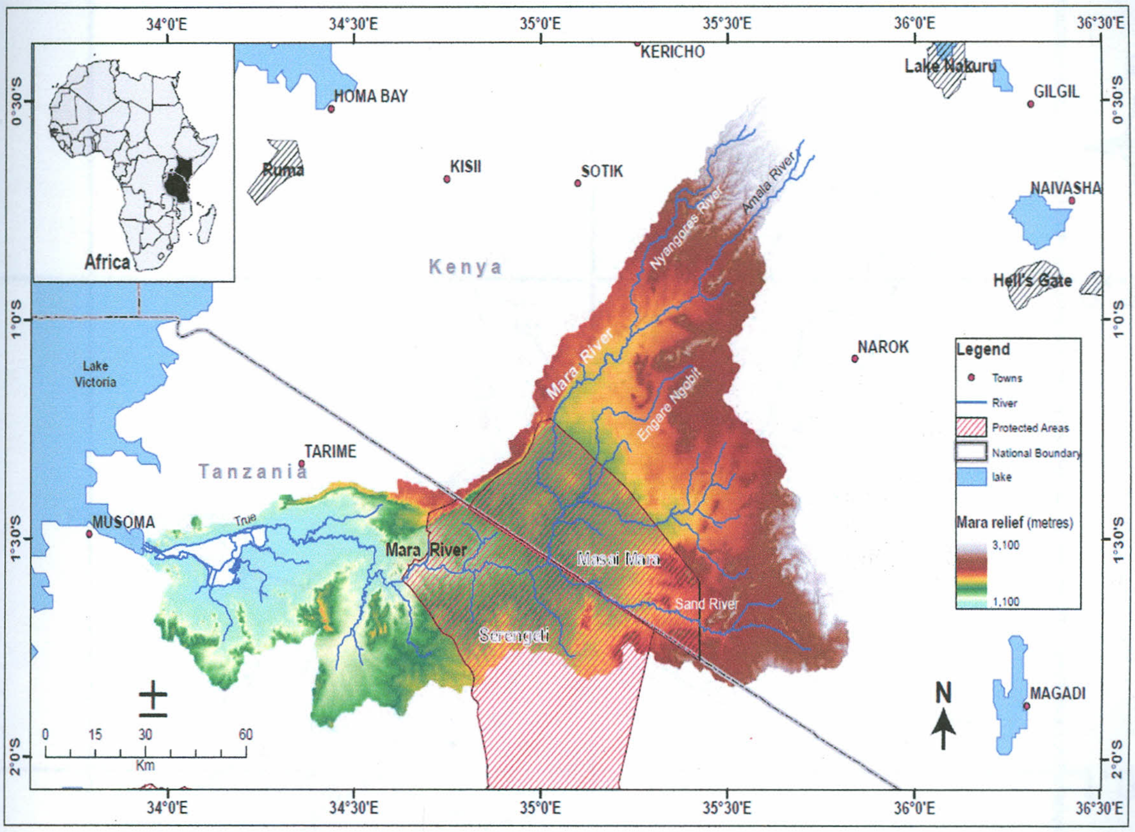


Figure 2: The map of the Mara River Basin, East Africa

The tributaries flow through the Mau Escarpment before meeting at the foot of the escarpment where they form the River Mara. The River Mara is known for the Maasai and the Serengeti National parks in which the tourist attraction of the famous wildebeest immigration is located. The tributaries traverse through a varying landscape which begins with a densely forested area which gives way to a fairly forested area mixed with farming, followed by urban centres which are densely populated then flow through a sparsely populated area before meeting at the confluence as indicated in Figure 2, Table 6 and 7. These presents different anthropogenic activities hence possible varying impacts on the quality of water flowing downstream. This is the criterion that was used to select the sampling sites along the Rivers Nyangores and Amala.

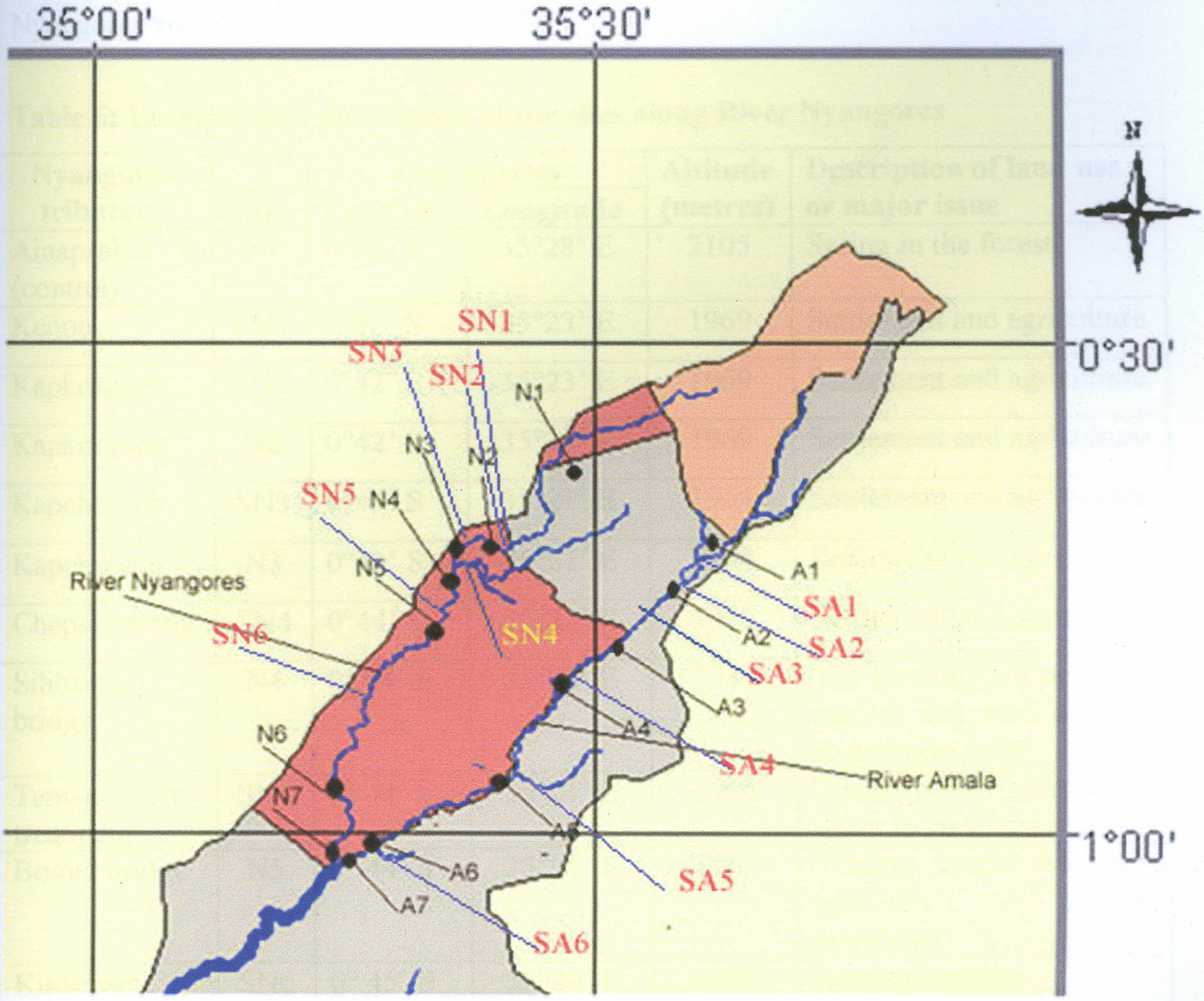


Figure 3: The map of the sampling sites along Rivers Nyangores and Amala at the upper reaches of Mara River Basin, East Africa

3.2 Sampling sites

There were thirteen sites at each tributary these comprised of seven sampling sites along each tributary (Figure 3, Tables 6 and 7) and six sites on streams joining the tributaries. The coordinates of the sampling sites and the description of the land use or major issue are indicated in Tables 6 and 7. The sampling sites N1 and A1 represent the control sites on River Nyangores and River Amala, respectively. The sampling sites on the tributaries are identified as N2 to N7 along River Nyangores and A2 to A7 along River Amala. The samples from the streams feeding the tributaries are identified as SN and SA for River Nyangores and River Amala, respectively

Table 6: Location and description of the sites along River Nyangores

Nyangores tributary	Site	Coordinates		Altitude (metres)	Description of land use or major issue
		Latitude	Longitude		
Ainapsabet (control)	N1	0°40' S	35°28' E	2105	Spring in the forest
Kenon	SN1	0°42' S	35°23' E	1969	Settlement and agriculture
Kapkorgwet	SN2	0°42' S	35°23' E	1969	Settlement and agriculture
Kapkorgwet	N2	0°42' S	35°23' E	1969	Settlement and agriculture
Kapcheluch	SN3	0°43' S	35°21' E	1964	Settlement and agriculture
Kapcheluch	N3	0°43' S	35°21' E	1964	Settlement and agriculture
Chepsokwony	SN4	0°44' S	35°22' E	1955	Settlement and agriculture
Silibwet bridge	N4	0° 44' S	35°22' E	1955	Tea farming and next to a market and thus a water abstraction point
Tenwek after treatment	SN5	0° 44' S	35°21' E	1960	Discharge of treated waste water from a hospital
Bomet bridge	N5	0° 44' S	35°21' E	1962	Trading centre which is relatively densely populated
Kipsewen	SN6	0° 45' S	35°20' E	1900	Less agriculture
Olbotyo	N6	0° 47' S	35°20' E	1871	Less agriculture
Confluence	N7	1°02' S	35°14' E	1665	Before convergence of the River Nyangores with the River Amala.

Table 7: Location and description of the sites along River Amala

Amala		**Coordinates**		**Altitude (metres)**	**Description of land use or major issue**
	Sites	**Latitude**	**Longitude**		
Kebenet (control)	A1	0°45' S	35°38' E	2096	Spring near the forest
Ndasasian	SA1	0°46' S	35°35' E	2096	Settlement and agriculture
Araranga	SA2	0°47' S	35°32' E	2021	Settlement and agriculture
Araranga	A2	0°47' S	35°32' E	2021	Settlement and agriculture
Ise	SA3	0°49' S	35°27' E	1950	Settlement and agriculture
Matecha bridge	A3	0°49' S	35°31' E	1934	Settlement and agriculture
Oljoro	SA4	0°56' S	35°25' E	1781	Settlement and agriculture
Kapkimolwa	A4	0°56' S	35°25' E	1781	Settlement and agriculture
Ngasiat	SA5	0°57' S	35°21' E	1722	Settlement and agriculture
Mulot bridge	A5	0°57' S	35°21' E	1722	Trading center, small-scale agriculture
Kukunoi	SA6	0° 58' S	35°16' E	1669	Less agriculture
Kukunoi	A6	0° 58' S	35°16' E	1669	Less agriculture
Confluence	A7	1°02' S	35°14' E	1665	Before convergence of the River Nyangores with the River Amala.

Sampling was done in three replicates at distance of 5 m apart for both water and sediments in two different rainfall seasons. A spring situated near the forest where there is less human interference acted as a control at each tributary. The criteria for picking these sites is that some of them included those previously used (WQBAR, 2007; McCartney, 2010) when studying the entire River Mara. There are specific anthropogenic activities taking place at the selected sites while the streams also flow through these areas of different anthropogenic activities. The sampling started from the highest point at an altitude of about 2100 m followed by points downstream as shown in Figure 3, Tables 6 and 7.

3.3 Chemicals and reagents

The chemicals and reagents used in the extraction and analysis of nutrients and heavy metals are listed in Table 8.

Table 8: Chemicals used in nutrient analysis

Chemicals for nutrient load analysis (Analar)	Manufacturer
Spongy Cadmium granules	Riedel-de Haën, Germany
Ammonium chloride	Riedel-de Haën, Germany
Sulphanilamide	Riedel-de Haën, Germany
Copper sulphate	Riedel-de Haën, Germany
N-1-Napthylethylene diamine dihydrochloride	Fluka, U.S.A
Hydrochloric acid	Riedel-de Haën, Germany
Potassium nitrate	Riedel-de Haën, Germany
Sulphuric acid	Unichem, India
Ascorbic acid	Unichem, India
Potassium antimony tartarate	Fluka U.S.A
A22 Potassium persulphate	Riedel-de Haën, Germany
Potassium dihydrogen phosphate	Riedel-de Haën, Germany
Ammonium molybdate	Riedel-de Haën, Germany
Phenol	Fluka U.S.A
Sodium hydroxide	Unichem India
Magnesium chloride	Unichem India
Potassium chloride	Unichem India
Activated carbon	Unichem India
Sodium nitroprusside	Riedel-de Haën, Germany
Sodium hypochlolite	Riedel-de Haën, Germany
Tri-sodium citrate dehydrate	Riedel-de Haën, Germany
Ammonium chloride	Fluka U.S.A

Standard solutions of the metals for atomic absorption spectrophotometer (AAS) analysis were obtained from Fluka, U.S.A. The instrument used for analyzing metals was Shimadzu AA-6200 atomic absorption flame emission spectrophotometer (Tokyo, Japan) and Genesys 10S Visible spectrophotometer (Massachusets, USA) was used to analyze nutrients.

3.4. Experimental Design

A two factor complete randomized design was used with sites as main treatment and seasons as a sub-treatment. Water and sediment samples were collected during the dry season (July 2011) and wet season (November 2011).

3.5. Sampling and sample preparation before extraction

Surface water samples were taken from each sampling site in 2 L plastic bottles and samples of surface sediments (15 cm deep) samples were collected in black plastic bags using a spade. The bottles used to collect water samples for nutrients analysis were rinsed using mercuric chloride. Sediment samples and water samples were transported to the laboratory and preserved at 4°C in a refrigerator prior to analysis. Before analysis, some sediment samples were air dried, homogenized by grinding using a pestle and motor then sieved through a 45 μm mesh sieve and kept in clean plastic bags ready for metals and phosphorous analysis.

3.6 Water analysis

3.6.1 Determination of ammonium-nitrogen

The method used for ammonium determination was the indophenol blue photometric determination (Koroleff, 1976; APHA, 1995). The water samples were reacted with phenol and hypochlorite under alkaline conditions to form indophenol blue.

The reagents required in this procedure were namely; phenol solution and hypochlorite in an alkaline. Phenol solution was prepared by dissolving 17.5 g of phenol and 0.2 g of sodium nitroprusside in 500 ml volumetric flask followed by adding milli-Q water to the mark and refrigerated, to be used when required. The hypochlorite was prepared by first dissolving 140 g of tri-sodiumcitrate- dihydrate and 11 g of sodium hydroxide in 300 ml of milli-Q water. Then after complete dissolution, 20 ml of sodium hypochlorite was added and made to a final volume of 500 ml and refrigerated until time of use.

Each sample was prepared by adding the reagents, that is, 3 ml of hypochlorite and 3 ml of the phenol solution into 50 ml of the water sample which was shaken thoroughly for ammonium to be converted to monochloroamine in an alkaline condition, resulting to the formation of the indophenol blue complex. The blue colour-forming reaction is called Berthelot reaction. Nitroprusside was used as a catalyst and precipitation of hydroxides was prevented by metal complexing sodium citrate. The samples were then stored in the dark at 4°C for 24 hours before analysis because

Berthelot reaction does not proceed rapidly enough to achieve adequate colour formation until after 24 hours.

A stock solution 1000 mg/L was made by dissolving 3.821 g of anhydrous ammonium chloride (NH_4Cl) in distilled water and making up to 1 litre solution. A substock solution (10 mg/L) was then made by adding 10 ml of the stock solution to double distilled water to make 1000 ml solution . Standard solutions were prepared in the range of 0, 10, 20, 40 and 60 μg NH_4-N/L by diluting to 50 ml the following volumes of the substock solution: 0, 0.05, 0.1, 0.2 and 0.3 ml, respectively. The standards were treated in the same manner as samples. The spectrophotometer, was calibrated using standards of NH_4-N and the absorbance measured using a spectrophotometer at 630 nm, using milli-Q water as a blank.

3.6.2 Determination of NO_2^-, NO_3^- and total oxidized nitrogen (TON)

The method prescribed by APHA (1995) was adopted for the nitrite, nitrate and total nitrogen analysis.

3.6.2.1 Total oxidized nitrogen, NO_2^- and NO_3

In the determination of total oxidized nitrogen; nitrates were quantitatively reduced to nitrites by running the filtered water samples through a copper-cadmium column containing cadmium filings coated with metallic copper. The nitrate in water was considered to be reduced almost quantitatively to nitrite when a sample was run through the copper-cadmium column. The total nitrite was then quantified as total oxidized nitrogen.

The copper-cadmium column was prepared by reacting 100 g of cadmium filings with 2% Copper sulphate (w/v) that is (10 g in 500 ml). Copper turnings were used to make a small plug which was pushed to the bottom of the column using wool. The column was filled with dilute ammonium chloride solution and Cd-Cu mixture to produce a column 30 cm in length. The column was washed thoroughly with the diluted ammonium chloride and plugged with cotton wool at the top. The cadmium reduction column is as shown in Figure 4.

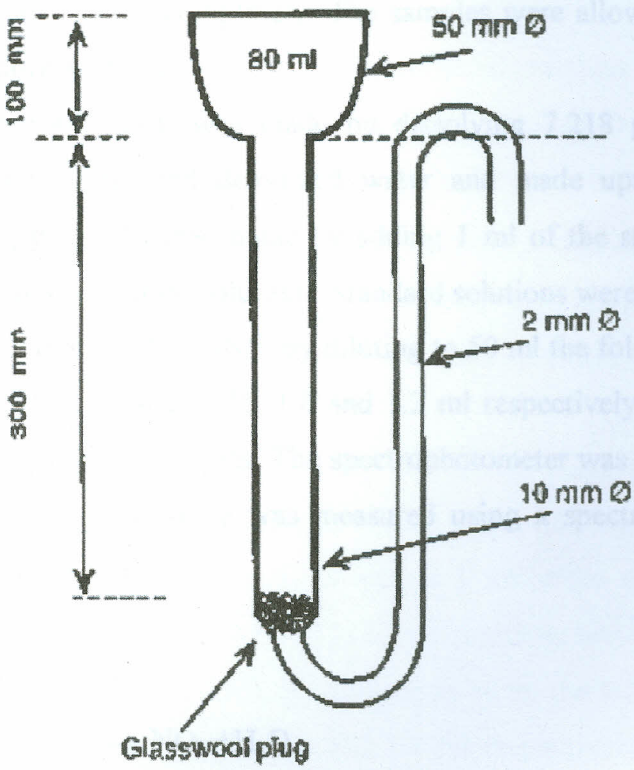


Figure 4: The cadmium reduction column

This method was used based on the reaction of nitrite ions with sulfanilamide in acidic medium. The nitrite thus produced was quantified by diazotizing and coupling with N- (1- napthyl) ethylene to form a highly coloured azo dye as indicated in equations 3, 4 and 5 (pg 31).

The reagents required in this procedure include; sulphanilamide and N-1-Napthyl ethylene diamine dihydrochloride ($C_{12}H_{14}N_2.2HCl$). The sulphanilamide was prepared by dissolving 5 g of sulphanilamide in 300 ml milli-Q water and 50 ml of concentrated HCl made to a 500 ml solution and N-1-Napthyl ethylene diamine dihydrochloride ($C_{12}H_{14}N_2.2HCl$) was prepared by dissolving 0.5g in milli-Q water and diluted to make a 500 ml solution and stored in dark bottles.

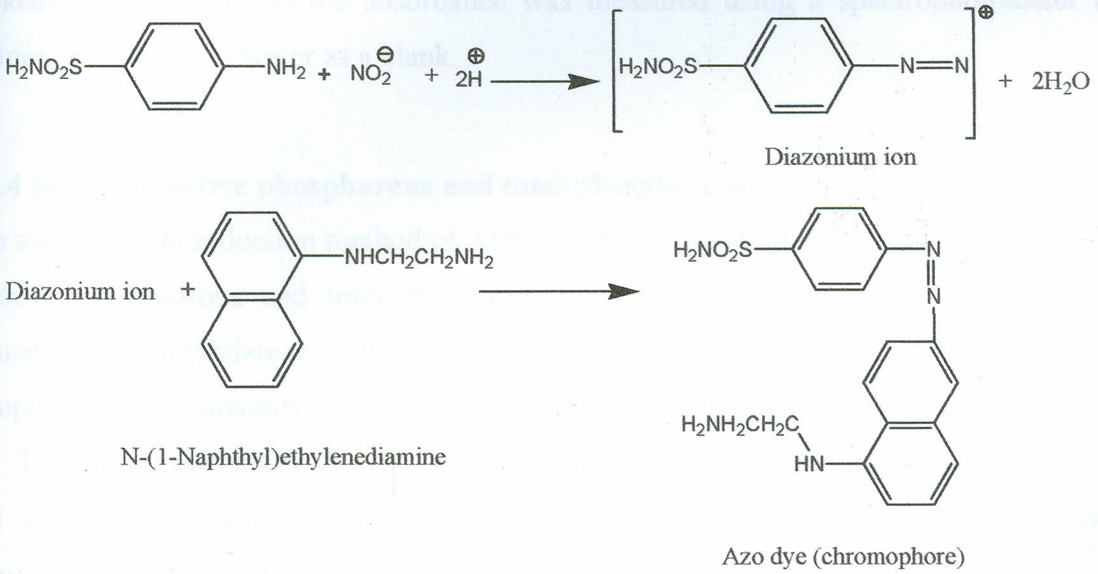
During the analysis 50 ml water sample were run through the column discarding the first 25 ml and saving the final 25 ml for analysis. To 25 ml of each sample 1 ml sulphanilamide was added and shaken thoroughly. The reagents were allowed to stand for 2-8 minutes and this was followed by the addition of 1 ml of N-(1-Napthyl) ethylene diamine dihydrochloride and mixed completely. The samples were allowed to settle for 10 minutes to 2 hours before analysis.

