`EFFECTS OF ANTHROPOGENIC ACTIVITIES ON SELECTED WATER QUALITY PARAMETERS IN SPRING WATER AND SEDIMENTS ALONG AMALA AND NYANGORES TRIBUTARIES IN THE MARA RIVER BASIN, KENYA

BY

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ABSTRACT

Replacing natural forests with commercial crops and/or other small scale farming activities including human settlement have several environmental impacts. The land use practices have the potential of contaminating aquatic ecosystems including spring water that are sources of major rivers like the Amala and Nyang'ores tributaries of the Mara River in Mau Complex, Kenya. Land use activities have been changing in the Mau Complex but no study has determined their impact on the quality of the spring waters. Most residents within Mara River Basin use the spring waters for domestic purposes despite the lack of awareness on their water quality status. The anthropogenic activities could negatively be affecting the physicochemical and other quality parameters of spring water within the Mau River Basin complex and cause water quality problems to users including aquatic life downstream. Therefore this study determined seasonal and site variations in pH, temperature, total nitrogen, ammonium-nitrogen, nitrites, total phosphates, soluble reactive phosphates, zinc, copper, selenium, manganese, chromium, cadmium and lead ions in waters and sediments within springs of Mau Complex that flow into and form the sources of Amala and Nyangores, the main tributaries of Mara River. Water and sediment samples were collected in triplicate from eight (8) springs feeding each tributary during the long dry and long wet seasons. The design of the experiment was a completely randomized design (CRD) in a two factorial arrangement with site (springs) as the main treatments and seasons as the sub treatment. A pH meter, a thermometer, ultraviolet spectrophotometer, and atomic absorption spectrophotometer were used in determining the selected parameters. Analysis of variance (ANOVA) and students t-test at $p \leq 0.05$ were used for data analysis. The results showed a water pH range of 6.4 to 6.6 and a temperature range of 13.00 to 15. 79°C (in Nyangores) and 15.21 – 17.70°C (in Amala) in both wet and dry seasons. The soluble reactive phosphate (SRP) varied significantly in springs, ranging from 42.01 to 22.00 ppb during the dry season to 64.11 to 19.55 ppb during the wet season. The total phosphate (TP) levels of the water samples varied significantly ($p \leq 0.05$) (ranging from 52.01 to 362.00 ppb). The concentration levels for all the nutrients fell within the World Health Organization guideline limits for domestic water. Heavy metals (Mn, Cu, Fe Zn, Pb, Cr, Cd, Zn) and Se concentrations in spring water samples differed greatly in springs along Amala and Nyangores. The springs had varying amounts of nutrients and heavy metals in the water. This could cause adverse water quality problems to streams and rivers downstream in the long run. Land use patterns in the complex did not significantly affect the quality of springs within Mara River Basin. These results demonstrate that anthropogenic activities are not yet causing adverse water quality problems and managing the anthropogenic activities is recommended. However, periodic monitoring of the springs to ascertain the quality of the water is also necessary.

CHAPTER ONE

1.1 INTRODUCTION

1.2. Background

A spring is a place on the earth's surface where groundwater emerges to the earth's surface naturally. It may also be defined as the surface exit point for water that has been traveling underground. The water source of most springs is rainfall that seeps into the ground. Spring water moves downhill through soil or cracks in rock until it is forced out of the ground by natural pressure. While springs may seem like an ideal water supply, they need to be selected with care, developed properly, and tested periodically for contamination (Gregory, 1996). The amount, or yield, of available water from springs may vary with the time of year and rainfall (Brian *et al.*, 1999). Groundwater obtained from springs is similar to water pumped from shallow wells. Like shallow wells, springs may be contaminated by surface water or other sources on or below the ground surface (Gregory, 1996; Brian *et al.*, 1999). They are susceptible to contamination by surface water, especially during rain storms.

Springs are susceptible to contamination because the water feeding them typically flows through the ground for only a short distance, limiting the amount of natural filtering that can occur. Consequently springs may not be a good choice for a water supply if the area uphill where the water collects is used for industry, agriculture, or other potential sources of pollution like is the case in the Mau Complex (McCartney, 2010 and UNEP, 2006). Contamination sources include livestock, wildlife, crop fields, forestry activities, septic systems, and fuel tanks located upslope from the spring outlet.

Changes observed in water from springs in terms of color, taste, odor, or flow rate indicate possible contamination by surface water (Gregory, 1996). These anthropogenic activities in water catchment areas obliterate the forest cover necessary in such areas as they aid in preventing soil erosion and sediment deposition into the water bodies (Hamilton and King, 1983; Wiersum 1984, Kunkle, 1974, Brooks *et al.*, 1997 and FAO, 2003). The composition of surface and underground water is dependent on natural factors such as geological, metrological, hydrological and biological in the drainage basin and varies with seasonal differences in runoff volumes, weather conditions and water levels (Kunkle, 1974, Brooks *et al.*, 1997 and FAO, 2003). The examination of the changes in water quality with time demonstrated that the anthropogenic activities taking place within the Mau Complex catchment area are affecting the water quality. However, it is not known if these anthropogenic activities which occur intensely during the wet season have adversely affected the water quality in the springs forming sources of Amala and Nyangores tributaries. Furthermore, to my knowledge, no study has been conducted on the seasonal dynamics of water quality in the spring water and sediments.

Most spring contamination results from direct flow of surface water into the shallow groundwater feeding the spring (Brian *et al.*, 1999). Spring water should be tested before and after heavy rains each year for bacteria, pH, turbidity, nutrients and conductivity levels to determine if surface-water contamination is a problem. If water levels change frequently when it rains, the spring is very susceptible to contamination (Gregory, 1996). Springs serve as habitats for most aquatic animals and plants. In most cases the organisms will reside in sediments of these springs hence contamination of springs will magnify itself in sediments due to sedimentation, precipitation, percolation and bioaccumulation processes, which will seriously affect these habitats (Odiete, 1999). The water levels of springs that feed Amala River and Nyangores River tributaries of Mara River have been reported to reduce seasonally, consequently they are suspected to have reduced water quality. This could be due to agricultural malpractices with consequent land degradation or deforestation of the Mau Forest up hill (UNEP, 2006). Such activities have been reported to affect spring water quality in other areas like Suwannee River Basin in Florida (Brian *et al.*, 1999). The effects of encroachment of the Mau Complex and related anthropogenic activities which occur seasonally on the quality of spring water of the Amala and Nyangores tributaries of the Mara River have not been quantified.

The Mau Complex, the largest forest of Kenya, covers some 400,000 ha (UNEP, 2006). It lies between 2,000 m and 2,600 m above the sea level, on the western slope of the Mau Escarpment, and is situated approximately 250 km from Nairobi and borders Kericho to the West, Nakuru to the North and Narok to the South. It comprises South West Mau, East Mau, Transmara, Mau Narok, Maasai Mau, Western Mau and Southern Mau. These seven forest blocks merge to form the larger Mau forest Complex. Out of all these blocks, only Maasai Mau is not gazetted (UNEP, 2006) as illustrated in the landsat images below. As a montane forest, the Mau Complex is one of the five main "water towers" of Kenya and feeds Lake Victoria, a major lake which is a shared resource among three countries: Kenya, Tanzania and Uganda through various rivers amongst them the Mara River (Kiragu, 2009). Studies have been carried out to ascertain the quality of both her tributaries, Amala and Nyangores, with respect to their nutrient and heavy metal load contribution to the main River, but none has been done on the springs that feed the two tributaries. Though most of Kenya's forests have been decimated by degradation among other factors, the Mau Complex Forests cover, and in particular that of the Maasai Mau Forest that forms the sources of Amala and Nyang'ores tributaries of Mara River, has been the most affected, and has receded drastically over time (UNEP, 2009). The effects of destruction by degradation on the quality of spring water of the Amala and Nyangores tributaries of the Mara River have not been quantified.

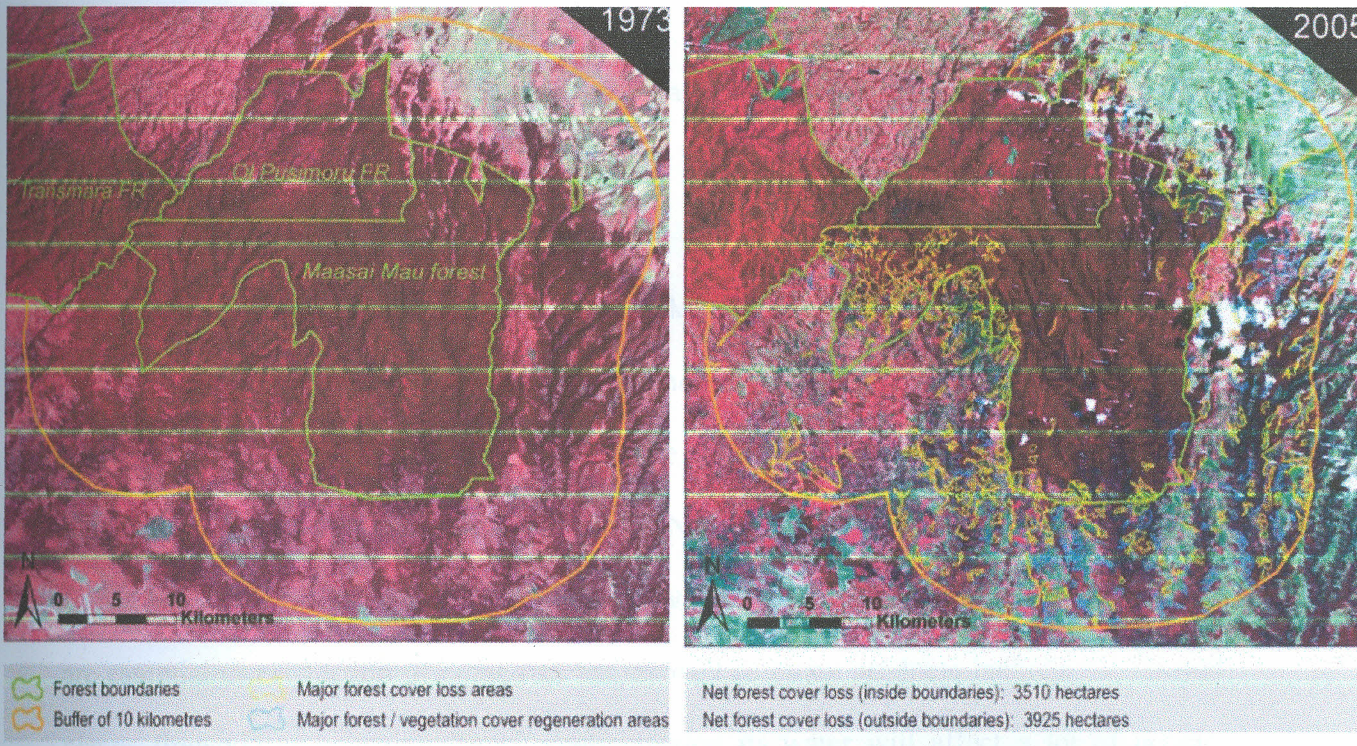


Figure 1.1 ***Forest Change Cover Between 1973 and 2005****(Source: Maasai Mau Forest Status Report 2005)*

The southern forests of the Mau Complex are rich in biological diversity in terms of fauna and flora. The forests host ungulates such as the bongo and the yellow-backed duiker; carnivores, including the golden cat and the leopard, and the forest elephant (Gereta *et al*., 2002). The forest of the Maasai Mau, in particular, comprises large stands of cedar and Podocarpus forests with scattered natural glades. All these animals and plants use spring water within this catchment hence its contamination affects them and to larger extent tourism, that is a major income generator for Kenya (UNEP, 2006). There are several reasons for interest in the spring water quality in the area. Recent extensive economic transformation of the area may result in a substantial change in farming practices including increased fertilizer use that may cause spring water degradation. Because the landscape in the region is attractive, tourism and associated development has increased, consequently wastes disposal systems are not regulated and may find their way into springs. However the influence of these activities on the water quality of the springs that form sources of Amala and Nyangores tributaries are not known.

A majority of Kenya's population lives in the Lake Victoria Basin. This region is crossed by major rivers flowing from the Mau Complex among them the Mara River. The water from Mau Forest serves more than 4 million people inhabiting more than 578 administrative locations in Kenya and several locations in Northern Tanzania. In addition, the Mau Complex provides continuous river flow and favourable micro-climatic conditions - which are essential to production of crops like tea, as well as many products including medicinal plants, firewood and grazing; hence contaminating its water will affect a lot of people, directly or indirectly (UNEP, 2006). Spring water contamination in farming areas originates from many different sources. Fissured aquifers are particularly vulnerable to contamination caused by fertilizer application, animal-feeding operations, leaching of solid wastes at sanitary landfills, and leakage from household waste-disposal systems. The impacts of these activities on the water quality of the springs that form sources of Amala and Nyangores tributaries are not known.

The forest is the home of the Ogiek community, who for a long time predominantly inhabit Mau forest in Rift Valley province and, until the 1950's, had been subsisting on sustainable hunting of wild game and gathering of wild fruits(Gereta *et al.*, 2002). As a result of modern laws, policies and the rapid spread of western religion and education, the Ogieks have lost their culture, traditions and territories. They now find themselves practising small scale agriculture and livestock keeping within the forest, hence contributing to possible contamination of surface water runoffs that end up in springs during rains (UNEP, 2006). The Mau Forest is also vital for the pastoral Maasai, who graze their animals there during the dry seasons (UNEP, 2006). It is however not known the extent to which the cultural practices of the Ogieks and the Maasai affect the spring water quality in the Mau forest Complex.

More than 46,000 hectares have been excised to convert the forest to other alternative land uses like settlement and agriculture during the last decade. The impact of the ensuing massive deforestation caused by factors including large-scale encroachment, charcoal production and logging of indigenous trees, is already impacting negatively on water resources, especially water quality (UNEP, 2006). The Maasai Mau Forest, with 46,278 hectares, is a major natural asset in terms of water catchment, micro-climate regulation and biological diversity. Between 1986 and 2003, it suffered a loss of 20,330 hectares of forest cover of the gazette and non gazatted areas of the forest (UNEP, 2006). In a Status Report of 2005, the aerial survey showed that approximately 11,095 hectares in the western part of the Maasai Mau Forest (Narok South Constituency) was destroyed or heavily impacted by settlements (UNEP, 2006). At the time of the survey, the forest was being actively cleared, with numerous plumes of smoke billowing out of the remaining forest canopy (UNEP, 2006) and the situation at present may be worse. Nevertheless the consequence of the apparent loss of forest cover in relation to spring water quality has not been quantified.

Forest excision for settlement is a complex problem. Often, forests are split off allegedly to resettle families that were forced to move from neighbouring forests (Aboud *et al.*, 2002). Most of the time, resettlement is carried out without local communities' participation with the result that they are distributed on small parcels while powerful people - well-connected grabbers, loggers and charcoal burners –take most of the land and convert it into farming fields unaware of the possible serious problems they are exposing to the environment including the aquatic organisms (UNEP, 2006). These activities have been going on in the Mau Complex for a long time but no study has been conducted to determine the impact of these activities on spring water quality. In developing countries, over one-third of human deaths are caused by the consumption of contaminated water (Palamuleni, 2002) and 60% of all infant mortality is linked to infectious and parasitic diseases, which are mostly water-related (Hinrichsen *et al.*, 1997). In addition the general sustainability of the spring's aquatic ecosystem life is at stake with contamination of these systems (Palamuleni 2002; Hinrichsen *et al.*, 1997). It is therefore necessary to obtain baseline data and establish the quality of the spring water within the Mau Complex with physicochemical parameters that are plausible causative agents of diseases in aquatic animals, plants and human beings at large upon accumulation. Contamination of aquatic ecosystems affects the health of people, aquatic plants and animals using or living within these aquatic systems. Anthropogenic source pollutants, irrespective of source, are transported over land and through the soil by rainwater. These pollutants ultimately find their way into groundwater, wetlands, springs, rivers and lakes and, finally, into oceans in the form of sediment and chemical loads carried by rivers. The ecological impact of these pollutants range from simple nuisance substances to severe impacts on fish, birds and mammals, and human health.

Sediments constitute a significant constituent of spring ecology, offering home to a large variety of benthic and epi-benthic organisms (Adeyemo *et al.*, 2008). Heavy metals contamination in sediments is known to affect water quality, with probable consequential long term repercussions on human health and ecosystem (Mango *et al.*, 2010). The spatial distribution of heavy metals in sediments is of significant importance in determining the pollution history of aquatic systems (Kiragu *et al.*, 2009) and provides basic information for identifying the possible sources of contamination (Almas *et al.*, 2009). Sediments evaluation in the catchment springs of Amala and Nyangores tributaries as a means of ascertaining probable causes of heavy metals loads in the springs has not been done.

1.3. Statement of the problem

Water for domestic and animal use in the Mara River Basin comes from below ground aquifers and is often used with little or no purification. Agricultural and other anthropogenic activities which intensify depending on the season are increasing in the Mau Forest Complex as a result of encroachment and settlement. These activities might be impacting negatively on the quality of spring water and associated sediments through inputs of contaminants such as nutrients and heavy metals, among others, leading to alteration of the water physicochemical composition in a way that may be environmentally adverse to the inhabitants within its watershed and further downstream users of the Mara River. However, there has been no evaluation in recent times to assess and provide a baseline status of the water quality of spring water in the Mau Forest Complex.

1.4. Objectives

1.4.1. Main objective

This research was aimed at determining whether the anthropogenic activities at the catchment of Amala and Nyangores, tributaries of Mara River have had an effect on the water quality of spring water and sediments within the springs of the catchment.

