

**EFFECTS OF SOME LAND USE PRACTICES ON WATER PHYSICO-CHEMICAL
PARAMETERS, NUTRIENT LOADS AND HEAVY METAL CONCENTRATIONS IN
WATER AND SEDIMENTS ALONG THE MARA RIVER**

BY

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ABSTRACT

Riverine land uses are among factors that influence water quality. Fresh water quality is declining and consequently impacting on the ecological health of the ecosystem. Within the Mara River Basin as a result of population increase over the years, deforestations has increased to create room for human settlement, agricultural activities, urbanization and industrial development. These activities have the potential to cause decline in water quality, however the effects of these activities on water quality in the Mara River Basin is very uncertain. The purpose of this study was to assess how land uses along the Mara River watershed impact on the water quality parameters and heavy metals levels in the river sediments, and concentration registered compared with acceptable standards limits as set by the National Environment Management Authority-Kenya (NEMA) and the World Health Organization (WHO) using documented standard methods of analysis. Water and sediment samples were collected in triplicates at 8 different sites based on distinct land use practices along the Mara River. A spring within the Mau Forest-Ainabsabet spring was used as the control 1 site (C1), while a stream of water emanating from a forested land and draining into the main river after the mine site was used as control 2 to establish changes in water quality due to land use downstream the main river. The water pH, dissolved oxygen, electrical conductivity, water turbidity, water temperature all registered a significant increase from the control site at a confidence limit of $p \leq 0.05$, other than the concentrations of dissolved oxygen and turbidity at site 10 (Kirumi wetland). The land uses along the river did alter the concentration of these physicochemical parameters, however they fell within acceptable standard limits of both NEMA and WHO. Other than ammonium nitrogen concentrations, all the nutrient concentration of silicates, nitrates, nitrites, soluble reactive phosphorous, total nitrogen and total phosphorous at Emarti site, Ngerende 1, Ngerende 2, Oldmara Bridge, New Mara bridge had a significant increase from the control site-Ainabsabet spring. At site 10-Kirumi wetland, all the nutrients other than silicates concentrations exhibited a significant reduction from the control site, and all fell within acceptable standard limits of NEMA, 2006 and WHO, 2011 for surface domestic water. All the heavy metals concentration registered significant increases from the control site, with concentrations such as Lead $49.80 \pm 0.20 \mu\text{g/l}$, Chromium $82.26 \pm 1.44 \mu\text{g/l}$ and Iron $41.00 \pm 1 \text{mg/l}$ after the mine site-site 8, registering concentration above the WHO, 2008 standard limits for surface domestic water of $10 \mu\text{g/l}$ for Lead, $50 \mu\text{g/l}$ for Chromium and 0.3mg/l for Iron. The results suggest that land uses along the Mara River are contributing to the nutrient and heavy metal loading of the river, however most parameters other than exhibiting significant increase from the control site are within acceptable standard limits for both NEMA 2006 and WHO 2011. As long as the land uses along the Mara River are sustained at their current levels, they don't pose a risk of polluting Lake Victoria. The wetland in Kirumi aided in reduction of most contaminants and should be well protected and conserved to ensure that the Mara River does not become a future reservoir for polluting the Lake Victoria waters.

Chapter 1

Background

Fresh water quality is declining (Johnson *et al.*, 2001). Lake Victoria and its basin have undergone enormous ecological changes with pollution levels from terrestrial, point source and atmospheric sources continuing to degrade its water quality (World Agroforestry Center, 2006). The Mara River Basin is one of the river basins within the Lake Victoria catchment and is shared between Kenya (65%) and Tanzania (35%) (LVBC & WWF-ESARPO, 2010a).

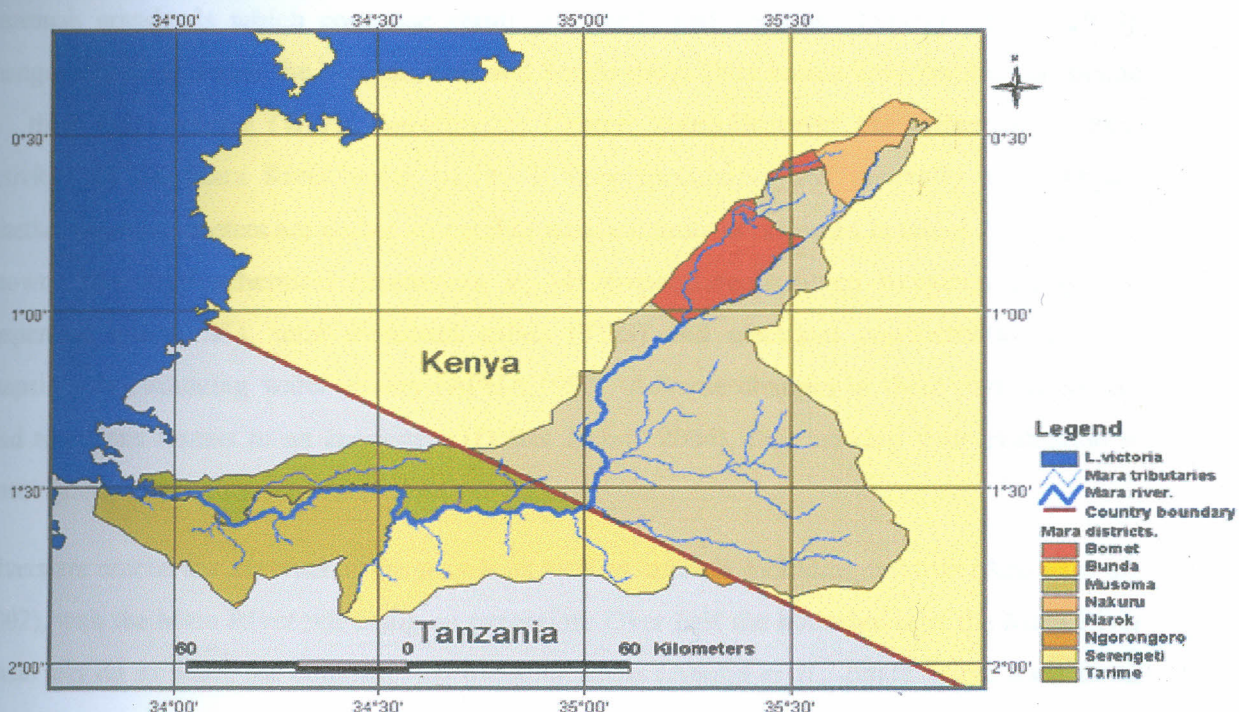


Fig 1: Map of the Mara River Basin (<http://nowater-nolife.org/watersheds/Mara/Map> .Accessed on 25th June 2013.)

The Mara River originates from the Mau Forest with high rainfall (above 1400 mm/year) in the South West Mau Escarpment in Kenya and descends in altitude from about 3000 m to below 2000 m, criss-crossing Narok, Trans Mara, then through the Mosirori Swamp in the North-Eastern part of Tanzania and finally into Lake Victoria. The 395 km long Mara River has for a long time been considered one of the pristine rivers draining into Lake Victoria, forming part of

the upper catchment of the River Nile basin. Its main perennial tributaries are the Amala and the Nyangores tributaries which originate from the Mau escarpment. Other prominent tributaries are Talek River, Engare Engito and the Sand River (Abulude *et al.*, 2007). The Mara River Basin was originally un inhabited, however due to population increase, large tracks of forest lands have been cleared and turned into settlements, Consequently, this river basin is now characterized by closed and open forests, tea plantations in the upper slopes of the Mau Escarpment, agricultural lands, shrub lands and grasslands used for livestock and game grazing or game reserves, savannah grasslands which comprise shrub grasslands and wetlands (Mango *et al.*, 2010). changes like these within the Nyando, Yala, and Sondu-miriu river basins have resulted in decline in their water quality (World Agroforestry Center, 2006). However the influence of these activities on the Mara River water quality is very speculative and generally unknown. and whether these parameters are within acceptable standard limits as reflected in tables 2 and 3 is not known. The physicochemical parameters ie; pH, temperature, dissolved oxygen, turbidity, total suspended solids (TSS), total dissolved solids (TDS) and electrical conductivity (EC) are snapshots in evaluating water quality (APHA, 1980). Adverse changes in these parameters can lead to serious threats to an ecosystem (Dallas & Day, 2004), thus making their evaluation in water quality mandatory.

Rivers are crucial for survival of the people as well as animals including wildlife (Aboud *et al.*, 2002), with the Mara River not being an exception. Over half the households in the Mara River Basin rely on its water for domestic and livestock needs (Aboud *et al.*, 2002). Large scale farms within the Mara River Basin are irrigated via water extractions from the Mara River while small scale farms are rain fed, with subsequent overflow in to the river. This river also provides critical in-channel and riparian habitats to a host of animals such as the hippopotamus, crocodiles, fish and various types of snakes and frogs, with the Mara-Serengeti ecosystem containing the most diverse combination of grazing mammals in the world, holding 400,000 wildlife and livestock (Aboud *et al.*, 2002). However the influence of these activities on the water quality in the Mara River is not known.

The dominant social economic activity for the majority of the populations within the Mara River Basin is crop farming, with 62% of the households being smallholder farmers (Aboud *et al.*, 2002). The agricultural farms are mostly bordering the river banks, and runoff water from these

farms result in nutrients, metals and sediments loading into the Mara River, however the contribution of agricultural activities and their influence on the Mara River water quality has not been evaluated.

Previous studies in the Mara River Basin suggest that the best approach to conservation of biodiversity is through conservation of plant and animal species, and through conservation of their habitats (LVBC & WWF-ESARPO, 2010b). A survey by the Global Water for Sustainable Development within the Mara River Basin in 2005 highlighted that the pattern in water quality along the Mara River varied as a function of position along the river (WQBAR, 2007). During the water quality baseline assessment of the Mara River in May 2005, nutrient concentrations were high in the agricultural sectors of the basin. However the concentrations of the nutrients were below existing WHO standard limits, but above natural levels and capable of causing eutrophication (WQBAR, 2007). Once there has been increase in population, demand for land for agriculture and human settlement. However, the effect of increased land uses on the water chemistry in the Mara River is not being quantified.

Water abstraction along the Mara River has continued to increase to sustain the growing urban areas, irrigated agriculture, tourism facilities and mining industries (LVBC & WWF-ESARPO, 2010a). The abstraction levels are usually highest during the dry seasons (GOK, 2002). The return of this abstracted water back into the river could lead to water pollution. There has been no evaluation of the effects of these water uses on the water quality in the Mara River.

The Mara River flows through the Maasai Mara National Reserve which is of great economic significance. The effect of the game reserve on the Mara River water quality remains unknown. Similarly there are mining activities and industries along the Mara River with the potential to contaminate the river water, such as the North Mara Gold Mine in Tarime region in the north eastern part of Tanzania (InfoMine Inc, 2012). There have been reports that untreated wastes are discharged from these industries into nearby water sources (Bitala, 2008). For example in May 2009, an accidental spill occurred from the North Mara Mines (Almas *et al.*, 2009). A study that followed the spill assessed the concentration of heavy metals and cyanide in water, soil and sediments surrounding this mine. In some places, levels of the heavy metals were higher than

what is permissible by the WHO, USEPA and Tanzania Government Standards (Bitala, 2008), but a follow-up of this study is lacking.

