LAND USE CHANGE AND TEMPORAL WATER QUALITY DYNAMICS ON THE SLOPES OF MOUNT MERU

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ABSTRACT

This work reports on the results obtained following the study on the land use change and temporal water quality change in rivers of the slopes of Mount Meru in Northern Tanzania between 2015 and 2016. Satellite images collected from United States Geological Survey (USGS) were used to model the land use change using ArcGIS and IDRISI software. Also, 419 water samples and two (2) rocks samples were collected from various geo-referenced points and assessed for sixteen (16) water quality changes using standard methods for water and wastewater from American Public and Health Association (APHA). The stable isotope studies were done at the University of Waterloo stable isotopes laboratory using the Los Gatos Research Laser processes analyzer with Integrated Cavity Output Spectroscopy (LGR-ICOS™).

The study showed significant land use changes in the area in every ten (10) years over a period of thirty (30) years such that, there is an increase in human settlement from 74.2 km^2 (1986) to 261.2 km^2 (2016), decrease in agricultural land from 545.8 km^2 to 531.5 km^2 (2016). Also, in similar years the bush-land decreased from 372.3 km^2 (1986) to 158.4 km^2 (2016) in favour of increase of settlement. Moreover, the mixed forest were improved from 139.7 km^2 (1986) to 116.0 km^2 (2016) whereas the water bodies decreased significantly from 14.0 km^2 (1986) to 4.2 km^2 (2016). In addition, the water quality in rivers deteriorated due to increased human activities, poor performing Wastewater Treatment Systems (WTS) which discharge its effluents in rivers, and bad agricultural practices. Few sampling points in rivers had Biochemical Oxygen Demand (BOD), NO_3^- and Total Soluble Phosphate (TSP) levels higher than the World Health Organization (WHO) standards of 10 mg/L, 50 mg/L and 0.1 mg/L, respectively. Fluoride contamination in Themi, Nduruma and Tengeru Rivers were within the WHO and Tanzania Bureau of Standards (TBS) maximum acceptable limits of 1.5 mg/L and 4.0 mg/L, respectively. Maji ya Chai River showed the highest levels of fluorides and dissolved organic matter of up to 69.01 ± 0.03 mg/L and 10 ± 0.2 mg/L, respectively, which are higher than the WHO standards. The study confirmed the main source of fluorides in water is rocks containing fluoride in which its leaching is favoured in alkaline environment. Also the stable isotopes studies revealed the origin of Dissolved Organic Matter (DOM) were plant materials and soil composites whereas NO_3^- originated from wastewater, urea fertilizers, and animal manures. The major sources for coloured dissolved organic matter

and fluoride contents in Maji ya Chai River were discovered at Kirurumu hill (M1) and Jamera (M2), respectively.

DECLARATION

I, Aldo Kitalika do hereby declare to the Senate of the Nelson Mandela African Institution of Science and Technology (NM-AIST) that this dissertation is my own original work and that it has neither been submitted nor being concurrently submitted for degree award in any other Institution.

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CERTIFICATION

The undersigned certify that they have read and hereby recommend for examination of a dissertation entitled; "Land Use Change and Temporal Water Quality Dynamics on the Slopes of Mount Meru", to be accepted in partial fulfillment of the requirements for the PhD Degree in Environmental Science and Engineering of the Nelson Mandela African Institution of Science and Technology (NM-AIST) Arusha, Tanzania.

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This work is dedicated to my parents; Japhet Kitalika, Redenta Mhegele, my lovely wife Clara, and my lovely children Baraka, Belinda and Bennett for their patience during my study.

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AG	Agriculture
ANP	Arusha National Park
APHA	American Public Health Association
BL	Bush Land
BDL	Below Detection Limit
BOD	Biochemical Oxygen Demand
CA	Cellular Automata
CA-MC	Cellular Automata-Markov Chain
CAN	Calcium Ammonium Nitrate
CDOM	Chromophoric/Coloured Dissolved Organic Matter
COD	Chemical Oxygen Demand
DAP	Double Ammonium phosphate
DDD	[1, 1-dichloro-2, 2-di (4-chlorophenyl) ethane]
DDE	[1, 1-dichloro-2, 2-di (4-chlorophenyl) ethylene]
DDT	Dichlorodiphenyl trichloroethane [1, 1, 1-trichloro-2, 2-di (4-Chlorophenyl) ethane
DIC	Danish Isotope Centre
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
EC	Electrical Conductivity
EDC	Endocrine Disrupting Chemicals
ETM	Enhanced Thematic Mapper
FC	Faecal Coliforms
FCU	Faecal Coliforms Units
GIS	Geographical Information System
GMWL	Global Metrological Water Line
GPS	Geographic positioning system
GW	Ground Water
HCH	Hexachlorohexane
KIA	Kappa Index of Agreement
LGR-ICOS	Los Gatos Research -Integrated Cavity Output Spectroscopy

LTM	Landsat Thematic Mapper
LULC	Land Use Land Cover Change
MC	Markov Chain
MCA	Markov Cellular Automata
NDVI	Normalized Difference Vegetation Index
MF	Mixed Forest
NM-AIST	Nelson Mandela African Institution of Science and Technology
NSF	National Sanitation Foundation
NTU	Nepherometric Turbidity Unit
OLI	Operational Land Imager
PBWO	Pangani Basin Water Office
PCA	Principal Component Analysis
POP	Persistence Organic Pollutant
POC	Particulate Organic Carbons
PP	Phosphate Phosphorus
PRB	Pangani River Basin
PTFE	Polytetrafluoroethylene
RCC	River Continuum Concept
QDS	Quarter Degree Sheet/Square
RFU	Relative Fluorescence Units
RGB	Red Green and Blue
RK	Rocks
RPM	Revolution per Minute
ST	Settlements
SWAT	Soil Water Agriculture and Transpiration
TBS	Tanzania Bureau of Standards
TDS	Total Dissolved Solids
TIR	Thermal Infra-Red
TISAB	Total Ionic Strength Adjustment Buffer
TM	Thematic Mapper
TOC	Total Organic Carbon
TP	Total Phosphate
TS	Total solids

TSP	Total Soluble Phosphate
TSS	Total Suspended Solids
TURB	Turbidity
UNEP	United Nations Environmental Protection
UNESCO	United Nations Educational, Scientific and Cultural Organization
US EPA	United States Environmental Protection Agency
US	United States
USGS	United States Geological Survey
UTM	Universal Transverse Mercator
VPDB	Vienna Pee Dee Belemnite
VSMOW	Vienna standard Mean Ocean Water
WAI	Weighted Arithmetic Index
WB	Water Bodies
WESE	Water Environmental Science and Engineering
WHO	World Health Organization
WSP	Waste Stabilization Ponds
WQI	Water Quality Index
WTS	Waste Treatment System
XRD	X-Ray Powder Diffraction

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CHAPTER ONE

General introduction

1.1 Background of the problem

Temporal water quality dynamics is a continuous change of water quality parameters and how they interact with each other in relation to its environmental changes. Water quality dynamics is based on the River Continuum Concept (RCC) which hypothesizes that a continuous gradient in physical condition of water exist from the catchment headwater to mouth (Vannote *et al.,* 1980). The concept views the river network as a product of a constantly incorporated series of physical modifications and resource gradients (such as land use and land cover changes) to which the biota and ecosystem processes adjust (McDonald *et al.,* 2004).

It is estimated that drinking unclean and unsafe water will cause 135 million people's deaths between 2000 and 2020 (Gleick, 2002; Schlager, 2005). Despite all water bodies present on earth, only 0.62% is fresh water in which among others, rivers are the main contributors (West, 2006). Despite the fact that the world's population is increasing every day, such small fresh water sources are decreasing due to unfriendly land use which include unsustainable agriculture, mining, natural disasters, climate change, emerging micro plastic pollution, and engineering activities (World Health Organisation (WHO), 2019). Water quality is contributed by biological, physico-chemical, micro-contaminants, and microbiological factors (Hellar-Kihampa *et al.,* 2013). The physico-chemical and microbiological factors account for the primary drinking water quality parameters while the biological factors regulate the secondary water quality parameters (World Health Organisation (WHO), 2017).

1.1.1 Water pollution studies in Tanzania

In the past most of the studies on water quality and pollution in Tanzania were conducted in major towns and cities which are densely populated like Dar es Salaam, Tanga and Zanzibar (Ngoile *et al*., 1978; Steinbach, 1974). Current studies were done by Ghiglieri *et al*. (2010; 2011; 2012) on Fluoride distribution in springs and ground water of the Eastern Africa Rift-Northern part of Tanzania and showed high fluoride levels of up to 68 mg/L. Such high levels of fluoride were associated with the presence of volcanic rocks containing such mineral element. Therefore, high fluoride levels in surface water are a result of an interference pattern between groundwater and the surface water. More studies on water

quality variability in the Pangani basin show the ongoing rapid expansion of human activities and population dynamics are the major cause for elevation of physico-chemical characteristics of water and change in geochemistry (Selemani *et al*., 2017). Thus, the low coverage of water quality studies in this basin necessitates further studies.

1.1.2 Dynamics of water quality in rivers

Several studies on water quality dynamics in rivers have been carried out in different areas of the world to evaluate how they are related with the surrounding environment. For example, in Tanzania the study spanned from domestic use in the Pangani basin to water quality for irrigation purposes. The study by Alavaisha *et al*. (2019) on assessment of water quality across irrigation schemes in Kilombero valley show agrochemicals and fertilizer run-off and leaching at local scales are the major contributors to the poor water quality. Also, water more studies were conducted in different parts of Tanzania and found that the main contributors were pesticides (Kitalika & Kishimba, 2011), nutrients (Mihale, 2015), organic contaminants (Aschermann *et al.,* 2016), microbes (Elisante & Muzuka, 2016b) and toxic and trace metals (Mataba *et al.,* 2016). On the other hand the physico-chemical and Dissolved Organic Carbon (DOC) dynamics studied by Harun (2006; 2013) in the lower Kinabatangan River in Malaysia revealed that the dynamics were derived from microbial activities and photo-degradation. Also Jawan (2008) assessed the water quality dynamics in river Billabong Kinabatangan and Sungai Padas which was associated with palm plantation with higher COD in wet than dry season. In addition, Josephine *et al.* (2004) studied the land use change in relation to water quality dynamics in the lower Kinabatangan catchment and established that there is a strong positive correlation between change in environment and water quality which is associated with active land development due to large palm plantations. They also found that, most water quality parameters were above the maximum recommended limits with very high levels of Fecal Coliforms (FC) of up to 1.4×10^7 FCU/100 mL.

1.2 Statement of the problem

The slopes of mount Meru have experienced different environmental changes which have affected the recharge potentials in their surrounding water sources (Makoba & Muzuka, 2019). This area has several rivers (Temi, Nduruma, Tengeru, Usa and Maji ya Chai) which are important for socio-economic development of its communities and the environment. While those communities are highly dependent on those rivers, there is limited information on the quality status of the river water. It is worth noting that the pollutions sources in rivers

and the pollutants dynamics in this area are not yet established. Furthermore, Arusha springs and rivers are known to contain high levels of fluoride and Dissolved Organic Carbon (DOC) but it is unknown which streams have major contributions to the main rivers. Therefore, undertaking this study is of profound importance for unveiling the pollution status, pollutant sources and their control measures which in turn will help to decrease the problems of scarce clean and safe freshwater sources in the Arusha City and its surrounding.

1.3 Rationale of the study

The knowledge for water quality dynamics in rivers in relation to environmental changes is important for sustainable freshwater bodies' development since environmental changes have a direct impact to the water quality and quantity. Currently, there are limited water quality data in rivers on the slopes of mount Meru in which the available (present) data are only based on water quality status collected from few monitoring stations solely for immediate use by Arusha Urban Water and Sewerages Authority (AUWSA) and the Pangani Basin Water Office (PBWO).

1.4 Research objectives

1.4.1 General objective

The general objective of this study is to assess the pollution status and its dynamics in Temi, Nduruma, Tengeru and Maji ya Chai Rivers in different hydrological periods.

1.4.2 Specific objectives

The specific objectives of this study are:

(i) To evaluate the past, present and future land management practices and land use changes in relation to recovery regimes of the mount Meru Rivers over past 30 years.

(ii) To evaluate the seasonal and spatial physical, biological, chemical and microbiological qualities and trends for selected rivers from the upper catchment to the flood plains.

(iii) To establish the sources of fluorides and DOC in streams.

(iv) To establish the spatial Water Quality Index (WQI) for each river and to assess its overall quality.

1.5 Research questions

The research questions investigated in this study are:

(i) What land use changes have taken place on the slopes of mount Meru Rivers over 30 years?

(ii) What land use changes on mount Meru Rivers are anticipated in the future 10 years?

(iii) What are the inter-seasonal and temporal spatial variations of physico-chemical and biological parameters of surface water from rivers on the slopes of Mount Meru?

(iv) What are the sources, amount and nature of pollutants are present in rivers?

(v) What are the fates of pollutants present in rivers?

(vi) What is the quality status of water in rivers on the slopes of Mount Meru?

1.6 Significance of the study

Therefore, results from this study will generate baseline information in addition to those from AUWSA and PBWO on the status, quality dynamics and proper management strategies which will hasten the river recovery regime, which in turn will help to reduce water treatment costs. Also, the results from this study will provide useful information to stakeholders; policy and decision makers at different levels on endorsing appropriate environmentally friendly interventions that will ensure sustainability of these fresh water sources. In addition, the suggested conservation measures in those rivers will increase the aesthetic value of rivers and improve the rivers environment hence make them attractive to other activities such as tourism and general recreation.

1.7 Delineation of the study

Several parameters contribute to water quality assessment. In this study, the primary water quality parameters have been studied. These include; Dissolved Oxygen (DO), Fecal Coliforms (FC), pH, Biochemical Oxygen Demand (BOD), Temperature Change, Nutrients, Turbidity, Total Dissolved Solids (TDS), fluorides status and sources and Dissolved Organic Carbons (DOC). Together with these, the land use changes in relation to the river conservation will be studied.

CHAPTER TWO

Literature review

2.1 Physical attributes of water quality

Physical attributes of water quality are the physical properties of water that can influence the quality of a particular water body. There are several attributes which includes water velocity, river depth and physico-chemical properties.

2.2 River hydrology and hydraulics

River hydrology such as flow regimes and it hydraulics (velocity, width and depth) plays an important role in water quality (King *et al*., 2008). The hydrological regime is of major importance in the functioning of the river and its influences differ depending on the constituent biotic and abiotic components. Thus, the natural historical and present flow regimes of the rivers are important to understand the variability in water quality and quantity. Rivers are characterized by uni-directional current with a relative flow velocity range of 0.1 ms^{-1} to 1 ms^{-1} (Vannote *et al*., 1980). The continuous vertical mixing is achieved in rivers when there are prevailing currents and turbulence (UNESCO/WHO/UNEP 1996; Vannote *et al*., 1980). The study done by King *et al*. (2008) reported many of the Pangani basin's rivers flow in only part of the year because of high water abstraction for domestic and different agricultural activities and reduced the capacity of discharge in the upper area of the Pangani River Basin (PRB). It is estimated that the discharge capacity of their watersheds has decreased from 26.8 m^3/s to 15.1 m^3/s and water abstraction has recently reached 900 million m^3/year (Shaghude, 2016).

2.3 Physico-chemical attributes

Physico-chemical attributes of rivers are important indicators of its water quality. The chemical attributes of water can affect the aesthetic qualities such as how water looks, smells, its potability and tastes. Physico-chemical parameters in water includes the levels of pH, temperature, turbidity, colour, conductivity, alkalinity, salinity, Total Solids (TS), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Dissolved Oxygen (DO), Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD). Others are calcium hardness, magnesium hardness, Total Hardness (TH), sulphates, chlorine, fluorine, heavy metals, Persistent Organic Pollutants (POPs), Endocrine Disrupting Chemicals (EDCs) and pesticides. It also include nutrients such as Ammonical-Nitrogen (NH_3-N), Nitrogen Nitrate (

NO_3^--N), Nitrogen Nitrite (NO_2^--N), Total Nitrogen (TN), Total Soluble Phosphates (TSP), Total Phosphates (TP) and Phosphate Phosphorus (PP).

2.3.1 pH

Water pH indicates the acidic or alkaline level it is. If the water in a stream is too acidic or basic, the H^+ or OH^- ion activity may disrupt the aquatic organisms' biochemical reactions by either harming or killing the stream organisms and accelerate the availability or unavailability of certain pollutants in water (United States Environmental Protection Agency (US EPA), 1997). Streams and natural water generally have a pH values between 6 and 8.5 depending on the presence of dissolved substances that come from bedrocks, soils and other materials in the watershed. Highly acidic or highly alkaline water are undesirable because of corrosion hazards and possible difficulties in treatment (Baird & Bridgewater, 2017). When the pH of water increases, smaller amounts of ammonia are needed to reach a level that is toxic to fish and when it is low may increase the concentration of metallic ions because higher acidity increases their ability to dissolve from sediments into water (Murdoch *et al.,* 2012).

2.3.2 Salinity and conductivity

Salinity indicates the concentration of dissolved salts in a water body. The ions responsible for salinity include the major cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and the major anions; carbonates (CO_3^{2-}), bicarbonates (HCO_3^-), sulphates (SO_4^{2-}) and chloride (Cl^-) (Friedl *et al.,* 2004). Salinity influences dissolved oxygen concentrations. Dissolved oxygen is low in highly saline waters and vice versa. Conductivity (Λ) is a measure of how well the water conducts the electrical current. This property is proportional to the concentration of ions in solution. Distilled water has an Electrical Conductivity (EC) range of 0.5 μS/cm to 3.0 μS/cm while EC in most streams range between 50 μS/cm to 1500 μS/cm and for freshwater streams EC is expected to be between 150 μS/cm to 500 μS/cm, which favours the aquatic life (Dodds, 2002). Waters in lower Pangani River Basin (PRB) have shown to be dominated with Na^+ and HCO_3^- which is one of the main contributors of salinity and temporary hardness. On the other hand the principal component analysis showed that, weathering of carbonate and Na^+ bearing rocks, gypsum dissolution and atmospheric deposition of sea salt are the major factors controlling the ionic composition, contributing more than 60% of the spatial variance in lower PRB (Kihampa *et al*., 2013). Also Selemani *et al*. (2017) showed the increase of dissolved silicates in the lower PRB is caused by chemical weathering of the

volcanic rocks from different sources. They further found that within similar areas of study, the nutrients levels were higher than that recommended for aquatic health. Similar study by Jokha, *et al*. (2014) showed the degradation of water quality in Weruweru was caused by nutrients and agriculture pesticides. Also Ngoye and Machiwa (2004) found that land use pattern had a significant influence in the water quality of Ruvu River. In addition, the land use change in the frontier settlement zone of Mount Meru has shown to affect the discharge pattern of their associated watersheds in an area (Ueda, 2011). In other countries Silva *et al*. (2015) found that the tropical estuary in northeastern Brazil was polluted by inorganic nutrients and chlorophyll–*a*. Currently, there is no current study on the pollution status of the main watershed catchment of the lower PRB.

2.3.3 Turbidity and temperature

Turbidity refers to water clarity. It is caused by suspended solids in water. The sources of turbidity in water are phytoplankton, particulates such as clays and silts from shoreline erosion, re-suspended bottom sediments, clastic particles from rocks and organic detritus from stream and/or water discharges. The source of sediments includes natural and anthropogenic activities in the watershed, such as natural or excessive soil erosion from agriculture, forestry or construction, urban run-off, industrial effluents and excess phytoplankton growth (United States Environmental Protection Agency (US EPA), 1997). Water bodies that have high transparency values typically have good water quality. The degree of turbidity of a stream is often used to measure the intensity of pollution. Turbidity blocks out the light needed by submerged aquatic vegetation for photosynthesis and lowers dissolved carbon. It can also raise surface water temperatures above normal since suspended particles near the surface facilitate the absorption of heat from sunlight.

Water temperature controls the rate of metabolic activities and reproductive activities of aquatic animals. Water temperatures can fluctuate seasonally, daily, and even hourly, especially in smaller sized streams. Water temperature is influenced by the canopy cover, discharge and velocity of stream flow. Changes in water temperature affects the amount of dissolved oxygen such that it becomes easily dissolved in cold water than in warm water (Murdoch *et al.*, 2012).

2.3.4 Solids in water

Solids in water can be measured in soluble and non–soluble forms. Thus, total solids (TS), Total Suspended Solids (TSS) and Total Dissolved Solids (TDS) are monitored in water quality. The TS is a measure of suspended and dissolved solids in water body. Total suspended solids are due to particles, which can be measured by filtering a sample through a fine paper surface (<0.45 µm). The common natural concentration of suspended solids in fresh water ranges between 3.0 to 15.0 mg/L. The principle constituents of TDS are Ca^{2+}, Mg^{2+}, Na^{+}, HCO_3^{-}, Cl^{-} and SO_4^{2-}. Suspended solids in streams interfere with photosynthesis, cause damage to benthic organisms, affect fishering, aesthetic of the river and affect the taste of water. The taste of water with a TDS <600 mg/L is generally considered to be good whereas drinking water with TDS >1200 mg/L becomes unpalatable (Wetzel, 2001).

2.3.5 Hardness

Water hardness is the total concentration of cations, specifically Ca^{2+}, Mg^{2+}, Fe^{2+} and Mn^{2+} in water. Water rich in these cations is said to be "hard." The hardness is said to be temporary when the above ions are combined with HCO_3^{-}, and CO_3^{2-} and permanent when combined with SO_4^{2-}, Cl^{-} and any other anions of mineral acids. Stream water hardness may reflects the geology of the catchment area (Wetzel, 2001). Despite causing hardness, calcium is an important mineral that is used by plants and animals and also buffers the stream's pH (Wetzel, 2001). Hardness can be measured in terms of calcium hardness, magnesium hardness and Total Hardness (TH). The scale of water hardness is categorized as indicated in Appendix 1. The sources of hardness in river water of lower Pangani basin have been shown to originate from bicarbonates and carbonates of magnesium cations which are a result of weathering of rocks (Kihampa *et al*., 2013).

2.3.6 Dissolved oxygen

Aquatic plants and animals depend on dissolved oxygen for their metabolic activities. High levels of dissolved oxygen are best for a healthy ecosystem and its amount depends on water temperature, time of the day, season, depth, altitude, magnitude of the pollutants present and flow rate. The main sources of oxygen in water are re-aeration and photosynthesis. The O_2 concentration of 0-2 mg/L is not enough to support life while 2-4 mg/L is enough for only few fish and aquatic insects to survive whereas 4-7 mg/L is good for many aquatic animals.

Usually streams with high dissolved oxygen concentrations >8 mg/L are considered healthy streams. Some human activities such as removal of riparian vegetation increase water temperature thus decrease oxygen dissolution. Others include discharge of oxygen demanding wastes from different sources such as sewerages, industries and agriculture (Murdoch *et al.,* 2012). In the case of rivers from Pangani basin, livestock keeping along the riparian environment and some agriculture activities have increased the oxygen demanding waste in water thus lowering the levels of DO to some extents (Kihampa *et al*., 2013).

2.3.7 Biochemical oxygen demand and chemical oxygen demand

The Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) accounts for the degree of organic matter pollution of a particular water body. The BOD measures the amount of oxygen removed from aquatic environments by aerobic micro-organisms for their metabolic requirements. Oxygen demanding wastes is a common problem to rivers passing in populated areas like cities (Myers, 2006). This is a case for Temi River which pass through the Arusha City and remain the only receiver of the treated waste water from the waste water stabilization ponds of the city in its floodplain environment. The COD is a measure of the oxygen equivalent of the organic matter in water sample that is susceptible to oxidation by a strong oxidant such as $Cr_2O_7^{2-}$ and MnO_4^- (United Nations Environmental Programe (UNEP), 1996). Unpolluted natural waters have a BOD level of 5 mg/L or less while raw sewage may have BOD levels ranging from 300 – 400 mg/L (Baird & Bridgewater, 2017; Murdoch *et al.,* 2012).

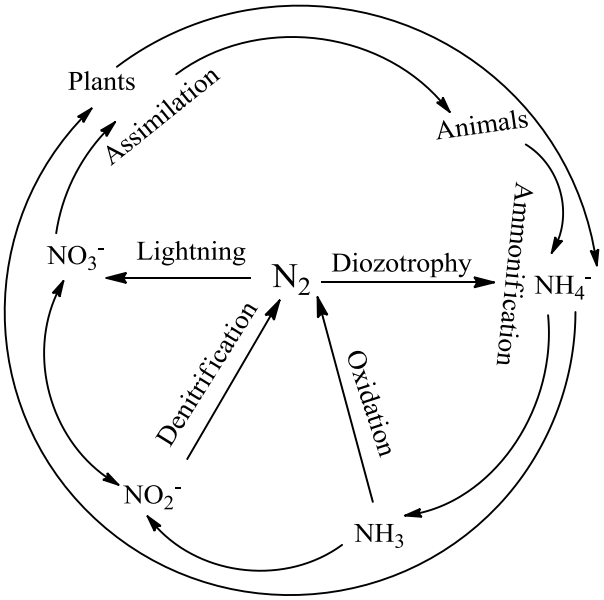
2.3.8 Fluorides

Fluoride originates from weathering of fluoride containing rocks. This is a serious problem in some parts of India, other Asian countries and many countries of Africa. In Tanzania, fluorides sources have been reported in Shinyanga, Singida, Kilimanjaro, Manyara, Kilimanjaro and Arusha. Fluorides sources in rivers of mount Meru slopes have been found to be associated with the volcanic rocks containing such minerals of which their levels of up to 68 mg/L in river water was reported (Ghiglieri *et al*., 2010; 2011; 2012). Higher levels (264 mg/L) of fluoride have been reported in other countries such as rift valley areas of Ethiopia (Redda *et al*., 2006). The work by Mamatha and Haware (2013) in India reported fluoride levels in lake waters of up to 3.0 mg/L. Most of the natural waters contain fluoride below 1.0 mg/L which is below the WHO maximum acceptable level of 1.5 mg/L. In

Tanzania the maximum permitted fluoride is 4.0 mg/L (TBS, 2014; World Health Organisation (WHO), 2004). Occasionally, high concentration of fluoride may enter a river as a result of industrial discharges. High concentration of fluoride is toxic to human and animal as they cause skeletal fluorosis (World Health Organisation (WHO), 2004; 2011; World Health Organization(WHO), 2004).

2.3.9 Nitrogen

The atmosphere consists of 78% nitrogen which plays an important and main source of nitrogen in the environment. The relation between different sources and forms of nitrogen is expressed well through the nitrogen cycle (Moir, 2011). The nitrogen cycle involves circulation of nitrogen in atmosphere, terrestrial and marine ecosystem. The processes of nitrogen cycle include fixation, ammonification, nitrification and denitrification. Fixation involves the conversion of nitrogen gas (N_2) into NO_3^- and NO_2^- which are the usable forms to plants. This process is done by nitrogen fixing bacteria, *Azotobacter* and *Rhizobium*. Plants absorb NO_3^-, NO_2^- and NH_4^+ from the soil via their root hairs by a process called assimilation (Kuypers *et al*., 2011). Ammonification involves conversion of organic nitrogen from dead plants and animals into NH_4^+. This process is also called mineralization. Nitrification involves conversion of NH_4^+ into NO_3^-. This process is done using soil living bacteria and other bacteria (nitrifying bacteria) such as *Nitrosomonas* which convert NH_3 to NO_2^- and *Nitrobacter* which oxidize NO_2^- into NO_3^-. Denitrification involves the reduction of NO_3^- into N_2 gas. This process is performed by *Pseudomonas* and *Clostridium* bacteria under anoxic environment. Another process which can fix nitrogen in the soil is lightning (Moir 2011; Moulton *et al*., 2016). This process involves conversion of atmospheric nitrogen into NH_3 and NO_3^- that enter soil with rainfall. The entire process for nitrogen cycle is summarized in Scheme 1.



Scheme 1: The nitrogen cycle

In natural water, nitrogen occurs in the form of NO_3^-, NO_2^- and NH_3. Nitrate (NO_3^-) is the most common tested form and the results are normally expressed as NO_3^- – N. Ammonia is the least stable form of nitrogen making it difficult to measure accurately. Nitrite (NO_2^-) is the most toxic form and less stable. It is present in much lower amounts than NO_3^-. These three compounds are interrelated through the process of nitrification which is the biological oxidation of NH_3 to NO_3^- through NO_2^-. The order of decreasing oxidation follows the trend: NO_3^- < NO_2^- < NH_3 < Organic Nitrogen (i.e. stable to unstable form (Van Der Maarel, 1996). It is unfortunate that scant studies have been done on nitrate trends in rivers except in sub catchments and lakes. The study by Kulekana (2004) in the Victoria basin showed nitrate levels of up to 1.54 mg/L which was lower than recommended standard levels for receiving waters in Tanzania. Another study by Nkotagu and Athman (2007) in the sub catchment area of Tanganyika showed the nitrate levels average of 2.6 mg/L.

NH_3 assumes two chemical forms of NH_4^+ (ionized and less/nontoxic) and NH_3 (unionized and toxic). The relative amount of NH_4^+ and NH_3 in given ammonia solution is basically a function of pH, temperature and its ionic strength of aqueous solution (Rand & Petrocelli, 1985).

Nitrate (NO_3^-) occurs in low quantities in surface water. It is among the macro nutrient which is necessary for photosynthesis and growth. It is commonly found in low levels in fresh domestic wastewater, but in effluents of nitrifying biological treatment plants, nitrate (NO_3^-–N) may be found in concentrations of up to 30 mg/L (Baird & Bridgewater, 2017). High amount of NO_3^-, may cause eutrophication and associated algal blooms become a problem (Rand & Petrocelli, 1985). Also, when NO_3^- is present in domestic fresh water it may cause methemoglobinemia (blue baby syndrome) if used in preparation of baby's food or drinking. Methemoglobinemia is a condition in which the red blood cells are prevented from transporting oxygen in the body thus causing suffocation to infants.

Nitrite (NO_2^-) is normally present only in trace amounts in freshwater due to its rapid oxidation to nitrate (NO_3^-). Its levels in water depend on pH such that when it is high it becomes less available since it is converted into NH_3 whereas when the pH is low it is oxidized into NO_2^-. High levels of NO_2^- inhibits both nitrobacteria and Nitrosomonas bacteria thus increasing more NO_2^- in solution (Rand & Petrocelli, 1985). The study shows that, few locations in rivers of lower Pangani were significantly enriched with nitrate and nitrite above the safe limits of exposure, with patterns indicating sources from anthropogenic activities (Kihampa *et al*., 2013).

2.3.10 Phosphorus

Phosphorus is usually present in river water as phosphates, and it is naturally found in very small amounts unless enriched by human activities. The natural scarcity of phosphorus is caused by its attraction to organic matter incorporated in soil particles. Phosphorus usually occurs in nature as phosphate (PO_4^{2-}). Phosphate that is associated in plant or animal tissue is termed as organic phosphate whereas that not bound with organic material is called inorganic phosphate (Hillbricht-Ilkowska *et al*., 2000). Other names given to inorganic phosphate is orthophosphate or reactive phosphorous or soluble phosphate (SP). It is a form that is assimilated by plants, and thus is the major cause of eutrophication (Dodds *et al*., 1998). It is recommended that the phosphate levels in rivers draining to the lake should not exceed 0.025 mg/L and if it is not should not exceed 0.1 mg/L. Inputs of phosphorus can originate from erosion, fertilizers, detergents and the draining of wetlands Taccogna, 1995). Phosphorus can be measured in terms of Total Soluble Phosphates (TSP), Total Phosphates

(TP) and Phosphate Phosphorus (PP). A study in phosphorus levels in Lake Victoria was done by Kulekana (2004) whereas Nkotagu and Athman (2007) studied the distribution of phosphorus in the sub catchment of Lake Tanganyika. Both studies showed higher levels of phosphorus than recommended by WHO.

2.3.11 Dissolved organic carbon

Dissolved Organic Carbons (DOCs) are organic material from living organisms with very small sizes; usually less than 0.22 μm in diameter hence can pass through a 0.45 μm filters. The remaining particles in such filter are termed as particulate organic carbons (POC) (Myers, 2006). They are food sources in aquatic food web. Their sources in aquatic ecosystems can be *allochthonous*, that is derived outside of the stream from soils and vegetation of the catchment and *autochthonous*, that is derived in stream from biota (Mook, 1986). The DOCs originating from a drainage basin are often composed of humic acids and may be yellow or brown in colour, imparting a characteristic colour to water. Sources of carbon dissolved in ground water are soil CO_2, geogenic CO_2, fluid inclusion CO_2, living and dead organic matter in soil and rocks, methane and carbonate minerals each contributing to total dissolved organic carbon in various proportions. The DOCs are characterized to be amino acids, phenolic compounds, fatty acids hydrocarbons, and carbohydrates. The stable form of DOC are fulvic acid and yellow organic (humic) acid (Oden, 1919; Shapiro, 1957; Kalle, 1966). They can also occur as aquatic humus (Gjessing, 1976) and 'unknown photo reactive chromophores' (Zafiriou, 1986). Humic acid is the major problem in Arusha waters thus it gives a yellowish-brown colored water similar to tea which this colour is named in Swahili “Maji ya Chai.” It is unfortunate that sources of these materials has not yet been studied in this region except in other rivers of the world such as McKenzie River, Oregon (USA) and their levels ranged between 0.3 mg/L to 2.0 mg/L (Kraus *et al*., 2010).

2.4 Microbiological attributes

The microbial aquatic community includes bacteria, viruses, protists and fungi. These organisms are important to aquatic ecosystem functioning. They are important decomposers of organic matter in aquatic ecosystems thus releasing nutrients and minerals in water that can be used to fuel metabolism of other organisms (Dolan, 2005). Viruses regulates production and diversity of the microbial food web through infecting them (Wommack & Colwell, 2000). The World Health Organization has identified the greatest health risk to human due to microbial contamination originates from consumption of water contaminated

by human or animal faeces (World Health Organisation (WHO), 2004). Measures of contamination from pathogenic organisms include total coliforms (TC) and faecal coliforms (FC) and high levels indicates discharge of untreated sewage effluents in rivers (Ashbolt *et al.,* 2001). Such coliforms are accompanied by non-pathogenic bacteria such as, enterococci bacteria and *Escherichia coli* bacteria which can be easily be detected. Thus the presence of *E. coli* in water is used as an indicator of contaminated water (Murdoch *et al.,* 2012). The recent study by (Mwakalobo *et al*., 2013) in the fresh, brackish and marine waters in Pangani and Ruvu estuary together with Mzinga creek has shown higher bacteria indicator in the fresh water but lower in the two environments. It should be noted that the Nduruma, Temi, Tengeru and Maji ya Chai Rivers are among the important rivers feeding River Pangani thus necessitates the study.

2.5 Stable isotopes of carbon

Organisms use the lighter isotopic species for its photosynthesis and metabolic activities since they are associated with lower bond energy breaking in those molecules. Thus due to existence of isotopes in an element there is significant fractionation between the substrates and biologically mediated products. Therefore, the ratio between heavier and lighter abundant stable isotope is useful for studying the origin, transport and fate of dissolved carbon (DC) in rivers (Mook, 1986). In order to be able to distinguish between the different carbon sources we have to know the $\delta^{13}C/^{12}C$ values of the various contributors and understand the isotopic fractionation processes in the water. Thus, stable isotopes signatures can be used to trace various pollution sources in environment (Hoefs, 2009; IAEA, 2000).

Fresh water plankton shows $\delta^{13}C$ of -32 to -44 ‰, organic carbon for terrestrial plants show $\delta^{13}C$ of -30 to -20 ‰, particulate organic carbon (POC) ranges between -20 ‰ and -26 ‰, organic matter have mean value of -25 ‰ and C_3 plants show at -28 ‰ to -25 ‰. In the absence of vegetation, atmospheric CO_2 may contribute to Dissolved Inorganic Carbon (DIC) by rock weathering, resulting in $\delta^{13}C$ values as high as -7 ‰ at low CO_2 concentrations (Hoefs, 2009; IAEA, 2000). Photosynthesis by upland trees involves a net fractionation of about 19 ‰, whereas that by tropical grasses including corn and maize involves a small fractionation of about 6 ‰ (Deines, 1980; Park & Epstein, 1961). River water DIC generally originates from groundwater with $\delta^{13}C$ values of the HCO_3^- fractionation of -12 ± 1 ‰. Particulate organic carbon isotope has fractionation at -20 to -25 ‰ at high and low temperatures, respectively, relative to dissolved bicarbonate with average of -23 ‰. The

schematic diagram for the major carbon pathways and the resulting isotope fractionation effects are shown in Appendix 2**.**

Stable isotopes have been used to study various pollution sources in environment, including the identification for sources of nitrogen and carbon in surface waters in the lower Susquehanna River Basin, Pennsylvania (Cravotta, 1997) and the sources of dissolved organic carbon (DOC) in the Rocky Mountain stream in North Boulder Creek catchment in the Green Lakes Valley, Colorado Front Range, USA (Hood, Williams & Mcknight 2005).

CHAPTER THREE

Land-Use and Land Cover Changes on the Slopes of Mount Meru-Tanzania[1]

Abstract

Environmental transitions analysis was done in part of the land on the slopes of the foothills of mount Meru in thirty (30) years' time from 1986 to 2016 using satellite-derived land use/cover maps and a Cellular Automata (CA) spatial filter under IDRISI software environment and assessed the important land use changes. Also, the future land use for 2026 which is the next ten (10) years was simulated based on Cellular-Automata Markov model. The results showed significant land use transitions whereby the bush land (BL) decreased from 372.3 km^2 (1986) to 158.4 km^2 (2016) and agriculture land (AG) decreased from 545.8 km^2 (1986) to 531.5 km^2 (2016) and were converted into human settlement (ST) which increased from 74.2 km^2 (1986) to 261.2 km^2 (2016) as a result of conversion of Arusha town into a City. In addition, the changes have caused slight changes in water bodies into mixed forest. Moreover, the future land use/land cover (LULC) simulations indicated that there will be unsustainable LULC changes in the next ten years since most of bush land (40.9 km^2) and large part of agriculture land (96.7 km^2) will be used for building different structures (72.6 km^2) thus interfering with fresh water sources and food availability in the City. These changes call upon the relevant planning authorities to put in place the best strategies for good urban development.

Key words: Cellular Automata; Markov Chain; Change Detection; Land Cover Change; Land Use Change; Remote Sensing; Spatial Modeling.

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3.1 Introduction

In the modern world Land Use Land Cover (LULC) change is inevitable since human use their environment for their socio-economic development. Human may use the atmosphere, surface and underground of the earth for development and by doing so they may affect the environment. Such changes occur as a result of complex processes that involve modifications in land-cover and land use (Noe, 2003) and they are determined by the interaction in space and time between biophysical and humans endeavors (Lambin *et al.,* 2001). Such processes include but not limited to expansion of agriculture, infrastructures, settlements, development of industries and natural disasters. In several areas on the earth, river ecosystems and land cover have changed as a result of various forces persisting on them which have led to modification of the flow regime and change in ecology (Richter, 2003).

In several areas on the earth, river ecosystems and land cover have changed as a result of various forces persisting on them which have led to modification of the flow regime and change in ecology (Richter, 2003). Such forces include deforestation, overgrazing, expansion of agriculture, and infrastructure development. Moreover, the increased competition for water use and changes in land use in the upstream of many rivers are said to have contributed to changes in hydrological regimes of many rivers and wetlands (Bisht & Tiwari, 1996; Mbonile, 2006). For example, more than 6.8 million people depend on water from Pangani River Basin (PRB) for their livelihood such as irrigation and domestic uses (Shaghude, 2006). Also, the same water source is used for hydroelectric power generation (Shaghude, 2016). Different government policies, political influences as well as technological changes can also lead to land use/land cover changes which can affect the watersheds and catchment areas (Notter *et al.,* 2013; Richter, 2003; Tu, 2006). The above mentioned forces are among of the several activities degrading large environment in many developing countries including Tanzania.

The study on impacts of land-use and land cover change has been a point of interest of many researchers. For example, Arsanjani*et al.* (2011), Lambin *et al.* (2001), Subedi *et al.* (2013) and Verburg *et al.* (2006) in their studies attempted to provide the insights and understanding of the causes and effects of land-use and land cover change with most emphasis of their studies on biophysical aspect of land-use and land cover change. Currently, large areas in Northern Tanzania are said to have been converted to agricultural land (such as large plantations of food and cash crops), expansion of settlements and development of infrastructures such as irrigation scheme systems, mining and other industries as a result of

increased migrations and internal population. Such areas include the slopes of Mount Meru in Tanzania which is among the important Pangani River Basin (PRB) sub catchment feeding the Pangani River (PBWO/IUCN, 2010; Turpie *et al*., 2005). This area is facing deforestation and poor agricultural expansion which includes increased furrow irrigation technology, establishment of new large commercial farms from virgin land, overgrazing, rapid increase in human population due to immigration and natural process threatened the land use and land cover of the area hence affecting the hydrological system of the area (Lalika *et al.,* 2014; Mbonile, 2006; Turpie *et al*., 2005). Currently, there has been a significant increase of farming and livestock activities in the PRB sub catchment (Mbonile, 2006). This has raised the dramatic conversion of grassland, woodland and forest into cropland and pasture which eventually results into negative changes in the wetlands size and river regimes.

Knowing the main drivers of LULC change in rivers and its aspects is vital. Such understanding includes both assessments of the expected rate and spatial pattern of land-use and land-cover change as well as familiarity of the principal human and biophysical drivers (Lambin *et al*., 2001). These complex questions can be answered through modeling the land use land cover change. Also, the process of analysis, forecasting and evaluating future land-use change of any place involves a complicated set of tasks and should be performed using better scientific knowledge of the physical extent, character and consequences of land transformation (Elservier, 2009). In analysis and modeling of LULC dynamics, remote sensing and GIS tools are widely used to study both quantitatively and qualitatively using Cellular Automata and Markov Chain (CA–MC) spatial models and predicting the future LULC scenario basing on historical land cover data (Arsanjani *et al.,* 2011; Behera *et al.,* 2012; Houet *et al.,* 2007; Marko *et al.,* 2016; Singh, 2010). These models finds its profound use since the input automata cells relates to the imagery cells with specific pixels resolution for each (Bolch *et al.,* 2006). Also, the MC model allows independent cell transition from one state into another state thus giving a plausible probability of change for a particular land use category. Thus, in Markov chain, the future depends only upon the present and not upon the past (Bolch *et al.,* 2006). Apart from that, Normalized Difference Vegetation Index (NDVI), principal component analysis (PCA), image rationing, image differencing, change vector analysis in terms of magnitude and direction, deviation and regression, are among the techniques which can be used in GIS environment to study the LULC changes (Lin *et al.,* 2008; Shively & Coxhead, 2004; Singh, 2010). In this study, CA-

MC has been used to assess the land use change and model the future LULC in upper part of the PRB catchment.

3.2 Land cover change and drainage

Land cover plays a vital role in drainage system and conservation of any catchment. Different studies have shown the land covered with different types of vegetations in relation to soil type can affect the drainage and sustainability of a particular catchment (Guzha *et al.*, 2017; Kundu & Olang, 2011). Further studies by Schilling *et al.* (2016) have shown that the pressure for change in land cover can particularly cause changes in the hydrological regime of an area especially when extensive deforestation has taken place. While this happens, the catchments study shows that the hydrological regime of any area can change with no significant changes of precipitation over long time (Heil, 2003). Also, other studies support further on the behavior of stream annual flow in relation to canopy cover where it is found to be high in forested areas than deforested area but does not show the effects of precipitations in different seasons whether they can affect the discharge potentials (Cristina *et al.*, 2015).

3.3 Cellular automata (CA)

Cellular automata (CA) is one of the methods used to model land change in terms of geospatial location of development as well as quantity of change. In this model, the geospatial dynamics are controlled by local rules determined either by the CA spatial filter or transition potential maps (Batty, 2011). The CA model is defined as a one or two-dimensional grid of identical automata cells of which each automata cell processes respective information, and proceeds in its actions based on data received from its environment and following rules that it stores or holds internally (Neumann, 1951). A simple CA have five components which are the grid space on which the model operates, cell states in the grid space and transition rules, which determine the spatial dynamic process. Others include status of neighborhoods that influences the central cell and iteration numbers (Moreno*et al.*, 2009). In addition, a grid of automata must be defined by a set of inputs from the states of neighbouring cells to become a CA. Moreover, two-dimensional CA must be considered on a grid lattice with the influencing neighborhoods containing four (von Neumann function) or eight (Moore function) adjacent cells (Benenson & Torrens, 2004). The most important advantage of the CA models is based on its ability to control complex spatially distributed processes, as well as affording insights into a wide variety of local behaviors and global patterns.

Furthermore, temporal and spatial complexities of many phenomena can be well simulated and represented by properly defining transition rules in CA models (Moreno *et al.*, 2009). With such vital advantages, CA models have been increasingly used for simulating different spatial phenomena including LULC Almeida *et al.* (2003) and urban growth (Syphard *et al.*, 2005). These features give most significant concern in CA modeling which requires defining appropriate transition rules based on training data which control the model. Furthermore, linear boundaries have been used to define the rules; however, land-use dynamics and many other geospatial phenomena, are extremely complex and require non-linear boundaries for the definition of rules (Moreno *et al.*, 2009). Mathematically, the CA model is expressed through Equation 1:

$$S(t, t+1) = f(S(t), N) \quad (1)$$

where S is the set of limited and discrete cellular states, N is the cellular field, t and $t + 1$ indicate the different times and f is the transformation rule of cellular states in local space (Subedi *et al.*, 2013).

3.4 Markov chain model

The Markov chain (MC) premise is a stochastic series that depicts the probability of how one state is altered to another state. It also produces a key descriptive outcome that determines the probability of change from one category to another category thus managing the temporal dynamics among the land use/cover categories, based on transition probabilities (e.g. conservation to built-up area), which is also called transition probability matrix (Arsanjani*et al.*, 2011; Kamusoko *et al.*, 2009). This model is highly used for studies of water resource systems and simulation of precipitation sequences, particularly to describe and predict lithological transition (Sinha *et al.*, 2015), plant succession (Maarel, 1996) and land use change (Muller & Middleton, 1994). The model works under assumption of several mathematical theories of transition probabilities are calculated through the Chapman–Kolmologov equation relating the joint probability distributions of different sets of coordinates on a stochastic process which gives the Markovian stochastic processes as explained in equation 2, 3 and 4 (Mathew 2014). In this study such mathematical manipulations are integrated in the IDRISI and GIS software and used for the same purpose. Equation (2) explains the calculation of the prediction of land use changes according to Burnham:

$$S(t, t+1) = Pij \times S(t) \quad (2)$$

where *S (t)* is the system status at time of *t*, *S* (*t* + 1) is the system status at time of *t* + 1; *Pij* is the transition probability matrix in a state which is calculated as follows:

$$\mathrm{P} = \|P\| = \begin{Vmatrix} P1,1 & P1,2 & \dots & P1,n \\ P2,1 & P2,2 & \dots & P2,n \\ \dots & \dots & \dots & \dots \\ Pn,1 & Pn,2 & \dots & Pn,n \end{Vmatrix} \quad (3)$$

P is the transition probability; *Pij* stands for the probability of converting from current state *i* to another state *j* in next time; *Pn* is the state probability of any time. Low transition will have a probability near (0) and high transition have probabilities near (1). Equation (2) must satisfy the next two conditions (Kumar *et al.,* 2014):

$$\sum_{j=1}^{n} Pij = 1, \text{ and } \quad (0 \leq Pij \leq 1) \quad (4)$$

The key step of the Markov model lies in getting a primary matrix and matrix of transition probability *(Pij).* Then the Markov forecast model is as follows:

$$P_n = P_{n-1} \text{ and } \quad Pij = P(0)P_{ij}^{n} Pn, \quad (5)$$

where P_n stands for state probability of any time and *P* (0) stands for primary matrix.