A stock solution 1000 mg/L was made by dissolving 7.218 g of anhydrous potassium nitrate (KNO_3) in distilled deionized water and made upto 1000 ml. A substock solution (1000 µg/L) was then made by adding 1 ml of the stock solution to double distilled water to make 1000 ml solution . Standard solutions were prepared in the range of 0, 5, 10, 15, 20 and 30 µg NO_3^--N/L by diluting to 50 ml the following volumes of the substock solution: 0, 0.25, 0.5, 0.75, 1.0 and 1.2 ml respectively. The standards were treated in the same manner as samples. The spectrophotometer was calibrated using standards of NO_3^--N and the absorbance was measured using a spectrophotometer at 543nm, using milli-Q water as a blank.

Equation 3: $Cd^{o} \rightarrow Cd^{2+} + 2e^{-}$

Equation 4: $NO_3 + 2H^{+} + 2e^{-} \rightarrow NO_2 + H_2O$

Equation 5:



Determination of nitrites was done as for TON but without passing the water samples through the cadmium-copper column. The nitrate concentration was obtained indirectly, that is

Nitrates = TON – nitrites

3.6.3 Total nitrogen

The total nitrogen was determined by digesting unfiltered samples using alkaline persulfate oxidation digestion (APHA, 1995) to convert total nitrogen to nitrates. Exactly 1.0 g of potassium persulfate ($K_2S_2O_8$) and 1 ml of 3.75 M NaOH were added to 50 ml unfiltered samples and digested in an autoclave steam sterilizer (Allamerican 25X-2), at 121°C and allowed to cool. The samples were then passed through the copper-cadmium column to be reduced to nitrites. The total nitrogen was then quantified as nitrites as it was described in section 3.6.2.1.

A stock solution 1000 mg/L was made by dissolving 7.218 g of anhydrous potassium nitrate (KNO_3) in distilled deionized water and made upto 1000 ml. A substock solution (1000 µg/L) was then made by adding 1 ml of the stock solution to double distilled water to make 1000 ml solution . Standard solutions were prepared in the range of 0, 5, 10, 15, 20 and 30 µg NO_3^--N/L by diluting to 50 ml the following volumes of the substock solution: 0, 0.25, 0.5, 0.75, 1.0 and 1.2 ml respectively. The standards were treated in the same manner as samples. The spectrophotometer was calibrated using standards of NO_3^--N and the absorbance was measured using a spectrophotometer at 543nm, using milli-Q water as a blank.

3.6.4 Soluble reactive phosphorous and total phosphorous

The ascorbic acid reduction method of APHA (1995) was adopted for analysis of soluble reactive phosphorous and total phosphorous. The method applies the basis of the formation of molybdate complex and its subsequent reduction to a highly coloured complex which is quantified using a spectrophotometer at a specific wavelength of 885 nm. The sample was allowed to react with a composite reagent containing molybdic acid and ascorbic acid, and trivalent antimony. The resulting complex heteropoli acid was reduced to give a blue complex (phosphomolybdate).

3.6.4.1 Soluble reactive phosphorous (orthophosphate (PO_4-P))

The reagents were prepared as follows; Ammonium paramolybdate $(NH_4) Mo_7O_{24}$ $.4H_2O)$ was prepared by dissolving 15 g in 500 ml of double distilled water and stored in a plastic container. Acidic medium was made by adding 140 ml of concentrated sulphuric acid 900 ml of distilled water; ascorbic acid was prepared by dissolving 27 g in 500 ml of distilled water. Exactly 0.34 g potassium antimonyl-tartarate ($C_8H_4K_2O_{12}Sb_2.3H_2O$) was dissolved in 250 ml of distilled water.

A mixture of the reagents was made by combining 100 ml ammonium molybdate solution, 250 ml sulphuric acid solution, 100 ml ascorbic acid solution and 50 ml potassium antimonyl tartarate. Exactly 5 ml of the mixed reagents was added to 50 ml of each filtered sample. The stock solution (0.1g PO_4-P/L) was prepared by accurately weighing 0.439 g of anhydrous potassium dihydrogen phosphate (KH_2PO_4) and dissolving it in distilled deionized water and made up to 1000 ml. A substock (1000 µg PO_4-P/L) was made by dissolving 1 ml of the stock solution in distilled deionized water and made up to 100 ml. Standard solutions were prepared in the range of 0, 5, 10, 20, 40 and 60 µg PO_4-P/L) by diluting to 50 ml the following volumes of the substock solution: 0, 0.25, 0.5, 1.0, 2.0, and 3.0 ml respectively. The standards were treated in the same manner as samples. The spectrophotometer, was calibrated using standards of PO_4-P and within 1 -2 hours the absorbance of the samples was measured using a spectrophotometer at 885 nm.

3.6.4.2 Total phosphorous

Total phosphorous was determined using the unfiltered samples. A volume of 50 ml of unfiltered samples digested by alkaline persulfate oxidation (APHA, 1995). Exactly 1.0 g of potassium persulfate ($K_2S_2O_8$) and 1 ml of 3.75 M NaOH were added to 50 ml unfiltered samples and digested in an autoclave steam sterilizer (Allamerican 25X-2) at 210°C and allowed to cool. Exactly 5 ml of the mixed reagent of antimony-molybdate was added to the sample to form a blue complex and the procedure followed as described in section 3.6.4.1

3.6.5 Measurement of pH, temperature and electrical conductivity

A 350 pH meter that measures both pH and temperature was used to measure pH and temperature in-*situ* and an electrical conductivity meter (AD8000) was used to determine electrical conductivity in the laboratory.

3.6.6 Determination of heavy metals

The procedure adopted by Mzimela *et al.* (2003) for total metal extraction was followed. A 200 ml water sample was filtered through a 1 μm cellulose acetate milli pore filter into an acid-washed 500 ml Erlenmeyer flask. The samples were acidified to 1% (2 ml) with concentrated nitric acid, placed on a hot plate at 60°C and allowed to evaporate to approximately 30 ml. The evaporated samples was transferred to a 50 ml volumetric flask and made up to volume with double distilled water after addition of 1.5 mg/ml of strontium chloride. The purpose of strontium chloride was to remove interference in absorption of the specific metal by other metals at the same wavelength by acting as a buffer and to minimize ionization of the metal atoms (Ikuo *et al*., 1965).

The pre-concentrated samples were analyzed for Cu, Cd, Fe, Zn, Cr, Mn, Pb and Se using Shimadzu AA-6200 Atomic Absorption Spectrophotometer with their respective Hamatsu hollow cathode lamps. Wavelengths of 324.8 nm, 213.9 nm, 243.3 nm, 213.9 nm, 243.3 nm, 279.5nm, 224nm and 196 nm were used to measure absorbance of Cu, Cd, Fe, Zn, Cr, Mn, Pb and Se, respectively. Before analysis was done, the AAS machine was calibrated. Standard solutions (1000 μg/L) of Cu, Cd, Fe, Zn, Cr, Mn, Pb and Se were used to prepare known concentrations of 0 μg/L, 20 μg/L, 40 μg/L, 80 μg/L, 100 μg/L, 120 μg/L, 160 μg/L and 250 μg/L per salt in 100 ml flasks after additions of 1.5 mg/ml of strontium chloride. These salts were used as standards and a calibration curve was drawn from them in the instrument before unknown samples were read.

3.7 Sediment Analysis

3.7.1 Determination of heavy metals.

The dry sediment samples were homogenized using mortar and pestle followed by sieving of 45 μm mesh. A portion (1 g) of each sediment sample was digested in 10 ml concentrated HNO_3 and HCI in a ratio of 1:1 according to Tack and Verloo (1999). The mixture was heated in a Gerhardt digester (105°C) continuously until all the brown fumes were exhausted leaving only white fumes. After cooling, the contents were filtered through 0.45 μm filter membrane into a 50 ml volumetric flask followed by addition of distilled water to the mark.

The extracts samples were analyzed for Cu, Cd, Fe, Zn, Cr, Mn, Pb and Se using Shimadzu AA-6200 Atomic Absorption Spectrophotometer with their respective Hamatsu hollow cathode lamps. Wavelengths of 324.8 nm, 213.9 nm, 243.3 nm, 213.9 nm, 243.3 nm, 279.5nm, 224nm and 196 nm were used to measure absorbance of Cu, Cd, Fe, Zn, Cr, Mn, Pb and Se, respectively. Before analysis was done, the AAS machine was calibrated. Standard solutions (1000 µg/L) of Cu, Cd, Fe, Zn, Cr, Mn, Pb and Se were used to prepare known concentrations of 0 µg/L, 20 µg/L, 40 µg/L, 80 µg/L, 100 µg/L, 120 µg/L, 160 µg/L and 250 µg/L per salt in 100 ml flasks after additions of 1.5 mg/ml of strontium chloride. These salts were used as standards and a calibration curve was drawn from them in the instrument before unknown samples were read.

Table 9 indicates a summary of the specific parameters used in the analysis of each metal in the Shimadzu AA-6200 Atomic Absorption Spectrophotometer. It shows the respective lamp current, wavelengths and machine detection limits of each metal.

Table 9: Atomic Absorption flame emission Spectrophotometer (Shimadzu AA-6200) experimental parameters

Element	**Mn**	**Cu**	**Fe**	**Zn**	**Pb**	**Cr**	**Cd**	**Se**
Lamp current (mA)	10	20	8	6	10	8	6	23
Wavelength (nm)	279.5	324	243.3	213.9	224	243.3	213.9	196.0
Slit width (nm)	0.2	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Mode	BGC-D2	BGC-D2	BGC-D2	BGC-D2	BGC-D2	BGC-D2	BGC-D2	HVG-1
Flame Type	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2
Fuel flow (L/min)	2	2	1.8	2	2	2	2	1.8
Prespraytime	3 Sec	3 Sec	3 Sec	3 Sec	3 Sec	3 Sec	3 Sec	3 Sec
Integration time	5 Sec	5 Sec	5 Sec	5 Sec	5 Sec	5 Sec	5 Sec	5 Sec
Calibrations (ppm)	0.5 - 2.0	0.8 - 3.2	1.0 -8.0	0.2 - 1.2	0.5 - 2.0	0.8 - 3.0	0.5 - 2.0	0.2 - 3.2
MDL	0.06 ppm	0.04 ppm	0.08 ppm	0.011 ppm	0.06 ppm	0.20 ppm	0.04 ppm	0.20 ppm

Key: MDL – machine detection limit; BGC-D_2 – Deuterium background correction (compensates for matrix interferences)

3.7.2 Determination of nutrients

3.7.2.1 Ammonium

Ammonium was extracted by centrifuging 2 g of moist sediment with 30 ml of 2 M KCl for 30 minutes. The extract was analyzed for ammonium as described in section 3.6.1.

3.7.2.2 Nitrite and Nitrate

Nitrate and nitrite was extracted by centrifuging 2 g of moist sediment with 30 ml of 2 M KCl for 30 minutes followed by filtration. The nitrates were reduced to nitrites by passing the extract through copper-cadmium column. The nitrite then reacted with sulfanilamide under acidic conditions to form a diazo compound. This in turn coupled with N-1-Napthylethylenediamine dihydrochloride to form a reddish purple azo dye. The procedure continued as described in section 3.6.2. Nitrite was determined by the same process but without using the copper- cadmium column and followed the procedure in section 3.6.2

3.7.2.3 Total nitrogen

The 0.2 g wet samples were digested in alkaline persulfate oxidation (APHA, 1995), by adding a mass of 1.0 g of potassium persulfate ($K_2S_2O_8$), 1 ml of 3.75 M NaOH and 40 ml of deionized water to each sample. The samples were then digested in an autoclave steam sterilizer (Allamerican 25X-2) at 121°C and allowed to cool. The extract was analyzed as described in section 3.6.3.

3.7 2.4 Soluble reactive phosphorous in sediments

Sediment reactive phosphorus was determined by using the method of Haggard *et al.*, (1999). A portion of 15g of sieved sediments was placed in a 250 ml Erlenmeyer flask, and mixed with 100 ml of 1 M $MgCl_2$ solution. The samples were shaken for an hour at 1000 revolutions per minute in an orbital shaker. Exactly 50 ml of the supernatant were diluted to 100 ml and pH adjusted to acidic using 1:1 hydrochloric acid to water. Exactly 0.2 g activated carbon was added followed by shaking for fifteen minutes. To 35 ml of the resultant solution in a 50 ml volumetric flask , 10 ml of antimony-molybdate reagent was added and topped to the mark with distilled water. The extract was then analyzed as described in section 3.6.4. 1.

3.7.2.5 Total Phosphorous

The samples were digested using alkaline persulfate oxidation (APHA, 1995). Exactly 1.0 g of potassium persulfate ($K_2S_2O_8$), 1 ml of 3.75 M NaOH and 40 ml of deionized water were added to 1 g of each dry sample and digested in an autoclave steam sterilizer (Allamerican 25X-2) at 200-250°F and allowed to cool and settle. Exactly 10 ml of the mixed reagent (the antimony-molybdate) was added to the samples in 50 ml volumetric flask and water added to the mark. The extract was analyzed as described in section 3.6.4.1.

3.8 Statistical Analysis

The means and ranges of the data collected were determined at confidence limits of 5% to test the significance of the analytical results. Analysis of variance (ANOVA) was done using a two factor completely randomized design and students T-test $p \leq 0.05$ was used to check the site and season variations. Statistical analysis was performed using SAS statistical application linear model. Sites on each river were the main treatment and season a sub-treatment.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Site variations in physicochemical parameters, nutrients and heavy metals in water along Rivers Nyangores and Amala

The mean site variations of pH, temperature and electrical conductivity for the water along Rivers Nyangores and Amala were determined and their results were as shown in Table 10 and 11. Site number N1 was the control site which was a spring, N2-N7 were main sites and SN1-SN7 were the streams along River Nyangores while A1 was the control site, A1-A7 main sites and SA1-SA7 were the streams along River Amala.

The pH at the control along River Nyangores was 5.70 and 5.44 in the dry and wet seasons, respectively and that along River Amala, was 6.38 and 6.83 in the dry and wet season, respectively. The mean pH range along the two tributaries along main sites was between 7.27 - 7.40 and 7.22 - 7.48 in the dry and wet seasons, respectively, along River Nyangores and 6.29 - 6.59 and 6.7 - 7.01 in the dry and wet seasons, respectively, along River Amala. River Nyangores indicated a gradual increase in pH downstream but River Amala had no specific trend. Generally, a significant difference ($p \leq 0.05$) was registered in pH among sites along Rivers Nyangores and Amala and with the control for pH (Table 10 and 11). This alterations in the pH indicate that there is an effect on water quality along these tributaries by the anthropogenic activities taking place around these tributaries.

The pH recorded in the two tributaries is within environmentally acceptable limits (USEPA, 1997) in which the expected pH range of any natural fresh surface water is 6.5-8.0. However, the pH may extend from around 4.5, for acid, peaty upland waters, to over 10.0 in waters where there is intense photosynthetic activity by algae (IEPA, 2001), and as observed in this study the mean pH of the control site of 5.70 in Nyangores was much lower compared to the pH at main sites because the site is found at the peaty upland which is densely forested. However, the pH of the control site of Amala (Table 11) was not as low as that of River Nyangores probably due to relatively less forest cover at its uplands caused by logging. The pH values recorded in this study are within the same

Table 10: Mean levels of pH, temperature and electrical conductivity along River Nyangores

	Nyangores	pH			Temperature °C			Conductivity (μS/cm)		
	Site	Dry	Wet	Mean	Dry	Wet	Mean	Dry	Wet	Mean
N1	Ainapsabet (control)	5.70	5.44	5.57	11.30	11.30	11.30	20	23	22
N2	Kapkorgwet	7.27	7.22	7.25	14.40	13.57	13.98	24	28	26
N3	Kapcheluch	7.30	7.30	7.30	14.40	14.73	14.57	28	28	28
N4	Silibwet Bridge	7.30	7.41	7.35	14.50	14.40	14.45	33	34	33
N5	Bomet Bridge	7.31	7.43	7.37	16.10	15.63	15.87	35	35	35
N6	Olbotyo	7.38	7.44	7.41	16.13	16.03	16.08	38	40	39
N7	Confluence	7.40	7.48	7.44	16.17	16.00	16.08	44	44	44
	Streams									
SN1	Kenon	7.08	6.84	6.96	14.00	12.50	13.25	29	35	32
SN2	Kapkorgwet	7.15	6.91	7.04	14.30	11.57	12.93	27	36	32
SN3	Kapcheluch	7.14	6.95	7.05	14.50	13.23	13.87	32	34	33
SN4	Chepsokwony	7.28	7.15	7.22	15.30	11.63	13.47	48	33	41
SN5	Tenwek after treatment	7.40	7.00	7.20	17.60	12.33	14.97	22	21	21
SN6	Kipsewen	7.52	7.10	7.31	17.50	18.33	17.91	40	42	41
	Mean	7.17	7.05		15.09	13.94		32	33	
	CV %		2.12			1.35			2.31	
	LSD, ($p \leq 0.05$)	0.07		0.18	0.09		0.23	NS		1

N1 is the control site, N2, N3, N4, N5, N6 and N7 were sampling sites along River Nyangores and SN1, SN2, SN3, SN4, SN5 and SN6 are the corresponding streams along River Nyangores.

Table 11: Mean levels of pH, temperature and electrical conductivity along River Amala

	Amala	pH			Temperature °C			Conductivity (µS/cm)		
	Site	Dry	Wet	Mean	Dry	Wet	Mean	Dry	Wet	Mean
A1	Kebenet (control)	6.38	6.83	6.61	14.00	11.70	12.85	34	50	42
A2	Araranga	6.59	6.71	6.65	14.50	12.01	13.30	35	55	45
A3	Matecha Bridge	6.52	6.74	6.63	14.50	12.25	13.40	37	53	45
A4	Kapkimolwa	6.29	6.77	6.53	15.33	12.60	14.00	75	87	81
A5	Mulot Bridge	6.50	6.80	6.65	14.00	13.40	13.55	99	91	95
A6	Kukunoi	6.42	7.01	6.72	16.60	13.57	15.15	80	63	72
A7	Confluence	6.29	7.01	6.65	15.33	14.47	14.90	81	70	76
	Streams									
SA1	Ndasasian	6.31	6.87	6.59	14.53	15.63	15.05	38	57	48
SA2	Araranga	6.34	6.78	6.56	15.53	15.60	15.60	40	84	62
SA3	Ise	6.62	7.01	6.82	15.53	12.87	14.05	44	37	41
SA4	Kapkimolwa	6.32	6.73	6.53	18.27	12.73	13.55	92	117	104
SA5	Ngasiat	6.54	6.78	6.66	15.57	13.30	14.35	95	89	92
SA6	Kukunoi	6.52	6.95	6.74	17.50	13.67	15.60	68	60	64
	Mean	6.43	6.85		15.46	13.37		63	70	
	CV %	0.35			1.05			2.15		
	LSD, ($p \leq 0.05$)	0.01		0.03	0.07		0.18	1		2

A1 is the control site, A2, A3, A4, A5, A6 and A7 were sampling sites along River Amala and SA1, SA2, SA3, SA4, SA5 and SA6 are the corresponding streams along River Amala.

range as those recorded in other rivers such as; River Sondu Miriu (Ongeri, 2008) and River Mara (WQBAR, 2007; McCartney 2010) as indicated in Table 16 except for the pH value from the control site (the spring) along River Nyangores.

The mean temperature ranged between 11.30-16.17°C and 11.30-16.03°C in the dry and wet seasons, respectively, in River Nyangores (Table 10) while the mean temperature along River Amala was 14.00-16.60°C and 11.00-14.47°C (Table 11) in the dry and wet seasons, respectively. Generally, the lowest temperature was recorded at the uplands followed by a gradual increase of temperature along the rivers which was possibly attributed to the fact that at higher altitude atmospheric air is cooler (Wikibooks, 2013) - hence its immediate surrounding - and another influence was change in forest cover which is dense uplands giving way to less forest cover downstream. However, apart from altitude and riverine vegetation, the temperature of any surface water is a function of latitude, time of day, air circulation, season, cloud cover and the flow and depth of the water body (Chapman and Kimstach, 1996).

The acceptable surface water temperature limit, as set in Kenya, is a maximum of 30°C (NEMA, 2006); at the same time the temperature of effluents getting into receiving waters should not raise or lower the temperature of the receiving water by more than 3°C (NEMA, 2006). Hence the water temperature recorded in the Rivers Nyangores and Amala is within the acceptable environmental limits. Similarly, the mean temperature recorded along these rivers is at the same range as those recorded in River Mara (McCartney 2010).

The mean electrical conductivity ranged between 20-44 µS/cm and 23-44 µS/cm in the dry and wet seasons respectively, in River Nyangores (Table 10) and 34-99 µS/cm and 60-91 µS/cm in the dry and wet season respectively, in River Amala (Table 11). There was steady increase along sites in River Nyangores and an increase in the first five sites followed by a drop along Amala River. This indicates that the alteration was resulting from the discharge into the rivers. In a previous study in the by WQBAR (2007), levels of conductivity in sites in Nyangores were found to be constant along the river which was a phenomenon characteristic to forested rivers (Chapman and Chapman, 2003; Nyoge and Machiwa, 2004) and in the Amala River, the conductivity levels were found to increase along the river. However, as observed in this study the levels of conductivity in sites in Rivers Nyangores and Amala were significantly ($p \leq 0.05$)

different and this could be probably due the relatively increasing anthropogenic activities that have taken place recently at the upper reaches of the Mara River Basin. However, The mean electrical conductivity values in this study were below those recorded in River Sondu Miriu of 170 µS/cm as indicated in Table 16.