Table 2. National Environment Management Authority (NEMA)-permissible quality standard limits for domestic and surface water

Parameter	Domestic water	Surface water
pH (Fresh water)	6.5 - 8.5	6.5-8.5
pH in Marine waters	No set guideline	5.0 -9.0
Dissolved oxygen	Above 6 mg/l	Above 6 mg/l
Total Suspended solids	30 mg/l	30 mg/l
Total Dissolved Solids	1200 mg/l	1200 mg/l
Ec (water conductivity)	No set guideline	400 μ S/cm
Turbidity	Below 10NTU	300NTU
Nitrate (NO ₃ -)	10 mg/l	10 mg/l
Ammoniacal- N (NH ⁴⁺ .)	0.5 mg/l	0.5 mg/l
Nitrite (NO ₂ -)	3 mg/l	3 mg/l
Lead	0.05 mg/l	0.01
Lead and its compounds	0.05mg/l	0.1
Cadmium	0.01 mg/L	0.01
Cadmium and its compounds	0.01 mg/l	0.1mg/l
Copper	0.05 mg/L	1 mg/l
Chromium	0.05 mg/l	0.05 mg/l
Zinc	1.5 mg/l	1.5mg/l
Dissolved Iron	0.3 mg/l	10 mg/l

(NEMA,2006)

Table 3. World Health Organization (WHO)-permissible quality standard limits for domestic and surface water

Parameter	Domestic water	Surface water
pH (Fresh water)	Below 8.0	6.5-9.2
pH in Marine waters	No set guideline	5.0 -9.0
Dissolved oxygen	No set guide	Above 6 mg/l
Total Suspended solids	5 mg/L	30 mg/l
Total Dissolved Solids	500 mg/l	1200 mg/l
Ec (water conductivity)	No set guideline	400 μ S/cm
Turbidity	10NTU	300NTU
Nitrate (NO ₃ -)	3 mg/l	10 mg/l
Ammoniacal- N (NH ₄ ⁺ .)	No set guideline	Below 0.2 mg/l
Nitrite (NO ₂ -)	0.05 mg/l	0.05-0.01mg/l
Lead	0.01	0.1
TN	No set guide	10 mg/l
TP	No set guide	10 mg/l
Lead and its compounds	0.01	0.1
Cadmium	0.003 mg/l	0.01
Cadmium and its compounds	0.003 mg/l	0.1mg/l
Copper	2 mg/l	10 mg/l
Chromium	0.05mg/l	0.05mg/l
Zinc	3 mg/l	5 mg/l
Iron	Below 0.3mg/l	10 mg/l
Silicates	No set guide	100 mg/l.

(WHO, 1984; WHO, 1996; WHO, 2004; WHO, 2011)

Sediments comprise an important component of aquatic ecosystems, providing habitats to a wide range of benthic and epi-benthic organisms (Adeyemo *et al.*, 2008). Heavy metals contamination in sediments affects water quality, resulting in potential long term implication on human health and ecosystem (Fernandes *et al.*, 2007). The spatial distribution of heavy metals in sediments is a major importance in determining the pollution history of aquatic systems (Birch *et al.*, 2001) and is basic information for identifying the possible sources of contamination (Sollito *et al.*, 2010). Sediments analysis along the Mara River with the aim of identifying the possible sources of heavy metals contamination in the Mara River is very obscure.

1.2 Statement of the Problem

Agricultural farming, human settlement, mining activities, deforestation, livestock grazing among other anthropogenic activities, are increasing within the Mara River Basin, due to population pressure. These activities may be impacting the water quality in Mara River through inputs of contaminants such as nutrients, heavy metals loads and sediments, leading to the alteration of the water physicochemical composition to be environmentally unfavourable to the inhabitants within its watershed. There is need to continuously monitor the effect of these land use conversions on the water quality and the river sediments in the Mara River to enable development of land use policies that protect the quality of water in Mara River and subsequently Lake Victoria.

1.3 Objectives

1.3.1 Main objective

This study aimed at assessing the effects of some land use practices along the Mara River on its water quality parameters such as the physico-chemical parameters, water nutrients loads and the river sediments heavy metal concentrations.

1.3.2 Specific Objectives

- 1) To assess the effects of land use along the Mara River on water physicochemical parameters:- pH, temperature, dissolved-oxygen, turbidity, total suspended solids, total dissolved solids, and water electrical conductivity concentrations.
- 2) To assess the effects of land use along the Mara River on water nutrient loads of nitrate (NO_3^-), nitrite (NO_2^-), ammoniacal nitrogen (NH_4^+), total nitrogen (TN), soluble reactive phosphorous (SRP), total phosphorous (TP) and silicates concentrations .
- 3) To assess the land use effects along the Mara River on water and sediments heavy metal concentrations of Chromium (Cr), Zinc (Zn), Copper (Cu), Iron (Fe), Cadmium (Cd), and lead (Pb) .

1.4 Null Hypothesis

- 1). The land uses along the Mara River do not have effects on its water physicochemical parameters: pH, temperature, dissolved-oxygen, turbidity, total suspended solids, total dissolved solids and water electrical conductivity concentrations.
- 2). The land uses along the Mara River do not have effects on its water nutrient loads of NH_4^+ , NO_3^- , NO_2^- , TN, SRP, TP and silicates concentrations.
- 3). The land uses along the Mara River do not have effects on its water and sediments heavy metals concentrations of Cr, Zn, Cu, Fe, Cd, and Pb.

1.5 Justification

This study will help in the decision on whether the present land use activities are negatively impacting on the water quality of the Mara River, and to formulate policies to mitigate the contamination of the Mara River and by extension Lake Victoria.

1.6 Significance of the Study

This study will be an update water quality monitoring process of the Mara River. The result shall be used to develop policies for the mitigation of water pollution and sustaining aquatic life forms in the Mara River and Lake Victoria.

1.7 Study limitations

Some of the sites of interest for sample collection were inaccessible due to the terrain and safety concerns, due to presence of wildlife.

CHAPTER 2

Literature Review

2.0 Introduction

Rivers play significant roles within a land scape, as they are at the receiving end of all human activities within their catchments. Analysis of the changes in river water quality often reveals the impacts of different activities taking place within a river basin (Hawkins *et al.*, 1993). Variation in watershed land use can translate to differences in lake water quality (Fraterrigo & Downing, 2008). In the Boeuf Basin, Los Angeles, United States of America, urban and agricultural developments were the two leading causes of poor water quality (LeBlanc, 2008). In the Castilla-La Mancha Region in Spain, there was significant strong relationship between nutrients and urban forested and dry agricultural land uses (Kroll *et al.*, 2009). A survey on water resources in Virginia, suggested agriculture and urban land use activities as the influx sources of nutrient loads into the surface water sources (Jones & Holmes, 1985). These activities also impacted the receiving waters through increased loads of sediments, pathogens and pesticides (Jones *et al.*, 1985), with the concentration of Metalachlor (a herbicide used in the control of weeds and grass in the croplands) in community water supply wells near surface aquifers directly relating to the amount of agricultural land within a half –mile radius of the wells (USGS, 1999). In the Wood River higher nutrients concentrations were at sites where agricultural land use dominated and sewage discharges were released (Holme, 2004). Runoff water from agricultural-ecosystems causes pollution to the adjacent semi-natural and natural terrestrial or aquatic ecosystems (Tsiouris *et al.*, 2001). Developed countries have had major problems of water pollution from agriculture and trends indicate that intensified farming systems and agrochemical consumption are being extended in emerging economies (FAO, 1994).

Surface water pollution is one of the serious environmental problems in many rivers in South Africa due to land use practices (Nkwonta & Ochieng, 2009). Nyabugogo River in Rwanda is heavily contaminated with high nutrient, suspended solids and heavy metal pollution, as a result of human settlement, urbanization and industrialization (Nhapi *et al.*, 2011).

In East Africa, land use changes caused by rapid urbanization and clearance of forests to create room for agriculture and human settlement have emerged as major stressors of streams and rivers (Kobingi *et al.*, 2009). Deforestation and cultivation cause an increase in water temperature, conductivity, total suspended solids, total dissolved solids and turbidity (Kobingi *et al.*, 2009). One of the major sediment contributors in the Kenyan portion of Lake Victoria Basin is the Nyando River (Ndwallah & Nyangaga, 2007). High sedimentation in Rivers; Nyando, Nzoia, Sondu and Yala have been attributed to increased destruction of forest to create room for human settlement (Abdalla & Ismail, 2008). Agricultural land use was a major factor contributing to changes in its water quality within the Nyando River Basin (Gathenya *et al.*, 2011). The physical and chemical analysis of water quality in Nzoia River Basin revealed high levels of phosphates and nitrates in the water along the agricultural zones (Twesigye *et al.*, 2011), while top soils samples from Nzoia sugarcane farms revealed the presence of elevated levels of heavy metals (Omwoma *et al.*, 2010). Repeated application of fertilizer is known to avail heavy metals in the soil (Mortvedt, 1995). Thus fertilizer applications in farms are a potential source of heavy metal pollution in neighbouring surface and ground water (Omwoma *et al.*, 2010).

One of the main anthropogenic sources of heavy metals contamination are mining industries (Mohanty *et al.*, 2001). Mining is a major economic activity in many developing countries (UNEP, 1997). The mining operations, whether small scale or large scale, are inherently disruptive to the environment, producing enormous quantities of waste that can have deleterious impacts on the environment for decades (Tauli-Carpuz, 1997). The gold mines produce pollutants, mainly heavy metals from waste rock piles, which come as acid mine drainage (Bitala, 2008). Acid drainage is a legacy of past as well as current mining operations, particularly where sulphide minerals are present (Ogola *et al.*, 2001). Once sulfuric acid is released, it gives the strong acidic property, which eventually breaks the minerals to release the heavy metals. Studies carried in Brahmani River along the tributaries of Angul Talcher region, highlighted the presence of heavy metals concentrations in water samples which were attributed to the concentrations of various mines and associated industries along the river course (Reza & Singh, 2010). Gold mining in Migori District in Kenya involves both open and underground operations. Mining in the area has left behind dredged out and contaminated streams (Ogola *et al.*, 2001).

Under natural conditions, the process of acid drainage is rather slow, but once mining takes place, the process is accelerated due to exposure of the minerals to oxygen and water (Taylor, 1998).

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 Mara River had for a long time been considered one of the more pristine rivers draining into the Lake Victoria, which forms the upper part of the Nile Basin (Mati *et al.*, 2005). It has long been suspected that deforestation and land cover conversion is manifested by declining water quality (World Agroforestry Center, 2006). Over the past 60 years, the Mara River Basin has undergone major changes in land cover (Mango *et al.*, 2010). The forests and savannah grasslands have been cleared and turned to agricultural areas, such as the forest excisions in the Mau Forest to create the Nyayo Tea Zones (Awiti *et al.*, 2001). By 2010 the riverine land uses included large scale agriculture, forestry, livestock keeping, fisheries, tourism, conservation areas and mining activities (Mango *et al.*, 2010). These activities are likely to have changed the environmental quality of the adjacent riverine lands, making them susceptible to soil erosion from water runoffs, and eventually leading to water pollution in the Mara River. However, the effects of these land conversion activities on the water quality in the Mara River have not been evaluated.