3.5 CA–Markov chain model

The CA–MC model is an integrated system which plays a great role in multi-criteria evaluation of LULC changes. It is among the best method and technique for quantity estimation, spatial and temporal dynamic modeling of LULC changes since GIS and remote sensing data can be well integrated to give a meaningful outcome (Kamusoko *et al.,* 2009). In this model, the MC tool is used to produce transitional probabilities statistics, transitional area statistics and conditional transition images data which are used as inputs to predict the later state of the particular pixels over space basing on the condition, location and proximity of the neighboring pixel in CA model (Aithal *et al.,* 2014; Arsanjani*et al*, 2011; Behera*et al*., 2012; Deep, 2014; Houet *et al.,* 2007; Marko *et al*., 2016; Omidipoor *et al.,* 2017; Yang *et al.,* 2015).

In the CA-MC model the potential of a cell to change from its existing land use to other land use types at a certain time period is calculated by using a combination of linear and geometric formulations giving us the model Equation (6) (Lau & Kam, 2005):

$$P_{z,i}(t+1) = [S_{z,i}(t)]\{[A_i(t) + H_i(t)][r_{x,i}(t) + \sum w_{j,y,z}(t)]\}, \square j \in \Omega_i, \; j \neq 1 \quad (6)$$

Where:

$P_{z,i}\,(t+1)$ is the pontential of a cell i to change to state z at time $t+1$, where z refers to a certain land use type, with $-2 \leq P_{z,i}\,(t+1) \leq 4$;

$S_{z,i}\,(t)$ is the suitability of a cell i for state z at time t, with $0 \leq S_{z,i}\,(t) \leq 1$;

$A_i\,(t)$ is termed the attribute effect, is an index for cell i at time t which is a weighted sum of normalized values of accessibility, population density, residential property value and passenger trip volume representing one aspect of a driving force of land-use changes, with $0 \leq Ai\,(t) \leq 1$;

$H_i\,(t)$ termed the heterogeneity effect, is an index for cell i at time t which is a weighted sum of normalized values of land-use balance and land-use mix representing the other aspect of the driving force of land-use changes, with $0 \leq Hi\,(t) \leq 1$;

$r_{x,i}\,(t) + \sum w_{j,y,z}\,(t)$ termed the gravity effect, is an index for cell i at time t which is a sum of resistance of cell i to land-use change and the push and pull forces exerted by other cells, j, in neighborhood Ωi representing a retarding force of land-use changes;

$r_{x,i}\,(t)$ is the inertia or resistance of the cell i with state x at time t to land-use change, with $0 \leq r_{x,\,i}\,(t) \leq 1$;

$w_{j,y,z}\,(t)$ is the weighting parameter applied to the cell, j, in neighborhood Ωi which is determined by the forces of attraction or repulsion between the state of the neighboring cell, y, at time t and the potential state of the center cell, z, at time $t+1$ as a result of compatibility or incompatibility of land uses, with $-1 \leq \sum w_{j,y,z}\,(t) \leq 1$;

Ω_i is a standard Moore neighborhood with eight cells j defined around the center cell i and $j \in \{1, 8\}$.

In this chapter, studies on the impacts of land use and land cover changes on water resources on the slopes of mount Meru is assessed using these two models by integrating it in IDRISI software v17.02.

3.6 Materials and methods

3.6.1 Description of study area

The study was carried out on the foothills of the eastern and south west parts of Mount Meru which is part of the entire upper Pangani basin sub catchment located in the Northern part of Tanzania sub catchment (Fig. 1) (Kitalika *et al.*, 2018). The natural vegetation in this area is typically tropical forest to savannah and topography is dominated by the Mount Meru volcanic cone of Pleistocene to recent origin. The local climate of the area is temperate Afro-Alpine with minimum and maximum daily temperature of 20.6 °C and 28.5 °C respectively. The rainfall is irregularly distributed between a main wet season from February to mid-May and a minor one from September to November both giving the mean annual rainfall of 535.3 mm (Gea, 2005; Hijmans *et al.*, 2005; UNDP, 2000). The catchment area of the river (headwater) is characterized by both artificial coniferous trees and mixed natural forest conservation; middle area of the river consists of mixed agriculture and urban settlement. The floodplain (downstream) region is characterized by bare land, intensive grazing, large scale agriculture, treated municipal sewage disposal and serious flooding in wet season (Kitalika *et al*., 2017).

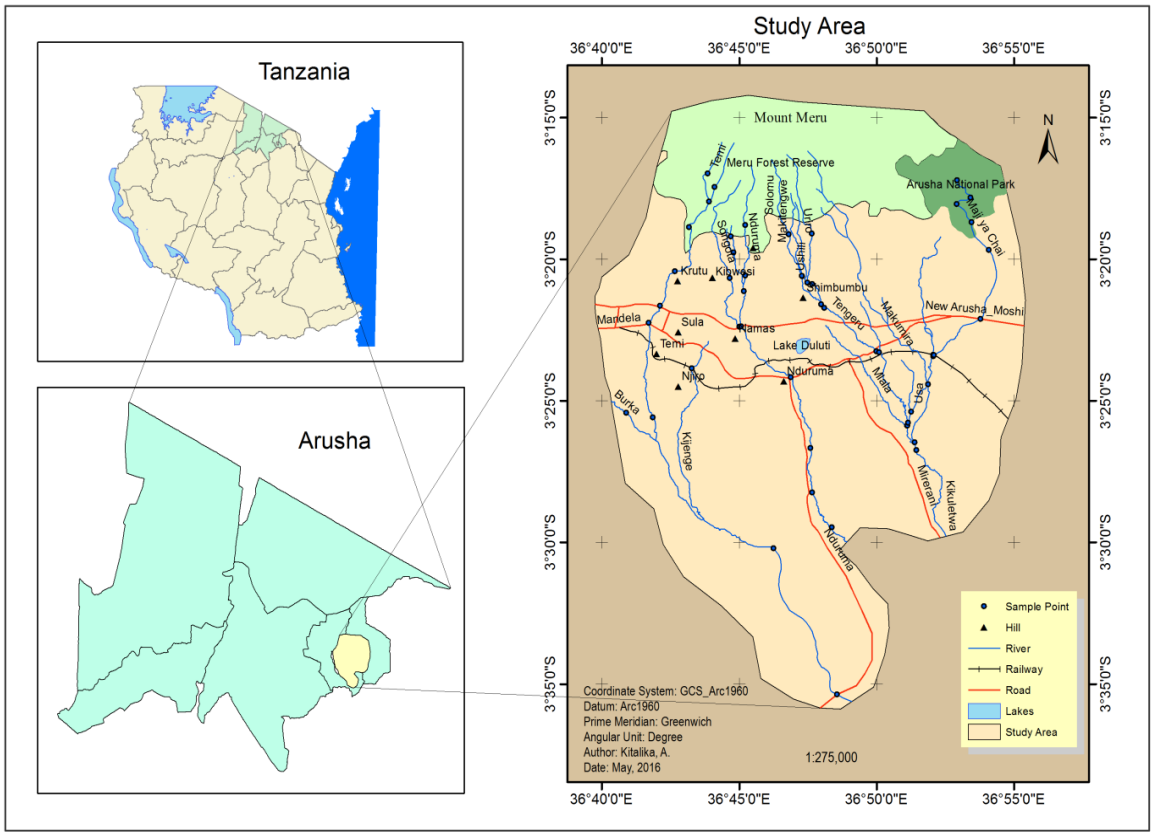


Figure 1: Study Area

3.6.2 Sources of data and data collection

In this study, both primary and secondary data were used. The primary data used include precipitation and water levels in rivers within the sub catchment for 2016, and the secondary data for precipitation in 1986, 1996 and 2006 were collected from the Pangani Basin Water Office (PBWO) (Table 1). Other secondary data includes the Landsat Thematic Mapper (LTM) images downloaded from United States Geological Survey (USGS) Earth Explorer as shown in Table 2. The collected satellite images were used to determine the change in land use/land cover of the area over time within thirty years (1986–2016). The classified satellite images were also used to predict the condition of land use /land cover condition in 10 years later in the Markov–Cellular Automata dynamic model (MCA) (Aithal *et al.*, 2014; Behera *et al.*, 2012; Deep, 2014; Houet *et al.*, 2007; Marko *et al.*, 2016; Omidipoor *et al.* 2017; Yang *et al.*, 2015).

Table 1: The average annual precipitation and discharge in rivers in 1986 to 2016

Year	Ann. Prec. (mm)	Discharge (m^3/s)				
		Temi	Nduruma	Tengeru	Maji ya Chai	Av. Level
1986	503.3	0.67	0.75	0.66	0.30	0.60
1996	225.4	0.29	0.34	0.28	0.13	0.26
2006	229.6	0.31	0.35	0.31	0.14	0.28
2016	464.3	0.61	0.75	0.38	0.19	0.48

Pangani Basin Water Office (2016)

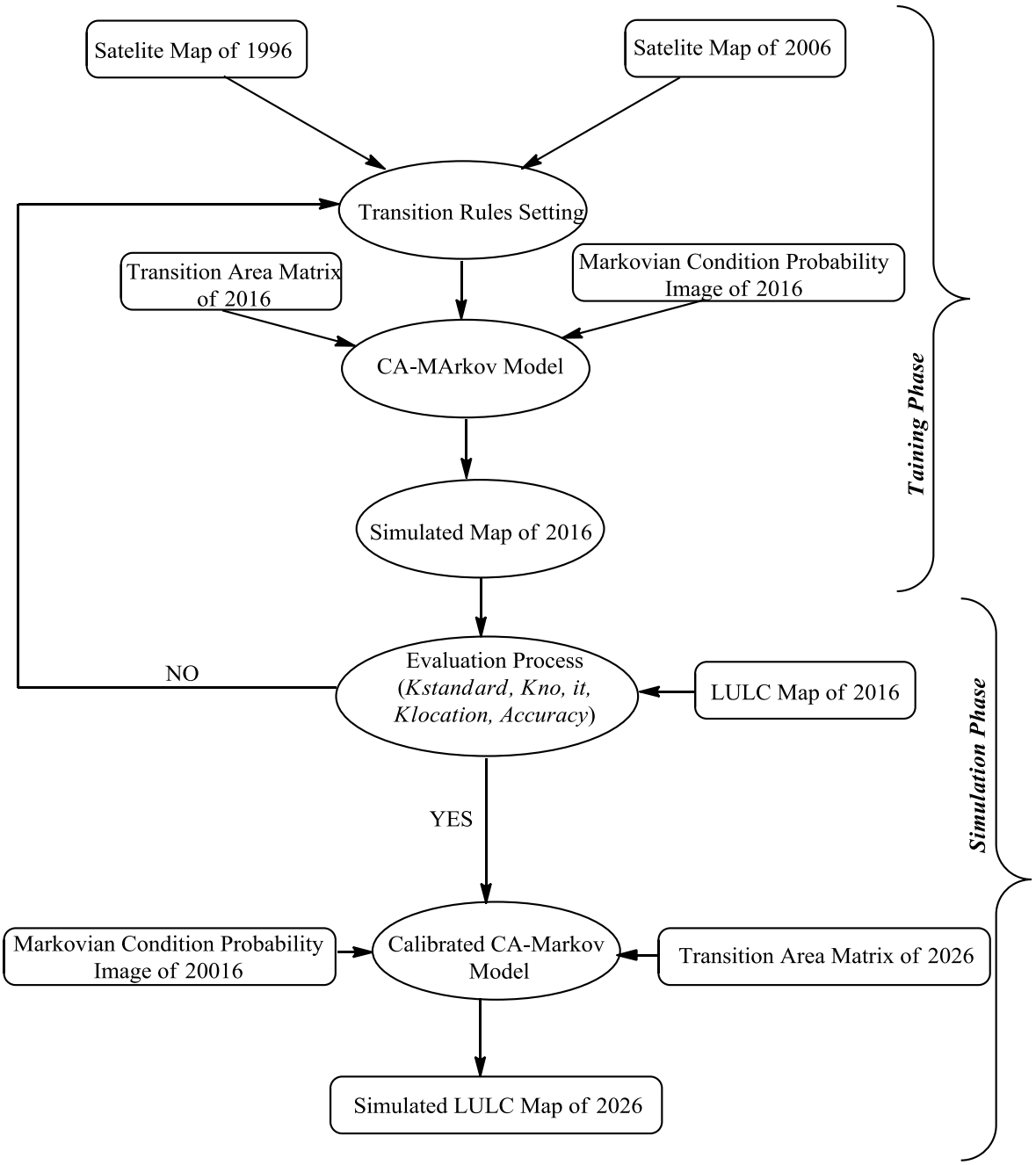
Table 2: United States geological survey collected landsat TM characteristics used for land use land cover change

Satellite Image	Resolution	Path	Row	Collection date
Landsat TM 4–5	30m × 30m	168	062	Sep–1986
Landsat TM 4–5	30m × 30m	168	062	Sep–1996
Landsat TM 4–5	30m × 30m	168	062	Sep–2006
Landsat ETM 8 TIR/OLI	30m × 30m	168	062	Oct–2016

3.6.3 Data analysis

The collected satellite images were pre-processed first before analyzing them, the process involved projecting them to UTM zone 36 S which corresponds to Arusha Region then RGB composite images were created for each year. The RGB were created by layer stacking which involved Band 2, 3 and 4 for Landsat TM 4–5 and Band 3, 4 and 5 for Landsat 8. Each image with composite colour was extracted to cover the study area by using the study area map. The satellite images were preprocessed then converted into composite images with false colors which could help to identify clearly the areas with different land uses like vegetation, settlements and water sources through supervised classification (Houet *et al*., 2007; Marko *et al*., 2016). Images were analyzed by using IDRISI–Selva software v 17.02 and the results were assessed basing on the changes occurred in the land uses and associating them with water reservoirs. Maximum likelihood (MAXLIKE) algorithm was used to classify the images for change detection analysis. Analysis of the net gain and loss of various land uses like forest cover, settlements and agricultural having a time step satellite images were performed and interpreted basing on Kappa Index of Agreement (KIA) (Arsanjani *et al*., 2011) for the best image representative image of the future land use land change prediction model. The whole procedural activities are summarized in Scheme 2. Also, the rainfall and

river water levels for some years were used to evaluate any correlation in relation to land use/land cover change if any.



Scheme 2: Flowchart for CA-Markov model process as explained by Arsanjani *et al.* (2011) and modified by Kitalika *et al*. (2018)

3.6.4 Satellite image classification, training, signature development and classification

Supervised image classification was adopted since the whole process is controlled by the user especially on deciding the number of classes to be identified, creation of training samples and

detailed knowledge about the real study area land use and land cover distribution. The training samples representing the pixels with particular land covers for 1986, 1996, 2006 and 2016 were created by using polygons with the aid of GPS points with support from Google earth image. In addition, the land use topographic maps for similar years representing the study area for Quarter Degree Square (QDS) 55−3 and 55−4 collected from the Cartography Department of the Ministry of Land were also used for the same purpose. Six classes of land LULC were identified which involved Mixed forest (MF), Bush land (BL), Agriculture (AG), Settlements (ST), water bodies (WB) and rocks (RK). Twenty-five (25) pixels were used for training and validation for each WB and RK land use class whereas for MF, AG and ST fifty (50) pixels were used for the same purpose in each land use class. The same training samples were stored and used to create signature file for entire image supervised classification process. Table 3 describes the land use classes identified in the study area and Table 4 gives their land class area sizes.

Table 3: Description of land use classification of the study area

Land Use	Description
Mixed Forest (MF)	Areas with plantation and natural forest, firewood, charcoal, pole wood and timber
Bush land (BL)	Areas with shrubs, agro forest, pasture and thickets
Agriculture (AG)	Areas with land for commercial and peasant agriculture
Settlements (ST)	All forms and types of buildings
Water bodies (WB)	All areas covered with water (rivers, snow, lakes, floods and wastewater treatment sites)
Rocks (RK)	All areas with rocks and mining

Supervised image classification was done after creation of signature file; each composite image was supplied in the maximum likelihood classification algorithm as input together with the associated signature file. After running the algorithm, the land use and land cover maps with trained classes were produced and was ready for classification accuracy assessment process. All these processes were performed on each individual image in ArcGIS 10.3 software

Table 4: Actual land use land cover change detection values and its projection from 1986 to 2026

LULUC	AREA (km^2)					NET GAIN/LOSS (km^2)					NET GAIN/ LOSS (%)				
	1986	1996	2006	2016	2026*	1996–1986	2006–1996	2016–2006	2016–1986	2026*–2016	1996–1986	2006–1996	2016–2006	2016–1986	2026*–2016
MF	139.7	174.9	166.7	166.0	172.5	35.2	–8.2	–0.7	+26.3	+6.5	+3.0	–0.7	–0.1	+2.3	+0.6
BL	372.3	281.8	237.0	158.4	199.3	–90.5	–44.9	–78.5	–213.9	4+0.9	–7.8	–3.9	–6.7	–18.4	+3.5
AG	545.8	587.4	498.6	531.5	434.7	+41.6	–88.8	+32.9	–14.3	–96.7	+3.6	–7.6	+2.8	–1.2	–8.3
ST	74.2	110.4	207.3	261.2	333.8	+36.2	+96.8	+53.9	+187.0	+72.6	+3.1	+8.3	+4.6	+16.1	+6.2
WB	14.0	5.6	3.4	4.2	2.5	–8.4	–2.2	+0.8	–9.8	–1.7	–0.7	–0.2	+0.1	–0.8	–0.1
RK	19.0	4.9	52.0	43.8	21.8	–14.1	47.1	–8.2	+24.8	–22.0	–1.2	4.0	–0.7	+2.1	–1.9

*Projected, +ve - net gain, -ve - net loss.

Table 5: Classification accuracy assessment for 2016 and other overall accuracy

LULC	MF	BL	AG	ST	WB	RK	Total	Accuracy (%)		Overall Accuracy (%)			
								User's	Producer's	Year	Total test points	Correct points	Accuracy
MF	4	1	0	0	0	0	5	80	100	1986	25	20	80
BL	0	4	1	0	0	0	5	80	80	1996	25	21	84
AG	0	0	5	1	0	0	6	83	63	2006	25	20	80
ST	0	0	1	6	0	0	7	86	75	2016	33	27	81.5
WB	0	0	0	0	5	0	5	100	100				
RK	0	0	1	1	0	3	5	60	100				
Total	4	5	8	8	5	3	33	81.5					

3.6.5 Accuracy assessment and change detection analysis

The assessment of classification accuracy was performed on each classified map by comparing the land use classes with 33 ground truth GPS points, then creating an error matrix table. The producers, users and overall accuracy were calculated from the table in Microsoft Excel sheet, as suggested by Coppin and Bauer (1996) which requires acceptable classification results to be at least from 70% and above. Table 5 gives a summary of accuracy assessment for year 1986 to 2016 which all qualified for further adoption. The overall accuracies were determined by the Equations given in (7) through (9):

$$\text{Overall Overall accuracy} = \sum \frac{\text{Correct classified}}{\text{Number of observations}} \times 100 \quad (7)$$

$$\text{User's accuracy} = \sum \frac{\text{Correct classified pixels in the row}}{\text{Pixels in the row}} \times 100 \quad (8)$$

$$\text{Producer's accuracy} = \sum \frac{\text{Correct classified pixels in the column}}{\text{Pixels in the column}} \times 100 \quad (9)$$

3.6.6 Change detection analysis

The statistics from classified land use and land cover maps of 1986, 1996, 2006 and 2016 were used to detect the changes occurred in the period of 30 years. Change detection involved finding the quantities of the land use land cover changed, locations where the changes occurred and the type of changes occurred at a certain defined time interval (Arsanjani *et al.*, 2011; Kashaigili *et al.*, 2006). In post classification process; quantitative changes were detected by comparing the successive pairs of classified maps by subtracting the quantities of the current land use class from the quantities of the past land use class; the differences obtained from each pair were converted to percentage of change using Equation (10):

$$\text{Percentage change} = \frac{\text{Observed change}}{\text{Total area}} \times 100 \quad (10)$$

Through change detection the deep understanding in terms of anthropogenic interference in the land use and land covers of an area will be possible hence this can facilitate in understanding the protection strategy of the environment.

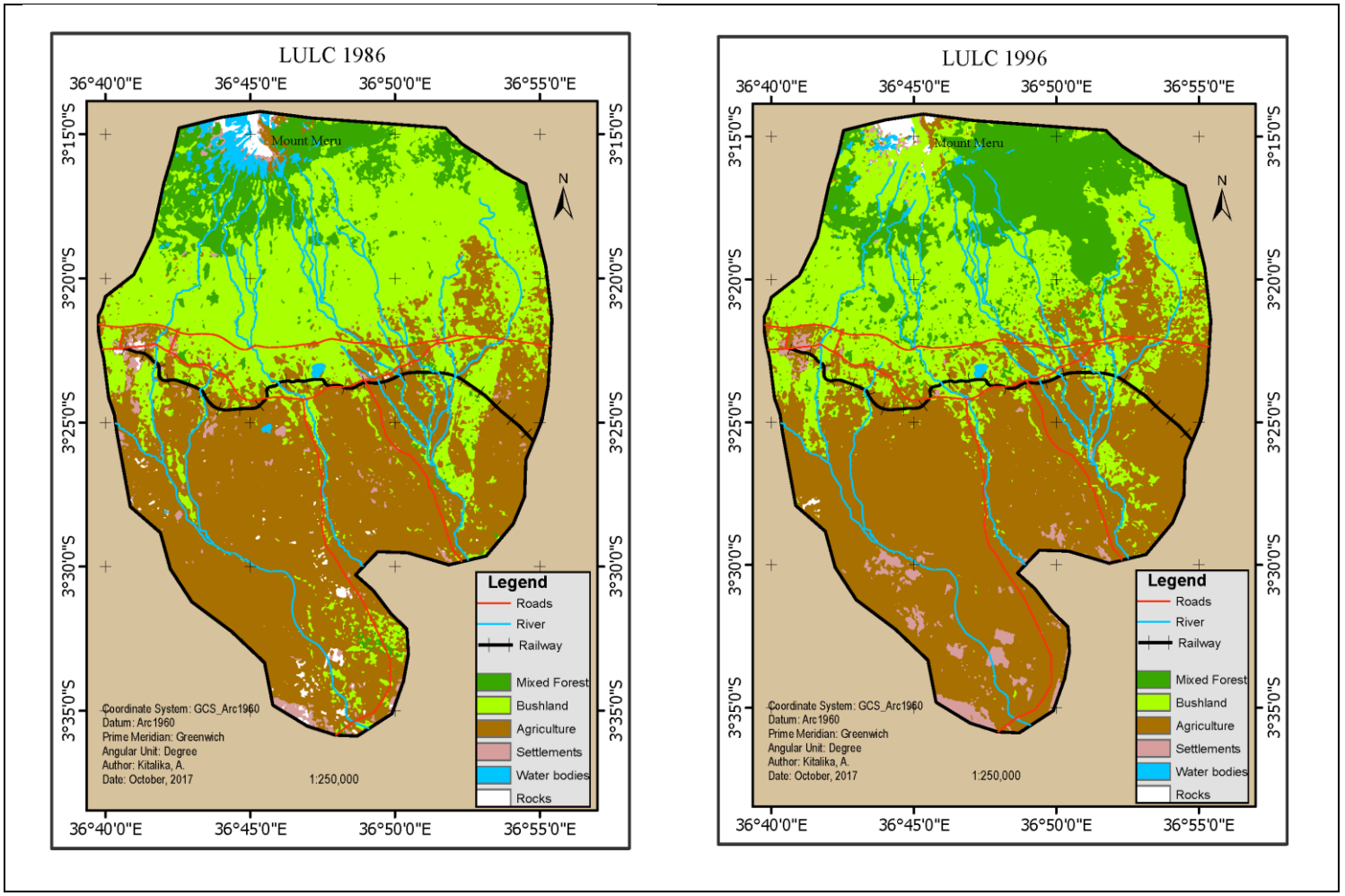
3.7 Results and discussion

3.7.1 Analysis of land use land cover change

Fig. 2 through 10 are LULC maps of the study area for 1986, 1996, 2006 and 2016 and their statistics are summarized in tables 4 through 8. The study shows that agriculture land increased from 46.85 % in 1986 to 50.42 % in 1996 with land use of 545.8 km^2 to 587.4 km^2, respectively. Also, within similar years the mixed forest increased from 139.7 km^2 to 174.9 km^2. The agriculture land mixed forest increased in favour of conversion of bush-land which decreased from 31.5 % to 24.19 % (Table 4 and 8). In addition, areas inhabited by human settlement increased in similar years from 74.3 km^2 (1986) to 110.4 km^2 (1996) that being the result of conversion of rock land and part of bush land (Table 8). The areas inhabited by water bodies decreased to 0.45 % in 1996 from 1.2 % in 1986. Several reasons may explain as why this happened due to the fact that water bodies are contributed by precipitations, groundwater, soil type and the canopy cover which accounts for evaporation index. Rainfall being the main source of surface water, then it is anticipated that fluctuation of rainfall is the best reason explaining the extent and existence of water bodies on surfaces.

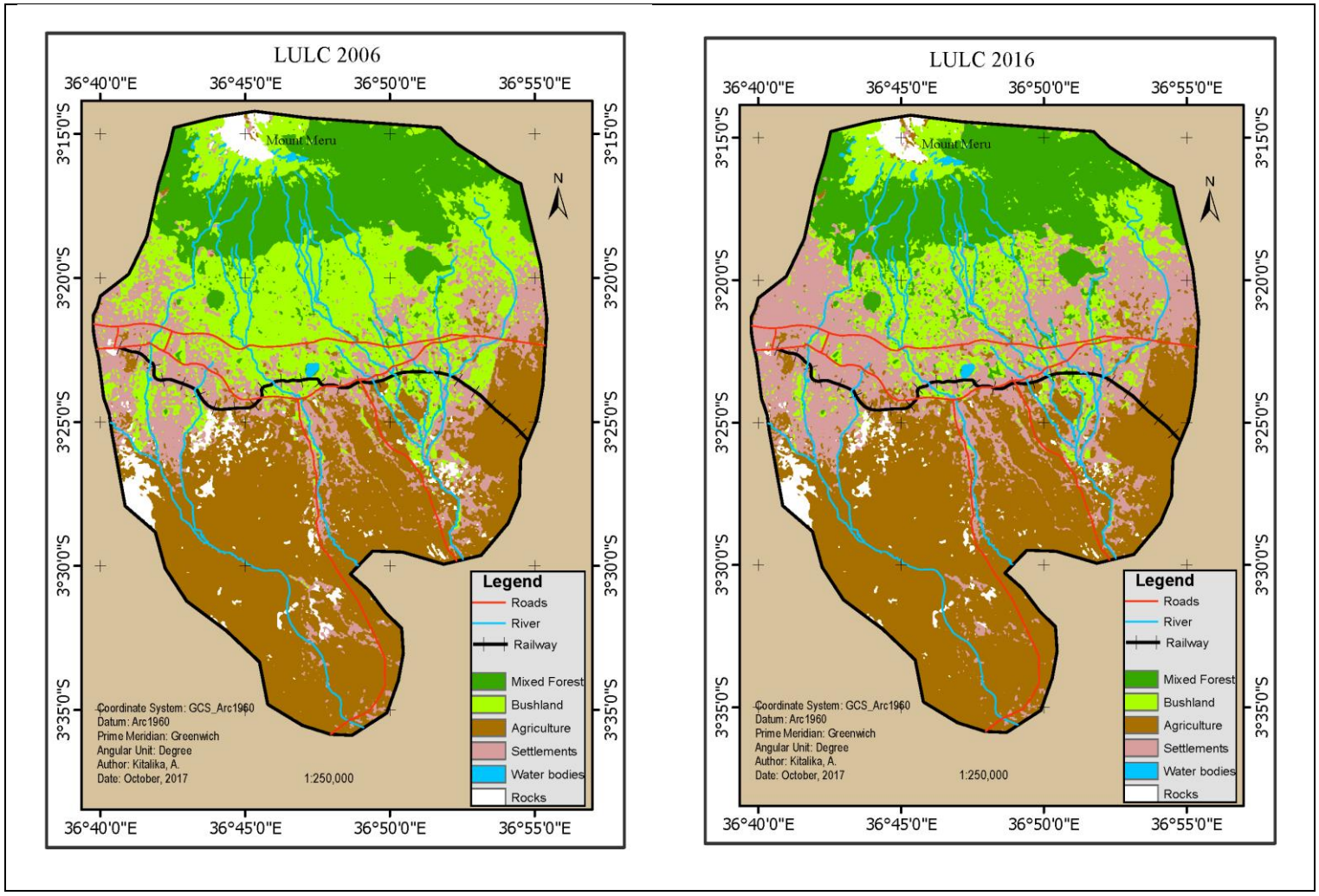
The agriculture land decreased in 2006 with only 42.8 % being used up compared to 50.42 % in 1996. The cross–tabulation study shows that the agriculture land was partly converted to bush land (15.5 km^2 uncultivated for long time and changed to bush land) and 90.6 km^2 was converted to settlement due to urbanization. Generally, settlements increased by 96.8 km^2 and 53.9 km^2 in 2006 and 2016, respectively (Table 7 and 8). However, ten years later (2016) agriculture land rose to 45.62 % (increase by 2.82 % with a net gain of 32.8 km^2) due to decreased rates of settlements constructions and part of the bush land was reconverted into agriculture land (Fig. 11, Table 4 and 8). More analysis shows mixed forest (MF) conservation decreased consecutively from 1996 to 2016 by 8.2 km^2 for the year 1996 to 2006 and a slow decrease of 0.7 km^2 in ten years later. It is within these years when the rehabilitation of the artificial Arusha Forest Reserve took place. Such improved forest plantations include the Midawe and Temi waterfalls catchment areas where big estates of artificial coniferous (pines) trees were raised. Also, the water bodies (WB) continued to decrease from 5.6 km^2 (1996) to 3.4 km^2 (2006) whereas in 2016 a slight increase by 0.8 km^2 occurred. The slight increase in 2016 is a result of increase in precipitation for the respective year. Generally, water bodies have decreased in 30 years (1986-2016) by 9.8 km^2 which can be an alarming situation to the availability of fresh water sources and water balance. It should

be noted that most rivers running in Arusha City have their main catchment sources being within the top hills of Mount Meru which is part of the study area and therefore it is an area of profound importance in terms of fresh water sources. Further analysis of LULC maps in the study area from Fig. 2, 3 and 4 shows a progressive decrease of water bodies at the top hills which is associated with melting of the ice caps, decreased precipitation, increased atmospheric temperature and evaporation. It is very unfortunate that different researchers had different ideas on the effect of canopy cover towards the water bodies whereby some advocates an increase in rivers discharge with increased deforestations (Heil, 2003) and others arguing differently (Cristina *et al.*, 2015). While these arguments remain contradictory, it should be remembered that runoff always increase with decrease in canopy cover which are the water breaks and facilitate infiltration in pervious rocks. Also, soil conditions (sandy, clay, loamy or rocks) account for water infiltration as a main recharge source for watersheds and aquifers. Loose soil is likely to allow more infiltration than compact soil and the vice versa is true.



(a) (b)

Figure 2: Land use land cover change detection for (a) 1986 (b) 1996 on the slopes of Mount Meru



(c) (d)

Figure 3: Land use land cover change detection for (c) 2006 (d) 2016 on the slopes of Mount Meru

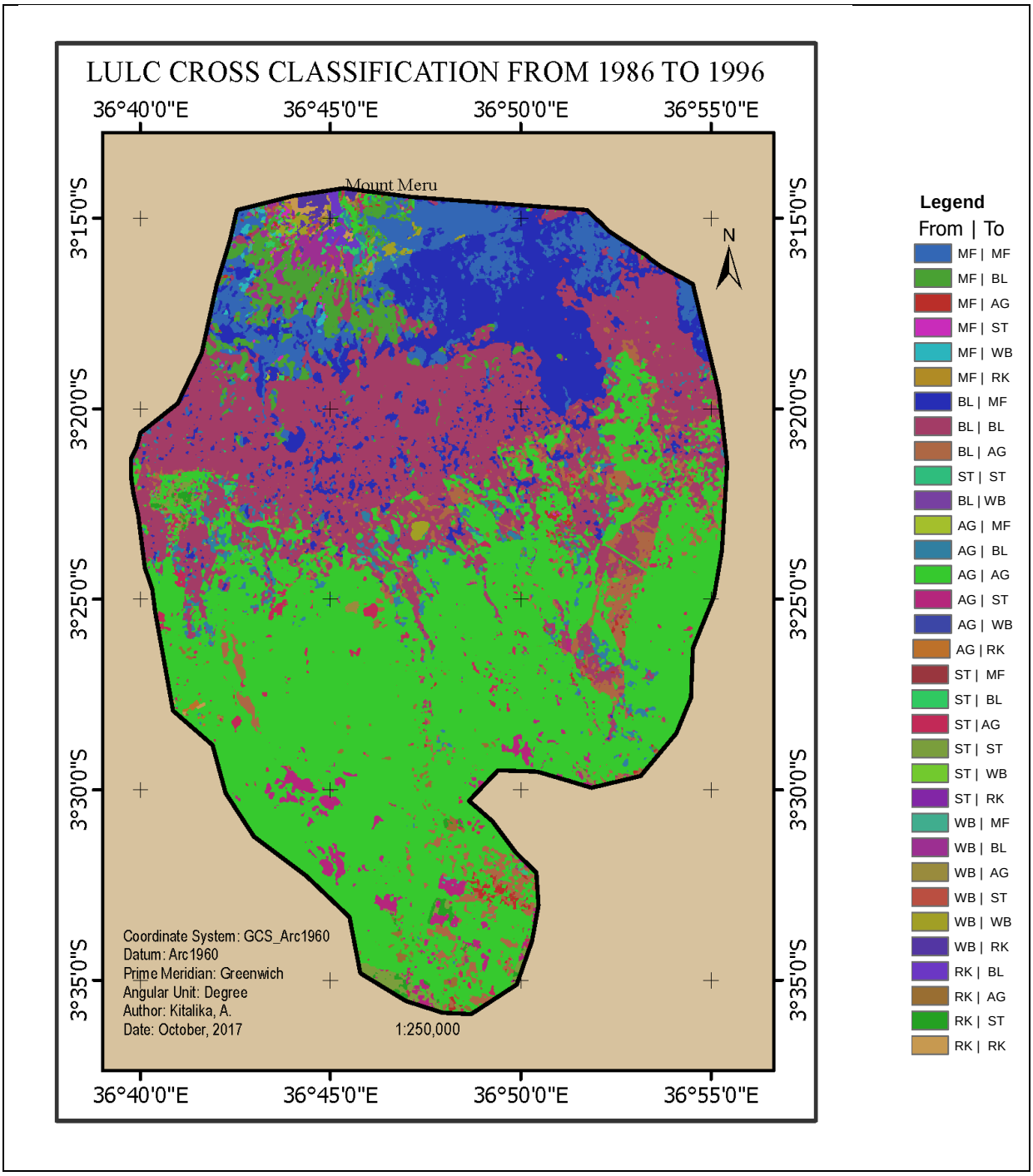


Figure 4: Cross tabulation for land use land cover change detection on the slopes of Mount Meru from 1986 to 1996

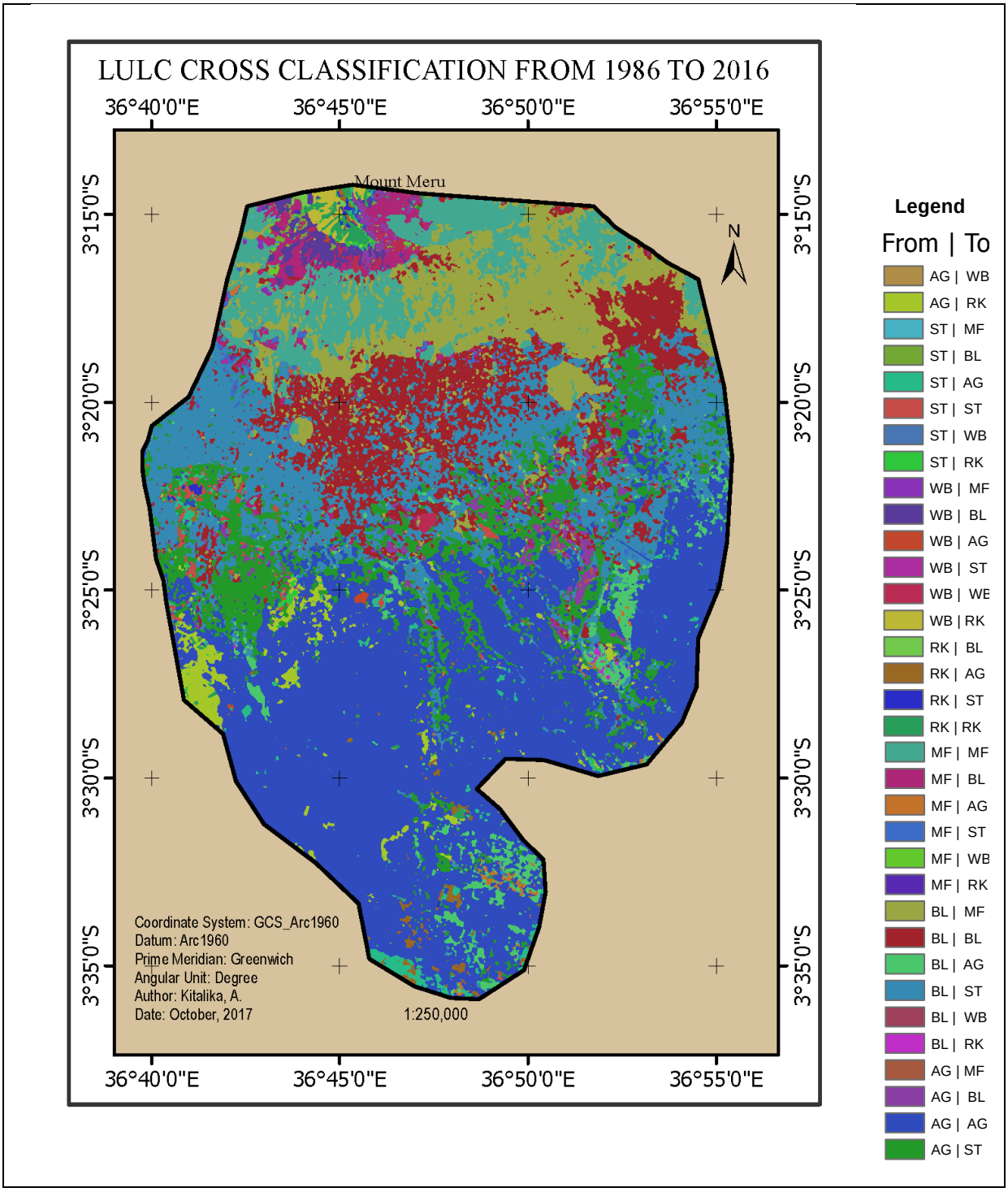


Figure 5: Cross tabulation for land use land cover change detection on the slopes of Mount Meru from 1996 to 2006

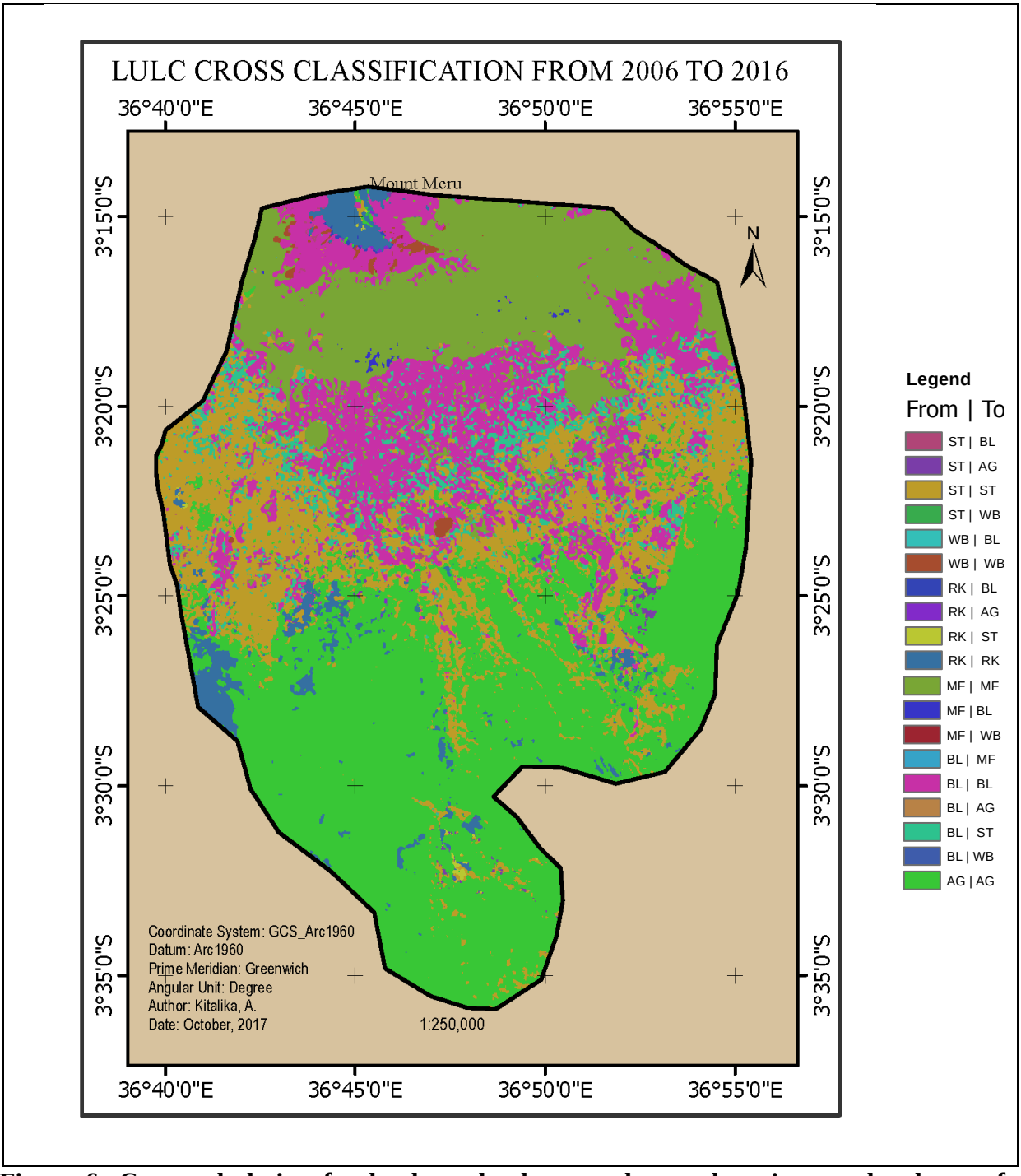


Figure 6: Cross tabulation for land use land cover change detection on the slopes of Mount Meru from 2006 to 2016

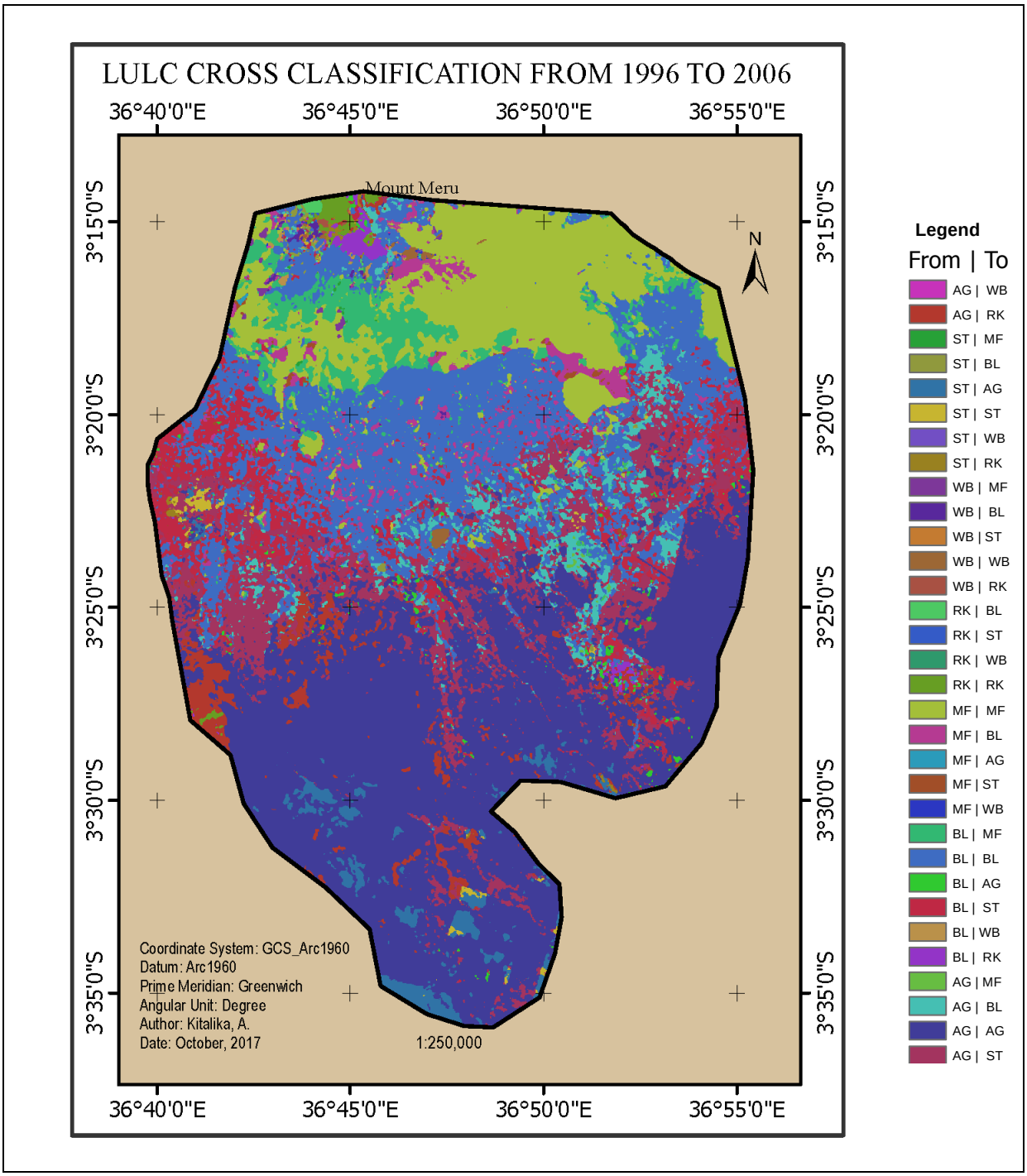


Figure 7: Cross tabulation for land use land cover change detection on the slopes of Mount Meru from 1986 to 2026