1.4.2. Specific objectives

1. Determine variations due to site and seasons of the levels of selected water quality parameters (temperature and pH), nutrients (phosphates, ammonium, nitrates and nitrites) and some heavy metals (Mn, Cu, Fe, Zn, Pb, Cr, Cd and Se) in selected springs of Mau Forest Complex that form the source of Amala and Nyangores tributaries of River Mara, Kenya.
2. Determine the changes due to site and seasons on levels of selected water quality parameters and some heavy metals in sediments of selected springs of Mau Forest Complex that form the source of Amala and Nyangores tributaries of River Mara, Kenya.
3. To compare the changes in physicochemical parameters in springs flowing into Amala and Nyangores tributaries of the Mara River, Kenya.

1.5. Null hypothesis (H_0)

1. Levels of selected water quality parameters and heavy metals are not different in water of selected springs of Mau Forest Complex that form the source of Amala and Nyangores tributaries of River Mara and do not vary with season.

2. Levels of selected water quality parameters and heavy metals are not different in sediments of selected springs of Mau Forest Complex that form the source of Amala and Nyangores tributaries of River Mara do not vary with season.
3. There are no changes of physicochemical parameters in springs flowing into Amala and Nyangores tributaries of the Mara River.

If the null hypothesis (H_0) is not true, then the alternative hypothesis (H_1) will be adopted

1.6. Justification of the research

The encroachment and consequent settlement, as well as enhanced untenable agricultural practices in the Mau Forest, may be negatively impacting the spring water quality. Human beings and animals use water from the status of it's springs and their quality is unknown. It is necessary to urgently assess the quality of the water to avoid further adverse effects if any on aquatic dependants. Little has been published concerning spring water in Kenya especially those that are sources of major rivers. This study is to establish the relationship between activities as a result of forest encroachment and the spring water quality variations with season in the Mau Forest Complex. It is necessary to understand how forest encroachment and related activities influence the levels of physicochemical parameters in sediments, which are sinks for spring water constituents. The results will provide baseline data which would help in developing sustainable policies to control possible water quality deterioration that can negatively affect life downstream. The generated data will also be used as a basis for further future studies.

1.7. Significance of the study

This study will enhance our understanding of the effects of encroachment of the Mau Forest Complex on spring water quality. Furthermore, it shall provide baseline data that could be used as a reference when introducing suitable mitigation measures towards the conservation and management of the Mara River Basin. This study will generate important information that stakeholders are alerted of the consequences of their activities and possible mitigation measures in which can be taken to avoid any future environmental disaster emanating from anthropogenic activities near springs that form sources of major rivers.

1.8. Scope and Limitation of the study

This research was conducted to assess the socio-economic and environmental impact of encroachment and the related anthropogenic activities to spring water of the Mara River Basin. However, this study is subject to the following limitations.

- Time series information from the settlers and the authority concerned was not collected to ascertain the type and nature of activity with regards to seasons.
- Geological, pesticide residues and soil analysis, which are very important to see the environmental effect of irrigation, was not done because of funds and time shortage.

CHAPTER TWO

2.1. LITREATURE REVIEW

2.2. Predominant Land Use Patterns around the Mau Forest

A number of forces continue to seriously affect our natural water resources. Many of these are the result of human activities (Mwichabe, 1986) and include ecosystem and landscape changes, sedimentation, pollution, over-abstraction and climate change (Mati *et al.*, 2005). The removal, destruction or impairment of natural forest is among the greatest causes of critical impacts on the sustainability of natural water resources (Kiragu, 2009).Water is an important source of trace elements in human health. Many elements and nutrients in trace amounts play vital roles in metabolic processes and are essential for the general well being of human beings (Merritts *et al.*, 1998). The deficiency or excess of any of these elements or nutrients may cause diseases and/or be deleterious to human health (O'Dell and Sunde, 1997). The trace elements can also pose both environmental and health problems (Almas *et al.*, 2009).

Water quality is important to humans as well as plants and organisms that live in and around water bodies (Merritts *et al.*, 1998). Chemical attributes of water are important indicators of water quality; they affect aesthetic qualities such as colour, smells, tastes and its toxicity. Springs play a significant role within a river profile, as they are the origin of some rivers; hence they may depict what the source of the river contains. Analysis of the changes in spring water quality revealed its relationship with the different activities taking place within a spring basin (Hawkins *et al.*, 1993). In Mau Forest, land use changes caused by clearance of forests to create room for agriculture, wetlands removal or reduction and a new roadwork for transportation have emerged as major stressors of springs and rivers (Baldyga *et al.*, 2007). Deforestation and cultivation cause an increase in water temperature, conductivity, total suspended solids, total dissolved solids and turbidity (Baldyga *et al.*, 2007). The Mau Forest, which hosts several springs that are the source of the Mara River, has for a long time been considered one of the more pristine rivers draining into Lake Victoria, which forms the upper part of the Nile Basin (Mati *et al.*, 2005).

In the recent past, the Mau Forest has undergone major changes in land cover. Large sections of the forests have been cleared and turned to agricultural and settlement areas (Kiragu, 2009). Interest in the Mara River water quality is due to the enormous importance of its water to the survival of a wide number of biodiversity within its watershed. The change in landuse in the Mau Forest has been enormous (Mati *et al.*, 2005). The land uses that may affect the spring water quality include large scale agriculture, forestry, livestock keeping, fisheries, tourism, and conservation areas activities (Mango *et al.*, 2010). It is not known if these activities have changed the environmental quality of the adjacent lands, making them susceptible to soil erosion from water runoffs, and the eventual pollution of the springs. For the management of the integrity of the springs there is an urgent need to evaluate the effects of these land use practices on its water quality.

The human settlement in the Mau Forest is increasing and has been accompanied by an increase in agricultural landuse at the expense of the basin forests and grasslands (LVBC and WWF ESARPO, 2010a). There is growing of Irish potatoes, maize, and beans with the main crop being maize (Mwichabe, 1986). Success of these activities depends on extensive use of chemical inputs including inorganic fertilizers, pesticides and herbicides. Runoff water from agricultural-ecosystems is known to cause pollution to the adjacent semi-natural and natural terrestrial or aquatic ecosystems (Tsiouris *et al.*, 2001). Within the Mau Forest, the fertilizer inputs and top soil from agricultural lands often end up as runoff - during rainfall - from the steep slopes into the springs. Depending on the physicochemical composition of the runoff, the quality of the spring water may be altered. It is not known if these human activities including agriculture have influence on the quality of spring water in Mau Forest.

2.3. Spring water and sediment physicochemical parameters

In addition to the dissolved load, springs from carbonate aquifers are significant sources of sediments. In aquifers based on marine deposits (such as in Florida) these particles may be derived from the direct surface connections with underground conduits, or from particles released through erosion or dissolution of the aquifer material itself. As a result, sediments in spring flows can vary in composition from small organic materials, to clay particles, to sands and carbonate minerals (McFarland and Hauck, 1999). The direct transport of surface derived materials also results in a strong dependence of sediment flux at the boil on the springshed characteristics and relationships with rainfall, runoff, recharge, and discharge (Aboud *et al.*, 2002). For example, some springs that are normally clear under low flow conditions may become turbid after storm events. The composition and distribution of sediment types influence spring water quality (Saunders, 2007). Not much is known about composition and distribution of sediment types in Mara River springs, including information regarding particle size, mineralogy or organic content.

In other stream environments, flow velocity is the most important determinant of sediment distribution patterns even where spring flow velocities range from *circa* 1 to 100 cms^{-1} (Gregory, 1996). In general, particle sizes of sediment decrease with passage downstream as channel widths widen, current velocity decreases, and progressively finer size classes are allowed to settle out. This pattern has been observed in the upper side of Chassahowitzka River USA where the areas near the boil are dominated by sands low in organic matter, and areas further downstream consists of finer sands with higher organic content (Saunders, 2007). Despite these facts, data on the springs feeding to the tributaries of Amala and Nyangores is inadequate and it is also not known how pH and temperature levels within these springs are influenced by anthropogenic activities.

The main biogeochemical feature of spring run sediments is the presence or absence of redox gradients (Saunders, 2007). In sediments, microbial respiration frequently consumes available oxygen leading to the formation of anaerobic zones at depth (Chróst, 1991). Under these conditions, oxygen contained in the water will diffuse downward to the anoxic sites creating a gradient of oxygen and the presence of both aerobic and anaerobic sediment zones. In aerobic zones, microbes are involved in biogeochemical reactions and use oxygen as the primary electron acceptor, while in anaerobic layers, facultative and obligate anaerobes function using alternate electron acceptors (e.g., NO_3^-, Fe(III), and SO_4^{2-}) in their respiration (Lontie and Vanquickenborne, 1974). Along the Mau Forest springs, the impact of nutrients loads from the activities related to biogeochemical reactions have not been examined.

One feature of sediments in high energy lotic systems is the high percentage of coarse particle size classes (e.g., sands) which greatly enhances advective processes. Sediments of high energy spring runs are also more likely to include varying stratigraphies with layers of different composition (e.g., organic matter) juxtaposed (Tchobanoglous and Shroeder, 1985). In a manner analogous to that in biofilms or benthic mats, these types of sediment distributions serve to enhance the potential for varying reactions where reactants and products are more easily exchanged between reactive zones to greatly increase reaction rates (Harvey and Wagner, 2000). Whether this is the scenario in spring waters along the Mau forest has not been documented.

2.4. Nutrients in spring water and sediment

Nutrients are chemical compounds that can be broken down through a series of reactions or assimilated to provide bio-elements that are necessary for normal growth of organisms (Fried *et al.*, 2003). These bio-elements include oxygen, hydrogen, carbon, nitrogen, calcium, phosphorous, sulphur, potassium and magnesium. However nitrogen and phosphorus are the most associated with ecosystem's nutrient enrichment resulting in excessive plant growth (Fried *et al.*, 2003). Elevated concentrations of these nutrients in the water ecosystem pose threats to aquatic organisms and enhance eutrophication (Haggard *et al.*, 2003). The increased use of agricultural chemical inputs, accompanied by runoff water from agricultural lands, have contributed to wide spread occurrence of eutrophication within Lake Victoria waters (LVBC and WWF- ESARPO, 2010).

2.4.1. Total nitrogen

In a river system, as well as spring system sediments have been widely used as environmental indicators and their chemical analysis can provide significant information on the assessment of anthropogenic activities (Singh *et al.*, 2007). Surface water run-offs, livestock, sewage discharge, fertilizers and waste water discharges all contribute to the abundance of total nitrogen in the environment (Armstrong, 1963). Nitrate ion (NO_3^-) is the common form of nitrogen in natural waters (Armstrong, 1963). Nitrite (NO_2^-) oxidizes into nitrate after entering an aerobic regime (Deborah and Kimstach, 1996). Nitrites exist normally in very low concentrations because it is the intermediate between ammonium and nitrates. Nitrate levels over 5 mg/L in natural waters normally indicate man made pollution, 200 mg/L is an extreme level (Ongley, 1996; USEPA, 2001c). Ammonia mainly exists in the ionized form (NH_4^+) but at high pH and temperature the ionized ammonia changes to un-ionized ammonia gas (NH_3). Ammonia is most harmful to freshwater aquatic life and fish, in particular (Ongley, 1996; USEPA, 2001a). In aerobic systems, ammonia breaks down by nitrifying bacteria to form nitrite and nitrate. Increased conversion of forest land into agricultural land and the expanding urban centers, require constant nitrate monitoring in order to maintain proper water quality. Whether this is the scenario depicted for spring waters along the Mau forest has not been documented.

2.4.2. Total phosphates and soluble reactive phosphate

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 bodies of water 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 (Ongley, 1996) in areas where phosphorous is naturally abundant in the soil. 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 (USEPA, 2001b). The monitoring of phosphorous levels is necessary to help in checking eutrophication in an aquatic system. It has not been established if this is the scenario for spring waters feeding into the tributaries of Mara River.

2.5. Heavy metals in spring water and sediment

Trace metals have been referred to as common pollutants, which are widely distributed in the environment with sources mainly from the weathering of minerals and soils (Merian, 1991; O' Neil, 1993). Thus, in water bodies, sediments form an important repository of heavy metals (Mzimela *et al.,* 2003; Mohiuddin *et al.*, 2011; Abdel-Baki *et al.*, 2011), and the heavy metal pollution of aquatic ecosystems is often most obviously reflected in high metal levels in sediments, other than in elevated concentrations in underlying water (Bryan, 1984 and Jaji *et al.*, 2007). However, the levels of these metals in the environment have increased tremendously in the past decades as a result of human inputs and activities (Preuss and Kollman, 1974; Prater, 1975; Merian, 1991). Heavy metals are usually available in little quantities in spring ecosystems, though the impact of these metals from anthropogenic activities have raised their natural concentrations causing serious environmental problems such as loss of some species or invasive species colonizing the springs (Aderinola *et al.*, 2009). Along the Mau Forest springs, there are natural and human activities which are potential sources of heavy metal loads into the springs; but the levels of heavy metal loads from the activities thereof have not been examined.

2.5.1. Zinc (Zn)

Although Zinc has low toxicity to man, prolonged consumption of large doses can result in some health complications such as fatigue, dizziness and neutropenia (Hess and Schmid, 2002). Zinc is also toxic to some aquatic organisms such as fish (Ailabaster and Lloyd, 1984). Continued use of inorganic fertilizers may lead to accumulations of zinc at the application sites which eventually get into aquatic systems. Thus, zinc levels in surface water should be checked regularly. Water is polluted with zinc, due to the presence of large quantities of zinc in the wastewater of industrial plants. This wastewater is not purified satisfactory. One of the consequences is that rivers are depositing zinc-polluted sludge on their banks. Zinc may also increase the acidity of waters.

Some fish can accumulate zinc in their bodies, when they live in zinc-contaminated waterways. When zinc enters the bodies of these fish it is able to bio magnify up the food chain. Large quantities of zinc can be found in soils. When the soils of farmland are polluted with zinc, animals will absorb concentrations that are damaging to their health. Water-soluble zinc that is located in soils can contaminate groundwater. Zinc cannot only be a threat to cattle, but also to plant species. Plants often have a zinc uptake that their systems cannot handle, due to the accumulation of zinc in soils (Hess and Schmid, 2002).

On zinc-rich soils only a limited number of plants has a chance of survival. That is why there is not much plant diversity near zinc-disposing factories. Due to the effects upon plants zinc is a serious threat to the productions of farmlands. Despite of this zinc-containing manures are still applied. Finally, zinc can interrupt the activity in soils, as it negatively influences the activity of microrganisms and earthworms (ASTDR, 1994). At the Mau Forest, the agricultural farms, as a result of encroachment and tea plantation forming forest buffers, are potential sources of zinc pollution; however, the levels of zinc in the spring waters of the Mau Forest have not been assessed.

2.5.2. Copper (Cu)

Copper (Cu) has a functional role in electron transfer and oxygen transport proteins as it has two common valence states: Cu (I) and Cu (II). The oxidation-reduction potential governing the relative predominance of these two valence states is sensitive to the nature and sterric arrangement of the surrounding ligand potentials (Reinhammar, 1979). For certain complexes, Cu (I) can bind oxygen and carbon monoxide (CO) reversibly (Lontie and Vanquickenborne, 1974) despite the fact that oxygen is a neutral symmetric molecule. Even though human body needs a trace amount of copper, it is toxic if the amount is too high. Excess tissue copper stimulates the biogenic amines, neurotransmitters associated with depression, anxiety, mood swings and schizophrenia.

Copper (Cu) is plentiful in the environment and essential for the normal growth and metabolism of all living organisms (Schroeder *et al.*, 1966; Carbonell and Tarazona 1994). Abnormal levels of copper intake may range from levels so low as to induce a nutritional deficiency to levels so high as to be acutely toxic USEPA (1999). Copper toxicosis in terrestrial higher plants is rare but occurs on mine spoils and where copper-rich manures or fungicides are used excessively (Schroeder *et al.* 1966 and Arduinietal. 1995). Copper is among the most toxic ofthe heavy metals in freshwater and marine biota (Schroeder *et al.*, 1966; Betzer and Yevich, 1975), and often accumulates and causes irreversible harm to some species at concentrations just above levels required for growth and reproduction. The Mau Forest encroachment leads to activities such as agricultural practices with likely fertilizer applications which are potential sources of pollution in the spring waters. However, there has been no study to assess the levels of copper in spring waters in the Mau Forest.

2.5.3. Selenium (Se)

Selenium is a metalloid found in soils, but exists mainly in insoluble forms in high-Fe, low-pH and certain leached soils, and hence is not readily available to plants (Lyons *et al.*, 2003; Clark *et al.*, 1996; Yu *et al.*, 1997). It is available to human beings through plants and animals. Selenium has anti-viral effect (Beck *et al.*, 1995; Baum *et al.*, 1997; Yu *et al.*, 1997) and the ability to contain cardiovascular diseases. It is therefore necessary to determine the levels of selenium in surface water of springs forming sources of Mara River, since this element is very important for human health.

2.5.4. Manganese (Mn)

Manganese is abundant in natural sources. Naturally, manganese is found 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+}; therefore, manganese tends to become more bioavailable with decreasing pH and redox potential (Heal, 2001). Manganese is a trace mineral that is present in very small amounts in the human body. The human body contains around 20 mg of manganese and most of it is found concentrated in the bones, kidneys, liver and pancreas (IMFNB, 2001). Manganese serves many functions in the human body. It primarily works as a coenzyme that facilitates various metabolic processes (Willis *et al.*, 2005). Again, it is involved in bone formation of connective tissues, sex hormone function, calcium absorption, blood sugar regulation, immune function and in fat and carbohydrate metabolism (NAS, 1980). Deficiency in Manganese leads to various health problems which include bone malformation, eye and hearing problems, high cholesterol levels, hypertension, infertility, heart disorders, memory loss, muscle contraction, tremors and seizures (NAS, 1980).