2.1 Agricultural Activities along the Mara River Basin

The human population in the Mara River Basin is estimated to be growing at an annual rate of more than 3% and has been accompanied by greater than 50% increase in agricultural land at the expense of the basin forests and grasslands (LVBC & WWF ESARPO, 2010a). Since the early 1970s, the land surrounding the Maasai Mara National Reserve has been steadily converted into agricultural land with large scale wheat farming being a major part of it. Between 1975 and 1995, wheat farming in the Loita Plains in the lower Mara River Basin increased by 44,000 hectares (Serneels *et al.*, 2001). Sunflower and wheat are grown around Olchoro Orogwa Ranch towards Emarti markets on the left bank of the Mara River, while around Emarti market on the right bank of the Mara River there is wheat, irish potatoes, maize, and beans with the main crop being maize (Mwichabe, 1986). Around the Maasai Mara National Reserve and Ngore Ngore area, land is now under large scale rain fed arable farming: ploughing, harrowing and planting

are done by tractors; weeding is by spraying of herbicides. The farmers use improved seeds and fertilizers (Mwichabe, 1986). Herbicides applied to crops eventually enter surface and ground water, while some of these herbicides enter the food chain, accumulate up the food chain and can potentially become toxic to organisms (WQBAR, 2007). Agricultural activities are among the most frequently cited sources for degradation and pollution of aquatic systems (Griffith *et al.* 2002). Unplanned agriculture is thus a potential threat to water quality. However, the effects of the agricultural activities along the Mara River on its water quality are unknown.

Within the Mara River watershed, the agrochemicals input and topsoil from agricultural lands often end up as runoff from the steep slopes during rainfall events. This situation has been made more serious by the loss of riparian vegetation (LVBC & WWF ESARPO, 2010b). Once the water runoff ends up in the Mara River, depending on its physicochemical composition, it may alter the water physicochemical characteristics. The effects of these agricultural-ecosystems on the water quality in the Mara have not been evaluated.

2.2 Maasai Mara National Reserve

The Maasai Mara National Reserve was established in 1961 to protect wildlife from hunters (Glover, 1966). The lower reaches of the Mara River in Kenya pass through Maasai Mara National Reserve. Human population is limited and clustered around hotels and lodges (LVBC-WWF ESARPO, 2010a). A number of environmental impacts can be associated with the development of these tourist facilities; these include water pollution resulting from discharge of waste water, litter from catering, accommodation and other tourist installation facilities within the reserve, which may eventually find its way into the Mara River. Both livestock and game animals are known to remove vegetation through grazing and habitation (Belsky *et al.*, 1999), exposing soils to energy of raindrops, facilitating and increasing amounts of runoff and ability to move sediments (USEPA, 2000). Animal wastes inputs are a source of nutrients contamination such as nitrates and phosphorous species such as soluble reactive phosphorous (McCartney, 2010) in aquatic systems. There is need to understand how water quality varies along the national reserve to refine the understanding on the effects of the reserve in totality to the water quality in the Mara River.

2.3 The Mining Activities along the Mara River Basin

Large scale gold mining in Tanzania started in 1998. The North Mara Gold Mine falls within the Mara River Basin (Almas *et al.*, 2009). In May 2009, a major spill occurred from the North Mara Mines (Almas *et al.*, 2009). Studies that followed to evaluate the effect of the spill, analyzed soil, sediments, and water within the vicinity of the mine and documented their findings as presented in Table 1. However the follow up to these studies has been lacking even though some sites had accumulated potentially hazardous concentrations of these trace elements

Table 1: Concentration of Trace Elements in the Vicinity of the North Mara Gold Mine in the Mara River Basin in May 2009

Element	level in mg/kg in soil	level in mg/kg in sediments	Levels in mg/l in water
Cd	ND	ND	0.00-224
Cr	1.6-38.2	5.7-72.2	0.00-951.9
Cu	11.0-63.1	3.1-25.2	0.5-4467.0
Pb	3.4 -61.4	6.9-18.8	0.00-7.80
Zn	17.7-252	14.6-142	1.0-94608

ND=Not detectable. Source: - Almas *et al.*, 2009

Water quality guidelines provide reasonable minimum requirements for safe practice to protect the health of consumers (WHO, 1996., WHO, 2011). They provide a scientific point for National Authorities to develop regulations and standards appropriate for the National situation (NEMA, 2006).

2.4 The Water Physicochemical Parameters

The water physical and chemical parameters are important attributes that define water quality (Adeyemo, 2003). Some of these include temperature, pH, electrical conductivity, dissolved oxygen, total dissolved solids, total suspended solids among others.

2.4.1 Temperature

Temperature changes can be described as a condition that is responsible for the transfer of heat within bodies (Bongomusa, 2010). Water temperature changes affects the solubility of H_2 , N_2 , CO_2 and O_2 , which play vital roles in aquatic ecosystems (Gillooly *et al.*, 2002). Temperature of running water is dependent in changes on the hydrology, climate and structural attributes such as depth, turbidity and the surrounding vegetation cover within the catchment (Appleton, 1976). Deforestation and cultivation increases water temperature (Kobingi *et al.*, 2009). Mean standard limits of surface water temperatures range between $25^{\circ}C$ to $35^{\circ}C$ (NEMA, 2006; WHO, 2011), and fluctuations outside these ranges affect aquatic life forms through influence of solubility of compounds and gases, decomposition rate and metabolism which subsequently affects dissolved oxygen demands (McCartney, 2010). How land uses influence the water temperature in Mara River is not known.

2.4.2 pH

pH is an indicator of the acidity, basicity or the hydrogen ions activity of a solution at a given temperature (APHA, 1995). The pH of a water body can be affected by industrial effluents, runoff water from mine tailings, agricultural farms and atmospheric deposition of acid forming substances (Deborah & Kimstach, 1996). Majority of fish populations live in a pH range of 6.3 to 9.0, but most of the water systems have a pH range of 6.7 to 8.6. The pH outside these ranges may be an indication of nutritional imbalance or presence of toxic ions (Ayers & Westcot, 1985). The variations in the water pH with respect to the various land use practices along the Mara River are not known.

2.4.3 Electrical Conductivity

Electrical conductivity is a measure of a solution's ability to conduct electrical current, and can be used to estimate the total salts that are dissolved in water (Guy, 1996). Water pollution and large quantities of land runoff contribute to increased salinity (Deborah & Kimstach, 1996), which is toxic to life forms causing a salinity hazard (Deborah & Kimstach, 1996). The conductivity for a given water body is related to the concentrations of total dissolved solids and major ions (Kihampa and Wenaty, 2013). Previous studies within the Mara River Basin attributed increase in conductivity to increase in concentration of salts, organic and inorganic materials as a result of discharges by feeder streams, effluents from mining areas and runoff from agricultural, domestic and other human activities into the river during rainy seasons (Kihampa and Wenaty, 2013). There is need to continuously monitor the conductivity concentration in the Mara River to keep check as per the standard limits of 400 μ S/cm (NEMA, 2006) for surface water and prevent the eventual pollution of Lake Victoria.

2.4.4 Dissolved Oxygen

Adequate water oxygen levels are necessary to provide for aerobic life forms which carry on natural stream purification processes (Hutchison, 1957). Healthy water should generally have dissolved oxygen concentrations above 6.5 mg/l to 8 mg/l (Jones & Holmes, 1985). As DO levels drop below 5.0 mg/l, aquatic life is put under stress. Oxygen levels that remain below 1-2 mg/l for a few hours can result in large fish kills. Low DO levels are generally an indication of high levels of dissolved organic matter (Chapman, 1996). Dissolved oxygen levels are also known to reduce as a result of natural decay of organic matter such as leaves that are washed into streams (Willimson *et al.*, 1998). Acceptable standard limits for dissolved oxygen levels capable of supporting aerobic life forms should be above 6 mg/l (NEMA, 2006; WHO, 2011). It is not known if the land use practices along the Mara River contribute to the presence of organic matter in the Mara River thereby impacting on the water dissolved oxygen levels and whether the concentration of dissolved oxygen in the Mara River are favourable for supporting aquatic life forms.

2.4.5 Turbidity, Total Dissolved Solids & Total Suspended Solids

Turbidity is a representation of the optical property of water that causes light scattering or absorption. Primary production of aquatic organisms is reduced in turbid waters as a result of decreased photosynthesis due to light scattering (Ryan, 1991). Likewise the amount of solids in water are common parameters which are constantly monitored because high concentrations cause environmental damage to ecological systems (Sartor & Boyd, 1992). The solids act as mobile substrates for the transportation of other pollutants such as heavy metals. TSS is a significant part of physical and aesthetic degradation and a good indicator of other pollutants, particularly nutrients and metals that are carried on the surface of sediments in suspension (Packman *et al.*, 1999), while the TDS represent mostly inorganic salts and small amount of organic matter present in water (WHO, 1996). The standard acceptable limits for : turbidity, total dissolved solids ,total suspended solids in surface water are 300 NTU, 1200 mg/l and 30 mg/l respectively (NEMA, 2006; WHO, 2011), however whether the cultivation and deforestation activities among other land use practices along the Mara River influence the turbidity, TDS and TSS in the Mara River water to make their concentration hazardous to aquatic life forms has not been established.

2.4.5 Nutrients: Nitrogen and Phosphorous

Nutrients are chemical compounds assimilated to provide bio-elements that are necessary for normal growth of organisms (Dallas & Day, 2004). These bio-elements include oxygen, hydrogen, carbon, nitrogen, calcium, phosphorous, sulphur, potassium and magnesium. However nitrogen and phosphorus are most associated with ecosystem's nutrient enrichment resulting in excessive plant growth (Dallas & Day, 2004). Elevated concentrations of these nutrients in the water ecosystem pose threats to aquatic organisms and enhance eutrophication (Campbell *et al.*, 1992). The increased use of agricultural chemical inputs, such as the NPK fertilizers majorly used in the tea growing regions in the upper tributeries of the Mara River (Othieno, 1988). Accompanied by runoff water from agricultural lands, have contributed to wide spread occurrence of eutrophication within Lake Victoria waters (Bugenyi & Balirwa, 2003).

The fertilizer application in agricultural lands culminates in high crop yields, thus making fertilizer application mandatory (EU, 1995). The major source of nitrogen input in agriculture is the commercial fertilizer, though input from animal manure is also important especially in regions of high animal density. Nitrogen ends up in the environment mainly from agricultural processes, eventually ending up in water bodies (Lenntech, 1998-2011). Excess nitrogen in water causes eutrophication resulting in stimulated algal and aquatic plant growth (Nixon, 1993). Water clarity is decreased, deep water become depleted of dissolved oxygen, fish and shell fish deaths may occur (Ryther & Dunstan, 1971). High concentrations of inorganic forms of nitrogen are also known to be poisonous to humans. Nitrate concentrations of above 10 mg/l in drinking water is usually harmful to babies and is known to cause blue baby syndrome, while nitrite concentration of about 4 mg/l is toxic to fish such as the Rainbow Trout (Mesner & Geiger, 2010). Total nitrogen in water comprises of dissolved inorganic nitrogen (nitrites, nitrates, and ammonia) and organic nitrogen. High organic nitrogen levels are due to decomposition of aquatic life and sewage runoff, while inorganic levels are enhanced by soil erosion and residential runoff of fertilizers (WRMA, 2007). Acceptable limits for Nitrogen species in surface water are; nitrate 10 mg/L, nitrite 0.01mg/l, ammonium nitrogen below 0.2 mg/L and total nitrogen 100 mg/l (WHO, 2011). It is not known how the land uses along the Mara River impact on the nutrient loads of nitrogen species in the Mara River.