4.1.2 Site and seasonal variations in nutrients in water along Rivers Nyangores and Amala

Nitrogenous compounds in an aquatic system undergo various decomposition and oxidation reactions depending on various conditions such as temperature, pH and dissolved oxygen. NO_3^-, NO_2^-,and NH_4^+ were determined in this study and the results were as shown in Tables 12 and 13.

The mean nitrate levels along River Nyangores were in the range of 101.24-256.38 µg N/L and 146.57-262.49 µg N/L (Table 12) in the dry and wet seasons, respectively, with the lowest level recorded at the control in both seasons but the highest was at Bomet Bridge in the dry season, while the highest was at Silibwet Bridge in the wet season. On the other hand, along River Amala, mean nitrate levels ranged between 80.15-208.16 µg N/L and 220.54-442.84 µg N/L (Table 13) in the dry and wet seasons, respectively. The lowest values in both seasons were at the controls, and the highest at Mulot Bridge in dry season while in the wet season the highest was at the confluence.

Mean nitrite levels ranged between 1.63-4.38 µg N/L and 3.13-7.59 µg N/L in the dry and wet seasons, respectively along River Nyangores (Table 12) with the lowest at Olbotyo and highest at Kapcheluch in the dry season and lowest at the control and the highest was at the confluence in the wet season. Similarly, along River Amala the mean nitrite levels ranged between 4.62-15.37 µg N/L and 5.31-19.37 µg N/L in the dry and wet seasons, respectively (Table 13), the lowest was at the controls and a highest at Kapkimolwa in both seasons.

The mean ammonium in River Nyangores ranged between 21.67-82.45 µg N/L and 32.67-53.11 µg N/L in the dry and wet seasons, respectively, with the lowest at Bomet Bridge and highest at Kapcheluch in the dry season while the lowest was at Olbotyo and the highest at the control in the wet season. The mean ammonium levels along River Amala ranged between 22.56-69.78 µg N/L, with the lowest at the control and highest at confluence in the dry season and it ranged between 31.00-65.11 µg N/L in the wet season, with lowest level at control but the highest at Kapkimolwa (Table 13).

Table 12: Mean levels of nitrates (NO_3^-), nitrites (NO_2^-), ammonium (NH_4^+) in water along River Nyangores

	Nyangores	NO_3^- (µg N/L)			NO_2^- (µg N/L)			NH_4^+ (µg N/L)		
	Site	Dry	Wet	Mean	Dry	Wet	Mean	Dry	Wet	Mean
N1	Ainapsabet (control)	101.24	146.57	123.91	3.12	3.14	3.13	56.56	53.11	54.83
N2	Kapkorgwet	111.80	224.00	167.90	3.42	4.42	3.92	36.00	33.78	34.89
N3	Kapcheluch	148.75	212.87	180.82	4.38	4.45	4.42	82.45	45.67	64.06
N4	Silibwet Bridge	118.85	273.72	196.29	2.21	4.60	3.41	27.67	37.11	32.39
N5	Bomet Bridge	189.31	227.77	208.54	4.01	5.59	4.80	21.67	34.67	28.17
N6	Olbotyo	185.76	237.89	211.82	1.63	5.48	3.56	36.22	32.67	34.45
N7	Confluence	256.38	262.49	259.44	4.31	7.59	5.95	62.67	47.33	55.00
	Streams									
SN1	Kenon	399.78	446.90	423.34	5.55	6.21	5.89	122.22	42.72	82.22
SN2	Kapkorgwet	422.27	448.77	435.52	6.45	9.58	8.02	34.22	86.89	60.55
SN3	Kapcheluch	323.95	351.37	337.66	4.94	6.17	5.56	77.55	49.11	63.33
SN4	Chepsokwony	432.69	516.84	474.76	16.90	22.24	19.57	56.22	70.22	63.22
SN5	Tenwek after treatment	176.42	259.96	218.19	2.81	3.40	3.11	22.55	3.44	13.00
SN6	Kipsewen	76.92	142.80	109.86	11.58	13.68	12.63	96.44	91.00	93.72
	Mean	226.73	288.61		5.48	7.43		56.34	48.25	
	CV %	8.97			3.76			3.77		
	LSD, ($p \leq 0.05$)	10.75		27.42	0.11		0.28	0.92		2.34

N1 is the control site, N2, N3, N4, N5, N6 and N7 were sampling sites along River Nyangores and SN1, SN2, SN3, SN4, SN5 and SN6 are the corresponding streams along River Nyangores

Table 13: Mean levels of nitrates (NO_3^-), nitrites (NO_2^-), ammonium (NH_4^+) in water along River Amala

	Amala	NO_3^- (µg N/L)			NO_2^- (µg N/L)			NH_4^+ (µg N/L)		
	Site	Dry	Wet	Mean	Dry	Wet	Mean	Dry	Wet	Mean
A1	Kebenet (control)	80.15	220.54	150.35	4.62	5.31	4.97	22.56	31.00	26.78
A2	Araranga	92.55	393.40	242.96	6.44	8.56	7.50	24.22	41.87	33.05
A3	Matecha Bridge	94.20	382.70	238.45	6.77	6.67	6.72	42.45	65.11	53.78
A4	Kapkimolwa	153.79	402.99	278.39	15.37	19.37	17.37	51.67	42.67	47.17
A5	Mulot Bridge	208.16	400.53	304.35	7.69	11.39	9.51	69.78	39.00	54.39
A6	Kukunoi	151.78	442.94	297.36	7.33	10.33	8.83	64.33	46.22	55.28
A7	Confluence	156.19	442.84	299.52	7.32	10.85	9.09	82.65	33.65	58.10
	Streams									
SA1	Ndasasian	208.49	451.26	329.88	6.76	21.40	14.08	69.00	64.55	66.78
SA2	Araranga	475.11	534.26	504.69	63.05	68.80	65.92	115.44	104.11	109.78
SA3	Ise	126.84	142.72	134.78	5.33	10.13	7.73	117.89	72.56	95.22
SA4	Kapkimolwa	94.20	349.10	221.65	15.50	23.84	19.67	122.56	122.56	122.56
SA5	Ngasiat	355.50	431.12	393.31	18.26	38.56	28.41	96.00	113.67	104.83
SA6	Kukunoi	124.28	467.99	296.14	7.09	7.43	7.26	87.78	140.55	112.67
	Mean	178.56	398.42		13.19	18.66		74.10	70.57	
	CV %	5.93			9.80			4.87		
	LSD, ($p \leq 0.05$)	7.84		19.98	0.73		1.85	1.64		4.18

A1 is the control site, A2, A3, A4, A5, A6 and A7 were sampling sites along River Amala and SA1, SA2, SA3, SA4, SA5 and SA6 are the corresponding streams along River Amala.

The mean total nitrogen levels were in the range of 919.67-1942.67 µg N/L and 930-2121.33 µg N/L (Table 14) in the dry and wet seasons, respectively, along River Nyangores, with the controls having the lowest levels in both seasons but the highest was at both Bomet and Silibwet Bridges in dry season and highest in Bomet Bridge in wet season. On the other hand, the mean total nitrogen levels along River Amala were in the range of 1146.33-1747.33 µg N/L and 1178.33-1750 µg N/L (Table 15) in the dry and wet seasons, respectively, with the controls recording lowest levels in both seasons and the highest at Mulot Bridge in the dry season and Araranga with the highest in the wet season.

Generally, there was significant difference ($p \leq 0.05$) in the nitrogen content between the control and sites along the Rivers Nyangores and Amala. The levels gradually increased along the tributaries with the exception of the ammonium levels along River Nyangores. This is an indication that the alteration in nutrient loads is due to a variation in the composition of discharge and surface runoffs into the tributaries related to anthropogenic activities taking place along the tributaries. The streams uplands discharged higher levels of nitrates (Tables 12, 13, 14 and 15) than the main sites because they flow through a region with relatively high agricultural activity but on joining the tributary the levels drop due to the dilution effect. The ammonium levels were high in the control and then decreased along the River Nyangores probably due to the changes in pH, because ionized ammonium is converted to un-ionized ammonia as pH and temperature increases as noted by Ongley (1996). Since nitrate levels of over 5 mg/L, 0.03 mg/L of nitrite and 0.1 mg/L of ammonium in natural waters indicate anthropogenic pollution (IEPA, 2001) then the levels indicated in this study are within environmentally acceptable limits.

The nutrient loads reported in a previous study in River Mara by McCartney (2010) at Bomet Bridge, along River Nyangores was 587 µg NO_3^--N/L, 2.91 µg NO_2^--N/L, 47.6 µg NH_4^+-N/L and 400 µg TN-N/L. In the same study along River Amala, at Mulot Bridge nutrient loads was reported as 892 µg NO_3^--N/L, 2.02 µg NO_2^--N/L, 58.14 µg NH_4^+-N/L and 1170 µg TN-N/L (Table 16). The nitrate level in this study was higher and nitrite level was lower than those reported in the current study, while ammonium level and total nitrogen were in the same range as those in the current study. This, therefore, indicates that the nutrient load along these rivers has been and still is within the environmentally acceptable limits with regard to nitrogen content.

Similarly, the soluble reactive phosphorous (SRP) site means levels ranged between 22.69-64.98 µg P/L and 33.48-46.48 µg P/L (Table 14) in the dry and wet seasons, respectively, along River Nyangores with the highest being at the confluence and lowest at the control in both seasons. Likewise, along River Amala, mean SRP levels ranged between 19.38-27.71 µg P/L with the lowest at the confluence and the highest at Kukunoi in the dry season, and in the wet season the mean SRP levels range was between 23.91-41.37 µg P/L with the control registering the lowest level and the highest at Mulot Bridge (Table 15). The levels of soluble reactive phosphorous (SRP) are considered to be at pollution levels when they are greater than 50 µg P/L (USEPA, 1997) and the drinking water permissible limit is 10 µg P/L. Most of the levels obtained in this study were below the pollution levels with some sites recording values slightly above 50 µg P/L, such as, the confluence site in the dry season on the River Nyangores. This may be considered negligible since in the wet season there was dilution effect. However, SRP was observed to be relatively higher than the USEPA limit in most of the streams along River Amala, although, on joining the River Amala there was again dilution. Generally, therefore, the SRP at this moment has not reached pollution levels but continued anthropogenic activities along these tributaries may with time result to pollution levels of SRP. The phosphates may then have a negative impact on the receiving waters (Lake Victoria) because they contribute to the eutrophication of water.

The mean total phosphorous, on the other hand, ranged between 50.89-471.38 µg P/L and 52.89-489.52 µg P/L in the dry and wet seasons, respectively, with the lowest at control and the highest at Bomet Bridge in both seasons (Table 14) along River Nyangores, while along River Amala the lowest value of 64.43 µg P/L was recorded at the control and the highest of 216.86 µg P/L was recorded at Mulot Bridge in the dry season and the lowest of 82.95 µg P/L was recorded at the control and the highest of 283.43 µg P/L was at Kukunoi (Table 15) in the wet season. For the total phosphorous just like in total nitrogen, the highest level was recorded at the Bomet Bridge and Mulot Bridge an indication that the change was due to the high domestic waste discharge from the highly populated urban centre combined with agricultural waste flowing from the upper reaches of the Mara River Basin.

Generally, the nutrient load along River Nyangores was relatively high at Silibwet and Bomet Bridges while along River Amala it was high at Mulot Bridge (regions with significantly high agricultural activities and large population). According to McCartney (2010), along River Mara, the highest level of ammonia 21.92 µg/L as indicated in Table 16 was recorded at the Bomet Bridge and another high value of 20.73 µg/L at Ngasiat- a stream just before Mulot Bridge. The study also indicated that the sites with high TON in the Mara River Basin were clustered in the Amala and Nyangores areas. While McCartney (2010) established that the Mara River Basin was generally in 'good health' based on the results obtained then, in this study, these elevated levels of nutrient loads are as result of anthropogenic activities at these sites by comparing them to the control sites. These results also indicated that the water quality is no longer in 'good health' as it was in 2010 since the levels of phosphorous recorded in the streams and some main sites along the two tributaries in this study exceeded the drinking water permissible limit (Table 16) of 0.1 ppm (USEPA 1997). Phosphates along with nitrates are known to cause eutrophication of surface water where algae and aquatic plant growth consume the oxygen rapidly (Ongley, 1996; Kenneth and Neeltje, 2002). Hence, the water flowing from these tributaries may contribute to algal bloom in the receiving water.

Table 14: Mean levels of total nitrogen (TN), soluble reactive phosphorous (SRP) and total phosphorous (TP) in water along River Nyangores

	Nyangores	TN (μg N/L)			SRP (μg P/L)			TP (μg P/L)		
	Site	Dry	Wet	Mean	Dry	Wet	Mean	Dry	Wet	Mean
N1	Ainapsabet (control)	919.67	930.00	924.83	22.69	33.48	28.09	50.89	52.89	51.89
N2	Kapkorgwet	1388.00	1520.00	1454.00	24.68	39.38	32.03	51.53	65.14	58.34
N3	Kapcheluch	1381.33	1968.00	1674.67	26.29	39.67	32.98	121.67	263.04	192.36
N4	Silibwet Bridge	1942.67	1991.33	1967.00	28.26	39.33	33.80	237.67	327.57	282.62
N5	Bomet Bridge	1942.67	2121.33	2024.00	38.27	37.71	37.98	471.38	489.52	480.45
N6	Olbotyo	1244.67	1660.33	1452.25	26.76	36.48	31.62	213.67	412.00	312.83
N7	Confluence	1530.00	1614.33	1572.17	64.98	46.48	55.73	219.57	359.62	289.60
	Streams									
SN1	Kenon	1980.67	2084.67	2032.67	33.14	39.28	36.26	85.62	96.29	90.95
SN2	Kapkorgwet	2148.00	2176.67	2162.33	41.62	44.76	43.19	82.29	85.09	83.69
SN3	Kapcheluch	1947.67	2023.00	1985.33	36.52	46.38	41.45	249.33	435.52	342.26
SN4	Chepsokwony	1453.33	1521.00	1487.17	53.26	56.72	54.99	466.47	464.81	465.64
SN5	Tenwek after treatment	1733.67	1952.00	1842.83	22.08	37.71	29.90	76.00	356.19	216.10
SN6	Kipsewen	1632.00	1637.00	1634.50	26.28	27.62	26.95	164.05	163.19	163.62
	Mean	1632.95	1784.59		34.22	40.39		191.51	274.53	
	CV %	3.20			3.25			7.18		
	LSD, ($p \leq 0.05$)	25.48		67.97	0.57		1.44	7.79		19.87

N1 is the control site, N2, N3, N4, N5, N6 and N7 were sampling sites along River Nyangores and SN1, SN2, SN3, SN4, SN5 and SN6 are the corresponding streams along River Nyangores.

Table 15: Mean levels of total nitrogen (TN), soluble reactive phosphorous (SRP) and total phosphorous (TP) in water along River Amala

	Amala	TN (μg N/L)			SRP (μg P/L)			TP (μg P/L)		
	Site	Dry	Wet	Mean	Dry	Wet	Mean	Dry	Wet	Mean
A1	Kebenet (control)	1146.33	1178.33	1169.83	20.62	23.91	22.26	64.43	82.95	73.69
A2	Araranga	1180.33	1750.33	1465.33	20.71	24.93	22.83	82.00	122.47	102.24
A3	Matecha Bridge	1292.67	1225.33	1259.00	22.14	27.38	24.76	104.38	122.00	113.19
A4	Kapkimolwa	1306.33	1226.67	1268.00	19.38	33.60	26.49	173.05	175.81	174.43
A5	Mulot Bridge	1747.33	1428.00	1587.67	24.52	41.37	32.95	216.86	247.33	232.10
A6	Kukunoi	1178.33	1256.67	1217.50	27.71	26.38	27.05	87.00	283.43	185.22
A7	Confluence	1280.33	1200.67	1240.50	11.86	29.48	20.67	135.71	233.29	184.50
	Streams									
SA1	Ndasasian	1241.33	1314.33	1277.83	17.90	33.50	25.70	102.86	342.52	222.69
SA2	Araranga	1713.33	1807.33	1760.33	17.57	82.11	49.84	264.23	165.43	214.83
SA3	Ise	1942.00	2122.67	2032.33	33.05	65.05	49.05	219.76	215.43	217.60
SA4	Kapkimolwa	1240.67	1541.00	1390.83	34.62	64.86	49.74	225.10	266.67	245.89
SA5	Ngasiat	1306.33	1296.33	1301.33	53.19	59.09	56.14	287.86	277.71	282.29
SA6	Kukunoi	1273.67	1318.67	1296.17	23.38	26.47	24.93	287.00	259.72	273.36
	Mean	1373.00	1485.87		25.13	41.39		173.02	214.98	
	CV %	3.24			2.87			8.00		
	LSD, (p≤0.05)	21.59	55.04		0.44		1.13	7.23		18.44

A1 is the control site, A2, A3, A4, A5, A6 and A7 were sampling sites along River Amala and SA1, SA2, SA3, SA4, SA5 and SA6 are the corresponding streams along River Amala.

Table 16: Comparing the levels of physicochemical parameters reported in this study with other studies and some international standards on domestic water

	Temp °C	pH	Cond µS/cm	NO_2^- (µg/L)	NO_3^- (µg/L)	NH_4^+ (µg/L)	TN (mg/L)	SRP (µg/L)	TP (µg/L)
River Nyangores (dry season)[a]	15.09	7.17	32	5.48	226.73	56.34	1.632	34.22	191.51
River Nyangores (wet season)[a]	13.94	7.05	33	7.43	288.61	48.25	1.784	40.39	274.53
River Amala (dry season)[a]	15.46	6.43	63	13.19	178.56	74.10	1.373	25.13	173.02
River Amala (wet season)[a]	13.37	6.85	70	18.66	398.42	70.57	1.485	41.39	214.98
KEBS[b] Standard		6.5-8.5							
NEMA[c] Standard	<30°C	6.5-8.5		3000	10000	500			
WHO[d] Standard		6.5-8.5			10000				
USEPA[e] Standard		6-9.5		20	10000		2 -6	50	100
Lake Victoria[f]		7.7	129.8						
Sondu Miriu River[f]	28.0	7.6	170.0						
Mara River[g] Nyangores*	17.1	7.7	32	2.91	587	47.6	0.4	0	34.72
Amala#	19.4	6.6	74	2.02	892	58.14	1.17	1.65	12.09
Mara River[h] Nyangores*	26.16	7.14	47		680			10.0	
Amala#	18.65	7.42	107		780	20.0		10.0	

Key

a-This study 2012 (n=13) along each tributary, **b**-KEBS (1996) maximum permissible limits, **c**-NEMA (2006), **d** -WHO (1998) maximum permissible limits, **e**-USEPA (1997) maximum permissible limits, **f**-Ongeri (2008), **g**-McCartney(2010), **h**-WQBAR (2007) Water quality baseline data. *for Bomet Bridge and #Mulot Bridge

4.1.3 Site and seasonal variations in heavy metals in water along Rivers Nyangores and Amala.

The mean levels of selected heavy metals in water were studied and recorded in Tables 17, 18, 19, 20, 21 and 22 they include; copper, cadmium, iron, zinc, chromium, manganese, lead and selenium all measured at parts per billion (ppb).

Copper levels were lowest at Ainapsabet (the control) 6.56 ppb and highest at Silibwet Bridge 11.52 ppb in the dry season and a lowest of 7.06 ppb at the control site and highest at Kapkorgwet of 26.11 ppb in the wet season, along River Nyangores (Table 17). The lowest along River Amala was 7.62 ppb at the control and 16.12 ppb as the highest at Kapkimolwa in the dry season, and the lowest of 8.04 ppb at the control (Kebenet) and a highest of 37.55 ppb at Araranga in the wet season (Table 18).

Cadmium levels, along River Nyangores, ranged between 0.26-4.14 ppb and 0.25-2.87 ppb in the dry and wet seasons, respectively (Table 17), with the lowest at the control and the highest at Kapcheluch in the dry season while the lowest was at the control and the highest at Kapkorgwet in the wet season. The range of cadmium along River Amala was from 1.68 ppb at the control (Kebenet) to 2.73 ppb at Mulot Bridge in the dry season and a lowest of 2.81 ppb at the control and a highest of 4.97 ppb at Matecha Bridge in wet season (Table 18).

Mean iron levels along River Nyangores ranged between 11.20-14.35 ppb and 12.57-24.86 ppb in the dry and wet seasons, respectively (Table 17) with the lowest at the control and the highest at the confluence in both seasons, while along River Amala the range was from 11.50 ppb at the control to 12.93 ppb at Matecha Bridge in the dry season and from 10.81 ppb at the control to 60.73 ppb at Kukunoi in the wet season (Table 18).

The range in mean zinc levels along River Nyangores was from 13.91 ppb at the control to 24.60 ppb at the confluence in the dry season while the range was from 14.01 ppb at the control to 213.19 ppb at Kapcheluch (Table 19) in the wet season, while along River Amala the range of zinc levels was from 15.01 ppb at the control to 31.75 ppb at the Mulot Bridge in the dry season, and in the wet season the range was from 45.21 ppb at the control to 85.82 ppb at Kukunoi (Table 20).