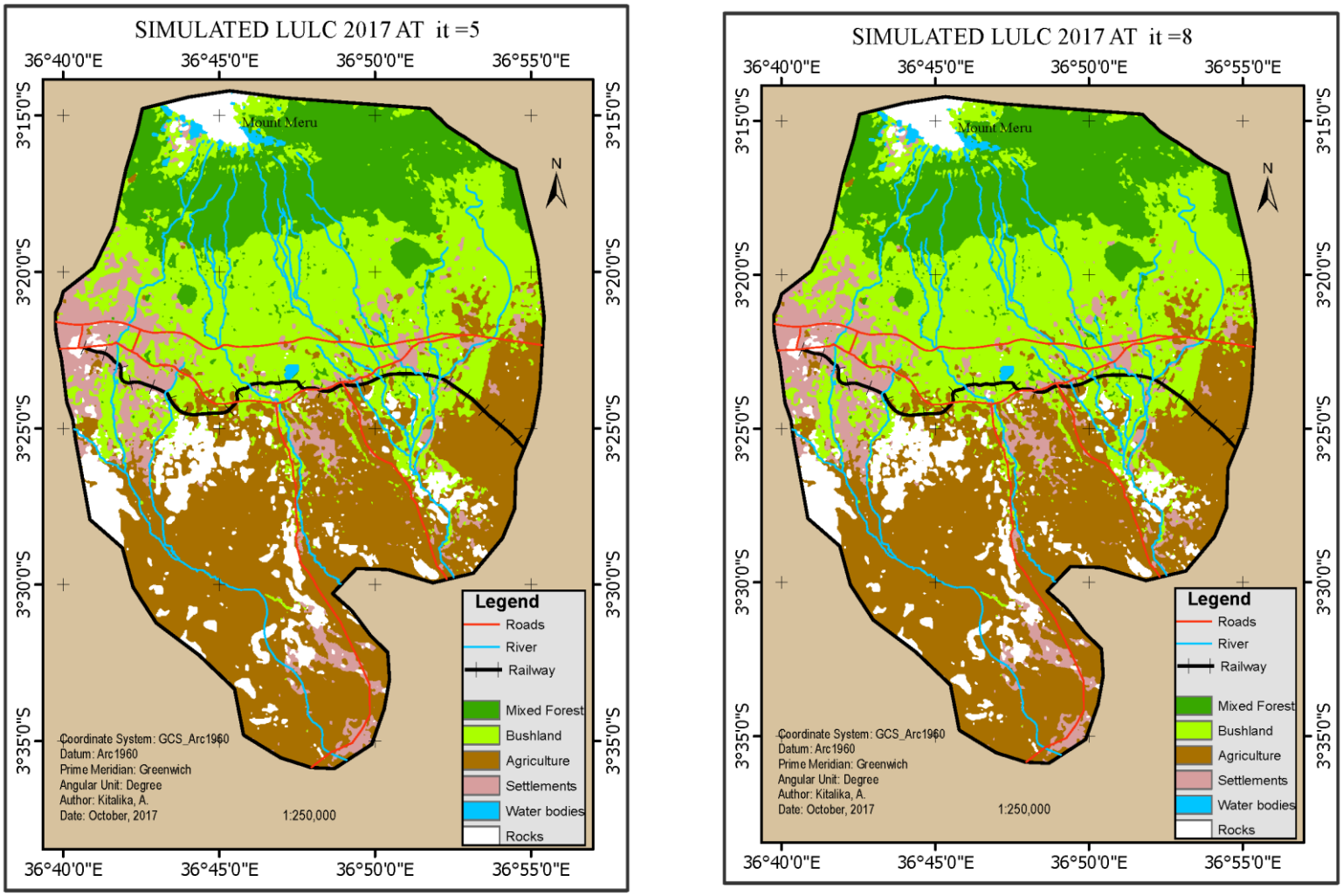
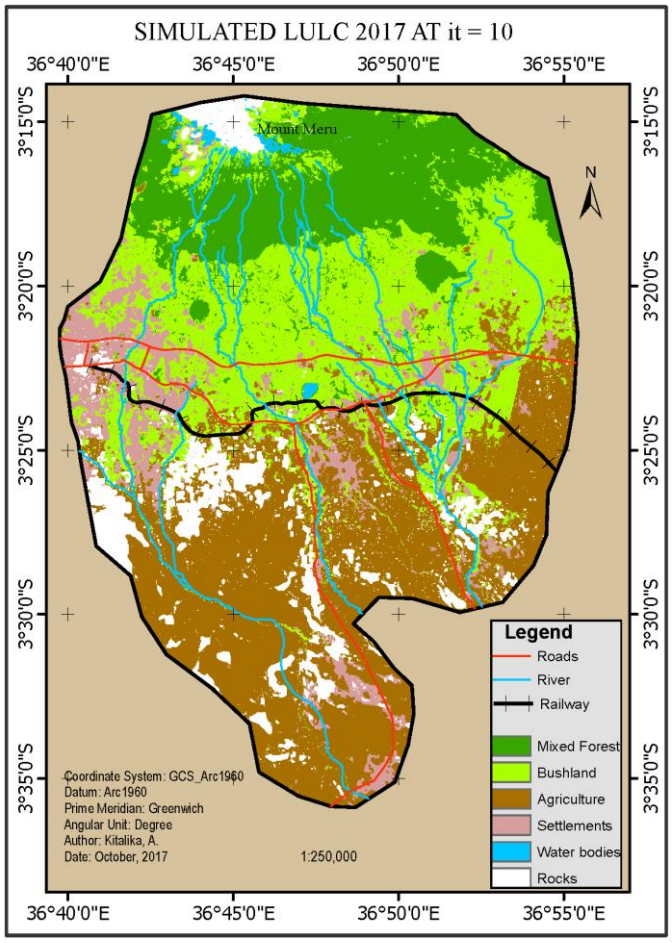
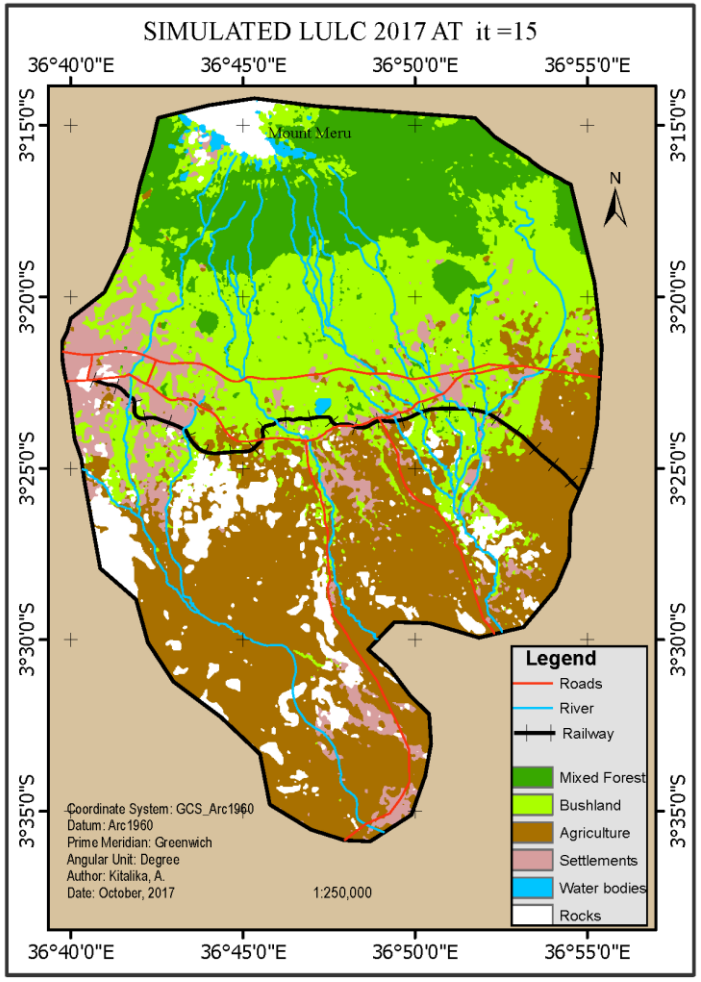


Figure 8: Simulated land use land cover change on the slopes of Mount Meru at (a) it = 5 (b)



(c)



(d)

Figure 9: Simulated LULC C on the slopes of Mount Meru at (c) it = 10 (d) it = 15

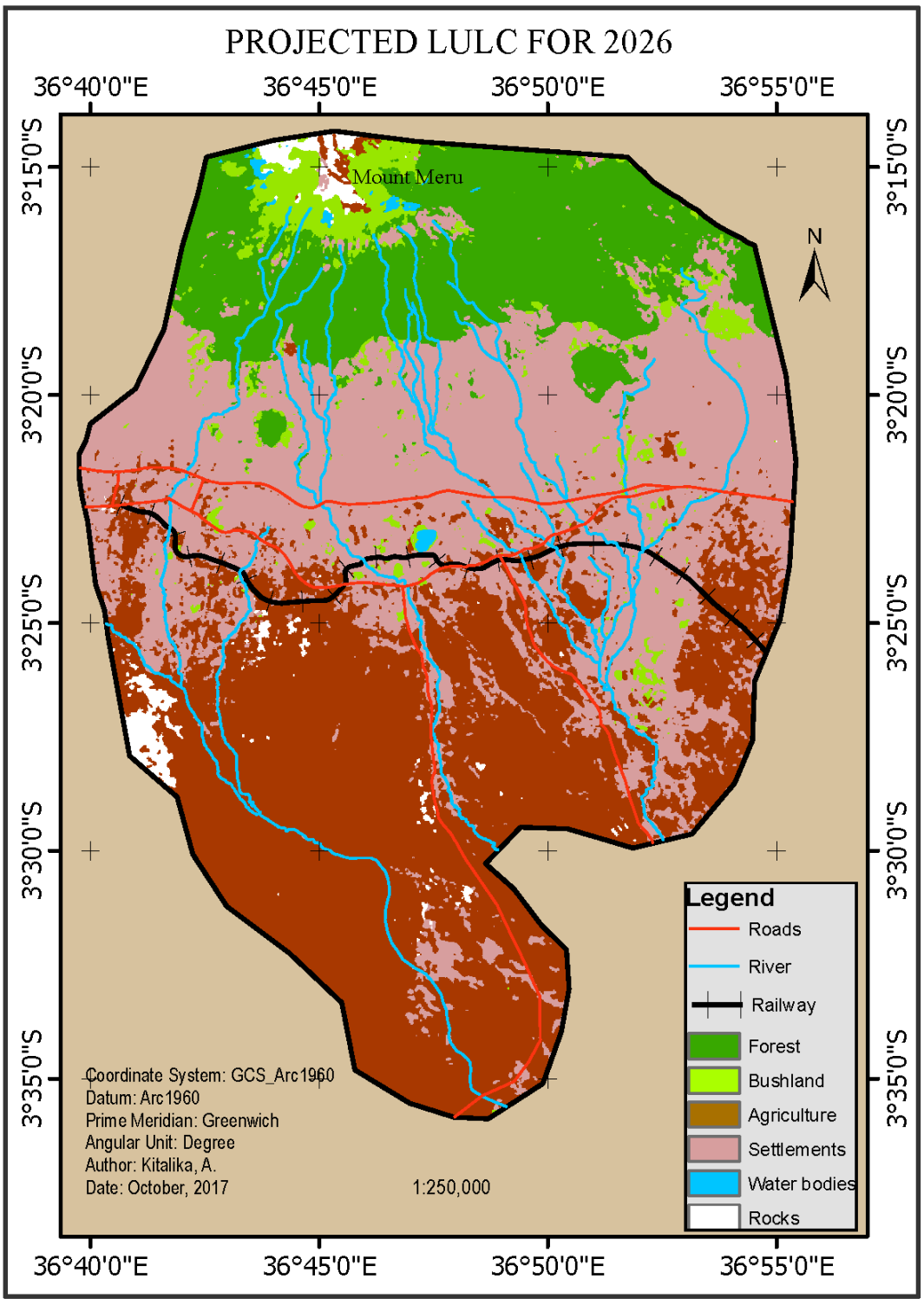
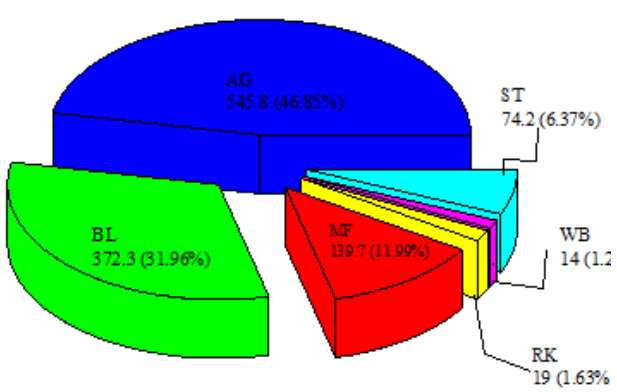
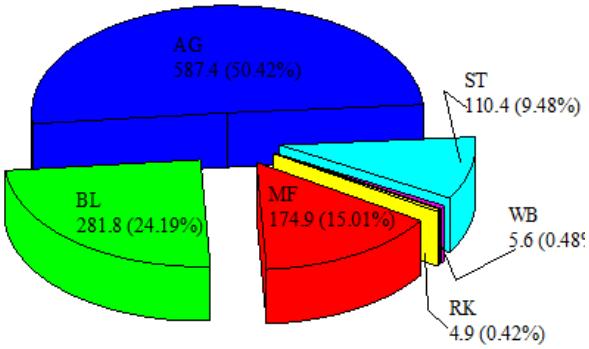


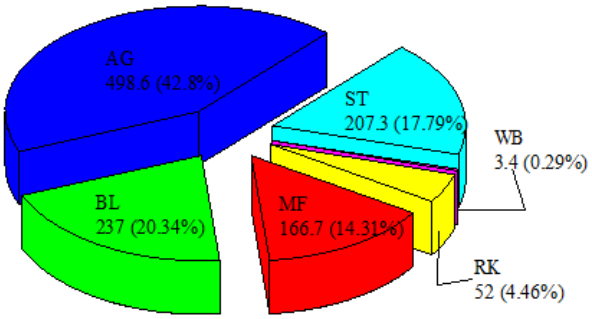
Figure 10: Projected LULC on the slopes of Mount Meru for 2026 at it = 10



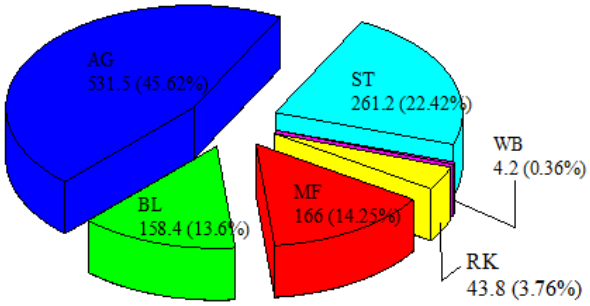
(d) 1986



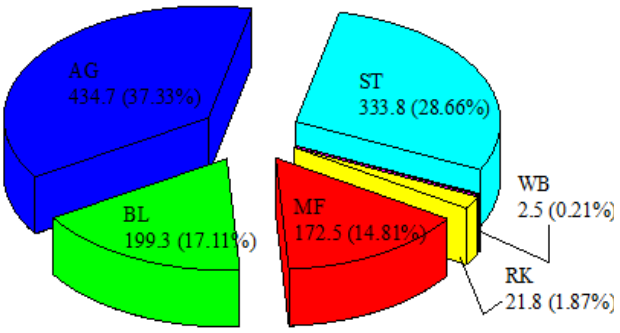
(d) 1996



(c) 2006



(d) 2016



(e) 2026

Figure 11: Analysis of land use land cover change from 1986 to 2016

Table 6: Markov transition probability matrix from 1996 to 2006

	MF	BL	AG	ST	WB	RK	Model Validation	
MF	0.7434	0.2178	0	0.032	0.003	0.004	Kstandard	0.87
BL	0.1243	0.5867	0	0.270	0.004	0.015	Kno	0.88
AG	0.0003	0.0638	0.7	0.192	0	0.057	Klocation	0.91
ST	0.0051	0	0.9	0.106	0.002	0.002	it	10
WB	0.3431	0.2284	0	0.014	0.303	0.112		
RK	0	0.2311	0	0.025	0.023	0.721		

Table 7: Cross tabulation proportions of change

					1986				Kappa Index (KIA)	
	LULC	**MF**	**BL**	**AG**	**ST**	**WB**	**RK**	**Total**	**1986**	**1996**
	MF	0.059	0.088	0.001	0.001	0.002	0.000	0.150	0.401	0.309
	BL	0.036	0.165	0.030	0.005	0.005	0.002	0.242	0.361	0.532
	AG	0.020	0.062	0.386	0.029	0.001	0.007	0.504	0.645	0.560
1996	**ST**	0.004	0.005	0.051	0.029	0.001	0.006	0.095	0.389	0.253
	WB	0.002	0.000	0.000	0.000	0.002	0.000	0.005	0.181	0.460
	RK	0.000	0.000	0.001	0.000	0.002	0.001	0.004	0.074	0.293
	Total	0.120	0.320	0.469	0.064	0.012	0.016	1.000	Overall	0.459
					1996				**Kappa Index(KIA)**	
	LULC	**MF**	**BL**	**AG**	**ST**	**WB**	**RK**	**Total**	**1996**	**2006**
	MF	0.102	0.037	0.002	0.001	0.002	0.000	0.143	0.627	0.663
	BL	0.038	0.123	0.039	0.002	0.001	0.001	0.203	0.383	0.478
	AG	0.001	0.013	0.336	0.078	0.000	0.000	0.428	0.417	0.567
2006	**ST**	0.008	0.063	0.094	0.012	0.000	0.000	0.178	-0.060	-0.029
	WB	0.001	0.001	0.000	0.000	0.001	0.000	0.003	0.227	0.372
	RK	0.001	0.005	0.034	0.002	0.001	0.003	0.045	0.626	0.056
	Total	0.150	0.242	0.504	0.095	0.005	0.004	1.000	Overall	0.393
					2006				**Kappa Index (KIA)**	
	LULC	**MF**	**BL**	**AG**	**ST**	**WB**	**RK**	**Total**	**2006**	**2016**
	MF	0.138	0.005	0.000	0.000	0.000	0.000	0.143	0.956	0.961
	BL	0.005	0.127	0.000	0.003	0.000	0.001	0.136	0.564	0.915
	AG	0.000	0.000	0.428	0.024	0.000	0.005	0.456	1.000	0.892
2016	**ST**	0.000	0.071	0.000	0.151	0.000	0.002	0.224	0.806	0.604
	WB	0.001	0.000	0.000	0.000	0.003	0.000	0.004	0.914	0.750
	RK	0.000	0.000	0.000	0.000	0.000	0.037	0.038	0.832	0.996
	Total	0.143	0.203	0.428	0.178	0.003	0.045	1.000	Overall	0.837
					1986				**Kappa Index (KIA)**	
	LULC	**MF**	**BL**	**AG**	**ST**	**WB**	**RK**	**Total**	**1986**	**2016**
	MF	0.061	0.078	0.001	0.001	0.002	0.000	0.143	0.425	0.349
	BL	0.024	0.085	0.018	0.004	0.005	0.001	0.136	0.150	0.446
	AG	0.017	0.038	0.347	0.043	0.001	0.010	0.456	0.522	0.549
2016	**ST**	0.016	0.117	0.078	0.012	0.001	0.001	0.224	-0.053	-0.013
	WB	0.001	0.000	0.000	0.000	0.002	0.000	0.004	0.159	0.540
	RK	0.001	0.001	0.025	0.004	0.002	0.004	0.038	0.223	0.095
	Total	0.001	0.320	0.469	0.064	0.012	0.016	1.000	Overall	0.311

Table 8: Cross tabulation by quantitative change (km^2)

		1986						
	LULUC	**MF**	**BL**	**AG**	**ST**	**WB**	**RK**	**Total**
1996	**MF**	68.6	102.5	1.2	0.9	1.7	0.0	174.9
	BL	41.6	192.0	34.7	6.2	5.6	1.7	281.8
	AG	22.7	71.8	449.9	33.4	1.0	8.6	587.4
	ST	4.4	5.5	59.4	33.2	0.9	7.0	110.4
	WB	2.1	0.5	0.1	0.2	2.6	0.0	5.6
	RK	0.2	0.0	0.6	0.3	2.2	1.5	4.9
	Total	139.7	372.3	545.8	74.2	14.0	19.0	1165.0
		1996						
	LULUC	**MF**	**BL**	**AG**	**ST**	**WB**	**RK**	**Total**
2006	**MF**	118.9	42.6	2.4	0.6	2.0	0.0	166.7
	BL	43.7	143.2	45.0	2.4	1.4	1.3	237.0
	AG	0.9	15.5	391.4	90.6	0.0	0.0	498.6
	ST	9.7	73.6	109.2	14.2	0.2	0.2	207.3
	WB	0.6	1.2	0.1	0.1	1.3	0.1	3.4
	RK	1.0	5.6	39.3	2.4	0.6	3.1	52.0
	Total	174.9	281.8	587.4	110.4	5.6	4.9	1165.0
		2006						
	LULUC	**MF**	**BL**	**AG**	**ST**	**WB**	**RK**	**Total**
2016	**MF**	160.4	5.6	0.0	0.0	0.0	0.0	166.0
	BL	5.7	147.6	0.0	3.7	0.2	1.2	158.4
	AG	0.0	0.3	498.5	27.4	0.0	5.2	531.5
	ST	0.1	82.9	0.0	176.1	0.0	2.0	261.2
	WB	0.6	0.3	0.0	0.0	3.1	0.0	4.2
	RK	0.0	0.0	0.1	0.1	0.0	43.6	43.8
	Total	166.7	237.0	498.6	207.3	3.4	52.0	1165.0
		1986						
	LULUC	**MF**	**BL**	**AG**	**ST**	**WB**	**RK**	**Total**
2016	**MF**	70.8	91.2	1.5	0.7	1.9	0.0	166.0
	BL	27.7	98.8	20.9	4.2	6.1	0.9	158.4
	AG	19.8	44.6	404.0	50.6	0.7	11.7	531.5
	ST	18.4	136.2	90.6	13.6	0.6	1.6	261.2
	WB	1.4	0.1	0.2	0.2	2.2	0.0	4.2
	RK	1.5	1.4	28.7	5.0	2.6	4.8	43.8
	Total	1.5	372.3	545.8	74.2	14.0	19.0	1165.0

3.7.2 Model validation

It was necessary to validate the customized CA-Markov model and assess whether it could be used for simulation of the 10 years (2026) prediction LULC. The process was done through comparison of several simulated maps of 2006 at iteration 5, 8, 10 and 15 (Fig. 8, 9 and 10) with the actual LULC map of 2006 and assessment of their Kappa Indices of Agreement (KIA) optimal values with their respective iterations. The validated model was observed at iteration 10 with satisfying required minimum value for model validation Kappa of 0.8 in which under this study Kstandard, Kno and Klocation of 0.87, 0.88 and 0.91 were obtained, respectively (Table 6) and therefore, the model was adopted (Pontius & Gil, 2000; 2002; Pontius & Suedmeyer, 2004; Pontius, 2005). Similar model validation for future land use in Tehran was done by Arsanjani *et al*. (2011) and found a strong correlation between the actual map and predicted model map at Kstandard of 0.91 and Klocation 0f 0.97 at 3000 iterations.

3.7.3 Land-use change prediction

The validated model was executed to project the LULC for the next 10 years (2026). The process was done together with the 2006 land-use map, the 1996–2006 transition area matrixes, as well as the 2006 transition potential maps. The resulting values for various land use changes are shown in Table 4 and Figure 11. Figure 11(e) shows that the total land for agriculture (AG) will decrease by 8.29 % which will be replaced by human settlement (ST) and bush land (BL) which will also increase by 6.2 % and 3.51 % respectively, by 2026. It is obvious that the increased human settlement will be caused by increased population which is among the expected major land use change for the land in transition to urbanization. It is also anticipated that in the next 10 years there will be a very little increase of mixed forest (MF) by 0.56 % which is a good sign of good forest conservation strategy by the government. It should be noted that the increase in urbanization process normally is associated with increase in demand for land for construction which can involve clearance of natural resources in some conserved areas such as forest and water bodies which in this study if the present government laws and rules will continue to be strictly followed the conserved forest will continue to survive. Also, the status of water bodies will be in a bad situation in relation to increased population since the demand for fresh water will be high if no other water sources will be invented. Furthermore, the study shows decrease in fresh water bodies (WB) by 0.15 % from 2016 to 2026 which is highly alarming for the rapid growing population of Arusha City. In addition, the area covered by rocks will decrease in the next 10 years by1.89 % which is

mostly expected to be converted into settlements due to the fact that there is minimum possibility of areas covered with rocks to be converted into any of the remaining land use categories.

Despite the anticipated land use changes expected to occur in the next 10 years, challenges may have occurred in the process of image and use land classifications hence in the projected model. For example, the study area has rocks on the mountain peak and other areas which its reflectance somehow resembled that of iron and the white corrugated plastic sheets, other white plastic coverings and several other greenhouses in flower farms. This must have led some confusion for actual land use category classification. It is unfortunate that the most common worldwide method for validation of the projected LULC map saves to use the validated model at stated three (3) Kappa values as stated at model validation section. On the other side, comparison between the projected and real image after the specified time lapse can also be used to observe what has happened in real environment. The second alternative is worthless since the aim of projecting the future LULC change of environment resides on protecting them from alarming current observed changes. However, there are some features which are necessary in any correct mapping process, such as scale and location which are sensitive to any feature presentations (Pontius *et al*., 2004). In this study this feature has been taken care by assuring similar scale is used for all analysis images through windowing and correct geo−referencing is done in addition to inspection for correct LULC classification in comparison with the simulated and real map. Difficulties appear in validation of simulated and projected maps since there are no true references as there is inexistence. Therefore, the best validation method in this study was designed in order to ensure that the model predicted reasonably, the locations and land use of the predicted cells for development and assessed their feasibilities in comparison to the real map (Arsanjani *et al*., 2011). Comparisons were done with true features based on the predictor model map of 2006 in relation to the true map of the same year and their outcomes were as summarized in Table 9. From this table the comparison showed correctness by 82 % which can also account for similar percentage correctness of the project LULC map for 2026.

Table 9: Position model validation for 2016

LULC	MF	BL	AG	ST	WB	RK	Total	Accuracy (%)
MF	7	1	0	0	0	0	8	87.5
BL	0	6	1	1	0	0	8	75
AG	0	1	6	1	0	0	8	75
ST	0	0	0	7	0	1	8	87.5
WB	0	0	0	0	8	0	8	100
RK	0	0	1	1	0	4	6	66.7
Total	7	8	8	10	8	5	46	82

3.7.4 Land use land cover change and discharge

A study was done to evaluate whether there is any effect on change of canopy cover in relation to river discharge when other parameters remained constant. The analysis show that there was a very weak correlation between the two ($r \leq 0.3$, $n = 4$, $p \leq 0.03$, Fig.12). These results suggest that the presence of good canopy cover feature around the catchment area does not maximize any recharge potential of the watershed rather it can add potentials for long term discharge and recharge of the river. Therefore, further analyses were needed to find out other contributing factors for discharge potentials of the river whereby the correlation analysis was done between precipitations of an area in relation to the discharge patterns of rivers in consecutive thirty (30) years in ten (10) years intervals. The analysis showed that there is a strong positive correlation between the two [(a) $r = 0.99$, $n = 4$, $p \leq 0.003$, (b) $r = 0.97$, $n = 4$, $p \leq 0.01$ (c) $r = 0.88$, $n = 4$, $p \leq 0.05$, (d) $r = 0.93$, $n = 4$, $p \leq 0.04$, (Fig. 13)] suggesting that the main water sources from rivers is precipitation which is charged in aquifers reservoirs.

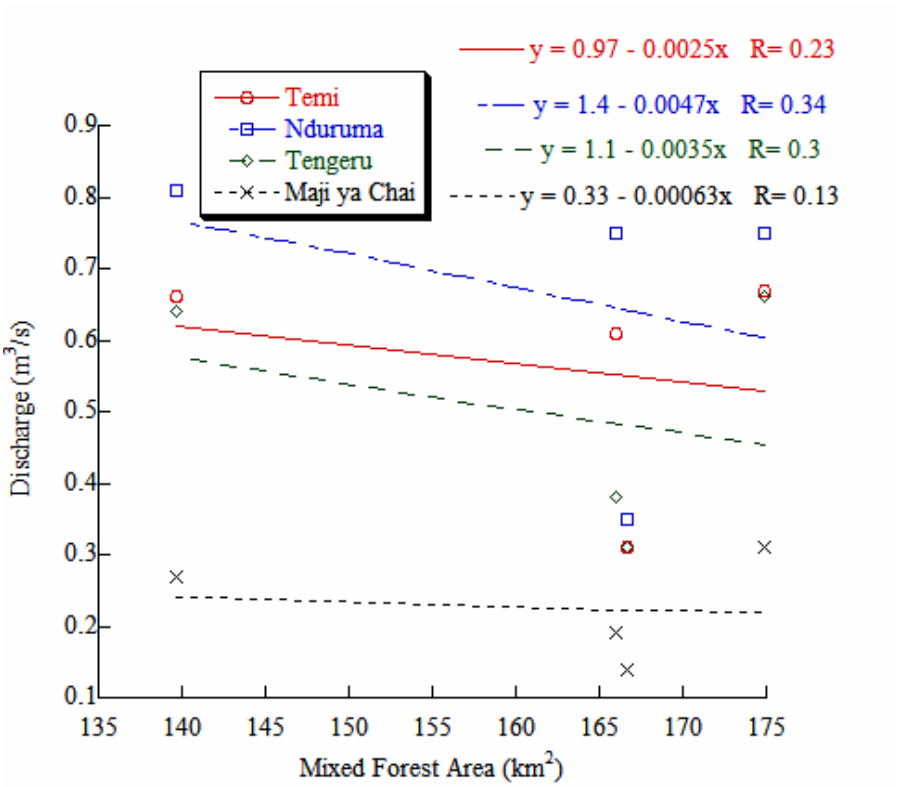
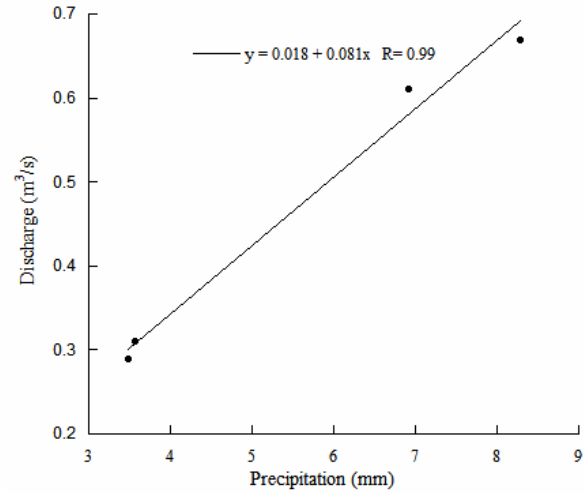
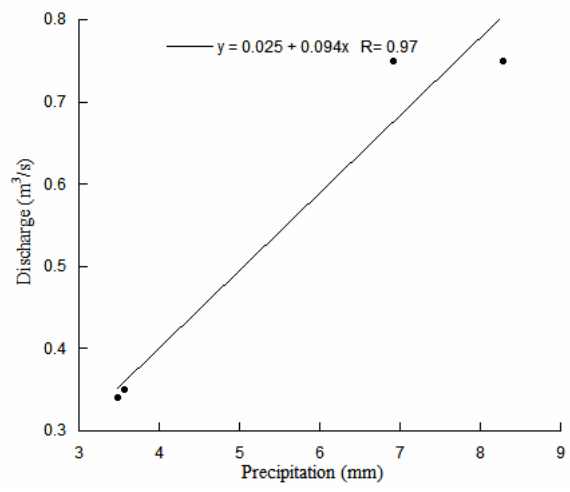


Figure 12: Correlation Analysis between MF and discharge from 1986 to 2016

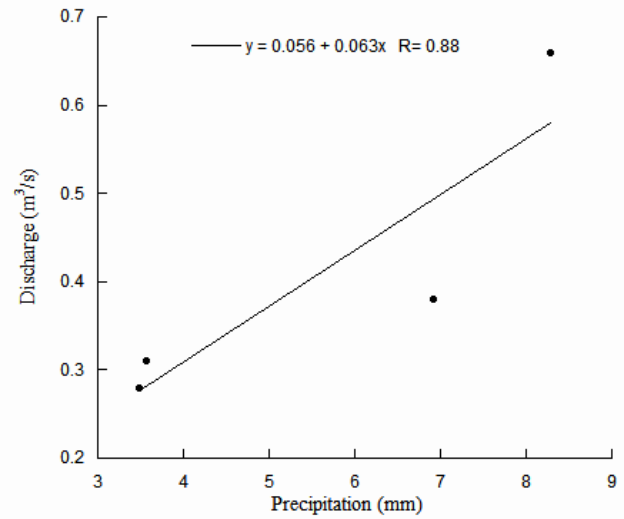
While this positive correlation is promising for the two relationships it should be remembered that the feasibility of the holding capacity of precipitated water is much more pronounced when there is good canopy cover of on area in order to minimize the runoff, evaporation and increase the soil holding capacity for water and porosity of aquifers which in turn will give a good recharge potential of any watershed. It should also be made clear that this assessment was done in the assumption that other confounding factors for discharge such as soil type, water, agriculture and transpiration (SWAT) remained constant throughout the year otherwise the analysis could be invalid. Also, most rivers from this study area originates from the top hills of mount Meru which the LULC study shows that water bodies from the mountain peak have been decreasing continuously from 1986 to 2016 (Fig. 2 &3, Table 4).



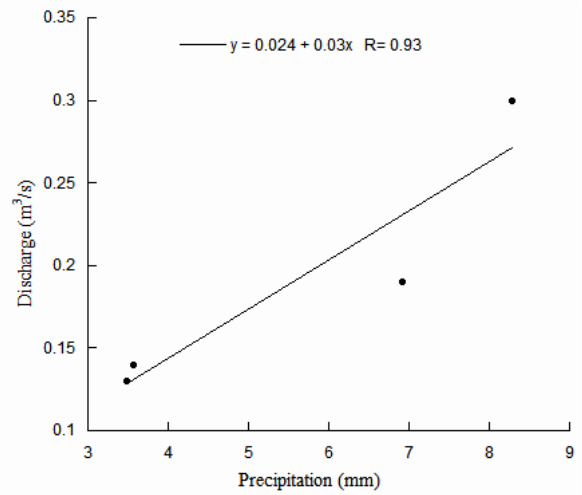
(a)Temi



(b) Nduruma



(c) Tengeru



(d) Maji ya Chai

Figure 13: Correlation for discharge in rivers and precipitation from 1986 to 2016

In addition, the analysis from Fig. 14 indicates that Themi and Nduruma Rivers had almost similar and higher discharge patterns compared to Tengeru and Maji ya Chai Rivers. Despite such similarity, the discharge capacity of Nduruma goes down during the dry season due to high water abstraction by AUWSA in the respective season the process which is further accelerated by the irrigation practices which is done by peasants in the downstream. A combination of the two factors have caused drying off of the river in the floodplain area during the dry season hence causing massive deaths of aquatic creatures and the riparian vegetations.

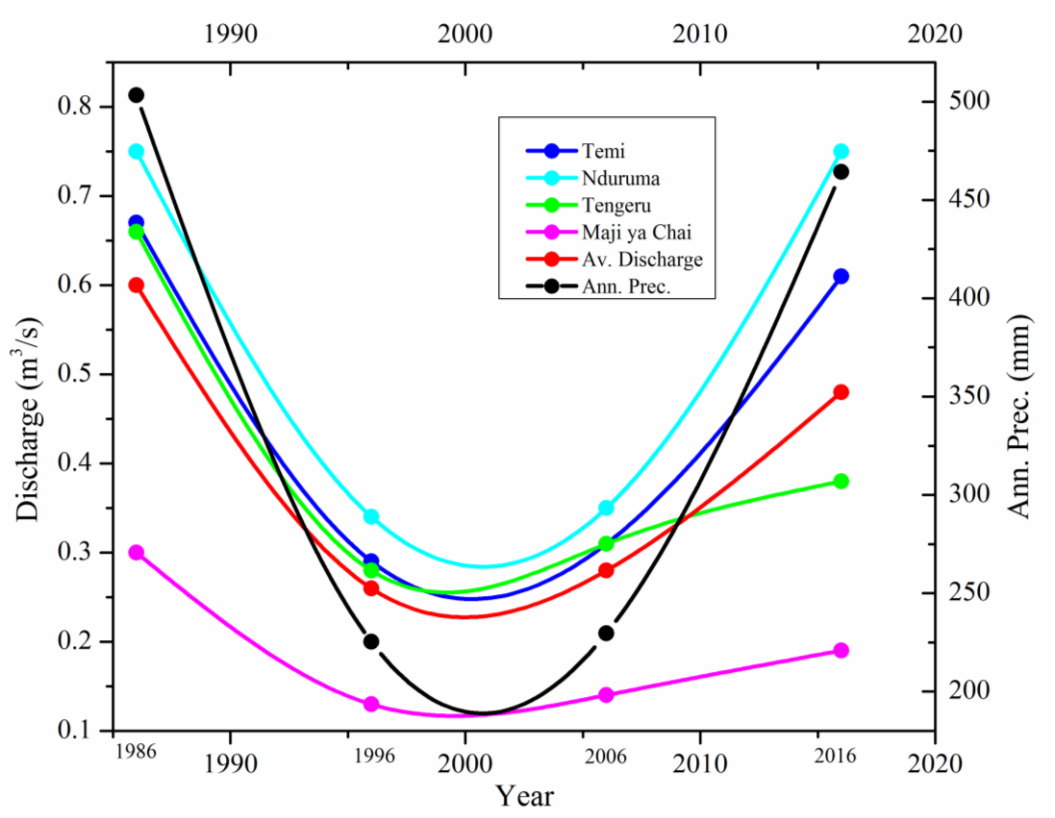


Figure 14: Precipitation and discharge patterns for rivers from 1986 to 2016

3.8 Conclusion

This study indicates a significant land use changes of the area which might have caused changes in biodiversity and water characteristics. The study has shown a rapid conversion of bush and agriculture land into human settlement which is likely to be a common case for any area which is in transition into urbanization. However, the challenge arises when there is an increase in human settlements which reflects the increase in human population at the expense of reduced agriculture land (AG) due to increase in buildings. That means while the population is increasing, the capacity to be fed by the same environment is minimized thus the sustainability of such urban population must involve importation of food and food products from other areas which will eventually increase the living cost. In addition, the present study has assessed the LULC of the area using only the features presented in the satellite images which are the outcomes of the influencing factors. Such factors which can affect the environment include social, political, scientific, technological, socio-economical and biophysical which if they were integrated in the CA-Markov model, could improve the accuracy of simulation thus giving the actual situation of the land use change by 100 %. Furthermore, errors must have happened in rock classification since in the study area there are greenhouses and roads which could show similar reflectance with rocks and therefore

some of the classification could have included in either settlements or rocks. Lastly, the observed continuous land use changes in the area attracts attention to further studies of other associated environmental features which are also likely to have been affected. In this context more studies of such changes are invested in water quality changes which have been covered in the next chapters.

CHAPTER FOUR

Inter-Seasonal Physico–Chemical, Microbiological, Nutrients Status and Their Sources in Themi River[2]

Abstract

This study reports on the sources of Dissolved Organic Carbons (DOC) and NO_3^- together with the physico-chemical, microbiological and nutrients changes observed in Themi River during wet and dry season. One hundred and five (105) water samples were collected in 2015 in both wet and dry seasons from various geo-referenced points along the river and various parameters were measured as per APHA standard methods for water and wastewater. Most parameters showed to increase downstream in both seasons. The highest levels of up to 352.11 ± 0.27 mg/L and 212.71 ± 0.37 mg/L were recorded in the wet season for HCO_3^- and CO_3^{2-}, respectively. These values decreased significantly in the dry season to126.00 ± 2.31 mg/L and 122.91 ± 9.2 mg/L, respectively. Levels of Cl^-, SO_4^{2-}, K^+, Na^+, Mg^{2+} and Ca^{2+} were up to 114 ± 1.6 mg/L and 40.51 ± 3.63 mg/L in wet and dry seasons, respectively. The floodplain part of the river had higher BOD and NO_3^- values than the WHO maximum permissible levels of 10 mg/L whereas other parameters remained lower in other parts. The stable isotope studies on the origin of dissolved organic carbon and NO_3^- indicated mainly to be from plant materials for DOC and from soil composite and wastewater for NO_3^-. Presence of high levels of fecal coliforms (FC) in water in both seasons was a major problem, an indicator for improper domestic sewage disposal/treatment and poor hygienic practices along the river. This calls upon treatment for un-piped water before domestic use to reduce waterborne diseases. Also, high nitrate content in the river soon after mixing with effluents from treated wastewater from Lemara indicates inefficient treatment system.

Key words: Water, physico–chemical, microbiological properties, Temi River, pristine, floodplain, stable isotopes.

[2] Manuscript.

4.1 Introduction

The worldwide human population increase has caused pollution of most fresh water resources by disposing of sewage, industrial and agricultural wastes which affect its physico–chemical characteristics and microbiological quality thus, making it unsafe for consumption (Baird & Bridgewater, 2017). Rivers are the most reliable fresh water sources for domestic use on earth. Understanding the hydro-physicochemical and biological properties of such water body is of great importance in monitoring its pollution and health status. A change in hydro-physicochemical and biological properties of the river is inevitable since environment also keep on changing. Such changes are hypothesized by the River Continuum Concept (RCC) stating that a continuous gradient in physical condition of water exist from the catchment headwater to mouth (Vannote *et al.,* 1980). Changes in physicochemical properties of water can be caused by natural or anthropogenic activities which can affect the safety of fresh water bodies and its surrounding environment (Yadav, 2006).

In the Tanzanian setting, early studies have characterized some physicochemical properties of Themi River (Lyimo, 2012), Msimbazi, Mzinga and Kizinga Rivers ((Napacho & Manyele, 2010; Mbuligwe & Kaseva, 2005). The studies which were conducted in rivers like Pangani, Kilombero, Kinabatangan, Sungai Padas and several others aimed at establishing the possible cause and source of water pollutants. For example, a study carried out in the Kilombero River assessed the effects of agrochemicals used in agriculture (Alavaisha *et al.,* 2019). Apart from Tanzania, the study conducted in the lower Kinabatangan River in Malaysia assessed the dynamics of dissolved organic matter (DOM) in a lowland tropical catchment (Harun, 2013). Another study by Jawan (2008) investigated the dynamicity of physicochemical properties in Billabong Kinabatangan and Sungai Padas River. Further studies in physicochemical parameters of River Tawi showed regular trends of concentration as a result of increase in sewage contamination in the river (Gandotra & Andotra, 2008). The distribution of dissolved organic matter have been studied in Mackenzie River (Tamara *et al.,* 2010), Potrero de los Funes River (San Luis-Argentina) (Almeida *et al*., 2007), River Ganga (Singh & Choudhary 2013). The nutrients variations was studied in Turag River (Tamanna*et al.,* 2013) and Yamuna river in Agra City (Gupta *et al.,* 2013). In Africa such studies have been done in flood waters in Nigeria (Ogoko, 2012) and Nile River (Ali *et al.,* 2014).

Establishment of sources for various pollutants in water has effectively been done through comparison and analysis of stable isotopes of the pollutant in-question. Some of these studies have been done in establishing the sources of dissolved organic carbon and nitrate in lake

Peter, Paul and Tuesday of the University of Notre Dame (USA) and found to originate from algae enrichment (Bade *et al.,* 2007). Other studies include the lower Mississippi River (Bianchi *et al.,* 2004), groundwater (Heaton *et al.,* 2012), surface water (Nestler *et al.,* 2011) and in ecosystems(Peterson & Fry, 1987). The Slopes of Mount Meru have several rivers which are important for socio-economic development of its community since its water is extensively used for domestic and irrigation activities. While increase in urbanization and agriculture activities along Themi River has caused water pollution from different sources little is known about their hydro physicochemical status. In this study, different methods have been employed to identify water pollutants in the river and establish the sources of DOC and NO_3^-. In addition, the inter-seasonal and spatial trends of such pollutants have also been studied.

4.2 Materials and methods

4.2.1 Description of study area

The study area involved Themi River which originates from common sub catchments foot hills of Mount Meru lying from the eastern part to the south west of the mountain (Fig. 15). The river runs downstream from the mountain to south east. The natural vegetation at the headwater of this river is typically tropical forest to savannah. The topography of the study region is dominated by Mount Meru volcanic cone of Pleistocene to recent origin. The local climate of the area is temperate Afro-Alpine, with an annual precipitation of 450 mm (Hijmans *et al.,* 2005) and their means minimum and maximum daily temperature of 20.6 °C and 28.5 °C, respectively. The rainfall is irregularly distributed between a main wet season from February to mid-May (contributing 70% of the annual precipitation) and a minor one from September to November which provides much of the remainder giving the mean annual rainfall of 535.3 mm (Gea, 2005; United Nations Development Programme (UNDP), 1989). The river was divided into three regions depending on the land development namely pristine (headwater) (3° 15’ 00” S to 3° 20’ 00” S), middle (3° 20’ 00” S to 3° 25’ 00” S) and flood plain (3° 25’ 00” S to 3° 35’ 00” S). The catchment area for the river (pristine) is characterized by both artificial coniferous trees and mixed natural forest conservation; and the middle area of the river consists of mixed agriculture and urban settlement. The floodplain (downstream) region is characterized by bare land, intensive grazing, large scale agriculture, treated municipal sewage disposal and serious flooding in wet season.

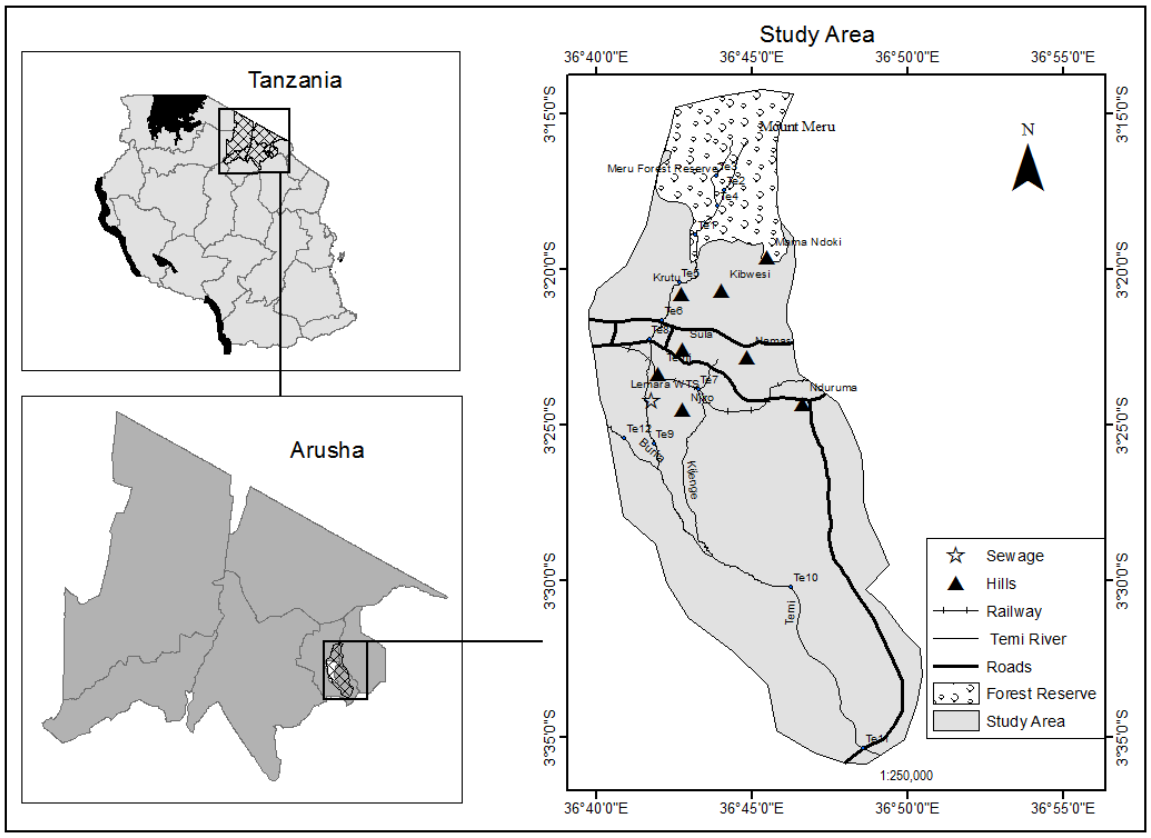


Figure 15: Location of the study area

4.2.2 Sampling

The geo-referenced sampling points were identified basing on confluence, accessibility and pre-established monitoring stations. Two liters water samples were collected in glass and plastic bottles which were both Teflon caped. Samples from glass bottles were used in nutrient and organic component analysis whereas the samples from plastic bottles were used in metal analysis. Samples for stable isotope analysis were collected in 100 mL polytetrafluoroethylene (PTFE) bottles and stored in cold box with ice caps to avoid fractionation of their isotopic composition. Also, preservations of all samples for stable isotopes analysis were done using $ZnCl_2$ and H_2SO_4 solutions to avoid bacterial degradation which could cause fractionation of stable isotopes. Sampling was done during the wet season (Mid–March to early April) and dry season (August) in 2015. In each season 52 representative samples were collected for analysis. Also, sampling of soil composite, sewerage effluents, manure and commonly used industrial fertilizer was done within the study area. All samples were immediately kept in cold box containing ice cubes and transferred directly to the laboratory of the Nelson Mandela African Institution of Science

and Technology (NM–AIST) ready for preservation and transport to Waterloo University in Canada.