The neurological effects of inhaled manganese have been well documented in humans chronically exposed to elevated levels in the workplace (Roels *et al.*, 1999 and ATSDR, 2000). The syndrome known as "manganism" is caused by exposure to very high levels of manganese dusts or fumes and is characterized by a "Parkinson-like syndrome", including weakness, anorexia, muscle pain, apathy, and slow speech, monotonous tone of voice, emotionless "masklike" facial expression and slow, clumsy movement of the limbs. In general, these effects are irreversible. Nevertheless the Manganese concentrations in water and sediments from springs forming sources of Mara River remain unknown despite the fact that communities upstream and downstream use this source of water.

2.5.5. Iron (Fe)

Iron is an essential mineral and thus a component of several co-factors including haemoglobin and cytochrome. It is a major control element and many enzymes require Fe for their activity in carbohydrate metabolism for example with aconitase (Beinert and Kennedy, 1989). Many enzymes that are involved in secondary metabolism require iron for their activity (Dasilva and Williams, 1991). Iron is virtually found in every food, with higher concentrations in animal tissues than in plant tissues (Hammond and Beliles, 1980). Soils contain different amounts of the element iron depending on the geographical area and agronomical practices of the area (Stalikas *et al.*, 1994). In spring and stream sediments dominated by iron minerals, reduction of ferric (Fe (III)) hydroxides and complexes results in ferrous Fe (Fe (II)) (Agarwal, 1990), and adsorbed phosphates. Such conditions are of particular importance in areas where organic matter (and reducing conditions) can be transient, or when ground water varies temporally between aerobic and anaerobic states (Wetzel, 2001). Under strongly reducing conditions, sulfate is reduced to hydrogen sulfide (Wetzel, 2001). Some S^{2-} can react with iron compounds (both Fe (III) and Fe (II)) resulting in the precipitation of Fe-S compounds. Sulfide formation due to sulfate reduction can displace iron-bound P to enhance the release of P into the interstitial waters (Wetzel, 2001). The relative P release from sediments can be significantly higher as sulfate concentrations increase from natural or anthropogenic sources, particularly in oligotrophic, soft water lakes and rivers. In highly reduced soils with low sulfate content, microbial reduction generates mostly Fe (II) compounds from microbial reduction of Fe (III) oxide. The anion PO_4^{-3} can be retained with Fe (II) compounds, but Fe-associated PO_4^{-3} is released when amorphous Fe (III) oxide is converted to iron sulphides (Agarwal, 1990). Thus, the conversion of reactive soil Fe compounds to iron sulphides by sulfate-reducing bacteria can lead to a more efficient release of Fe-associated PO_4^{-3} than does direct microbial Fe (III) oxide reduction. Estimates of the minimum daily requirement for iron depend on age, sex, physiological status, and iron bioavailability and range from about 10 to 50 mg/day (ASTDR, 2000). The average lethal dose of iron is 200–250 mg/kg of body weight, but death has occurred following the ingestion of doses as low as 40 mg/kg of body weight (ASTDR, 2000). Autopsies have shown haemorrhagic necrosis and sloughing of areas of mucosa in the stomach with extension into the submucosa. At the Mau Forest, the agricultural farms, as a result of encroachment and tea plantation forming forest buffers are potential sources of iron pollution; but the levels of iron in the spring waters of the Mau forest has not been assessed.

2.5.6. Lead (Pb)

Lead has been classified as being potentially hazardous and toxic to most forms of life (USEPA, 1986). Lead has been responsible for quite a number of ailments in humans such as chronic neurological disorders especially in foetuses and children (Goyer and Clarkson, 2001). Automobile exhaust fumes have been reported to account for about 50% of the total inorganic Pb absorbed by human beings (Mohan and Hosetti, 1998). Lead poisoning can cause mental retardation and hyperactivity in children, and violent behaviour in adults other inputs of lead into the environment are from used dry-cell batteries, sewage effluent, runoff of wastes and atmospheric deposition while lower levels are found in fertilizers (Mortvedt, and Beaton, 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 in myriad of problems in organisms as highlighted above. The levels of lead in the Mau spring waters are not known.

2.5.7. Chromium (Cr)

The main entries of chromium into surface water are through sewer sludge, cement works and municipal waste (ARB, 1986). The most stable oxidation states of chromium are Cr^{3+} and Cr^{6+}. A daily intake of 50 – 200 μg Cr^{3+} is essential for normal glucose, protein and fat metabolism in human beings (ATSDR, 2003). The USEPA has classified Cr^{6+}as a human carcinogen and though the body is able to reduce it to Cr^{3+} which is less harmful, it readily damages cell walls being a strong oxidizer (USEPA, 1994b). It is for this reason that the quantities of chromium in water should be monitored so that it does not magnify itself to higher living organisms through the food chain. The cation Cr^{6+} is a byproduct of industrial applications and textiles. At the Mau Forest, the agricultural farms, as a result of encroachment and tea plantation forming forest buffers, are potential sources of chromium pollution. However, the levels of chromium in the spring waters of the Mau Forest have not been assessed.

2.5.8. Cadmium (Cd)

Cadmium is found in soils, rocks, coal and mineral fertilizers. Its entry into water is mainly due to surface run offs and industrial discharges such as paints, plastics and landfill leachates. cadmium is very strongly adsorbed on mud, humus and organic matter, leading to the possibility of entry into the food chain via fish and fish food, and subsequent accumulation in tissue. Following extended exposure, cadmium is highly toxic causing bone damage, chronic kidney disease, cancer and hypertension in human beings (WHO, 1992; Goyer and Clarkson, 2001). Cadmium is one of the most toxic elements with reported carcinogenic effects in humans (Goering *et al.,* 1995). Cadmium accumulates mainly in the kidney and liver and high concentrations lead to chronic kidney dysfunction. Cadmium induces cell injury and death by interfering with calcium (Ca) regulation in biological systems. It is toxic to fish and other aquatic organisms (Woodworth and Pascoe, 1982). Cadmium has been implicated in endocrine disrupting activities, which could pose serious health problems. Apart from the health implications, the metal (Cd), together with other elements, e.g. Zn form a toxic "soup" that often acts synergistically. Sources of Cd include wastes from Cd-based batteries, incinerators and runoff from agricultural soils where phosphate fertilisers are used since Cd is a common impurity in phosphate fertilisers (Stoeppler, 1991). In the Mau Forest there are agricultural activities which are possible sources of cadmium pollution in the spring water. However, the levels of cadmium from agricultural activities have not been assessed in springs in the Mau Forest.

Water quality degradation problem is not a new phenomenon in Kenya. Initial research reports on the problem in the country dates back in the 1950's. In Kenya, the problem of water quality degradation was first exposed in the MOWD (1976 a) and MOWD (1976 b) containing case studies of three rivers; Nzoia, the Nyando and Kerio. These reports contain the chemical characteristics of water shortly before and after establishment of factories along their courses. Nzoia River which drains into Lake Victoria carries the effluents discharged from Pan Africa Paper Mill in Webuye upstream and from Mumias Sugar Factory downstream; Nyando which also discharges its waters into Lake Victoria receives Molasses from Sugar Factories, Chemilil and Muhoroni. Kerio River drains the Kerio Valley with intermittent flow into Lake Turkana. This is now periodically polluted by effluents from fluorspar factory established three decades ago. All these three reports are a clear indication of the effects of industrial growth on the quality of water courses and their effluents are a major contributing factor to water quality degradation at the extreme vicinity of industrial activities. This was once more confirmed by a recent study done by the Ministry of Land Reclamation and Regional Development (MLRRD, 1993). Many studies indicate that groundwater resources are not seriously threatened with water pollution problem but the major concern has been on the surface waters especially in river systems.

Other research reports which indicated water quality deterioration in Kenya are those by Ongwenyi (1979) and Njunguna (1978). Njunguna (1978) also added that pollution in the river (Nairobi-Athi-Sabaki) was chiefly due to domestic waste, industrial wastes and runoff (both rural and urban).

The most recent studies by Kithiia (1992, 2006), Okoth and Otieno (2000) and Mavuti (2003) revealed degradation trends in water quality within the river system due to changes and intensity in land use activities. The study by Kithiia (1992) in the same area revealed high concentration levels of Mercury and Lead surpassing the critical WHO and the Kenya standards guideline values (Mercury 0.03 and Lead 0.1 mg l-1). In the study by Kithiia (2006) within the same river systems indicated a downstream increase in water pollutants and water quality degradation. Sediment and Heavy metal concentrations were found to increase downstream the river courses. The increasing trends in pollution levels and water quality deterioration are attributed to increased land use activities and population growth rates within the urban area and the basins in general. This calls for stringent measures to address the problem and reduce the ever increasing water pollutants and water quality degradation.

CHAPTER THREE

3.1. MATERIALS AND METHODS

3.2. Site Description

The springs studied are sources of Nyangores and Amala rivers, tributaries of Mara River, and are located in the Mau Forest Complex that is located in Narok and Bomet counties, in Kenya. Mara River Basin is a transboundary basin shared by Kenya and Tanzania. This is part of the larger Nile River Basin. The Mara River Basin lies between Latitudes 0°38' and 1° 03' South and between longitudes 35° 01' and 35° 33' East as illustrated in Figure 3.1a and the Google earth imagery on Figure 3.1 b and Table 3.2. The area was heavily forested (G.O.K., 2008a, 2008b), but parts are now characterized by large and small scale farming and a buffer zone of tea plantation introduced by the government to stop encroachment into the forest, which is an important water tower for the region (G.O.K., 2008a, 2008b). These land use activities have severely altered the previous natural environment.

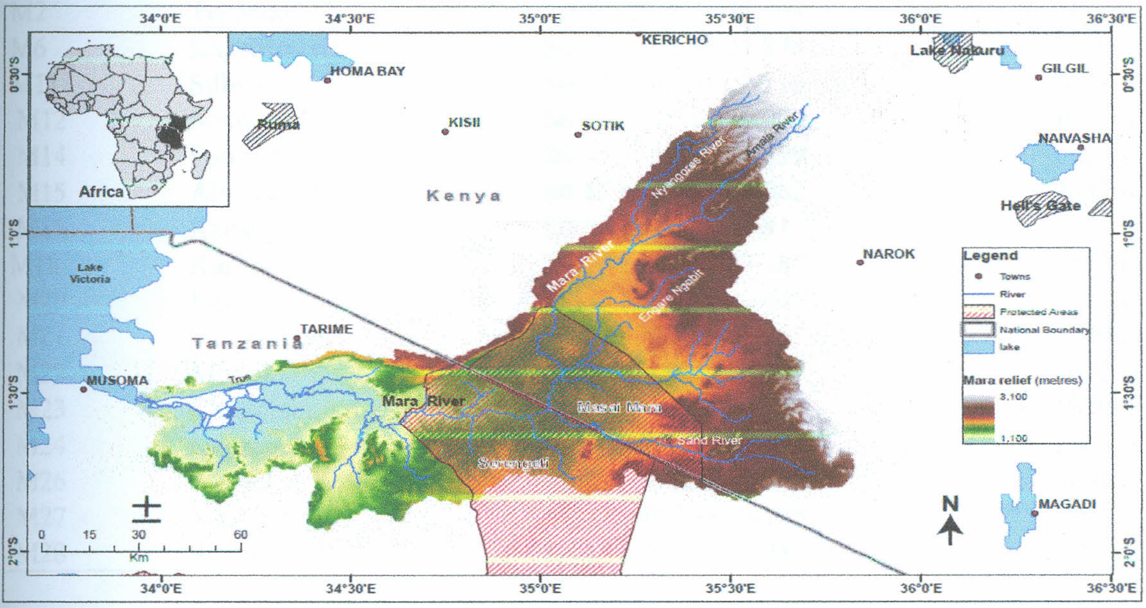
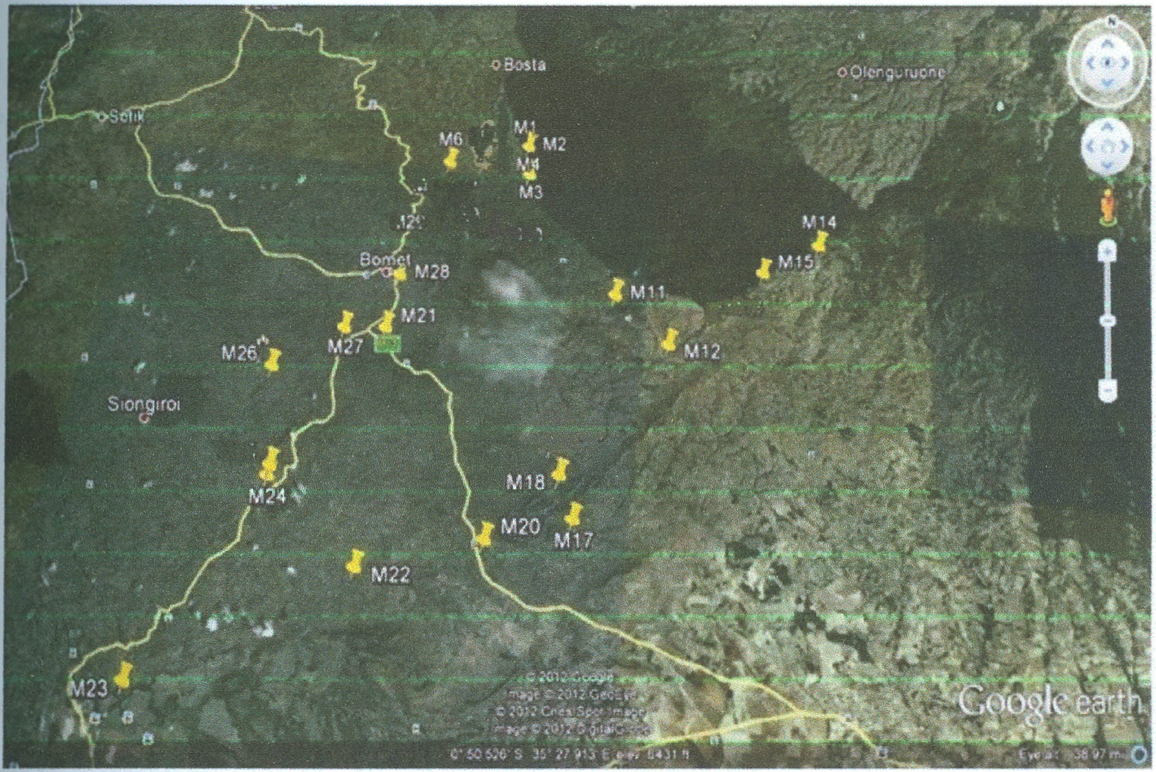


Figure 3.1a. The of Mara River Basin



Key: Sampling point: M1 – M23: Sampling points for springs.

Figure 3.1b. A Google earth map of Mara River Basin and sampling points

Table 3.1: GPS Coordinates of sampling points for springs

Site	Local Name of Spring	Coordinates	Elevation
M2	Teganda	S0 41.257 E35 24.964	2131m
M6	Kapsosrurwa	S0 42.343 E35 21.878	2036m
M11	Silbwet	S0 47.327 E35 29.116	2038m
M12	Sotionik 1	S0 49.023 E35 31.270	1964m
M14	Sotionik 2	S0 45.825 E35 34.659	2109m
M15	Ainabsabet	S0 47.881 E35 32.762	2053m
M17	Kapsoen 1	S0 54.197 E35 27.812	1971m
M18	Kapsoen 2	S0 53.159 E35 27.385	1870m
M20	Kebenet	S0 49.580 E35 20.677	1826m
M21	Chepudonge	S0 57.992 E35 21.303	1749m
M22	Motiok	S1 02.221 E35 14.534	1692m
M23	Chepkesoi	S0 55.368 E35 17.687	1880m
M24	Kapangas 1	S0 55.004 E35 17.619	1904m
M26	Kapangas 2	S0 49.740 E35 19.126	1894m
M27	Ndong Ndong	S0 47.408 E35 20.785	1901m
M28	Siongiroi	S0 44.788 E35 21.787	1993m

3.3 Chemicals and reagents

Potassium persulphate, ammonium chloride, ammonium molybdate, ascorbic acid, copper sulphate, hydrochloric acid and magnesium chloride were obtained from Riedel- de Haën (Germany); N-1- napthylethylene diamine dihydrochloride, phenol, potassium antimony tartarte, potassium chloride and potassium nitrate were obtained from Fluka (U.S.A.); sodium hydroxide, sodium hypochlolite, sodium nitroprusside, spongy cadmium granules, sulphanilamide, sulphuric acid and tri-sodium citrate dehydrate were obtained from Unichem (India), the perecentage purity of most of the reagents ranged from ≥95% to ≥99% depending on the supplier. The standard solutions for AAS for zinc, selenium, manganese, lead, iron, copper, chromium and cadmium were obtained from Fluka (USA), all the standards used were of purity ≥95%; for general laboratory use.

3.4. Sampling design and sample collection

A completely randomized design was used in sampling and sampling springs (sites) as per the coordinates on Table 3.1 were randomly selected within the basin draining into River Amala and Nyangores. Both sediment and water sampling were done over two seasons, dry season and wet season. The dry season sample collection was carried out from 15th to 17th March, 2011 while the wet season sample collection was carried out from 24th to 17th November, 2011.