Table 17: Mean levels of copper (Cu), cadmium (Cd) and iron (Fe) in water along River Nyangores

	Nyangores	Cu (ppb)			Cd (ppb)			Fe (ppb)		
	Site	Dry	Wet	Mean	Dry	Wet	Mean	Dry	Wet	Mean
N1	Ainapsabet (control)	6.56	7.06	6.81	0.26	0.25	0.25	11.20	12.57	11.87
N2	Kapkorgwet	7.24	26.11	16.67	1.95	2.87	2.41	12.69	16.06	14.38
N3	Kapcheluch	10.64	17.34	14.00	4.14	2.69	3.41	11.71	21.94	16.82
N4	Silibwet Bridge	11.52	17.72	14.62	3.08	2.59	2.83	12.17	17.82	14.99
N5	Bomet Bridge	6.66	8.03	7.34	2.39	2.37	2.38	13.31	25.07	19.19
N6	Olbotyo	7.87	12.29	10.08	2.14	2.65	2.40	12.76	23.46	18.11
N7	Confluence	9.78	12.16	10.97	2.64	2.51	2.58	14.35	24.86	19.60
	Streams									
SN1	Kenon	9.30	21.22	15.26	1.45	3.45	2.45	11.96	23.15	17.56
SN2	Kapkorgwet	10.52	37.62	24.07	2.39	2.38	2.38	12.35	19.58	15.96
SN3	Kapcheluch	17.36	9.62	13.49	3.31	2.93	3.12	11.79	33.83	22.81
SN4	Chepsokwony	5.85	25.77	15.81	2.72	3.13	2.89	11.55	16.12	13.83
SN5	Tenwek after treatment	6.22	7.94	7.08	1.78	2.53	2.15	10.66	23.02	16.84
SN6	Kipsewen	1.96	13.38	7.67	2.83	3.62	3.23	15.08	42.27	28.68
	Mean	8.57	16.63		2.39	2.61		12.43	22.90	
	CV %	4.97			4.59			2.47		
	LSD, (p≤0.05)	0.29		0.74	0.11		0.27	0.20		0.52

N1 is the control site, N2, N3, N4, N5, N6 and N7 were sampling sites along River Nyangores and SN1, SN2, SN3, SN4, SN5 and SN6 are the corresponding streams along River Nyangores

Table 18: Mean levels of copper (Cu), cadmium (Cd) and iron (Fe) in water along River Amala

	Amala	Cu (ppb)			Cd (ppb)			Fe (ppb)		
	Site	Dry	Wet	mean	Dry	Wet	Mean	dry	wet	Mean
A1	Kebenet (control)	7.62	8.04	7.87	1.68	2.81	2.25	11.50	10.81	11.15
A2	Araranga	7.70	37.55	22.63	2.07	3.20	2.63	12.27	29.74	21.00
A3	Matecha Bridge	9.13	8.98	9.05	1.88	4.97	3.43	12.93	23.83	18.38
A4	Kapkimolwa	16.12	8.48	12.30	2.17	4.05	3.11	12.49	33.4	22.95
A5	Mulot Bridge	12.38	19.08	15.73	2.73	3.95	3.34	12.45	23.73	18.09
A6	Kukunoi	11.09	18.94	15.02	2.10	4.58	3.34	12.75	60.73	36.74
A7	Confluence	13.38	21.12	17.25	2.32	3.48	2.90	12.31	28.32	20.32
	Streams									
SA1	Ndasasian	4.20	4.64	4.42	2.87	2.46	2.67	12.27	53.20	32.74
SA2	Araranga	3.30	9.60	6.45	2.00	2.34	2.17	12.84	29.46	21.15
SA3	Ise	4.27	12.80	8.53	2.21	3.11	2.66	12.39	57.04	34.72
SA4	Kapkimolwa	9.05	37.43	23.43	1.66	3.11	2.38	11.86	13.07	12.46
SA5	Ngasiat	8.33	10.87	9.60	2.20	3.07	2.63	12.12	49.29	30.70
SA6	Kukunoi	13.97	12.42	13.20	2.37	4.25	3.31	12.24	57.94	35.09
	Mean	9.27	16.15		2.16	3.49		12.34	36.20	
	CV %	5.05			4.07			2.12		
	LSD, (p≤0.05)	0.30		0.76	0.11		0.27	0.24		0.61

A1 is the control site, A2, A3, A4, A5, A6 and A7 were sampling sites along River Amala and SA1, SA2, SA3, SA4, SA5 and SA6 are the corresponding streams along River Amala.

In the dry season mean chromium levels ranged between 2.15 ppb at the control to 2.91 ppb at Silibwet Bridge and in the wet season, the range was between 0.36 ppb at the control to a highest of 1.29 ppb (Table 19) at Kapcheluch along River Nyangores. The mean chromium levels along River Amala ranged between 2.17 ppb at the control to 3.14 ppb at the confluence in the dry season, and between 1.04 ppb at the control to 2.10 ppb (Table 20) at Matecha Bridge in the wet season. Manganese mean levels, on the other hand, rang at d between 0.19 ppb at the confluence to 0.52 ppb Kapkorgwet in the dry season and in the wet season, the lowest value was at the control at 0.31 ppb and highest value was 5.53 ppb at Bomet bridge along River Nyangores (Table 19), while along River Amala the range was between 0.65 ppb at the control to 1.03 ppb at the confluence in the dry season and manganese mean levels ranged from 2.41 ppb at the confluence to 4.70 ppb at Kapkimolwa in the wet season (Table 20).

The mean levels of lead ranged from 2.04 ppb at the control to 8.55 ppb at Olbotyo in the dry season and from 2.38 ppb at the control to 7.78 ppb at Bomet Bridge (Table 21) in the wet season along River Nyangores, while along River Amala the range was between 6.37 ppb at the control to 9.62 ppb at the confluence in the dry season and it ranged between 1.90 ppb at the control to 5.77 ppb at the confluence in the wet season (Table 22). Selenium mean levels, on the other hand, along River Nyangores ranged between 0.26 ppb at Silibwet Bridge to 1.87 ppb at Kapkorgwet in the dry season (Table 21). and in the wet season it ranged between 0.21 ppb at the control to 1.83 ppb at Kapkorgwet, while along River Amala the lowest selenium level was 0.47 ppb at Kapkimolwa and highest of 4.50 ppb at the confluence in the dry season and in the wet season the range was between 0.22 ppb at Mulot Bridge to 1.73 ppb at the control site (Table 22).

Generally, the levels of heavy metals were significantly different ($p \leq 0.05$) among the sites and with the control site, this could be attributed to the changing anthropogenic activities along the tributaries. Significantly high values of heavy metals were registered at the agriculturally dominant areas; for instance, along Nyangores copper levels were significantly high at Kapkorgwet while iron, zinc and chromium were significantly high at Kapcheluch (Tables 17, 18 19 and 20). Similarly, copper levels were found to be significantly higher at Araranga - a relatively highly agricultural region along River Amala.

Table 19: Mean levels of zinc (Zn), chromium (Cr) and manganese (Mn) along River Nyangores

	Nyangores	Zn (ppb)			Cr (ppb)			Mn (ppb)		
	Site	Dry	Wet	Mean	Dry	Wet	Mean	Dry	Wet	Mean
N1	Ainapsabet (control)	13.91	14.01	13.96	2.15	0.36	1.25	0.31	0.31	0.31
N2	Kapkorgwet	16.11	100.94	58.52	2.26	0.58	1.42	0.52	4.19	2.35
N3	Kapcheluch	17.48	213.19	115.33	2.82	1.29	2.06	0.48	5.03	2.75
N4	Silibwet Bridge	17.09	138.65	77.87	2.91	0.48	1.70	0.21	4.73	2.47
N5	Bomet Bridge	14.87	143.09	79.98	2.53	0.43	1.48	0.34	5.53	2.94
N6	Olbotyo	23.12	100.94	62.03	2.18	0.42	1.30	0.29	4.61	2.45
N7	Confluence	24.60	69.55	47.08	2.17	0.39	1.28	0.19	2.56	1.38
	Streams									
SN1	Kenon	11.41	203.83	107.62	1.83	1.17	1.50	0.96	5.56	3.26
SN2	Kapkorgwet	14.54	293.63	154.03	1.54	1.07	1.30	2.00	6.00	4.00
SN3	Kapcheluch	20.80	221.69	121.24	2.16	3.80	2.98	1.44	5.16	3.30
SN4	Chepsokwony	16.87	164.32	90.60	2.54	2.64	2.59	0.58	4.05	2.31
SN5	Tenwek after treatment	13.01	91.02	52.01	3.06	0.34	1.70	0.10	5.27	2.69
SN6	Kipsewen	11.19	380.48	195.83	2.29	1.45	1.87	1.64	7.26	4.45
	Mean	16.53	164.25		2.34	1.11		0.70	4.64	
	CV %	1.62			3.40			1.58		
	LSD, (p≤0.05)	0.68		1.73	0.03		0.07	0.02		0.05

N1 is the control site, N2, N3, N4, N5, N6 and N7 were sampling sites along River Nyangores and SN1, SN2, SN3, SN4, SN5 and SN6 are the corresponding streams along River Nyangores

Table 20: Mean levels of zinc (Zn), chromium (Cr) and manganese (Mn) along River Amala

	Amala	Zn (ppb)			Cr (ppb)			Mn (ppb)		
	Site	dry	Wet	Mean	Dry	Wet	Mean	dry	wet	Mean
A1	Kebenet (control)	15.01	45.21	30.11	2.17	1.04	1.61	0.65	2.60	1.62
A2	Araranga	16.30	48.02	32.16	2.70	1.51	2.11	0.79	4.24	2.52
A3	Matecha	16.79	46.96	31.87	2.46	2.10	2.28	0.68	4.01	2.35
A4	Kapkimolwa	17.61	49.91	32.26	2.44	1.43	1.93	0.88	4.70	2.79
A5	Mulot	31.75	63.50	47.63	2.22	1.35	1.79	0.77	2.95	1.89
A6	Kukunoi	29.07	85.82	57.45	3.11	1.07	2.09	1.00	3.13	2.07
A7	Confluence	29.46	80.82	55.14	3.14	1.11	2.13	1.03	2.41	1.72
	Streams									
SA1	Ndasasian	14.66	73.25	43.95	0.54	2.78	1.66	0.39	3.25	1.82
SA2	Araranga	13.31	27.50	20.41	0.67	2.81	1.74	0.43	4.21	2.32
SA3	Ise River	21.00	72.27	46.64	3.02	2.53	2.77	0.69	4.15	2.42
SA4	Kapkimolwa	14.32	43.42	28.87	3.02	0.14	1.58	0.59	7.60	4.09
SA5	Ngasiat	27.03	52.35	39.69	2.10	2.16	2.13	3.11	10.08	6.59
SA6	Kukunoi	33.26	140.68	86.97	0.18	0.50	0.34	1.87	2.34	2.11
	Mean	21.51	63.59		2.14	1.58		0.99	4.28	
	CV %	1.63			3.69			5.87		
	LSD,(p≤0.05)	0.32		0.83	0.03		0.08	0.07		0.18

A1 is the control site, A2, A3, A4, A5, A6 and A7 were sampling sites along River Amala and SA1, SA2, SA3, SA4, SA5 and SA6 are the corresponding streams along River Amala.

Table 21: Mean levels of lead (Pb) and selenium (Se) in water along River Nyangores

	Nyangores	Pb (ppb)			Se (ppb)		
	Site	Dry	Wet	Mean	Dry	Wet	Mean
N1	Ainapsabet (control)	2.04	2.38	2.21	0.59	0.21	0.40
N2	Kapkorgwet	2.72	3.61	3.16	1.87	1.83	1.85
N3	Kapcheluch	3.00	3.27	3.13	1.44	1.44	1.44
N4	Silibwet Bridge	2.18	4.48	3.33	0.26	0.37	0.31
N5	Bomet Bridge	8.23	7.78	8.00	1.37	0.98	1.18
N6	Olbotyo	8.55	7.72	8.13	1.66	0.83	1.25
N7	Confluence	6.49	7.67	7.08	1.24	0.85	1.05
	Streams						
SN1	Kenon	2.41	7.28	4.84	0.53	0.57	0.54
SN2	Kapkorgwet	7.08	4.18	5.63	0.66	0.20	0.43
SN3	Kapcheluch	9.41	7.00	8.20	1.04	0.34	0.69
SN4	Chepsokwony	6.86	10.39	8.63	2.05	0.71	1.38
SN5	Tenwek after treatment	7.40	4.39	5.89	0.33	0.24	0.28
SN6	Kipsewen	1.26	13.00	7.13	1.29	0.85	1.07
	Mean	5.20	6.39		1.10	0.72	
	CV %	1.16			1.20		
	LSD, ($p \leq 0.05$)	0.03		0.08	0.01		0.01

N1 is the control site, N2, N3, N4, N5, N6 and N7 were sampling sites along River Nyangores and SN1, SN2, SN3, SN4, SN5 and SN6 are the corresponding streams along River Nyangores

Table 22: Mean levels of lead (Pb) and selenium (Se) in water along River Amala

	Amala	Pb (ppb)			Se (ppb)		
No.	Site	Dry	Wet	mean	Dry	wet	Mean
A1	Kebenet (control)	6.37	1.90	4.14	0.53	1.73	1.13
A2	Araranga	7.35	3.29	5.32	1.37	1.20	1.29
A3	Matecha Bridge	7.13	3.71	5.43	0.49	0.34	0.42
A4	Kapkimolwa	7.87	3.81	5.84	0.47	0.37	0.42
A5	Mulot Bridge	7.58	3.57	5.57	3.84	0.22	2.03
A6	Kukunoi	6.50	4.42	5.46	3.33	0.24	1.79
A7	Confluence	9.62	5.77	7.70	4.50	0.24	2.37
	Streams						
SA1	Ndasasian	2.24	5.37	3.81	1.03	0.90	0.96
SA2	Araranga	9.82	5.18	7.50	2.39	0.96	1.67
SA3	Ise	6.10	4.31	5.21	1.97	1.06	1.52
SA4	Kapkimolwa	20.25	2.22	11.23	0.74	0.52	0.63
SA5	Ngasiat	4.23	3.33	3.78	0.47	0.37	0.42
SA6	Kukunoi	1.08	3.53	2.30	0.41	0.24	0.33
	Mean	7.40	3.88		1.66	0.65	
	CV %	1.95			3.46		
	LSD, ($p \leq 0.05$)	0.05		0.13	0.02		0.05

A1 is the control site, A2, A3, A4, A5, A6 and A7 were sampling sites along River Amala and SA1, SA2, SA3, SA4, SA5 and SA6 are the corresponding streams along River Amala.

The significant ($p \leq 0.05$) mean site and season variations in the heavy metals is an indication that trace elements are introduced to water systems through agricultural activities such as application of fungicides, sewage, vegetation, wood production and phosphate fertilizer application (Dameron and Howe, 1998; USEPA, 2007). Manganese was seen to be significantly high in the wet season at Bomet Bridge- a relatively populated urban centre lacking a water treatment plant- this indicated domestic waste discharge containing manganese which is used in making a wide range of domestic and agricultural products, including: manganese dioxide used for dry-cell batteries, manganese chloride as a catalyst in the chlorination of organic compounds, manganese sulfate used as a fertilizer, livestock supplement and fungicide, potassium permanganate used for bleaching, as a purifier in water and waste treatment plants (USEPA, 1984; HSDB,1998).

A comparison of the levels of heavy metals obtained in this study with those recorded in the other rivers feeding Lake Victoria such as Rivers Nyando and Sondu Miriu and other water sources, shows that the values of most heavy metals obtained in this study were lower (Table 23). However, zinc values in the wet season in some streams along River Nyangores and the main site (Kapcheluch) were close to those recorded in Rivers Nyando and Sondu Miriu. The mean heavy metal levels from River Nyando were reported as 52.40 ppb (Cu), 2835 ppb (Fe), 232.3 ppb (Zn) and 14.4 ppb (Pb) while River Sondu Miriu had 47.00 ppb (Cu), 2320 ppb (Fe), 225.2 ppb (Zn) and 18.4 ppb (Pb) as recorded by Ongeri (2008). In the Nile Delta the mean levels of heavy metals are reported as 15.00 ppb (Cu), 25.0 ppb (Cd), 142.0 ppb (Fe), 36.0 ppb (Zn), 5.0 ppb (Cr), 98.0 ppb (Mn) and 32.0 ppb (Pb) as reported by El Bouraie *et al.* (2010).

A comparison of the heavy metals in this study with internationally set permissible limits for heavy metals in domestic water in Table 4 and 23, shows that generally, the levels of heavy metals recorded from along Rivers Nyangores and Amala in this study are within the permissible environmental limits. According to WHO guidelines for drinking water, all the values of heavy metals are within the environmentally permissible limits (WHO, 1998). This indicates that currently the heavy metals in water flowing downstream from these tributaries have minimal impact on water quality. However, continued and uncontrolled destruction of the natural water catchment in the upper reaches of Mara River Basin for human settlement and cultivation may eventually lead to actual water quality impairment by the heavy metals.

Table 23: Comparison of data in this study with some international standards on domestic water (ppb) and data from other studies for heavy metals in surface water.

River	Cu	Cd	Fe	Zn	Cr	Mn	Pb	Se
River Nyangores dry season [a]	8.57	2.39	12.90	16.53	2.34	0.6962	5.20	1.10
River Nyangores wet season [a]	16.63	2.61	22.90	164.25	1.10	4.6352	6.39	0.72
River Amala dry season[a]	9.27	2.18	12.34	21.51	2.14	0.9910	7.40	1.66
River Amala wet season[a]	16.14	3.49	36.20	63.59	1.58	4.2415	3.88	0.66
KEBS[b] Standard	100		300	5000			50	
WHO[c] standard	1000	5	300	5000		50	10	10
USEPA[d]	50	5	300	5000	100	50	5	10
Canadian W Q Guidelines[e]	100	5	300	5000	50	50	10	10
Nile Delta[f]	15.0	25.0	142.0	36.0	5.0	98.0	32.0	
Winam gulf[g]	53.60		2778	237			14.2	
Rain water[g] (L. V. Basin)	47.90		216.5	228.5				
Well water[g] (L. V. Basin)	48.00		132.5	213.5			13.8	
Municipal water[g] (L. Victoria)	44.7		522.6	267.5			20.8	
Nyamasaria River[g]	52.40		3.049	253.1			4.6	
Nyando River[g]	57.50		2835	232.3			14.4	
Sondu Miriu River[g]	47.00		2320	225.2			18.4	
BIS[h]	50	10	300	5000	50	10	50	10

Key

a-This study 2012 (n = 13) along each tributary, **b**-KEBS (1996), **c**-WHO (1998), **d**-USEPA (1980), **e**-Health Canada (2012), **f**- El Bouraie *et al.* (2010), **g**-Ongeri (2008), **h**-BIS (2010)

4.2 Site and seasonal variations in nutrients and heavy metals in sediments along Rivers Nyangores and Amala

The nutrient load in dry sediments was determined in this study; the nitrites, nitrates, ammonium, total nitrogen, soluble reactive phosphorous and total phosphorous was determined in (µg/g) and recorded as indicated in Tables 24, 25, 26 and 27.

The mean nitrate levels along River Nyangores ranged between 5.37 µg/g at the control to 11.33 µg/g at Bomet Bridge (Table 24) in the dry season, and in the wet season it ranged between 7.55 µg/g at the control to 16.78 µg/g at the confluence. On the other hand, along River Amala mean nitrate levels ranged between 5.32-14.03 µg/g with the lowest at the control and the highest at Kapkimolwa in the dry season and in the wet season, the range was between 7.48-19.55 µg/g, with the lowest at the control and the highest at Kukunoi (Table 25). Mean nitrite levels ranged between 0.94-1.41 µg/g and 0.97-2.19 µg/g in the dry and wet seasons, respectively, along River Nyangores (Table 24) with the lowest at the control in both seasons and highest at Kapcheluch in both seasons. Similarly, along River Amala the mean nitrite levels ranged between 1.94-4.39 µg/g and 2.00-3.66 µg/g in the dry and wet seasons, respectively (Table 25), the lowest was at Matecha Bridge and a highest at Araranga in the dry season while the lowest was at the control and highest at Matecha Bridge in the wet season. The mean ammonium levels in River Nyangores ranged between 1.59-3.27 µg/g and 3.67-5.47 µg/g in the dry and wet seasons respectively with the lowest at control and the highest at Kapcheluch in both seasons. The mean ammonium levels along River Amala, range between 2.73-3.75 µg/g in dry season and a range 3.72-5.29 µg/g in the wet season with the lowest at the control and highest at Matecha Bridge in both seasons (Table 25).

The mean TN levels ranged between 27.90-54.69 µg/g and 32.64-84.78 µg/g in the dry and wet seasons, respectively along River Nyangores, with the controls having the lowest levels in both seasons but the highest was at Kapcheluch in dry season and the highest in Bomet Bridge in wet season (Table 24). On the other hand, the mean total nitrogen levels along River Amala ranged between 25.62-44.52 µg/g and 36.45-56.22 µg/g (Table 25) in the dry and wet seasons, respectively, with the controls recording lowest levels in both seasons and a highest at Mulot Bridge in the dry season and highest at Matecha Bridge in the wet season.