Diamonium phosphate is widely used as a phosphorous fertilizer to stimulate root growth and plant health (Othieno, 1988). It gets into water in both urban and agricultural settings (USGS, 2011). The phosphorous fertilizers are less mobile in the soil as a result of strong adsorption to soils (Ayers & Westcot, 1985), and thus move into water bodies via runoff water. Phosphate fertilizers are usually manufactured or blended with nitrogen, potassium or both to form mixed blends (Sauve *et al.*, 1996). The main source of nutrients in tea grown areas in the upper tributeries of the Mara River is the NPK fertilizer (Othieno, 1988). Application of this fertilizer as well as other manures leads to build up of phosphorous in soils, increasing the potential for phosphorous losses via water runoff and soil erosion (Sauve *et al.*, 1996). The anthropogenic activities are the major sources of phosphorous through the use of fertilizers, pesticides and industrial and cleaning activities using soaps (Boron *et al.*, 2003). Phosphorous in natural water is divided into three components: soluble reactive phosphorous (SRP), soluble unreactive

phosphorous (SUP), and particulate phosphorus (PP) (Rigler, 1973). It is an essential nutrient for living organisms that occurs in natural water and in waste waters, mostly as phosphates. Being the limiting nutrient for algal growth, it is rarely found in high concentrations in fresh waters (Edwin, 1996). However eutrophication is the greatest threat facing aquatic life when there is an unnatural increase of nutrients such as phosphorous and nitrogen that increase algal growth (Schindler & Vallentyne, 2008). As a result of eutrophication, oxygen levels in water bodies is depleted, posing a threat to aquatic life forms due to suffocation (Rao, 2008).

In Lake Lowell in the treasure valley of Idaho, nuisance algal blooms were found to be stimulated by an average phosphorous concentrations of 80 $\mu\text{g/l}$. Lakes with 30 to 100 $\mu\text{g/l}$ are classified as eutrophic, while those of greater than 100 $\mu\text{g/l}$ are classed as hypereutrophic (Newton & Jarrell, 1999). The eutrophic classifications of the Mara River is uncertain. Scientist agree that the main causes of eutrophication in surface water bodies is increasing inputs of phosphorous and nitrogen, which are abundant in human sewage, excrement of livestock and synthetic fertilizers applied to agricultural lands (Schindler, 2012). USEPA recommends soluble reactive phosphorous concentrations of 0.05 mg/ L for streams that discharge in to a lake or estuary and 0.10 mg/ L for streams that do not and 0.10 mg/ L (McCartney, 2010). whether the anthropogenic activities along the Mara River have extensively polluted the river water phosphate concentrations beyond acceptable standard limits for humans, aquatic life forms and domestic uses is not known.

2.5 Heavy Metals in Water and Sediments

Heavy metal contaminations in aquatic environment are of critical concern due to the toxicity of the metals and their accumulation in aquatic habitats. Heavy metals, in contrast to most pollutants, are not biodegradable and undergo an ecological cycle in which natural waters are pathways (Tam & Wong, 1995). Sediments represent an important sink for trace metals in aquatic systems. Sediment associated metals pose a direct risk to detrital and deposit feeding benthic organisms, and may represent a long term source of contamination to higher trophic levels (Luoma, 1983). Heavy metals are generally present in small amounts in natural aquatic environments. However, contributions of these metals from anthropogenic activities usually raises their natural concentrations causing serious environmental problems (Aderinola *et al.*,

2009). Studies carried out in Tarkwa mining region in Ghana, surface and ground water in the mining areas is contaminated by heavy metals, with some metals concentrations exceeding the WHO guideline values for Cd 0.003 mg/l, Fe 0.3 mg/L, Pb 0.01mg/l (Armah *et al.*, 2011). Along the Mara River, there are a number of land use practices which are a potential source of heavy metal loads into the river. Whether heavy metals concentration contributed by the land uses along the Mara River pose a health hazard by exceeding the standard limits is not known.

2.5.1 Lead

Lead is a dangerous heavy metal whose consumption should be minimized (Ogola *et al.*, 2001). It causes impairment of the nervous system and is a possible human carcinogen (UN, 1998). Lead accumulates in surface horizons of soils, and this has been attributed to its low water solubility within an environmentally neutral pH range, which results in very low mobility. Due to past uses of lead in industrial processes and consumer products like paints and leached gasoline, urban soils often contain high concentrations of lead (Lawrence & Brian., 2002). Lead occurs as galena and is associated with gold mineralization, thus during ore crushing and panning it is released into the environment (Ogola *et al.*, 2001). It is also a component in some fertilizers (Mortvedt, 1995), and repeated application of these fertilizers results in the accumulation of lead in soils followed by leaching and transportation into water bodies (Stoking, 1981). NEMA and WHO standard set allowable permissible limits of lead concentration in surface water are 0.01mg/l (NEMA, 2006; WHO, 2011) The contribution effects of land uses along the Mara River on lead pollution in the Mara River water quality has not been quantified.

2.5.2 Cadmium

Cadmium is a natural element in the earth's crust. It often occurs in small quantities associated with zinc ores, such as sphalerite (Anderson, 1992). This element has no beneficial biological importance in the human body and it is a pollutant of global concern (Ayers *et al.*, 1994). Cadmium in water bodies originates from natural as well as anthropogenic sources. Some of the anthropogenic sources of cadmium in water include discharge of effluents from mining and processing industries as well as agricultural runoff (Rai *et al.*, 2003). Acceptable standard limits of Cadmium in surface water is 0.01mg/l (NEMA, 2006; WHO, 2011). Along the Mara River

There are agricultural activities as well as mining industries which are possible sources of cadmium pollution into the Mara River. However the risk assessment of cadmium pollution beyond acceptable NEMA and WHO standard limits in the Mara River basin due to its riverine land uses is not known.

2.5.3 Copper

Copper metal exists by itself as an element or in combination with other elements in various mineral and compounds (Merck Index, 1983). The largest release of copper to the environment by anthropogenic activities includes mining operations, fertilizer and fungicides application in agriculture, landfills and waste disposals (Sauve *et al.*, 1996). Copper in water has been noted to be exceedingly toxic to aquatic biota in contrast to its low toxicity to mammalian consumers of water (USEPA, 1980). Concentrations as low as 0.005 to 0.025 ppm are lethal to some invertebrate and fish species within 4 days. (USEPA, 1980). Tributaries of Msimbazi River have also been found to contain heavy metals such as Cadmium, Zinc, Copper and Lead at different levels and the study suggested the metals are mostly in the ionic forms which are easily accessible to ingestion by animals and aquatic plants (Othman, 2002). NEMA sets acceptable standard limits of copper concentration in surface water at 1 mg/l (NEMA, 2006). Along the Mara River there are land use practices such as mining industries, agricultural practices with probable fertilizer and fungicides applications, landfills which are potential source of copper pollution into the river. However there pollution effects of copper concentrations beyond set standard limits in the Mara River has not been evaluated.

2.5.3 Chromium

Chromium usually appears commonly in the environment as a trivalent salt Cr^{3+} (ATSDR, 2003) found in air, water, soil and some foods. Chromium attaches tightly to soil particles and the usual exposure pathways are due to dust and sediments (ATSDR, 2003). Only a small part of the chromium that ends up in water will eventually dissolve. Excess chromium (III) has a number of negative health effects such as skin rashes (Cheryl & Susan, 2000). The International Agency for Research on Cancer categorizes chromium as carcinogenic to human beings (ATSDR, 2000). Associated effects of excess chromium are growth depression, kidneys, liver

damage and cancer (Frisbie *et al.*, 2002). Chromium enters the environment from mining operations, runoff water from agriculture farms and leaching into ground water (USGS, 2011). WHO and NEMA set the standard limits of Chromium acceptable in surface water at 0.05 mg/l (NEMA, 2006; WHO, 2011). Along the Mara River the agricultural farms and the mining operations are potential sources of chromium contamination. The contribution of chromium into the waters of the Mara River from its riverine land use practices are not known.

2.5.5 Iron

Iron is virtually found in almost every food, with higher concentrations in animal tissues than plant tissues (Beinert & Kennedy, 1989). Allowable limits for Fe in drinking water in the UK, EU, and USA are 0.2, 0.2, and 0.3ppm respectively (EPA, 2001; Lemtech, 1998; DWI, 1990). Intake of excess iron is dangerous and acute poisoning of children can occur following ingestion in excess of 1g of iron (Stokinger, 1981; Forbes, 1947). Anthropogenic sources of iron include mining operations, industrial waste and corroding metals. NEMA set acceptable standard limits of iron in surface water at 10 mg/l (NEMA, 2006). Along the Mara River, although there are potential sources of Iron pollution such as the mining operations among others. The contributions of iron in the Mara River water from its riverine land use practices is still very obscure and whether the concentration are beyond acceptable standard limits is not known.

2.5.6 Zinc

Zinc is released in the environment by natural processes, it attaches to soil, sediments and dust particles in air and water (ATSDR, 1994). However zinc concentrations are rising unnaturally due to addition of zinc through human activities such as mining, purifying of zinc, lead and cadmium ores, burning of coal and industrial wastes (ATSDR, 1994). Zinc is also an amendment in most commercial fertilizers (Moetvedt, 1995) and hence its continued use may lead to accumulation at application sites and runoff water will carry it eventually to the nearby water bodies. NEMA and WHO acceptable standard limits of Zinc in surface water is 1.5mg/l (NEMA, 2006; WHO, 2011). Along the Mara River the land use practices such as mining and agricultural activities are potential sources of zinc pollution. However the contributions of zinc in the Mara River water

CHAPTER 3

from these land use practices and their effects of pollution beyond standard limits posing a threat to life forms is not known.

Although many researchers agree that land uses have a major effects on the surface water quality, the effects of the land use along the Mara River on it water quality are very obscure thus necessitating this study.

along the Mara River. A study was conducted in the area of the Mara River in Kenya to determine the effects of land use on water quality. The study was conducted in the area of the Mara River in Kenya to determine the effects of land use on water quality. The study was conducted in the area of the Mara River in Kenya to determine the effects of land use on water quality.



Fig. 3.1: Location of the study area

The sampling points were selected based on the accessibility of the study area. The study employed a complete

CHAPTER 3

Materials and Methods

3.1 The Study Area and Sampling Design

This study was carried along the Mara River (longitudes 33°47' E and 35°47' E and latitudes 0°38' S and 1°52' S). The altitudes in the basin range from 2,932, m above mean sea level (amsl) around the sources in the Mau Escarpment to 1,134, m (amsl) around Lake Victoria. Water and sediments samples were collected in triplicates at 8 sites based on distinct land use practices along the Mara River. All the parameters analyzed were compared to deviation from control 1 (Ainabsabet spring) which is the site upstream within the Mau forest characterized by dense forested tress with no anthropogenic activities within it vicinity. Control 2 (Nyahenda spring) only used as a gauging factor on the alteration effects of the water quality parameters before the river drains into the wetland in Kirumi.