Water sampling was done using a pre-cleaned water sampler. The water samples were collected just below the water surface and stored in pre-cleaned amber coloured 2.5 litre glass bottles. The bottles had prior to sampling been cleaned by soaking in 10% nitric acid over night and rinsed on the day of sampling with distilled water. Each sample was treated 10 mL of 6 N HNO_3 solution. The samples were then transported to the laboratory and filtered immediately using watman filter paper and stored at -20°C pending extraction. Sediment sampling was done using a pre-cleaned sediment grab sampler. Approximately 200 g samples were kept in pre-cleaned 250 mls sample jars with lids lined with aluminum foil and were stored in a cooling box kept at low temperatures with dry ice before transportation to the laboratory according to the procedures of APHA, (1985); APHA, (1995) and AOAC, (2000). Triplicate sample analysis was used to determine reproducibility or consistency in the method. Triplicates (or split samples) are three samples taken from the same source, digested, distilled or otherwise processed, and then analyzed identically. The acceptable level or variation between triplicates varies by test and by concentration of analyte. The percent recovery was calculated by dividing the difference between the three results by their average as follows:

$$\% \text{ difference} = (x - y - z) / ((x + y + z)/3) \times 100\%$$

where x = result of first analysis

y = result of second analysis

z = result of third analysis

3.5. Determination of parameters

3.5.1. Measurement of water and sediment pH and water temperature

Water pH and temperature were measured in-*situ* in the field using a pH meter (3071 Jenway, USA) and a mercury thermometer, respectively. For sediment pH a method adopted from Rhodes (1982) was used. Briefly, 50 mL of deionized water was added to 20 g of crushed dry sediments, stirred well for ten minutes and then allowed to stand for 30 minutes before stirring again for two minutes; then the pH was measured using a pH meter according to a method described by Omwoma (2010).

3.5.2. Determination of ammonium -nitrogen, oxidized nitrogen and nitrites in water

3.5.2.1. Determination of ammonium-nitrogen in water

The method used for ammonium determination is the indophenol blue photometric determination (Koroleff, 1969; APHA, 1995). The water samples were reacted with phenol and hypochlorite under alkaline conditions to form indophenol blue. The intensity of the blue color formed is proportional to the concentration of ammonium ions within a given range (0-1000µg NH_4-N/L). The absorbance was measured in a UV-1650 PC-UV-Vis spectrophotometer (Shimadzu, Japan) at 630 nm using highly purified water as a blank. Ammonium chloride (NH_4Cl) was dissolved in distilled water and the volume made up to 1 litre was used to make the calibration standard solutions.

3.5.2.2. Determination of oxidized nitrogen in water

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

$$NO_3^- + 2H^+ + 2e^- \longrightarrow NO_2^- + H_2O$$

$$Cd^o \longrightarrow Cd^{2+} + 2e^-$$

The total nitrite was then quantified as total oxidized nitrogen. The cadmium-copper column was made by reacting cadmium with copper sulphate and dilute ammonium chloride solution. The method used was based on the reaction of nitrite ions with sulfanylamide in acidic medium. The nitrite thus produced was quantified by diazotising and coupling with

N- (1- napthyl)ethylene to form a highly coloured azo dye. The nitrite ion concentration was then determined by measuring the absorbance of the azo color at 543 nm. In calculating the NO_3-N values, for samples and standards, two times the absorbance reading at 275 nm was subtracted from the reading at 220 nm to obtain absorbance due to NO_3-N. A standard curve was constructed by plotting absorbance due to NO_3-N against NO_3-N concentration of standard. Using corrected sample absorbance, sample concentrations were determined from the standard curve.

3.5.2.3. Determination of nitrites in water

The method prescribed by APHA (1995) was adopted for the nitrite analysis. It was determined by using the unfiltered samples which were digested before addition of sulphanilamide and N-1-napthylethylene diaminedihydrochloride. The samples were digested in an autoclave steam sterilizer (Gerhadt Bunn –kjedatherm.480322, Germany) at 120°C and allowed to cool. It was then passed through the copper cadmium column and the absorbance read at 543 nm and concentration determined against the standard calibration curve.

3.5.3. Determination of Soluble Reactive Phosphate and Total Phosphate

3.5.3.1. Soluble Reactive Phosphorous (orthophosphate (PO4-P)

A mixed reagent consisting of analytical grades ammonium molybdate solution, 250 mL sulphuric acid solution, 100 mL ascorbic acid solution and 50 mL potassium antimonyl tartrate were prepared. To 50 mL of filtered sample was added 5 mL of the mixed reagent and after 3 hours the extinction of the solution was measured in a UV-1650 PC-UV-Vis spectrophotometer (Shimadzu, Japan) at a wavelength of 885 nm. Absorbance's of a blank and calibration standards that were prepared from solutions of phosphate, 220 g KH_2PO_4/L;

1 ml = 50 µg PO_4 carried through the same steps were measured. A calibration curve was prepared and total concentration of phosphates per litre determined

3.5.3.2. Determination of total phosphorus in water

Total phosphorous was determined using the unfiltered samples. To 50 mL of unfiltered sample was added 5 mL of the mixed reagent. This was then digested in an autoclave at 120 °C for 2 hours, then allowed to cool. The absorbance of the solution was measured at a wavelength of 880 nm in a UV-1650 PC-UV-Vis spectrophotometer (Shimadzu, Japan). Total phosphorous concentration was determined against a standard calibration curve prepared from analytical grade potassium dihydrogen phosphate $(KH_2PO_4)^{-}$. Absorbance's of a blank and calibration standards that were prepared from solutions of phosphate, 220 g KH_2PO_4/L; 1 ml = 50 µg PO_4 carried through the same steps were measured. A calibration curve was prepared and total concentration of phosphates per litre determined

3.5.4. Analysis of heavy metals in water.

A standard procedure described in AOAC (2000) was followed for the preparation of samples for analysis of heavy metals in water. A volume of 200 mL of each water sample was accurately measured for analyzing Mn, Cu, Se, Fe, Zn, Pb, Cr and Cd. The samples were treated using aqua regia (concentrated hydrochloric and nitric acids in a 1:1 ratio). This was then transferred into digestion tubes and eventually into a digester for digestion at 300^{o}C for four hours. The final residue was dissolved in 0.05 M hydrochloric acid solution for extraction and made up to 25 mL for Mn, Cu, Fe, Zn, Pb, Cr, Se and Cd analysis. Working standard solutions were prepared by diluting the stock solution with 0.05 M hydrochloric acid. The Mn, Cu, Fe, Zn, Pb, Cr, Cd and Se in sediment samples were analyzed using atomic absorption spectrophotometer (Shimadzu AA-6200 Model, Japan) under standard instrumental conditions (Table 3.4 and Appendix III).

Table 3.4: 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-D_2	BGC-D_2	BGC-D_2	BGC-D_2	BGC-D_2	BGC-D_2	BGC-D_2	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
Callibrations (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 – Deterium background correction (compensates for matrix interferences)

3.4.5. Analysis of heavy metals in sediments.

A standard procedure described in AOAC (2000) was followed for the preparation of samples for analysis of heavy metals in sediments. The dry sediment samples were weighed on a digital analytical balance. A mass of 1.0000 g of sediment was weighed for analyzing Mn, Cu, Fe, Zn, Pb, Cr and Cd while 2.0000 g of sediment was weighed for Se analysis. The samples were treated using aqua regia and hydrogen peroxide in the ratio of 2:3. This was transferred into digestion tubes and eventually into a digester for digestion at 300°C for six hours. The final residue was dissolved in 0.05 M hydrochloric acid solution for extraction and made up to 25 mL for Mn, Cu, Fe, Zn, Pb, Cr and Cd analysis and to 10 mL for Se analysis. Working standard solutions were prepared by diluting the stock solution with 0.05M hydrochloric acid. The Mn, Cu, Fe, Zn, Pb, Cr, Cd and Se in sediment samples were analyzed using atomic absorption spectrophotometer (Shimadzu AA-6200 Model, Japan) under standard instrumental conditions (Table 3.4 and Appendix III).

3.5.6. Determination of total phosphorous in sediments

Sediment total phosphorus was determined by using the method of Haggard *et al.* (2003). A mass of 15g of pre-sieved sediments was placed in a 250 mL Erlenmeyer flask, and mixed with 100 mL of 1 M $MgCl_2$ solution. The sample was shaken for 1 hour on the orbital shaker. A volume of 50 mL of the supernatant was diluted to 100 mL in 100 mL volumetric flask and pH adjusted to acidic using 1:1 hydrochloric acid. 0.2 g activated carbon was added followed by shaking for fifteen minutes. The samples were filtered through double Whatman filter paper. To 35 mL of the filtrate, 10 mL of Vanado-molybdate reagent was added and topped to the mark with distilled water in a 100 mL volumetric flask. Absorbance measurements were taken after 15 minutes at 470 nm.

3.5.7. Determination of ammonium -nitrogen, oxidized nitrogen and nitrites in sediments

Sediment samples were thawed before the extractions for the different analysis.

3.5.7.1. Ammonium - nitrogen

Ammonium was extracted by centrifuging 3 g of moist sediment with 30 mL of 2 M KCl for 30 min. as described by Page (1982). The extract was analyzed for ammonium as described for the water samples by indophenol blue photometric determination.

3.5.7.2. Nitrite and nitrate.

Nitrate and nitrite was extracted by centrifuging 3 g of moist sediment with 30 mL of 2 M KCl for 30 min followed by filtration. The nitrates were reduced to nitrite 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. Nitrite was determined by the same process but without using the copper- cadmium column.

3.5.7.3. Total nitrogen

The 0.20 g wet samples was digested in alkaline persulfate media in an autoclaved steam sterilizer at 121°C and allowed to cool and sediment. After addition of sulphanilamide and N-1-Napthylethylene diaminedihydrochloride the contents were passed through the copper cadmium column and the absorbance measured at 543 nm in a UV-1650 PC-UV-Vis spectrophotometer (Shimadzu, Japan). The concentration was determined against a standard calibration curve.

3.6. Statistical analysis

The data from the water and sediment samples was subjected to statistical analysis to give the means, LSDs and standard deviations. The concentration of nutrients and heavy metals were statistically analyzed using a two factor completely randomized design. SAS statistical package was used for Analysis of Variance (ANOVA) to separate the means ($p \leq 0.05$) and to check the variations while GraphPad Prism for students't-test ($p \leq 0.05$) to compare the contribution of springs flowing into the tributeries of the Mara River. (Appendix I).

CHAPTER FOUR

4.1. RESULTS AND DISCUSSION

4.2. Levels, site and seasonal variations of physicochemical parameters in spring water.

4.2.1. Temperature and pH

The mean in-*situ* water physicochemical parameters at different sites of the Nyangores and the Amala springs are as presented in Table 4.1

Table 4.1: Levels of physicochemical parameters of water from springs of Amala and Nyangores Rivers.

		NYANGORES SPRINGS								
Item		Teganda	Kapsosrurwa	Silbwet	Sotionik 1	Sotionik 2	Ainabsabet	Kapsoen 1	Kapsoen 2	Mean season
Temperature(°C)	Wet season	12.57	12.90	13.07	13.13	12.90	13.07	13.13	13.23	13.00
	Dry season	14.70	15.78	16.05	16.07	15.44	16.06	16.10	16.15	15.79
	Mean Sites	13.64	14.34	14.56	14.60	14.17	14.56	14.61	14.69	
	CV(%)					1.17				
	LSD ($p \leq 0.05$)					0.20				0.10
pH	Wet season	6.37	6.90	6.24	6.23	6.15	6.42	6.47	6.90	6.46
	Dry season	6.51	6.10	6.37	6.67	6.14	6.44	6.48	6.10	6.35
	Mean Sites	6.44	6.50	6.31	6.45	6.15	6.43	6.48	6.50	
	CV(%)					0.00				
	LSD($p \leq 0.05$)					0 .00				0 .00

Item		AMALA SPRINGS								
Temperature(°C)		Kebenet	Chepudonge	Motiok	Chepkesoi	Kapangas 1	Kapangas2	Ndong Ndong	Siongiroi	Mean season
	Wet season	13.13	29.70	8.81	13.87	13.77	14.09	14.11	14.21	13.13
	Dry season	16.20	32.34	9.81	16.94	16.97	16.38	16.73	16.21	16.20
	Mean Sites	14.67	31.02	9.31	15.40	15.37	15.24	15.42	15.21	
	CV(%)						1.36			
	LSD ($p \leq 0.05$)						0.26			0.13
pH	Wet season	6.24	6.20	6.23	6.66	6.83	6.83	6.27	6.27	6.24
	Dry season	6.37	7.59	6.67	6.30	6.11	6.79	6.72	6.44	6.37
	Mean Sites	6.31	6.90	6.45	6.48	6.47	6.81	6.50	6.33	
	CV (%)						0 .00			
	LSD($p \leq 0.05$)						0 .00			0 .00

4.2.1.1. Site variation of temperature

The levels and site variations of temperatures in Springs of Nyangores and Amala are given in Table 4.1. The temperatures of springs flowing into Nyangores varied significantly ($p \leq 0.05$) and ranged from 13.64°C to 14.69°C. Teganda recorded the least temperature of 13.64 °C while Kapsoen 2 registered the highest temperature of 14.69 °C. Whereas in Amala the temperatures varied significantly ($p \leq 0.05$) and ranged between 31.02 °C at Chepudonge which was a hot spring to 9.31 at Motiok which was a cold spring. The temperatures were relatively low probably due to the spring locations in the highland and may be due to different timing of collection and influence of season (Jayaraman *et al.*, 2003). The temperature ranges were generally below 30 °C, except at the Chepudonge Hot spring which was 32.02°C which is the recommended limit for no risk according to the World Health Organization (WHO) water quality guidelines for domestic use (WHO, 1996). These ranges were similar with the ranges reported for other tropical spring waters (Khana and Ejike, 1984; Ovie and Adeniji, 1993) at 12°C to 15°C in West Africa. The temperature of the water from both springs flowing in Amala and Nyangores Rivers did not appear to pose any threat to the homeostatic balance of the receiving water bodies as noted in the study of River Ogun in west of Nigeria (Jaji *et al,* 2007).

4.2.1.2. Seasonal variation of temperature

The seasonal variation of the temperature of the water samples are presented in Table 4.1. The temperature regimes of the spring water samples varied significantly ($p \leq 0.05$) with season and ranged from a mean season of 15.79°C to a mean season of 13.00°C in springs flowing into Nyangores during the wet season while springs flowing into Amala registered a mean season of 16.20°C in dry season to a mean season of 13.13°C in the wet season. The spring waters were generally cool in both seasons and within the acceptable temperature range acceptable by (WHO, 1996). At the Chupudonge hot spring, the temperature was 29.70°C in the wet season and 32.34°C in the dry season, while the Motiok cold spring was 8.81°C in the wet season and 9.81 in the dry season. The seasonal variation in the water temperature may be due to different timing of collection and influences of season as reported by a study by (Jayaraman *et al*., 2003) similar results were also recorded by (Jeppesen *et al*., 1997).

4.2.1.3. Site variation of pH

The levels and site variation of pH in springs flowing into Nyangores and Amala are given in Table 4.1. The pH of springs along Nyangores ranged ($p \leq 0.05$) from 6.15 at Sotionik 2 to 6.50 at Kapsoruwa and Kapsoen 2, and did not vary significantly whereas the pH of springs flowing into Amala also did not vary significantly ($p \leq 0.05$) from 6.90 at the Chepudonge to a of 6.31 at Kebenet. The pH of the hot spring was relatively higher than the other springs and this could be attributed to the hot spring probably extracting more salts from the source, thus raising pH. The mean pH range ($p \leq 0.05$) of springs flowing into the two tributaries ranged from 6.15 to 6.90 which are within the acceptable pH limits of 6.50 to 8.00 by KEBS, (1996), NEMA, (2006), USEPA (1999) and WHO, (1996) for drinking water. This tendency, of increased pH at hot springs, is similar to that exhibited in a hot spring such as in the Western United States, although the use of nitrogenous fertilizers on the cultivated areas was expected to lower pH as per studies by Mortvedt and Beaton (1995), this was not observed. This indicates the use of nitrogenous fertilizers in farms around the springs might not have reached excessive levels. Generally, the obtained pH values fell within the (WHO, 1996) standard of 6.5 to 8.5 for full contact recreation water (WHO, 1984; 1989). The EU also sets pH protection limits of 6.0 to 9.0 for fisheries and aquatic life (WHO, 1996). The results indicate that pH levels are generally less than the neutral value of 7.0, indicating slight acidity. The pH of water is important because many biological activities occur only within a narrow range. Thus, any variation beyond an acceptable range could be fatal to a particular organism. The results show no significant variations in pH with seasons and this is in agreement with previous studies on conditions that are important secondary determinants of heavy metal transport and fate at the application sites (Alloway, 1995).

4.2.1.4. Seasonal variation of pH

The levels and seasonal variations of pH in springs flowing into Nyangores and Amala are given in Table 4.1.The pH profile of the water samples did not vary significantly ($p \leq 0.05$) and ranged from a mean season of 6.24 in the wet season and 6.37 in the dry season for springs flowing into Amala to a mean season of 6.46 in the wet season and 6.35 in the dry season for springs flowing into Nyangores. The wet season exhibited relatively higher pH in the springs along both rivers. This was probably due to excessive drainage of acidifying nitrogenous salts from farming activities during the wet season. The pH values obtained were generally lower in wet season than in dry season. The lower pH could be attributed to enhanced ammonification and nitrification processes in the wet season (Oliver, 2004). The results show a trend of variations in pH with seasons though not significant. This is comparable with similar studies on conditions that are important secondary determinants of heavy metal transport and fate at the application sites (Alloway, 1995).