Table 24: Mean levels of nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+) along River Nyangores (dry sediments)

		NO_3^- (µg N/g)			NO_2^- (µg N/g)			NH_4^+ (µg N/g)		
		Season			Season			Season		
	River Nyangores	Dry	Wet	Mean	Dry	Wet	Mean	Dry	Wet	Mean
N1	Ainapsabet (control)	5.37	7.55	6.46	0.94	0.97	0.95	1.59	3.67	2.63
N2	Kapkorgwet	10.72	12.35	11.54	1.02	1.90	1.46	2.81	4.08	3.45
N3	Kapcheluch	7.89	12.96	10.42	1.41	2.19	1.80	3.27	5.47	4.37
N4	Silibwet Bridge	9.91	12.57	11.24	1.30	1.95	1.62	2.87	3.83	3.35
N5	Bomet Bridge	11.33	14.68	13.01	1.32	1.91	1.62	2.84	3.71	3.28
N6	Olbotyo	10.64	14.57	12.61	1.40	1.90	1.65	2.78	4.09	3.43
N7	Confluence	9.46	16.78	13.12	1.28	2.01	1.64	3.22	4.88	4.05
	Streams									
SN1	Kenon	11.90	22.19	17.04	1.65	2.19	1.92	3.07	6.86	4.97
SN2	Kapkorgwet	17.96	22.67	20.32	1.88	1.90	1.89	3.81	4.03	3.92
SN3	Kapcheluch	15.04	21.81	18.42	2.13	2.19	2.16	3.27	5.33	4.30
SN4	Chepsokwony	19.22	21.98	20.60	5.17	2.77	3.97	3.86	4.69	4.28
SN5	Tenwek after treatment	7.47	12.29	9.88	0.84	1.87	1.36	1.88	3.67	2.76
SN6	Kipsewen	4.28	7.14	5.71	3.94	2.81	3.38	4.65	5.89	5.27
	Mean	10.86	15.35		1.87	2.04		3.07	4.63	
	CV %	3.83			4.74			2.44		
	LSD, ($p \leq 0.05$)	0.23		0.60	0.04		0.11	0.04		0.11

N1 is the control site, N2, N3, N4, N5, N6 and N7 were sampling sites along River Nyangores and SN1, SN2, SN3, SN4, SN5 and SN6 are the corresponding streams along River Nyangores

Table 25: Mean levels of nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+) along River Amala (dry sediments)

		NO_3^- (µg N/g)			NO_2^- (µg N/g)			NH_4^+ (µg N/g)		
Site	**River Amala**	Dry	Wet	Mean	Dry	Wet	Mean	Dry	Wet	Mean
A1	Kebenet (control)	5.32	7.48	6.40	2.02	2.00	2.01	2.73	3.72	3.23
A2	Araranga	9.75	13.61	11.68	4.39	2.74	3.57	3.06	4.73	3.89
A3	Matecha Bridge	11.78	8.41	10.09	1.94	3.66	2.80	3.75	5.29	4.52
A4	Kapkimolwa	14.03	13.78	13.90	2.32	2.61	2.47	3.38	4.68	4.03
A5	Mulot Bridge	13.52	14.24	13.88	2.31	2.44	2.38	2.97	4.27	3.62
A6	Kukunoi	10.79	19.55	15.17	2.28	2.41	2.35	3.19	4.55	3.87
A7	Confluence	11.78	13.42	12.60	2.30	2.43	2.36	2.81	5.47	4.14
	Streams									
SA1	Ndasasian	14.26	11.18	12.67	2.01	2.40	2.21	4.90	5.07	4.97
SA2	Araranga	18.45	18.04	18.25	6.48	2.74	4.61	6.75	6.76	6.76
SA3	Ise River	9.80	22.53	16.67	4.26	3.66	3.96	6.61	6.90	6.75
SA4	Kapkimolwa	11.83	15.47	13.65	1.34	2.82	2.08	3.89	4.27	4.08
SA5	Ngasiat	13.67	16.94	15.30	5.37	3.46	4.41	5.66	5.90	5.78
SA6	Kukunoi	12.77	18.54	15.65	3.18	2.02	2.60	6.46	6.75	6.61
	Mean	12.13	14.86		3.09	2.72		4.32	5.26	
	CV %		5.47			5.49			5.02	
	LSD, ($p \leq 0.05$)		0.34	0.88		0.07	0.19		0.11	0.29

A1 is the control site, A2, A3, A4, A5, A6 and A7 were sampling sites along River Amala and SA1, SA2, SA3, SA4, SA5 and SA6 are the corresponding streams along River Amala.

Similarly, the soluble reactive phosphorous (SRP) site mean levels ranged between 3.46-7.81 µg/g and 5.43-8.76 µg/g (Table 26) in the dry and wet seasons, respectively along River Nyangores with the highest at confluence in the dry season and highest at Bomet Bridge in wet season and the lowest at the control in both seasons. Likewise, along River Amala, mean SRP levels range between 4.49-7.35 µg/g in the dry season, and in the wet season the mean SRP levels range was 5.48-9.71 µg/g, the control registered the lowest level and the highest was at Mulot Bridge in both seasons (Table 27).

The mean total phosphorous, on the other hand, ranged between 12.39-80.89 µg/g and 15.37-89.78 µg/g along River Nyangores in the dry and wet seasons, respectively, with the lowest level at the control and the highest at confluence in both seasons (Table 26) and along River Amala the lowest level of 15.65 µg/g was recorded at the control and highest at 65.87 µg/g at Mulot Bridge in the dry season and a similar trend was observed in the wet season with the lowest level of 18.02 µg/g obtained at the control and the highest at Mulot Bridge (Table 27).

Table 26: Mean levels of total nitrogen (TN), soluble reactive phosphorous (SRP) and total phosphorous (TP) along River Nyangores (dry sediments)

		TN(µg N/g)			SRP(µg P/g)			TP(µg P/g)		
Site	**River Nyangores**	Dry	Wet	Mean	Dry	Wet	Mean	Dry	Wet	Mean
N1	Ainapsabet (control)	27.90	32.51	30.21	3.46	5.43	4.45	12.39	15.37	13.88
N2	Kapkorgwet	37.59	51.30	44.45	4.62	6.57	5.60	28.03	35.66	31.75
N3	Kapcheluch	54.69	80.43	67.56	6.43	8.24	7.34	36.59	42.23	39.41
N4	Silibwet Bridge	43.74	67.23	55.49	6.62	7.24	6.93	33.19	34.33	33.76
N5	Bomet Bridge	50.64	84.78	67.71	7.19	8.76	7.98	62.38	80.43	71.41
N6	Olbotyo	34.80	67.35	51.07	6.57	8.24	7.41	72.09	79.95	76.02
N7	Confluence	34.44	54.99	44.72	7.81	6.48	7.15	80.89	89.78	85.34
	Streams									
SN1	Kenon	49.53	68.22	58.88	6.47	6.41	6.44	45.19	38.67	41.93
SN2	Kapkorgwet	46.29	73.92	60.11	4.49	8.67	6.58	38.35	36.63	37.49
SN3	Kapcheluch	54.69	67.50	61.10	6.19	6.24	6.22	66.40	42.21	54.31
SN4	Chepsokwony	40.62	52.68	46.65	6.62	7.67	4.15	76.71	76.42	76.57
SN5	Tenwek after treatment	43.56	73.01	58.28	6.57	7.71	7.14	47.33	55.86	51.60
SN6	Kipsewen	35.10	57.96	46.54	5.30	7.35	6.33	49.82	47.52	48.67
	Mean	42.59	64.00		6.03	7.31		49.95	51.91	
	CV %	1.76			3.56			8.31		
	LSD, (p≤0.05)	0.44		1.11	0.11		0.28	NS		5.03

N1 is the control site, N2, N3, N4, N5, N6 and N7 were sampling sites along River Nyangores and SN1, SN2, SN3, SN4, SN5 and SN6 are the corresponding streams along River Nyangores

Table 27: Mean levels of total nitrogen (TN), soluble reactive phosphorous (SRP) and total phosphorous (TP) along River Amala (dry sediments)

		TN(µg N/g)			SRP(µg P/g)			TP µg P/g)		
	River Amala	Dry	Wet	Mean	Dry	Wet	Mean	Dry	Wet	Mean
Site										
A1	Kebenet (control)	25.62	36.45	31.05	4.49	5.48	4.99	15.65	18.02	16.83
A2	Araranga	28.68	46.17	37.44	5.62	7.81	6.71	42.00	37.43	39.72
A3	Matecha Bridge	34.89	56.22	45.54	5.67	6.66	6.17	38.07	42.14	40.10
A4	Kapkimolwa	37.83	44.37	41.13	5.43	8.22	6.82	47.21	47.38	47.30
A5	Mulot Bridge	44.52	47.19	45.87	7.35	9.71	8.53	65.87	94.29	80.08
A6	Kukunoi	40.23	47.79	44.01	6.33	7.76	7.05	38.33	38.10	38.22
A7	Confluence	40.77	44.43	42.6	6.38	6.43	6.40	43.38	43.09	43.23
	Streams									
SA1	Ndasasian	44.01	63.54	53.79	6.49	7.57	7.03	40.52	51.48	46.00
SA2	Araranga	66.75	69.09	67.92	6.18	8.21	7.20	56.40	40.71	48.56
SA3	Ise	53.70	67.26	60.48	6.71	7.76	7.24	51.87	56.67	54.27
SA4	Kapkimolwa	40.44	52.71	46.59	6.56	7.19	6.88	52.31	57.38	54.85
SA5	Ngasiat	43.89	45.81	44.85	5.68	10.55	8.12	58.52	81.09	69.81
SA6	Kukunoi	37.56	47.22	42.39	6.38	7.71	7.05	44.90	48.00	46.45
	Mean	42.58	61.69		6.10	7.77		45.77	50.44	
	CV %		5.16			2.49			3.67	
	LSD, ($p \leq 0.05$)	1.11		2.84	0.08		0.20	0.82		2.10

A1 is the control site, A2, A3, A4, A5, A6 and A7 were sampling sites along River Amala and SA1, SA2, SA3, SA4, SA5 and SA6 are the corresponding streams along River Amala.

Generally, there was significant difference ($p \leq 0.05$) in the nutrient loads levels among the sites and with the control along the Rivers Nyangores and Amala indicating that anthropogenic activities have had an influence on the levels of nutrient loads along the two tributaries. The levels gradually increased along the tributaries and general pattern was similar to that of nutrients in water although in the sediments the levels of nutrient loads were much higher. This confirms that sediments act as sinks for pollutants (Biney *et al.*, 1994; Barbour *et al.*, 1998, 1999) and they have an effect on the quality of the overlying water. A comparison with a study reported of Catatumbo River in Venezuela (Table 28) indicates that the levels of ammonium, total phosphorous and total nitrogen obtained in this study were lower.

Table 28: Comparison of data with some international standards on sediment reported and in other studies nutrients in dry sediments (µg/g)

	NO_3^-	NO_2^-	NH_4^+	TN	SRP	TP
River Nyangores (dry season)[a]	10.86	1.87	3.07	42.56	6.03	49.95
River Nyangores (wet season)[a]	15.35	2.04	4.63	64.00	7.31	51.91
River Amala (dry season)[a]	12.13	3.09	4.32	42.58	6.10	45.77
River Amala (wet season)[a]	14.86	2.72	5.26	61.69	7.77	50.44
Thailand[b]	1.08	NG	50.8		2.6	
Catatumbo River (Bravo tributary 1994) Venezuela[c]				1761		487
Key **a**-This study 2012 (n = 13) from each tributary, **b**- Funges-Smith (1996), **c** -Rivas *et al.* (1998)						

The levels of a selected number of heavy metals in dry sediment were studied and recorded in Tables 29, 30, 31, 32, 33 and 34 (in dry weight), of metals including; copper (Cu), cadmium (Cd), iron (Fe), zinc (Zn), chromium (Cr), manganese (Mn), lead (Pb) and selenium (Se) in µg/g.

Copper levels ranged between 0.11–0.32 µg/g with the highest at Silibwet Bridge in the dry season, and in the wet season it ranged between 0.38-0.83 µg/g with the highest at Kapkorgwet and Kapcheluch along River Nyangores (Table 29). The range of copper along River Amala was between 0.10-0.51 µg/g with the highest value at Matecha Bridge in the dry season, and in the wet season it ranged between 0.12–0.73 µg/g with the highest at the confluence (Table 30). Cadmium mean levels, along River Nyangores, ranged between 0.04-0.12 µg/g and 0.07-0.14 µg/g in the dry and wet seasons, respectively (Table 29), with the highest at the confluence in the dry season and the highest at Kapcheluch in wet season. The range along River Amala was between 0.10-0.22 µg/g and 0.06 - 0.11 µg/g in the dry season and wet seasons, respectively, with the highest at Kapkimolwa in both seasons (Table 30). The control (Ainapsabet) had the lowest Cu and Cd levels in both seasons and in both Rivers Nyangores and Amala.

Table 29: Mean levels of copper (Cu), cadmium (Cd) and iron (Fe) in sediments along River Nyangores

		Cu (μg/g)			Cd (μg/g)			Fe (μg/g)		
Site	**River Nyangores**	Dry	Wet	Mean	Dry	Wet	Mean	Dry	Wet	Mean
N1	Ainapsabet (control)	0.11	0.38	0.25	0.04	0.07	0.06	68.11	68.72	68.41
N2	Kapkorgwet	0.28	0.83	0.55	0.07	0.14	0.10	68.26	75.67	71.97
N3	Kapcheluch	0.24	0.83	0.53	0.06	0.14	0.10	69.37	68.56	68.96
N4	Silibwet Bridge	0.32	0.50	0.41	0.08	0.12	0.10	68.33	69.81	69.07
N5	Bomet Bridge	0.14	0.54	0.34	0.09	0.08	0.09	68.78	67.39	68.09
N6	Olbotyo	0.26	0.55	0.41	0.09	0.12	0.11	68.74	75.96	72.35
N7	Confluence	0.22	0.61	0.41	0.12	0.13	0.13	66.34	68.64	67.49
	Streams									
SN1	Kenon	0.36	0.57	0.46	0.10	0.12	0.11	67.21	67.55	67.38
SN2	Kapkorgwet	0.19	0.66	0.42	0.12	0.10	0.11	67.57	67.17	67.37
SN3	Kapcheluch	0.21	0.79	0.50	0.09	0.13	0.11	68.44	69.65	69.04
SN4	Chepsokwony	0.49	0.51	0.50	0.06	0.11	0.09	68.40	69.78	69.09
SN5	Tenwek after treatment	0.17	0.54	0.35	0.09	0.09	0.09	66.23	65.19	65.71
SN6	Kipsewen	0.15	0.33	0.24	0.09	0.11	0.10	68.32	67.04	67.68
	Mean	0.24	0.59		0.09	0.11		68.00	69.31	
	CV %	4.40			7.51			1.70		
	LSD, (p≤0.05)	0.01		0.02	0.01		0.01	0.54		1.39

N1 is the control site, N2, N3, N4, N5, N6 and N7 were sampling sites along River Nyangores and SN1, SN2, SN3, SN4, SN5 and SN6 are the corresponding streams along River Nyangores

Mean iron levels along River Nyangores were at a range of 66.34-69.37 μg/g and 67.39-75.96 μg/g in the dry and wet seasons, respectively (Table 29), with the lowest level at the confluence and highest at Kapcheluch in the dry season and in the wet season the lowest was at Bomet Bridge and the highest at Olbotyo, while along River Amala the range was between 63.17-67.18 μg/g and 65.39-69.63 μg/g in the dry and wet seasons, respectively. The lowest was at Kukunoi and the highest at Araranga in the dry season while the lowest was at the control and the highest at Matecha Bridge in the wet season (Table 30).

The range in mean zinc levels along River Nyangores was from 4.45-5.60 μg/g with the highest at Kapcheluch in the dry season, while it ranged between 25.13-26.59 μg/g in the wet season with the highest at Olbotyo (Table 31).

Table 30: Mean levels of copper (Cu), cadmium (Cd) and iron (Fe) in sediments along River Amala

		Cu (µg/g)			Cd (µg/g)			Fe (µg/g)		
	River Amala	Dry	Wet	Mean	Dry	wet	Mean	Dry	Wet	Mean
A1	Kebenet (control)	0.10	0.12	0.11	0.10	0.06	0.08	63.63	65.39	64.51
A2	Araranga	0.12	0.13	0.12	0.14	0.09	0.11	67.18	68.83	68.01
A3	Matecha	0.51	0.24	0.37	0.15	0.07	0.11	66.51	69.63	68.07
A4	Kapkimolwa	0.31	0.35	0.33	0.22	0.11	0.17	65.41	65.51	65.46
A5	Mulot	0.25	0.60	0.43	0.12	0.08	0.10	63.65	66.14	64.90
A6	Kukunoi	0.30	0.61	0.46	0.11	0.08	0.10	63.17	65.78	64.47
A7	Confluence	0.18	0.73	0.45	0.12	0.10	0.11	64.20	67.11	65.65
	Streams									
SA1	Ndasasian	0.17	0.34	0.26	0.13	0.10	0.11	66.97	67.03	67.00
SA2	Araranga	0.31	0.48	0.40	0.15	0.11	0.13	67.07	73.93	70.50
SA3	Ise River	0.15	0.30	0.22	0.11	0.12	0.11	67.49	67.57	67.53
SA4	Kapkimolwa	0.03	0.07	0.05	0.09	0.08	0.09	64.88	66.44	65.66
SA5	Ngasiat	0.18	0.33	0.26	0.13	0.09	0.11	64.22	67.34	65.98
SA6	Kukunoi	0.22	0.43	0.33	0.13	0.09	0.11	64.52	70.11	67.32
	Mean	0.22	0.37		0.13	0.09		65.30	67.78	
	CV %		4.41			5.12			1.17	
	LSD, (p≤0.05)	0.01		0.02	0.01		0.01	0.36		0.93

A1 is the control site, A2, A3, A4, A5, A6 and A7 were sampling sites along River Amala and SA1, SA2, SA3, SA4, SA5 and SA6 are the corresponding streams along River Amala.

The mean zinc level along River Amala ranged between 2.06-3.75 µg/g and 25.11-26.58 µg/g in the dry and wet seasons, respectively with the highest at Matecha Bridge in the dry season and the highest at Kapkimolwa (Table 32). The lowest zinc mean levels were lowest at the control in both seasons. In the dry season, mean chromium levels ranged between 13.44-16.94 µg/g (Table 31) with the highest at Kapkorgwet and in the wet season it ranged between 21.56-24.91 µg/g with highest value at Silibwet Bridge and the lowest was at the control in both seasons along River Nyangores. The range of mean chromium levels along River Amala was between 13.53-14.65 µg/g (Table 32) with the lowest at the control and the highest at the confluence in the dry season and a lowest of 22.80 µg/g at Matecha Bridge and a highest of 25.51 µg/g (Table 32) at the confluence in the wet season.

Table 31: Mean levels of zinc (Zn), chromium (Cr) and manganese (Mn) in sediments along River Nyangores

		Zn (µg/g)			Cr (µg/g)			Mn (µg/g)		
Site	**River Nyangores**	Dry	Wet	Mean	Dry	Wet	Mean	Dry	Wet	Mean
N1	Ainapsabet (control)	4.45	25.13	14.79	13.44	21.56	17.50	24.87	25.11	24.99
N2	Kapkorgwet	5.32	25.50	15.40	16.94	24.14	20.54	25.74	25.86	25.80
N3	Kapcheluch	5.60	25.22	15.41	15.53	24.18	19.86	25.56	25.46	25.51
N4	Silibwet Bridge	5.58	25.39	15.48	15.94	24.91	20.42	25.56	26.67	26.12
N5	Bomet Bridge	5.33	25.90	15.62	15.62	24.55	20.09	26.16	26.73	26.44
N6	Olbotyo	5.22	26.59	15.90	16.51	23.37	19.94	26.44	26.04	26.24
N7	Confluence	5.23	25.95	15.74	14.51	23.73	19.12	25.77	26.15	25.96
	Streams									
SN1	Kenon	5.52	8.42	6.97	16.51	23.29	19.90	25.10	26.08	25.59
SN2	Kapkorgwet	4.78	9.04	6.91	18.11	23.30	20.70	25.42	26.30	25.86
SN3	Kapcheluch	5.56	8.59	7.08	15.99	23.51	19.75	24.93	26.43	25.68
SN4	Chepsokwony	5.62	8.54	7.08	15.79	21.75	18.77	24.62	25.10	24.86
SN5	Tenwek after treatment	5.70	8.32	7.01	14.84	21.91	18.38	24.70	25.64	25.17
SN6	Kipsewen	4.80	8.63	6.72	14.64	23.00	18.82	24.88	25.27	25.08
	Mean	5.31	17.79		15.72	23.32		25.36	25.91	
	CV %	1.86			3.70			1.47		
	LSD, ($p\leq0.05$)	0.10		0.25	0.34		0.86	0.18		0.45

N1 is the control site, N2, N3, N4, N5, N6 and N7 were sampling sites along River Nyangores and SN1, SN2, SN3, SN4, SN5 and SN6 are the corresponding streams along River Nyangores

Table 32: Mean levels of zinc (Zn), chromium (Cr) and manganese (Mn) in sediments along River Amala

		Zn (µg/g)			Cr (µg/g)			Mn (µg/g)		
Site	**River Amala**	Dry	Wet	Mean	Dry	Wet	Mean	Dry	Wet	Mean
A1	Kebenet (control)	2.06	25.11	13.59	13.53	23.00	18.27	24.86	25.19	25.03
A2	Araranga	3.35	25.25	14.30	13.89	24.53	19.21	25.18	25.72	25.47
A3	Matecha Bridge	3.75	25.67	14.71	14.06	22.80	18.42	25.77	25.77	25.90
A4	Kapkimolwa	3.11	26.58	14.84	14.07	23.22	18.64	26.89	26.52	26.70
A5	Mulot Bridge	2.19	26.05	14.12	14.37	23.62	19.00	25.95	26.21	26.08
A6	Kukunoi	2.07	26.02	14.04	14.40	24.93	19.67	25.45	25.59	25.52
A7	Confluence	2.43	25.90	14.16	14.65	25.51	20.08	26.13	25.85	25.98
	Streams									
SA1	Ndasasian	3.25	7.92	5.59	12.52	23.68	18.10	25.41	25.77	25.59
SA2	Araranga	5.29	8.23	6.76	13.78	23.66	18.72	25.28	25.52	25.39
SA3	Ise	6.34	8.27	7.30	13.55	23.55	18.43	25.62	25.24	25.43
SA4	Kapkimolwa	4.23	7.22	5.92	12.72	26.42	19.57	25.24	25.03	25.13
SA5	Ngasiat	4.70	8.07	6.34	14.42	29.30	21.86	25.24	25.76	25.65
SA6	Kukunoi	3.07	8.08	5.58	15.33	24.45	19.86	24.98	24.71	24.85
	Mean	3.54	17.58		13.94	24.51		25.56	25.63	
	CV %		2.31			2.34			1.81	
	LSD, ($p \leq 0.05$)		0.11	0.29		0.21	0.53		NS	0.55

A1 is the control site, A2, A3, A4, A5, A6 and A7 were sampling sites along River Amala and SA1, SA2, SA3, SA4, SA5 and SA6 are the corresponding streams along River Amala.