4.2.3 Extraction, pretreatment and cleanup of water samples

Extraction and treatment of soil organic matter and manure was done following the procedure by Thornton and McManus (1994) whereas the method by Heaton *et al.* (2012) was used for preparation of manure and fertilizer samples. In addition, the soil samples were treated with 5 % HCl to remove all inorganic carbonates before further processing and the resulting solution was filtered using a 0.45 µm Whatman membrane filter prior to preservation. Water samples for NO_3^- analysis were acidified using concentrated H_2SO_4 to a pH below 2 and frozen until respective analysis. Samples for stable isotope analysis of $\delta^{13}C$, $\delta^{15}N$ were preserved with few drops $ZnCl_2$ (aq) to prevent all biological activities, whereas samples for $\delta^{18}O$ and $\delta^{2}H$ analysis were kept cooled at below 4°C before and on transport to Stable Isotope laboratory at Waterloo University in Canada (Hoefs 2009; Myers & Mark, 2006).

4.2.4 Analysis and confirmation

Temperature, pH, total dissolved solids (TDS), dissolved oxygen (DO) and electrical conductivity (EC) were measured in situ using a HANNA multi-parameter Model HI9829 whereas the total hardness was measured by acid titrimetric method. Other parameters such as BOD, nitrates (NO_3^-), fecal coliforms and the total suspended solids (TSS) were measured at NM–AIST laboratories following standard methods as per APHA (2012) (Appendix 3). In addition, total phosphates (TP) and soluble phosphates (SP), sulphates and chlorides were measured using HACH 2800™ while turbidity and alkalinity were measured using a 2100Q01 HACH portable turbidimeter with formazin turbidity standard 4000 NTU in serial dilutions to the required standards and HANNA alkalinity checker HI 755, respectively. The chromophoric dissolved organic matter (CDOM) was measured in situ by a submersible fluorometer Turner™ Cyclops–7(P/N–2100–000–U) integrated with a data logger. Samples for dissolved organic carbon (DOC) were filtered in a 0.45 µm Whatman membrane filters. Concentration of organic carbon and isotopic analysis of $\delta^{13}C$ were done at Stable Isotope Centre, California University using a Shimadzu TOC-5000 Elemental analyzer Total Organic Carbon Analyzer equipped with an on-dispersive CO_2 detector (Brooks *et al.,* 2015) and Isotope Ratio Mass Spectrometry (TOCA-IRMS), respectively, following the procedure by

Gandhi *et al*. 2004). The isotopic measurement and identification for Nitrogen sources was carried out by continuous flow IRMS following the standard procedure using the LGR-ICOS technology (Hood & Mcknight, 2005). Analysis of $\delta^{15}N$ stable isotopes was done using a modern technology of Los Gatos Research Laser processes analyzer with Integrated Cavity Output Spectroscopy (LGR-ICOS™) machine. All isotopes analyses were done using international standards from the Vienna Pee Dee Belemnite (V−PDB) and Vienna standard Mean Ocean Water (V−SMOW) (International Atomic Energy Agency, 2000; De Troyer *et al.*, 2010). The Data analysis for $\delta^{13}C$ and NO_3^- were reported as per mill (‰) as given in the Equation (11):

$$\delta^{13}C \text{ or } \delta^{15}N = \left(\frac{Rs}{Rstd} - 1\right)1000 \qquad (11)$$

Where Rs− is the ratio of $^{13}C/^{12}C$ in the sample.

Rstd− is the standard ratio (V−PDB) which equates to 0.0112372.

For $\delta^{15}N$, Rs −is the ratio 15N/14N in the sample.

Rstd− is the standard ratio (VSMOW).

4.2.5 Analytical quality assurance

The analytical laboratory report needs quality assurance data to allow independent assessment of the methods, laboratory performance, credibility and reliability of results. In this study all plastic and glass sampling bottles were washed and rinsed with double distilled water then oven dried before sampling. Samples for nutrients analysis were kept at appropriate conditions before and upon analysis to avoid fractionation of its original components. Electrodes for in-situ multi-parameter analysis, CDOM and fluoride analysis were rinsed thrice in double distilled water and its sensitivity were reconfirmed through calibration using standard solutions.

4.3 Results and discussion

The average physicochemical and microbiological trends for Temi River are shown in Table 10 and 11**.**

4.3.1 Physicochemical and microbiological changes in Temi River

The major cations and anions varied downstream as shown in Fig. 16. Generally, high levels of cations and anions were observed in the wet season than dry season. The highest levels of major cations and anions were observed in the floodplain area of the river during the wet season at Te10 and Te11 and low levels were observed in the headwater and middle area of the river. The levels of HCO_3^- and CO_3^{2-} in the wet season were up to 352.11 ± 0.27 mg/L and 212.71 ± 0.27 mg/L, respectively. These levels decreased in the dry season to 126.00 ± 2.31 mg/L and 122.91 ± 9.20 mg/L, respectively. The remaining ions (Cl^-, SO_4^{2-}, K^+, Na^+, Mg^{2+} and Ca^{2+}) were up to114 ± 1.6 mg/L and 40.51 ± 3.63 mg/L in wet and dry seasons, respectively (Appendix 4). This trend was accelerated in the wet season due to the presence of runoff which might have collected various dissolved ions to the river from various sources. Also, the low water velocity in the floodplain which gives more interaction time of water with rocks which in turn it increases the dissolution of ions from rocks. Most ions and nutrients had significant correlation with each other meaning that they originated from similar soluble salt species in the environment (Table 10 and 11). Also, such strong positive correlation indicates a common transformation pattern of the respective salts in water. Generally, the major ions in this river were higher in the wet than dry season and such high levels in the wet season were highly contributed by runoff.

Table 10: Correlation matrix for major ions in Themi River

Ion	Ca^{2+}	Mg^{2+}	Na^+	K^+	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}
Ca^{2+}	1							
Mg^{2+}	0.8071*	1						
Na^+	1*	0.8067*	1					
K^+	1*	0.8066*	1	1				
CO_3^{2-}	0.855*	0.7815*	0.8548*	0.8548*	1			
HCO_3^-	1*	0.8069*	1*	1*	0.8549*	1		
Cl^-	0.6122*	0.8319*	0.6118*	0.6118*	0.7415*	0.6122*	1	
SO_4^{2-}	0.8056*	0.6398*	0.8058*	0.8058*	0.9549*	0.8055*	0.5783*	1

*Correlation are significant at n = 12, p = 0.05.

Table 11: Correlation matrix for nutrients in Themi River

Ion	NH_3	NH_3–N	NH_4^+	NO_3^-	NO_3^-–N	TSP	TP
NH_3	1						
NH_3–N	0.9999*	1					
NH_4^+	0.9997*	0.9997*	1				
NO_3^-	0.7248*	0.7228*	0.7091*	1			
NO_3^-–N	0.7166*	0.7146*	0.7007*	0.9998*	1		
TSP	0.5815*	0.5794*	0.5643	0.9359*	0.9379*	1	
TP	0.5815*	0.5794*	0.5643	0.9359*	0.9379*	1	1

*Correlation are significant at n = 12, p = 0.05.

The oxygen demanding wastes were higher in the wet season than dry season with the highest level of Biochemical Oxygen Demand (BOD) being 34.1 ± 4.62 mg/L and its Chemical Oxygen Demand (COD) being 52.0 ± 1.74 mg/L in the wet season while in the dry season these levels decreased to 24.7 ± 0.99 mg/L and 37.0 ± 3.71 mg/L for BOD and COD, respectively.

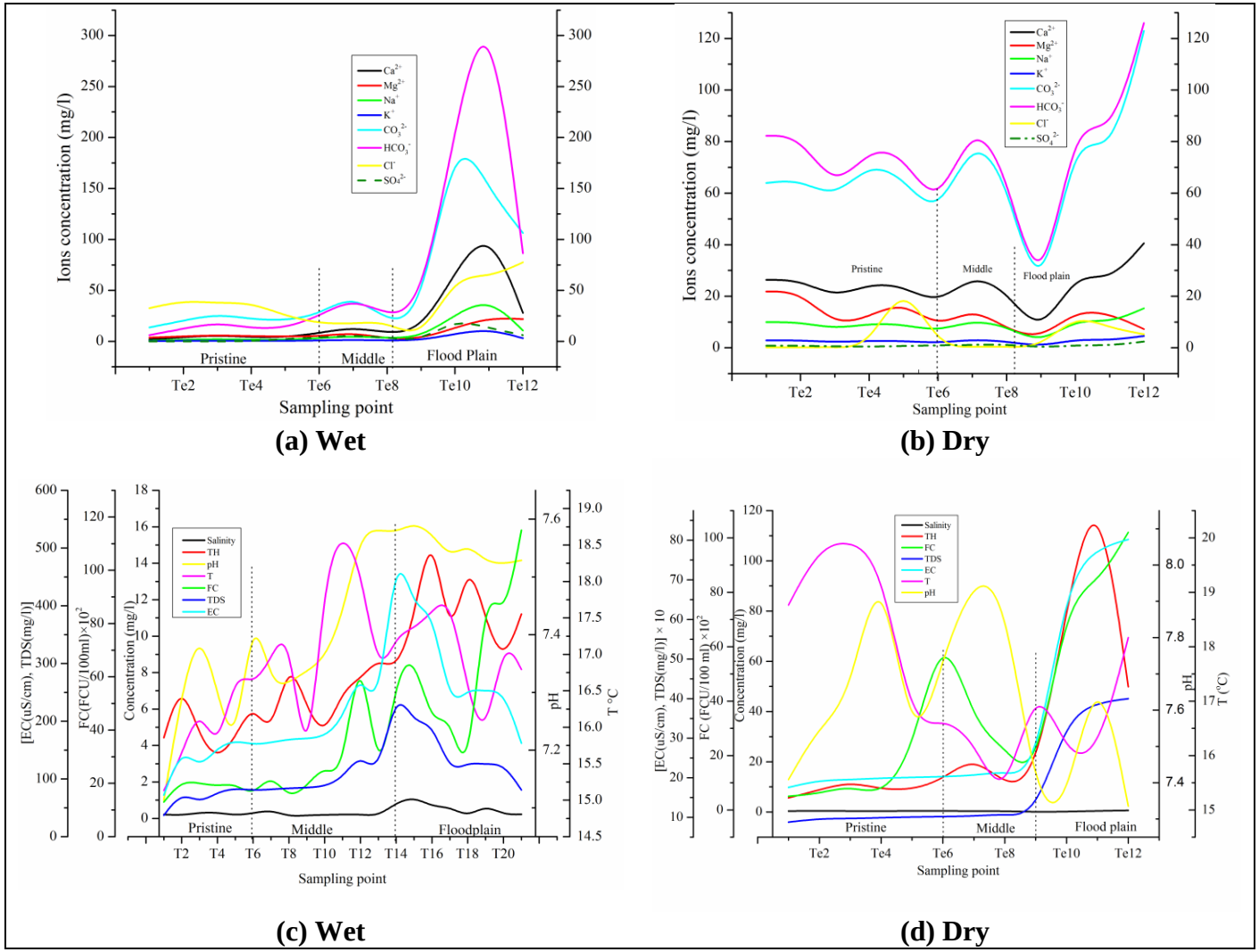


Figure 16: Variation of physicochemical and microbiological parameters in Themi River during wet and dry seasons

These observations were recorded at Te10 which is next to the confluence point between Lemara waste water treatment system and Themi River (Fig. 16). High levels of BOD and COD in the river is caused by terrestrial runoffs which are associated with inputs of oxygen demanding wastes from different sources. Also, the high BOD and COD values to the downstream just after the river receiving waste water from WSPs in Lemara indicate the low performance of the treatment system towards removal of oxygen demanding waste since effluents from discharge point to the receiving water recorded high BOD and COD values of 61.4 ± 4.81 mg/L and 84.7 ± 2.74 mg/L, respectively. These values are relatively higher than their immediate upstream samples at Te 9. Thus, some sampling points had values greater than the TBS maximum acceptable values for wastewater of 30 mg/L (TBS, 2014). Also, the COD and BOD increased proportionally to each other an indication that similar waste compositions affect the two parameters. Despite such relatively high levels at Lemara, the oxygen demanding wastes decreased at the floodplain is observed at Te11, and Te12 an indication of river recovery as it runs downstream from the point source. Interestingly, the headwaters in this river recorded very low levels of such waste an indication of minimum runoff of oxygen demanding wastes to the river but these levels were elevated soon after crossing the city area. Since the oxygen demanding waste consumes much oxygen, the levels of dissolved oxygen (DO) in water varied inversely proportional to the wastes with the highest level being 10.10 ± 1.86 mg/L and 9.16 ± 0.92 mg/L at the river source (Te1), 7.91 ± 0.33 mg/L and 4.20 ± 2.11 mg/L both in the floodplain (Te10) during wet and dry seasons, respectively (Appendix 4). Normally, a river with DO values of 4 –7 mg/L is good for many aquatic animals and if the concentration of oxygen exceeds 8 mg/L such river is considered as healthy (Murdoch *et al.*, 2012). Therefore, the above values are relatively high to support the aquatic life. Also, these values are within the acceptable limits of Tanzania Bureau of Standards(TBS) for drinking water (TBS, 2014). In addition, the Total Suspended Solids (TDS) showed to increase proportionally with COD an indication that they are among of the wastes which consume oxygen.

The presence of chromophoric/coloured dissolve organic matter (CDOM) is an indication of presence of oxidized dissolved organic carbon in water which appears in form of fulvic and humic acids. The intensity of fluorescence (in this study measured in relative fluorescence unit (RFU) reflect the amount of total organic carbon) in water. In this study the highest and lowest fluorescence was 19.4 ± 3.77 RFU at Te11 and -162 ± 28.51 RUF at Te2, 441 ± 37.21 RFU at Te 12 and -160 ± 35.02 RFU at Te1 in wet and dry season, respectively (Appendix

4). Negative fluorescence in the pristine environment indicates that the dissolved organic matter (DOM) in water were below the detection limit (BDL) of the instrument while in the floodplain their positive values indicates presence of DOM. The sources of such carbons are discussed in the preceding sections through stable isotope analysis.

The nutrient flows in this river were high after they mix with the waste waters from Lemara in which nitrates (NO_3^-) were the highest in both seasons. The maximum NO_3^- levels were 97± 1.33 mg/L at Te 10 and 82 ± 7.15 mg/L at Te 11with their minimum levels being < 0.23 mg/L and below detection limit (BDL) in the dry and wet seasons, respectively (Appendix 4). The levels in both seasons for some sampling points exceeds the maximum levels recommended by WHO for drinking water which is 50 mg/L (World Health Organisation (WHO), 2011). In this river the NO_3^- levels were higher in the dry season than wet season. This condition is expected to occur due to the fact that the floodplain is lowland dominated with pastoralists with large groups of animals which depend on the same river for animals drinking especially in the dry season. Once they spent the whole day in the same area, they increase nitrogenous waste in water through excretion.

Other parts of the river had low levels of NO_3^- in both seasons but in the dry season the levels were slightly elevated at pristine environment (Te1, and Te4). Increase in nitrates in this area is caused by excretory wastes from wild animals which use this river as the only water source for them since most streams dry in the dry season. The nitrate transformation in all points followed similar patterns depending on the concentration of nitrates present as shown in Fig. 17 (a) (b). The correlation studies for NO_3^- transformations showed a strong positive relation between themselves which is an indication for transformation of NO_3^-, NH_3 and NH_4^+ into either one depending on the pH (Table 11). Generally, the nitrates levels in the pristine environment were below the WHO maximum permissible levels.

Phosphate nutrients were also recorded in similar areas as those of nitrates. Under normal conditions, the river that is not flowing into a lake should not drain off the TSP exceeding 0.1 mg/L (Murdoch *et al.*, 1991). In this study the maximum TSP was 4.16 ± 0.99 mg/L at Te 10 in the wet season whereas in the dry season their levels raised to 4.74 ± 0.36 mg/L. A strong positive correlation was observed between the TP and TSP an indication that, the TSP originates from both organic and inorganic phosphates which are represented by total phosphates (TP) (Table 11).

The floodplain area of the river showed PO_4^{2-} concentration > 0.1 mg/L in both seasons an indication that the main phosphate source is from the improperly treated effluents from Lemara wastewater treatment system (Appendix 4).

Other parameters measured in this river were fecal coliforms (FC), salinity, pH, water temperature (T), the amount of total dissolved solids (TDS), conductivity (EC) and its total hardness (TH). The number of FC was an alarming parameter in both seasons since no water sample was free from FC. The elevated levels of FC were observed in the wet season than dry season basically as a cause of runoff which carried feces contaminated wastes onto the river. The highest level of FC (10200 ± 1720 FCU/100 mL) was recorded at Te12 in the floodplain and 4800 ± 410 FCU/100 mL which was recorded at Te6 in middle section area of the river during wet and dry seasons, respectively. The lowest level in the wet season was 500 ± 230 FCU/100 mL being recorded in the pristine environment at Te4 while in the dry season the values slightly decreased to 300 ± 110 FCU/100 mL at the same point in the headwater (Appendix 4). Presence of FC even in pristine environment shows how it is necessary for portable water to be treated before drinking regardless the water source. Yet, the headwater had low FC than the rest parts of the river in both seasons. Since the number of FC is elevated soon after the mixing of effluents from Lemara WTS, then it is necessary to modify the system to trap enough microorganisms hence reduce its amount in the downstream receiving water.

The salinity ranged between 0.04 ± 0.02 mg/L and 275.99 ± 24.81 mg/L whereas pH values were between 7.32 ± 0.52 and 9.70 ± 0.55 both being within the acceptable levels of 100 mg/L and 6.5-9.2 in both seasons, respectively, except at Te 8 where it was 9.7 ± 0.55 (National Health and Medical Research Council (NHMRC) & National Resource Management Ministerial Council(NRMMC), 2016). Also TDS, TH and EC were within the acceptable levels of 200-1200 mg/L, 200 mg/L and 2500 µS/cm for drinking water in both seasons, respectively (NHMRC & NRMMC, 2016; WHO, 2011) (Fig. 16). The water temperature showed to increase downstream in both rivers. This trend is also evidenced by δ^2H and $\delta^{18}O$ enrichment which is a sign for increase in evaporation downstream. High temperature might have slightly influenced the physico-chemical activities in water and their concentration gradient.

Table 12: Stable isotope signatures and dissolved organic carbon levels for Themi River

Sampling point	Te1	Te3	Te5	Te6	Te8	Te9	Te10	Manure	Soil Composite	GW	Wastewater	Fertilizers* (CAN/NPK)	Plant materials
DOC (mg/L)	0.20	0.20	-	1.41	1.46	1.98	1.97	-	-	-	-	-	-
$\delta^{13}C \pm 0.20$ ‰	-13.01	-	-	-	-21.30	-22.82	-22.50	-21.25	-17.4	-13.11	-20.07	-24.81	-22.1
$\delta^{15}N–NO_3^- \pm 0.30$‰	+6.82	-	-	-	+8.08	+10.11	+10.36	+6.77	+9.47	+2.59	+`10.19	-6.91	-
$\delta^{18}O–NO_3^- \pm 0.80$ ‰	+1.64				+1.65	+1.68	+1.71	+1.62	+1.69	-	+1.73	+1.65	

*CAN– Calcium Ammonium Nitrate;*NPK– Nitrogen Phosphorus Potassium; *GW– Ground water

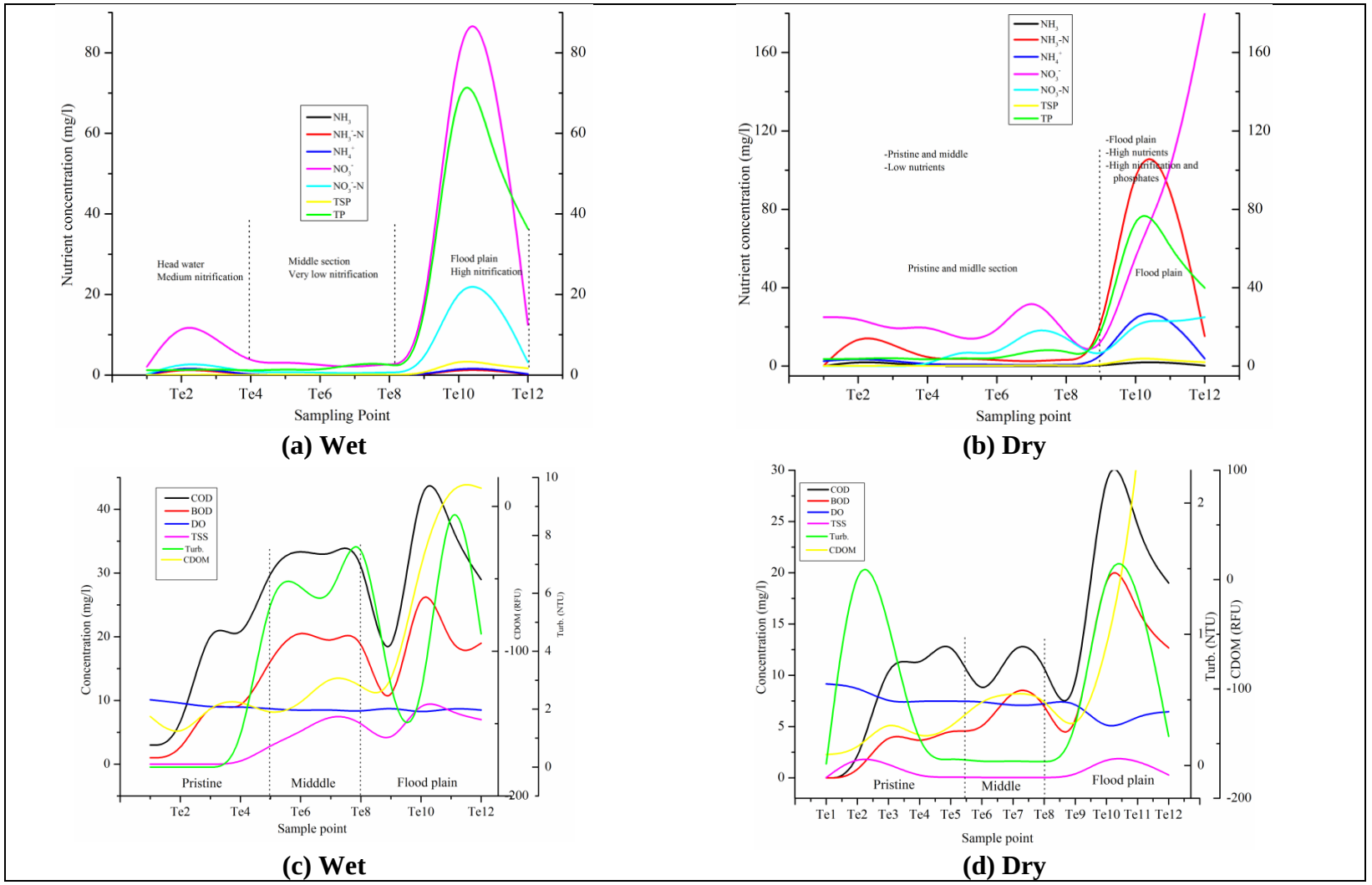


Figure 17: Variation of Nutrients and physicochemical parameters in Themi River during wet and dry seasons

4.3.2 Dissolved organic carbon and nitrate sources

The dissolved organic carbons (DOC) trends showed to increase from the pristine water downstream. The minimum levels for DOC (0.21 ± 0.20 mg/L) were measured at Te1 and Te3 located at the pristine environment of the river whereas the maximum level of 1.97 ± 0.02 mg/L was recorded in the floodplain region of the river at Te10 (Fig. 18; Table 12). The increased levels of DOC in the floodplain can be due to increase in waste loading due to runoff and municipal sewage discharge from the treatment point at Lemara which empty its contents in Temi River.

Also, increase in decomposition of organic matters by microorganisms can be another cause of increase in DOC. Past works has shown that DOCs from rivers systems are mainly derived from terrestrial vegetation and it dominates in all rivers (Malcolm, 1990; Opsahl & Zepp, 2001).

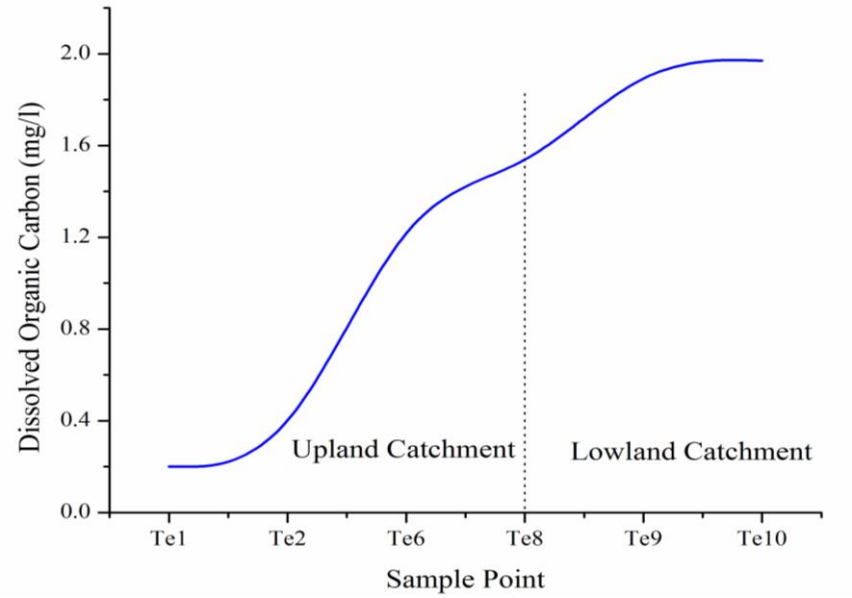


Figure 18: Levels of dissolved organic carbon in Themi River

Since this river passes through different environment it was necessary to establish the sources of DOC. This process was done by comparing the stable isotopes of carbon in water (^{13}C and ^{12}C) with the stable isotopes of the same material from different surrounding possible sources (Mook, 1980; 1986) as shown in Table 12. The results from this table show that the headwaters (Te1) from this river showed $\delta^{13}C$ fractionation of −13.01 ± 0.20 ‰ which was close to the isotopic signature of −13.11 ± 0.20 ‰ for ground water. This range shows that the main source of dissolved carbon is mainly inorganic carbonates indicating that; groundwater is mixing with surface water. The middle and downstream had $\delta^{13}C$

fractionation range between −21.3 ± 0.20 ‰ to −22.82 ± 0.20 ‰. This range is within the manure and plant materials signatures of −21.25 ± 0.20 ‰ and −22.1 ± 0.20 ‰, respectively, indicating the source of dissolved carbon in water is mainly wastewater and terrestrial plants. Generally, since the main composition of manure is plant materials, it can be concluded that the main source of DOC in this part of the river is plant materials as it was reported elsewhere by Malcolm (1990), Opsahl and Zepp (2001), Kendall *et al*. (2001) and Mook (1980; 1986).

The fractionation of $\delta^{15}N$ stable isotope in the pristine environment of the same water was +6.82 ± 0.30 ‰ indicating a significant contribution of NO_3^- from inorganic nitrogenous fertilizers (anthropogenic) as supported by isotopic signatures from the commonly used sampled fertilizers and manure which were +6.91 ± 0.30 ‰. Thus, small scale agriculture around those catchment areas spills off fertilizers and animal manure into water through run off. The fractionation of $\delta^{15}N$ stable isotope in the rest part of the river ranged between +8.08 ± 0.30 ‰ to ± 10.36 ± 0.30 ‰ signifying that, the main source of NO_3^- is organic N from soil (natural) and waste waters from Lemara wastewater stabilization system. This is evidenced by similarities in isotopic signatures in the soil composite and waste water with isotopic signatures of +9.47 ± 0.30 ‰ and +10.19 ± 0.30 ‰, respectively. Similar fractionations patterns were shown in the corresponding $\delta^{18}O–NO_3^-$ signatures which supported further the nitrates pollutants components as shown in Table 12.

4.4 Conclusions

The physicochemical and microbiological parameters have shown to deteriorate downstream the river as a result of increased human activities and runoff. Excessive increase in fecal coliforms in the river is alerting on the hygienic practices along the river and in the urban areas which the river passes. The study shows the elevated levels for most parameters to occur downstream soon after receiving the treated wastewater which is an indication for poor performing wastewater stabilization ponds. Thanks to the AUWSA for planning the construction of new ponds with advanced wastewater treatment technology that will give a permanent solution for the existing problem.

CHAPTER FIVE

Interseasonal Physicochemical, Microbiological Temporal Variations, And Nutrients Sources in Rivers on the Foothills of Mount Meru, Tanzania[3]

Abstract

The physicochemical, microbiological changes and the DOCs and NO_3^- sources in three rivers (Nduruma, Tengeru and Maji ya Chai) on the foothills of Mount Meru were studied during wet and dry seasons in 2015. Three hundred and fourteen (314) water samples from various geo–referenced points along rivers were analyzed for major physico–chemical and microbial contents using APHA standard methods for fresh and wastewater. Pollution levels in Tengeru River were lower than those of Nduruma and Maji ya Chai Rivers. The fecal coliforms were observed in all water samples while other parameters were within the WHO maximum permissible limits. Few samples had BOD, NO_3^- and TSP levels higher than the WHO standards of 10 mg/L, 50 mg/L and 0.1 mg/L, respectively. Most areas in the wet season recorded COD levels higher than the WHO recommended values of 10 mg/L. Few areas in the dry season had EC of up to 1722 ± 29.71 µS/cm which is above the WHO maximum recommended level. Also, dissolved organic carbons originating from the drainage basin was the major problem in Maji ya Chai River. The stable isotopes studies in water samples revealed sources of DOC in Nduruma River was from plant materials and soil composite with its NO_3^- being mainly from urea fertilizers applied by farmers. Ground water was the main source of DOC in headwater of Tengeru while manure was its main source in the floodplain. Furthermore, the NO_3^- from this river originated from animal manure. COD in Maji ya Chai River originated from plant materials whereas NO_3^- were from wild animal manure.

Key words: Physico–chemical Parameters, Microbiological Parameters, Nduruma River, Tengeru River, Maji ya Chai River, Stable Isotopes.

[3]**This chapter is based on the published paper:**
Aldo J. Kitalika, Revocatus R. L. Machunda, Hans C. Komakech and Karoli N. Njau, *International Journal of Scientific and Engineering Research*8(9): (2017) 1320-1346, http://dx.doi.org/10.14299/ijser.2017.09.005

5.1 Introduction

Tanzania is among the countries with abundant fresh water sources which conservation outside of large towns is lacking or minimal at best (Aller *et al*., 2013). Among these sources include rivers and lakes. It is known that over 1.6 billion people lack access to clean water with more than 2.6 billion do not have proper sanitation the situation being most dominant in developing countries including Tanzania (UNDP, 2008).Themi, Nduruma, Tengeru and Maji ya Chai Rivers are among the fresh water sources in the Pangani basin supplying the Arusha and Meru Urban in Tanzania (Munishi *et al.*, 2009). The mentioned rivers pass through the human settlements and downstream to the areas with several human activities which include farming, building material mining and pastoralism. Such different environmental changes cause changes in the water chemistry which result into polluted water as it moves. Water pollution which leads to physicochemical changes and other parameters does not only threaten the human health but also increase the cost of water processing for domestic and other purposes of use. Such water pollution include the change in physical, chemical and biological properties of water which prevent its suitability for various purposes (Taha *et al*., 2004). The changes in water quality in these rivers is advocated to be caused by poor wastewater stabilization ponds (WSP) effluent quality, which does not meet the Tanzania effluent quality standard for receiving rivers (African Development Bank (ADB), 2015), poor agricultural practices, poor urban planning, poor hygienic conditions of human settlements and mining activities.

Despite the established causes for water deterioration in these rivers, the pollutants and extent of such pollution in different aspects is unknown. Considering the importance of these rivers, a study was designed to unveil and assess such unknown pollutants through different scientific methods. Therefore, this work reports the changes in physicochemical and biological properties of water together with the sources of DOC and NO_3^- in the three rivers namely, Nduruma, Tengeru and Maji ya Chai and how the rivers are affected by seasonal changes and the surrounding environment.

5.2 Materials and methods

5.2.1 Description of study area

The study area involved Nduruma, Tengeru and Maji ya Chai Rivers. These rivers originates from common sub catchments of upper Pangani River Basin (PRB) in the foot hills of Mount

Meru lying from the eastern part to the south west of the mountain (Fig. 19) The rivers run downstream from the mountain to the south east draining their contents into the Indian Ocean through Kikuletwa and Pangani Rivers (Pangani Basin Water Board (PBWB), 2009).

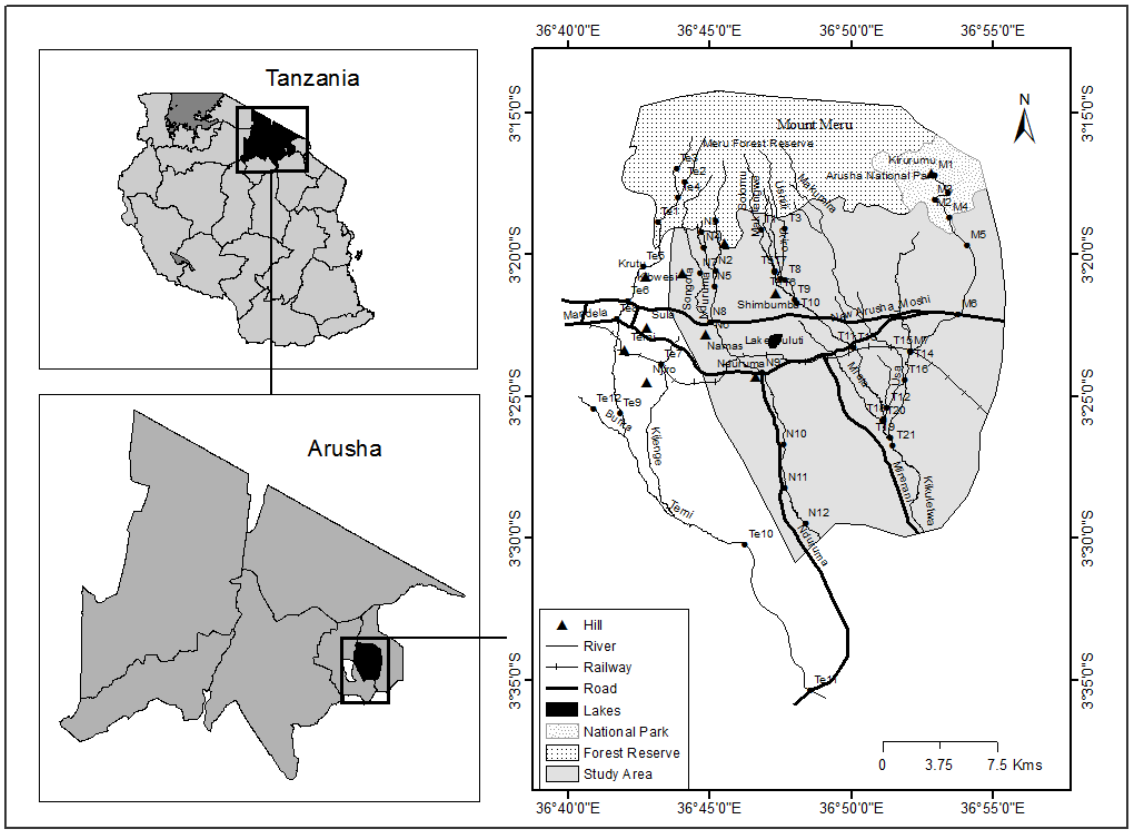


Figure 19: Location of the study area

5.2.2 Sampling

The georeferenced sampling points were identified basing on confluence, accessibility and pre-established monitoring stations. In each sampling point, two liters of water samples were collected in Teflon capped 1 liter glass bottles and another 1 liter plastic bottles of which samples from the glass bottles were used in analysis of organic components and nutrients analysis and samples from plastic bottles were used in metal ions and microbiological analysis. Samples for stable isotopes were collected in – situ using 100 mL PTFE bottles and immediately preserved with few drops of $ZnCl_2$ (for stable isotopes of carbon) and H_2SO_4 (nitrates). Sampling was done thrice in one-week interval during the wet season (Mid–March to early April) and dry season (August). All samples were kept in iced cold boxes ready for transport to the laboratory. In each season 157 representative samples were collected for analysis.

5.2.3 Extraction, pretreatment and cleanup of water samples

Samples for NO_3^- analysis were acidified with conc. H_2SO_4 to a pH below 2 and frozen until respective analysis. Samples for other parameters were not pretreated with any chemical. Samples for stable isotope analysis of $\delta^{13}C$, $\delta^{15}N$ were preserved with few drops of $ZnCl_2$ (aq) to prevent from all biological activities, whereas samples for $\delta^{18}O$ and $\delta^{2}H$ analysis were cooled at 4 °C ready for transport at Stable Isotope laboratory in Waterloo University - Canada.

5.2.4 Analysis and confirmation

Temperature, pH, total dissolved solids (TDS), dissolved oxygen (DO) and electrical conductivity (EC) were measured in situ using a HANNA multi-parameter Model HI9829 whereas the total hardness was measured by acid titrimetric method. Other parameters such as BOD, nitrates (NO_3^-), fecal coliforms and total suspended solids (TSS) were measured following standard methods (American Public Health Association (APHA), 2012). In addition, total phosphates (TP) and soluble phosphates (SP), sulphates and chlorides were measured using HACH 2800™ while turbidity and alkalinity were measured using a 2100Q01 HACH portable turbidimeter with formazin turbidity standard 4000 NTU prepared by serial dilutions to the required standards and HANNA alkalinity checker HI 755, respectively. The chromophoric dissolved organic matter (CDOM) was measured in situ by a submersible fluorometer Turner™ Cyclops–7(PIN–2100–000–U) integrated with a data logger. Analysis for $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$ and $\delta^{2}H$ stable isotopes was done using a modern technology of Los Gatos Research Laser processes analyzer with Integrated Cavity Output Spectroscopy (LGR–ICOS™) instrument.

5.3 Results and discussion

The average physicochemical and microbiological trends for the three rivers are shown in appendix 5, 6 and 7**.** Also, the results are further summarized in Fig. 20 through 25. The signatures of the four stable isotopes elements for C, N, H and O are shown in Table 20.

5.3.1 Physicochemical and microbiological changes in Nduruma River

The distribution of major ions in Nduruma River is shown in Appendix 5 and summarized in Fig. 20 and 21.

The major ions pattern in this river showed high levels of chloride (Cl^-) than carbonates (CO_3^{2-}). The highest levels of ions were observed in dry season than wet season. Highest chloride levels (44.99 ± 3.81 mg/L) were observed in wet season in the pristine environment (N5) whereas in the dry season the levels were elevated to 122.5 ± 7.31 mg/L at N7. The two levels were monitored at Songota River which is among the tributaries feeding Nduruma River. Therefore, under such trend, we can justify that Songota was the main contributor to such higher Cl^- levels to the downstream despite other sources. Despite the high levels observed in dry season, still they are within the maximum permissible threshold levels for Australia of 250 mg/L (NHMRC & NRMMC, 2016).

Sulfates (SO_4^{2-}) is another ion of interest in the river whereby the maximum level of (23.49 ± 1.58 mg/L) was detected at the pristine environment (N3) during dry season. Other ions (HCO_3^-, CO_3^{2-}, K^+, Na^+, Mg^{2+} and Ca^{2+}) were all in low amount in both seasons and complied with the WHO prescribed standards, despite their high levels in dry season compared to wet season. The WHO requires K^+ levels of 300 mg/L/day and Na^+ at aesthetic level of 180 mg/L whereas Mg^{2+} and Ca^{2+} are prescribed in total hardness standards (Gorchev & Ozolins, 2011; NHMRC & NNRMMC, 2016; UNEP, 2008). In addition, a strong positive correlation was observed between CO_3^{2-} and HCO_3^- of K^+, Na^+, Mg^{2+} and Ca^{2+} whereas for their chlorides and sulphates their correlation were weak. Similar results were reported by (Ghiglieri *et al.*, 2012) whereby Na^+ and HCO_3^- were found to be dominant in all water samples in the volcanic environment of north east of Mount Meru slope in their study on hydrochemistry of water surrounding those areas. A strong positive correlation observed in those ions indicates their originality from common source salts in the form of Na_2CO_3, $NaHCO_3$, K_2CO_3, $KHCO_3$, $MgCO_3$, $Mg(HCO_3)_2$, $CaCO_3$ and $Ca(HCO_3)_2$ (Table 13).

Fig. 20 describes the distribution of fecal coliforms with respect to other physicochemical parameters. The wet season recorded higher counts of fecal coliforms than the dry season. Higher counts were recorded in the flood plain than in the other parts of the river during wet season.

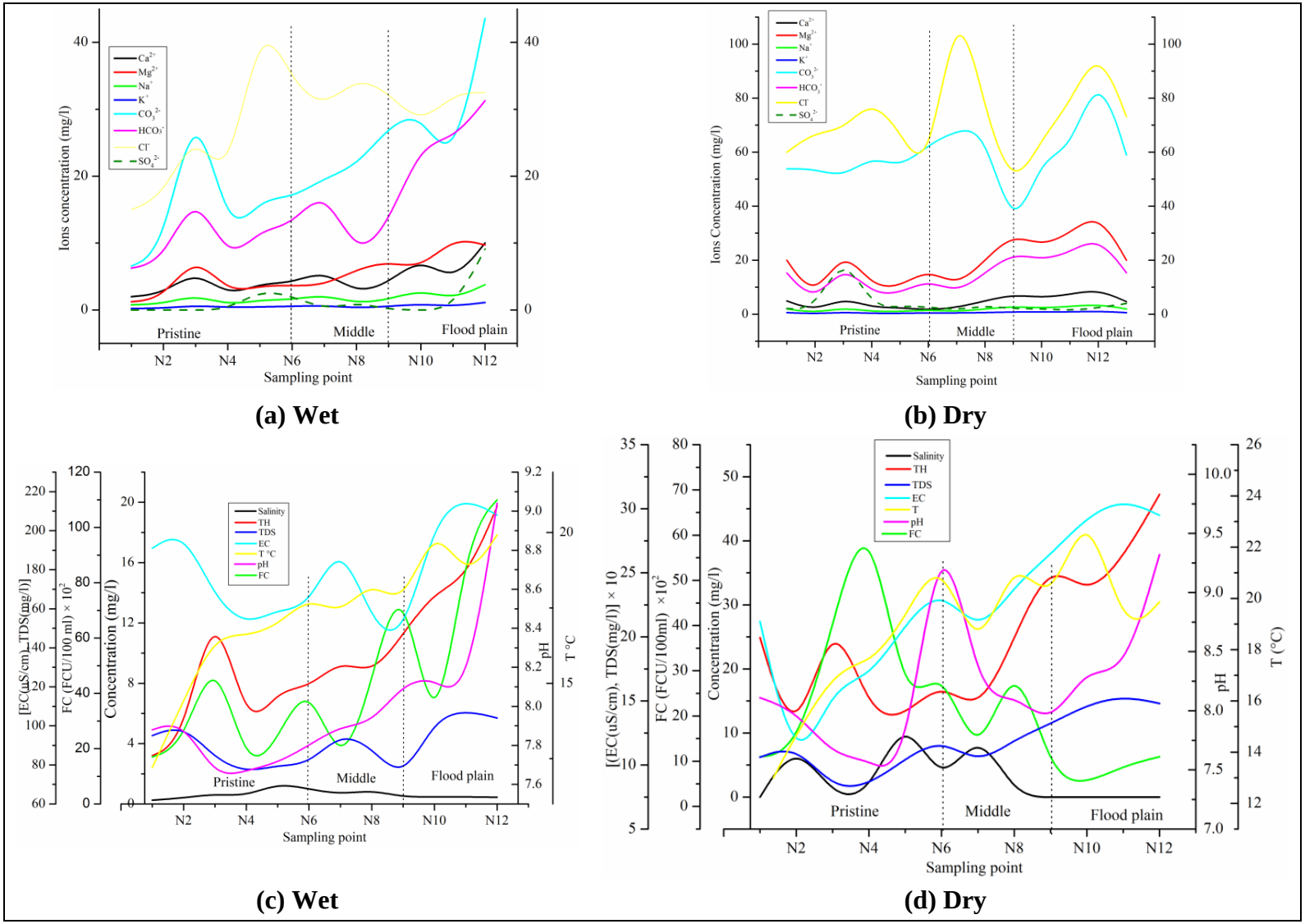


Figure 20: Variation of major ions and physicochemical parameters along Nduruma River in wet and dry seasons

Table 13: Correlation matrix data for major ions in Nduruma River

	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO_3^{2-}	HCO_3^{-}	Cl^{-}	SO_4^{2-}
Ca^{2+}	1.00							
Mg^{2+}	0.57	1.00						
Na^{+}	0.99955*	0.58629*	1.00					
K^{+}	0.98157*	0.61741*	0.98052*	1.00				
CO_3^{2-}	0.86843*	0.8032*	0.87433*	0.86769*	1.00			
HCO_3^{-}	0.89693*	0.77376*	0.90121*	0.91446*	0.79644*	1		
Cl^{-}	0.31593	0.45202	0.33004	0.32392	0.43423	0.3451	1	
SO_4^{2-}	0.59837*	0.3338	0.59486*	0.59609*	0.56263	0.48658	0.39343	1

*Correlation are significant at n = 12, p = 0.05

The middle part of the river experienced high amount of FC in the dry season whereas its floodplain the amount decreased significantly. Higher amounts of FC in the wet season may be caused by contaminated wastes which are carried to the river by runoff. The headwater of the river (N1 and N2) recorded low amounts of FC in both seasons. The highest amount of FC (11000 ± 630 FCU/100 mL) was recorded in the wet season at N12 where the highest amount of 4000 ± 150 FCU/100 mL was recorded at N3 in the dry season. Higher salinity content was recorded in the dry season than wet season probably the latter being affected by dilutions from runoff. The highest level in the dry season was 1.19 ± 0.37 mg/L while in the dry season they were elevated to 13.90 ± 1.71 mg/L both values being recorded at N5. The maximum recorded levels were lower than the maximum permissible levels of 100 mg/L (NHMRC & NRMMC, 2016). Acceptable pH range were recorded in most points of the river except at one point (N6) in the dry season which had pH 9.90 ± 0.01. This value is above the maximum WHO recommended level of 8.5 (WHO, 2011). Such elevated levels of pH may be attributed by runoff from flower farms which have constructed outlet furrows for emptying their excess water after irrigation. Water for irrigation in those farms is mixed with fertilizers and other pesticides before irrigation which the excess water may be associated with such agrochemicals. The levels of TH, EC and TDS were within the recommended limits as per WHO standards.