4.2.2. Nutrients concentration levels, site and seasonal variations in spring water

4.2.2.1. Site variation of Soluble Reactive Phosphate (SRP) and total phosphate(TP).

The levels and site variations of SRP in springs flowing into Amala are given in Table 4.2 and in Nyangores are given in Table 4.3 respectively. The SRP levels in springs flowing into the Amala river significantly ($p \leq 0.05$) varied and ranged from 43.06 ppb at Motiok to 26.35 ppb at Kapangas (Table 4.2), while the SRP regime in springs flowing into Nyangores varied significantly ($p \leq 0.05$) and ranged from a high of 41.35 ppb at Kapsoen1 and a low of 26.35 ppb at Kapsoen 2 (Table 4.2). SRP concentrations seemed to be generally low as a result of most of the springs being located in the forested land within the catchment. Several studies have shown that agricultural land use (i.e., pasture) can influence water chemistry in ground and surface waters in relation to SRP concentrations (Petersen *et al.*, 1999, Haggard *et al.*, 2003, McFarland and Hauck, 1999). This was not the case in the springs flowing into both tributaries. Phosphorus concentrations in springs generally show a sequential decrease with increasing distance from source as observed in streams, rivers and lakes (Fox *et al.*, 1989; Chambers and Prepas, 1994; House and Denison, 1998; Haggard *et al.*, 2001, 2004). Springs often require longer distances to temporarily retain significant portions of P inputs from sources (Haggard *et al.*, 2001, 2004; Martí *et al.*, 2004). In Spring Creek and Sager/Flint Creek, the sequential decrease in SRP concentration was likely from sediment sorption, biotic uptake, and dilution from groundwater and lateral tributaries. Phosphorus concentrations in streams generally showed a sequential decrease with increasing distance from the anthropogenic source (Fox *et al.*, 1989; Chambers and Prepas, 1994; House and Denison, 1998; Haggard *et al.*, 2001, 2004). In Springs flowing into Amala and Nyangores, the sequential decrease in SRP concentration was likely from sediment sorption, biotic uptake, and dilution from groundwater and lateral tributaries.

The levels and site variations of TP in springs flowing into Nyangores are given in Table 4.3 and in Amala are given in Table 4.2 respectively. The average concentrations of TP did not vary significantly ($p \leq 0.05$) and ranged between 288 ppb in the wet season to 118 ppb in the dry season at the sampling springs flowing into Amala (Table 4.2), whereas TP varied between 142.33 ppb in the wet season to 240.59 ppb in the dry season at the sampling springs flowing into Nyangores (Table 4.3). The observed high concentration of TP in the two last sites - Ndong Ndong and Siongiroi springs (Table 4.2) - that flow into Amala, as well as Kapsoen 1 and 2 springs (Table 4.3) that flow into Nyangores, is probably related to the increasing inputs of concentrated inorganic phosphorus from fertilizer sources and dissolved P from domestic sewage, which are the most important anthropogenic sources of phosphorus in aquatic ecosystems (Wither, 1994). It is important to note that spring runs and other lotic ecosystems can transform inorganic nutrients into organic material, thus preventing or reducing the downstream export of inorganic nutrients. However, these lotic ecosystems can become saturated with respect to relatively conservative inorganic nutrients such as phosphorus and may not be able to further assimilate inorganic forms through uptake, microbial and utilization. It is unclear at what concentration or loading rate saturation can occur, but likely it is dependent on whether it is an acute or chronic nutrient load and on the magnitude of other limiting chemical constituents or forcing functions such as light availability Bernot and Dodds (2005). Allen (1946) made similar observations on phosphorus in Florida spring ecosystems remains uncertain in most cases and is obviously a function of individual spring biogeochemistry.

4.2.2.2. Site variation of ammonium, nitrates, nitrites and oxidised nitrogen

The levels and site variations of Ammonium in springs flowing into Nyangores are given in Table 4.3 and in Amala are given in Table 4.2 respectively. The Ammonium levels varied significantly ($p \leq 0.05$) in springs flowing into Nyangores and ranged from 131.61 ppb at Teganda to 21.01 ppb at Kapsoen 1 in the dry season, and from 50.42 ppb at Motiok to 147.20 ppb at Sotionik 1 in the wet season. The average concentrations of NH_4^+ in the study ranged from 50.96 ppb in the wet season to 62.97 ppb in the dry season for springs flowing into Nyangores (Table 4.3), while for springs flowing into Amala the mean concentration was 75.20 ppb in the wet season to and 55.46 ppb in the dry season (Table 4.3).

The levels and site variations of Nitrites in springs flowing into Nyangores are given in Table 4.3 and in Amala are given in Table 4.2 respectively. The Nitrites profile of the water samples varied significantly ($p \leq 0.05$) and recorded the lowest concentration at Kapsoen 2 (2.68 ppb) while the spring at Silbwet exhibited the highest concentration at 10.58 ppb, for springs flowing into Nyangores. The average concentration of NO_2^- ranged from 14.23 ppb at Motiok to 3.04 ppb at Siongiroi in the springs flowing into Amala.

The levels of site variation for Oxidised Nitrogen in Nyangores are given in Table 4.3 and in Amala are given in Table 4.2 respectively The Oxidised Nitrogen regime did not vary significantly ($p \leq 0.05$) and ranged from 95.07 ppb to 485.92 ppb for springs flowing into Nyangores and 88.80 ppb to 553.96 ppb.

The levels and site variations for nitrates in springs flowing into Nyangores are given in Table 4.3 and in Amala are given in Table 4.2 respectively. The nitrates levels also did not vary significantly ($p \leq 0.05$) and ranged from 485.92 ppb to 95.07 ppb for springs flowing into Nyangores and 109.79 ppb to 23.23 ppb in the springs flowing into Amala. Naturally, in unpolluted rivers, the concentration of NH_4^+ is generally higher during the wet season because the nitrification process in rivers is more effective at higher summer temperatures as reported by Haag and Westrich, (2002). In paddy soils, NO_3^-containing fertilizers are ineffective because of N lost by denitrification process. Some NO_3^- is always present, however, since a portion of NH_4^+ in the aerobic zone of plant-soil water system is converted to NO_3^-, when NO_3^- diffuses into anaerobic subsoil, where it is rapidly and completely denitrified (Tisdale *et al.*, 1993). But NH_4^+ is usually bound to soil particles through cation exchange, which reduces the risk of leaching loss (Peter *et al.*, 1997). However, some NH_4^+ could discharge into the river via soil erosion by fine soil particles in agricultural lands. Furthermore, water logging of soil results in rapid denitrification by impeding diffusion of O_2 to sites of microbiological activities in these soils (Tisdale *et al.*, 1993). Nitrification—the biological conversion of NH_4^+ to NO_3^- requires free O_2. As a result it is restricted in submerged soils to oxidized zones. The magnitude of nitrification is regulated by the availability of O_2, which determines the fraction of the total volume occupied by aerobic zones, and NH_4^+ concentration in these aerobic zones.

Table 4.2: Concentration levels of nutrients (ppb) in water from springs flowing into Amala River.

Spring		Kebenet	Chepudonge	Motiok	chepkesoi	Kapangas 1	Kapangas 2	Ndong Ndong	Siongiroi	**Mean Season**
SRP	Dry Season	33.44	42.01	22.01	24.86	33.43	26.29	36.29	22.00	30.04
	Wet Season	31.54	19.55	64.11	31.54	29.84	26.41	46.96	31.54	35.19
	Mean sites	32.49	30.78	43.06	28.20	31.64	26.35	41.63	26.77	
	CV (%)					0.02				
	LSD(p≤0.05)					0.01				0.00
TP	Dry Season	52.01	82.01	63.43	50.57	86.29	122.01	362.00	130.57	118.61
	Wet Season	105.25	48.69	561.25	197.84	134.41	91.54	607.54	563.14	288.71
	Mean sites	78.63	65.35	312.34	124.21	110.35	106.78	484.77	346.86	
	CV (%)					0.00				
	LSD(p≤0.05)					0.00				0.000
Ammonium -nitrogen	Dry Season	57.67	34.33	21.00	36.00	122.67	82.67	77.67	69.33	62.67
	Wet Season	33.20	33.20	67.20	115.21	63.21	27.21	25.21	43.21	50.96
	Mean sites	45.44	33.77	44.10	75.61	92.94	54.94	51.44	56.27	
	CV (%)					0.013				
	LSD(p≤0.05)					0.009				0.01
Oxidized nitrogen	Dry Season	155.54	431.61	114.64	114.94	407.36	138.27	434.33	132.52	241.15
	Wet Season	157.93	145.20	557.56	62.66	519.02	301.560	233.56	975.39	369.11
	Mean sites	156.74	288.41	336.10	88.80	463.19	219.92	333.95	553.96	
	CV (%)					0.00				
	LSD(p≤0.05)					0.00				0.00
Nitrates -nitrogen	Dry Season	28.66	59.26	31.42	31.42	50.90	45.38	64.86	28.66	42.54
	Wet Season	27.75	24.44	188.15	161.32	57.69	31.05	44.47	17.73	69.09
	Mean sites	28.20	41.89	109.79	96.37	54.30	38.22	54.66	23.24	
	CV (%)					0.00				
	LSD(p≤0.05)					0.00				0.00
Nitrites-nitrogen	Dry Season	3.12	6.45	3.42	3.42	5.54	4.94	7.06	3.12	4.63
	Wet Season	3.02	2.66	20.48	17.56	6.28	3.38	4.84	1.93	7.52
	Mean sites	3.07	4.56	11.95	10.49	5.91	4.16	5.95	2.53	
	CV (%)					0.15				
	LSD(p≤0.05)					0.01				0.01

4.2.2.3. Seasonal variation of soluble reactive phosphate and total phosphate.

The levels and seasonal variation of SRP in springs flowing into Nyangores are given in Table 4.3 and in Amala are given in Table 4.2 respectively The SRP concentration levels of the water samples varied significantly ($p \leq 0.05$) seasonally from a mean wet season concentration of 30.04 ppb and 35.19 ppb in the dry season for springs flowing into Amala, whereas the mean concentrations for springs flowing into Nyangores were 29.32 ppb and

36.05 ppb in the wet and dry seasons, respectively. In wet seasons, due to decreasing levels of biological activities, the amount of phosphate and therefore total phosphate could rise while this phenomenon is reversed in the other seasons.

The levels of seasonal variation for TP in Nyangores are given in Table 4.3 and in Amala are given in Table 4.2 respectively. The TP levels did not vary significantly ($p \leq 0.05$) and ranged from 118.610 ppb to 288.710 ppb in the dry and wet seasons respectively. In this study, higher levels of TP were observed in the wet season (Table 4.2 and 4.3). Similarly studies such as Garhwal Springs by Avnish *et al.* (2011) reported higher phosphates levels during intense agricultural seasons.

The seasonal variations of water column nutrients in many springs are controlled by underground discharge (Petersen *et al.*, 1999; Haggard *et al.*, 2003; McFarland and Hauck, 1999). Haggard *et al.* (2003) investigated the relationship between the water column nutrients in springs and the daily discharge of the Chikugo River. The results indicated that the water column nutrient concentration was high in summer and low in winter.

4.2.2.4. Seasonal variation of ammonium, nitrites, nitrates and oxidised nitrogen

The levels and seasonal variation of ammonium in springs flowing into Nyangores are given in Table 4.3 and in Amala are given in Table 4.2 respectively. The ammonium levels varied significantly ($p \leq 0.05$) and ranged from 55.460 ppb in the dry season to 75.200 ppb in the wet season.

Ammonium in aerobic zones originates from formation by ammonification within the aerobic zone, inputs of external N including fertilizer, and diffusion of NH_4^+ from adjacent anaerobic soil zones. Nitrate formed by nitrification is stable within an aerobic zone, but it can be readily reduced in adjacent anaerobic zones. Oxygen availability is typically the factor most limiting nitrification in paddy soils (Kengara, 2010). Nitrate does not accumulate in the anaerobic zone because of the high demand for NO_3^- to serve as an electron acceptor in the absence of O_2. Denitrification is of NO_3^-, whereby NO_3^- serves as a terminal electron acceptor and is reduced to gaseous end products of nitrous oxide (N_2O) and nitrogen gas (N_2). Denitrification is mediated by heterotrophic microorganisms; and its rate is regulated by NO_3^- concentration and available C, which serves as an energy source or electron donor. The supply of NO_3^- originating from the aerobic zones is typically the factor limiting denitrification in submerged soils (Aulakh *et al.*, 2000 and Kengara, 2010). The seasonal variations of NH_4^+ concentrations in this study were consistent with this observation (Table 4.2 and 4.3). Moreover, the springs flowing into Nyangores were characterized by higher concentrations of NH_4^+ (Table 4.3). In the springs where higher levels were observed, the prevalent land-use practice is agriculture as the most common cultivation in which redox potential is suitable for NH_4^+ formation.

The levels and seasonal variations of nitrites in springs flowing into Nyangores are given in Table 4.3 and in Amala are given in Table 4.2 respectively. The seasonal profile of Nitrites varied significantly ($p \leq 0.05$) for springs flowing into Amala with a mean concentration of 5.56 ppb in the dry season and 8.98 ppb in the wet season. On the other hand, for springs flowing into Nyangores, the mean concentration was higher in the dry season at 10.77 ppb compared to 9.50 ppb registered in the wet season. These temporal differences might be due to the fact that the nitrate loading is usually highest in the wet season. Therefore, soil-water recharge in the dry season causes N-mineralization to be increased when soil is drying, followed by a re-wetting period Peter *et al.* (1997). The rise of NO_3^- concentration in the water column due to NO_3^- release from the sediments in wet season has been noted in several studies (Petersen *et al.*, 1999; Haggard *et al.*, 2003; McFarland and Hauck, 1999) Haggard *et al.* (2003) suggested that not only the NO_3^- release from the sediments but also nitrification in the water column contribute to the high NO_3^- concentration in the water column in the springs of Eastern Aegean.

Table 4.3: *Concentration levels of nutrients (ppb) in water from springs flowing into Nyangores River.*

Spring		Teganda	Kapsosrurwa	Silbwet	Sotionik 1	Sotionik 2	Ainabsabet	Kapsoen 1	Kapsoen 2	Mean season
SRP	Dry Season	26.280	16.290	53.420	26.290	24.860	22.010	39.140	26.290	29.320^{a}
	Wet Season	40.120	50.420	26.410	29.830	40.120	31.550	43.550	26.400	36.050^{b}
	Mean sites	33.200^{d}	33.360^{c}	39.920^{b}	28.060^{f}	32.490^{e}	26.780^{g}	41.350^{a}	26.350^{h}	
	CV (%)					0.022				
	LSD($p \leq 0.05$)					0.008				0.004
TP	Dry Season	87.710	40.570	467.710	164.860	112.010	76.290	506.290	469.280	240.590^{a}
	Wet Season	62.410	98.410	76.120	60.680	103.540	146.410	434.400	156.680	142.330^{b}
	Mean sites	75.060^{g}	69.490^{h}	271.920^{c}	112.770^{d}	107.78^{f}	111.350^{e}	470.350^{a}	312.980^{b}	
	CV (%)					0.005				
	LSD($p \leq 0.05$)					0.011				0.006
Ammonium-nitrogen	Dry Season	131.610	27.670	56.000	96.010	52.670	22.670	21.010	36.010	42.460^{b}
	Wet Season	69.210	41.190	25.200	43.200	147.200	99.200	93.200	83.190	75.200^{a}
	Mean sites	100.410^{a}	34.430^{h}	40.600^{g}	69.600^{b}	99.940^{a}	60.940^{c}	57.110^{e}	59.600^{d}	
	CV (%)					0.012				
	LSD($p \leq 0.05$)					0.008				0.004
Oxidised nitrogen	Dry Season	131.610	121.000	464.640	52.210	432.520	251.300	194.640	812.820	307.590^{a}
	Wet Season	186.650	517.930	137.560	137.920	488.830	165.930	521.200	159.020	289.380^{b}
	Mean sites	159.130^{g}	319.470^{d}	301.100^{e}	95.070^{h}	460.68^{b}	208.620^{f}	357.920^{c}	485.920^{a}	
	CV (%)					0.000				
	LSD($p \leq 0.05$)					0.000				0.000
Nitrates-nitrogen	Dry Season	28.663	59.256	31.420	23.151	20.303	156.730	134.498	48.140	25.815^{a}
	Wet Season	27.745	24.437	188.150	34.359	71.107	37.667	37.667	61.094	54.479^{b}
	Mean sites	28.204^{g}	41.893^{e}	109.785^{a}	28.755^{b}	45.751^{d}	97.198^{f}	86.082^{c}	54.663^{h}	
	CV (%)					0.000				
	LSD($p \leq 0.05$)					0.000				0.004
Nitrites - nitrogen	Dry Season	2.520	2.210	17.060	14.640	5.240	2.810	4.030	1.610	6.270^{a}
	Wet Season	3.740	7.740	4.100	4.100	6.650	5.930	8.470	3.740	5.560^{b}
	Mean sites	3.130^{g}	4.980^{e}	10.580^{a}	9.370^{b}	5.950^{d}	4.370^{f}	6.250^{c}	2.680^{h}	
	CV (%)					0.158				
	LSD($p \leq 0.05$)					0.011				0.006

4.2.3. Nutrients concentration levels in sediments

4.2.3.1. Site variation of total phosphate.

The results of the nutrients concentration levels in sediments from springs flowing into Rivers Amala and Nyangores were determined and the results shown in Tables 4.4 and 4.5, respectively. The TP regimes varied significantly ($p \leq 0.05$) in springs during the study and ranged from 67.95 ppb at Chepudonge to 503.85 ppb at Ndong Ndong, in Amala tributary.

A similar trend was observed in the Nyangores tributary with Kapsoen1 recording the highest TP level of 945.56 ppb, while Kapsosrurwa recorded the lowest level at 139.18 ppb. The high phosphates concentration in sediments at springs closer to tea plantation is probably indicator of the agricultural inputs being a source of these nutrients. Previous studies carried out in springs in North Carolina, USA indicated that agricultural land use is a major contributory factor in variation in water quality particularly its nutrients concentration (Gregory *et al.*,1996). Sediments often play an important role in the temporary retention and release of P in spring's systems. The inputs of P from anthropogenic increased the sediment pool of readily bioavailable P in these streams, and reduced the P buffering capacity. Several studies have shown similar results, suggesting that abiotic processes (sediment sorption) are a substantial factor in P retention (Fox *et al.*, 1989; House and Denison, 1998) but are not solely responsible for decreases in P concentrations downstream from anthropogenic sources; biotic processes are also important determinants (Chambers and Prepas, 1994; House and Denison, 1998). However, it is possible for enriched systems to become saturated with P and even release P when inputs are reduced below a threshold concentration (Haggard *et al.*, 2004). The amount of loosely exchangeable P in sediments has been observed in streams with finer sediments in the south–central Great Plains of Oklahoma (Haggard *et al.*, 2001). It is conceivable that once effluent P concentrations are reduced in springs flowing into Amala and Nyangores, sediments will release P into the water column and maintain elevated P concentrations for several distances downstream for an undetermined period of time. Bottom sediments are often sources of P in aquatic systems, especially lakes and reservoirs as noted by Haggard *et al.* (2001).