Mean manganese levels, on the other hand, ranged between 24.87-26.44 µg/g with the highest at Olbotyo in the dry season and 25.11-26.73 µg/g with the highest at Bomet bridge in the wet season along River Nyangores (Table 31). The range along River Amala was between 24.86-26.89 µg/g with the highest at Kapkimolwa in the dry season and manganese ranged between 25.19-26.52 µg/g at Kapkimolwa in the wet season (Table 32), the control had the lowest value in both seasons and in both tributaries.

The mean levels of lead ranged between 0.14-0.53 µg/g with the highest at Olbotyo in the dry season and 0.17-1.15 µg/g with the highest at Kapcheluch in the wet season along River Nyangores (Table 33), while along River Amala the range was between 0.11-0.34 µg/g with the at the highest at the confluence in the dry season and it ranged between 0.24-1.13 µg/g with the highest at Mulot Bridge in the wet season (Table 34), the control had the lowest value in both seasons and in both tributaries.

Selenium, on the other hand, ranged between 0.08-0.12 µg/g with the lowest at Bomet Bridge and the control, while the highest was at Kapcheluch and Olbotyo in the dry season (Table 33). In the wet season the lowest was 0.09 µg/g at the control and was highest 0.23 µg/g at Kapcheluch. The range along River Amala was between 0.05-0.07 µg/g with the highest at Kukunoi in the dry season and in the wet season it ranged between 0.08-0.13 µg/g at the with the highest at Mulot Bridge (Table 34).

Table 33: Mean levels of lead (Pb) and selenium (Se) in sediments along River Nyangores

		Pb (µg/g)			Se (µg/g)		
Site	**River Nyangores**	Dry	Wet	Mean	Dry	Wet	Mean
N1	Ainapsabet (control)	0.14	0.17	0.16	0.08	0.09	0.09
N2	Kapkorgwet	0.38	0.76	0.57	0.08	0.17	0.13
N3	Kapcheluch	0.27	1.15	0.71	0.12	0.23	0.18
N4	Silibwet Bridge	0.17	0.40	0.29	0.09	0.18	0.14
N5	Bomet Bridge	0.35	0.74	0.54	0.08	0.18	0.13
N6	Olbotyo	0.53	0.74	0.64	0.12	0.21	0.17
N7	Confluence	0.15	0.61	0.38	0.09	0.21	0.15
	Streams						
SN1	Kenon	0.51	1.02	0.77	0.09	0.15	0.12
SN2	Kapkorgwet	0.32	0.45	0.36	0.09	0.12	0.10
SN3	Kapcheluch	0.48	0.77	0.62	0.04	0.08	0.06
SN4	Chepsokwony	1.09	1.02	1.05	0.13	0.23	0.18
SN5	Tenwek after treatment	0.52	0.57	0.55	0.03	0.07	0.05
SN6	Kipsewen	0.37	0.96	0.67	0.16	0.22	0.19
	Mean	0.41	0.72		0.09	0.17	
	CV %	5.93			10.10		
	LSD, (p≤0.05)	0.02		0.04	0.01		0.02

N1 is the control site, N2, N3, N4, N5, N6 and N7 were sampling sites along River Nyangores and SN1, SN2, SN3, SN4, SN5 and SN6 are the corresponding streams along River Nyangores

The levels of most of the heavy metals in sediments were significantly different (p≤0.05) among main sites and with the control this could be attributed to the changing anthropogenic activities along the tributaries. However, cadmium levels along River Amala significantly decreased ($p \leq 0.05$) in the wet season implying that variation in cadmium levels may not be due to anthropogenic activities as there were no new inputs.. The trace metals in sediments did not register a pattern similar to that of metals in water like observed in nutrients this could be attributed to other factors including geochemical processes such as weathering of rocks (Forstner and Wittmann, 1983; Nriagu, 1989; Veena *et al.*, 1997; Habes and Nigem, 2006), solubility of metals and sorption ability of the sediments along the rivers. The mean levels of heavy metals obtained in this study were generally lower than those recorded in other studies done in the rivers feeding Lake Victoria. River Sondu Miriu as reported by Ongeri (2008) had 20.90 µg/g (Cu), 651.4 µg/g (Fe), 258.4 µg/g (Zn), 25.10 µg/g (Pb) among other rivers as indicated in Table 35.

Table 34: Mean levels of lead (Pb) and selenium (Se) in sediments along River Amala

		Pb (µg/g)			Se (µg/g)		
Site	**River Amala**	Dry	Wet	Mean	Dry	Wet	Mean
A1	Kebenet (control)	0.11	0.24	0.17	0.05	0.14	0.10
A2	Araranga	0.28	0.33	0.30	0.07	0.09	0.08
A3	Matecha Bridge	0.12	0.31	0.22	0.06	0.17	0.12
A4	Kapkimolwa	0.27	0.73	0.50	0.06	0.16	0.11
A5	Mulot Bridge	0.31	1.13	0.72	0.06	0.19	0.13
A6	Kukunoi	0.33	0.41	0.37	0.07	0.13	0.10
A7	Confluence	0.34	0.72	0.53	0.06	0.08	0.07
	Streams						
SA1	Ndasasian	0.37	0.45	0.41	0.08	0.16	0.12
SA2	Araranga	0.69	0.97	0.83	0.08	0.11	0.09
SA3	Ise	0.86	0.19	0.53	0.13	0.23	0.18
SA4	Kapkimolwa	0.43	0.56	0.50	0.07	0.14	0.10
SA5	Ngasiat	0.26	0.48	0.37	0.07	0.18	0.13
SA6	Kukunoi	0.35	0.85	0.60	0.07	0.11	0.09
	Mean	0.36	0.64		0.07	0.14	
	CV %		6.43			6.45	
	LSD, ($p \leq 0.05$)		0.02	0.04		0.01	0.01

A1 is the control site, A2, A3, A4, A5, A6 and A7 were sampling sites along River Amala and SA1, SA2, SA3, SA4, SA5 and SA6 are the corresponding streams along River Amala.

Similarly, the international environmental limits on aquatic contamination as shown in Table 35 indicate that the heavy metals levels recorded in this study are below the threshold concentrations that may have an effect on the overlying surface water (USEPA, 2010)

Table 35: Comparison of data on heavy metals in this study with some studies done on sediments from other rivers (dry sediments in µg/g)

RIVER	Cu	Cd	Fe	Zn	Cr	Mn	Pb	Se
River Nyangores dry season [a]	0.24	0.09	68.01	5.31	15.72	25.36	0.36	0.09
River Nyangores wet season [a]	0.59	0.11	69.31	17.79	23.32	25.91	0.64	0.17
River Amala dry season [a]	0.22	0.13	65.30	3.54	13.94	25.56	0.41	0.07
River Amala wet season [a]	0.37	0.09	67.78	17.58	24.51	25.63	0.72	0.14
River Sio Kenya [b]	18.50		9.60	37.70			8.10	
River Sondu Miriu Kenya [b]	20.90		651.4	258.4			25.10	
River Nyamasaria Kenya [b]	28.30		418.30	131.8			25.10	
River Nyando Kenya [b]	56.30		685.60	172.2			17.00	
Nile Delta Egypt [c]	255.82	1.43	$5.25*10^4$	266.7	129.8	166.8	87.0	
Lake Malawi [d]	37.30			0.05			14.60	
Lake Naivasha Kenya [e]	15	<0.17		160	BDL		<0.3	
River Gadilam -India [f]	0.295	0.172		62.36		0.419	0.386	
Environment Canada [g]	36	0.6		123	37		35	
USEPA [h]	31.6	0.99		121	43.3		35.8	

a – This study 2012 (n = 13) along each river, **b**-Ongeri (2008), **c**-El Bouraie, *et al.*, (2010), **d**-Kidd *et al.* (1998), **e**-Tarras-Wahlberg, *et al.*(2002), **f**-Usha and Vikram (2012), **g**- Canadian Council of Ministers of Environment (2002), **h**-USEPA (2010) threshold effect concentration on surface water.

BDL- Below Detection Limit

4.3 Seasonal variations of the levels of physicochemical parameters, nutrients and heavy metals along Rivers Nyangores and Amala

The mean pH was significantly different ($p \leq 0.05$) in the different seasons and this points to a change in the composition of surface runoffs resulting from anthropogenic activities (Tables 10 and 11). Therefore, the alternate hypothesis holds. The mean pH along River Amala significantly increased in the wet season, that is, 6.43 and 6.85 in the dry and wet seasons, respectively, while the pH along River Nyangores significantly decreased in the wet season, it was 7.17 and 7.05 in the dry and wet seasons, respectively. This could be attributed to different farming activities along each river which possibly require different farm inputs. The mean temperature was also significantly lower ($p \leq 0.05$) during the wet season in both rivers due to increased precipitation; that is, River Nyangores 15.09°C and 13.94°C during dry and wet seasons, respectively and River Amala 15.46°C and 13.37°C in the dry and wet seasons, respectively (Tables 10 and 11).

Generally most of the parameters registered a significant increase ($p \leq 0.05$) during the wet season which is a function of concentration and solution effect. The levels of electrical conductivity registered during the wet season (Tables 10 and 11) were significantly ($p \leq 0.05$) higher than those during dry season, an indication of "solution" effect - a situation where salts contained in dry lands such as fertilizers and dead vegetation get into the waters during the heavy down pour (Welcome, 1992). Equally, there was a significant increase ($p \leq 0.05$) in the nitrates, nitrites and total nitrogen levels (Tables 12, 13, 14 and 15) during rainy season caused by solution effect.

Nitrates are known to build up in during dry seasons and high levels of nitrates are observed during early rainy seasons because initial rains flush out deposited nitrate from near-surface soils and nitrate level reduces drastically as rainy season progresses (Wolfhard and Reinhard, 1998). Therefore, there was significant increase $p \leq 0.05$ in the nitrogen content levels during rainy season which could also be attributed to change in the composition and quantity of surface runoffs in the rainy season thus an effect of anthropogenic activities. The phosphorous levels were also significantly ($p \leq 0.05$) higher in the wet season an indication of the solution effect.

Most of the heavy metal levels in water were also significantly higher ($p \leq 0.05$) in the wet season in both tributaries than dry season (Tables 17, 18, 19, 20, 21 and 22) except for chromium, lead and selenium. The fact that chromium, lead and selenium were significantly ($p \leq 0.05$) lower in the wet season is an indication that the variation of these heavy metals is not due to anthropogenic activities because there were no new inputs in the wet season. In sediments all the heavy metals significantly ($p \leq 0.05$) increased in the wet season (Tables 29, 30, 31, 32, 33 and 34) indicating a solution effect, except for the level of cadmium in River Amala that decreased significantly ($p \leq 0.05$) in the wet season implying there were no new cadmium inputs.

4.4 Comparing variations in physicochemical parameters, nutrients and heavy metals in water and sediments between Rivers Nyangores and Amala.

The sampling sites along the two tributaries were different, for comparison purposes the last sampling site at the confluence on each river was used. This was in consideration that these sites are situated at the same latitude and altitude, and they contain the levels of nutrients and heavy metals that eventually get into the River Mara and ultimately may have direct influence on the quality of water flowing downstream from this point.

The mean pH at the confluence of River Amala were compared to that of River Nyangores at the confluence in the dry and wet seasons (Fig 5). The result shows that in both seasons mean pH of River Amala is significantly lower ($p \leq 0.05$) than that of the corresponding sites at River Nyangores in both seasons (Fig 5).

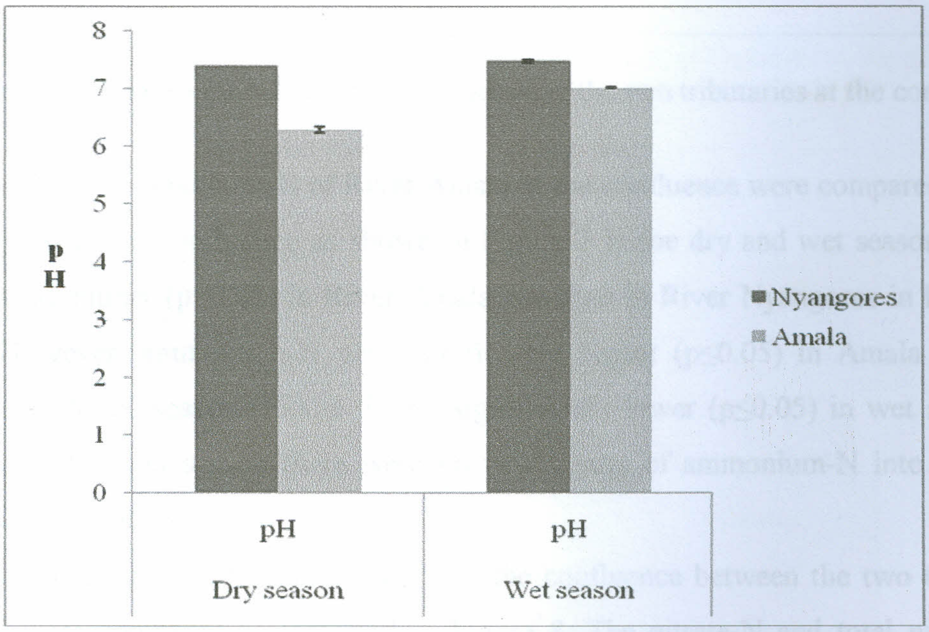


Figure 5: Comparing pH at the confluence between the two rivers

The mean electrical conductivity of River Amala at the confluence was compared to that of River Nyangores at the confluence as shown in Figure 6 in the dry and wet seasons. The conductivity in River Amala site was significantly higher ($p \leq 0.05$) than that of River Nyangores in both seasons (Figure 6). Indicating that more dissolved matter are washed into River Mara by River Amala than River Nyangores.

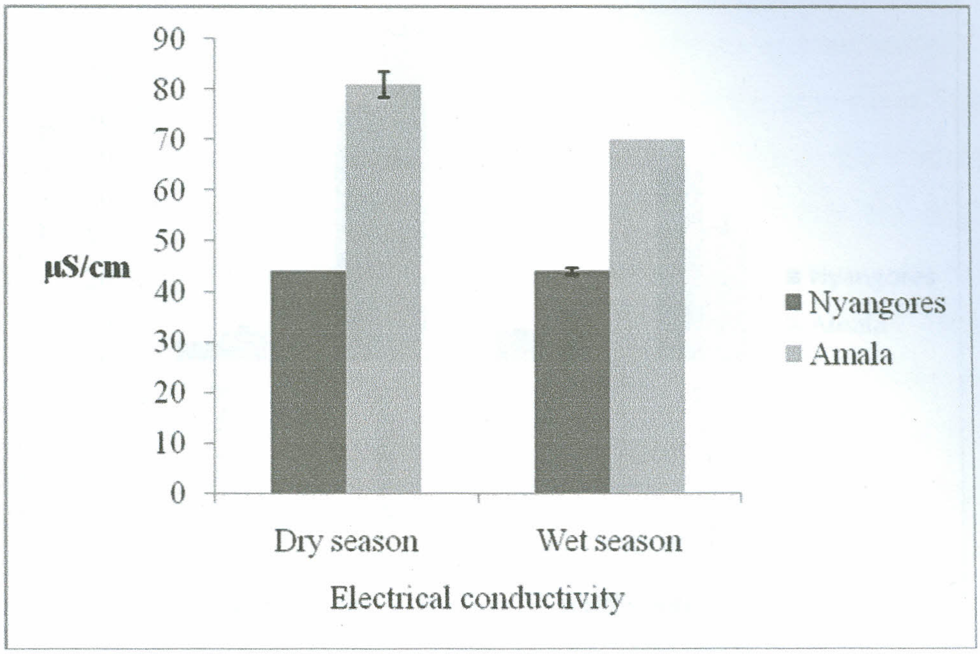


Figure 6: Comparing the electrical conductivity between the two tributaries at the confluence.

Nitrite-N and ammonium-N of River Amala at the confluence were compared to those of River Nyangores at the confluence as shown in Figure 7 in the dry and wet seasons. Nitrite-N was significantly higher ($p \leq 0.05$) in River Amala site than in River Nyangores in both seasons (Figure 7). However, ammonium-N was significantly higher ($p \leq 0.05$) in Amala site than at Nyangores' site in dry season (Figure 7) but significantly lower ($p \leq 0.05$) in wet season. This indicates that in the wet season there were no new inputs of ammonium-N into River Mara coming from River Amala.

The mean nitrate-N and total nitrogen at the confluence between the two tributaries in both seasons were compared as indicated in Figure 8. The nitrate-N and total nitrogen were significantly lower ($p \leq 0.05$) in River Amala than in River Nyangores in the dry season but in the wet season mean nitrate-N was significantly higher ($p \leq 0.05$) in River Amala than in River Nyangores while mean of total nitrogen remained significantly lower ($p \leq 0.05$) in River Amala than in River Nyangores in the wet season (Figure 8). This indicates that River Amala brought more dissolved nutrients than River Nyangores into River Mara.

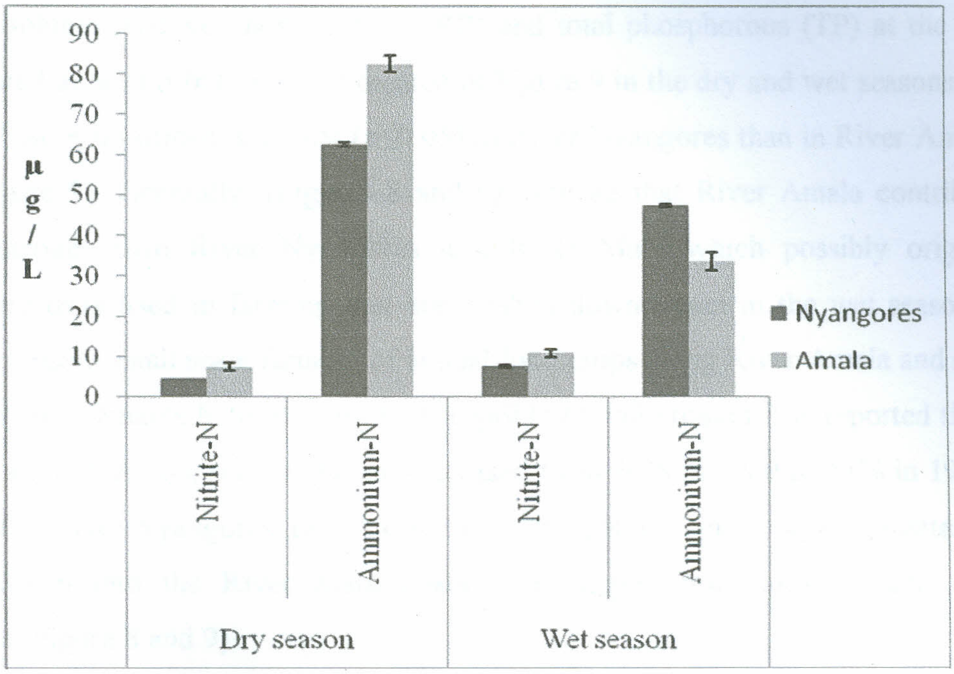


Figure 7: Comparing the nitrite-N and ammonium-N between the tributaries at the confluence

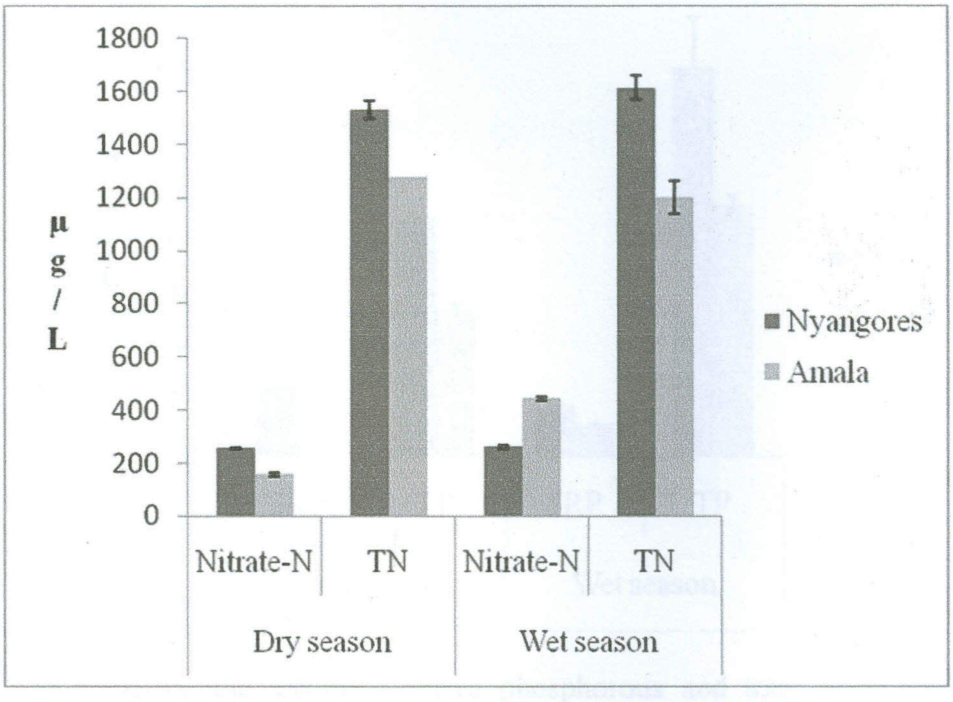


Figure 8: Comparing the nitrate-N and total nitrogen (TN) between the tributaries at the confluence

The soluble reactive phosphorous (SRP) and total phosphorous (TP) at the confluence were compared at both tributaries as indicated in Figure 9 in the dry and wet seasons. The mean SRP and TP were significantly higher ($p \leq 0.05$) in River Nyangores than in River Amala in both seasons (Figure 9). Generally, (Figures 8 and 9) indicate that River Amala contribute higher dissolved nitrogen than River Nyangores into River Mara which possibly originate from inorganic fertilizers used in farming that are washed downstream in the wet season. There is relatively extensive small scale farming of annual food crops along River Amala and some of the uncultivated land remains bare, making it susceptible to soil erosion it is reported that the land under cultivation in Amala sub-catchment increased from 20% in 1960 to 51% in 1991 (Mati *et al.*, 2005). The River Nyangores, on the other hand, contributed more organic matter in form of organic nitrogen into the River Mara resulting to higher total nitrogen and also higher phosphorous (Figure 8 and 9).