The status of oxygen demanding wastes were relatively higher in the wet season than dry season **(**Fig. 21). The maximum levels of COD and BOD in the wet season were 39 ± 3.82 mg/L and 23.00 ± 9.42 mg/L, respectively whereas in the dry season they were 6 ± 0.26 mg/L and 31 ± 2.49 mg/L, respectively. Low values for these pollutants in the dry season are a result of absence of runoff thus no inputs for oxygen demanding wastes from outside the river. Many BOD values in both seasons were higher than WHO prescribed values of 10

mg/L (Gorchev & Ozolins, 2011) in most sampling points these values being within the recommended limits in the dry season at N1, N11 and N12 in wet, N3 and N7 in dry season. The DO trends were inversely related to COD and BOD with the highest DO being 10.58 ± 0.19 mg/L and 8.22 ± 0.31 mg/L in wet and dry season, respectively. These values are indicators for presence of low oxygen demanding waste thus a healthy river. Similar trends of TSS were measured in respective sampling points. The CDOM were detected in sampling points with low COD and BOD an indication that at low oxygen, most organic carbons are converted into fulvic and humic acids. The highest level of 18.10 ± 1.02 RFU was registered at N12 in the dry season. Such low RFU levels in all sampling points indicate low levels of dissolved organic carbons in the river (Fig. 21)**.**

The NO_3^- and PO_4^{3-} nutrients were also detected in both seasons. High nitrates (NO_3^-) were recorded in the dry season than wet season. High levels of NO_3^- were recorded in samples with high levels of DO such as N5, N9 and N12 (Fig. 21). Denitrification was slightly favoured at N3 due to low pH (6.4 ± 0.48).In acidic condition, transformation of NO_3^- into reduced states is much favored (Murdoch *et al*.,1991) but in this study there is no elevated levels of NH_3 and NH_4^+ since the water pH in most sampling points could not favour such high transformation due to high pH (alkaline environment). The maximum levels of NO_3^- was 60 ± 0.72 mg/L in the wet season and in the dry season the levels were elevated to 73.8 ± 2.68 mg/L both being higher than the WHO maximum recommended levels of 50 mg/L (WHO, 2011). Transformations of NO_3^-, NH_3 and NH_4^+ showed a very strong positive correlation between them an indication of common source of originality of the nutrients with similar transformation patterns (Table 14). These results were similar to studies done on groundwater by (Elisante & Muzuka, 2016a) and showed NO_3^- transformations in ground water depended on amount of DO present. In similar study strong positive correlations between COD and BOD were noted which is an indication that the oxygen demanding wastes in both measurements are similar. However, very strong negative correlations were observed between COD and DO, BOD and DO meaning that the main components depleting the dissolved oxygen in water were the oxygen demanding wastes (Table 19).

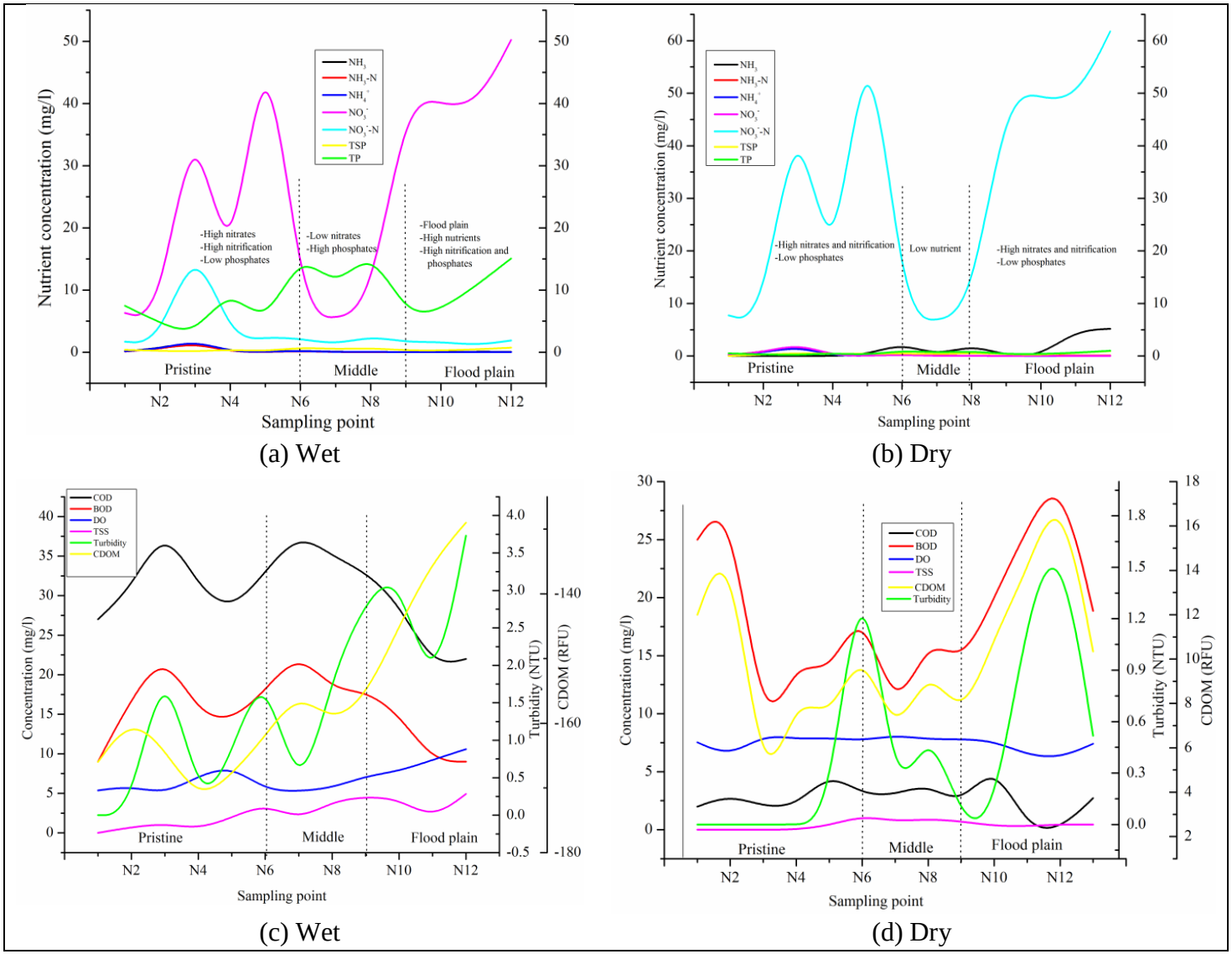


Figure 21: Variation of nutrients and physicochemical parameters along Nduruma River in wet and dry seasons

The levels of TP were significantly higher in wet season with the highest level (0.77 ± 0.39 mg/L) being detected at Songota stream (N6) while the dry season recorded very low levels. In wet the season the TSP were above the recommended levels for the river while most parts of the river recorded levels below the maximum recommended level of 0.1 mg/L. There was weak positive correlation between TP and TSP which is an indication that there are different input sources of PO_4^{3-} in water (Table 14). Figure 21 summarizes all nutrients trends in the river in both seasons.

Table 14: Correlation matrix data for nutrients in Nduruma River

	NH_3	NH_3-N	NH_4^+	NO_3^-	NO_3^-–N	TSP	TP
NH_3	1						
NH_3–N	0.99789*	1					
NH_4^+	0.99916*	0.99742*	1				
NO_3^-	0.11377	0.09547	0.12444	1			
NO_3^-–N	0.93963*	0.92299*	0.94702*	0.27267	1		
TSP	–0.4439	–0.45457	–0.45369	–0.33539	–0.39084	1	
TP	–0.45523	–0.46223	–0.4605	–0.38843	–0.38598	0.97429*	1

*Correlation are significant at n = 12, p = 0.05

5.3.2 Physicochemical and microbiological changes in Tengeru River

Figure 22 summarize the general trends of major ions in Tengeru River. The wet season was dominated by HCO_3^- and CO_3^{2-} while the other ions remained moderately low. The highest recorded values for HCO_3^- and CO_3^{2-} were 39.13 ± 2.17mg/L at T20 and 42.46 ± 1.84 mg/L at T16 both being in the floodplain. The dry season recorded higher levels of other ions in addition to SO_4^{2-}. The highest levels of HCO_3^-, CO_3^{2-} and SO_4^{2-} were 62.44 ± 3.71 mg/L at T10 and 73.22 ± 4.18 mg/L at T14 and 137.00 ± 31.95 mg/L at T8, respectively. The maximum Cl^- levels were within the maximum threshold levels for Australia of 250mg/L (NHMRC & NRMMC, 2016). A strong positive correlation for CO_3^{2-} of Ca^{2+} and Mg^{2+} is an indication of common originality of the two salts. Also, HCO_3^- of K^+ and Na^+ showed a strong positive correlation between them which indicates that most of them are found in water in common form of $NaHCO_3$ and $KHCO_3$. The Cl^- and SO_4^{2-} of all salts had weak correlation an indication of different source of origin in environment (Table 15).

Distribution of oxygen demanding wastes, carbon chromophores and other solids are presented in Fig. 23.

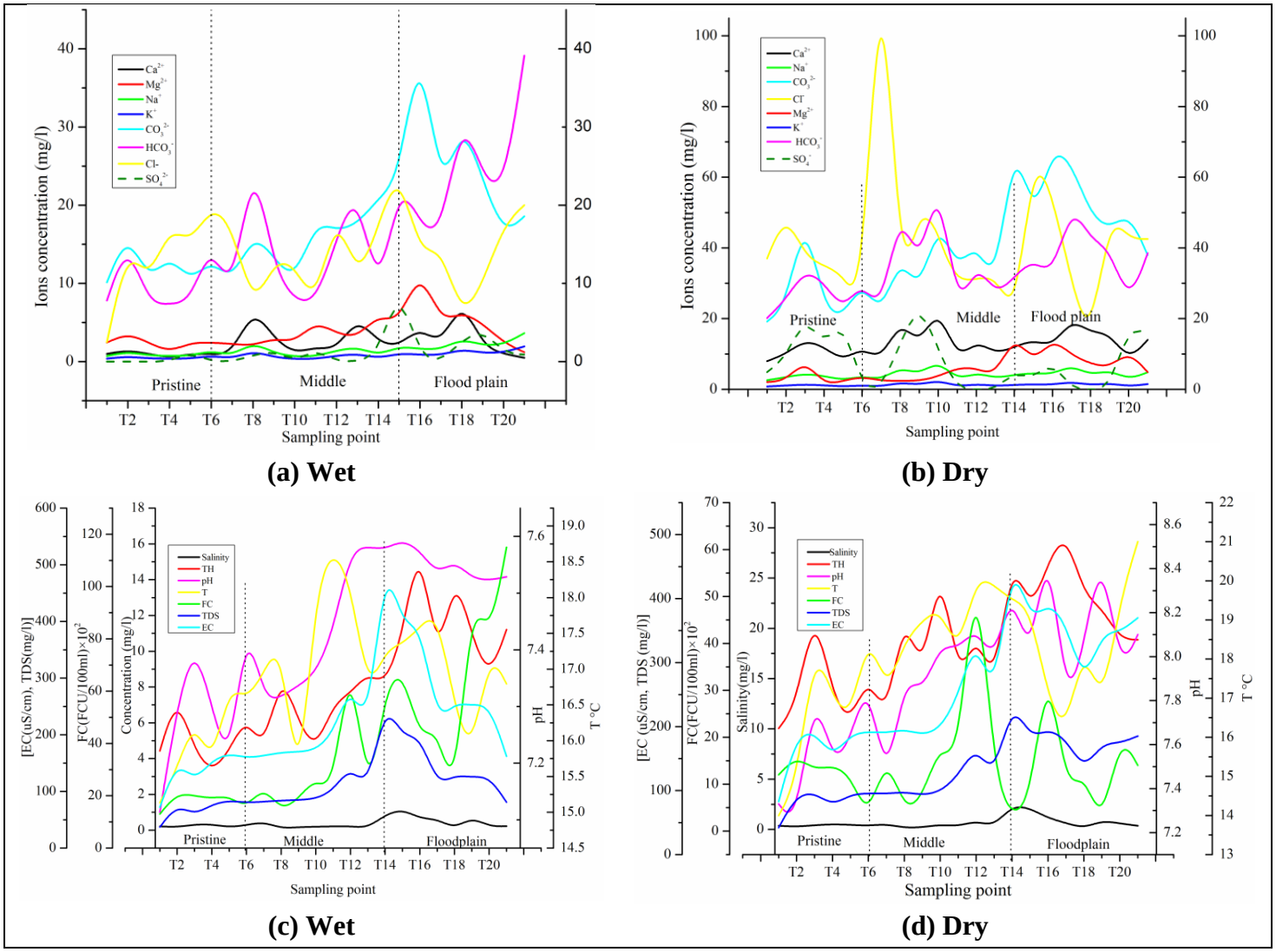


Figure 22: Variation of major ions and physicochemical parameters along Tengeru River in wet and dry seasons

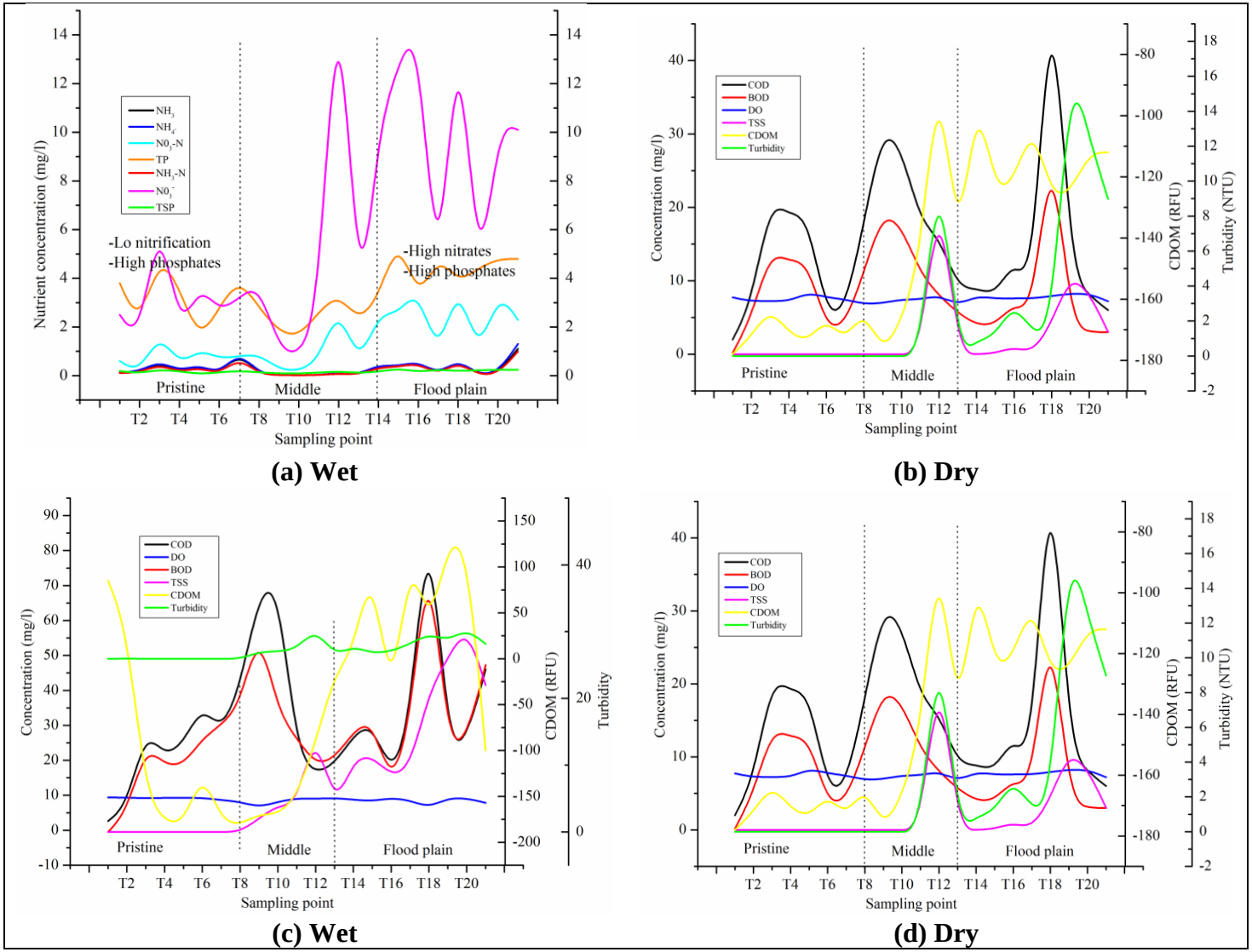


Figure 23: Variation of nutrients and physicochemical parameters along Tengeru River in wet and dry seasons

The highest levels of BOD (44.9 ± 9.52 mg/L and 31.0 ± 6.72 mg/L) were recorded at T18 in both wet and dry season, respectively. These levels increased proportionally with increase in COD where the highest levels (97.00 ± 2.91 mg/L and 56.00 ± 3.72 mg/L) were recorded in the same point. Most water from the middle and floodplain exceeded the maximum WHO recommended limits (World Health Organisation (WHO), 2011). The DO trends were inversely proportional to the COD and BOD levels which is an indication that similar oxygen demanding wastes are responsible for oxygen depletion. High levels of DO (9.19 ± 1.83 mg/L and 9.37 ± 1.29 mg/L) were recorded in the headwater whereas in the floodplain the highest level were 9.29 ± 1.32 mg/L all being in the wet season. A slight fall in the dry season were recorded at T5 (8.38 ± 1.33 mg/L), T19 (8.25 ± 1.42 mg/L) and T20 (8.24 ± 1.93 mg/L). The rest part of the river in the dry season had DO range between 6.45 ± 1.37 mg/L and 8.38 ± 1.33 mg/L. Usually streams with high dissolved oxygen concentrations > 8 mg/L are considered healthy streams thus in our study, most part of the river was healthy.

The chromophoric dissolved organic matters (CDOM) were higher in the floodplain during wet season an indication of high dissolved organic carbons in the floodplain. The negative values in the dry season are an indication of low dissolved organic matter, normally below the detection limit (BDL) of the level. The general trends for total suspended solids (TSS) increased with increase in COD and BOD an indication that TSS is part of oxygen demanding wastes. The TSS levels were up to 31.00 ± 2.31 mg/L and 24.17 ± 2.61 mg/L in the wet and dry season, respectively and most of them exceeded the recommended values of 5 mg/L in the floodplain (WHO, 2004; TBS, 2014). In addition, the study showed a very strong positive correlation between COD and BOD an indication that the oxygen demanding wastes in both measurements were similar. However, very strong negative correlations were observed between COD and DO, BOD and DO meaning that the main components depleting the dissolved oxygen in water were the BOD and COD wastes.

Turbid water exceeding the maximum permissible levels was noted at T12 (33.90 ± 2.18 NTU), T18 (27.39 ± 0.44 NTU) and T21 (32.80 ± 3.15 NTU) in wet the season whereas in dry season it decreased to 11.98 ± 11.98 NTU, 1.42 ± 0.18, and 8.98 ± 0.79, respectively. The dry season recorded a maximum of 16.92 ± 0.44 NTU with its pristine environment being BDL.

The fecal coliforms (FC) in Tengeru River were higher in the wet season than dry season with the headwater environment counting low numbers (Fig. 22). The minimum number of fecal coliforms in the wet season was 1300 ± 70 FCU/100 mL where as its highest was

11,500 ± 1600 FCU/100 mL in the wet season. These values dropped significantly in the dry season to a range between 9 ± 3 FCU/100 mL (being recorded in the floodplain) and 6200 ± 710 FCU/100 mL. Fecal coliforms in the human settlement parts of the river can be associated with poor hygienic practices of the surrounding environment which involve improper use of latrines and sewage waste disposal. The floodplain experienced higher amount of FC than other parts of the river in the wet season. Very low salinity levels in this river were recorded where the highest levels in the wet and dry seasons were 1.18 ± 0.41 mg/L and 2.41 ± 0.11 mg/L, respectively. The pH of water was within the WHO standards and ranged between 7.12 ± 0.11 and 8.59 ± 0.21 in both seasons.

Table 15: Correlation matrix data for major ions in Tengeru River

Ion	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO_3^{2-}	HCO_3^{-}	Cl^{-}	SO_4^{2-}
Ca^{2+}	1							
Mg^{2+}	0.41005	1						
Na^{+}	0.46495*	0.06595	1					
K^{+}	0.46495*	0.06595	1*	1				
CO_3^{2-}	0.54605*	0.89348*	0.4641*	0.4641*	1			
HCO_3^{-}	0.4779*	0.0726	0.99295*	0.99295*	0.47052*	1		
Cl^{-}	–0.48986*	–0.09578	0.05328	0.05328	–0.02608	0.05741	1	
SO_4^{2-}	0.10369	0.20799	0.29475	0.29475	0.31454	0.33468	0.26699	1

*Correlation are significant at n = 21, p = 0.05

The TDS were within the prescribed standards of 1200 mg/L (WHO, 2011) in both seasons where the highest level of 260 ± 57.29 mg/L was recorded at T14 in the wet season. Similar trends were demonstrated by EC where the maximum recorded level (518 ± 83.2 µS/cm) was within the permissible standards. Hardness is another issue of concern whereby its maximum levels of 16.68 ± 1.73 mg/L and 29.71 ± 1.50 mg/L were recorded in the wet and dry season, respectively (Fig. 22).

The NO_3^- levels were recorded in all sampling points in both seasons. Higher levels were recorded in dry than wet season. The NO_3^- levels in the wet season ranged between 0.8 ± 0.21 mg/L to 18.40 ± 0.53 mg/L where as in the dry season the values were 0.98 ± 0.18 mg/L to 22.63 ± 1.52 mg/L. Other NO_3^- intermediates (NH_4^+ NH_3 and NO_2^-) were very low. The highest levels of NO_3^- in the wet season and in the dry season were detected at T12 of the floodplain. In addition, the NO_3^- levels of this river were lower than those of Nduruma and Maji ya Chai Rivers due to less agricultural practices along the river which could be among

the main NO_3^- sources in the river. All NO_3^- levels in this river were within the maximum permissible levels of 50 mg/L as stipulated by WHO (Fig. 23).

However, phosphates nutrients (PO_4^{3-}) were lower than nitrates in most samples. The amount of readily available phosphates (TSP) ranged between 0.07 ± 0.02 mg/L to 0.29 ± 0.05 mg/L and 0.12 ± 0.09 mg/L to 0.48 ± 0.03 mg/L in wet and dry seasons, respectively. Higher levels of PO_4^{3-} were recorded in the dry than wet season and their low levels in the wet season may be associated with dilution and adsorption of phosphate molecules in organic matter due to its higher affinity in it. A strong positive correlation for transformation of NO_3^-, NH_3 and NH_4^+ into either one was observed which indicates a common origin of the nutrients. However, there was a weak correlation between TP and TSP an indication of different input sources of such nutrients accounts for their introduction in water (Table 16). Despite the overall low levels of readily available phosphates in water, most levels were above the maximum recommended limits of 0.1 mg/L for a river discharging into the lake or ocean (World Health Organisation (WHO), 2011). A strong positive correlation was observed between NH_3, NH_4^+ and NO_3^- an indication of common origin of the three components (Table 16). Nutrients variations in rivers showed to vary in different areas as a result of changes in land use and microbial activities as it was shown in Great Ruaha River (GRR) whereby the levels of NO_3^- ranged between 0.01 mg/L and 0.51 mg/L and that of PO_4^{3-} were up to 79.11 mg/L. Also a strong correlation were observed between the two nutrients (Mihale, 2015). In this study the levels of NO_3^- showed to be lower than the findings in most areas of Temi, Nduruma, Tengeru and Maji ya Chai Rivers but for PO_4^{3-} their levels are quite higher.

Table 16: Correlation matrix data for nutrients in Tengeru River

	NH_3	**NH_3–N**	**NH_4^+**	**NO_3^-**	**NO_3^-–N**	**TSP**	**TP**
NH_3	1						
NH_3–N	0.99768*	1					
NH_4^+	0.99988*	0.99766*	1				
NO_3^-	0.90876*	0.90492*	0.91315*	1			
NO_3^-–N	0.91813*	0.91642*	0.92236*	0.99899*	1		
TSP	–0.0503	–0.05383	–0.03534	0.2816	0.26794	1	
TP	–0.09464	–0.09429	–0.07992	0.20381	0.19588	0.9857*	1

*Correlation are significant at n=21, p=0.05

5.3.3 Major ions and microbiological changes in Maji ya Chai River

As it is displayed in Figure 24, SO_4^{2-}, Cl^-, CO_3^{2-} and HCO_3^- dominated in the wet season. Sulphates recorded the highest concentration (39.99 ± 4.72 mg/L) compared to other ions followed by CO_3^{2-} (32.86 ± 2.06 mg/L) both being recorded at the headwater of the river (M1 and M2). Other ions remained relatively low in most sampling points. However, the highest concentrations of ions were recorded in the dry season. In this season, higher concentrations for Cl^- and HCO_3^- were recorded at a level of up to 87.0 ± 9.27 mg/L and 43.59 ± 4.72 mg/L, respectively, whereas other ions were significantly low. In this season, the floodplain environment recorded the highest levels of ions than the headwater environment. Other ions ranged between 0.22 ± 0.02 mg/L and 1.53 ± 0.35 mg/L (K^+), 1.52 ± 0.17 mg/L to 5.28 ± 0.37 mg/L (Na^+), 1.21 ± 0.33 mg/L to 7.28 ± 0.99 mg/L (Mg^{2+}) and 0.49 ± 0.31 mg/L to 14.00 ± 1.77 mg/L (Ca^{2+}). Strong positive correlations were observed between carbonate of Mg^{2+} and Ca^{2+} whereas as for other ions their correlations were weak (Table 17). All ions concentrations levels were below the maximum recommended limits by WHO (2011).

Table 17: Correlation matrix data for major ions in Maji ya Chai River

Ion	Ca^{2+}	Mg^{2+}	Na^+	K^+	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}
Ca^{2+}	1							
Mg^{2+}	1	1						
Na^+	0.22518	0.22518	1					
K^+	0.22518	0.22518	1	1				
CO_3^{2-}	0.99886*	0.99886*	0.22791	0.22791	1			
HCO_3^-	0.22518	0.22518	1	1	0.22791	1		
Cl^-	0.05163	0.05163	0.1601	0.1601	0.0737	0.1601	1	
SO_4^{2-}	–0.3368	–0.3368	–0.2689	–0.2689	–0.3565	–0.2689	–0.8860*	1

*Correlation are significant at n = 7, p = 0.05

The oxygen demanding wastes was another important parameter studied in this river. The headwater and middle part of this river showed highest oxygen demanding wastes than other rivers specifically during dry season. Higher values of COD and BOD in the dry season were observed in this river. This is due to the fact that there is a major common source for the oxygen demanding wastes in which high amount of organic matters are released. This source resides on the foothills of Kirurumu, such that during wet season there is continuous dilutions lowering their concentration and in the dry season the levels are elevated. The COD and BOD varied proportionally to each other with higher amounts being recorded in pristine environment in both seasons. In the wet season, the highest COD level (74.00 ± 5.93 mg/L)

was recorded at the entry point source (M2) and its lowest (4.00 ± 0.81 mg/L) was recorded at M4. The highest level in the dry season was 149.00 ± 8.03 mg/L whereas the lowest was 3.35 ± 0.92 mg/L. Despite the high levels of COD in the dry season, most areas in the wet season also recorded values greater than the WHO maximum recommended values of 10 mg/L for fresh water (WHO), 2004).

Also, the river had high chromophoric dissolved organic matter (CDOM) especially in the dry season where values of up to 326.60 ± 18.39 RFU were recorded in wet and 180.7 ± 11.83 RFU in dry season. High values of CDOM indicate higher levels of dissolved organic matter in water. Such high amounts of chromophores have affected the aesthetic quality of water to its brownish colouration hence its name in Swahili "Maji ya Chai" In addition, high levels of CDOM reflect high levels of fulvic and humic acids in water since most CDOM's exist in the two mentioned forms. Generally, the CDOM increased with decrease in DO indicating that organic matters responsible for the colour transmissions are in high oxidation states.

The nutrient variation in Maji ya Chai River is illustrated in Fig. 25. Nitrates (NO_3^-) dominated the pristine environment of the river with low transformation into NH_3 and NH_4^+. High NO_3^- levels (15.9 ± 1.38 mg/L and 16.5 ± 1.71 mg/L, 22.26 ± 0.33 mg/L and 23.10 ± 0.41 mg/L) were recorded at M1 and M2 in the wet and dry seasons, respectively. These levels were lower than the WHO maximum recommended levels (50 mg/L) for drinking water (WHO, 2011). High nitrates values in the pristine environment are contributed by the high nitrogenous wastes produced by wild animals in the National Park which most animals spent most of their time along the river for drinking water. The levels of total phosphates (TP) ranged between 1.31 ± 0.94 mg/L and 1.60 ± 0.44 mg/L, 0.15 ± 0.03 mg/L and 1.60 ± 0.26 mg/L in wet and dry seasons, respectively. All values were higher than the WHO maximum recommended level of 0.01 mg/L for freshwater in rivers (Dodds *et al*., 1998). The levels of total soluble phosphate ranged between 0.05 ± 0.03 mg/L and 0.51 ± 0.26 mg/L in wet season whereas in the dry season they raised to 0.08 ± 0.02 mg/L and 0.81 ± 0.20 mg/L, respectively. Most of these levels were above the recommended values of 0.1 mg/L for the river draining its content to the sea/ocean (WHO, 2011). A weak correlation between TP and TSP indicates different input sources for the nutrient (Table 18).

Table 18: Correlation matrix data for nutrients in Maji ya Chai River

Ion	NH_3	NH_3–N	NH_4^+	NO_3^-	NO_3^-–N	TSP	TP
NH_3	1						
NH_3-N	0.99674*	1					
NH_4^+	0.99641*	0.99656*	1				
NO_3^-	0.4302	0.44852*	0.41374	1			
NO_3^-–N	0.46799*	0.4796*	0.44814*	0.95034*	1		
TSP	0.33753	0.35571	0.34715	0.3937	0.41168	1	
TP	0.33753	0.35571	0.34715	0.3937	0.41168	1	1

*Correlation are significant at n=7, p=0.05

The DO concentration at M2 was below the detection limit (BDL**)** with absence of aquatic life in water hence a dead river. The amount of DO increased downstream due to dilution of oxygen demanding wastes from different freshwater streams. The highest levels (8.87 ± 1.72 mg/L, 8.75 ± 0.92 mg/L and 8.85 ± 1.37 mg/L) were recorded in the downstream at M4, M5 and M6, respectively during the wet season with persistence of such levels in the dry season. These levels dropped down in the dry season to 6.00 ± 1.02 mg/L, 7.89 ± 0.85 mg/L and 7.97 ± 0.83 mg/L, respectively. The study showed a very strong positive correlation between COD and BOD an indication that the oxygen demanding wastes in both forms of measurements are from common source. However, very strong negative correlations were observed between COD and DO, BOD and DO indicating that the main components depleting the (DO) in water were the BOD and COD wastes (Table 19). Despite the high CDOM, the turbidity levels were low in the dry season indicating that most of the coloured substances in water are in its dissolved form of the two organic acids. The highest value of turbidity (361.60 ± 19.04 NTU) was recorded at M6 in the wet season whereas in the dry season the values decreased to 4.61 ± 0.91 NTU (at M2). Most parts of the pristine environment of the river recorded NTU levels BDL during wet season. The amount of TSS changed inversely to its DO and were direct proportional to the BOD and COD an indication that TSS is another major contributor to the oxygen demanding wastes in the river. Despite such variations of TSS its overall amount was quite lower than the maximum WHO recommended values of 5 mg/L for fresh water (WHO, 2004).

Table 19: Correlation matrix for oxygen demanding waste in river water

	Nduruma			Themi			Maji ya Chai		
	COD	**BOD**	**DO**	**COD**	**BOD**	**DO**	**COD**	**BOD**	**DO**
COD	1			1			1		
BOD	0.9718*	1		0.9577*	1		0.9971*	1	
DO	–0.8978*	–0.9179*	1	–0.8191*	–0.6866*	1	–0.9314*	–0.9114*	1

*Correlation are significant at n =12, for Temi and Nduruma, 21 and 7 for Tengeru and Maji ya Chai, respectively at p=0.05

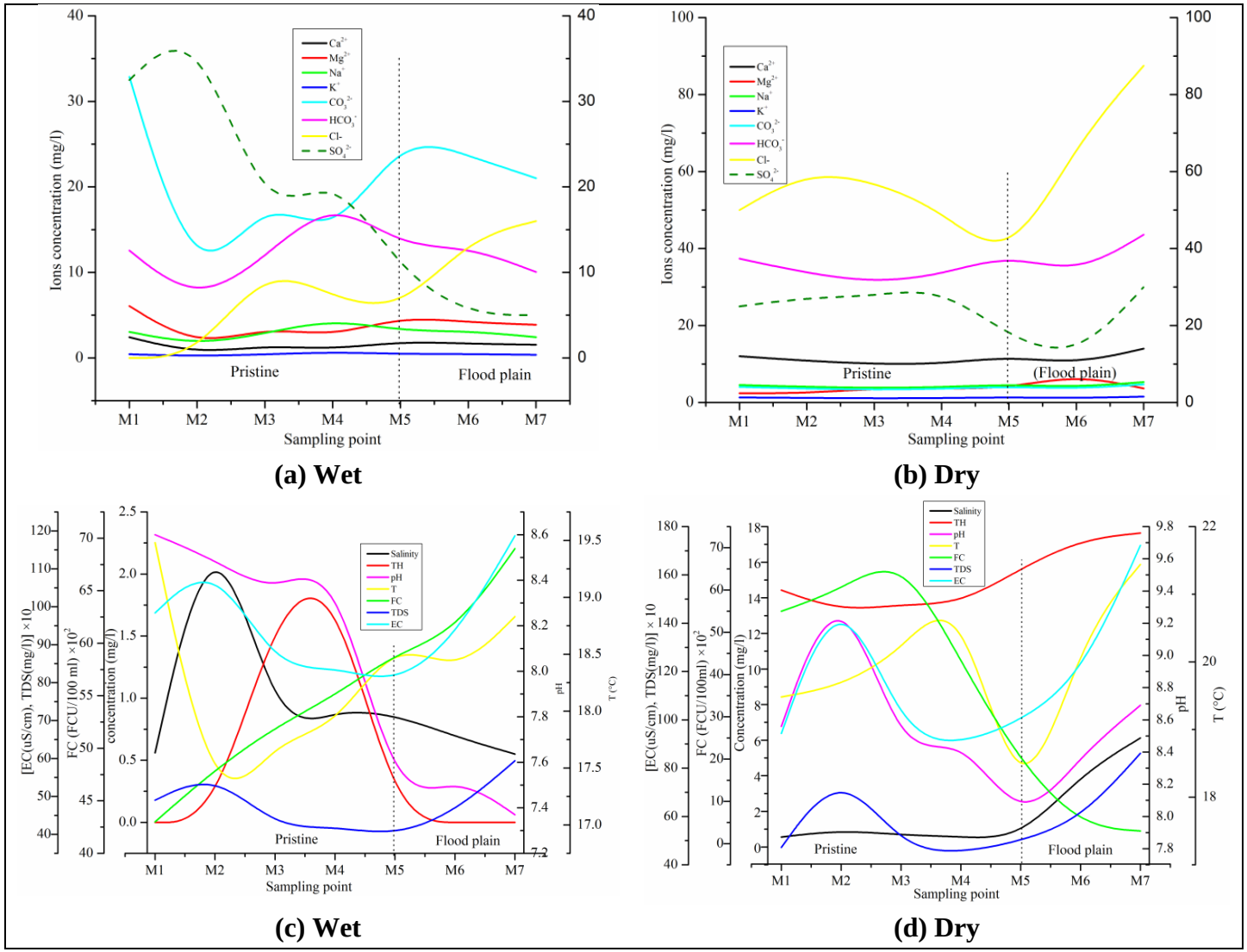


Figure 24: Variation of major ions and physicochemical parameters along Maji ya Chai River in wet and dry seasons

Higher levels of FC were noted in the floodplain during wet season while in the dry season such levels were noted in the pristine environment. This trend is explained by the fact that in wet season there are many water sources in the river thus animals are evenly distributed for water sources therefore the catchment area is likely to be little affected by wild animals. But in the dry season the river remains the major water source for drinking; therefore, animals congregate along the river for water. The pristine environment in this river is entirely in the park while the rest part is in human settlement area (urban). When animals drink water in the rivers they tend to excrete in water thus elevating the FC counts in the dry season. Salinity and total hardness remained to be minor problems in the river in both seasons since very low levels (< 6.0 mg/L) were recorded.

Maji ya Chai River had the highest levels of EC and TDS among the three rivers. High levels of EC can be caused by high pH as a result of increased level of OH^- ions and presence of high amount of dissolved fulvic and humic acids which are weak electrolytes. Also, the high levels of Cl^- and SO_3^{2-} ions as discussed earlier can further account for elevated conductivity of water. During the wet season the conductivity was up to 1187 ± 0.3 µS/cm (recorded at M7) and this amount was elevated to 1722 ± 29.71 µS/cm in the dry season.

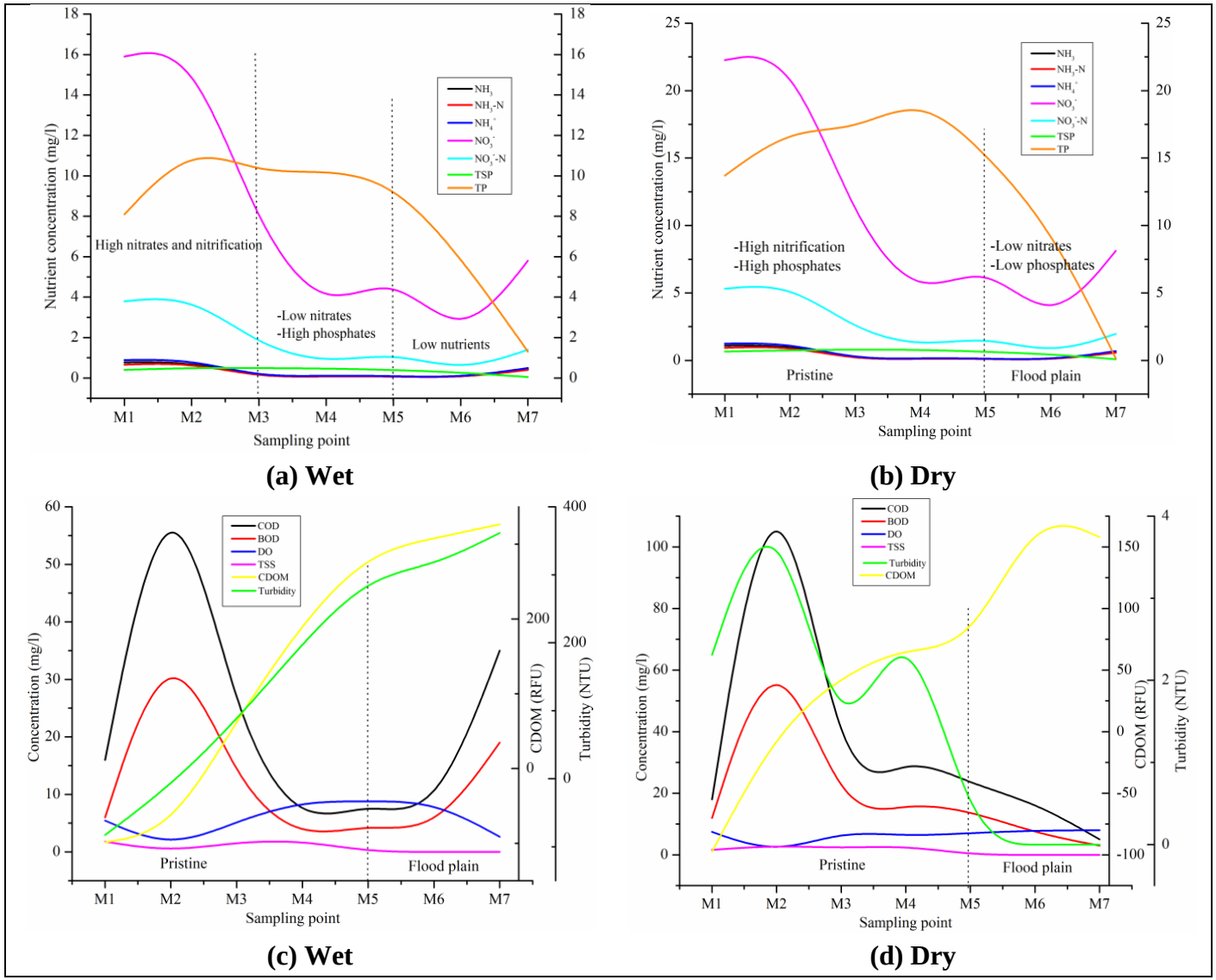


Figure 25: Variation of nutrients and physicochemical parameters along Maji ya Chai River in wet and dry seasons

This value was above the maximum WHO recommended level of 1500 µS/cm (WHO, 2011). Accordingly, the total dissolved solids (TDS) followed similar trends such that the maximum levels during wet and dry season were 594 ± 36.82 mg/L and 861 94.52 mg/L, respectively. These values were within the maximum permissible levels as stipulated by WHO and Australian standards of 600-1200 mg/L (NHMRC, 2011; WHO, 2011).

5.3.4 Dissolved carbons and nitrate sources in rivers

The stable isotopes of ^{13}C, ^{18}O and ^{16}N for wastewater, ground water, manure, soil composite and plant material in relation to the water sample composition in rivers were studied to assess their relationship with surrounding environment. Since 60−70% of water enters large rivers from first to third order streams, it was necessary to take samples from headwater, middle and a fully developed river (floodplain) of which their differences could also reflect different dissolved organic carbons and nitrates sources (Billy *et al.*, 2011).

5.3.5 Sources of dissolved organic carbon in rivers

Traces of dissolved organic carbon in water can be detected through their colours if they are chromophoric. Oxidized state of organic carbons can exist as humic and fulvic acids which are chromophoric. Large amounts of these compounds can even change the water color to a brownish yellow the characteristic experienced by “Maji ya Chai” River which is a translated Swahili language to mean “tea water.” Low concentrations of these may not change the aesthetic quality of water.

Water samples from the three rivers were screened for dissolved organic carbons. Maji ya Chai River contained the highest levels (2.31 ± 0.20 mg/L) of dissolved organic carbon of up to 2.31 ± 0.20 mg/L in the head water (M1). This was expected due to the closeness of the sampling area to the point source of the pollutant, the foothills of Kirurumu. Tengeru River showed the concentration range between 0.74 ± 0.2 mg/L and 1.3 ± 0.20 mg/L whereas for Nduruma River the levels were up 0.21 ± 0.20 mg/L (Table 20).

The stable isotopic signatures of Carbon were measured from water samples and then compared with the stable isotopic signatures of carbon for nearby soil composite, manure, groundwater, plant materials and common fertilizers used by farmers. The stable isotope studies showed different origins of dissolved organic carbons (DOC).

Table 20: Stable isotope signatures and dissolved organic carbon levels for Nduruma, Tengeru and Maji ya Chai Rivers

River/Material	Nduruma			Tengeru			Maji ya Chai			Manure		
Sampling Point	**N1**	**N6**	**N12**	**T3**	**T9**	**T19**	**M1**	**M5**	**M7**	**N**	**T**	**M**
DOC (mg/L)	Bdl	0.21	0.23	0.74	0.99	1.3	2.31	2.26	1.96	–	–	–
$\delta^{13}C \pm 0.20$ ‰	–	–20.36	–22.42	–15.30	–15.47	–13.39	–22.81	–22.23	–22.08	–20.11	–17.11	–22.1
$\delta^{15}N–NO_3^- \pm 0.30$ ‰	+3.72	+7.91	+8.07	+8.16	+9.33	+9.84	+10.46	+10.04	+10.37	+8.29	+8.06	+10.12
$\delta^{18}O–NO_3^- \pm 0.80$ ‰	+0.94	+1.70	+1.92	+1.97	+7.73	+7.91	+8.64	+8.01	+8.02	+1.94	+1.90	+8.11
Sample Material	**Soil Composite**			**GW**			**Plant Materials**			**Fertilizers**		
Sampling Point	**N**	**T**	**M**	**N**	**T**	**M**	**N**	**T**	**M**	**UREA**	**DAP**	
DOC (mg/L)	–	–	–	–	–	–	–	–	–	–	–	
$\delta^{13}C \pm 0.20$ ‰	–20.87	–17.94	–19.47	–17.91	–15.13	–15.33	–21.07	–21.31	–22.1	–	–	
$\delta^{15}N–NO_3^- \pm 0.30$ ‰	+10.61	+9.02	+10.16	+13.06	+3.11	+12.96	+10.46	+10.13	+9.79	+7.95	+6.64	
$\delta^{18}O–NO_3^- \pm 0.80$ ‰	+8.50	+7.69	+8.12	+9.02	+0.93	+8.99	+8.12	+8.12	+7.87	+1.72	+1.57	

Note: **N**-Nduruma, **T**-Temi, **M**-Maji ya Chai. **DAP**-Double Ammonium Phosphate, **GW**- Ground Water

Nduruma River showed δ^{13}Cisotopic signatures of −20.56 ± 0.20 ‰ (N6, middle) and −22.4 ± 0.20 ‰ (N12, floodplain) whereas the nearby materials had δ^{13}C values of −20.87 ± 0.20 ‰ (soil composite) and −22.10 ± 0.20 ‰ (plant materials) whereas the headwater had dissolved carbon levels below the detection limit (BDL). From these data, the middle part of the river confirmed dissolved carbon to originate mainly from soil composite meaning that the organic carbon incorporated in soil undergoes dissolution in water. The study by Quails and Raines (1992) showed the occurrence of dissolved organic carbon in the soil composite can happen from leaching of dissolved organic matter from different sources into the rain water which pass through the canopy and forest flow and eventually percolate into the soil. A similar pattern occurred for NO_3^- composition in the soil. Dissolved carbons in the floodplain showed mainly to originate from dead plant materials which are swept with water from different points due to runoff.

Tengeru River had δ^{13}C of −15.30 ± 0.20 ‰ (T3, headwater); −15.47 ± 0.20 ‰ (T9, middle/human settlement area), −13.39 ± 0.20 ‰ (T19, floodplain) and other results are as shown in Table 20. These results were also compared with different nearby common materials and showed δ^{13}C of −15.13 ± 0.20 ‰ (groundwater); −15.11 ± 0.20 ‰ (manure) indicating the origin of dissolved organic carbons is from ground water mixing with surface water.

In addition, Maji ya Chai had δ^{13}C fractionation of −22.81 ± 0.20 ‰ (M1, headwater), −22.23 ± 0.20 ‰ (M5, human settlement/middle) and −22.08 ± 0.20 ‰ (M7, floodplain). All other associated materials showed different fractionation except for plant materials which had δ^{13}C fractionation of −22.10 ± 0.20 ‰ an indication that the brownish yellow colour of water originates from rotten plant material from the point source of the foots of Kirurumu hill as discussed earlier. The basin of Kirurumu hill is an accumulation centre for most plant material swept from the east south of Mount Meru and various uphill points down the mountain which its dead plants stockpiles rot and dissolve with the brownish characteristic colour in form of fulvic and humic acids.

5.3.6 Sources of nitrates in rivers

Nduruma river had $\delta^{15}N-NO_3^-$ fractionation of +3.72 ± 0.30 ‰ (N1, headwater) corresponding to +3.11 ± 0.30 ‰ for groundwater meaning that the nitrogen sources were from the ground water containing nitrogen mixing with surface water. The fractionation of +7.91 ± 0.30 ‰ and 8.07 ± 0.30 ‰ (N6, middle/human settlement and N12, floodplain, respectively) indicated nitrogen sources from Urea fertilizers applied in farms which showed similar fractionation of +7.95 ± 0.30 ‰. In such area the farming activities in the steep slopes experienced transportation of soil and dissolved Urea fertilizer to the river. Similar fractionations were depicted by $\delta^{18}O\text{-}NO_3^-$ indicating similar sources of nitrogen as shown in Table 20. A similar comparison technique was used by Aravena *et al*. (1993) in their study on identification of nitrate from the septic system by comparing the stable isotopes of oxygen and nitrogen from the septic system and the surrounding materials in the environment.