4.2.3.2. Site variation of ammonium, nitrites, nitrates and oxidised nitrogen.

The levels and site variation of ammonium in sediments in springs flowing into Nyangores are given in Table 4.5 and in Amala are given in Table 4.4 respectively. The ammonium levels in the sediment sites varied significantly ($p \leq 0.05$) and recorded the lowest concentration at Chepudonge (38.05 ppb) while the sample from Kapangas exhibited the highest concentration at 104.74 ppb in springs of Amala. For springs in Nyangores, the highest levels were recorded in Sotionik 2 (188.55 ppb) and the lowest in Kapsoen (64.74 ppb).

The levels of site variation for nitrites in sediments in Nyangores are given in Table 4.5 and in Amala are given in Table 4.4 respectively. The nitrites in sediments of Amala varied significantly ($p \leq 0.05$) and ranged from 14.23 ppb to 3.04 ppb, while in Nyangores it also varied significantly ($p \leq 0.05$) ranging from 18.20 ppb to 4.56 ppb.

The levels and site variations of oxidised nitrogen in sediments in springs flowing into Nyangores are given in Table 4.5 and in Amala are given in Table 4.4 respectively. The oxidised nitrogen in sediments varied significantly ($p \leq 0.05$) and ranged from a mean of 1024.46 ppb to 200.60 ppb for springs flowing into Nyangores and 614.75 ppb to 173.64 ppb.

The levels and site variations of nitrates in sediments in springs flowing into Nyangores are given in Table 4.5 and in Amala are given in Table 4.4 respectively. The Nitrates in sediments in springs flowing into springs flowing into Amala varied significantly ($p \leq 0.05$) and ranged from 130.731 ppb to 27.928 ppb, while in Nyangores it also varied significantly($p \leq 0.05$) ranging from 167.20 ppb to 41.89 ppb. The levels are within the acceptable limits by WHO, (1996) and USEPA, (2001); the trend exhibited can be attributed to ammonia changing in proportion between its ionized and un-ionized forms, depending on water pH and temperature. Concentrations of total ammonia seldom reach toxic levels naturally, unless anaerobic conditions persist and nitrification is impeded (Wither, 1994). Similar trends have been observed in the works reported for Garhwal springs (Avnish *et al,* 2011).

Significantly ($p \leq 0.05$) higher levels of oxidised nitrogen were observed at both springs of Amala and Nyangores but with significantly ($p \leq 0.05$) higher levels in the wet season. The site levels for springs of Amala were highest at Siongiroi (614.75 ppb) and lowest at Chepkesoi (98.57 ppb), whereas in Nyangores the mean site concentration was highest at Kapsoen 2 (1024.46 ppb) and lowest at Teganda (336.05).

Table 4.4: Concentration levels of nutrients(ppb) in sediments from springs flowing into Amala

Spring		Kebenet	Chepudonge	Motiok	Chepkesoi	Kapangas 1	Kapangas 2	Ndong Ndong	Siongiroi	**Mean Season**
TP	Dry Season	53.76	85.19	65.64	52.39	90.11	127.22	376.15	136.13	123.32
	Wet Season	109.79	50.70	583.70	205.52	139.42	95.13	631.55	585.43	300.15
	Mean sites	81.77	67.95	324.67	128.95	114.76	111.18	503.85	360.78	
	CV (%)				0.25					
	LSD($p \leq 0.05$)				0.61					0.31
mmonium - nitrogen	Dry Season	65.40	38.79	23.58	40.78	138.38	93.14	87.85	78.21	70.77
	Wet Season	37.68	37.32	75.61	130.42	71.09	30.75	28.65	48.50	57.50
	Mean sites	51.54	38.05	49.60	85.60	104.74	61.94	58.25	63.35	
	CV (%)				0.89					
	LSD($p \leq 0.05$)				0.67					0.34
Oxidised nitrogen	Dry Season	172.08	479.09	127.78	127.58	452.51	153.32	482.36	147.05	267.72
	Wet Season	175.19	161.11	618.59	69.55	576.06	334.40	259.16	1082.45	409.56
	Mean sites	173.64	320.10	373.19	98.57	514.29	243.86	370.76	614.75	
	CV (%)				0.12					
	LSD($p \leq 0.05$)				0.49					0.25
Nitrates-nitrogen	Dry Season	34.36	71.20	37.67	37.58	61.37	54.11	77.99	34.36	51.08
	Wet Season	33.35	29.03	223.80	193.20	69.09	37.21	53.01	21.59	82.50
	Mean sites	33.81	50.07	130.73	115.39	65.23	45.66	65.50	27.93	
	CV (%)			0.11						
	LSD($p \leq 0.05$)			0.47						0.49
Nitrites-nitrogen	Dry Season	3.74	7.75	4.10	4.09	6.68	5.89	8.49	3.74	5.56
	Wet Season	3.63	3.16	24.36	21.03	7.52	4.05	5.77	2.35	8.98
	Mean sites	3.68	5.45	14.23	12.56	7.10	4.97	7.13	3.04	
	CV (%)				1.35					
	LSD($p \leq 0.05$)				0.12					0.06

The mean concentration for springs flowing into Amala were 267.72 ppb in the dry season and 409.56 ppb in the wet season, while for those flowing into Nyangores the mean seasonal concentrations recorded were 648.93 ppb and 610 ppb for dry and wet seasons, respectively. It was also observed, that significantly ($p \leq 0.05$) lower levels of nitrites were noted in the springs of both tributaries. The levels varied from a high of 14.23 ppb at Motiok and a low of 3.04 for springs flowing into Amala, and a high of 18.20 ppb and low of 4.56 ppb were recorded for the springs flowing into Nyangores. The risk of NO_2^- leaching is particularly high after the harvest, when plant uptake is low, but N-release as mineralization continues. Moreover, denitrification and leaching cause most N loss from a catchment. For example, aerobic conditions created by ploughing enable ammonification and subsequent nitrification that results in NO_2^- release from organic compounds in soils (Tisdale *et al.*, 1993). However, in forest soils, inorganic N concentrations are generally low and most N is in organic complexes associated with biological materials (Charkhabi and Sakizadeh, 2006).

Generally there was a significant ($p \leq 0.05$) increase in the levels of most of the measured nutrients during wet season caused by surface runoffs resulting in washing out of excess nutrients from the surrounding farms into the springs.

4.2.3.3. Seasonal variation of total phosphate.

The levels and seasonal variation of TP in sediments in springs flowing into Amala and Nyangores are presented in Tables 4.4 and 4.5 respectively. The seasonal variations were significant ($p \leq 0.05$) in both springs of Amala and Nyangores. The mean concentration for TP in sediments in springs of Amala was 123.32 ppb in the dry season and 300.15 ppb in the wet season, while springs in Nyangores registered a mean concentration of 483.17 ppb and 285 ppb in the dry and wet season, respectively. These high levels of TP in sediments can be explained by the fact that dissolved phosphate mineralized from organic phosphorus in marsh soil is less mobile than nitrate and tends to be retained in mineral soils (Tisdale *et al.*, 1993). Phosphorus retention capacity differs greatly among wetland types depending on the mineral content of their soils (Richardson, 1985). Organic-rich sediment is a major part of the peat which forms from decaying plants, but decaying plants also trap detrital mineral matter which becomes an integral part of sediment. The high levels of TP in springs are attributable to the increasing inputs of concentrated inorganic phosphorus from fertilizer sources, which are the main anthropogenic sources of phosphorus in aquatic ecosystems (Wither, 1994).

4.2.3.4. Seasonal variation of ammonium, nitrites, nitrates and oxidised nitrogen.

The levels and seasonal variations of Ammonium in sediments in springs flowing into Amala and Nyangores are presented in Tables 4.4 and 4.5 respectively. The mean seasonal concentration for ammonium varied significantly ($p \leq 0.05$) at 70.77 ppb and 57.50 ppb in dry and wet seasons, respectively, for springs in Amala, while springs in Nyangores registered mean concentrations of 80.01 ppb and 141.77 ppb ppb in dry and wet seasons, respectively.

The levels of seasonal variation of oxidised nitrogen in sediments in Amala and Nyangores are presented in Tables 4.4 and 4.5 respectively. The mean seasonal concentration for oxidised nitrogen varied significantly ($p \leq 0.05$) at 267.72 ppb and 409.56 ppb in dry and wet seasons, respectively, for springs in Amala, while springs in Nyangores recorded mean concentrations of 98.94 ppb and 87.28 ppb in dry and wet seasons, respectively.

The springs in both Amala and Nyangores catchment areas showed a significant increase in as expected in the wet season and could be attributable to anthropogenic activities, though the levels were within maximum allowable limits for drinking water as provided for by (WHO, 1996). A related scenario was reported in studies of springs in United States of America (Avnish *et al*, 2001; Charkhabi and Sakizadeh 2006 and Gregory, 1996)

Table 4.5: Concentration levels of nutrients (ppb) in sediments from springs flowing in Nyangores River.

Spring		Teganda	Kapsosrurwa	Silbwet	Sotionik 1	Sotionik 2	Ainabsabet	Kapsoen 1	Kapsoen 2	**Mean season**
TP	Dry Season	179.62	81.55	940.09	330.38	221.47	153.00	1018.30	940.93	483.17
	Wet Season	125.78	196.81	153.00	122.30	207.79	292.95	872.81	314.60	285.76
	Mean sites	152.70	139.18	546.55	226.34	214.63	222.98	945.56	627.77	
	CV (%)				1.37					
	LSD($p \leq 0.05$)				6.18					3.09
Ammonium -nitrogen	Dry Season	51.96	52.29	105.51	181.12	98.55	42.85	40.04	67.73	80.01
	Wet Season	131.47	77.19	47.63	81.32	278.54	187.16	175.82	154.57	141.71
	Mean sites	91.71	64.74	76.57	131.22	188.55	115.00	107.93	111.15	
	CV (%)				1.28					
	LSD($p \leq 0.05$)				1.67					0.83
Oxidised Nitrogen	Dry Season	277.93	255.32	980.72	110.17	911.95	530.58	411.02	1713.72	648.93
	Wet Season	394.16	1092.17	289.93	291.02	1031.09	350.11	1096.72	335.20	610.05
	Mean sites	336.05	673.75	635.33	200.60	971.52	440.35	753.87	1024.46	
	CV (%)				0.24					
	LSD($p \leq 0.05$)				1.78					0.89
Nitrates-nitrogen	Dry Season	39.78	35.00	269.64	231.24	82.77	44.47	63.48	25.08	98.94
	Wet Season	59.07	120.99	64.86	64.86	103.90	93.71	132.38	58.80	87.28
	Mean sites	49.43	78.00	167.20	148.09	93.34	69.09	97.93	41.89	
	CV (%)				1.49					
	LSD($p \leq 0.05$)				1.87					1.83
Nitrites-nitrogen	Dry Season	4.33	3.81	29.35	25.17	9.01	4.84	6.91	2.73	10.77
	Wet Season	6.43	13.17	7.06	7.06	11.31	10.20	14.41	6.40	9.50
	Mean sites	5.38	8.49	18.20	16.12	10.16	7.52	10.66	4.56	
	CV (%)				1.35					
	LSD($p \leq 0.05$)				0.16					0.08

4.2.4. Levels of heavy metals in spring water

4.2.4.1. Site variation of heavy metals in spring water

Results of heavy metals analysis in water from springs flowing into Amala and Nyangores are presented in Table 4.6 and 4.7. All the heavy metals with exception of Zn varied significantly ($p \leq 0.05$) in both springs flowing into Amala and Nyangores. Dissolved heavy metals in this study ranged between the lowest limit in Chepudonge for Pb (0.009 ppb) and Mn (0.014 ppb); Kapangas for Cu (0.073 ppb), Zn (0.004 ppb) and Se (0.055 ppb); Kebenet for Fe (0.448 ppb) and Cr (0.015 ppb) and Motiok for Cd (0.093 ppb) and the highest limit in Chepkesoi for Se (0.465 ppb) and Zn (0.602 ppb); Ndong Ndong for Mn (0.051 ppb) and

Zn (0.602 ppb); Kapangas 1for Cu (0.609 ppb) and 2 for Cd (0.988 ppb) in springs flowing into Amala. In Nyangores the highest values were recorded at Silbwet for Mn (0.058 ppb); Pb (0.020 ppb) and Fe (0.561 ppb); Ainabsabet for Cr (0.094 ppb) and Se (0.386 ppb); Kapsoen 1 for Zn (0.235 ppb) and Kapasoen 2 for Cd (0.042 ppb) and Sotionik for Cu (0.302 ppb). Whereas the lowest values were Sotionik 2 for Mn (0.017 ppb); Kapsoen1 for Cu (0.137 ppb); Kapsoen 2 for Zn (0.109); Ainabsabet for Fe (0.439 ppb) and Pb (0.003 ppb); Kapsosurwa for Cr (0.064 ppb); Tenganda for Cd (0.013) and Silibwet for Se (0.095 ppb). Heavy metals (Mn, Cu, Fe Zn, Pb, Cr, Cd, Zn and Se) concentrations in spring water samples differed greatly in Amala and Nyangores.

The springs contributions to River Amala and Nyangores was statistically significantly ($p \leq 0.05$) different. This was probably due to the fact that the solubility of all the studied heavy metals increased with reduction in pH (Alloway, 1995); the pH of the spring water was on average 6.0, a value at which the heavy metals start being soluble hence easily transported in the aquatic environment. The same results can also be supported by the fact that the heavy metals correlated positively with each other further indicating their common origin. The increase in the concentrations during the wet season can be attributed to surface runoffs that acted as transport agents for the heavy metals from the farms to the springs. Furthermore, soil erosion and leaching also aid in heavy metal transport from the tea plantations to the springs hence the increased concentrations in water samples during the wet season.

All the heavy metals analyzed in water recorded a low concentration within the springs across the sites. The low concentration of the heavy metals in the springs is attributed to presence of these trace elements in the agricultural inputs, applied in the farm lands and natural degradation of rocks containing the elements. Comparable differences in levels of some heavy metals of springs from the same catchment had been observed in other studies.

Table 4.6: Heavy metals concentration levels (µg/L) in waters from springs flowing in Amala River.

Spring		Kebenet	Chepudonge	Motiok	Chepkesoi	Kapangas 1	Kapangas 2	Ndong Ndong	Siongiroi	Mean Season
Mn	Dry Season	0.01	0.01	0.04	0.03	0.02	0.02	0.05	0.03	0.03
	Wet Season	0.02	0.02	0.06	0.03	0.02	0.03	0.06	0.04	0.03
	Mean sites	0.02	0.02	0.05	0.03	0.02	0.02	0.05	0.03	
	CV (%)					8.03				
	LSD(p≤0.05)					0.00				0.00
Cu	Dry Season	0.69	0.17	0.16	0.27	0.28	0.06	0.173	0.376	0.273
	Wet Season	0.08	0.22	0.21	0.34	0.94	0.08	0.223	0.485	0.324
	Mean sites	0.39	0.20	0.19	0.31	0.61	0.073	0.198	0.431	
	CV (%)					2.09				
	LSD(p≤0.05)					0.01				0.002
Fe	Dry Season	0.00	0.60	0.83	0.50	0.73	0.54	0.58	0.80	0.57
	Wet Season	0.89	0.78	1.07	0.64	0.94	0.69	0.75	1.04	0.85
	Mean sites	0.45	0.69	0.95	0.57	0.83	0.62	0.66	0.92	
	CV (%)					3.48				
	LSD(p≤0.05)					0.02				0.01
Zn	Dry Season	0.01	0.00	0.01	0.38	0.01	0.00	0.53	0.24	0.15
	Wet Season	0.01	0.01	0.10	0.50	0.01	0.00	0.68	0.31	0.20
	Mean sites	0.01	0.01	0.05	0.44	0.01	0.00	0.60	0.28	
	CV (%)					0.85				
	LSD(p≤0.05)					0.00				0.00
Pb	Dry Season	0.85	0.01	0.03	0.02	0.02	0.00	0.01	0.02	0.12
	Wet Season	0.01	0.01	0.05	0.03	0.03	0.01	0.02	0.03	0.02
	Mean sites	0.43	0.01	0.04	0.03	0.02	0.01	0.01	0.02	
	CV (%)					8.87				
	LSD(p≤0.05)					0.00				0.00
Cr	Dry Season	0.01	0.03	0.04	0.04	0.03	0.02	0.03	0.05	0.03
	Wet Season	0.02	0.04	0.05	0.05	0.04	0.03	0.04	0.06	0.04
	Mean sites	0.02	0.04	0.04	0.05	0.04	0.02	0.04	0.06	
	CV (%)					6.02				
	LSD(p≤0.05)					0.010				0.005
Cd	Dry Season	0.14	0.19	0.08	0.40	0.48	0.86	0.27	0.72	0.39
	Wet Season	0.19	0.24	0.11	0.52	0.62	1.11	0.34	0.92	0.51
	Mean sites	0.17	0.22	0.09	0.46	0.55	0.99	0.31	0.82	
	CV (%)					10.87				
	LSD(p≤0.05)					0.00				0.00
Se	Dry Season	0.69	0.17	0.08	0.40	0.48	0.03	0.04	0.06	0.25
	Wet Season	0.05	0.17	0.58	0.53	0.01	0.08	0.03	0.27	0.21
	Mean sites	0.37	0.17	0.33	0.47	0.25	0.06	0.04	0.16	
	CV (%)					0.40				
	LSD(p≤0.05)					0.00				0.00

In Florida, the Fe and Al (Hamilton and King, 1983) and Cu (Harvey and Wargner, 2000) levels from different springs significantly varied in the past studies. In North Carollina, Fe and Mn levels in springs from different catchement were significantly different (Gregory, 1996).