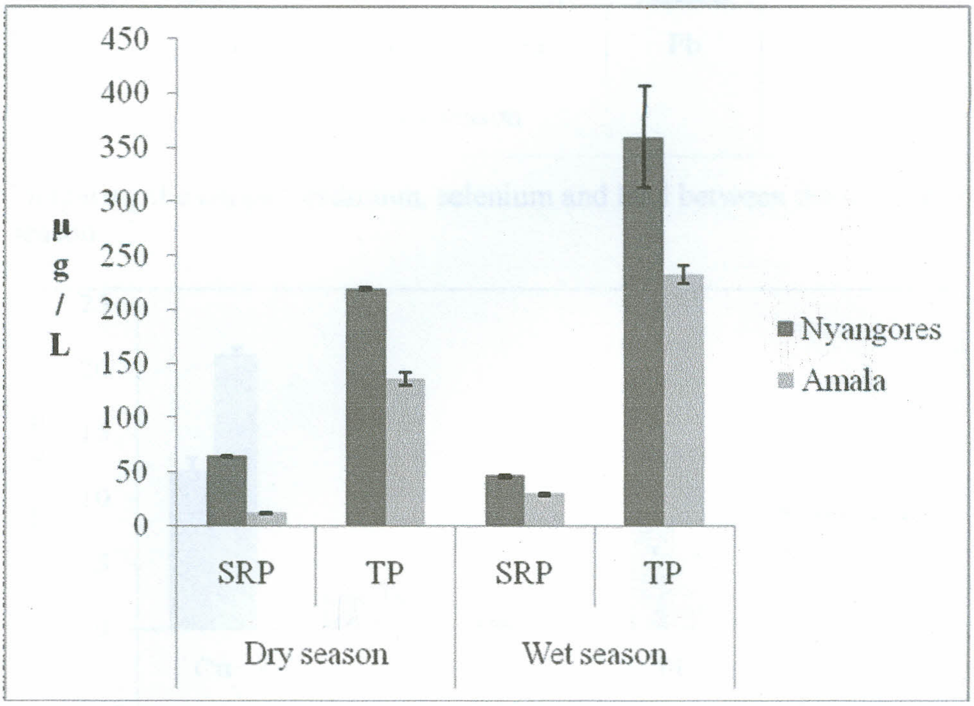


Figure 9: Comparing the soluble reactive phosphorous and total phosphorous between the tributaries at the confluence

Generally, the levels of most of the metals at the confluence were significantly higher ($p \leq 0.05$) in River Amala than in River Nyangores as shown in Figures 10, 11,12 and 13. Metals such as copper, selenium, lead in the dry season were significantly higher ($p \leq 0.05$) in River Amala than River Nyangores. In the wet season copper was still significantly higher ($p \leq 0.05$) in River Amala than River Nyangores and so was cadmium, but lead and selenium were lower in both tributaries in the wet season at the confluence.

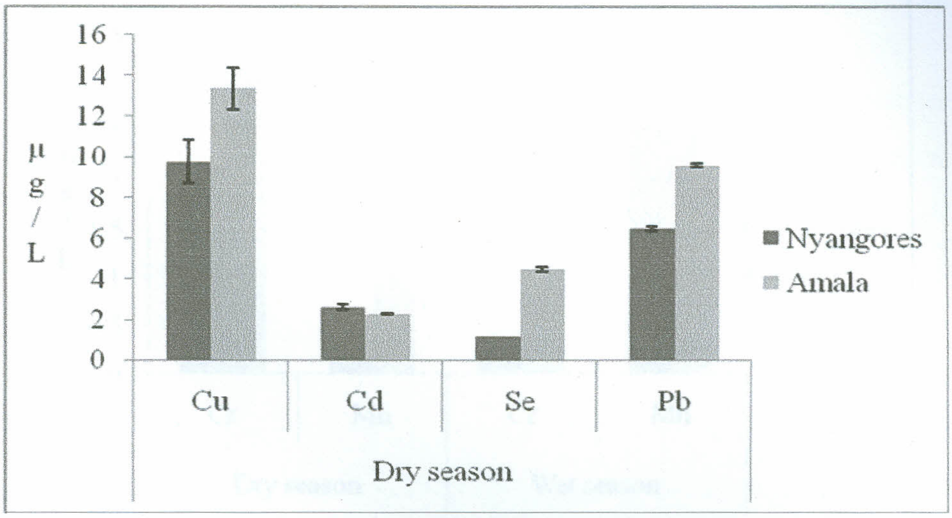


Figure 10: Comparing the copper, cadmium, selenium and lead between the tributaries in the dry season

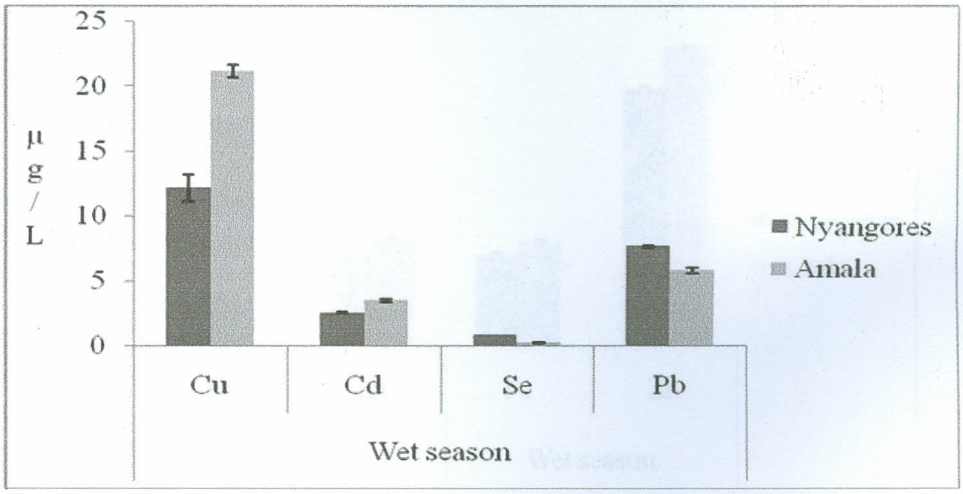


Figure 11: Comparing the copper, cadmium, selenium and lead between the tributaries in the wet season

The mean levels of Cr and Mn in water were significantly higher ($p \leq 0.05$) at River Amala in the confluence than in River Nyangores in the dry season but in wet season Mn was significantly higher ($p \leq 0.05$) in River Nyangores than River Amala (Figure 12). Similarly, the levels of iron and zinc in the confluence were significantly higher ($p \leq 0.05$) at River Amala in the confluence than in River Nyangores in the wet season.

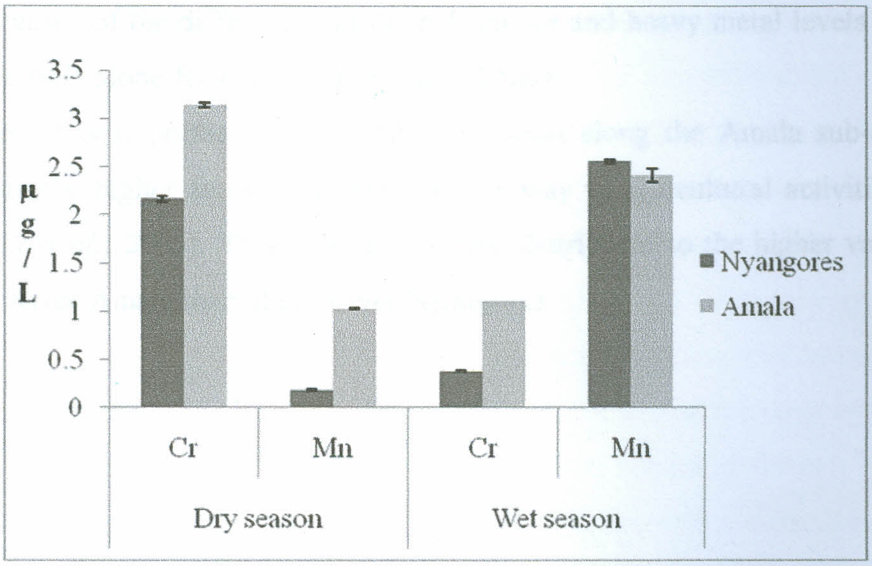


Figure 12: Comparing chromium and manganese levels at the confluence between the tributaries

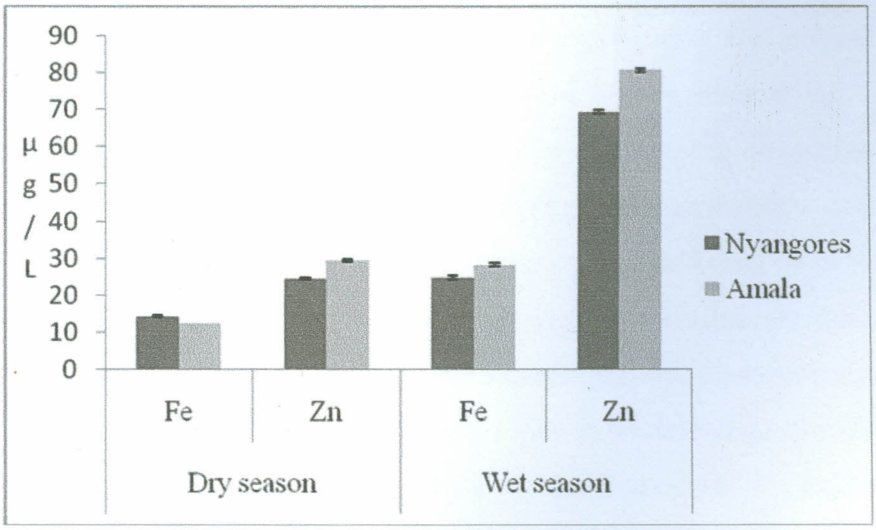


Figure 13: Comparing iron and zinc levels at the confluence between the tributaries

The chemistry of metals is diverse, there occurrence in water is a function of the geology of a place (Forstner and Wittmann, 1983; Nriagu, 1989; Veena *et al.*, 1997; Habes and Nigem, 2006), the pH of water and anthropogenic activities. Due to the geochemical processes factors involved the natural occurrence of metals in the soil along the two tributaries; the differences in the mean levels of the metals between the two tributaries recorded in this study may not be explained comprehensively. This is a possible area that need be researched on and possibly determine the causes of the differences in the pH, nitrate and heavy metal levels between these tributaries in the soils along Rivers Nyangores and Amala.

However, it is important to note that the region along the Amala sub-catchment has undergone relatively higher forest clearance to give way to agricultural activities and human settlement (Mati *et al.*, 2005). This to an extent has contributed to the higher values of metals recorded along River Amala than along River Nyangores.

CHAPTER 5

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary

Human settlement at the upper reaches of the Mara River Basin has led to different anthropogenic activities at different regions which may cause an alteration of the water quality flowing along the tributaries. To study the relationship between anthropogenic activities and the water quality status the strategy used to select sites in this study depended on the varying activities being undertaken along the tributaries including a control site upstream where there has been less human interference. This study established that the physicochemical parameters, nutrient load and heavy metal levels registered significant differences ($p \leq 0.05$) among these sites and with the control both in water and sediments. The significant difference ($p \leq 0.05$) between the sites and the control is an indication that anthropogenic activities have had an effect on the water quality, hence the alternative hypothesis holds. The levels of nutrients and heavy metals recorded at the streams flowing through the selected regions were significantly higher ($p \leq 0.05$) than those registered in main sites indicating that anthropogenic activities have had an effect on the water quality .

The levels of most of the parameters studied namely electrical conductivity, NO_3^- -N, NO_2^- -N, TN, SRP, TP, Fe, Mn, Cd, Pb, Cu and Zn were significantly higher ($p \leq 0.05$) during the wet season compared to the dry season. This confirms the alternative hypothesis that anthropogenic activities have an effect on the quality of water flowing downstream from Rivers Amala and Nyangores since the surface runoffs through the agricultural areas and human settlements brought new inputs of nutrients and some heavy metals during the wet season.

The pH of water along River Amala was observed to be significantly lower ($p \leq 0.05$) than that of River Nyangores. Generally, a significantly higher ($p \leq 0.05$) dissolved nutrient loads and heavy metal content was recorded along River Amala than in River Nyangores. The River Amala had significantly higher ($p \leq 0.05$) mean site levels of electrical conductivity, nitrates, nitrites, Cu, Zn, Cr and Fe by comparing the contribution of each river at the confluence, into the River Mara. However, significantly higher ($p \leq 0.05$) levels of total nitrogen and total phosphorous were recorded along Nyangores River than at River Amala. The same trend was also established in the heavy metals levels obtained from the sediments.

Some heavy metals namely; Cr, Pb and Se along River Amala and Cr and Se along River Nyangores were significantly lower ($p \leq 0.05$) in the wet season indicating they are not as a result of anthropogenic activities. The levels of phosphorous recorded in the streams and some main sites along the two tributaries exceeded the permissible domestic water limit of 0.1 ppm (USEPA 1997). Except for total phosphorous, the other nutrient loads and heavy metals are below the environmentally acceptable limits at present and are of no immediate danger to the aquatic system and domestic consumption.

5.2 Conclusions

1. Anthropogenic activities have had an influence on the pH and electrical conductivity of the water flowing along Rivers Amala and Nyangores. However the levels of pH and electrical conductivity are within the environmentally acceptable limits.
2. Anthropogenic activities have had an effect on the levels of NO_3^--N, NO_2^--N, TN, SRP, TP, Fe, Mn, Cd, Cu, Zn and Pb in the water and sediment of the water flowing along Rivers Amala and Nyangores when compared to those from the control sites. Most of the nutrient loads and all heavy metals are below the environmentally acceptable limits at present and are of no immediate danger to the aquatic system and domestic consumption. However, the levels of total phosphorous recorded in the streams and some main sites along the two tributaries exceeded the permissible domestic water limit of 0.1 ppm (USEPA 1997).
3. The levels of NO_3^--N, NO_2^--N, NH_4^+-N, TN, SRP, TP, Fe, Mn, Cd, Pb, Cu, Zn, Se and Cr in water and sediments varied with change in seasons. The electrical conductivity, NO_3^--N, NO_2^--N, TN, SRP, TP, Fe, Mn, Cd, Pb, Cu and Zn were significantly higher ($p \leq 0.05$) during the wet season compared to the dry season.

5.3 Recommendations

The current status of the water quality flowing from these tributaries is within the environmentally accepted limits. However, efforts should be made to prevent further encroachment within the water catchment area, since with time, it could seriously impact the water quality of River Mara negatively and by extension that of Lake Victoria.

5.4 Suggestions for future research

1. A study should be done to establish the heavy metals and nutrient loads in the immediate soils in the region to ascertain the effect of soil erosion and surface runoffs.
2. A study should be done to determine the possible causes of the differences between the two tributaries in the water quality parameters with reference to their geological parameters.

REFERENCES

Aboud, A.A., Bowyer, G.O., Melinda, M.M., Raini, J.A. (2002). A Rapid participatory socioeconomic assessment of the Mara River Basin. Mara River catchment basin initiative work. Eastern Africa Regional Programme Office (EARPO). WWF Nairobi.

Agarwal, K.N. (1990). Effects of malnutrition and iron deficiency on mental functions and study of possible mechanism in animal model. *Proceedings of the Indian Science Academic Board.* **56**, 43-50

Alloway, B.J. (1995). *Soil processes and the behavior of heavy metals in Soils.* Second Edition. Blackie, New York, 11-37.

APHA (1995). *Standard Method for Examination of Water and Wastewater*, American Public Health Association. Washington, DC, 23-89.

ARB (1986). Public hearing to consider the adaptation of a regulatory amendment. Identifying hexavalent chromium as toxic air contaminant. Stationary Source Division; Sacramento, California.

ATSDR (2003). Case Studies in Environmental Medicine – Chromium Toxicity http://www.atsdr.cdc.gov/HEC/CSEM/chromium/exposure_pathways.html (accessed on 03 March 2011)

Baird, D., Ulanowicz, R.E. (1989). The seasonal dynamics of the Chesapeake Bay ecosystem. *Ecology Monograph*. **59**, 329–364

Barbour, M.T., Gerritsen, J., Snyder, B.D., Stripling, J.B. (1998). *USEPA rapid bioassessment protocols for use in streams and wadeable rivers. Periphyton, benthic macro invertebrates and fish.* 2nd Ed. U.S. Environmental Protection Agency; Office of Water, EPA/841-B-98-010. Washington, D.C.

Barbour, M.T., Gerritsen, J., Snyder, B.D., Stribling J.B. (1999). *USEPA rapid bioassessment protocols for use in streams and wadeable rivers—Periphyton, benthic macro invertebrates, and fish.* 2nd Ed. U.S. Environmental Protection Agency, Office of Water, EPA 841–B—99–002. Washington, DC.

Baum, M.K., Shor-Posner, G., Lai, S. (1997). High risk of HIV related mortality is associated with selenium deficiency. *Journal of Acquired Immune Deficiency Syndromes.* **15**, 370–374.

Beck, M.A., Shi, Q., Morris, V.C., Levander, O.A. (1995). Rapid genomic evolution of a non-virulent Coxsackievirus B3 in selenium-deficient mice results in selection of identical virulent isolates. *Nature Medicine.* **1**, 433–436

Biney, C., Amazu, A.T., Calamari, D., Kaba, N., Mbome, I.L., Naeve, H., Ochumba, P.B.O., Osibanjo, O., Radegonde, V., Saad, M.A.H. (1994). Review of heavy metals in the African aquatic environment, *Ecotoxicology and Environmental Safety.* **31**, 134-159.

Binkley, D., Burnham, H., Allen, H.E. (1999). Water quality impacts of forest fertilization with nitrogen and phosphorus. *Forest Ecology and Management.* **121**, 191-213

BirdLife International (2008). BirdLife's online world bird database. Cambridge, UK: BirdLife International. http://www.birdlife.org. (Accessed on 6 January 2011)

BIS (2010). Bureau of Indian Standards. Indian Standard for Drinking Water as per BIS specification. http://www.indian portal.org. (Accessed on 10 October 2013)

Brooks, K.N., Folliott, P.F., Gregersen, H.M., DeBano, L.F. (1997). *Hydrology and the management of watersheds.* 2nd Ed. Iowa State University Press. Iowa, USA.

Bryan, G.W., Langston, W.J. (1992). Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. *Environmental Pollution.* **76**, 89-131

Burnell, J.N. (1988). The biochemistry of manganese in plants. In: *Manganese in Soils and Plants.* (Graham R.D., Hannam, R.J., Uren, N.C., eds). Dordrecht, Kluwer Publishers, pp. 125–137.

Canadian Council of Ministers of the Environment. (2002). Canadian sediment quality guidelines for the protection of aquatic life: Summary tables. Updated. In: *Canadian environmental quality guidelines,* 1999. Canadian Council of Ministers of the Environment, Winnipeg. pp.: 1–10.

Carley, M., Spapens, P. (1998). *Sharing the World: Sustainable Living and Global Equity in the 21st Century*, Earthscan, London. 15-19

Carpenter, S.R., Caraco, N.F., Correll, D.L. (1998). Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecological Applications 8, pp. 559-568. In *Wastewater Engineering Treatment, Disposal and Reuse*. (Clark, B.J and John M.M., Ed). 3rd edition McGraw- Hill International Editions Singapore. 87-15

Chapman, D., Kimstach, V. (1996). Water quality assessments – A guide to use of biota, sediments and water environmental monitoring. 2nd Ed. Selection of water quality variables. 1992/1996 UNESCO/ WHO /UNEP

Chapman, L.J., Chapman. C.A. (2003). Fishes of the African Rain Forests: Emerging and Potential Threats to a Little-Known Fauna. In : *Conservation, Ecology, and Management of African Fresh Waters.* (Crisman, T.L., Chapman L.J. and Chapman C.A., eds.) The University Press of Florida, Gainesville, Florida. 176-209.