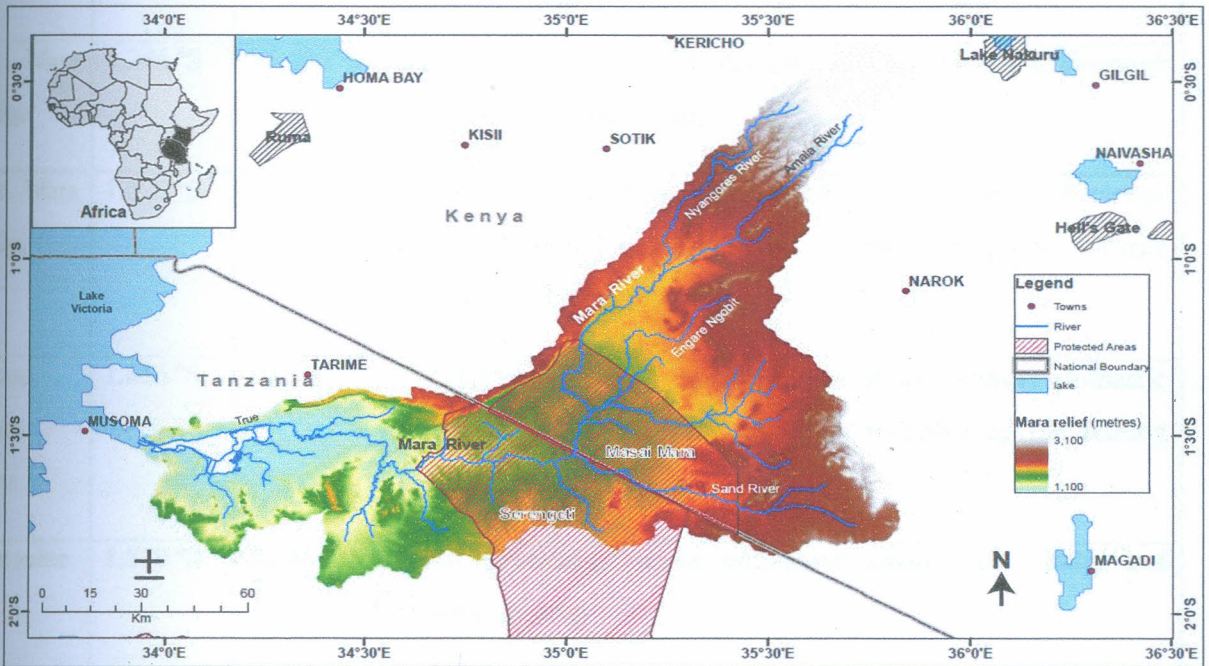


Fig 2-Map of the mara river basin(Mati *et al.*, 2005)

The sampling points were selected based on the dominant land use activity within the area, accessibility of the sampling points and safety was also taken into consideration. This study employed a completely randomized design.

Table 4. Sample sites sampling coordinates, land use and riverside characteristics

Name	Sampling coordinates		land use and riverside characteristics within the sampling site
Ainabsabet	0.658°S	35.544°E	Dense forested tress, thick grasslands and shrubs
Emarti site	1.043 °S	35.240 °E	Large scale wheat and maize farming
Ngerende 1	1.109 °S	35.166 °E	Wildlife conservation-pools of hippopotamus upstream of the sampling point, isolated shrubs and trees within the river bank
Ngerende 2	1.137 °S	35.142 °E	Wildlife conservation- tourist lodges (Ngerende Campsites), game animals (Zebras, Gazelle, Hippos, Crocodiles, buffalos).
Old Mara Bridge	1.246 °S	35.032 °E	Isolated pockets of tall grasses,wildlife browsers and livestock (Maasai cattle and sheep).
New Mara Bridge	1.529 °S	35.021 °E	Wildlife Conservation, evidence of intense browsing. Presence of trenches and gullies used as paths by game animals assessing drinking water points
Tarime before mines	1.616 °S	34.531 °E	Pockets of human settlement, livestock, human domestic activities, excavated heaps of soils neighboring the mining industries.
After mine	1.510 °S	34.465 °E	Sand harvesting, human settlement, small scale maize and banana farming
Nyahenda stream	1.476 °S	34.414 °E	It's a stream of clear water draining into the main Mara River. Emanating from a small forested land upstream, thick grasslands/shrubs.
Kirumi wetland	1.493 °S	34.258 °E	Fishing activities, pockets of human settlement, the water mass covered by aquatic vegetation(wetland)

3.2 Chemicals and Reagents

Ammonium molybdate tetrahydrate (99% purity) and Potassium persulphate (99% purity) were obtained from Riedel-de-Haen-Germany. Ammonium chloride (99% purity), potassium nitrate (95% purity), potassium dihydrogen phosphate (95% purity), Sodium hexafluorosilicate (96% purity), Potassium antimony tartarate (99% purity), Phenol, Ascorbic acid, and sulfuric acid (reagent grade ACS) were obtained from Fisher Scientific, Bishop Meadow Rd, United Kingdom. Mercuric chloride, Nitric acid (72%), Hydrochloric acid (37% reagent grade ACS) were obtained from Sigma Aldrich, Milwaukee, USA. Cadmium filings, Sulphanilamide, N-1-Naphyl ethylene diamine dihydrochloride were obtained from Fluka Analytical Products (Switzerland). Double distilled-deionized water (pH 7.02) was prepared using the Vaposet 20-distillation unit (Gerhardt, Germany). Standard solutions of metals salts were obtained as follows: Cu-1000mg/l \pm 2mg/l and Pb-1000mg/l \pm 2mg/l (Fluka Analytical Products, Switzerland); Cr-1000mg/l \pm 2mg/l (Sigma Aldrich, Milwaukee, USA); Fe-1000ppm (Fisher Scientific, Bishop Meadow Rd, United Kingdom); Zn-1000 \pm 0.04 g/l (AA Panreac Quimic A.SA, Barcelona, Spain). 0.45 μ m GF/C filter paper, Whatman-no 1 -11cm filter paper-M06150125 from Machery Nagel Duran, Germany.

3.3 Sample Collection

The water and surface sediments were collected from the sampling sites according to the methods adopted by the APHA (2005).

3.3.1 Water Samples for Nutrient Analysis

Grab samples of surface water were collected in 3 replicates, 10 meters apart and 15 cm into the water along the Mara River within each given site. The water was collected using a clean beaker, which was rinsed with the river water prior to each sample collection. These were then transferred into labeled 500 ml plastic bottles containing 0.2 g of HgCl₂ each as the preservation agent for the nutrient analysis samples. These were then stored in an ice box and transported to the laboratory for analysis.

3.3.2 Water Samples for Heavy Metals Analysis

The surface water samples were collected as grab samples in 3 replications into 1 liter plastic bottles. Preservation was done by addition of 3 drops of concentrated nitric acid, 72% purity (Sigma Aldrich Milwaukee, USA) in each bottle. These were then transported to the laboratory for elemental analysis.

3.3.3 Surface Sediments for Heavy Metal and Nutrient Analysis

The river bank surface sediments were collected at depths of 1 to 15 cm along the river, using a trowel into black polythene bags in three replications. The replicate samples were collected 10 meters apart from each other along the river bank at the same point of collection of the water samples. These were then stored in an ice box, and transported to the laboratory for heavy metal extraction and analysis as dry weights.

3.4 Analytical Methods

3.4.1 The pH, Temperature, Turbidity Dissolved Oxygen, and Electrical Conductivity

The water pH, temperature, turbidity, dissolved oxygen, and electrical conductivity were measured *in-situ* at the points of sample collection using a multi parameter-water quality meter (WQC-24-TOACOK, Analyticon Instruments Corporation, Springfield, USA).

3.4.2 Total Dissolved Solids and Total Soluble Solids

The total dissolved solids and total soluble solids were determined by the method adopted by APHA (1989). For each water sample, 20 ml was filtered through 0.45 μm GF/C filter paper using a filtering apparatus (Suction Pump P18990, All Favor Enterprise Co Ltd, Taichung, Taiwan). The collecting beakers and filter papers were dried in an oven at 90°C for 24 hours prior to being used and their weight measurements recorded. The collected residues were then dried in the oven at 90°C for 8 hours and the filtrate in the beaker evaporated to dryness at the same temperature. All the weights measurement were taken using an analytical balance (Wagtech GR-202, Gerhardt, Germany).

The TDS for each sample was then calculated as follows:

$$\frac{(BS-B) \times 1000 \times 1000}{20 \text{ mL}}$$

BS= (B X S); B=Mass of beaker, S= Mass of sample

to give concentration in mg/L.

The TSS for each sample was then calculated as follows:

$$\frac{(FR-F) \times 1000 \times 1000}{20 \text{ mL}}$$

FR= (F X R); F=Mass of filter, R=Mass of residue

To give concentration in mg/L.

3.4.3 Ammonium-nitrogen

Ammonium-nitrogen was determined by the indophenol blue photometric method (Koroleff, 1969). Accurately weighed 17.5 g of phenol and 0.2 g of sodium nitroprusside was dissolved in Millipore milli Q water to make a final volume of 500 ml and this was denoted as reagent 1. Accurately weighed 140 g of trisodiumcitrate-dihydrate and 11 g of sodium hydroxide was dissolved in 300 ml of Millipore milli Q water. After complete dissolution, 20 ml of sodium hypochlorite was added and made to a final volume of 500 ml with distilled water prepared by Vaposet 20- distillation unit (Gerhardt, Germany). This was denoted as reagent 2. To 50 ml of the water sample were added 3 ml each of reagent 1 and 2 with vigorous shaking between additions of each reagent. The samples were then kept at room temperature for 24 hours prior to analysis. The absorbance's were then measured at 630 nm on the Uv-Vis Spectrophotometer (Genesys 10s, Thermo Fisher Scientific, UK). The concentration of ammonium nitrogen was quantified by use of calibration curves prepared within the linear ranges of 20, 50, 80, 100, 200 $\mu\text{g NH}_4\text{-N/l}$ from a substock of 10 mg $\text{NH}_4\text{-N}$ prepared from Analar (AR) anhydrous ammonium chloride (NH_4Cl).

3.4.4 Nitrite

The method described by Wetzel (1991) was adopted for nitrite, nitrate and total nitrogen analyses. For nitrites, to 25 ml of each filtered water sample was added 1 ml of sulphanilamide followed by vigorous shaking and standing for 5 minutes, before a further 1 ml of N-1-naphthylethylene diamine dihydrochloride was added and mixed completely. The absorbance's of the solutions were then measured against distilled water as the blank at a wavelength of 543 nm on the Uv-Vis Spectrophotometer (Genesys 10s, Thermo Fisher Scientific, UK). The nitrite concentration was quantified by use of a calibration curve prepared within the linear range of 5, 10, 15, 20, 30 $\mu\text{g NO}_2\text{-N/l}$ from a working sub stock solution of 1000 $\mu\text{g NO}_2\text{-N/l}$ prepared from potassium nitrate (KNO_3).

3.4.5 Nitrate

Nitrates were determined as nitrites by first passing the water sample through a copper cadmium column to reduce the nitrates to nitrites (Wetzel, 1991). The first 25 ml of each sample were discarded and the final 25 ml analyzed as nitrites at a wavelength of 543 nm (Genesys 10s, Thermo Fisher Scientific, UK) as per the nitrite method in section 3.4.4.

3.4.6 Total nitrogen

Total nitrogen was determined as the (Wetzel, 1991) method, by using the unfiltered sample, after addition of sulphanilamide and N-1-naphthylethylene diamine dihydrochloride. The samples were digested in an autoclave steam sterilizer at 93°C-120°C (electric model no.25x-Wisconsin Aluminium Foundry Co.Inc, Manitowec USA). These were allowed to cool, then passed through a copper cadmium column and the absorbance read as per section 3.4.4.

3.4.7 Soluble reactive phosphorous

The soluble reactive phosphorus was determined by the ascorbic acid reduction method (Murphy and Riley, 1962). A mixed reagent consisting of ammonium molybdate, sulphuric acid, ascorbic acid and potassium antimonyl tartrate in the ratio of 2:4:2:1, respectively was prepared. To 50 ml of each filtered sample was added 5 ml of the mixed reagent, and within 3 hours the extinction of the solutions were measured, (Genesys 10s Vis spectrophotometer, Thermo Fisher Scientific,

(K) at a wavelength of 885 nm. The soluble reactive phosphorous concentration was quantified by use of calibration curve prepared within the linear ranges of 5, 10, 20, 40, 60 $\mu\text{g PO}_4\text{-P/l}$ from a working substock solution of 1mg $\text{PO}_4\text{-P/l}$, prepared from (AR) potassium dihydrogen phosphate (KH_2PO_4).