Tengeru River showed fractionation of +8.16 ± 0.30 ‰ (T3, headwater) which corresponded with +8.06 ± 0.30 ‰ for manure meaning that the main source of nitrate in headwater is from animal manure. The results obtained correlate with farming activities around the steep slopes on headwater banks which involve heavy application of cattle manure which are eventually driven to the river in the wet season. The middle (human settlement) and floodplain areas of the river had $\delta^{15}N-NO_3^-$ fractionation value of +9.33 ± 0.30 ‰ (T9) and +9.84 ± 0.30 ‰ (T19), respectively, which corresponded to the fractionation values of soil composite of + 9.02 ± 0.30 ‰ meaning that the origin of nitrates from those areas are mainly dominated by soil incorporated with nitrogen/nitrate which can originate from different nitrogen containing matters including living and non-living materials.

The headwater of Maji ya Chai River had fractionation of +10.46 ± 0.30 ‰ and the human settlement/middle area of the river showed fractionation of +10.04 ± 0.30 ‰ whereas the floodplain area had a fractionation of +10.37 ± 0.30 ‰. All areas correspond to nitrate contamination as a result of manure inputs with the fractionation of +10.12 ± 0.30 ‰. The source of manure from this river is mainly from wild animals in the Arusha National Park since this river is the main source for drinking water in the park thus animals spent most of their time to drink and feed along the river. Meanwhile as the animals feed along the river they excrete within the same area thus their dung and urine are carried along with rainwater

in the river. NO_3^- sources in ground water in this study area has shown to be derived from manure and sewage waters (Elisante & Muzuka, 2016a).

5.4 Conclusions

Monitoring the physicochemical and biological changes of rivers is of profound importance since it informs the river status on regular basis along the time line and assist in designing immediate measures/remediation which should be taken to overcome the potential negative impacts before they appear. However, due to limited resources, assessment on such changes is done in sporadic unplanned manner thus missing the intended purpose. In this study, the physicochemical, biological changes and sources of DOC and NO_3^- in each river due to different environmental changes were evaluated. Most parameters showed to be within the WHO maximum permissible levels whereas FC, COD, BOD, EC and NO_3^- were above the limits. The headwater of all rivers had low counts compared with the middle /human settlement and floodplain areas. Increase in FC in the two parts of all rivers was accelerated by different human activities such as poor management of domestic wastes and discharging of inadequately treated domestic wastewater into the rivers. Farming activities along the river with steep slopes was another cause for increase in turbidity and nutrients loading due to runoff from rain water into rivers. Farming activities in such areas should be controlled to preserve the riparian environment of rivers as per the Tanzania environmental conservation law which requires 60 meters from each side of the river bank to be conserved as a buffer zone for catchment and runoff protection (United Republic of Tanzania (URT), 2014).

CHAPTER SIX

Fluoride Temporal Variations in Rivers on the Slopes of Mount Meru in Tanzania[4]

Abstract

This chapter reports on the variations of fluoride ions in rivers on the slopes of Mount Meru in the northern part of Tanzania. Four hundred and nineteen (419) water samples were collected from Temi, Nduruma, Tengeru, and Maji ya Chai Rivers in both wet (mid-March and April) and dry (August) seasons. The samples were analyzed for fluoride levels using Ion Selective Electrode (ISE). The minimum and maximum average fluoride levels in the wet season were 0.24 ± 0.03 mg/L and 65.20 ± 0.03 mg/L, respectively whereas the average lowest and highest levels in the dry season were 1.02 ± 0.02 mg/L and 69.01 ± 0.03 mg/L, respectively. Tengeru River had the lowest fluoride levels in both seasons, whereas Maji ya Chai recorded the highest fluoride levels in both seasons. The headwater of all rivers, with the exception of Maji ya Chai, met the WHO maximum acceptable fluoride levels of 1.50 mg/L and the downstream environment qualified for Tanzania Bureau of Standards (TBS) maximum permissible fluoride concentration in drinking water of 4.00 mg/L. Also, the laboratory experiments showed that fluoride containing rocks which were collected in the study area when exposed to pH above 7.6 display high leaching of F^- in solution which gradually increased with the increase in pH, indicating that dissolution of fluoride from rocks is a function of pH.

Key words: Fluoride level, alkaline environment, Mount Meru, Temperature, Electrolytic Conductivity, t–test, Pearson correlation (r).

[4]**This chapter is based on the published paper:**

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6.1 Introduction

The understanding of fluoride distribution in Tanzanian rivers is of great importance since majority of the Tanzanian population obtain their domestic fresh water from rivers, springs, and lakes. It is reported that 30% of these are water sources with fluoride concentration exceeding 1.5 mg/L (Latham & Gretch, 1967). Despite the fact that fluoride has health benefits, consumption above the optimal level is unhealthy. The WHO and TBS recommend the healthy intake of fluoride in water should not exceed 1.5 mg/L and 4.0 mg/L, respectively (WHO, 2004; 2011; WHO, 2004). Excessive consumption of fluoride has shown to cause crippling skeletal fluorosis due to the reaction of F and Ca in the bones thus it is extremely reactive in biological systems thus affecting the enzymes and the whole organism as well (Edmunds & Smedley, 2013; Johansen, 2013; WHO, 2004). In Tanzania, fluorides are distributed in the most areas of Arusha, Moshi, Singida and Shinyanga Regions with severely affected area being on the foot hills of Mount Meru and Kilimanjaro (Davies, 1996; Deocampo, 2003). Fluoride rich waters are associated with sediments of marine origin in Mountainous areas, volcanic, granitic and gneissic rocks (Nair *et al*., 1984). Being the case in Tanzania, the problem occurs in both the rift valley zones in northern and south-western part of the country associated with volcanic activity and in the crystalline basement complex of the central plateau (Nanyaro *et al.,* 1984). Enrichment of fluoride minerals in water occurs through evaporation, weathering of volcanic rocks and geothermal solutions in the rift valley system and from dissolution of saline rocks associated with fluoride (Kilham & Hecky, 1973; Nanyaro *et al*., 1984).

Fluorine is the most electronegative element with the electronegativity value of 3.98 on the Pauling Scale thus it is very reactive (Pauling, 1960). Therefore, this property makes the element exists in different forms of mineral salts in the environment rather than its pure form (Hem, 1989). The fluoride containing minerals are grouped into fluorides, phosphates, silicates and mica (Teotia *et al*., 1981). In Tanzania fluorapatite, fluorite, topaz, phlogopite and lepidolite predominate. All these minerals are water insoluble hence their ability to release fluoride ions in surface and ground water depends on the conditions which favor their solubility such as high temperature and pH. Consequently, fluorides enter surface water by leaching (being the main cause), surface runoff from fertilizers containing phosphates which are complexed with fluoride ions, industrial emissions and effluents (Aswathanarayana *et al*., 1986). The average dissolved fluoride content in major rivers of the world is between 0.01 mg/L and 0.02 mg/L whereas in lakes it is below 0.5 mg/L (WHO, 2004), but in Tanzania the

concentrations are above the mentioned values in the vulnerable regions (Aswathanarayana *et al*., 1986).

Previous studies carried out to establish sources of high fluoride concentrations and distribution in the environment on the slopes of Mount Meru have mostly put emphasis on ground water. In surface water, studies reported the fluoride levels of 12–13 mg/L, 21–26 mg/L, 61–65 mg/L and 690 mg/L for Maji ya Chai and Engare Nanyuki Rivers, pond water, and Lake Momela, respectively (Aswathanarayana *et al*., 1986; Mcharo 1986; Mjengera 1988; Mungure 1984; Nanyaro *et al*., 1984; WHO, 1966). The contaminated areas have shown health implications to some children and adults living around the foot of Mount Meru (Johansen, 2013; WHO, 2004). Further studies on fluoride levels were carried out in ground waters within the same area and found a concentration of up to 68 mg/L which was highly associated with the alkaline volcanism and high pH (Ghiglieri *et al*., 2010; 2012). The vulnerability of alkaline soil for fluoride dissolution in soil has recently been associated with presence of bicarbonate ions (HCO_3^-) which accelerates the alkalinity and fluoride availability (Mkungu *et al.*, 2014). Since surface/river water is a contribution of ground water discharge and precipitation, fluorides in water are mainly from leaching of rocks from ground water and fluoride containing substances.

Despite the above facts, the general trends of fluorides in rivers after interaction with different environment of this study area have been scantily studied and, thus raising its importance of this study. Therefore, this work was conducted to investigate the spatial distribution of fluorides in rivers after such interactions have occurred. Equally important, the study aimed at tracing point source of contamination if existent. Studies in these rivers are of profound importance since water from these rivers is used for various domestic activities including cooking and drinking in Arusha City.

6.2 Materials and methods

6.2.1 Description of study area

The study area involved four rivers namely Themi and Nduruma which lie within the Arusha City and Tengeru and Maji ya Chai which lie within the Meru District. The four rivers originate from a common sub catchment of foot hills of Mount Meru lying from the eastern part to the south west of the mountain (Fig. 1). The rivers run downstream from the Mountain to the south east. The natural vegetation is typically tropical forest to savannah. The

topography and climate of this study area are as described by Hijmans *et al.* (2005) in the second chapter of this dissertation.

6.2.2 Sampling

The GPS predetermined sampling points were identified basing on confluence, accessibility and pre-established monitoring stations. Two liters (2 L) of water samples were collected at each point using a 1 liter Teflon capped glass bottle and another 1 liter Teflon capped plastic bottle downstream from the source of each river as shown in Fig. 1. Samples from plastic bottles were used for metal analysis and other parameters whereas samples in glass bottles were used for nutrients and other organic components analysis. Samples for $\delta^{2}H$ and $\delta^{18}O$ stable isotope analysis were collected using 100 mL PTFE bottles and kept cold at 4 °C and thereafter frozen at 0 °C before and after transport to the laboratory for analysis. Sampling was done thrice in one week interval during the wet season (Mid–March to early April) and dry season (August) in 2015. All samples were kept in cold boxes ready for transport to the laboratories. In each season 159 representative samples were collected for analysis.

6.2.3 Chemicals

Analytical, grade reagents from Sigma Aldrich (Merk) reagents for preparation of Total Ionic Strength Adjustment Buffer (TISAB) II and TISAB IV were prepared from glacial acetic acid, NaCl, NaOH and HCl, Tris (hydroxymethyl) amino methane and Sodium tartarate dihydrate, respectively. Also, the analytical grade of Ion Electrolyte Reference Filling Solution (P/N 51344750) was obtained from the same company.

6.2.4 Extraction, Pretreatment and Cleanup of Water Samples

Samples for major ions measurements were not pretreated with any chemical except the samples with solids and other organic debris were filtered using a 0.45 µm filter before measurement. Samples for $\delta^{18}O$ and $\delta^{2}H$ analysis were kept cooled at 4 °C before and on transport to the Stable Isotope laboratory at Waterloo University in Canada.

6.2.5 Detection limit of the instrument and calibration

The calibrated detection limit of the instrument was reconfirmed by measuring in triplicate the serial diluted primary standard solution with lowest concentration of 0.02 mg/L, which was the calibrated Minimum Detection Limit (MDL) and the maximum instrument detection

limit was calibrated at 100 mg/L. Therefore, any undetected concentration measurement of a highly diluted sample was regarded to be below 0.02 mg/L and thus it was Below the Detection Limit (BDL) of the instrument and for the same purpose similar measurement in double distilled water used for rinsing apparatus its cleaners and TISAB were all considered as fluoride free matrices.

6.2.6 Analysis and confirmation

The sample's physic−chemical parameters (temperature, pH, conductivity, velocity and TDS) were measured in situ from the sampling points. Quantification of free fluoride ions was done by mixing equal volumes of TISAB to provide a constant background ionic strength, decomplex fluoride ions and adjust the solution pH. Thorough mixing was done using a magnetic stirrer. Measurement was done by using the Ion Selective Electrode (ISE) from Mettler Toledo, perfectION™, with a Bayonet Neill-Concelman (BNC) connector, P/N 51344775. The electrode was immersed in serial diluted fluoride primary standard solution of 0.1 mg/L and 10 mg/L from Sigma-Aldrich (Merk) for calibration followed by measurement of the mixture and the steady readout was recorded. The electrode was filled with Ion Electrolyte Reference Filling Solution (P/N 51344750) to maintain its maximum sensitivity. Analysis for $\delta^{18}O$ and $\delta^{2}H$ stable isotopes was done using a modern technology of Los Gatos Research Laser processes analyzer with Integrated Cavity Output Spectroscopy (LGR-ICOS™) machine using the Vienna standard Mean Ocean Water (VSMOW) with a standard error of ± 0.8 ‰. The experimental rock identification was done in the Geology Department of the University of Dar es Salaam (UDSM) using the X-Ray Diffraction (XRD) machine. The Geostatistic Analyses for the spatial distribution of Fluoride and other related parameters were done using ArcGIS Software, Version 10.1 in the GIS Laboratory of the Nelson Mandela African Institution of Science and Technology-Arusha, Tanzania.

6.2.7 Analytical quality assurance

The double distilled water that was used for rinsing all the instruments and apparatus was tested to check whether it is fluoride free before use. Instruments were rinsed thrice with double distilled water to ensure no traces of fluoride outside the sample before another consecutive measurement was done. Thereafter, the glass electrode cleanliness was reconfirmed by immersing in a beaker containing distilled water and its cleaners were measured for fluoride free ions and thereafter TISAB solution was also monitored for any

traces of fluoride to assess its purity before measurement of the analyte was made. Also, the linearity of the electrode was monitored in every two samples measurements by measuring a known concentration (0.1 mg/L and 10 mg/L in serial dilutions) primary standard fluoride solution.

6.2.8 Statistical tests

The strength of linear relationships between fluorides levels with other physico–chemical parameters was assessed by calculating the Pearson's correlation coefficient (*r*) using Sigma Plot Software, Version 11. Also, the student-*t* test at the stated *p* value was carried out to assess whether the fluoride levels between seasons are significantly different. Significant difference was considered when the *p* values were < 0.05.

6.2.9 Geostatistical mapping

Fluoride concentration mapping was done by graduated symbols proportional to values using Arc Map Version 10.1. The Fluoride concentration ranges in water were grouped based on WHO (0.0 – 1.5 mg/L) and TBS (0.0 – 4.0 mg/L) standards simply for the purpose of assessing the status of the rivers according to the mentioned standards (WHO, 2004).

6.2.10 Identification and laboratory experiments of fluoride leaching rocks

A laboratory experiment was setup to assess the effect of pH in dissolution of fluoride containing rocks at 25 °C. Two rocks were collected in the catchment river banks of Nduruma and Tengeru rivers and two more rocks were collected in Maji ya Chai River whereby the first rock was collected from Maksoro (M1, area with low fluoride levels) and the second rock was collected from Jamera (M2, with high fluorides in water). The rock types were initially identified by X–Ray Diffraction (XRD) and confirmed to be feldspar-quartz extrusive volcanic igneous rocks. All rocks were separately grounded at variable grain size (Table 25). A 2.00 g sample of each ground rock was mixed with 200 ml of de ionized water and the mixture was constantly stirred with magnetic stirrer on hot plate at 150 rpm and 25 °C for three consecutive days. Monitoring of fluoride concentration was done in every twelve hours in all days and the results were recorded.

6.3 Results and discussion

The isotopic signatures of $\delta^{18}O$ and $\delta^{2}H$ from LGR–ICOS laser process analyzer of water in the four rivers in different points is shown in Table 21. The average physicochemical trends for the four rivers are shown in Table 22 and 23. The fluoride levels at various points of the rivers are shown in Table 23. The particle size distribution of the grounded rock and its pH dependence for fluoride leaching results are shown in Table 25 and 26, respectively.

6.3.1 Isotopic characteristics of water

Table 21 shows the different stable isotopic composition of water on the slopes of Mount Meru. The Oxygen and Deuterium isotopic composition from each river on these slopes show its water balance to be controlled by meteoric precipitation, evaporation and ground water. The results indicated enrichment in $\delta^{18}O$ and $\delta^{2}H$ in springs downstream due to evaporation effects. There is a large difference between water from precipitation and running water with progressive variation from the catchment downstream. The isotopic data show enrichment downstream with an increase in water temperature (Fig. 26). Such trend shows a sign of evaporation which can be an important factor contributing to the slight increase of some dissolved salts in water. Despite such isotopic variations, the data differ slightly from the Global Meteoric Water Line (GMWL) as explained by (Chacha *et al.*, 2018) (Fig. 26). Also, variations are noted within the river from the catchment area to the downstream. Such isotopic variations are further experienced in each river from the catchment to the downstream which can be caused by the different environment the rivers they pass and ground water recharged mixing with surface water.

Also, more observations showed $\delta^{2}H$ and $\delta^{18}O$ enrichment was relatively higher in Maji ya Chai and Temi Rivers with expectation that the evaporation effect would be much pronounced in the two rivers compared to Nduruma and Tengeru Rivers.

Table 21: Isotopic signatures of $\delta^{18}O$ and $\delta^{2}H$ from LGR-ICOS laser process analyzer of water

Temi River			Nduruma River			Tengeru River			Maji ya Chai River		
Point Name	**$\delta^{2}H$ ‰**	**$\delta^{18}O$ ‰**	**Point Name**	**$\delta^{2}H$ ‰**	**$\delta^{18}O$ ‰**	**Point Name**	**$\delta^{2}H$ ‰**	**$\delta^{18}O$ ‰**	**Point Name**	**$\delta^{2}H$ ‰**	**$\delta^{18}O$ ‰**
Prec.	–28.97	–6.16	Prec.	–28.96	–6.25	Prec.	–28.35	–6.22	Prec.	–28.41	–6.21
Te1	–24.71	–5.08	N1	–28.54	–5.80	T3	–21.95	–4.84	M1	–21.68	–4.68
Te5	–22.31	–4.70	N6	–24.83	–5.22	T8	–21.36	–4.69	M3	–20.12	–4.58
Te6	–20.36	–4.45	N9	–20.59	–4.60	T9	–20.85	–4.57	M5	–19.11	–4.20
Te9	–17.42	–3.77	N10	–19.24	–4.25	T19	–19.70	–4.40	M6	–16.14	–3.62
Te10	–14.50	–3.01	N12	–18.04	–3.99	T21	–18.58	–4.24	M7	–14.85	–3.28

Note:Te – Temi River, **N** – Nduruma River, **T** – Tengeru River, **M** – Maji ya Chai River, **Prec**.= Precipitation, $\boldsymbol{\delta^{2}H} = x \pm 0.20$ ‰, $\boldsymbol{\delta^{18}O} = x \pm 0.80$ ‰ where x are isotopic values from the table.

Table 22: The Average seasonal physico and hydrochemical parameters of Temi and Nduruma Rivers

Season		Temi River											
		pH	**T (°C)**	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}**	**K^{+}**	**CO_3^{2-}**	**HCO_3^{-}**	**Cl^{-}**	**SO_4^{2-}**	**TDS**	**EC(µS/cm)**
Wet	**Min.**	7.32 ± 0.52	14.95 ± 0.69	2,00 ± 0.0.29	2.43 ± 0.29	0.76 ± 0.17	0.21 ± 0.11	13.71 ± 0.92	6.18 ± 1.82	BDL	BDL	88.00 ± 11.82	176.00 ± 16.26
	Max.	8.07 ± 0.62	20.00 ± 0.93	114.00 ± 9.24	23.085 ± 3.21	43.33 ± 3.61	12.23 ± 1.36	212.71 ± 14.72	352.18 ± 24.18	77.47 ± 2.61	6.18 ± 0.52	400.00 ± 97.00	802.00 ± 92.67
	AV.	7.70 ± 0.26	17.01 ± 1.80	22.5 ± 34.17	7.96 ± 7.20	7.96 ± 12.98	2.42 ± 3.66	57.08 ± 64.34	69.58 ± 105.51	33.28 ± 22.69	4.38 ± 6.67	169.83 ± 127.50	339.75 ± 255.38
Dry	**Min.**	7.37 ± 0.30	14.95 ± 0.49	3.66 ± 1.03	2.16 ± 0.28	1.38 ± 0.28	0.41 ± 0.22	9.78 ± 0.92	11.40 ± 0.73	0.11 ± 0.03	0.06 ± 0.02	41.00 ± 2.93	82.00 ± 3.64
	Max.	9.70 ± 0.55	25.09 ± 3.71	40.51 ± 3.72	21.84 ± 1.64	15.30 ± 2.91	4.58 ± 0.37	117.91 ± 23.81	126.00 ± 25.14	13.00 ± 2.83	2.38 ± 0.37	698.00 ± 55.92	1396.00 ± 59.04
	AV.	8.31 ± 0.67	20.44 ± 2.44	23.97 ± 8.72	12.60 ± 6.09	9.05 ± 3.29	2.68 ± 0.99	67.89 ± 26.17	74.74 ± 27.13	4.58 ± 8.21	0.92 ± 0.57	245.42 ± 240.99	491.5 ± 481.11
		Nduruma River											
Wet	**Min.**	6.42 ± 0.48	12.21 ± 1.35	2.00 ± 0.16	1.21 ± 0.72	0.70 ± 0.28	0.22 ± 0.09	6.57 ± 1.32	6.25 ± 1.92	15.00 ± 0.27	BDL	71.00 ±28.72	142.00 ± 12.81
	Max.	9.04 ± 0.39	20.48 ± 0.04	10.00 ± 1.82	10.86 ± 2.91	3.78 ± 0.72	1.11 ± 0.27	43.57 ± 7.16	31.26 ± 4.82	44.99 ± 3.96	9.10 ± 0.83	108.00 ±17.92	217.00 ± 28.46
	AV.	7.98 ± 0.37	17.20 ± 2.24	4.57 ± 2.51	5.40 ± 3.19	1.74 ± 0.95	0.54 ± 0.26	21.25 ± 10.94	15.35 ± 8.41	28.82 ± 8.70	1.28 ± 2.66	90.67 ± 12.48	179.33 ± 26.73
Dry	**Min.**	7.40 ± 0.08	12.01 ± 0.06	1.21 ± 0.38	5.00 ± 0.63	0.48 ± 0.26	0.14 ± 0.05	26.92 ± 2.91	3.81 ± 0.77	45.00 ± 11.92	1.35 ± 0.32	81.00 ± 6.83	88.00 ± 10.62
	Max.	9.90 ± 0.01	24.32 ± 0.07	9.22 ± 2.93	38.00 ± 0.69	3.61 ± 0.94	1.06 ± 0.22	92.20 ± 15.72	28.92 ± 3.81	122.50 ± 27.69	23.49 ± 1.93	154.00 ± 17.42	308.00 ± 38.92
	AV.	8.22 ± 0.72	19.00 ± 3.25	4.63 ± 2.62	20.00 ± 10.04	1.95 ± 0.95	0.58 ± 0.28	59.00 ± 15.00	15.28 ± 7.70	73.12 ± 21.18	3.96 ± 6.18	117.83 ± 24.14	223.42 ± 64.31

Note: All concentration measurements are in mg/L. **Min**. – Minimum, **Max**. – Maximum, **Av**. – Average

Table 23: Average seasonal physico and hydrochemical parameters of Tengeru and Maji ya Chai Rivers

Season		Tengeru River											
		pH	**T (°C)**	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}**	**K^{+}**	CO_3^{2-}	HCO_3^{-}	**Cl^{-}**	SO_4^{2-}	**TDS**	**EC(µS/cm)**
Wet	**Min.**	7.12 ± 0.11	15.00 ± 1.73	0.48 ± 0.25	1.21 ± 0.35	0.62 ± 0.21	0.33 ± 0.14	10.14 ± 1.69	7.27 ± 1.92	2.50 ± 0.27	BDL	37.00 ± 3.96	72 ± 13.85
	Max.	7.58 ± 0.43	18.81 ± 1.84	8.20 ± 0.97	12.18 ± 1.83	3.62 ± 0.72	1.94 ±0.22	42.46 ± 3.94	39.13 ± 6.94	24.99 ± 1.93	10.00 ± 3.02	260.00 ± 57.29	518 ± 21.18
	AV.	7.34 ± 0.13	17.53 ± 1.12	2.35 ± 2.19	3.76 ± 1.21	1.48 ± 0.84	0.79 ± 0.79	17.74 ± 7.82	16.29 ± 9.24	13.79 ± 5.70	1.20 ± 2.28	110.81 ± 52.62	221.52 ± 105.06
Dry	**Min.**	7.23 ± 0.16	14.00 ± 1.96	8.00 ± 0.94	1.21 ± 0.35	2.56 ± 0.96	0.79 ± 0.21	19.14 ± 2.95	20.15 ± 4.82	12.50 ± 2.94	BDL	42.00 ± 12.03	83.00 ± 11.92
	Max.	8.59 ± 0.21	21.00 ± 0.59	24.00 ± 3.71	15.78 ± 3.01	8.27 ± 0.38	2.56 ± 0.94	73.22 ± 12.36	62.44 ± 2.84	137.00 ± 28.81	25.00 ± 2.27	243.00 ± 12.52	474.00 ± 83.52
	AV.	7.90 ± 0.36	18.04 ± 1.80	12.95 ± 4.41	5.88 ± 2.10	4.25 ± 1.51	1.32 ± 0.47	39.99 ± 16.17	33.95 ± 11.44	42.71 ± 15.96	7.89 ± 1.27	131.43 ± 50.75	262.33 ±100.41
		Maji ya Chai River											
Wet	**Min.**	7.37 ± 0.16	17.00 ± 0.61	0.49 ± 0.29	1.21 ± 0.37	1.52 ± 0.31	0.22 ± 0.07	6.57 ± 1.04	6.27 ± 0.81	BDL	5.00 ± 1.03	395.00 ± 27.41	791.00 ± 0.6
	Max.	8.60 ± 0.14	19.48 ± 0.12	2.43 ± 0.92	6.08 ± 0.72	4.56 ± 0.54	0.67 ± 0.28	32.86 ± 3.94	18.82 ± 0.92	16.00 ± 0.99	39.99 ± 5.22	594.00 ± 85.94	1187.00 ± 0.3
	AV.	8.03 ± 0.57	18.27 ± 0.82	1.50 ± 0.63	3.75 ± 1.58	2.95 ± 0.91	0.43 ± 0.13	20.46 ± 8.61	12.21 ± 3.77	7.63 ± 6.38	18.56 ± 13.68	477.14 ± 77.17	954.86 ± 153.96
Dry	**Min.**	7.91 ±0.52	17.37 ±1.25	10.00 ± 099	2.43 ±0.77	3.77 ±0.92	1.10 ± 0.28	3.35 ± 0.93	31.14 ± 4.22	35.00 ± 3.91	11.00 ± 1.41	448.00 ± 92.05	896.00 ± 0.3
	Max.	9.60 ± 0.02	21.44 ± 0.73	14.00 ± 2.91	7.28 ± 02.91	5.28 ± 0.84	1.53 ± 0.29	4.69 ± 1.72	43.59 ± 3.92	87.50 ± 14.06	30.00 ± 4.95	861.00 ± 93.57	1722 ± 29.71
	AV.	8.57 ± 0.52	19.95 ± 1.35	11.25 ± 1.50	3.81 ± 1.63	4.33 ± 0.52	1.26 ± 0.15	3.85 ± 0.47	35.81 ± 4.32	58.23 ± 16.44	23.98 ± 7.24	591.86 ± 173.82	1183.43 ± 47.54

Note: All concentration measurements are in mg/L. **Min**. - Minimum, **Max**. - Maximum, **Av**. – Average

Table 24: Fluoride levels in Temi, Nduruma, Tengeru and Maji ya Chai Rivers

Latitude	Longitude	Point Code	River	F^- _Wet(mg/L)	F^-_Dry(mg/L)	Latitude	Longitude	Point Code	River	F^- _Wet(mg/L)	F^-_Dry(mg/L)
-3.318744	36.780114	T1	Tengeru	0.94 ± 0.07	1.45 ± 0.48	-3.313160	36.753599	N1	Nduruma	0.84 ± 0.05	1.33 ± 0.58
-3.343263	36.788113	T2	Tengeru	0.24 ± 0.03	1.25 ± 0.94	-3.319881	36.744824	N3	Nduruma	1.60 ± 0.48	1.78 ± 1.57
-3.318238	36.794051	T3	Tengeru	0.68 ± 0.03	1.11 ± 0.56	-3.329416	36.746495	N4	Nduruma	1.13 ± 0.38	1.34 ± 0.38
-3.343263	36.788113	T4	Tengeru	1.17 ± 0.32	1.44 ± 0.72	-3.344450	36.744286	N7	Nduruma	0.92 ± 0.49	1.02 ± 0.02
-3.343118	36.788072	T5	Tengeru	1.48 ± 0.53	1.51 ± 0.06	-3.373071	36.750155	N8	Nduruma	1.59 ± 1.07	2.68 ± 0.47
-3.347191	36.791335	T6	Tengeru	0.66 ± 0.02	0.97 ± 0.01	-3.402712	36.781335	N9	Nduruma	1.59 ± 0.36	2.16 ± 0.01
-3.343113	36.788064	T7	Tengeru	1.32 ± 0. 47	1.50 ± 0.48	-3.444499	36.793244	N10	Nduruma	1.67 ± 0.48	2.43 ±0.69
-3.361913	36.801558	T10	Tengeru	1.20 ± 0.28	1.56 ± 0.69	-3.470623	36.794341	N11	Nduruma	1.82 ± 0.42	BDL
-3.387562	36.833290	T11	Tengeru	1.13 ± 0.48	1.34 ± 0.57	-3.491149	36.806301	N12	Nduruma	1.71 ± 0.60	BDL
-3.388095	36.834787	T13	Tengeru	1.27 ± 0.33	1.53 ± 0.97	-3.342963	36.753636	N2	Nduruma	0.81 ± 0.38	1.20 ± 0.41
-3.390375	36.867836	T14	Tengeru	2.30 ± 0.95	5.96 ± 0.28	-3.352160	36.752858	N5	Nduruma	1.39 ± 0.05	1.69 ± 0.49
-3.389705	36.867828	T15	Tengeru	2.19 ± 0.51	3.13 ± 0.04	-3.372934	36.751276	N6	Nduruma	2.16 ± 0.39	2.90 ± 0.05
-3.431228	36.851936	T17	Tengeru	1.47 ± 0.84	1.89 ± 0.74	-3.314420	36.719588	Te1	Temi	1.02 ± 0.01	1.60 ± 0.76
-3.441064	36.856352	T19	Tengeru	1.31 ± 0.77	1.53 ± 0.09	-3.340386	36.711055	Te5	Temi	1.40 ± 0.21	1.87 ± 0.22
-3.431185	36.852054	T20	Tengeru	1.77 ± 0.64	1.92 ± 0.28	-3.360737	36.701942	Te6	Temi	1.19 ± 0.41	1.83 ± 0.58
-3.445723	36.857519	T21	Tengeru	2.23 ± 0.01	3.13 ± 0.03	-3.397515	36.721275	Te7	Temi	0.61 ± 0.69	0.94 ± 0.17
-3.286817	36.882092	M1	Maji ya chai	20.10 ± 0.99	26.10 ± 1.49	-3.370857	36.695152	Te8	Temi	1.26 ± 0.40	1.83 ± 0.12
-3.297030	36.890270	M2	Maji ya chai	65.20 ± 0.03	69.01 ± 0.03	-3.426367	36.697539	Te9	Temi	1.41 ± 0.65	2.15 ± 0.54
-3.300897	36.882034	M3	Maji ya chai	14.50 ± 0.36	17.70 ± 0.47	-3.503508	36.770893	Te10	Temi	1.54 ± 0.03	2.68 ± 0.02
-3.311596	36.890981	M4	Maji ya chai	14.80 ± 1.04	18.20 ± 0.39	-3.589528	36.809305	Te11	Temi	1.36 ± 0.38	3.38 ± 0.16
-3.327916	36.901406	M5	Maji ya chai	13.80 ± 0.97	18.00 ± 0.42	-3.282948	36.730934	Te3	Temi	1.36 ± 0.28	1.96 ± 0.47
-3.368379	36.896311	M6	Maji ya chai	11.75 ± 0.7	16.40 ± 0.92	-3.290865	36.735081	Te2	Temi	1.02 ± 0.59	1.27 ± 0.44
-3.389771	36.868054	M7	Maji ya chai	10.17 ± 0.43	15.70 ± 0.37	-3.423636	36.681599	Te12	Temi	1.37 ± 0.49	2.01 ± 0.54
-3.348050	36.794225	T8	Tengeru	0.92 ± 0.58	1.14 ± 0.72	-3.299415	36.731638	Te4	Temi	1.27 ± 0.07	1.39 ± -0.27
-3.359968	36.799709	T9	Tengeru	1.02 ± 0.02	1.28 ± 0.48						
-3.406998	36.864624	T16	Tengeru	2.03 ± 0.62	2.64 ± 0.73						
-3.429589	36.852371	T18	Tengeru	1.10 ± 0.83	1.40 ± 0.49						
-3.423187	36.854269	T12	Tengeru	0.94 ± 0.05	1.19 ± 0.49						

Table 25: Particle size distribution for igneous rocks

Diameter	Solomu		Nduruma		Maksoro		Jamera	
	Weight (g)	%	Weight (g)	%	Weight (g)	%	Weight (g)	%
≥2 mm	23.99	17.38	19.51	14.13	21.73	15.75	23.55	17.07
1.5 mm	14.73	10.67	13.97	10.12	10.94	7.93	13.14	9.52
1 mm	19.34	14.01	19.46	14.10	17.93	12.99	17.84	12.93
0.35mm	39.55	28.66	37.08	26.14	34.41	24.94	40.16	29.10
250 µm	5.71	4.14	9.00	6.89	9.20	6.67	9.11	6.60
180µm	8.93	6.47	6.01	4.36	8.54	6.19	6.60	4.78
125µm	14.86	10.77	15.90	11.53	10.44	7.57	17.84	12.93
90µm	4.12	2.98	11.32	8.20	14.62	10.59	5.03	3.65
63µm	4.00	2.90	4.01	2.90	7.22	5.23	3.28	2.38
45µm	1.50	1.08	0.91	0.66	1.79	1.30	0.63	0.46
32µm	0.54	0.39	0.66	0.48	0.61	0.44	0.41	0.29
20µm	0.59	0.43	0.47	0.34	0.39	0.28	0.38	0.27
Total	137.85	99.89	137.80	99.86	137.82	99.87	137.96	99.97

The total weight of the sample was 138.00 g

Table 26:The pH dependence of Fluoride leaching from igneous rocks at 25 °C

Tengeru(Solomu)		Nduruma		Maksoro(M1)		Jamera(M2)	
pH	*[F^-]	pH	*[F^-]	pH	*[F^-]	pH	*[F^-]
3.72	0.26	3.82	0.28	3.85	0.43	3.75	1.28
4.20	0.29	4.17	0.31	4.32	0.49	4.00	1.44
5.00.	0.33	5.44	0.72	5.63	0.46	4.05	1.77
6.95	1.37	6.37	0.97	6.76	0.64	4.33	2.15
7.22	2.83	7.47	1.74	7.49	0.68	4.6	2.15
8.51	3.86	8.82	2.73	8.03	1.21	5.69	2.17
9.72	3.95	9.49	2.53	9.17	3.71	6.24	2.28
10.21	3.95	10.73	2.53	10.6	5.95	7.07	2.79
11.94	3.94	10.99	2.53	11.3	6.20	8.25	9.05
12.64	3.94	12.01	2.53	12.34	26.60	9.48	10.3
13.08	3.94	13.37	2.53	13.17	26.85	10.85	18.75
13.55	3.94	-	-	13. 35	26.89	11.07	29.55
-	-	-	-	-	-	12.61	72.5
-	-	-	-	-	-	12.79	73.95
-	-	-	-	-	-	13.17	74.3

*[F^-] in mg/L

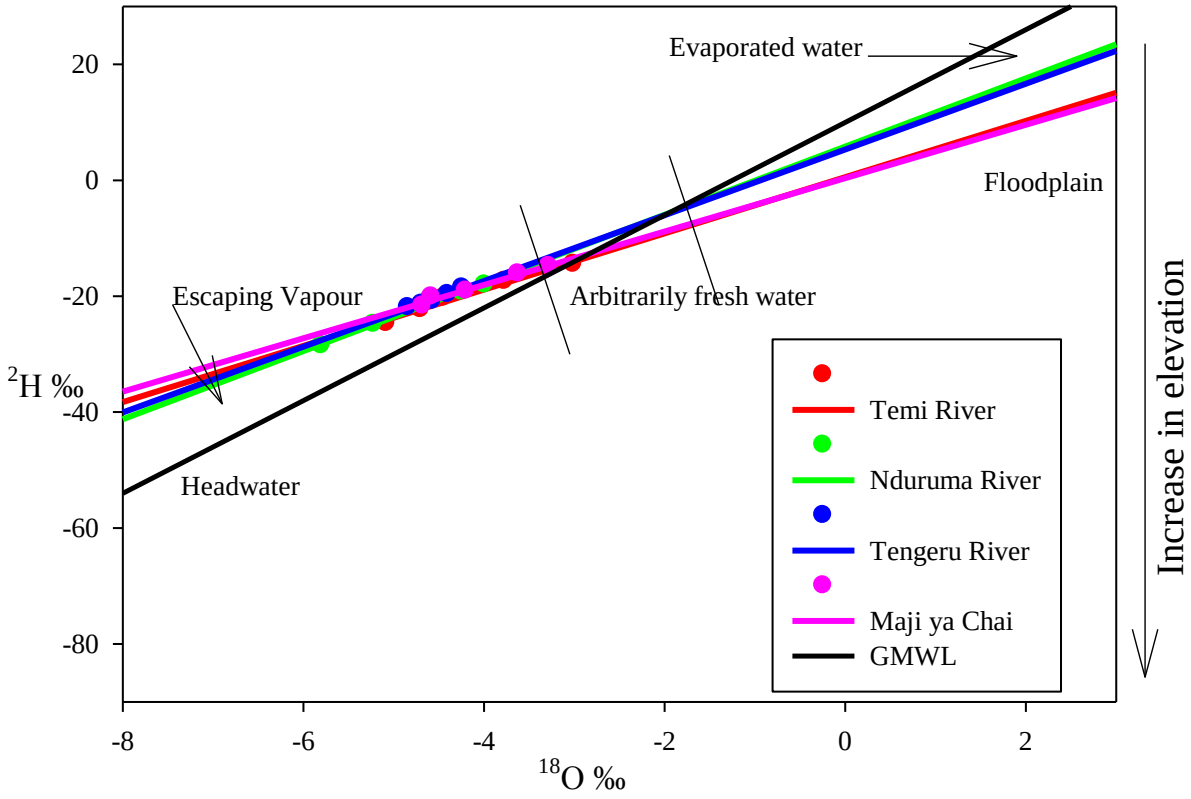


Figure 26: A plot of $\delta^{2}H$ versus $\delta^{18}O$ indicating increase in evaporation downstream

6.3.2 Physicochemical trends

The pH of all rivers was above 7 in both seasons with the lowest pH being in the catchment areas of all rivers. The lowest pH (7.12 ± 0.11) was measured at Tengeru catchment during the wet season whereas the highest value (9.90 ± 0.14) was measured in Nduruma River downstream during the dry season. Tengeru River showed the lowest pH in both seasons which averaged to 7.12 ± 0.11 in the wet season and 7.70 ± 0.36 in the dry season. Maji ya Chai had the highest average pH in both seasons with the values of 8.03 ± 0.57 and 8.57 ± 0.52 for wet and dry seasons respectively (Appendix 7). The minimum water temperature (12.21 °C) was measured in the catchments area of Nduruma River with its highest temperature of up to 25 °C being measured in the dry season. The lowest average temperature of 17.01 ± 1.80 °C was recorded at Themi River in the wet season while its highest temperature of 20.44 ± 4.22 °C was recorded in dry season. The temperature variations in all rivers were generally associated with canopy cover of the riparian environment and its

elevation such that the low water temperature was measured in high canopy cover environment and vice versa for the high water temperature.

The lowest conductivity of 82 ± 3.64 *µS/*cm was measured at the catchments of Themi River an indication of less salt being dissolved in it whereas the lowest average value of 179.33 ± 26.73 *µS/*cm was measured at Nduruma River in wet the season. The highest EC of 1722 ± 29.71 *µS/*cm was measured in the downstream of Maji ya Chai River during the dry season with the highest average value of 1183.43 ± 47.54 *µS/*cm being measured in the same river during the wet season.

6.3.3 Distribution of major cations and anions in the rivers

The distribution of dissolved major cations and anions summarized in the Piper diagram as shown in Fig. 27. For Themi River, neither ions predominated in both seasons thus the Ca–Mg or Na^+ and K^+ were all very low with SO_4^-, HCO_3^- and Cl^- also being low resulting in low EC and TDS and hence soft water.

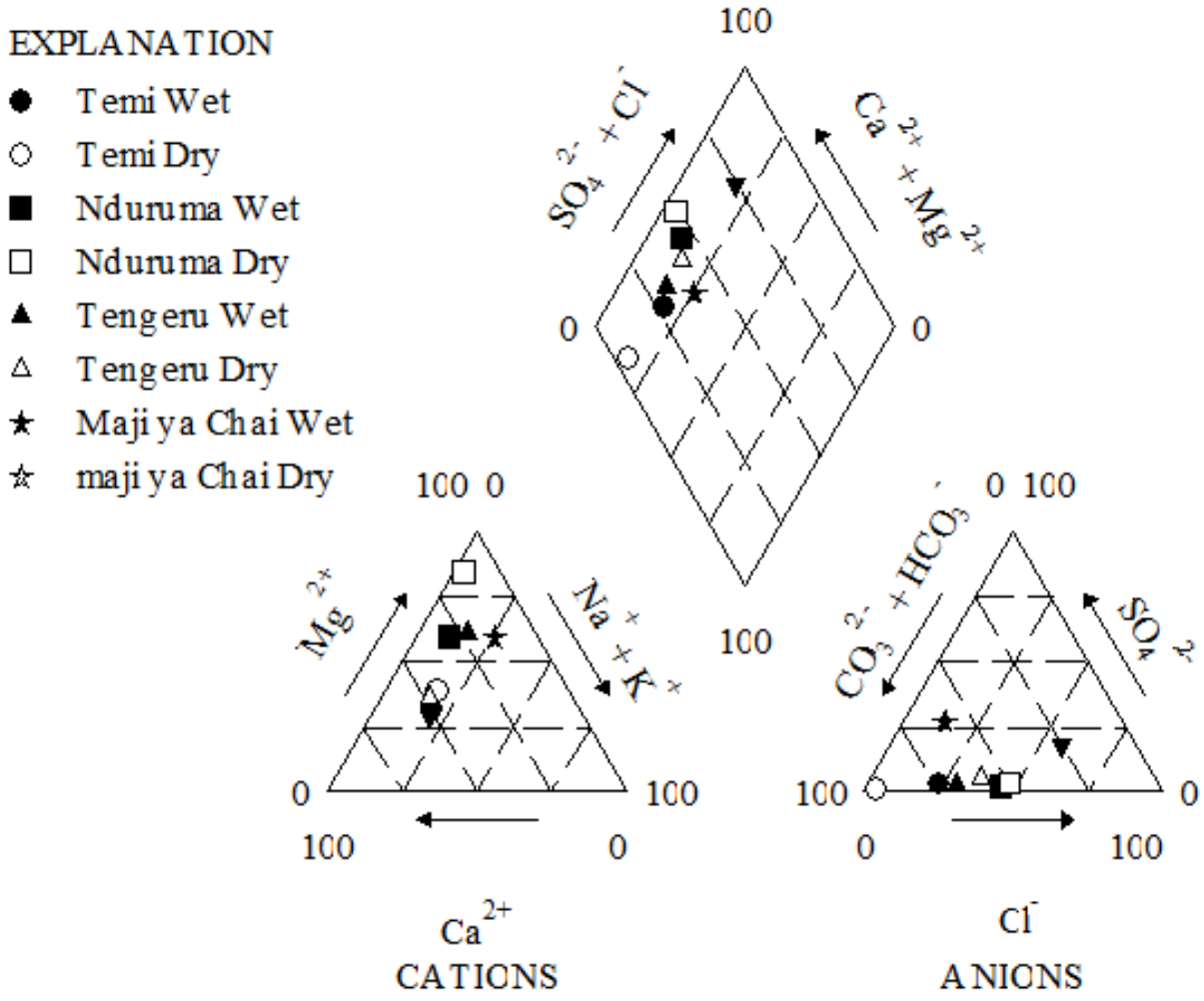


Figure 27: Piper Diagrams for distribution of major cations and anions

This trend was different in Nduruma River in both seasons whereby Ca–Mg and CO_3^{2-}, HCO_3^- SO_4^{2-} and Cl^- were moderate but with low concentrations of Na^+ and K^+ thus the water alkalinity in this river was mainly contributed from hydrolysis of CO_3^{2-} and HCO_3^- which increase the levels of OH^- as shown in Equation (12) and (13), thus, the higher levels of CO_3^{2-} and HCO_3^- the higher the river pH.

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq) \qquad K_b = 2.0 \times 10^{-4} \qquad (12)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(l) + OH^-(aq) \qquad K_b = 2.5 \times 10^{-8} \qquad (13)$$

Thus, the total carbon alkalinity (A_C) of water is practically contributed by hydrolysis of both CO_3^{2-} and HCO_3^- (Equation 14) (IAEA, 2000).

$$A_C = [HCO_3^-] + [CO_3^{2-}] \quad (14)$$

The increased levels of SO_4^{2-} and Cl^- in the downstream can be attributed by the point source pollution from peasant horticultural farming in river banks where some practices use high amounts of fertilizers, herbicides and pesticides containing such formulations. Generally the SO_4^{2-} and Cl^- were relatively low, which is one of the characteristics for most natural water systems (Davies, 1996).

The levels of Ca–Mg in Tengeru River were higher in the dry season than wet season with the Na^+ and K^+ being low. The anions SO_4^{2-} and Cl^- were relatively increasing in the wet compared to the dry season whereas CO_3^{2-} and HCO_3^- were low in the wet season compared to the dry season. A similar trend was shown in Maji ya Chai River. A similar study on major ions in this area showed a high relation on dominance between Na^+ and HCO_3^- an indication that they might probably be originating from $NaHCO_3$ salt (Ghiglieri *et al.,* 2012) .