4.2.4.2. Seasonal variation of heavy metals in spring water

The seasonal variations of heavy metals in spring water of springs flowing into Amala and Nyangores are presented in Tables 4.6 and 4.7 respectively. All the heavy metals varied significantly ($p \leq 0.05$) with exception of Zn in both catchment areas. The heavy metals in study sites in springs flowing into Amala ranged between 0.026 ppb for Cu in dry season and 0.034 ppb in wet season to 0.245 ppb for Se in the dry season and 0.214 ppb in the wet season, while on Nyangores it ranged between 0.023 ppb for Cu in the dry season and 0.034 ppb in the wet season to 0.245 ppb for Se in the dry season and 0.214 ppb in the wet season. Variability in the distribution of metals appeared to be more related to hydro biological conditions (Sankar *et al.*, 2010). The components may also have been washed from the atmosphere through run-off, windblown dust, forest fire and some agricultural inputs, adding to the distribution of heavy metals in water as noted in other past studies by Govindasamy *et al.*, (2000) and Bryan, (1984). Seasonal variation in heavy metals concentration in the spring water may have arisen as a result of the rapid growth of population and increased agricultural activities Abdel-Baki *et al.*, (2011). The level of heavy metals recorded in water in this study are generally low when compared with the limit values suggested by WHO (1996), and USEPA (1986).

Table 4.7: Heavy metals concentration levels (µg/L) in water from springs flowing into Nyangores River.

Spring		Teganda	Kapsosrurwa	Silbwet	Sotionik 1	Sotionik 2	Ainabsabet	Kapsoen 1	Kapsoen 2	**Mean Season**
Mn	Dry Season	0.013	0.012	0.039	0.023	0.014	0.018	0.041	0.026	0.023^{b}
	Wet Season	0.032	0.027	0.076	0.021	0.020	0.022	0.026	0.018	0.030^{a}
	Mean sites	0.023^{c}	0.020d^{c,e}	0.058^{a}	0.022d^{c}	0.017^{c}	0.020^{d,c,e}	0.034^{b}	0.022^{c}	
	CV (%)					9.435				
	LSD($p \leq 0.05$)					0.003				0.002
Cu	Dry Season	0.057	0.154	0.143	0.237	0.247	0.057	0.153	0.334	0.173^{b}
	Wet Season	0.456	0.183	0.214	0.367	0.265	0.285	0.121	0.026	0.240^{a}
	Mean sites	0.257^{a,b}	0.169b^{c}	0.179b^{c}	0.302^{a}	0.256^{b,a}	0.171b^{c}	0.137^{c}	0.180b^{c}	
	CV (%)					43.010				
	LSD($p \leq 0.05$)					0.104				0.052
Fe	Dry Season	0.613	0.537	0.733	0.443	0.647	0.477	0.513	0.713	0.585^{a}
	Wet Season	0.268	0.508	0.388	0.628	0.507	0.400	0.544	0.256	0.437^{b}
	Mean sites	0.441^{d}	0.523^{b}	0.561^{a}	0.536^{b}	0.577^{a}	0.439^{d}	0.529^{b}	0.485^{c}	
	CV (%)					3.095				
	LSD($p \leq 0.05$)					0.019				0.009
Zn	Dry Season	0.003	0.004	0.005	0.341	0.005	0.003	0.467	0.215	0.130^{a}
	Wet Season	0.002	0.002	0.006	0.004	0.002	0.002	0.002	0.002	0.003^{b}
	Mean sites	0.003^{f,e}	0.002^{f,e}	0.006^{d}	0.173^{b}	0.003^{e}	0.003^{e}	0.235^{a}	0.109^{c}	
	CV (%)					0.901				
	LSD($p \leq 0.05$)					0.001				0.000
Pb	Dry Season	0.007	0.007	0.026	0.020	0.018	0.003	0.011	0.018	0.016^{a}
	Wet Season	0.019	0.013	0.014	0.011	0.002	0.002	0.025	0.019	0.013^{b}
	Mean sites	0.013^{d}	0.010^{e}	0.020^{a}	0.016^{c}	0.010^{e}	0.003d^{e}	0.018^{b}	0.019^{a}	
	CV (%)					9.602				
	LSD($p \leq 0.05$)					0.002				0.001
Cr	Dry Season	0.753	0.072	0.063	0.093	0.083	0.096	0.074	0.064	0.162^{a}
	Wet Season	0.067	0.056	0.076	0.068	0.081	0.091	0.078	0.089	0.076^{b}
	Mean sites	0.410^{a}	0.064^{f}	0.070^{e}	0.081^{c}	0.082^{c}	0.094^{b}	0.076^{d}	0.077^{d}	
	CV (%)					2.147				
	LSD($p \leq 0.05$)					0.003				0.002
Cd	Dry Season	0.012	0.028	0.031	0.036	0.028	0.018	0.027	0.042	0.028^{a}
	Wet Season	0.013	0.017	0.025	0.040	0.013	0.032	0.037	0.041	0.027^{a}
	Mean sites	0.013^{f}	0.023^{e,d}	0.028^{c,b}	0.038^{a}	0.020^{e}	0.025^{c,d}	0.032^{b}	0.042^{a}	
	CV (%)					11.933				
	LSD($p \leq 0.05$)					0.004				0.002
Se	Dry Season	0.128	0.167	0.072	0.359	0.427	0.766	0.237	0.635	0.349^{a}
	Wet Season	0.190	0.023	0.128	0.168	0.083	0.006	0.030	0.071	0.087^{b}
	Mean sites	0.159^{c}	0.095^{h}	0.100^{g}	0.264^{c}	0.255d	0.386^{a}	0.134^{f}	0.353^{b}	
	CV (%)					0.439				
	LSD($p \leq 0.05$)					0.001				0.001

* Means with the same letters are not significantly ($p \leq 0.05$) different

4.2.5. Levels of heavy metals in sediments of spring waters

4.2.5.1. Site variation of heavy metals in sediments

The site variations of heavy metals in sediments of springs flowing into Amala and Nyangores are presented in Table 4.8 and 4.9, respectively. The levels of all the heavy metals in springs flowing into Amala and Nyangores varied significantly ($p \leq 0.05$). Generally, the trend observed is the levels of heavy metals in the spring sediments were slightly higher than those of the water samples. For sediment sample of springs flowing into

Amala, Motiok recorded the highest levels for Mn (0.05 ppb); Kapangas 1 for Cu (0.609 ppb); Siongiroi for Fe (0.920 ppb) and Cr (0.055 ppb); Ndong Ndong for Zn (0.602 ppb) and Kapangas 2 for Cd (0.988 ppb) and Se (0.055 ppb). The lowest site levels in springs flowing into Amala were recorded at Chepudonge for Mn (0.015 ppb); Motiok for Cu (0.185); Kebenet for Fe (0.448), Cr (0.015) and Cd (0.165) and Siongiroi for Se (0.164). In Nyangores, the highest values were recorded at Silbwet for Mn (0.082 ppb); Sotionik 1 for Cu (0.020 ppb); Zn (0.005 ppb) and Fe (0.387 ppb); Tenganda for Pb (0.023 ppb) and Se (0.224 ppb) and Kapsoen 2 for Cd (0.048 ppb). The lowest values for springs in Nyangores were recorded at Kapsoen 2 for Mn (0.002 ppb), Fe (0.158 ppb) and Cu(0.136 ppb); Sotionik 2 for Pb (0.003 ppb) and Cd (0.015 ppb); Tenganda for Se (0.002) and all sites for Zn (0.002 ppb) except Silbwet and Sotionik 1. Sediments represent one of the ultimate sinks for heavy metal discharges into the environment; mean seasonal levels of sediment heavy metals in the study sites of springs flowing into Amala and Nyangores are presented in Table 4.6 and 4.8 respectively. The results showed low levels of heavy metals in residual phase of sediment in the springs under study.

The low levels of heavy metals observed in the springs could probably be as a result of a geomorpholical gradient traversed by spring water before emerging on the surface. Contrary observations were made on studies by Mohiuddin *et al.* 2011 wheras similar observations were made in studies by Mzimela *et al.* (2003) in South Africa and (Harvey and Wagner, 2000) in Florida, USA. The range of the levels revealed that nearly all the profiles for Mn, Cu, Fe, Zn, Pb, Cr, Cd and Se fell into class I (Table 4.16) of the Turkish environmental guideline values. The levels of heavy metals for all the springs surveyed are <50 µg/L indicating practically unpolluted spring sediments. This trend is not surprising since these springs are located at a distance from the probable anthropogenic pollution sources due to farming and agricultural chemicals and or most of them are protected. However, Siongiroi and Kapangas 1 and 2 are slightly higher and could be affected by effects of some anthropogenic and natural sources of the elements examined.

The levels of heavy metals in sediments of springs flowing into Nyangores are outlined in Table 4.8, and they are significantly low, although they exhibit a high coefficient of variation. These levels ranged between 0.026 ppb for Mn in the dry season (as minimum level) and 0.850 ppb for Fe in the wet season (as maximum level) for springs flowing into Amala. The moderately high concentrations recorded in the sediments of some springs may be attributed to discharge from commercial fertilizers and pesticides or insecticides used in farming in areas close to the springs, that may contain metals as well as the ability of the sediments to act as sinks (Olowu *et al.*, 2010). Heavy metal contamination in sediment can affect the water quality and bioaccumulation of metals in aquatic organisms, resulting in potential long term implications on human health and ecosystems (Olowu *et al.*, 2010). In addition, excretion and elimination of exoskeletons by abundantly occurring plankton and by settlement of particulate matter may probably have played a significant role in enhancing the concentration of heavy metals in the sediments (Sankar, *et al.*, 2010). The behavior and distribution of heavy metals in sediments may be affected by water hydrology and many biological, chemical and geological operations occur in aquatic systems (Mohiuddin *et al.*, 2011).

Table 4.8: *Concentration levels (ppb) of heavy metals in sediments from springs flowing into Amala River.*

Spring		Kebenet	Chepudonge	Motiok	Chepkesoi	Kapangas1	Kapangas 2	Ndong Ndong	Siongiroi	Mean Season
Mn	Dry Season	0.01	0.01	0.04	0.03	0.02	0.02	0.05	0.03	0.03
	Wet Season	0.02	0.02	0.06	0.03	0.02	0.03	0.06	0.04	0.03
	Mean sites	0.02	0.02	0.05	0.03	0.02	0.02	0.05	0.03	
	CV (%)					2.50				
	LSD(p≤0.05)					0.00				0.00
Cu	Dry Season	0.69	0.17	0.16	0.27	0.28	0.06	0.17	0.38	0.19
	Wet Season	0.08	0.22	0.21	0.34	0.94	0.08	0.22	0.49	0.25
	Mean sites	0.39	0.20	0.19	0.31	0.61	0.07	0.20	0.43	
	CV (%)					1.72				
	LSD(p≤0.05)					0.01				0.00
Fe	Dry Season	0.00	0.60	0.83	0.50	0.73	0.54	0.57	0.80	0.66
	Wet Season	0.89	0.78	1.07	0.64	0.94	0.69	0.75	1.04	0.85
	Mean sites	0.45	0.69	0.95	0.57	0.83	0.62	0.66	0.92	
	CV (%)					3.69				
	LSD(p≤0.05)					0.03				0.03
Zn	Dry Season	0.01	0.00	0.01	0.38	0.01	0.00	0.53	0.24	0.15
	Wet Season	0.01	0.01	0.10	0.50	0.01	0.00	0.68	0.31	0.20
	Mean sites	0.01	0.01	0.05	0.44	0.01	0.00	0.60	0.28	
	CV (%)					0.45				
	LSD(p≤0.05)					0.00				0.00
Pb	Dry Season	0.85	0.01	0.03	0.02	0.02	0.00	0.01	0.02	0.12
	Wet Season	0.01	0.01	0.05	0.03	0.03	0.01	0.02	0.03	0.02
	Mean sites	0.43	0.01	0.04	0.02	0.02	0.01	0.01	0.02	
	CV (%)					1.12				
	LSD(p≤0.05)					0.00				0.00
Cr	Dry Season	0.01	0.03	0.04	0.04	0.03	0.02	0.03	0.05	0.03
	Wet Season	0.02	0.04	0.05	0.05	0.04	0.03	0.04	0.06	0.04
	Mean sites	0.02	0.037	0.04	0.05	0.04	0.02	0.04	0.06	
	CV (%)					4.76				
	LSD(p≤0.05)					0.01				0.01
Cd	Dry Season	0.14	0.19	0.08	0.40	0.48	0.86	0.27	0.76	0.39
	Wet Season	0.19	0.24	0.11	0.52	0.62	1.11	0.34	0.92	0.51
	Mean sites	0.17	0.22	0.09	0.46	0.55	0.99	0.31	0.82	
	CV (%)					2.10				
	LSD(p≤0.05)					0.00				0.00
Se	Dry Season	0.69	0.17	0.08	0.40	0.48	0.03	0.04	0.06	0.25
	Wet Season	0.05	0.17	0.58	0.53	0.01	0.08	0.03	0.27	0.21
	Mean sites	0.37	0.17	0.33	0.47	0.25	0.06	0.04	0.16	
	CV (%)					0.20				
	LSD(p≤0.05)					0.01				0.00

4.2.5.2. Seasonal variation of heavy metals in sediments

The seasonal variations of heavy metals in sediments flowing into Amala and Nyangores are presented in Tables 4.8 and 4.9, respectively. All the heavy metals of sediments of springs flowing into Nyangores varied significantly with season whereas for sediments of springs flowing into Amala, Cu, Fe, Cr and Se varied significantly as Pb,Mn and Zn did not vary significantly. The mean seasons ranged from 0.026 ppb for.Mn in springs of Amala in dry season to 0.850 ppb for Fe in the wet season. Teganda, Kapsosrurwa and Silbwet located upstream of Nyangores River and are associated with intensive farming recorded higher levels of heavy metals in water samples than Ainabsabet, Kapsoen 1 and Kapsoen 2 that are downstream of Nyangores River with low human activity. There was significant ($p \leq 0.05$) interaction effect for all the heavy metals, indicating that the responses did not occur in a uniform pattern. Results of this study agree with levels reported earlier by Palamuleni (2002), Schulze *et al.* (2001) and Tsiouris *et al.* (2001).

Table 4.9: *Concentration levels (ppb) of heavy metals in sediments from springs flowing into Nyangores River.*

Spring		Teganda	Kapsosrurwa	Silbwet	Sotionik 1	Sotionik 2	Ainabsabet	Kapsoen 1	Kapsoen 2	**Mean season**
Mn	Dry Season	0.03	0.03	0.07	0.02	0.02	0.02	0.02	0.02	0.03
	Wet Season	0.04	0.03	0.09	0.03	0.03	0.03	0.03	0.02	0.04
	Mean sites	0.04	0.03	0.08	0.02	0.02	0.02	0.03	0.02	
	CV (%)					11.76				
	LSD(p≤0.05)					0.01				0.00
Cu	Dry Season	0.25	0.47	0.36	0.59	0.48	0.38	0.51	0.24	0.41
	Wet Season	0.56	0.22	0.26	0.45	0.33	0.35	0.15	0.03	0.29
	Mean sites	0.41	0.35	0.31	0.52	0.40	0.36	0.33	0.14	
	CV (%)					30.89				
	LSD(p≤0.05)					0.13				0.06
Fe	Dry Season	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
	Wet Season	0.33	0.62	0.48	0.77	0.62	0.49	0.67	0.31	0.54
	Mean sites	0.16	0.31	0.24	0.39	0.31	0.25	0.34	0.16	
	CV (%)					2.10				
	LSD(p≤0.05)					0.01				0.003
Zn	Dry Season	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
	Wet Season	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00
	Mean sites	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	
	CV (%)					28.97				
	LSD(p≤0.05)					0.00				0.001
Pb	Dry Season	0.02	0.02	0.02	0.01	0.00	0.03	0.03	0.02	0.02
	Wet Season	0.02	0.02	0.02	0.01	0.00	0.03	0.03	0.02	0.02
	Mean sites	0.02	0.02	0.02	0.01	0.00	0.03	0.03	0.02	
	CV (%)					12.54				
	LSD(p≤0.05)					0.00				0.00
Cr	Dry Season	0.08	0.06	0.09	0.08	0.09	0.10	0.09	0.10	0.09
	Wet Season	0.08	0.07	0.09	0.08	0.10	0.11	0.10	0.11	0.09
	Mean sites	0.078	0.07	0.09	0.08	0.10	0.11	0.09	0.11	
	CV (%)					2.79				
	LSD(p≤0.05)					0.00				0.00
Cd	Dry Season	0.02	0.02	0.03	0.05	0.01	0.04	0.04	0.05	0.03
	Wet Season	0.02	0.02	0.03	0.05	0.02	0.04	0.05	0.05	0.03
	Mean sites	0.02	0.02	0.03	0.05	0.02	0.04	0.04	0.05	
	CV (%)					16.93				
	LSD(p≤0.05)					0.01				0.00
e	Dry Season	0.21	0.03	0.14	0.19	0.09	0.01	0.03	0.08	0.10
	Wet Season	0.23	0.03	0.16	0.21	0.10	0.01	0.04	0.09	0.11
	Mean sites	0.22	0.03	0.15	0.20	0.10	0.01	0.04	0.08	
	CV (%)					1.35				
	LSD(p≤0.05)					0.00				0.00

4.3. Comparison of the water quality parameters from the different sites and seasons with the national, international standards and other studies

4.3.1. Comparison of water quality parameters of springs flowing in Amala and Nyangores

The means of the water quality parameters were subjected to a student t- test to compare if the water levels of water quality parameters of springs flowing into Amala are equal to those of springs flowing into Nyangores with the assumption that their variances are equal. The results are presented in Tables 4.10 to 4.13.