3.4.8 Total phosphorous

Total phosphorous was determined using the ascorbic acid reduction method described by Murphy and Riley (1962). To 50 ml of each unfiltered sample was added 5 ml of the mixed reagent, followed by digestion in an autoclave -pressure steam sterilizer at 200-250°F (electric model no.25x Wisconsin Aluminium Foundry Co. Inc, Manitowec USA) for 2 hours. The solutions were then allowed to cool and their absorbance read at a wavelength of 885 nm on the UV-Vis Spectrophotometer (Genesys 10s, Thermo Fisher Scientific, UK). The soluble reactive phosphorous concentration was quantified by use of a calibration curve prepared within the linear ranges of 5, 10, 20, 40, 60 $\mu\text{g PO}_4\text{-P/l}$ from a working substock solution of 1mg $\text{PO}_4\text{-P/l}$, prepared from (AR) potassium dihydrogen phosphate (KH_2PO_4).

3.4.9 Silicates

Silicates were analyzed according to the procedure adopted by Wetzel (1991). To 25 ml of each filtered sample was added 5 ml of 0.25 M HCl, followed by swirling, addition of 5 ml of 5% ammonium molybdate, further swirling, addition of 5 ml of 1% disodium EDTA and vigorously swirling. After 5 minutes, 10 ml of 17% sodium sulphite was added in each sample solution and these were allowed to stand for 30 minutes after which their absorbance were measured at 700 nm. The silicates concentrations were quantified by use of calibration curve prepared within the linear ranges of 0.4, 1, 2, 3, 4 mg $\text{SiO}_2\text{/l}$ from a working stock solution of 100mg $\text{SiO}_2\text{/l}$ prepared from (AR) sodium hexafluorosilicate (Na_2SiF_6).

3.4.10 Heavy metals in water

The heavy metals in water were extracted by the procedure adopted by Mzimela *et al.* (2003). For each water sample, 100 ml was filtered through a cellulose acetate filter paper into 250 ml collecting beakers, acidified with 1 ml concentrated nitric acid, 72% purity (Sigma Aldrich,

Milwaukee, USA). This was transferred into 100ml digestion tubes and digested at 60°C on a KB 40 Kjeldatherm Block Digester (Gerhardt, Germany). These were allowed to evaporate to 15 ml. The samples were then transferred into 25 ml volumetric flasks and made up to volume with double distilled water for subsequent heavy metal analysis. The extraction filtrates were all analyzed for heavy metals using a double-beam Shimadzu AA-6200 Atomic Absorption Flame Emission Spectrophotometer (Tokyo, Japan): Cr at a wavelength of 425.4 nm, Zn at wavelength of 636.2nm, Cu at a wavelength of 324.8nm, Fe at a wavelength of 372.0 nm, Cd at a wavelength of 326.1 nm, and Pb at a wavelength of 405.8 nm. The concentrations of the metal ions were then quantified by linear curves from working standards prepared from standard stock solutions for the various metals.

3.4.11 Heavy metals in sediments

The heavy metals (Pb, Cd, Cr, Cu, Zn, Fe) in sediments were extracted according to the method adopted by Tack and Verloo (1999). The sediments samples were dried in an oven to constant weight at 100°C for 24 h after which 1 g of each sample was weighed into 250ml beaker, acidified with 20ml of concentrated nitric acid -72% purity (Sigma Aldrich, Milwaukee, USA). These was then transferred into a 100ml digestion tube, and digested on a KB 40 Kjeldatherm block digester (Gerhardt, Germany) at 130°C for 3 hours. The digests were allowed to cool to room temperature followed by filtration using Whatman no. 1 filter papers-Mn 615 Ø125 (Machery-Nagel, Germany), into 50 ml volumetric flasks, and the filtrate made to volume using distilled water. The extraction filtrates were then analyzed for their heavy metal concentration as per water filtrates above, using a double-beam Shimadzu AA-6200 Atomic Absorption Flame Emission Spectrophotometer (Tokyo, Japan).

3.5 Validity and reliability

The instruments and equipments used for the field data collection were calibrated and pretested before the field visits, while the laboratory methods and procedures used were standardized in conformity to the reference methods provided.

3.6 Data analysis

The generated data was statistically analyzed using Statistical Analysis System (SAS) version 9.2 SAS Inc, 2002. And the variation along sites compared at a confidence limit of ($p \leq 0.05$). And parameters analyzed compared with permissible levels sets by NEMA and WHO standard and the change effects compared in relation to the concentration registered at control 1 (Amahsabet Spring).

Table 3.10: Mean and standard deviation of different parameters along the study area.

Site	Mean	Standard deviation
Amahsabet	1.2	0.5
Forest	1.5	0.6
Highway	1.8	0.7
Nyabisi	2.1	0.8
Old Market	2.4	0.9
New Market	2.7	1.0
Uganda	3.0	1.1
Abuja	3.3	1.2
Nyabisi	3.6	1.3
Kumasi	3.9	1.4
CVI	4.2	1.5
ESB	4.5	1.6

Chapter 4

Results and Discussion

4.1 Mean *In-situ* water physicochemical parameters

The mean *In-situ* water physicochemical parameters at different sites along the Mara River are as outlined in Table 5.

Table 5. Mean *in-situ* \pm SE water physicochemical parameters at different sites along the Mara River

Sites no	Names	pH	DO (mg/l)	EC (μ S/cm)	Turbidity (NTU)	Temperature $^{\circ}$ C
1	Ainabsabet Spring	5.23 ± 0.01	6.45 ± 0.01	34.32 ± 0.45	98.45 ± 1.15	11.53 ± 0.06
2	Emarti site	7.48 ± 0.01	7.28 ± 0.05	67.00 ± 0.01	160.37 ± 29.21	18.83 ± 0.15
3	Ngerende 1	7.53 ± 0.06	7.62 ± 0.38	66.30 ± 5.03	143.17 ± 48.97	19.73 ± 0.32
4	Ngerende 2	7.56 ± 0.02	7.53 ± 0.09	65.00 ± 2.65	109.87 ± 1.86	19.70 ± 0.1
5	Old Mara	7.47 ± 0.01	7.28 ± 0.05	67.00 ± 0.01	176.20 ± 28.19	18.83 ± 0.06
6	New Mara	7.27 ± 0.01	6.92 ± 0.15	81.00 ± 3.60	280.97 ± 2.54	23.73 ± 0.06
7	Before mine	7.75 ± 0.01	7.94 ± 0.01	108.00 ± 6.08	364.17 ± 29.56	23.50 ± 0.29
8	After mine	8.04 ± 0.01	7.56 ± 0.10	112.00 ± 3	369.47 ± 15.69	23.03 ± 0.15
9	Nyahenda Stream	7.47 ± 0.06	8.18 ± 0.03	42.33 ± 0.6	90.55 ± 0.90	18.07 ± 0.12
10	Kirumi(Wetlands)	7.58 ± 0.12	6.14 ± 1.55	252.00 ± 5.57	65.77 ± 21.58	23.26 ± 0.13
	CV (%)	0.68	6.98	3.91	12.61	0.73
	LSD, ($p \leq 0.05$)	0.08	0.87	5.97	39.92	0.25

SE = Standard error

4.1.1 pH

The mean pH along the Mara River ranged between 5.4 ± 0.01 at the control site and 8.04 ± 0.01 after the mine site. Exhibiting a significant increase downstream from the control site (Ainabsabet spring). Other than the control site, all sites along the river registered pH concentration acceptable within standard limits of both WHO and NEMA of 6.5 to 9.2 and 6.5 to 8.5 respectively for surface water (WHO, 2011; NEMA, 2006). The trend of a significantly higher concentration being registered after the mining site, is similar to the trend exhibited in other areas of the world such as gold mining in the Western United States as the cyanide that is used in the leaching of gold ores results in higher pH in the adjacent water (Vladimir and Robert, 2006). Abundance of organic acids due to natural organic decomposition tend to increase water acidity (Chapman, 1996). The low pH at the control site (Ainabsabet Spring), where there was no human habitation or evidence of anthropogenic activity, is attributed to the abundance of natural organic acids due to the decomposition of leaves and twigs at this site. Organisms use nitrogen, phosphorous and other nutrients to live and develop and upon decaying, the organic nitrogen is reduced to organic acids and ammonia (Aggie-horticulture, 2009). Carbon from the organic compounds such as leaves which is not utilized in cell protein is liberated mainly in the reduced form of methane CH_4 and small portion of carbon respired as carbon dioxide CO_2 (Aggie-horticulture, 2009). The land uses along the Mara River, such as the gold mining activities, contribute to increased water pH in this river. However, other than the control site at the Ainabsabet Spring, all the values of pH in the Mara River fell within acceptable standard limits of both WHO and NEMA limits (WHO, 2011; NEMA, 2006). Thus the land uses along the Mara River do not pose a health hazard in regards to the water pH. This trend in pH is comparable to the concentration of past study which indicated health pH concentrations being within the standard range limits in consideration of the upper limit, 4.8 to 7.6 (GLOWS, 2005). Though previously a low concentration of 4.8 was registered, at a confidence limit of ($P \leq 0.05$) LSD 0.08, this was insignificant to the concentration of 5.23 registered at the control site.

4.1.2 Dissolved Oxygen (DO)

The mean dissolved oxygen concentration along the Mara River ranged from 6.14 ± 1.55 mg/l at the wetland to 7.94 ± 0.01 mg/l before the mine and 7.56 ± 0.10 mg/l after the mine site. Nyahenda stream (control 2) which was off the main river registered a mean of 8.18 ± 0.03 mg/l,

however this wasn't used to evaluate the land use effects, only to evaluate its alteration of the water quality downstream after this site. As it's a source of high purity water feeding into the main river. There is generally more oxygen in cold, flowing water with many obstacles and moderate plants, as compared to stagnant and slow flowing water (Wetzel, 1983). At the control site 1 (Ainabsabet spring), the water was slow flowing with pockets of natural decaying vegetative matter (plant leaves and twigs) on the water surface. This is the resultant cause for an increase in oxygen demand (Williamson *et al.*, 1998), however the registered concentrations still fell within acceptable standard limits (WHO, 2011). During a previous study along the Mara River in 2005, the mean DO concentration ranged from 0.49 mg/l at the river mouth before draining into the wetland in Kirumi to 7.35 at the Mara mines sites. With exception of swampy location all the DO levels were above the guideline criteria as set by the Tanzania government for surface water suitable for fisheries and domestic use of 6 mg/l (Glows, 2005), this was comparable to DO concentrations in this study in which the mean DO values fell within acceptable NEMA and WHO guidelines (NEMA, 2006; WHO, 2011). An indication of sustainability of dissolved oxygen concentrations in Mara River over the years, though there is a trend of fluctuations in DO concentrations along the river. This should be monitored periodically to keep check such that the concentrations do not go below the acceptable standard limits, particularly at the wetland where the registered levels were just above 6 mg/l registering 6.14 ± 1.55 mg/l.