Clark, B.J, John M.M. (1991). *Wastewater Engineering Treatment, Disposal and Reuse*. 3rd edition McGraw- Hill International Editions Singapore. 87-150.

Clark, L.C., Combs, G.F., Turnbull, B.W., Slate, E.H., Chalker, D.K., Chow, J., Davis, L.S., Glover, R.A., Graham, G.F., Gross, E.G., Krongrad, A., Lesher, J.L., Park, H.K., Sanders, B.B., Smith, C.L., Taylor, J.R.(1996). Effects of selenium supplementation for cancer prevention in patients with carcinoma of the skin. *Journal of the American Medical Association.* **276**, 1957–1963.

Dalzell, D.J.B., Macfarlane, N.A.A. (1999). The toxicity of iron to brown trout and effects on the gills: a comparison of two grades of iron sulfate. *Journal of Fish Biology.* **55**, 301-315.

Dameron, C., Howe, P.D. (1998). Environmental health criteria for copper. International Programme on Chemical Safety. A publication of World Health Organization, Geneva.

Dwasi, J.A. (2002). Trans-boundary environmental issues in East Africa: An assessment of the environmental and socio-economic impacts of Kenya's forestry policy on Tanzania. Manuscript.

Eisler, R. (1993). Zinc hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Fish and Wildlife Service Biological Report. U.S Dept. of interior, fish and wildlife service. Washington, DC.

El Bouraie, M.M., El Barbary, A.A, Yehia, M.M., Motawea, E.A. (2010). Heavy metal concentrations in surface river water and bed sediments at Nile Delta in Egypt. *Suoseura — Finnish Peatland society.* **61**(1): 1–12

FAO (2003). Sustainable use and management of fresh water response: *Role of forests. States of the worlds forests, population and Water Resources.* Food and Agriculture Organization Food of United Nations. Rome, 2002. 74-85

Fargašová, A., Bumbalova, A., Havranek, E. (1999). Ecotoxicological effects and uptake of metals (Cu^+, Cu^{2+}, Mn^{2+}, Mo^{6+}, Ni^{2+}, V^{5+}) in freshwater alga *Scenedesmus quadricauda*. *Chemosphere*. **38**(5):1165–1173.

Fernandez, L.G., Olalla, H.Y. (2000). Toxicity and bioaccumulation of lead and cadmium in marine protozoan communities. *Ecotoxicology and Environmental Safety.* **47**, 266 -276.

FOC (Friends of conservation) (2000). Fact Sheet No. 2. The impacts of human activities on the Serengeti-Mara Ecosystem. Lillesand, T.M. and Kiefer, R.W 1987. Remote sensing and image interpretation. John Wiley & Sons. New York

Ford, R.G., Scheinost, A.C., Sparks, D.L. (2001). Frontiers in metal adsorption/precipitation mechanisms on soil mineral surfaces. *Advanced Agronomy.* **74**, 41-62.

Forstner, U., Wittmann, G.T.W. (1983). *Metal Pollution in the Aquatic Environment.* Springer-Verlag, Berlin. 147-150

Fred H/WWF-EARPO (2010). Biodiversity Strategy and Action Plan for Sustainable Management of the Nairobi and Kisumu, Kenya.

Funges-Smith, J.S. (1996). Water and sediment quality in different intensive shrimp culture systems in Southern Thailand. Institute of Aquaculture, Stirling University, Stirling, Scotland, FK9 4LA

Gereta, E.,Wolanski, E.M., Serneels, S. (2002). Use of an ecohydrology model to predict the impact on the Serengeti ecosystem of deforestation, irrigation and the proposed Amala Weir Water Diversion Project in Kenya. *Hydroecology*. **2**(14): 135-142

GOK (2009). Government of Kenya: Rehabilitation of the Mau Forest Ecosystem. Mau Forest complex concept paper. Government printer. Nairobi, Kenya

Goyer, R.A. (1996). Toxic effects of metals. In: *Casarett and Doull's Toxicology: Basic Science of Poisons*, (Klaassen C.D. ed). McGraw-Hill, New York, 811-867.

Goyer, R.A., Clarkson, T.W. (2001). Toxic effects of metals. In: *Casarett and Doullis Toxicology: The Basic Science of Poisons*, Sixth Edition (Klaassen, C.D. ed.) Mc-Graw-Hill, New York, 811-867.

Habes, G., Nigem, Y. (2006). Assessing Mn, Fe, Cu, Zn, and Cd pollution in bottom sediments of Wadi Al-Arab Dam, Jordan. *Chemosphere*. **300**: 300

Haggard B. E., Stanley E. H., Hyler R., (1999). Sediment phosphorus relationship in three north central Oklahoma streams. *Trans. ASAE42*. 1709-1714.

Hamilton, L.S., King, P.N. (1983). *Tropical forested watersheds. Hydrologic and soils response to major uses or conversions*. A Westview Press, Boulder.

Hammond, P.B., Beliles, R.P. (1980). Metals. In: *Casarett and Doull's toxicology, the basic science of poisons*, (Doull, J., Klassen, C.D., Amdur, M.O., Eds). New York. Macmillan, Chapter 17, pp. 409–467.

Heal, K.V. (2001). Manganese and land-use in upland catchments in Scotland. *Science of the Total Environment*. **265**(1 –3):169–179.

Health Canada (2012). Guidelines for Canadian Drinking Water Quality—Summary Table. Water, Air and Climate Change Bureau, Healthy Environments and Consumer Safety Branch, Health Canada, Ottawa, Ontario.

Horne, M.T., Dunson, W.A. (1995). Effects of low pH, metals, and water hardness on larval amphibians. *Archives of Environmental Contamination and Toxicology*. **29**, 500-505.

HSDB, (1998). *Hazardous substances data bank*. Bethesda, MD, National Institutes of Health, National Library of Medicine.

HSDB, (2001) *Manganese compounds*. Hazardous Substances Data Bank. Bethesda, MD, National Library of Medicine

IEPA (2001). *Parameters and water quality interpretation and standards*. EPA, Ireland.

Ikuo, A., Shigero I., Hidehiro G. (1965). A study of Atomic Absorption Spectrometry: Determination of Magnesium and Calcium in Slag. *Science Reports of the Research Institute, Tohoku University. Ser. A., Physics, Chemistry and Metallurgy*. **(17/18)** 76b-85b.

Ishimaru T., Takeguchi T., Fukuyo, Y., Kodama, M. (1989). The selenium requirement of *Gymnodinium nagasakiense*. In: *Red Tides: Biology, Environmental Science and Toxicology*. (Okaichi T., Anderson, D.M., Nemoto, T.,eds) Elsevier Science. New York, p 357-360

IUCN (2000). Forest cover and forest reserve in Kenya. Policy and Practice. Working paper No 5.

Joachim, W.H., Felistas, P.P. (2000). *Handbook on ingredients for aquaculture feeds*. Pp 478

Joly, C. (1993). Plant nutrient management and the environment, In: *Prevention of Water Pollution by Agriculture and Related Activities*. Proceedings of the FAO Expert Consultation, Santiago, Chile, 20-23 Oct. 1992. Water Report 1. FAO, Rome. pp. 223-245.

KBS (2009). Kenya Bureau of Statistics. Kenyan population census 2009.

KEBS (1996). *Kenya Bureau of Standards*, KS 05-459: Part 1 pg. 6. ICS 13.060.20 Nairobi, KEBS.

Kenneth, K.T., Neeltje, C.K. (2002). Agricultural drainage water management in arid and semi arid areas. FAO Irrigation and Drainage Paper 61. Food and Agrculture Organization of United Nations. Rome.

Kidd, K.A., Lochart W.L., Wilkinson P. and Muir D.C.G. (1998). Pesticides, metals and other persistent contaminants in water, sediments and biota from Lake Malawi. In: *Water quality Report*. Boosma, H.A., Heckey, R.E. (Eds.),. SADAC/GEF Lake Malawi/Nyasa Biodiversity conservation Project **43,** unpublished.

Kiffney, P., Knight, A. (1990). The toxicity and bioaccumulation of selenate, selenite, and seleno-L-methionine in the cyanobacterium Anabaena flos-aquae. *Archeological Environmental Contamination Toxicology*. **19**, 488-494

Kishe, M., Machiwa, J. (2001). Distribution of heavy metals in sediments of Mwanza Gulf of Lake Victoria Tanzania. Paper presented at LVEMP conference, Kisumu, Kenya.

Koroleff, F. (1976). Determination of NH_4–N. In: *Methods of seawater analysis*. (K. Grasshoff, Ed.). Weinheim: Verlag Chemie. 127–133.

Kreuzinger, N. (2009). Water Quality Monitoring & Bio-indicators. Vienna, Lecture Notes. IPGL course.

Kunkle, S.H. (1974). Water- Its quality often depends on forester. *Unasylva.* **25**(105); 10-16

Lawrence, R.C., Brian, W.S. (2002). Heavy metals in fertilizers: Considering for setting regulations in Oregon, Oregon Department of Agriculture Salem Oregon. Department of Environmental and Molecular Toxicology Oregon State University, Corvallis Oregon

Lehtinen, K., Klingstedt, G. (1983). X-ray microanalysis in the scanning electron microscope on fish gills affected by acidic, heavy metal containing industrial effluents. *Aquatic Toxicology.* **3**, 93-102.

Lemly, A.D. (1999). Selenium Impacts on Fish: An insidious time bomb. *Human and Ecological Risk Assessment.* **5**, (6) 1139-1151.

Lin, H.C., Dunson, W.A. (1993). The effect of salinity on the acute toxicity of cadmium to the tropical, estuarine, hermaphroditic fish, *Rivulus marmoratus* – a comparison of Cd, Cu and Zn tolerance with *Fundulus heteroclitus*. *Archeological Environmental Contamination Toxicology.* **25**, 41 – 47.

Loska, K., Wiechula, D. (2003). Application of principal component analysis for the estimation of source heavy metal contamination in surface sediments from Rybnik Reservoir. *Chemosphere.* **51**, 723–733.

LVBC & WWF-EARPO (2010). Biodiversity Strategy and Action Plan for Sustainable Management of the Nairobi and Kisumu, Kenya.

Machiwa, P. (2002). Water quality management and sustainability: In: *The experience of the Lake Victoria Environmental Management Project (LVEMP). 3rd*

WaterNet/Warfsa Symposium 'Water Demand Management for Sustainable Development', Dar es Salaam. 30-31

Marschner, H. (1995). *Mineral nutrition in higher plants*. Academic Press: London.

Mati, B.M., Mutie, S., Home, P., Mtalo, F., Gadain, H. (2005). Land use changes in the Africa. 8th International River Symposium. Brisbane, Australia. September 6th-9th 2005.

McCartney, B.A. (2010). *Evaluation of water quality and aquatic ecosystem and health in the , East Africa*. MSc Thesis. Florida International University.

Morris, J.T. (2000). Effects of sea level anomalies on estuarine processes. In: *Estuarine Science: A synthetic Approach to Research and Practice*, (Hobbie J.E. ed.), Island Press, Washington, DC, pp. 107–127.

Mortvedt, J.J. (1995). Heavy metal contaminants in inorganic and organic fertilizers: *Nutrient cycling in agroecosystems*. **10**, 55-61

Mousa, M.A., Khattab, Y.A. (2003). The counteracting effect of vitamin – C (L – ascorbic acid) on the physiological perturbations induced by ochratoxin intoxication in the African catfish (*Clarias gariepinus*). *Journal of Egypt Academic Environmental Development*. **4(1)**: 117 – 128.

Murdoch, T., Cheo, M., O'Laughlin, K. (2001). Streamkeeper's field guide: Watershed inventory and stream monitoring methods. Adopt-A-Stream Foundation, Everett, WA.

Mutie, S.M., Mati, B., Home, P., Gadain, H. (2006a). Land cover change effects on flow regime of Mara River. Second International ISCRAM Conference, Brussels – Belgium.

Mutie, S.M., Mati, B., Home, P., Gadain, H., Gathenya, J. (2006b). Evaluating land use change effects on river flow using Usgs Geospatial Stream Flow Model in , Kenya. Second Workshop of the EARSeL SIG on Land Use and Land Cover, Bonn

Mzimela, H.M., Wepener, V., Cyrus, D.P. (2003). Seasonal variation of selected metals in sediments, water and tissues of groovy mullet, *Liza dumerelii* (Mugilidae) from the Mhlathuze Estuary, South Africa. *Marine Pollution Bulletin*. **46,** 659-676.

Nassef, M., Hannigan, R., El Sayed, K.A, Tahawy, M.S. (2006). Determination of some heavy metals in the environment of Sadat industrial city. Proceeding of the 2nd Environmental Physics Conference, Cairo University, Egypt, pp. 145-152.

NEMA (2006). Environmental Management and Co-Ordination (Water Quality) Regulations, 2006. NEMA. Ministry of Environment and Natural Resources. Kenya

Nolan, B.T. (2005). Probability of nitrate contamination of recently recharged ground water in the Coterminous, United States. *Environmental Science & Technology.* **36**, 2138-2145

Nriagu, J.O. (1989). A global assessment of the natural sources of atmosphere trace metals. *Nature.* **338**, 47–49.

NTZDC (1986). Nyayo Tea Zones Development Corporation. http://www.teazones.co.ke. (Accessed on 16 June 2013)

Nyoge, E., Machiwa. J.F. (2004). The influence of land-use patterns in the Ruvu river watershed on water quality in the river system. *Physics and Chemistry of the Earth.* **29**:1161-1166.

Odiete, W.O. (1999). *Environmental Physiology of Animals and Pollution.* Diversified Resources Ltd, Lagos. 261

Ogoyi D.O., Mwita, C.J., Nguu E.K., Shiundu P.M. (2011). Determination of Heavy Metal Content in Water, Sediment and Microalgae from Lake Victoria, East Africa. *The Open Environmental Engineering Journal.* **4**, 156-161.

Ongeri, D.M.K. (2008). *Physicochemical Parameters, Heavy Metal Residue levels and their Speciation Studies in Lake Victoria Basin.* PhD thesis Maseno University.

Ongley, E.D. (1996). Control of pollution from Agriculture – FAO Irrigation and Drainage Paper 55. GEMS/Water Collaborating Centre. Canada Centre for Inland Waters, Burlington, Canada. Food and Agriculture Organization of United Nations.

Onyari, J.M., Wandiga, S.O. (1989). "Distribution of Cr, Pb, Cd, Zn, Fe and Mn in lake Victoria sediment, East Africa", *Bulletin of Environmental Contamination and Toxicology.* **42**, 807-813.

Othieno, C.O. (1975). Surface run-off and soil erosion on fields of young tea. *Tropical Agriculture.* **52**, 299–308.

Peuranen, S., Vuorinen, M.P.J., Hollender, A. (1994). The effects of iron, humic acids and low pH on the gills and physiology of Brown Trout (*Salmo trutta*). *Annales Zoologic Fennici.* **31**, 389-396.

Pollit, E., Kotchabhakodi, N.J., Missel, L., Valyasevi, A. (1989). Iron deficiency and educational achievement in Thailand. *Journal of American Clinical Nutrition.* **50**, 687-697.

Prasad, A.S., Oberleas, D. (1976). *Trace elements in human health and disease*, vol I &II. Academic press, India, 201-205.

Rivas, Z., Ledo de Medina, H., Gutiérrez, J. and Gutiérrez, E. (1998). Nitrogen and phosphorus levels in sediments from tropical Catatumbo River (Venezuela). *Water, Air, and Soil pollution.* **117**, 27–37

Romkens, M.J.M., Nelson, D.W., Mannering, J.V. (1973). Nitrogen and phosphorus composition of surface runoff as affected by tillage method. *Journal of Environmental Quality.* **2** (2), 292–295.

Skipton, S., Hay, D. (1998) Drinking water: Nitrate and methemoglobinemia ("Blue Baby" Syndrome); Publication G98-1369; University of Nebraska Cooperative Extension: Lincoln, NE, 1998, http://www.ianr.unl.edu/pubs/water/g1369.htm (accessed Feb 2011)

Smil, V. (2001). Enriching the earth: Fritz Haber, Carl Bosch and *the Transformation of World Food Production*; MIT Press: Cambridge, MA, USA.

Snyder, W.S., Cook, M.J., Nasset, E.S., Karhausen, L.R., Howells, G.P., Tipton, I.H. (1975). International Commission on Radiological Protection. Report of the task group on reference man. New York, *ICRP publication 23*

Stokinger, H.E. (1981). The metals. In: *Pathy's industrial hygiene and toxicology*:(3rd edition vol.2A Clayton G.D, Clayton F.E. Eds) New York. A *Wiley-Interscience publication,* John Wiley and Sons, pp. 1493-2060

Stronkhorst, J., Brils, J., Batty, J., Coquery, M., Gardner, M., Mannio, J., O'Donnell, C., Steenwijk, J., Frintrop, P. (2004). Discussion document on sediment monitoring guidance for the EU water framework directive. Version 2. EU Water Framework Directive expert group on Analysis and Monitoring of Priority Substances.

Tack, F.M.G. and Verloo M.G., (1999). Single extraction versus sequential extractionfor estimation of heavy metal fractions in reduced and oxidised dredged sediments. *Chemical Speciation Bioavailability.* **11,** 43-50.

Tarras-Wahlbergl, H., Everard, M. & Harper, M.D. (2002). Geochemical and physical characteristics of river and lake sediments at Naivasha, Kenya. (D.M. Harper, R. Boar, M. Everard & P. Hickley, eds) Lake Naivasha, Kenya. *Hydrobiologia.* **488**, 27–41.

Underwood, E.J. (1977). *Trace elements in human and animal nutrition.* New York, NY, Academic Press.

UNEP (2002). Africa environment outlook: Past, present and future perspectives. http://www.unep.org/africa.html (accessed March 7, 2011)

UN-HABITAT (2003). Water and Sanitation in the World's Cities: Local Action for Global Goals, United Nations Human settlements Programme, Nairobi, Kenya

USEPA (1980). U.S Environmental Protection Agency. Ambient water quality criteria for copper and lead. Springfield, VA: *National Technical Information Service.* **81**,117-681

USEPA (1984). Health assessment document for manganese. Final draft. Cincinnati, OH, US Environmental Protection Agency, Office of Research and Development (Report No.EPA/600/8-83/013F).

USEPA (1994a). Water quality effects and non-point source control practices for forestry: an annotated bibliography, EPA 841-R-97-008, Washington DC

USEPA (1994b). Review Draft of the Health, Effects Notebook for hazardous Air pollutants. Air Risk Information support Centre, Research Triangle Park, North Carolina. Contract No. 68-D2-0065.

USEPA (1997). Volunteer Stream Monitoring: A Methods Manual, Office of Water. EPA 841-B-97-003.Washington, DC

USEPA (2007). Aquatic life ambient freshwater quality criteria–copper 2007 Revision. Office of water, Office of Science and Technology, Health and Ecological Criteria Division. EPA-822-F-07-001.Washington, DC.

USEPA (2010). Guidance on Evaluating Sediment Contaminant Results. Division of Surface Water. Standards and Technical Support Section. Washington, DC

UshaD., Vikram, M.R. (2012). Assessment of trace metal pollution of water and sediment of River Gadilam (Cuddalore, south east coast of India) receiving sugar industry effluents. *Continental Journal of Environmental Sciences.* **6** (3): 8 – 24

Veena, B., Radhakrishnan, C.K., Chacko, J. (1997). Heavy metal induced biochemical effects in an estuarine teleost. *Indian Journal of Marine Science.* **26**,74–78.

Vosylienė, M.Z., Kazlauskienė, N. (2004). Evaluation of the Svede pond water effect on fish (after accidental discharge of the Kairiai dump filtrate into the environment). Protection and management of water bodies. Proceedings of International Science Conference Kaunas, 219–223.

Welcome, R.L. (1992). Pasco fluvial. In: *Technical document of fishing* (FAO editors). No. 262. Roma, 303 pp. http://www.fao.org/docrep/003/T0537S/T0537S00.HTM. (accessed 08 February 2011).

WHO (1992). Cadmium, environmental health criteria, No. 134, World Health Organization, Geneva.

WHO (1998). *Guidelines for Drinking Water Quality.* International programme on chemical safety (UNEP, ILO, WHO), Geneva, Switzerland, 204-215.

Wikibooks (2013). Basic Geography http://www.wikibooks.org. (Accessed on 10 October 2013.

Wolfhard S., Reinhard B. (1998). The heterogeneity of runoff and its significance for water quality problems, *Hydrological Sciences Journal des Sciences Hydrologiques.* **43**, 103-113.

Woolhouse, H.W. (1983). Toxicity and tolerance in the responses of plants to metals. In: (Lange OC, Nobel PS, Osmond CB, Ziegler H, eds). *Encyclopedia of Plant Physiology II.* **12**. 245–300.

WQBAR (2007). *Mara River Basin, Kenya-Tanzania. Global Water for Sustainability (GLOWS) Program*, Florida International University, Miami, Fl, USA.

Yu, M.W., Horng, I.S., Chiang, Y.C., Liaw, Y.F., Chen, C.J. (1999). Plasma selenium levels and the risk of hepatocellular carcinoma among men with chronic hepatitis virus infection. *American Journal of Epidemiology.* **150**, 367–374.

Yu, S.Y., Zhu, Y.J., Li, W.G. (1997). Protective role of selenium against Hepatitis B virus and primary liver cancer in Qidong. *Biological Trace Element Research.* **56**, 117–124.