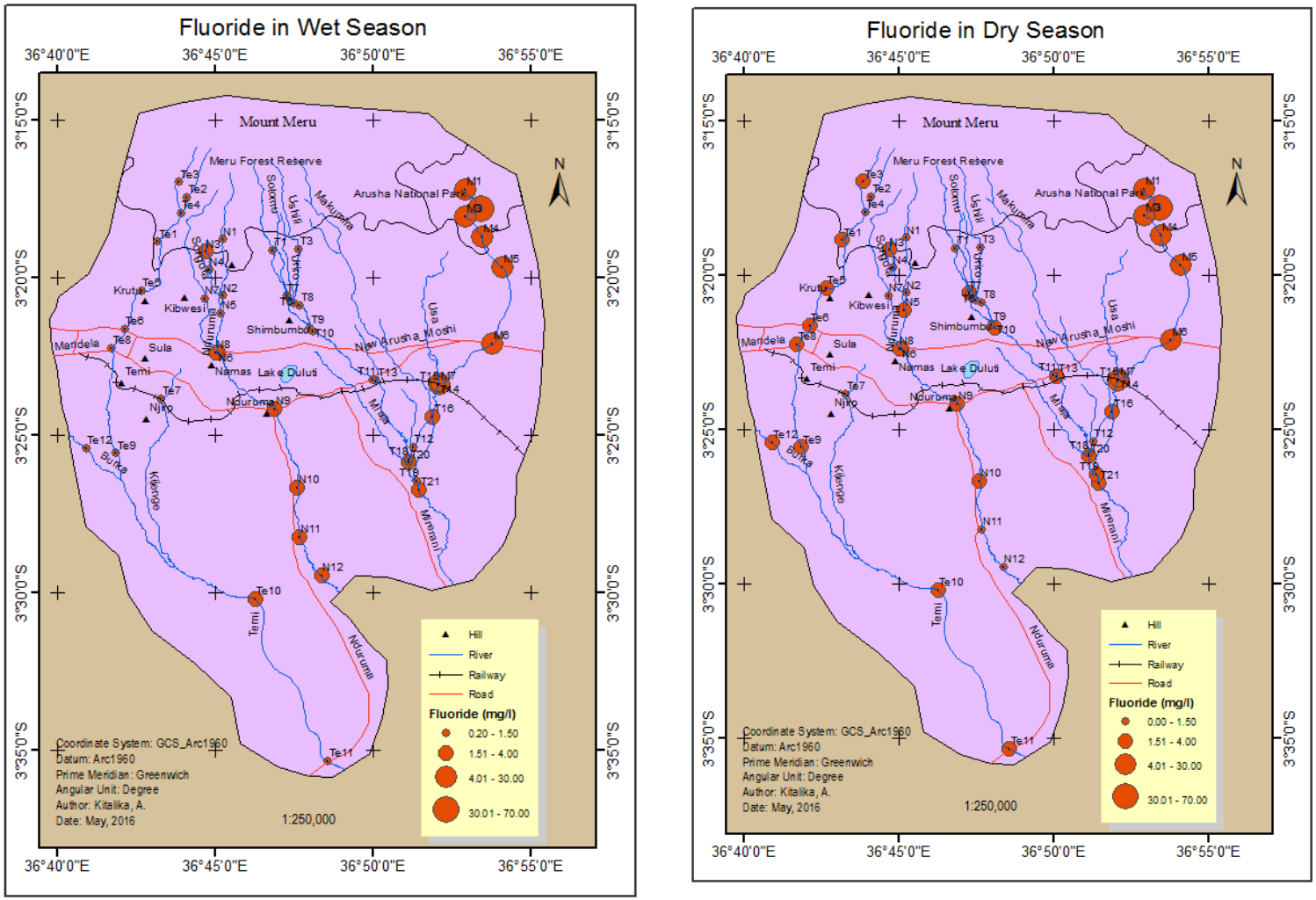
6.3.4 Fluoride ions trends

The Fluoride levels in various points of the respective rivers are indicated in Table 24. They are further summarized with Geostatistical analysis and mapped as shown in Figures 28a, b. The pH spatial distribution reflecting the pH dependency for fluoride levels in water is shown in Fig. 29 a, b. The study shows pH to play a great role in the availability of fluoride ions in water. The lowest average fluoride level of 0.24 ± 0.03 mg/L was recorded during the wet season in Maktengwe stream which is a tributary sub catchment of Tengeru River. In the same season the highest average fluoride levels of 65.20 ± 0.03 mg/L was measured in River Maji ya Chai (Fig. 28a). This river is located at Arusha National Park (ANP) and is used as one of the major drinking water sources for wildlife.

The average lowest fluoride levels in the dry season was recorded in Kijenge stream in Themi River with an average level of 0.94 ± 0.07 mg/L whereas the highest average level of 69.01 ± 0.03 mg/L was recorded in Maji ya Chai River (Fig. 28 b). The increase in fluoride levels in the dry season may be attributed to the absence of runoff to the river which may cause dilutions and hence in that period the river flow is mainly from ground water (old

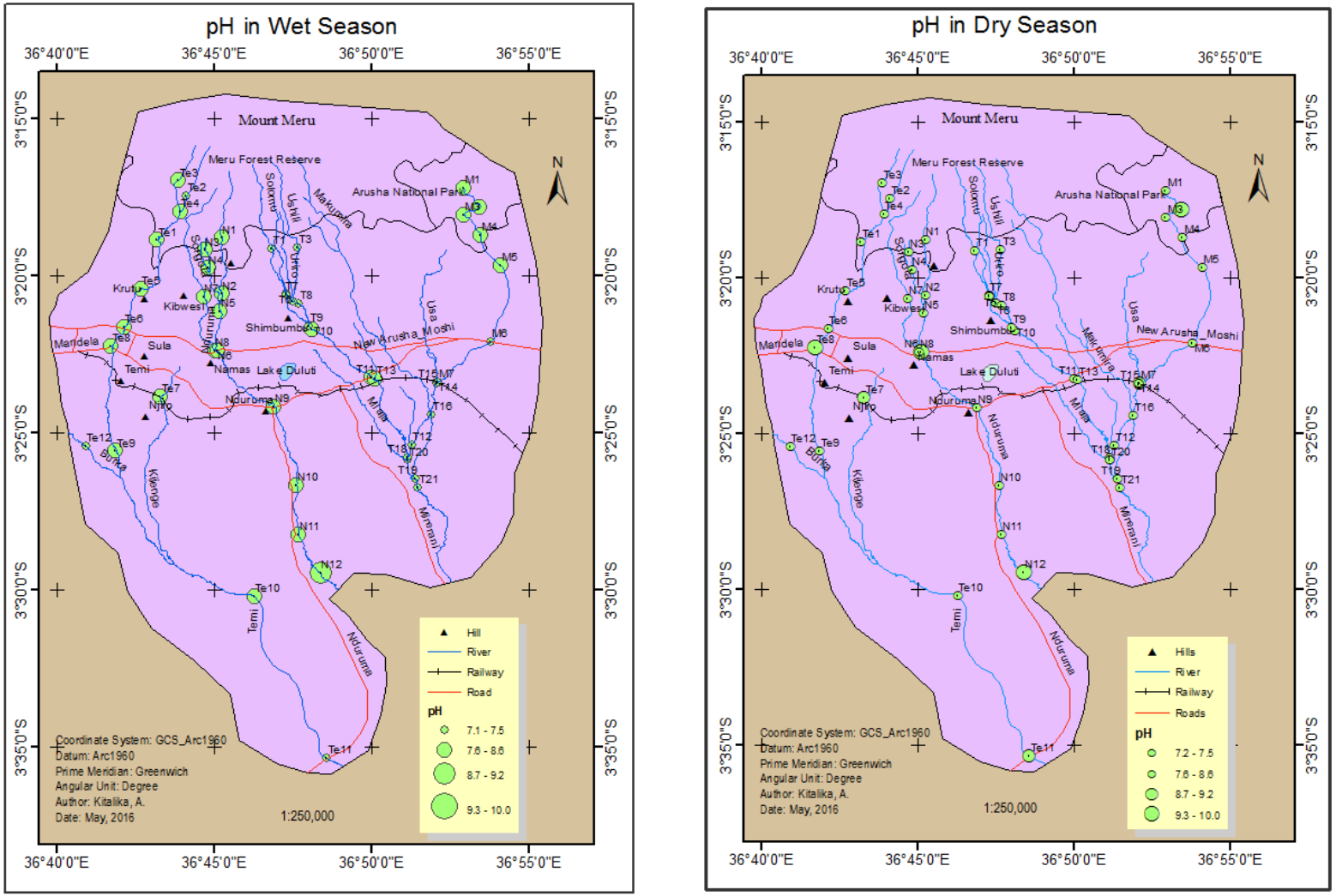
water) containing more fluoride ions. It should be noted that the ground water mixing with surface water has enough time for interaction with fluoride containing rocks which allow dissolution of more fluoride ions in it.

The headwater environment of the three rivers (Themi, Nduruma and Tengeru) showed low fluoride level of < 4.0 mg/L which is in line with the standards recommended by WHO and TBS except for the headwater environment of Maji ya Chai River which had extremely high fluoride levels of up to 69.01 ± 0.03 mg/L. Low fluoride levels in the three rivers (Themi, Nduruma and Tengeru) in both seasons are mainly caused by low fluoride composition in the phonolite feldspar rocks which predominates at the upstream main catchment areas of these rivers thus discharging low fluorides amount in water. Another general trend of interest is observed on the spatial distribution of fluoride at the headwater where fluorides showed to increase from the south western part to the south eastern part (0.24 ± 0.03 mg/L to 69.01 ± 0.03 mg/L) with respect to Mount Meru. This trend can be explained by the fact that its head water from the south western part is at a high altitude with low temperature thus the lower temperature the lower dissolution rate of fluoride from rocks. Also, the aquifer lithology at such high altitude is predominantly phonolite which is characterized by low fluoride contents (Ghiglieri *et al*., 2010). The headwater source in Maji ya Chai River is from lowland (foothills of Mount Meru) in the south eastern region of the mountain characterized by relatively high temperature incidence due to low canopy cover and its aquifer lithology is basalt which is characterized by high fluoride levels (Table 24) (Ghiglieri *et al*., 2010). All these features favour high fluoride contents in water of the river.



(a) **(b)**

Figure 28: Fluoride Variation in wet (a) and dry (b) season



(a) (b)

Figure 29: Water pH in wet (a) and dry (b) seasons

The average fluoride levels in the three rivers increase downstream up to 3.38 ± 0.16 mg/L at the floodplain in Themi River. Such observed trend does not happen at Maji ya Chai River where the fluoride levels showed to decrease downstream. This is caused by dilutions from Ngurdoto and Shoripanga streams feeding to the main river in between with averaged fluoride concentration of 3.32 ± 0.26 mg/L and 4.21 ± 0.17 mg/L, respectively. Also, the extreme high difference in fluoride levels in the headwater environment of Maji ya Chai compared to other sampling areas of the same river indicates the main point source pollution of fluoride in the river which has been identified at Jamera (Fig. 28). In similar study, water samples showed that fluoride was low in the main cone group, mantling ash and Tengeru lahar whereby the median concentration was 1mg/L but it was high in Ngarenanyuki and Ongadongishu lahars whereby the median concentrations were 4 mg/L and 9 mg/, respectively (Mkungu *et al.,* 2014). The statistical tests showed good positive correlations (*r*) in the dry season between fluorides levels and pH, EC, together with temperature simply because there was only ground water (old water) recharge with the absence of runoff which may increase dilutions of river water at various rates.

6.3.5 Fluoride spatial distribution in Temi River

Fluoride levels in Themi River increased from the headwater downstream to the floodplain in both wet and dry seasons. The minimum average fluoride level was in the upstream headwater region of the river with average values of 1.02 ± 0.01 mg/L and 1.27 ± 0.07 mg/L during the wet and the dry seasons, respectively. The maximum level was measured at the floodplain with the average values of 1.54 ± 0.03 mg/L and 2.68 ± 0.02 mg/L in wet and dry seasons, respectively [Fig. 28 (a), (b)]. Furthermore, the headwater and middle regions of the river had fluoride levels lower than the WHO permissible levels for drinking water of 1.50 mg/L(WHO, 2004) whereas the remaining part had fluoride level higher than WHO permissible standards but within the TBS maximum permissible level of 4.0 mg/Lin both seasons [Fig. 28 (a), (b)] (TBS, 2014). Higher fluoride levels in the floodplain can be explained by low water velocities which in turn increase the interaction time of water with basalt aquifers containing high fluoride element. Together with this, the slightly alkaline condition in the flood plain favours the availability of fluorides in water as suggested by Saxena and Ahmed in their experiments (Saxena & Ahmed, 2001).

In addition to increase in fluoride levels downstream to the flood plain, the study shows a strong positive Pearson correlation of fluoride levels between wet and dry seasons (*r = 0.87,*

n = 13, p ≤ 0.005) which suggest common pollution sources between seasons (Fig. 29a). Using the-two sample t-test for unequal variance the means of fluoride levels were significantly different between seasons, thus the fluoride levels were significantly higher in the dry season than in the wet season (*n = 13, p ≤ 0.001*). The higher fluoride levels in the dry season can be explained by the river recharge from ground water containing high fluoride levels as the major source without dilutions from runoff. Increase in pH showed a strong positive Pearson correlation with fluoride levels (*r= 0.9, n = 13, p ≤ 0.0001* (Fig. 30 a). Similar correlation trends have been shown by Saxena and Ahmad on their study in water rock interaction on dissolution of fluoride containing feldspar rocks (Saxena & Ahmed, 2001).

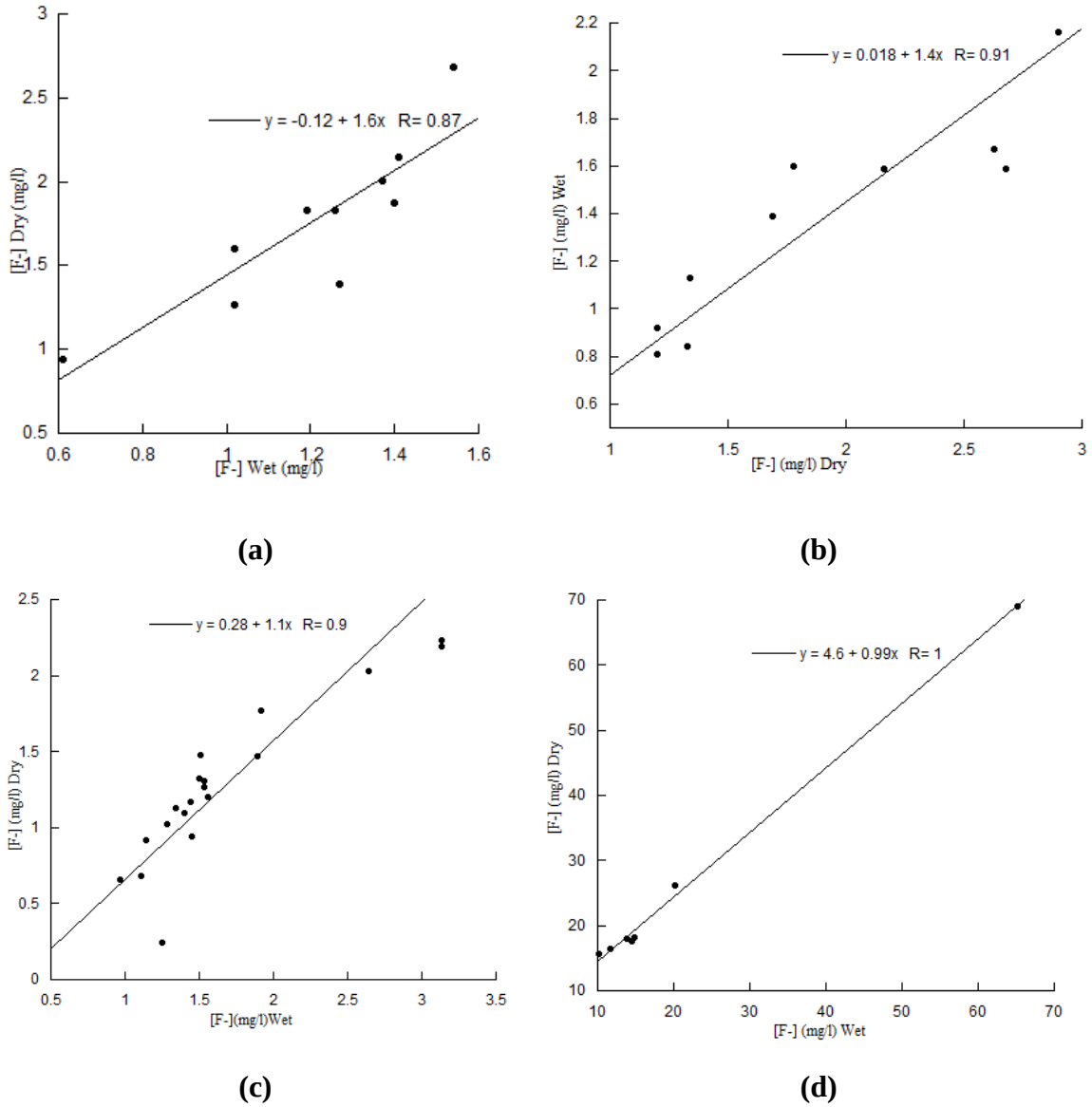


Figure 30: Correlation of Fluoride between wet and dry season in (a) Temi, (b) Nduruma,(c) Tengeru and (d) Maji ya Chai

6.3.6 Fluoride distribution in Nduruma River

Nduruma River had fluoride levels of 0.84 ± 0.05 mg/L to 2.16 ± 0.01 mg/L and 1.02 ± 0.02 mg/L to 2.90 ± 0.05 mg/L during the wet and dry seasons, respectively. The headwater and middle regions had fluoride levels within the WHO maximum permissible levels while the rest region was within the TBS standards [Fig. 28 (a), (b)]. Also, the fluoride concentrations in this river were shown to increase from the upstream to the floodplain in favour of the increase of some its physicochemical properties including downstream water temperature, pH and EC. These good trends were much more pronounced in the dry season depicting that the river water recharge was mainly from ground water (old water) which had good interaction time with rocks containing salts. The very strong positive correlation in fluoride levels between wet and dry seasons ($r = 0.9$, $n = 12$, $p \leq 0.0002$) also suggest the common pollutant sources in the two seasons (Fig. 30 b).

The minimum and maximum average water temperature in wet season were 12.01 ± 0.06 °C and 20.48 ± 0.04 °C, respectively whereas during the dry season the minimum and maximum average water temperature were 12.61 ± 0.03 °C and 24.32 ± 0.07 °C, respectively. While the pH trends in the wet season showed many irregularities due to various external factors such as surface runoffs, the minimum and maximum average pH range was from 7.63 ± 0.01 to 9.4 ± 0.03 and 7.4 ± 0.08 to 9.9 ± 0.01 for the wet and dry seasons, respectively. A strong positive correlation between fluoride levels and pH in dry season ($r = 0.93$, $n = 12$, $p \leq 0.02$) suggests that increase in water pH, increases the ability of dissolution of fluoride containing rocks in water (Fig. 31 b) (Saxena & Ahmed, 2001) hence an increase in fluoride ions in water. Also, the mean fluoride levels between seasons were significantly not different ($p \leq 0.7$, $n = 12$) suggesting that seasonal dilution in this river had no significant impact in the fluoride availability in water.

6.3.7 Fluoride distribution in Tengeru River

The fluoride levels in this river were shown to fluctuate as a result of dilution from inputs of several tributaries such as Ngaresero and Malala which had very low fluoride levels. The headwater of this river showed lower values than the WHO standards while the floodplain showed higher values due to effects from Maji ya Chai River [Fig. 28 (a), (b)]. Despite such fluctuations, fluorides levels in this river increased when the confluence between Usa River and Maji ya Chai contributed its water to form the main Kikuletwa River. Higher levels in this downstream were caused by Maji ya Chai River which have the highest fluoride levels

among the studied rivers. Despite their low levels, the wet season had lower levels than the dry season such that the minimum average levels in this river were 0.24 ± 0.03 mg/L and 0.97 ± 0.01 mg/L whereas its average maximum levels were 2.23 ± 0.01 mg/L and 3.13 ± 0.03 mg/L for the wet and dry seasons, respectively. In addition, the higher values in the flood plain did not exceed the TBS standards of 4.0 mg/L. Generally, this river showed the lowest fluoride levels in the study area.

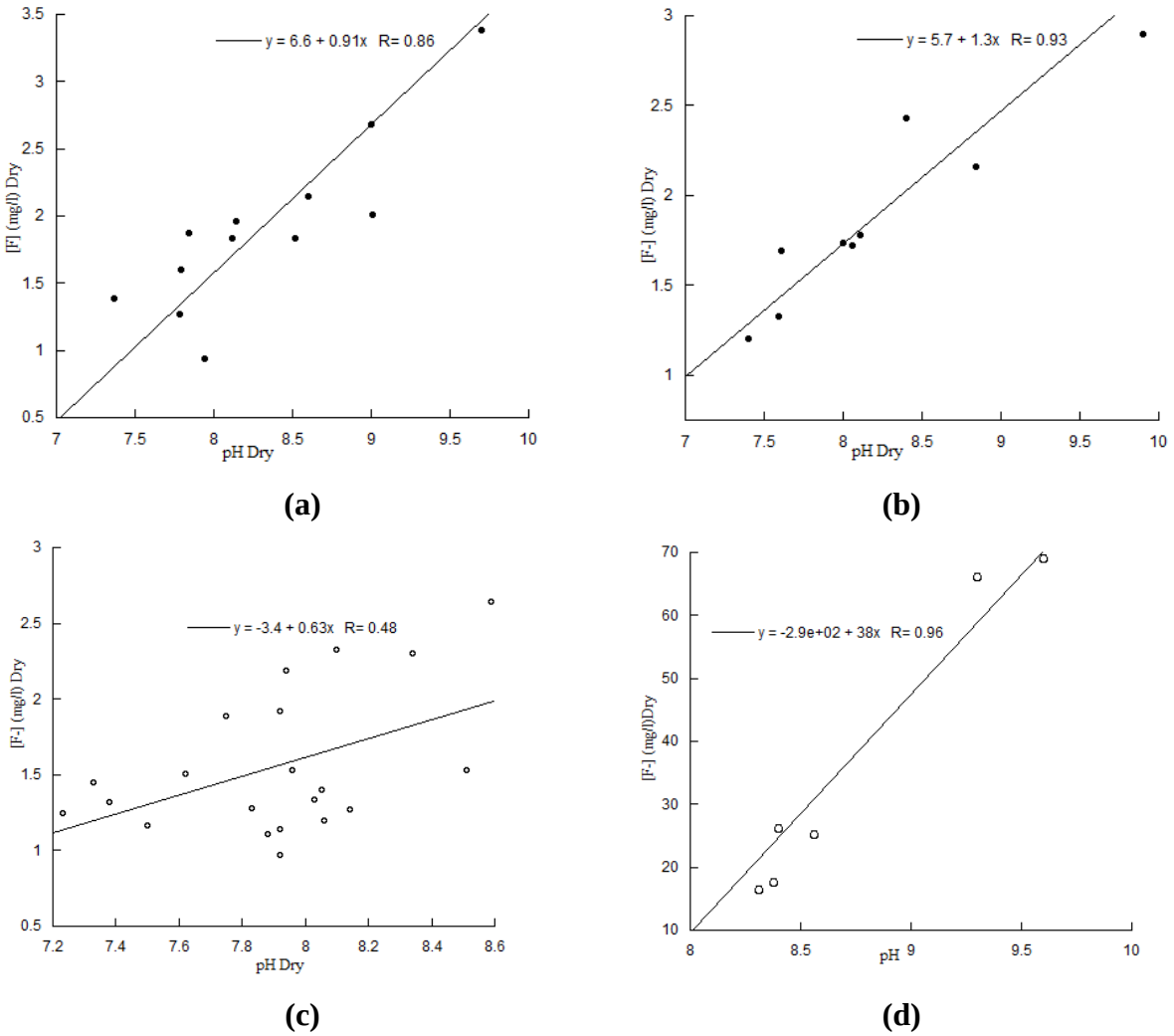


Figure 31: Correlation of Fluoride with pH for dry season in (a) Temi (b) Nduruma, (c) Tengeru and (d) Maji ya chai

Water temperature in this river had slight changes due to high canopy cover in its riparian environment throughout whereby the minimum temperature were 14.00 ± 0.02 °C and 15.00 ± 0.01 °C with its maximum temperature being 18.71 ± 0.02 °C and 21.00 ± 0.04 °C for the wet and dry seasons, respectively.

The statistical test showed a very strong positive correlation in fluoride levels between the two seasons ($r = 0.9$, $n = 21$, $p \leq 0.0002$) suggesting a common source of the pollutant in the two seasons (Fig. 30 c). In addition to this, a very weak positive correlation ($r = 0.4$, $n = 21$, $p \leq 0.4$) was shown between fluoride levels and pH during the dry season suggesting that the slight changes in pH had no significant effect on fluoride variations (Fig. 31 c). Together with these, their mean fluoride levels between seasons were shown to be significantly different ($n = 21$, $p = 0.02$) indicating that water from rainfall had a significant effect to the water quality changes and the contributing water in dry season was mainly from ground water recharge.

6.3.8 Fluoride distribution in Maji ya Chai River

During the wet season the average fluoride levels were between 11.75 ± 0.70 mg/L and 65.20 ± 0.03 mg/L whereas its minimum average levels in dry season ranged from 16.40 ± 0.05 mg/L to 69.01 ± 0.03 mg/L both highest being recorded in the headwater at Jamera (**M2**). A Similar concentration of fluoride of 59 mg/L – 68 mg/L was recorded in the past five years in the nearby hydrothermal spring feeding its water in Engare Nanyuki River which is a lowland river with respect to Maji ya Chai River (Ghiglieri *et al.,* 2010). These similarities may entail common fluoride containing rock in all rivers around the area. Interestingly, Jamera (**M2**) was discovered to be the main point source for fluoride ions in this river and contains the highest fluoride concentration among others. This area is characterized by high fluoride levels in its river bank rocks (Table 26) and highest pH (9.6 ± 0.02) among all measurements recorded creating a good alkaline environment which favours high fluoride dissolution from rocks compared to other areas. Also, this area is characterized by very low water velocity of 0.27 m/s which favours a good interaction time of water with fluoride containing rocks.

Low fluoride concentration in the downstream of Maji ya Chai River is due to dilutions from springs contributing water to the main river which have a low fluoride level range of 1.62 ± 0.01 mg/L and 3.01 ± 0.04 mg/L in the wet season, 3.32 ± 0.26 mg/L and 4.21 ± 0.17 mg/L in the dry seasons namely, Ngurdoto and Shoripanga springs, respectively. The contributed values are quite lower than minimum levels observed in the two seasons of the main river. In addition, waters from this river had very high EC compared to other nearby rivers indicating that the river contains more soluble salts/rocks. The area noted with the highest fluorides and pH had also had the highest EC (1958 ± 0.7 μS/cm and 1187 ± 0.3 μS/cm) with their average minimum values being 896 ± 0.3 µS/cm and 791 ± 0.6 `µS/cm in the dry and wet seasons, respectively. This good pH dependence correlation was previously shown by Saxena and

Ahmed in their experiment in pH rock interaction in dissolution of fluoride containing granitic rocks and it was found that the pH range of 7.6–8.6 favours the rock dissolution (Saxena & Ahmed, 2001).

The comparison of fluoride levels between seasons indicated a very strong positive correlation between seasons (*r = 1, n = 7, p <= 0.002*) indicating that the pollutant originates from a common source (Fig. 31 d). Also, a very strong positive correlation (*r = 0.9, n = 7, p ≤ 0.005*) was observed between the fluoride levels and pH in the dry season an indication that dissolution of fluoride rocks is a function of pH (Fig. 31 d) (Ghiglieri *et al.*, 2012; Saxena & Ahmed, 2001).

6.3.9 The pH dependence in fluoride leaching from rocks

The laboratory experiments to establish the patterns in leaching of fluoride were performed from basalt rocks collected from Maksoro and Jamera (M2) (Maji ya Chai) Rivers catchment banks with its results being shown in Table 25 and 26. In this experiment the rocks collected from the three rivers have been shown to release a low fluoride amount at various pHs with further negative response even at high alkaline environment which favours fluoride leaching. The low fluoride leaching in these rocks even at highly alkaline environment is an evidence of low fluoride amounts contained in rocks. More experiments from the high fluoride containing rocks show high amounts of fluoride leaching which acquires its maximum levels in the alkaline environment with no further changes upon increase of its pH. At such point complete fluoride leaching from the rocks is assumed (Fig. 32; Table 26). The study from this figure shows three phases of rock leaching whereby phase I involves pH below 7.6 where there is little response of fluoride leaching until neutral pH. Phase II involves the pH range of 7.6 to 11 where there is a good response to the increase of alkalinity (pH) with fluoride leaching. Phase III which starts at pH 11 shows a quick response in fluoride leaching in the rock. The pH of water samples ranged from 7.12 to 9.90 which it is slightly above neutral to alkaline thus all corresponding to Phase II in our experiment. These results are supported by Saxena and Ahmad in similar study for granite rock which showed good response in pH 7.6–8.8 (Saxena & Ahmed, 2001).

At low pH slow fluoride leaching is expected from rocks in the environment. However, there were some water samples which had high pH with low fluoride concentration than expected. Such results depict an important massage to scientists that the availability of fluoride ions in solution depends mainly on the nature of rocks that they interact with whether they contain

fluoride or not and also their response to leaching under favorable conditions. From this experiment it was found that the amount of fluoride in rocks is another major limiting factor for presence of this pollutant in water which its availability is favoured by alkaline environment.

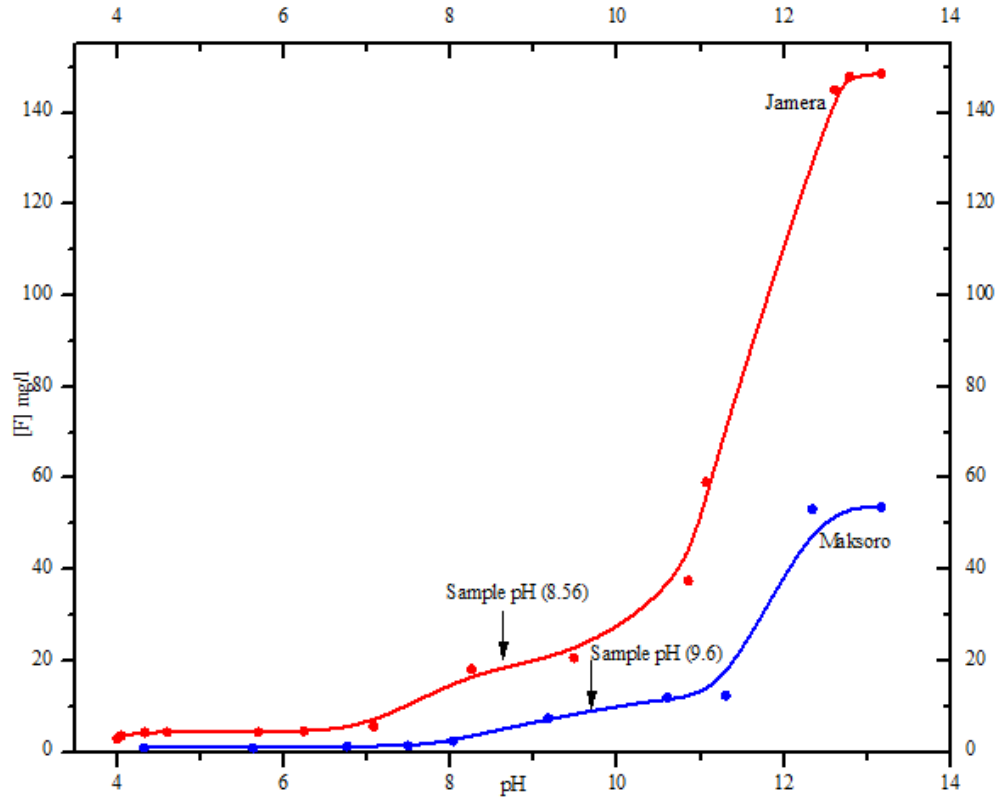


Figure 32: Fluoride leaching in feldspar-quartz igneous rock at 25°C

6.3.10 The role of OH– in fluoride leaching from rocks

The alkaline environment associated with fluoride leaching occurs as a result of several reactions including the reaction between fluorite (CaF_2) and HCO_3^- which release fluoride ions (Equation 15) (Ghiglieri *et al.*, 2012).

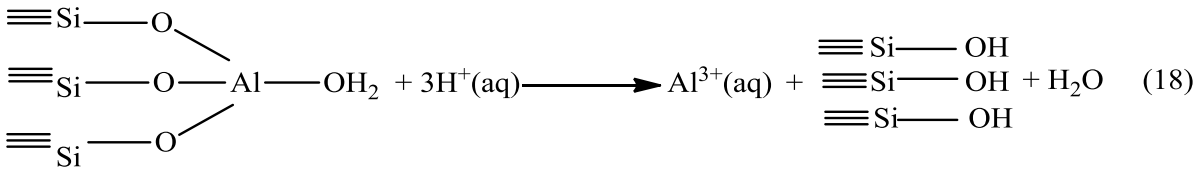
$$CaF_2(s) + 2HCO_3\text{-}(aq) \longrightarrow CaCO_3(s) + 2F\text{-}(aq) + CO_2(l) + H_2O(l) \qquad (15)$$

Also, the carbonate ions present in the aqueous solution increase the alkalinity of water through Equation (12). When $CO_2(g)$ (atmospheric) is dissolved in water it gives carbonic acid (Equation 16) where in turn the acid decreases the pH of water due to increased H^+ (Equation 17). This process proceeds at a limited extent due to low solubility of CO_2 (g) in water and the resulting acid is weak.

$$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq) \quad (16)$$

$$H_2CO_3(aq) \rightleftharpoons HCO_3\text{-}(aq) + H^+(aq) \qquad K_a = 2.5x10^{-4} \quad (17)$$

The formed HCO_3^- from (17) accelerates further the dissolution of $CaF_2(s)$ rock to release more $F^-(aq)$. However, in this experiment since the fluoride containing rock is a feldspar, at low pH (acidic) alumina surfaces can be hydrogenated into a neutrally charged species which it also gives free aluminum ions (Equation 18) (Walther, 1997).



(18)

Thus, one Al^{3+} will polarize three water molecules to give three H^+ which increase the acidity of water (Equation 19):

$$Al^{3+}(aq) + 3\ H_2O(l) \longrightarrow Al(OH)_3(aq) + 3H^+(aq) \quad (19)$$

(This reaction reduces the free fluorides ions in solution since it combines with the HCO_3^{2-} responsible for reaction Equation (15)). Since the CO_3^{2-} did not react with CaF_2 previously, it was hydrolyzed in water to give more OH^- which is consumed by H^+ in reaction Equation (19) increasing the dissolution of feldspar surfaces containing fluoride which in turn further exposes the new surfaces from feldspar to the reaction since more H^+ are consumed (Phase II responses).This decreases the resistance of igneous rock against weathering exposing more free fluorides in water (Phase III). Therefore, the different phases in the rock dissolution are caused by a mixture of reactions and nature of the rock; when these processes actively work in a particular environment, their collective effect becomes substantial.

6.4 Conclusions

The present study shows that the fluoride levels in all rivers were spatially distributed from the headwater to the floodplain. The fluoride levels in pristine (headwater) regions of Temi, Nduruma and Tengeru rivers were lower than what WHO and TBS maximum recommendation (1.5 mg/L and 4.0 mg/L, respectively). The spatial variation of fluoride in rivers is a function of rock composition (the amount of fluoride present in it) and availability of HCO_3^- and CO_3^{2-} which accounts for the alkaline environment favourable for fluoride

leaching. Moreover, interaction of groundwater and surface water patterns and external inputs such as surface runoff, salinity and climate change which affects the water temperature also governs its availability. Also, these findings show the importance of environmental conservation in water sources and catchment areas in which the well conserved environment reduce several physical and chemical processes which alters the natural water composition due to low water temperature that minimizes several chemical reactions. The availability of fluoride in water is highly affected by pH such that it is more favoured in alkaline environment. This is evidenced in the laboratory through experiments which indicated that rise in pH could favour fluoride leaching from the feldspar rocks. The floodplain areas of all rivers have shown higher levels of the pollutant as they are accelerated by external factors such as high-water temperature, high water–rock interaction time due to low water velocity, several agriculture activities, and the rock lithology. An exception is observed in Maji ya Chai River where the pristine (headwater) environment showed elevated fluoride levels which is basically caused by its high alkaline environment and fluoride contents in rocks and soil surrounding the river which contain high levels of fluoride containing salts. Also, this study is of great help to different authorities such as AUWASA and the PBWO as it enlightens some of the best practice of catchment area and its management which can minimize pollution of water sources and the cost for water processing.

CHAPTER SEVEN

Assessment of Water Quality Variation in Rivers through Comparative Index Technique and Its Reliability for Decision Making[5]

Abstract

The National Sanitation Foundation (NSF) and Weighed Arithmetic Index (WAI) methods for water quality index (WQI) have been studied to evaluate their reliability in water quality assessment in rivers. Water samples were collected in various GPS predetermined points in Temi, Nduruma, Tengeru and Maji ya Chai rivers−Tanzania during wet and dry seasons and were analyzed for several water quality parameters using standard methods as per APHA. Medium to excellent water qualities were observed for pristine environment in three rivers except Maji ya Chai under NSF and WAI methods, respectively. Excellent water quality was observed in the pristine environment of Temi and Tengeru rivers during wet season. Maji ya Chai water was identified as unsuitable for drinking throughout the year. Fecal Coliforms (FC), Nutrients content, BOD and Fluorides (F^-) were the major contributors to the poor water quality in Maji ya Chai whereas FC and Nutrients were a serious problem in floodplain for other rivers. The two methods showed different overall Water Quality Indices using the same data thus, making them unreliable tools for water quality assessment when used simultaneously for the same purpose. Therefore, selection of the method for water quality assessment and decision making may depend on the water use.

Key words: Water quality Index, Mount Meru Rivers, National Sanitation Foundation, Weighted Arithmetic Index, Water Quality Parameters, Pristine, Floodplain.

[5]**This chapter is based on the published paper:**
Kitalika, Aldo J., Machunda, R. L., Komakech, H. C., & Njau, K. N. (2018). Assessment of water quality variation in rivers through comparative index technique and its reliability for decision making, *Tanzania Journal of Science, 44* (3), 163-193.

7.1 Introduction

Water resources are of great environmental issues and studied by a wide range of specialists including hydrologists, engineers, ecologists, chemists, geologists and geomorphologists (Kumar & Dua, 2009). This is because water affects not only human uses but also plant and animal life. Mount Meru is one of the major catchment areas of several rivers and streams feeding the Pangani main river. While Arusha city, Monduli and Arumeru districts depend on water sources from this area, its overall quality at different river management levels is not well known (UNDP, 2000; Pangani River Basin Management Project (PRBMP), 2006; Kihampa *et al*., 2013). Judgments on water quality in different water sources remain a debate due to the fact that several parameters can be used to contribute in its quality depending on the water use type. Quality of water is defined in terms of its physical, chemical, and biological parameters. However, the water quality is difficult to evaluate from a large number of samples, each containing different values for many parameters (Almeida *et al*., 2007).

Several approaches are used to assess the water quality in respective rivers, this includes; multivariate factor analysis for water quality assessment and water quality indices (WQI) (Qian *et al*., 2007; Tyagi *et al.*,2013) . Among these, the water quality index (WQI) is the most prominent acceptable water quality scaling tool for assessment of water quality for different purposes (Brown *et al*., 1972; Almeida *et al*., 2007). Water quality index method has been developed by establishing the overall water quality using a single scale from contribution of several water parameters to a clearly and simple understood water quality scale such as excellent, poor, good, bad and so on, thus, making it simple for reporting to management and the public, the status of water in understandable and consistent manner. The first WQI was proposed by Horton and it made a great deal for consideration towards development of index methods (Horton, 1965). The method has undergone several modifications to fit different purposes such as inclusion or exclusion of some other factors which have potentials to different health defects such as carcinogens and weighed contributing factors balance (Debels *et al*., 2005; Abtahi *et al*., 2015). However, the basic components and purpose of WQI methods being a mathematical instrument used to transform large quantities of water quality data into a single number which represents the water quality level while eliminating the subjective assessments of water quality and biases of individual water quality experts remain unchanged. Basically, a WQI attempts to provide a mechanism for presenting a cumulatively derived, numerical expression defining a certain level of water quality (Miller *et al*., 1986). Several methods have been used to develop WQI for different

use. The commonly used methods includes, the National Sanitation Foundation (NSF) method being the most prominent and the Weighted Arithmetic Index (WAI) Method. In this study, the two methods are used to evaluate their reliability in assessment of water quality by using Temi, Nduruma, Tengeru and Maji ya Chai Rivers and thus, its overall quality for each river will be unveiled.

7.2 Materials and methods

7.2.1 Description of study area

The study was conducted in Themi and Nduruma rivers and their catchments which lie within the Arusha City together with Tengeru and Maji ya Chai Rivers which lie within the Meru District. The four rivers originate from common sub-catchments of foot hills of Mount Meru lying from the eastern part to the south west of the mountain (Fig. 1). The rivers run downstream from the mountain to the south east. The study area was divided into three regions depending on the river and land development namely, pristine (headwater) (3° 15' 00"S to 3° 20' 00"S), middle (3° 20' 00"S to 3° 25' 00"S) and flood-plain (3° 25' 00"S to 3° 35' 00"S).

7.2.2 Sampling and analytical methods

Two-liters (2 L) of water samples were collected at each point using a 1-liter Teflon capped glass bottle and another 1-liter Teflon capped plastic bottle downstream from the source of each river as shown in Fig. 1. Water samples were collected downstream from monitoring stations established by the Pangani Basin Water Office (PBWO) and other points depending on the confluence and accessibility of the riparian environment. The sampling stations and number of samples collected were dictated by the length of the rivers and their feasibilities. Therefore, eleven (11) sampling stations were identified for Themi River where as twelve (12) sampling stations were identified in Nduruma River. In addition, twenty-one (21) sampling points were identified in Tengeru River together with seven (7) stations which were identified in Maji ya Chai River. Samples from plastic bottles were used for metal analysis and other parameters whereas samples in glass bottles were used for nutrients and other organic components analysis. The sampling was done during the wet season (Mid–March to early April) and dry season (August) in 2015 in order to compare their seasonal quality differences and usability. Several water quality parameters were measured as explained thereafter. Temperature, pH, total dissolved solids (TDS), dissolved oxygen (DO) and

electrical conductivity (EC) were measured in-situ using a HANNA multiparameter Model HI9829 whereas the total hardness were measured by acid titrimetric method. Samples for nitrate analysis were collected in half liter glass sampling bottles and immediately acidified with concentrated sulphuric acid to a pH below 2 to stop any further nitrate transformation. All samples were stored in a cold box and immediately transferred to the laboratory for analysis and preservation in the second day. The analysis for BOD, nitrates (NO_3^-), fecal coliforms (FC) and total suspended solids (TSS) were done following standard methods (APHA, 2012). In addition, total phosphates (TP) and soluble phosphates (SP), sulphates and chlorides were measured using HACH 2800™ while, turbidity and alkalinity were measured using a 2100Q01 HACH portable turbidimeter with formazin turbidity standard 4000 NTU in serial dilutions to the required standards and HANNA alkalinity checker HI 755, respectively.

7.2.3 Assessment of WQI

Two approaches for calculation of WQI, the WAI and the NSF were used to evaluate the water quality of each river. Measurements were made basing on the average value for water quality parameter of different sampling points in the respective river region.

7.2.4 The weighted arithmetic index method

Brown *et al.* (1970; 1972) considered several variables for weighted arithmetic index method which follows some steps for its estimation. The first step involves calculation of sub index of quality rating (*qn*) (Equation 20); qn is calculated basing on the number of water quality parameters involved in establishing the WQI. Suppose there are *n* water quality parameters where the quality rating or sub index (q_n) corresponds to the n^{th} parameter, then the number reflecting the relative value of this parameter in the polluted water with respect to its standard permissible value is given by the expression.

$$q_n = \frac{(V_n - V_o)}{(S_n - V_{io})} \qquad (20)$$

Where,

q_n = quality rating for the nth water quality parameter.

V_n = estimated value of the nth parameter at a given sampling station.

S_n = standard permissible value of nth parameter

V_{io} = ideal value of nth parameter in pure water.

All the ideal values, V_{io} are taken as zero for drinking water except for pH 7.0 and dissolved oxygen concentration of 14.6 mg/L (Tripaty & Sahu, 2005).

The second step involves calculation of proportionality constant (K) for all water quality parameters which is the reciprocal of the sum of reciprocals of the standard permissible values for each parameter (Equation 21).

$$K = \frac{1}{\left(\frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3} + \cdots \frac{1}{S_n}\right)} \tag{21}$$

The third step involves calculation of unit weight (W_n) for various water quality parameters which is inversely proportional to the recommended standards for the corresponding parameters (Equation 22).

$$W_n = \frac{K}{S_n} \tag{22}$$

Lastly is to develop an equation for determination of WQI using the WAI Method (Equation 23).

$$WQI = \frac{\sum_{n=1}^{n} q_n W_n}{\sum_{n-1}^{n} W_n} \tag{23}$$

The excel file was prepared for all variables in equations (19 through 22) using ten (10) water quality parameters namely; pH, Dissolved oxygen (DO), Total dissolved solids (TDS), Fluorides (F^-), NO_3^-, Total phosphates (TP), water temperature (T), turbidity, Fecal Coliforms Units (FCU), and Biochemical oxygen demand (BOD) and were GIS integrated for computation of overall WQI for each sampling point.

7.2.5 The NSF method for water quality index

This method was developed in the early 1970's and later was adopted by NSF (Brown *et al.*, 1970). Nine water quality parameters namely, DO, pH, temperature, TDS, BOD, nitrates, FC, TP and turbidity were considered each with its weighing factor totaling to 1. Thus, this method is specific to particular water quality parameters which were assembled by 142 water quality experts in the United States (US). The pre-established rating curves for quality index values (QI) for each water quality parameter is used to establish the overall WQI of particular water since each parameter has a fixed weighing factor. The QI value is then multiplied by

weighing factor to get the WQI for that parameter (Kesharwani *et al*,. 2004). The results are then summed to get the Overall WQI as given by Equation (24).

$$WQI = 0.17_{DO} + 0.11_{pH} + 0.10_{\Delta T} + 0.07_{TDS} + 0.11_{BOD} + 0.10_{NO_3^-} + 0.16_{FC} + 0.10_{TP} + 0.08_{TURB} \quad (24)$$

7.2.6 Conversion of dissolved oxygen concentration to percentage (%) saturation

All values for calculating the WQI by NSF method are used in their standards of measured values. However, the amount of DO in water is much affected by the atmospheric pressure and temperature: the two being an altitude function. These effects can be corrected by the Equations (25) through (29) (Mortimer, 1956). The equilibrium oxygen concentration at any pressure C_p is given by:

$$C_p = C^* \times P\left[\frac{(1-Pwv/P)(1-\theta P)}{(1-Pwv)(1-\theta)}\right] \quad (25)$$

Where;

C*= equilibrium oxygen concentration at standard pressure of 1 atm, mg L^{-1}

P = measured pressure, atm

P_{wv} = partial pressure of water vapour at temperature, t (atm).

$$\theta = 0.00095 - (1.426 \times 10^{-5} t) + (6.436 \times 10^{-8} t^2) \quad (26)$$

where;

t = temperature, °*C*

$$\ln P_{wv} = 11.8571 - \left(\frac{3840.7}{T}\right) - \left(\frac{216,961}{T^2}\right) \quad (27)$$

Where;

T= temperature, K

But, the measured pressure (*P*) at altitude *h* is given by:

$$\ln P = 5.25 \times \ln\left(1 - \frac{h}{44.3}\right) \quad (28)$$

Hence, the % saturation of DO concentration (mg/L) is given by:

$$\% \text{ Saturation} = \frac{100 \times DO}{C_p} \quad (29)$$

Where; DO is the measured (experimental) value.

The measured DO for each sample was corrected before including it in the calculations and the spread sheet for excel file was prepared to calculate the DO % saturation at recorded temperature.

7.2.7 GIS based water quality analysis

In this study, the two water quality assessment techniques (WAI and NSF) were integrated with ArcGIS to determine the overall water quality at various sampling points. Each water quality parameter was calculated in excel spread sheet using Equation (23) and (24) and its components were filled in the ArcMap attribute table. The effective weights of the each water quality parameter were calculated using ArcGIS analyst tool and the water quality grades were marked by quantitative classification using graduated colours based on prescribed NSF and WAI standards as shown in table 1 (Şener *et al.,* 2017). Nine water quality parameters including BOD (mg/L), NO_3^- (mg/L), TDS (mg/L), fecal coliforms (FCU/100 mL), DO (% saturation), pH, turbidity (NTU), total phosphates (mg/L) and temperature (°C) were combined in both models. Also, since the WAI method is flexible to addition of more parameters, another model which includes fluoride ions was run to assess its effect in water quality since the pollutant is available in waters of these rivers and has potential health effects in development and strength of human skeleton.

7.2.8 GIS based WAI technique spatial distribution

This technique employed both the excel spreadsheet and ArcGIS software as explained before. The Quality rating (qn) for the n^{th} water quality parameter for each sample point and the unit weight (W_n) for n^{th} water quality parameter were calculated in excel environment using Equation (23). The standard grades used for classification of water quality by WAI and NSF method in this study are shown in Appendix 4 and 5. The overall WQI for each GPS predetermined sample point for both seasons was calculated using equation (23) under field calculator tool in ArcGIS 10.1 environment.

7.2.9 GIS based NSF technique spatial distribution

In this technique the quality index of each water quality parameter was determined from their respective rating curves. Then, the overall WQI for each GPS predetermined sampling point was calculated as per Equation (24) using field calculator tool in ArcGIS software 10.1.