4.1.3 Electrical Conductivity

The mean conductivity concentration along the Mara River ranged from 34.32 ± 0.45 to 252.00 ± 5.57 μ S/cm. These exhibited a steady increase downstream from control 1 site -Ainabsabet spring, which was upstream along the river. And likewise control 2 which was a stream feeding into the Main Mara River after the mining site. Farm inputs that avail mineral ions into surface water are a primary cause of increased conductivity concentrations within agricultural lands (Williamson, 2001). The conductivity concentrations registered at Emarti site resulted from farm inputs via runoff finding way into the river. Livestock herding that was evident before the mining site also contributed to soil erosion, enhancing the ionic inputs into the water. Mining operations

are also known to accelerate the chemical oxidation processes of the earth crust, releasing acids, metals and sulphates into surface and ground water (Lupankwa *et al.*, 2004). Along the Mara River the most significant input of ions was from the mining activities as is evident by the conductivity concentration registered at downstream of this site. However all the conductivity concentration fell within acceptable standard limits of 400 μ S/cm in surface water (WHO, 2011).

4.1.4 Turbidity

The mean turbidity concentrations along the Mara River ranged from a mean of 65.77 ± 21.58 NTU at Kirumi wetland to 369.47 ± 15.69 NTU after the mine site. All sites registered an increased turbidity concentration compared to the control site 1 (Ainabsabet spring), other than the wetland in Kirumi. Turbidity is mainly from runoff from both non-point and point sources (Wood & Armstrong, 1997), insufficient soil conservation practices is one main entry of sediment loading into surface water (Bugenyi & Balirwa., 2003).

The increase in turbidity downstream along the Mara River is as a result of sediment loading resulting from the land use practices. With the main contributor being the mining activities as per the reflected turbidity concentration after the mining sites. Other contributors of increase turbidity along the Mara River include land tillage from agricultural farms, livestock herding and the game accessibility of drinking water points. As reflected with the registered concentrations within the Ngerende Sites, which the predominant land use is game conservancy. The turbidity concentration after the mine site exceeded the standard limits of 10 NTU for drinking water and 300 NTU for surface water safe for domestic use and some aquatic life forms (WHO, 2011) thus posing a health risk to consumers at this point.

4.1.5 Temperature

The mean water temperature along the Mara River ranged between $11.53^{\circ}\text{C} \pm 0.06$ to $23.73^{\circ}\text{C} \pm 0.06$. All the sites downstream from the control site exhibited a significant variation from control site 1. However all the mean temperature registered fell within acceptable NEMA upper limits of 35°C (NEMA, 2006) for natural surface water.

4.1.6 Total Dissolved Solids

Along the Mara River the lowest TDS concentration was registered at control 1 site (Ainapsabet spring), registering a mean TDS concentration of 45.22 ± 0.65 mg/l. This was comparable to control 2 (Nyahenda stream) with a mean concentration of 59.00 ± 1 mg/l. Low total dissolved solids are often characteristic of forested rivers (Chapman and Chapman, 2003) as reflected in table 6. Both the control sites are inhabited by forested riverbanks, and this explains their trend. Downstream along the river all sampled sites registered a significant increase in TDS comparable to the control 1 site. With the wetland site in Kirumi registered the highest TDS concentration with a mean of 308.33 ± 2.08 mg/l. The increase in TDS concentration downstream is attributed to mineral ions availing themselves as a result of land uses such as land tillages downstream availing the ions into the water body, mining activities, vegetative destruction via grazing thus enhancing mineral ions entry through runoff water to the river. However the TDS concentration at all sites along the river fell within acceptable standard limits of 1200 mg/l (WHO, 2011) and do not pose a health concern for the Mara water users only as per the total concentration but not the individual chemical components.

4.6.7 Total Suspended Solids

Along the Mara River, the highest TSS concentration (110 ± 1.50 mg/l) was registered after the mining site (site 8), with the lowest TSS concentration of 6.33 ± 2.31 mg/l being registered at Emarti site as reflected in table 6, which was characteristic of large wheat and maize farming within its vicinity. Thus the large scale farming within Emarti site does not contribute to the influx of total suspended solids, as this site registered concentrations non significant to control 1 site concentration of 9.22 ± 0.13 mg/l. Insufficient soil conservation practices in agricultural regions is known to increase total suspended solids (TSS) values (Bugenyi and Balirwa, 2003). Increase in TSS concentration along the Mara River is much attributed to mining activities other than

agricultural activities, as is evidence by the highest mean TSS concentration of (110±1.50 mg/l) registered after the mining site. On a quality criteria for surface domestic water based on TSS value, the Mara River fell beyond the 5 mg/l WHO permissible limits (WHO, 2011). However at the wetland before draining into lake Victoria the registered (24.67±1.53 mg/l) was just short within the 30 mg/l NEMA permissible limit (NEMA, 2006).

Table 6. Mean±SE water total dissolved solids and total suspended solid at different sites along the Mara River

Site no	Site name	TDS(mg/l)	TSS(mg/l)
1	Ainabsabet Spring (Control 1)	45.22 ± 0.65	9.22±0.13
2	Emarti site	129.33 ±4.04	6.33±2.31
3	Ngerende 1	183.33 ±4.93	41.67±1.15
4	Ngerende 2	180.68 ±1.15	42.00±2
5	Old Mara bridge	183.68±1.15	73.33±2.89
6	New Mara bridge	106.67±10.4	11.67±2.89
7	Tarime-(Before Mines)	193.24±0.17	107.33±0.19
8	Tarime-(After Mines)	221.33±12.66	110.56±1.50
9	Nyahenda Stream(control 2)	59.00±1	9.33 ±1.15
10	Kirumi(Wetlands)	308.33±2.08	24.67±1.53
	CV (%)	3.50	4.18
	LSD (P ≤ 0.05)	9.60	3.11

SE= standard error

4.2.1 Nitrogen Nutrient Analysis

The dominant species of the inorganic nitrogen along the Mara River was the nitrate nitrogen ($\text{NO}_3\text{-N}$) followed by the ammonium nitrogen ($\text{NH}_4^+\text{-N}$) and then the nitrite nitrogen ($\text{NO}_2\text{-N}$). The highest mean $\text{NO}_3\text{-N}$ concentration of $243.65 \pm 5.26 \mu\text{g/l}$ at Emarti Site which is the closest site to large scale agricultural plantation is an indicator of the agricultural farms upstream being a source of these nutrients. This generally agrees with the finding by Kihampa and Wenaty (Kihampa and Wenaty, 2013) on lower portion of the Mara River in Tanzania surrounding the mining regions where they attributed the mean concentrations of NO_3^- and PO_4^{3-} to be originating from the nearby agricultural soils. Previous studies carried within the Nyando River basin indicated that agricultural land use was major contributory factor in variation in water quality particularly its nutrients concentration (Raburu *et al.*, 2002). Livestock and game animals also had an input on the nutrient concentrations, more so nitrates and phosphorous, as was evident by the concentration of these nutrients registered at the Ngerende Site which was after a pool of Hippopotamats and crocodiles. This resulted as nutrient loading from these animal wastes. Further downstream, sections with limited agricultural farms - other than small pockets of subsistence farm lands such as at site 6 (Tarime) before mines and site 7 (Tarime after mines) - there was a decrease in both nutrients (nitrogen and phosphorus). Aquatic vegetation are known to utilize phosphate and nitrates as nutrients thereby lowering their concentrations in aquatic environments (Belke, 2007), this tends to agree with the low nutrients concentrations of both nitrates ($3.16 \pm 0.20 \mu\text{g/l}$) and soluble reactive phosphates ($5.53 \pm 1.22 \mu\text{g/l}$) registered at this site. However the nutrient species of nitrogen in the Mara River is sustainable, as the all fell within acceptable standard limits for both NEMA and WHO standard (NEMA, 2006; WHO, 2011) as reflected in Tables 2 and 3 and permissible limit of Total nitrogen of 10 mg/l (WHO, 1984).

4.2.2 Soluble reactive phosphorous (SRP), Total phosphorous (TP)

The mean nutrients concentrations of soluble reactive phosphorous and total phosphorous is at illustrated in Table 7. The soluble reactive phosphorous registered it high concentrations within the Ngerende sites, which were inhabited by a pool of hippopotamus upstream during the period of sampling. During the water analysis along the Mara River in 2007, high soluble reactive phosphorous concentration were registered at the New Mara Brige was attributed to presence of livestock wastes and livestock within this area (Mc Cartney, 2010). Other than the natural

phosphate, human and animal excreta are some of the most important sources of phosphate inputs into surface water (Golterman, 1993). The registered concentration of phosphorous at the Ngerende sites is as a result of the hippopotamus upstream of these sites. Along the Mara River both game animals and livestock are a source of nutrient loadings particularly phosphorous loads in to the Mara River. However the phosphorous concentrations are still sustainable, as they all fell within the permissible WHO limit of 10 mg/l (WHO, 1984) for the total phosphorous concentrations in surface water.

Table 7.

Mean \pm SE Nutrients Concentrations at different sites along the Mara River

Site name	Silicates mg/l	NO ₃ ⁻ µg/l	NO ₂ ⁻ µg/l	NH ₄ ⁺ µg/l	SRP µg/l	TN µg/l	TP µg/l
Amabsabet Spring (Control 1)	Nd \pm 0.0	111.97 \pm 1.50	3.20 \pm 0.1	56.57 \pm 0.91	32.95 \pm 1.37	923.24 \pm 5.77	52.00 \pm 0.01
Emarti Site	29.50 \pm 1.70	243.65 \pm 5.26	15.58 \pm 3.96	15.26 \pm 4.18	78.40 \pm 1.48	1515.67 \pm 7.63	581.00 \pm 2 5.35
Ngerende 1	30.00 \pm 0.00	142.97 \pm 2.17	32.03 \pm 1.05	30.33 \pm 0.58	122.68 \pm 0.58	1209.33 \pm 3.06	479.33 \pm 1 5.14
Ngerende 2	30.33 \pm 0.58	141.73 \pm 2.06	33.06 \pm 0.96	30.43 \pm 0.81	123.33 \pm 0.58	1206.33 \pm 1.53	483.67 \pm 4. 72
Old Mara Bridge	29.02 \pm 2.89	149.14 \pm 6.49	30.50 \pm 0.81	31.95 \pm 1.92	79.46 \pm 1.94	1309.33 \pm 61.85	681.23 \pm 6 8.8
New Mara Bridge	28.83 \pm 1.31	145.36 \pm 3.11	13.83 \pm 2.81	15.48 \pm 2.68	69.10 \pm 1.73	1630.00 \pm 96.56	373.47 \pm 8. 66
Tarime (Before Mines)	26.08 \pm 0.10	41.41 \pm 2.05	21.73 \pm 6.35	24.23 \pm 1.97	46.38 \pm 2.28	1285.13 \pm 4.39	456.00 \pm 2
Tarime (After Mines)	32.50 \pm 3.83	8.08 \pm 2.35	8.07 \pm 1.79	13.15 \pm 0.27	17.78 \pm 2.92	1093.40 \pm 24.48	505.33 \pm 3. 05
Nyahenda Stream (Control 2)	21.47 \pm 0.33	5.37 \pm 0.30	0.10 \pm 0.01	5.73 \pm 0.46	6.13 \pm 0.42	223.57 \pm 2.22	42.32 \pm 0.34
Kirumi (Wetlands)	65.80 \pm 0.65	3.16 \pm 0.20	0.37 \pm 0.46	8.18 \pm 0.57	5.53 \pm 1.22	442.07 \pm 5.25	95.19 \pm 2.50
CV (%)	5.76	3.19	16.70	8.06	2.82	4.70	6.38
LSD (P \leq 0.05)	2.88	5.39	4.51	3.17	2.78	86.69	40.76

Nd = not detected, SE = Standard error

4.2.3 Silicates

The mean silicates concentrations along the Mara River is as illustrated in Table 7. All sites registered an increase from the control sites, with the wetland in kirumi registering the highest silicates concentrations. Previous studies established that mining and dust were inseparable, with the main dust component being silica (Ogola *et al.*, 2001). This is comparable to the increase in silicates concentration after the mining sites downstream along the River. The most significant man-made land use that affects the silicates concentration along the Mara River is the mining activities. The vegetative destruction via mining and the heaps of sandy soil within the mining vicinity is the main route of silica dust finding its way into the Mara River thus tending to increase its concentration. However the concentrations of silicate registered at Kirumi wetland, is above the standard who limits of 1 to 30 mg/l in surface water (WHO 1987). Confirming the Mara River as one of the source of silicate pollution in Lake Victoria.