Table 4.10: Student t test of Amala and Nyangores data for Temperature and pH in water samples

Table Analyzed	Temperature Paired t test data	pH Paired t test data
Column B vs. Column A	Amala vs. Nyangores	Amala vs. Nyangores
Paired t test		
P value	0.3849	0.1428
P value summary	ns	Ns
Significantly different? (p≤ 0.05)	No	No
One- or two-tailed P value?	Two-tailed	Two-tailed
t,	t=0.9267	t=1.651
df	df=7	df=7
Number of pairs	8	8
How big is the difference?		
Mean of differences	2.059	0.1275
SD of differences	6.284	0.2185
SEM of differences	2.222	0.07725
95% confidence interval	-3.195 to 7.312	-0.05516 to 0.3102
R squared	0.1093	0.2802
How effective was the pairing?		
Correlation coefficient (r)	-0.09142	0.2077
P value (one tailed)	0.4148	0.3108
P value summary	ns	Ns
Was the pairing significantly effective?	No	No

From Table 4.10, the *P*-value obtained is larger than 0.05, because of the random variation, the difference between the tributaries means in this experiment is unlikely to be equal to the difference between population means. There is no way to know what the true difference is;

hence the treatment has no effect or the effect is so small or it is an informative negative experiment.

Table 4.11: Student t test of Amala and Nyangores data for nutrients in water samples

	SRP	TP	Ammonium	Oxidized Nitrogen	Nitrites
Table Analyzed	Paired t test data	Paired t test data	Paired t test data	Paired t test data	Paired t test data
Column B	Amala	Amala	Amala	Amala	Amala
vs.	vs.	vs.	vs.	vs.	vs.
Column A	Nyangores	Nyangores	Nyangores	Nyangores	Nyangores
Paired t test					
P value	0.9006	0.0798	0.2530	0.5768	0.5188
P value summary	ns	ns	ns	ns	Ns
Significantly different? ($p \leq 0.05$)	No	No	No	No	No
One- or two-tailed P value?	Two-tailed	Two-tailed	Two-tailed	Two-tailed	Two-tailed
t, df	t=0.1295 df=7	t=2.048 df=7	t=1.245 df=7	t=0.5852 df=7	t=0.6792 df=7
Number of pairs	8	8	8	8	8
How big is the difference?					
Mean of differences	-0.07375	12.20	-8.516	6.645	0.1637
SD of differences	1.611	16.85	19.34	32.11	0.6819
SEM of differences	0.5694	5.957	6.838	11.35	0.2411
95% confidence interval	-1.420 to 1.273	-1.888 to 26.29	-24.69 to 7.653	-20.20 to 33.49	-0.4063 to 0.7338
R squared	0.002390	0.3746	0.1814	0.04665	0.06183
How effective was the pairing?					
Correlation coefficient (r)	0.9719	0.9965	0.6249	0.9811	0.9948
P value (one tailed)	< 0.0001	< 0.0001	0.0488	< 0.0001	< 0.0001
P value summary	****	****	*	****	****
Was the pairing significantly effective?	Yes	Yes	Yes	Yes	Yes

It is evident from the student t-test for nutrients in water samples that the *P*-value obtained is larger than 0.05 as seen in Table 4.11, because of the random variation; the difference between the tributaries means in this experiment is unlikely to be equal to the difference between population means. There is no way to know what the true difference is; hence the treatment has no effect or the effect is so small or it is an informative negative experiment.

Table 4.12: Student t test of Amala and Nyangores data for heavy metals in water samples

Table Analyzed	Mn Paired t test data	Cu Paired t test data	Fe Paired t test data	Zn Paired t test data	Pb Paired t test data	Cr Paired t test data	Cd Paired t test data	Se Paired t test data
Column B	Amala	Amala	Amala	Amala	Amala	Amala	Amala	Amala
vs.	vs.	vs.	vs.	vs.	vs.	vs.	vs.	vs.
Column A	Nyangores	Nyangores	Nyangores	Nyangores	Nyangores	Nyangores	Nyangores	Nyangores
Paired t test								
P value	0.3999	0.1204	0.0076	0.0729	0.3025	0.1059	0.0070	0.8791
P value summary	Ns	ns	**	ns	ns	ns	**	Ns
Significantly different? (p≤0.05)	No	No	Yes	No	No	No	Yes	No
One- or two-tailed P value?	Two-tailed	Two-tailed	Two-tailed	Two-tailed	Two-tailed	Two-tailed	Two-tailed	Two-tailed
t,	t=0.8962	t=1.768	t=3.704	t=2.109	t=1.113	t=1.856	t=3.763	t=0.1578
df	df=7	df=7	df=7	df=7	df=7	df=7	df=7	df=7
Number of pairs	8	8	8	8	8	8	8	8
How big is the difference?								
Mean of differences	0.003125	0.09188	0.1998	0.1071	0.05713	-0.08325	0.4224	0.0115
SD of differences	0.009862	0.1470	0.1525	0.1437	0.1452	0.1269	0.3175	0.2062
SEM of differences	0.003487	0.05196	0.05393	0.05080	0.05133	0.04486	0.1122	0.07290
95% confidence interval	-0.005120 to 0.01137	-0.03099 to 0.2147	0.07223 to 0.3273	-0.01301 to 0.2273	-0.06426 to 0.1785	-0.1893 to 0.02283	0.1569 to 0.6878	-0.1609 to 0.1839
R squared	0.1029	0.3087	0.6621	0.3884	0.1503	0.3297	0.6692	0.003543
How effective was the pairing?								
Correlation coefficient (r)	0.7662	0.5635	0.5552	0.9984	0.008387	-0.6991	0.3621	-0.1955
P value (one tailed)	0.0133	0.0729	0.0766	< 0.0001	0.4921	0.0268	0.1890	0.3213
P value summary	*	Ns	ns	****	ns	*	Ns	Ns
Was the pairing significantly effective?	Yes	No	No	Yes	No	Yes	No	No

A treatment of data set from Amala and Nyangores for heavy metals as observed in Table 4.12 reveals that the *P*-value obtained is larger than 0.05 for Mn, Cu, Zn, Pb, Cr and Se for the Amala and Nyangores groups while *P*-values obtained for Fe and Cd were lower than 0.05 meaning that the difference or correlation observed would rarely occur due to random sampling. A closer look at this mix, we can conclude that the null hypothesis is false, there is truly a difference but the difference is so small that is scientifically uninteresting, the difference is real but trivial.

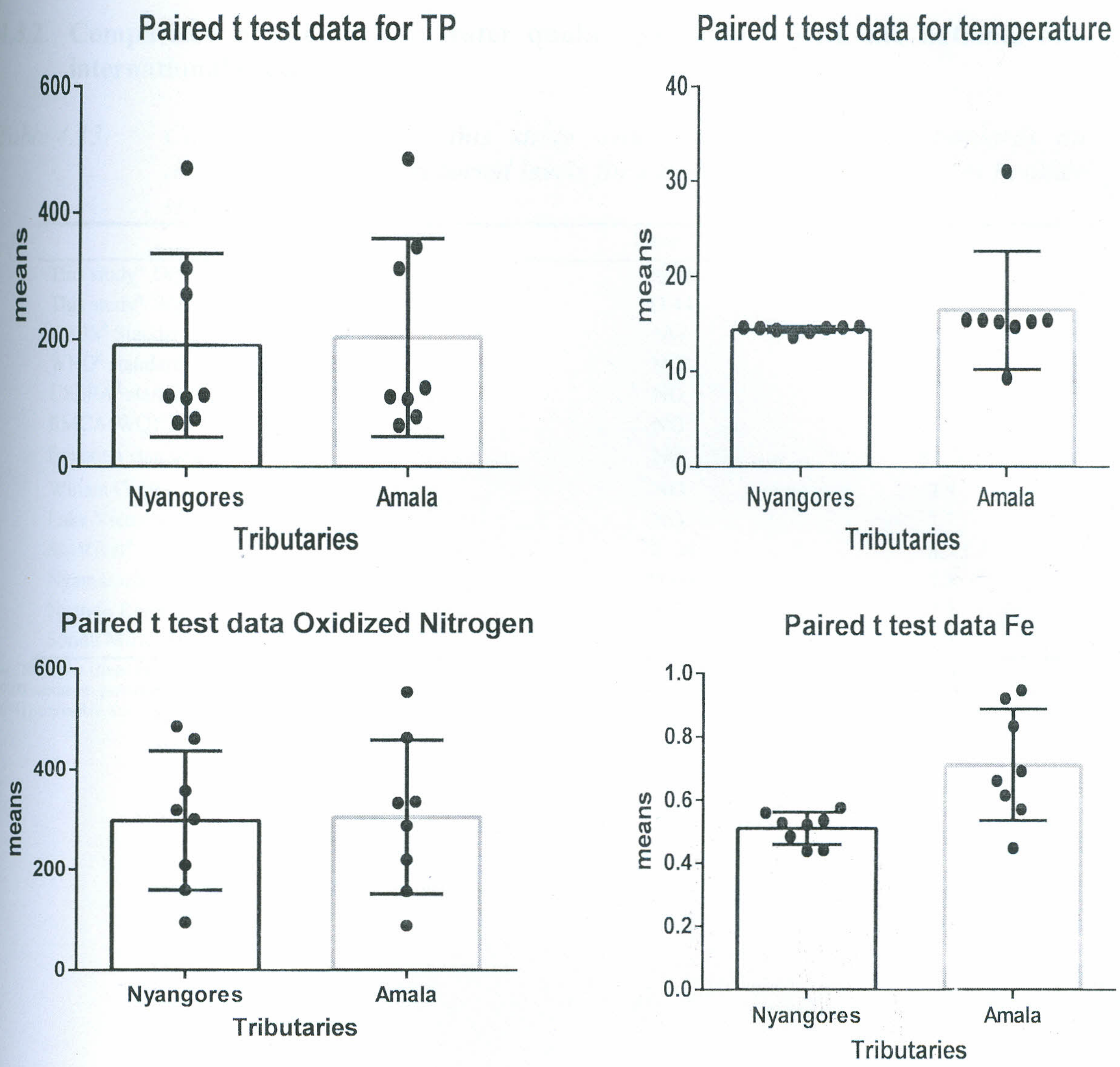


Figure 4.1. Graphical representation of Student t test results for selected parameters in water samples

4.3.2. Comparison of the seasons water quality parameters with the national and international standards

Table 4.13: Comparison between this study with some international standards on domestic water and reported levels for physicochemical parameters in other studies

	Temp ^{0}C	pH
This study[a] Dry season	26.35	7.44
This study[a] Wet season	23.44	6.22
KEBS[b] Standard	NG	6.5-8.5
WHO[c] standard	NG	6.5-8.5
USEPA[d] standard	NG	6.0-9.5
EMCA(WQ)[g]2006 std	NG	6.5-8.5
Egyptian standard[f]	NG	6 – 9
Winam Gulf[e]	NG	7.8
Lake Victoria[e]	NG	7.7
Sio River[e]	28. 00	8.5
Nyamasaria River[e]	28.00	7.3
Nyando River[e]	26.00	7.5
Sondu Miriu River[e]	28.00	7.6

Key: NG – Not Given in literature. **a** – This study 2010 Kenya (number of examined samples:36), **b** – KEBS (1996) maximum permissible limits, **c** – WHO (1993) maximum permissible limits, **d** – USEPA (1979) permissible limits, **e** – Ongeri (2008) downstream for rivers, **f** – ECS (Egyptian chemical standards) (1994) permissible limits, **g** – Kenyan EMCA (WQ) (2006) Standards.

Table 4.14: Comparison between this study with other studies for heavy metals in domestic water

	Mn µg/L	Cu µg/L	Fe µg/L	Zn µg/L	Pb µg/L	Cr µg/L	Cd µg/L	Se µg/L
This study[a] Nyangores Dry season	0.026	0.273	0.572	0.147	0.120	0.031	0.393	0.245
This study[a] Nyangores Wet season	0.034	0.324	0.850	0.201	0.021	0.040	0.507	0.214
This study[a] Amala Dry season	0.023	0.173	0.585	0.130	0.014	0.162	0.028	0.349
This study[a] Amala Wet season	0.030	0.240	0.437	0.003	0.013	0.076	0.027	0.087
KEBS[b] Standard	NG	50	100	5000	300	300	300	300
WHO[c] standard	NG	10	1000	5000	300	300	300	300
Waterquality criteria[d] CMC	16	65	13	120	NG	NG	NG	NG
CCC	11	25	9	120	NG	NG	NG	NG
Turkish env. Guideline[e]: Class	20	10	20	200	NG	NG	NG	NG
i	50	20	50	500	50	20	50	500
Class ii	200	50	200	2000	200	50	200	2000
Class iii	>200	>50	>200	>2000	>200	>50	>200	>2000
Class iv								
Dil Deresi Stream[f]	16-110	11-370	11-94	150-4100	NG	NG	NG	NG
Indian River Florida[g]	0.15	0.025	1.1	0.8	NG	NG	NG	NG
Lambro River Italy[h]	2-66	2.2-138.8	1.1-134.4	NG	NG	NG	NG	NG
Gediz River Turkry[i]	1-17	10-110	4.84	3-46	NG	NG	NG	NG
USEPA[j]	NG	5	50	5000	300	300	300	300
UK[k]	NG	NG	50	5000	200	200	200	200
EU[k]	NG	5	10	100-5000	200	200	200	200
Canada[k]	NG	5	50	5000	300	300	300	300
USA[k]	NG	5	15	5000	300	300	300	300
Russia[k]	NG	3	100	5000	300	300	300	300
Winam gulf[m]	NG	14.2	53.60	237	2778	2778	2778	2778
Rain water[m] (L. Victoria basin)	NG	NG	47.90	228.5	216.5	216.5	216.5	216.5
Well water[m] (L. Victoria basin)	NG	13.8	48.00	213.5	132.5	132.5	132.5	132.5
Municipal water[m] (L. Victoria basin)	NG	20.8	44.7	267.9	522.6	522.6	522.6	522.6
Nyamasaria river[m]	NG	4.6	52.40	253.1	3.049	3.049	3.049	3.049
Nyando river[m]	NG	14.4	57.50	232.3	2835	2835	2835	2835
Sondu mirio river[m]	NG	18.4	47.00	225.2	2320	2320	2320	2320
Dipsiz river[n]	0.092	0.405	0.365	1.051	NG	NG	NG	NG
Background Conc. World average	NG	0.2	1.00	10	NG	NG	NG	NG

Key: NG – Not Given in literature. ND Not Detected **a** – This study 2010 Kenya (number of examined samples: 16 for spring water) **b** – KEBS (1996), **c** – WHO (1998), **d** - USEPA (1999), **e** – Turkish Environmental guidelines (1988), **f** – Perkey *et al.* (2004), **g** – Trocine and Trefry (1996), **h** – Pettine *et al.* (1996), **i** – Bakaa and Kumru (2001), **j** - USEPA (1980), **k** – Neubauer and Wolf (2004), **l** – Klavins *et al.* (2000), **m** – Ongeri (2008), **n** – Ahmet *et al.* (2005), Class i – Clean water for domestic use, Class ii - Fairly clean water for domestic use, Class iii – Polluted water, Class iv – Heavily polluted water.

CHAPTER FIVE

5.1. CONCLUSIONS AND RECOMMENDATIONS

5.2. Summary

This study revealed that physical parameters investigated temperature and pH did vary significantly with spring (site) and also with season in both Amala and Nyangores catchment areas, water temperatures of the springs of Nyangores and Amala were generally low, though within the acceptable limits for drinking water standards. The nutrient concentration in the springs with regard to nitrogen and phosphorus were slightly higher in the wet season than the dry season an indication that anthropogenic activities were affecting the spring waters albeit to a minimal extent.

Heavy metals were to a lesser extent anthropogenically enriched in the sediments. The heavy metals concentrations in both water and sediments were generally low in relation to acceptable limits for drinking water standards for both WHO, (1996) and KEBS, (1996) with higher concentrations in sediments than in water. The overall physicochemical load was higher in the wet season than in the dry season, and none of the tributaries contributed more physicochemical load into the River Mara as a result of physicochemical load of the spring water and sediments. There was no statistically significant contribution of nutrients from springs flowing into the Amala and Nyangores tributaries and subsequently into the Mara River. However, for heavy metals the contribution was so small that it can be ignored.

5.3. Conclusions

- Anthropogenic activities at the catchment of Amala and Nyangores, tributaries of Mara River had minimal effect on the water quality flowing in springs and sediments within the springs of the catchment.
- The spring water and sediments quality parameters examined were within the maximum permissible limit prescribed by (WHO, 1996). Spring water in and around Mau water towers are suitable for drinking, as the levels of the parameters are not beyond acceptable standards.
- The physicochemical parameters were higher in the wet season compared to the dry season.
- There was no contribution of physicochemical load to River Mara from water and sediments from springs flowing into the tributaries of the Amala and Nyangores

5.4. Recommendations

- The anthropogenic activities around Mau water catchment should be maintained at the current levels.
- Although the risk from nutrients and heavy metal load was not prominent, continuous surveillance of their levels in the catchment is advisable.
- Periodic monitoring of the springs is is particularly called for since a trend of seasonal variation is evident so as to maintain the fidelity of the springs.

5.5. Suggestions for further studies

- There is need to assess the biological water quality parameters on these springs in order to conclude on the impacts of anthropogenic activities.

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