The wetland site in kirumi registered the most significant reduction in all the nutrients concentrations other than the silicates. This decrease in nitrogen and phosphorous nutrients is as a result of their uptake by the population of aquatic vegetation within the wetland. However the silicate concentration in the Mara River fell within acceptable WHO limits of 100 mg/l (2011) in surface water.

4.4 Heavy metals in water and sediments

The variation in the mean heavy metals concentrations in water and sediments are as illustrated in Tables 8 and 9 respectively.

4.4.1 The heavy metals in water and sediments

Previous studies carried around the Mara Mines along Mara River in Tanzania revealed that the surface and sediment in the studied areas were grossly contaminated with heavy metals (Kihampa & Wenaty, 2013). with some of the water heavy metals mean ranges quite comparable to the concentrations registered in this study within the after mine site(site 8); Cu 20 ± 0.006 ug/l, Fe 33.49 mg/l ± 15.90 in the previous study carried within the mining areas and the mean concentration of Cu 24.53 ± 0.71 ug/l, Fe 41.00 ± 1 mg/l during this study.

All the heavy metals analyzed at a confidence limit of ($P \leq 0.05$) exhibited a significant increase from the control site 1(Ainapsabet spring). The concentration of the heavy metals upstream

before the mining site and downstream from control site 1, is attributed to presence of these trace elements in the agricultural inputs, applied in the farm lands. The larger concentrations increases after the mining site (site 8). Further downstream at the wetland, there was a significant decrease in all the heavy metals concentrations. Aquatic vegetation are known to utilize ionic elements as nutrients thereby lowering their concentrations in aquatic environments (Belke, 2007). The low concentrations registered within the Kirumi wetland is attributed to uptake of these heavy metals by the aquatic plants. The concentration of the heavy metals in sediments exhibited a similar trend of increase similar to the concentration in water but registered higher concentrations due to continuous sedimentation of the metals from the water surface.

At the wetland in kirumi, before discharging into lake Victoria, all the metals other than lead concentration fell within the WHO 2008 permissible limits for domestic surface water. but the lead concentration of 12.07 ± 0.41 ug/l was within the NEMA 2006 permissible limit of 50 ug/l.

Mean heavy metals concentration in rivers Nyando, Nzoia and Yala range from Pb : 29.5 to 93.6 $\mu\text{g/l}$, Cu : 10 to 57.9 $\mu\text{g/l}$, Zn : 25 to 124.8 $\mu\text{g/l}$ (Lalah *et al.*, 2008). Other than the site after the mining, the Mara River as per the concentrations registered at Kirumi wetland, the Mara River would hold as one of the river within the lake Victoria basin that is least as a pollutant to Lake Victoria waters in regards to heavy metals pollution, other than the zinc concentrations.

The Iron concentration in Mara River, even at the least concentration site (Kirumi wetland) was higher than the recommended EPA limits of 2.0 mg/l and WHO limits of 0.3 mg/l in surface waters (EPA, 2008). However even the control sites registered concentrations above this limit an indication of high background iron concentration within this river basin. All the other metals analyzed in this study fell within the NEMA, WHO, limits for concentrations in surface waters. (NEMA, 2006; WHO, 2011) as reflected in tables 2 and 3.

Table 8: The Mean \pm SE heavy metals concentrations in water at different sites along the Mara River

Site name	Pb $\mu\text{g/l}$	Cd $\mu\text{g/l}$	Cr $\mu\text{g/l}$	Cu $\mu\text{g/l}$	Zn $\mu\text{g/l}$	Fe mg/l
Ainabsabet Spring (control 1)	3.88 ± 0.05	0.11 ± 0.01	21.01 ± 1.00	1.30 ± 0.02	77.69 ± 0.55	12.49 ± 0.03
Emarti Site	23.13 ± 0.13	0.60 ± 0.02	28.78 ± 0.19	3.80 ± 0.02	173.30 ± 0.61	31.49 ± 0.53
Ngerende 1	21.12 ± 0.27	0.50 ± 0.02	30.76 ± 0.11	3.61 ± 0.01	169.41 ± 2.07	23.82 ± 0.17
Ngerende 2	27.10 ± 0.90	0.50 ± 0.02	29.03 ± 0.06	4.10 ± 0.1	109.60 ± 0.53	24.00 ± 1.22
Old Mara	25.17 ± 1.10	0.51 ± 0.02	27.57 ± 0.58	3.50 ± 0.02	107.07 ± 0.90	22.17 ± 0.59
New Mara	16.0 ± 0.20	0.50 ± 0.02	29.18 ± 0.25	5.28 ± 0.06	103.67 ± 1.52	25.97 ± 0.32
Tarime(Before Mines)	19.47 ± 0.64	0.60 ± 0.04	32.62 ± 0.56	9.03 ± 0.67	206.10 ± 1.95	25.43 ± 1.08
Tarime (After Mines)	49.80 ± 0.20	0.72 ± 0.02	82.26 ± 1.44	24.53 ± 0.71	935.67 ± 6.66	41.00 ± 1
Nyahenda Stream (control 2)	6.21 ± 0.21	0.10 ± 0.02	6.87 ± 0.06	4.29 ± 0.14	92.00 ± 4	10.77 ± 0.39
Kirumi (Wetlands)	12.07 ± 0.41	0.20 ± 0.01	8.27 ± 0.22	3.70 ± 0.02	129.00 ± 1	7.79 ± 0.15
CV (%)	2.66	4.86	2.12	5.89	1.26	2.87
LSD ($P \leq 0.05$)	0.92	0.04	1.07	0.63	4.52	1.10

SE=Standard error

Table 9: Mean \pm SE Concentration of heavy metals in sediments at different sites along the Mara River

Site No	Site Name	Pb $\mu\text{g/g}$	Cd $\mu\text{g/g}$	Cr $\mu\text{g/g}$	Cu $\mu\text{g/g}$	Zn $\mu\text{g/g}$	Fe $\mu\text{g/g}$
1	Ainabsabet Spring	57.67 ± 1.53	13.00 ± 1.00	581.33 ± 1.53	109.33 ± 0.58	12.00 ± 0.50	2256.67 ± 10.41
2	Emati Site	182.00 ± 2.00	123.00 ± 1.00	746.00 ± 22.7	210.67 ± 2.08	653.33 ± 11.37	6065.67 ± 61.21
3	Ngerende 1	167.00 ± 6.24	130.33 ± 1.53	682.00 ± 12	325.00 ± 5.00	633.33 ± 10.41	4748.67 ± 1.15
4	Ngerende 2	156.67 ± 6.11	121.33 ± 1.53	689.67 ± 2.08	326.00 ± 2.00	631.33 ± 1.53	4764.67 ± 5.13
5	Old Mara Bridge	139.00 ± 1.00	123.00 ± 2.64	654.67 ± 4.94	318.00 ± 2.00	640.00 ± 4.00	4393.00 ± 4.58
6	New Mara Bridge	138.67 ± 0.56	142.33 ± 1.53	636.00 ± 6.00	305.00 ± 3.21	642.33 ± 6.03	4206.00 ± 5.50
7	Tarime (Before Mines)	187.00 ± 2.65	156.00 ± 2	619.00 ± 1.00	408.00 ± 6.08	746.00 ± 2.00	4590.00 ± 9.71
8	Tarime (After Mines)	922.00 ± 7.21	157.33 ± 2.08	1654.67 ± 16.04	922.33 ± 17.62	1347.67 ± 41.19	6533.67 ± 4.04
9	Nyahenda Stream	102.33 ± 1.52	6.67 ± 2.08	528.00 ± 2.00	219.67 ± 3.51	310.00 ± 8.00	2070.00 ± 2.00
10	Kirumi(Wetlands)	109.00 ± 1.00	10.00 ± 1.00	531.67 ± 5.03	175.00 ± 6.08	608.67 ± 8.62	2015.00 ± 7.09
	CV (%)	1.77	1.75	1.37	2.03	2.35	0.49
	LSD (P \leq 0.05)	6.51	2.93	17.03	11.49	24.864	34.68

SE= standard error

Chapter 5

5.1 SUMMARY AND CONCLUSION

Although most of the water physicochemical parameters; pH, temperature, dissolved oxygen, turbidity, total dissolved solids, total suspended solids and electrical conductivity fell within acceptable mean ranges of both WHO and NEMA (WHO, 2011, NEMA, 2006) quality standards, there was a tendency of a build up on some parameters such as TDS, EC, Turbidity, TSS and lower concentration of dissolved oxygen (6.14 ± 1.55 mg/L) as evidenced by the registered concentration at Kirumi posing a future threat to the river ecosystem.

The land uses along the Mara River do impair the water nutrient concentrations, with the most abundant nutrient influxes being Total Nitrogen and Total phosphorous. The main nitrogen sources along the Mara River are agricultural farms courtesy of agricultural inputs such as manures and fertilizers, while phosphorous is mainly from animal waste /manures as evidenced by high phosphorous concentrations after pool of hippopotamus at Ngerende sites. However these are within acceptable standard limits.

Land use along the Mara River contributes to heavy metal loading in the river, with mining activities being the most significant influx of heavy metals. The heavy metals concentrations in sediments are higher in concentration than in water due to the strong binding affinity of the heavy metals to the sediments. The sediments in the Mara River are thus a sink of Lead, Cadmium, Chromium, Copper, Zinc and Iron metals.

The wet land in Kirumi plays a significant role of water purification, thus reduction of these contaminants just before the Mara River drains into Lake Victoria, hence mitigating the pollution effects upstream.

5.2 Recommendations

Most of the land uses along the Mara River in regards to surface water quality are sustainable. But these should be periodically monitored as is evidence by a buildup of some contaminants, to remedy for future pollution.

Inhabitants within the Mara River basin should be discouraged from land tilling up to the banks of the river and, instead, be encouraged to conserve the bank vegetation as this will aid in soil conservation by reducing erosion as well as sediment loading in the Mara River.

There is need for the conservation of the wetland in Kirumi as it played a significant role in the reduction of both nutrients and heavy metals concentrations. Thus this wetland plays a significant role in minimizing pollution levels entering Lake Victoria from within the Mara River basin.

Artificial wetlands could be constructed at each and every bank adjacent to farming lands that utilize fertilizer applications, as a control measure to minimal entry of fertilizer residues finding way into the river.

5.3 Suggestions for future studies

There is need to widen up the scope for other elements of interest not covered in these study that are of environmental concern, There is need for further studies within the wetland to understand the implications that might arise in case of a shift in the algal species/decay of the aquatic vegetation or decomposition of the aquatic vegetation in terms of the nutrients and heavy metal concentrations.

Chapter 6

6.0 References

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