7.2.10 Principal component analysis

The Principal Component Analysis (PCA) is an important tool used to reduce multiple observed variables contributing to a particular property to a small number of variables called principal component (Jolliffe, 2002). In this study the PCA for determination of the major contributing parameters (factors) in the water quality variation to the respective point was performed using OriginLab software version 8.6. The variables were supplied in the worksheet of the software and the multivariate for PCA was done as explained in the software manual (Origin Lab, 2010). The contributing factors were retained based on whether they could satisfy both the Kaiser and Cattell criteria conditions (Cattell, 1966; Kaiser, 1960). The two criteria were used in order to maximize the number of stronger contributing factors to a particular water quality and thus, minimizing the errors for omitting any necessary water quality parameter. In the Kaiser criterion, the contributing factors with Eigen value ≥ 1 were selected whereas using the Cattell criterion the Eigen values were plotted in descending order against the principal components to screen the variables and from the scree plot the principal components were selected basing on the significant break off of the graph (Cattell, 1966; Kaiser, 1960,).

7.2.11 Reliability of WAI and NSF methods

Assessment for the test whether the two methods are consistent and could give the same result upon using the same water quality parameters were tested by comparing the results obtained after data processing. The assessment was done by comparing the water quality levels of the respective class for a particular method using the same water quality parameters with expectation that the two methods cold give similar results.

7.3 Results and discussion

The WAI and NSF quality status scales and the calculated WQIs are summarized in Table 27 and 28. Also, Fig. 33, 34 and 35 shows the results for GIS based spatial analysis of water quality in the study area and thoroughly discussed in their respective sections.

7.3.1 The PCA criteria for major contributing components

Three components/parameters were retained in Themi River during wet season with Eigenvalue in brackets (4.95935, 2.19463 and 1.12749 where 82.8% are covered) and four components (4.59504, 2.43857, 1.17054 and 0.6224 where 82.04% are covered) were retained in dry season whereby, for Nduruma River three components (4.1363, 1.8552, and 1.3858 where 83.67% are covered) and four components (4.76565, 2.0851, 1.13421, 1.04259 where 90.28% are covered) were retained in wet and dry seasons, respectively. Tengeru River retained four components with (4.26557, 1.93561, 1.15874 and 0.90464 where 82.69% are covered) and (3.94866, 1.60458, 1.27979, 0.86643 where 84.80% are covered) were retained in wet and dry seasons, respectively. Maji ya chai River had two components (7.24753and 2.08298 where 97.21% are covered) and three components (5.98628, 2.7757 and 0.73816 where 97.21% are covered) during wet and dry seasons, respectively. Other components were not retained since they had less representation to the overall effect of water quality of the respective sampling point.

Table 27: Status of water quality based on WAI and NSF

WQI		STATUS	
NSF	**WAI**	**NSF**	**WAI**
0–25	<50	Very bad	Excellent
26–50	50–100	Bad	Good
51–75	100–200	Medium	Poor
76–100	200–300	Good	Bad
Above 100	>300	Excellent	Unsuitable for drinking and fish culture

Ramakrishniah C. R., Sadashivaiah, C., & Ranganna, G. (2009). Assessment of Water Quality Index for the Groundwater in Tumkur Taluk. *E-Journal of Chemistry*, *6*(2), 523–530

Table 28: Water quality index statuses based on WAI and NSF techniques

SAMPLE POINT	RIVER	WQI		NSF		RELIABILITY
		WET	DRY	WET	DRY	
Te1	Temi	Excellent	Excellent	Good	Medium	Differed
Te2	Temi	Excellent	Excellent	Medium	Medium	Differed
Te4	Temi	Excellent	Excellent	Medium	Medium	Differed
Te6	Temi	Excellent	Excellent	Medium	Medium	Differed
Te8	Temi	Good	Poor	Medium	Medium	Differed
Te10	Temi	Unsuitable	Unsuitable	Bad	Bad	Differed
N1	Nduruma	Good	Excellent	Medium	Medium	Differed
N3	Nduruma	Good	Poor	Bad	Medium	Differed
N5	Nduruma	Good	Good	Medium	Medium	Similar
N7	Nduruma	Poor	Good	Bad	Medium	Differed
N9	Nduruma	Good	Good	Medium	Medium	Differed
N11	Nduruma	Poor	Poor	Medium	Medium	Differed
T1	Tengeru	Excellent	Good	Medium	Medium	Similar
T3	Tengeru	Good	Poor	Medium	Medium	Similar
T7	Tengeru	Good	Good	Medium	Medium	Differed
T10	Tengeru	Excellent	Good	Medium	Medium	Differed
T13	Tengeru	Excellent	Excellent	Medium	Medium	Differed
T18	Tengeru	Good	Poor	Medium	Medium	Differed
M1	Maji ya Chai	Good	Poor	Bad	Bad	Differed
M2	Maji ya Chai	Poor	Bad	Bad	Bad	Differed
M3	Maji ya Chai	Poor	Poor	Bad	Bad	Differed
M4	Maji ya Chai	Good	Poor	Medium	Bad	Similar
M5	Maji ya Chai	Good	Poor	Medium	Medium	Differed
M6	Maji ya Chai	Good	Poor	Medium	Medium	Differed

7.3.2 Water quality index by NSF method

The established WQI by NSF was done by using nine (9) water quality parameters. However, there are other parameters with crucial importance in safe and clean water which were not included in this method. For example, in this study area, fluoride is among the major water pollutants as it causes serious health problems on human health. Therefore, additional method which could accommodate more important parameters for further evaluation of the same water body is discussed in subsequent sections. Thus, the results discussed in this section are based on the nine water quality parameters and their output shown in Fig. 33.

The pristine environment (headwater) in Themi River showed to have a medium water quality despite the fact that it is a conserved area. In this area the FC (11-29 %), TP (2-35 %) and temperature (19-31 %) contributed more to the low water quality in both seasons. The presence of FC in the pristine environment of the river might be contributed by the living primates in forests such as baboons, simians and monkeys which dominate in the forest. The pristine environment of this river has no any kind of human activities such that the most likely source of FC could be from human closely related wild animals, the primates. These animals excrete in catchment areas with their feces being transported through runoff. Furthermore, the presence of FC in the downstream with human inhabitants can be due to transport of feces from animals in the pristine environment and open defecation of people along the river. Studies show that FC is common on surface water of Arusha City and Arumeru Districts in which two studies reported more than 100 FCU/100 mL of water (Lyimo *et al*., 2016; Kitalika *et al*., 2017). However, the presence of high TP can be of geological reason due to the nature of surrounding rocks. Also, dead animals buried in soil such as birds may contribute to elevated levels of phosphates.

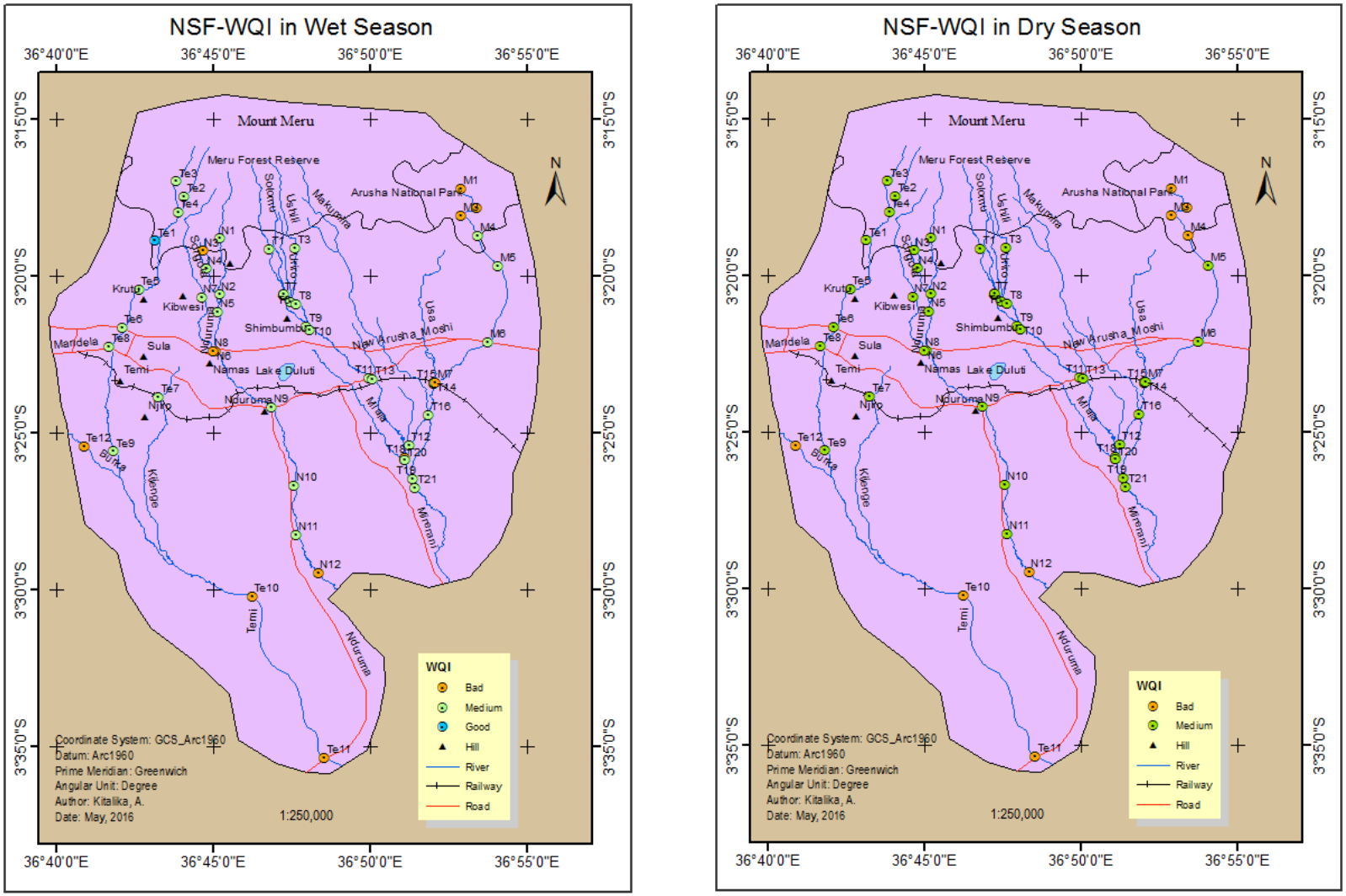
Contributions of other parameters to high water quality are quite good with turbidity (99%) being the best contributing parameter followed by BOD (95 %). The good contributions of these parameters are due to the good conservation practices of Mount Meru Forest Reserve. Also, in the dry season NO_3^- increased due to the fact that, in this season, rivers are the only water sources for wild animals: as they drink water, they also excrete in those water sources. Despite all these, the overall water quality in pristine environment is medium and thus, pretreatment is necessary. The good water quality at Te1 can be contributed by low pollutant loads which had less effect in the water quality.

When water from the pristine environment passes through the human settlements from pristine environment, its quality is maintained. This indicates low pollution inputs in the river from anthropogenic activities in both seasons. The flood-plain showed bad water quality due to low contributions from FC (20 %), NO_3^- (1 %), TP (2 %) and BOD (15 %).

These inputs were much pronounced from Burka (Te12) which is a feeding tributary of the main river. Also, the bad water quality in this part of the river may be attributed by the fact that the flood plain is connected with the waste water treatment systems at Lemara (Te9) which accumulates domestic and industrial waste and thus, raising the pollutant levels with high effects being from nutrients (Figh. 35I). In addition, the low water velocity in the flood-plain (Te10 and Te11) favoured more interactions time of surface water with rocks and wastes together with groundwater surface water interactions which might have increased the pollutants loads in fresh water. Similar pollution patterns were observed in both seasons for this part of the river.

The water quality for Nduruma River was medium in the pristine environment in both seasons. It is expected that the pristine environment in this river should have excellent water quality, but that is not the case due to poor or very low-quality index which is contributed by FC (19-22 %) and nitrates (29 %) in both seasons. While temperature is not an issue in this mountainous region, FC increase especially in the dry season can be a contribution from primates' littering since there are limited water sources in the dry season which are used by wild animals for drinking. Other factors remain of less contribution in water quality in this region.

When the river flows across the human settlement and floodplain, the water quality response in the two seasons is maintained except at one sampling point (N8) which has bad water quality due to increase in oxygen demanding wastes caused by runoff from the households during the wet season. However, this situation is recovered along as the river runs to the flood-plain where its water quality is medium. To the extreme downstream (N12), the water quality deteriorates due to nutrients inputs from farming activities such as manure and industrial fertilizers runoff. While nutrients can be contributed by fertilizers runoff from small and big horticultural farms around it, the high BOD in such water is another problem. This phenomenon may be due to such nutrients and their associated organic wastes being high oxygen demanding.



(a) **(b)**

Figure 33: The NSF based water quality in (a) wet and (b) dry Season

Tengeru River had medium water quality in both seasons throughout despite of the different inputs from other several streams which had also medium water quality. This important river behavior is contributed by well conserved riparian environment of the river and its feeder streams. The water quality downstream was expected to be distorted due to contributions from Maji ya Chai River which have bad quality. However, that was not the case due to its insignificant dilution by the main river. A similar water quality throughout the river indicates constant contributions of pollutants in all areas along the river.

The headwater from Maji ya Chai River had bad water quality in both seasons. Most parameters contributed negatively to the good water quality with exception of turbidity (92-99 %) which had good contribution. In this river, despite its water colour to be excessively brown due to dissolved organic carbons and hence, its name in Swahili "Maji ya Chai" meaning that tea coloured water, it is not turbid. More interestingly, this river has little or no fish lives in headwater (M2) an indication for bad water quality even for aquatic life. The larger part of this river is situated in the Arusha National Park which is among the highly conserved area. Thus, the bad water quality in the pristine environment is mainly caused by high amount of oxygen demanding wastes due to river source deterioration done by wild animals especially elephants and buffalos which dominate the catchment area. Moreover, high pH (alkaline water) adds more problems to its quality. The downstream of the river have medium water quality which is a result of dilutions from streams with medium water quality (Fig. 33). A similar study was done in Ruvu River and found the quality rating of 49.9, 52.0 and 57.8 for the year 2014, 2016 and 2017 respectively. The overall rating of 53.2 indicated that water quality of river in study stretch is in the medium range. The BOD, DO and FC was found to be most stressing parameters overall sampling locations due to improper sanitation systems, discharge of untreated and partially treated wastewaters from industries and domestic into the river (Alphayo & Sharma, 2018).

7.3.3 Water quality index by WAI

The results of water quality status by WAI in the four rivers are presented in Figure 34. Water quality index by WAI assess unlimited parameters to establish the overall water quality of a particular water body. For the purpose of reliability of the two methods, nine (9) water quality parameters used in NSF were employed for assessment by WAI. In addition, since F^- is also a serious problem in this area, a new assessment including such pollutant was done to evaluate its contribution to the overall water quality for all rivers. Despite using the same data

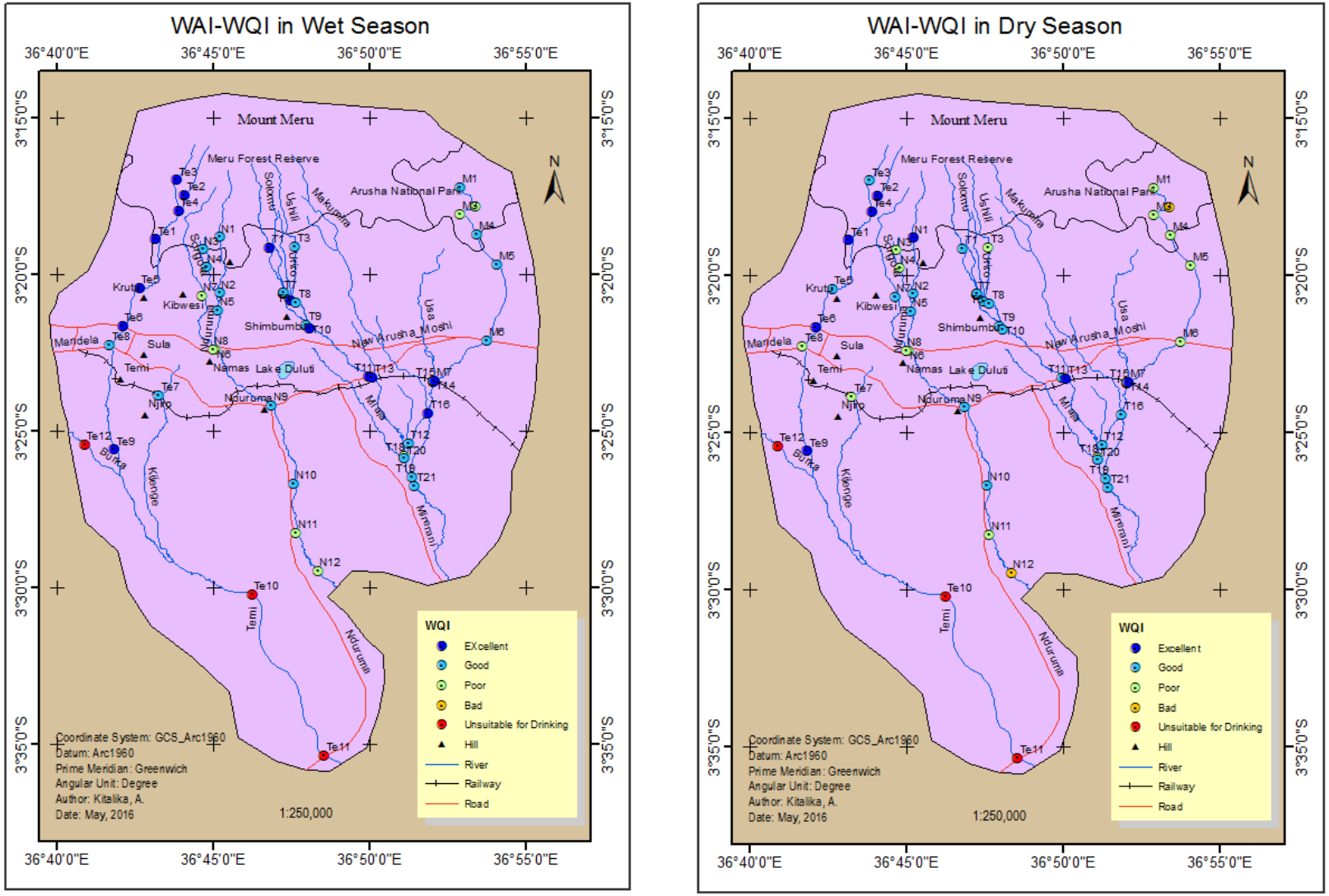
values in assessment, the water qualities by this method differed from NSF method such that in some areas it has been higher or lower than NSF. Under this method, both seasons in most parts of pristine environment (headwater) in Themi River showed excellent water quality with some few points (Te3 and Te5) indicating good water quality during dry seasons whereas in comparison with the NSF method the water quality was medium in most parts.

Meanwhile, the human settlement areas showed medium to poor water quality in both seasons compared to NSF method in which the medium water quality predominated. While these results occurred on the upper part of the river, its flood-plain water quality appeared to be unsuitable for drinking. In this area, the water quality by NSF method appeared to be bad.

For Nduruma River, the WAI method showed good water quality in pristine and human settlement areas in both seasons with some few areas (N3, N4, N6 and N7) being poor in both seasons. Its flood-plain had poor (N11 and N12) to bad (N12) water quality similar to NSF scales in both wet and dry seasons respectively. Similar reasons with NSF accounts for the poor water quality in the flood-plain of this river under this technique.

Similar water quality patterns are shown in Tengeru River by WAI method in both seasons. While the overall water quality for the whole river in both seasons is medium by NSF method, WAI shows good water quality in the two areas during wet season with its wet season being excellent in some areas (T1, T8 and T10) and good for pristine and urban areas respectively. This quality rating is higher than NSF rating for the same water body. The excellent water quality in dry season may be attributed by absence of runoff which is one of the major waste input sources in rivers during wet season. However, since waters of this area contain some pollutants grading its water quality in excellent condition is questionable.

For Maji ya Chai River, better water quality scales (good) were observed by this method in the wet season whereas, in the dry season the water quality was regarded as poor throughout the river with exception of Jamera (M2) which had poor to bad water in wet and dry seasons respectively. This area is exceptional due to absence of DO and also very high pH of up to 9.9. It should be noted that the main water pollutants in this river are mainly fluorides and chromophoric organic matters which are naturally occurring humus in Kirurumu hill located in the western part of Jamera. The WAI method for water quality analysis was employed in different water quality studies in rivers and ponds of Egypt and Argentina and showed good and comparable results for water quality monitoring similar to this study (Kesharwani *et al*., 2004; Moscuzza *et al*., 2007; Ali *et al*., 2014).



(a) **(b)**

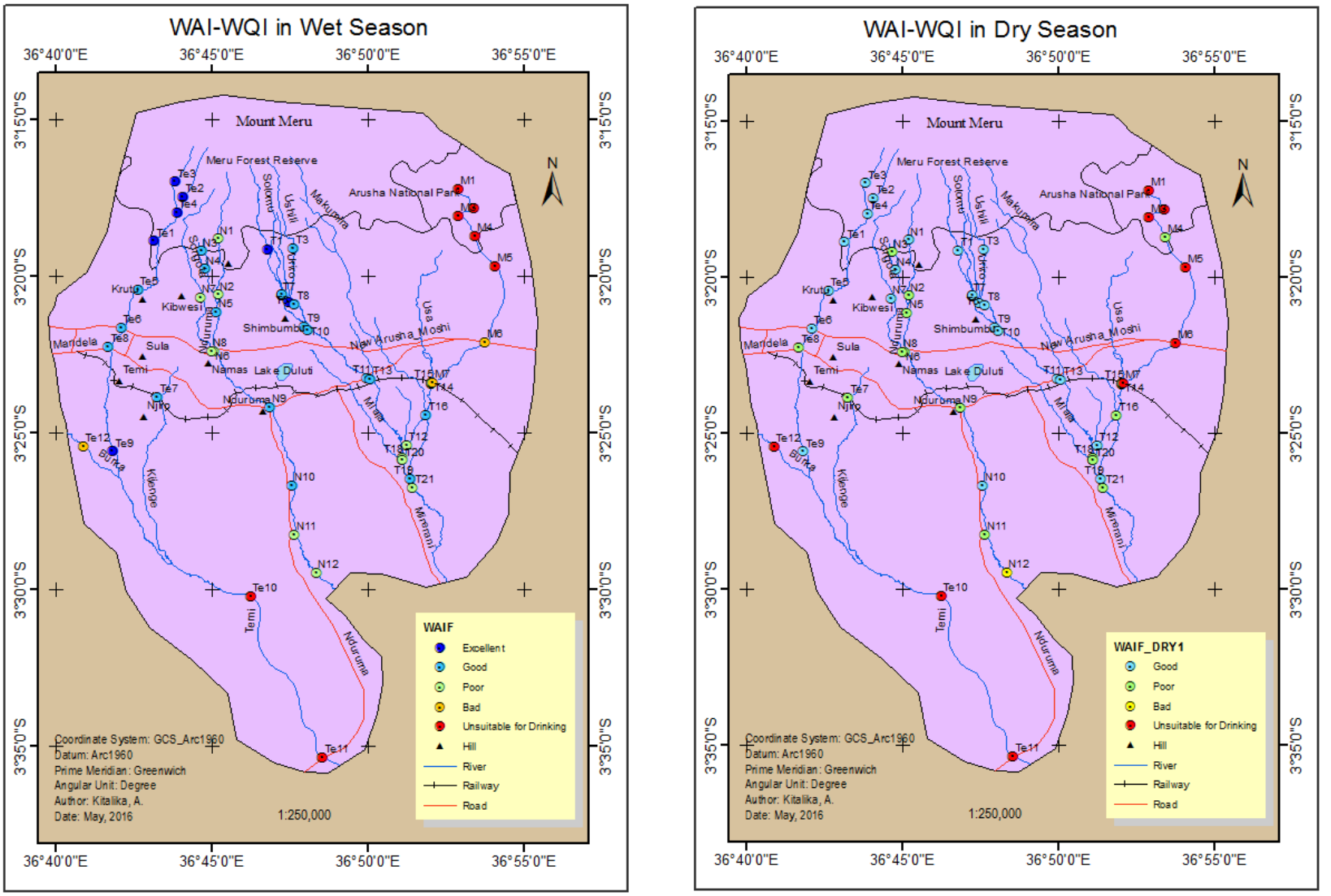
Figure 34: The WAI based water quality in (a) wet and (b) dry season

7.3.4 The WAI with fluoride pollutant source

Inclusion of fluorides concentrations in establishing the WQI in the four rivers is necessary due to its prominence as the major pollutant in the study area since its presence in drinking water compromises with the health of human skeleton. Their results of water quality status by this method in the four rivers are presented in Fig. 35. The presence of fluoride among pollutants changed the whole trend of water qualities in their respective points with Maji ya Chai River being mostly affected due to its high fluoride contents.

The excellent water quality in the pristine environment of Themi River was maintained due to the low fluoride contents compared to its standard permissible values of 1.5 mg/L and 4.0 mg/L as per WHO and Tanzania Bureau of Standards (TBS), respectively (WHO 2004, TBS 2014). However, its flood-plain part maintained its status of unsuitability for drinking. The water quality in Nduruma River was slightly affected in the dry season at N2, N5 and N8 from good to poor water quality. The situation is different for Tengeru River in the dry season where by most parts of the flood-plain, presence of fluorides decreased its water quality from good to poor. Such changes can be attributed by increase in fluorides in Makumira and Maji ya Chai rivers.

The serious changes were observed in Maji ya Chai River in both seasons whereby the water quality for most parts of the river were unsuitable for drinking. Despite the high BOD levels due to presence of high amount of humic and fulvic acids, the unsuitability of this river throughout is caused by very high fluoride concentrations of up to 69.01 ± 0.03 mg/L which are quite higher compared to its maximum standards of 1.4 mg/L and 4.0 mg/L for WHO and TBS, respectively (WHO, 2004; TBS, 2014). From this observation, it is clear that including several important water quality parameters like fluorides in water quality assessment has an added advantage for understanding the actual quality of the river. Previous studies on WQI from various scholars through modified WAI in different rivers showed no significant changes in the water quality studies based on temporal but at spatial analysis level being significant (Debels *et al.*, 2005; Abtahi *et al.*, 2015). In this study, similar results have been observed in both modified and unmodified WAI methods as discussed above.



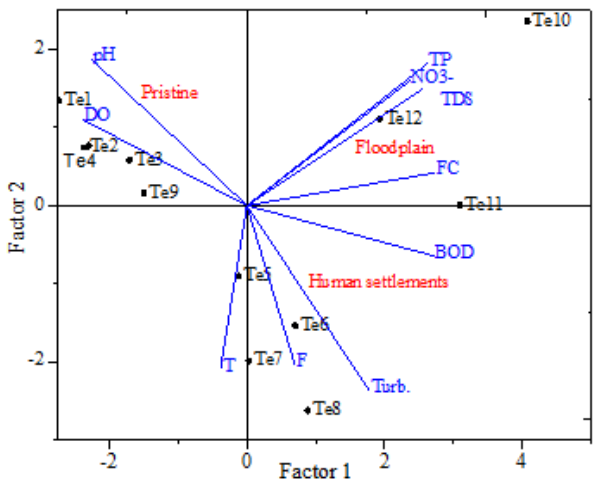
(a) **(b)**

Figure 35: The WAI based water quality in (a) wet and (b) dry season with fluoride

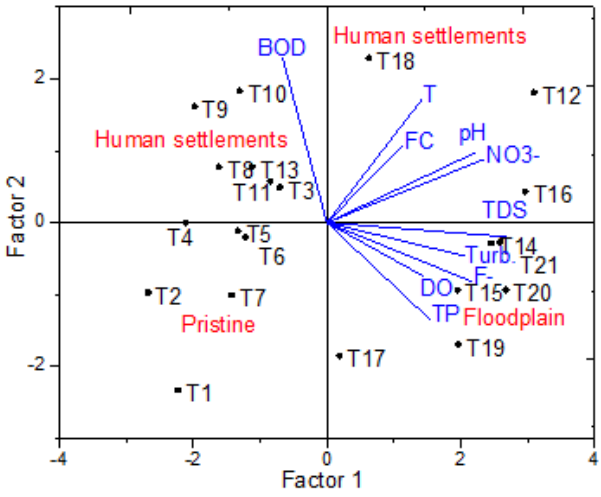
7.3.5 The Principal component analysis for the major contributing factors

The Principal component analysis (PCA) was performed to assess the principal factors (variables) which caused water quality changes in their respective points. The study shows that in wet season DO and variation in water pH were major factors for water quality changes in the pristine (headwaters) environment of Themi River whereas in the human settlement environment temperature (T), F^{-}, turbidity and oxygen demanding waste were the significant cause for water quality change. In addition, the water quality in the flood-plain environment was much affected by increase in nutrients (NO_3^- and TP) loads, increase in total dissolved solids (TDS) and FCs. While the nutrients in the flood-plain are loaded from the city wastewater treatment system, increase in FC, NO_3^- and TP may be caused by loading of ineffective treated domestic and industrials wastes from the city sewage treatment system. A different situation was noted in the dry season where in the pristine environment neither the parameter contributed strongly to the water quality variation perhaps due to absence of runoff. Water temperature, FC, pH, NO_3^- and TDS were the major contributing factors in human settlement environment whereas, turbidity, fluorides, DO, and phosphates contributed much in the flood-plain (Fig. 36 I). The presence of phosphates in the flood-plain during dry season indicates poor performance of the city waste treatment system towards phosphates (TP) removal since NO_3^- was readily removed.

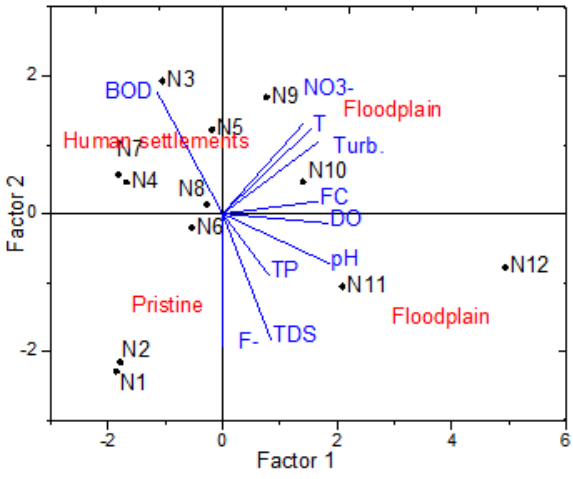
There was no dominant pollutant in the pristine water in Nduruma River during wet season despite the dominance of DO, FC and NO_3^- nutrients in dry season. Pollutant dilution by precipitation in wet season can be the main cause of their low levels whereas dominance of NO_3^- and FC in dry season can be caused by pollution from animals which migrate near the water sources during dry season, and thus adulterating it since a few water sources (catchment areas) in dry season produce water for wild animals' drinking (Fig. 36 II). Under such circumstances the remaining water source are used above their capacity which in turn lower the quality of water sources through defecation and other physical disturbance of the catchment areas.



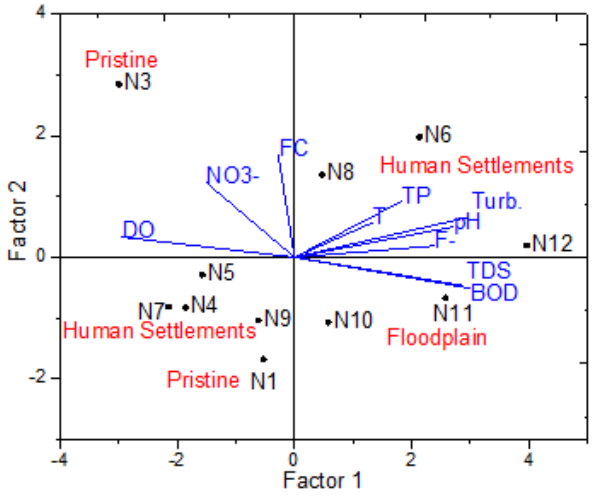
I (a)Temi Wet



I(b) Temi Dry



II (a)Nduruma Wet

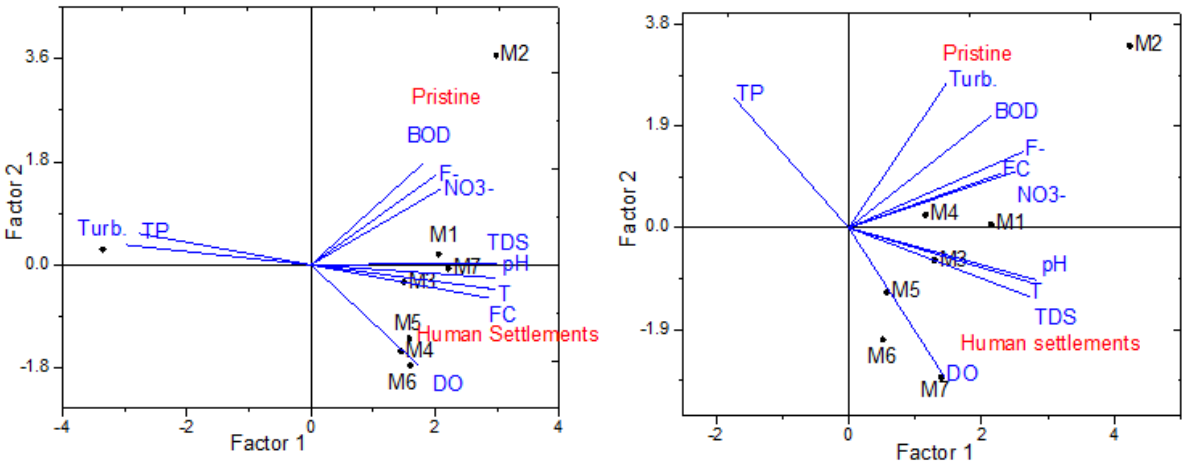


II (b)Nduruma Dry

Figure 36: The principal component analysis for Temi (Te) and Nduruma (N) Rivers

I (a)Tengeru Wet

I(b) Tengeru Dry



II(a) Maji ya Chai Wet **II(b) Maji ya Chai Dry**

Figure 37: The principal component analysis for Tengeru (T) and Maji ya Chai (M) Rivers

Similar reasons can account for this change. The water quality in the human settlement areas were compromised mainly by oxygen demanding wastes (BOD, low DO) whereas in the dry season TP, pH, turbidity and F^- were the main sources for water quality change.

The flood-plain in the wet season were more affected by NO_3^- inputs, turbidity and FC loads, while in dry season TDS and oxygen demanding waste were the major issues of concern.

Interestingly, the pristine water in Tengeru River was less affected by a combination of pollutant sources. While this happened, other parts of the river were compromised by nutrients loads, F^-, FC, pH and slightly warmer water thus lowering the water quality in both seasons (Fig. 37 I). The flood-plain water was much affected by oxygen demanding wastes probably due to runoff due to poor farming activities while turbid water, F^- and DO variations were significant in both seasons. Tengeru River is much associated with Maji ya Chai River, the latter feeding its waters into the former. Thus, its water in human settlement areas were similarly affected by change in DO, pH and temperature in both seasons with FC affecting much in the wet season while presence of TDS being a problem in the dry season. The pristine water was much affected by NO_3^- and oxygen demanding wastes these being expected due to the continuous loading of humus in the river (Fig. 37 II). Increase in dissolved humic and fulvic acids in such water in both seasons results into increased TDS in it and hence, its brown colored of "Maji ya Chai." The previous study on stable isotopes of $^{15}N\text{-}NO_3^-$ revealed nitrate sources in the headwater to be from ground water such that the ground water containing nitrate are mixed with surface water. The NO_3^- sources in the floodplain were from nitrogenous industrial fertilizers spilling from farms through runoff especially during the wet season (Kitalika *et al*., 2017).

7.3.6 Reliability of NSF and WAI methods

Reliability is among the necessary conditions for different scientific methods to give similar experimental results when the same data set is used. In this study the WAI and NSF methods were expected to provide similar results in overall water quality despite their differences in their approaches for water quality assessment. However, in this study some differences between these methods were noted. Despite the similarity in number and values of water quality parameters used for assessment of water quality in the two methods, yet they both showed variation in its overall water quality with WAI carrying higher grades than water

qualities indicated by NSF. Only a few observations showed some similarities. Also, in some other few cases the NSF method carried higher grades than WAI. More interesting the WAI was able to rate the water containing large number of FC to be in "excellent" conditions especially in the head water environment as shown in Table 28. From this table most parts of the river had different quality outcomes. To mention a few examples from some rivers the pristine environment of Themi River rated "excellent" water quality by WAI where as the "good" and "medium" water quality are rated by NSF method from the same water quality parameters and part of the river during wet and dry seasons, respectively. Excellent water quality ratings were obtained in some sampling points under the WAI. At this rating level the water condition is normally regarded as "portable water" indicating high aesthetic value and absence of all disease-causing pathogens the case which is different from the real observation in all samples. Under such conditions, the water quality assessment by WAI can be regarded as over-scaling since it is difficult to get the excellent water quality from its natural environment of the river. More differences are observed in the pristine environment of Nduruma River where the WAI ranked "good" water quality in both seasons while with similar quality parameters a "bad" to "medium" qualities are experienced and so on. From these few pointed examples, we can establish a good fact of no doubts that the two methods can be good when used together to establish particular water quality but unreliable when one method is used for water quality judgments.

7.4 Conclusion

The flexibility of WAI to accept addition of several other water quality parameters adds more advantages for its adoption than the NSF method in terms of extensive water quality examination. Moreover, addition of FC parameter adds some errors in the whole meaning for WAI-WQI since we cannot set its standard amount of the pathogens which are tolerable in human body. The question is which method is to be adopted for decision making? Using this case study, the answer can be any method if the two could give similar results. However, the noted differences in this study may give a benefit of doubts to users under either the technique. An individual can decide to adopt both methods separately depending on the intended water use. Also, under such situations and for the purpose of decision making, precautions should be made by considering the parameters that are expected to be harmful in water and thus, the flexibility of WAI gives more advantages for use.

In this study the water quality in the pristine environment was good in all rivers except that of Maji ya Chai while in the flood-plain the quality was bad in all rivers in wet seasons. Bad water quality in flood-plain was mainly contributed by runoff and flooding in those areas. Maji ya Chai River showed exceptions in its water quality since it had bad quality throughout. The two methods for water quality assessment (NSF and WAI) seem to work but their differences in its overall quality should be worked separately for proper decision making depending on intended water use. Some accentuated water parameters such as FC showed to accelerate the difference between the WAI and NSF methods since it is difficult in tropical areas to find water in rivers without FC.

Furthermore, since the fully developed parts of the river indicated medium water quality, then it is likely that a well conserved riparian environment of the river gives a high possibility to harvest water in its fully developed parts. This practice will decrease the chances of affecting the major watersheds and catchment areas through constructions of water collection points. Also, tapping water in fully developed parts of the rivers will optimize the quantity of water harvested in rivers since they offer maximum discharge compared to the pristine environment which most parts of them contains potential springs to recharge the main river. In addition, it is necessary to establish the water quality of the whole river before deciding at what point water taping should be done to minimize water processing cost and maximize output. Moreover, the standard water temperature can be modified to start from a value just above 0 °C which is the temperature at which water exist as liquid instead of 35 °C which is a higher temperature since most catchment areas for many rivers start from mountainous areas which are normally colder than the established standards. Despite the observed differences, the two methods cannot be abandoned but used with precautions as reminded by the precautionary principle demanding precaution to be taken for anything harmful or seems to be harmful even if the scientific reason is not yet established as why that happened (Myers, 2002). Lastly, the water quality study using WQI technique under WAI and NSF method when integrated with GIS describes more about the river status which can be useful for management strategy of a particular place and its output map can easily be understood used in the society.

CHAPTER EIGHT

General discussion, Conclusions and Recommendations

8.1 Land use change of the study area

Chapter one has discussed on the land use change occurring on the slopes of Mount Meru vesting on changes which has occurred in thirty–year period of time. The results of profound importance were noted on depletion of bush land and mixed forest for agriculture and human settlements. The study has shown a good achievement in increase of forest conservation from 139.7 km^2 in 1986 to 174.9 km^2 in 1996 which is a good success towards environmental conservation. However, the success which occurred in the ten (10) years dropped in 2006 when parts of the forest were converted into settlements. Perhaps, the economic transitions which occurred in those years (which included privatization of various government plantations) stimulated development which accelerated the urbanization process of the Arusha City and Meru District. Conservation were maintained in the period of 2006 to 2016 since more strict laws on natural resources were put in place in various areas. During this time the society increased their settlement (hence its population) and agricultural (AG) from 207.3 km^2 to 261.2 km^2 and 498.6 km^2 to 531.5 km^2, respectively by clearing the bush land (BL) area from 237 km2 which decreased to 158.4 km^2. The urbanization process also utilized the area covered with rocks which decreased from 52 km^2 to 43.8 km^2. Such decrease mostly occurred to the rocks residing in the downstream of the area since the most part assessed as rocks in this study area is located on the top of Mount Meru where there are no human activities taking place. The ten (10) years projection shows a massive increase in settlement, hence its population. This will take place through clearing of agriculture land (AG) that will cause scarcity of land for cultivation of food crops an indication that, increase in population will increase the demand for fresh water sources and food that will require outsourcing source resources from other areas.

8.2 Physicochemical and nutrients status in rivers

Chapter Two and Three have discussed on different physicochemical and nutrients status in rivers. Most parameters showed to increase downstream in both seasons. Few samples had BOD, NO_3^- and TSP levels higher than the WHO standards of 10 mg/L, 50 mg/L and 0.1 mg/L, respectively. Most areas in wet season recorded COD levels higher than the WHO recommended values of 10 mg/L. The highest levels of up to 352.11 ± 24.18 mg/L and

212.71 ± 14.72 mg/L were recorded in the wet season for HCO_3^- and CO_3^{2-}, respectively. In the dry season these levels decreased to 126.00 ± 25.14 mg/L and 122.91 ± 13.61 mg/L, respectively. Levels of Cl^-, SO_4^{2-}, K^+, Na^+, Mg^{2+} and Ca^{2+} were < 114 mg/L and 40.51 mg/L in wet and dry seasons, respectively. The floodplain part of the rivers had higher BOD and NO_3^- levels than the WHO maximum permissible levels of 10 mg/L whereas other parameters remained low in other parts. The stable isotope studies on the origin of dissolved organic carbon and NO_3^- indicated mainly to be from plant materials for DOC and from soil composite, [6]wastewater and animal manure for NO_3^-.

8.3 Riverine fluoride levels

Fluoride contamination in water of this area has been discussed in Chapter Four. Fluoride contamination in this area has been found to be a common problem since then. Several expatriates have vested more effort to solve the problem with different approaches and technology. Among these technologies include; the use of nano filtration membrane, dialysis, electro dialysis, ion-exchange processes, electro-coagulation and adsorption through bio char (Waghmare & Arfin, 2015). Despite the Fluoride problem in this study area being chronic, most studies didn't unveil its distribution and persistence in the environment especially in rivers. This study managed to map the Fluoride distribution in most major rivers on this sub catchment area whereby three rivers namely Themi, Nduruma and Tengeru recorded Fluoride concentration lower than the WHO and TBS maximum permissible levels of 1.5 mg/L to 4.0 mg/L, respectively during the wet season. The down streams of these rivers had higher levels than permissible whereby the highest levels of up to 69.01 ± 0.03 mg/L in both wet and dry seasons was recorded in Maji ya Chai River. Mostly important, the study discovered the point source for elevated fluoride pollution in Maji ya Chai which was found to be at Jamera (M2). This discovery built up one step ahead towards the laboratory study of behavior and persistence pattern of fluoride leaching and what is the contribution of water pH in rock dissolution and fluoride leaching as shown in Chapter 5. The study has explained as why fluoride is produced slowly in water for quite long time the main cause being the slightly solubility of the igneous feldspar rock containing fluoride ions in various forms being a function of pH. It should be noted that most soil in this study area originates from feldspar-quartz extrusive volcanic igneous parent material which is resistant to various physical and

[6] The wastewater contributing to high levels of nutrients in rivers are mainly based in Temi River which receives treated wastewater from WTS in Lemara an indication of poor performing system.

chemical processes thus eliciting fluoride ions in aqueous solution, is a slow process and takes a long time.

8.4 Riverine water quality

The water quality in rivers in this study area has been compromised by various biological, physicochemical and chemical parameters of which some were found to be above the maximum healthy acceptable levels from various standards established by quality assurance bodies. Poor quality of water in most rivers have been contributed mostly by contamination of high levels of fecal coliforms bacteria, oxygen demanding wastes and elevated levels of fluoride ions. However, in some rivers their flood plain parts had poor water quality which was a result of high nutrients contamination in water, specifically nitrates (NO_3^-) and phosphates (PO_4^{3-}).

The pristine environment of Temi, Nduruma and Tengeru Rivers showed good water quality due to limited human activities. In addition, the rest part of these rivers had bad to poor quality all these being accelerated by several human activities including poor disposal of domestic wastes which are carried into rivers through runoff, poor quality of sewage and industrial effluents discharged in the receiving rivers which is caused by poor performance of the waste treatment and stabilization ponds (WSP) located at Lemara (Fig. 34)and poor agriculture practices ranging from crop production and livestock keeping which accelerates deforestation, soil erosion and destruction of the buffer zones and riparian environment of the rivers.

The interesting challenge in grading the water quality status of rivers was noted when the two methods (WAI and NSF) were employed such that in most cases they gave different results compared to the anticipated. Also the flexibility of WAI gave more chances for important water quality parameters to be employed in quality rating. Together with the mentioned findings, the point source for fulvic and humic acids which is the main cause of brown colouration in water for Maji ya Chai River was established and found to be at the foothills of Kirurumu hill in Maksoro spring. The stable isotope studies revealed the main sources of such colour was from manure and plant materials which have accumulated for quite long time in this area. Such materials have also caused a maximized oxygen demanding wastes which consume most of dissolved oxygen thus causing limited or absence of aquatic life.

8.5 Conclusions

In this study, statuses of various land use change have been evaluated. The land use statuses on the slopes of Mount Meru have significantly changed in the thirty years' time line. Such changes have affected the riparian environment in most rivers. Also, the decrease of bush land which supports various lives is alarming the sustainability of biodiversity in the entire area. In addition, water conflicts have become common in several villages surrounding the study area and the whole Lower Pangani River Basin (LPRB) area which have eventually affected some of the socioeconomic status of people living in the area. This calls upon the society and other responsible authorities to establish a continuous monitoring programme for sustainable use of the upper PRB environment.

Most water quality parameters in the pristine environment along Temi, Nduruma and Tengeru rivers were within the TBS and WHO standards. This signifies the well conserved catchments which in turn protect the environment. The water quality shows to deteriorate in the middle and floodplain environment of those rivers due to improper sanitation measures and some economic activities which deteriorate the environment. The water quality of the entire Maji ya Chai river have shown to be poor throughout the year due to presence of high levels of DOM and fluorides. The DOM has further affected even the aesthetic values of water in this river due to presence of implausible brown colouration. The poor water quality in the floodplain environment of Themi River is mainly contributed by the discharge of effluents from the poorly performing wastewater treatment system of the city at Lemara. This calls upon designing a new technology for water treatment to suffice the present city needs.

8.6 Suggestions and recommendations for further studies

This study has managed to unveil a small part of knowledge within several environmental problems which occur in this area. Despite all the achievements made in this study, several gaps have been identified which need further studies to bring about a good status of our environment. Among those necessary areas which need further improvement include and but are not limited to the following:

(i) Studies should be invested on sustainable use of the present land for future generations.

(ii) Thorough assessment should be conducted to evaluate the extent in which the societies depending on the studied environments have been affected. This will help

the policy and decision makers to resort into the right policies and decision for sustainable development of the surrounding communities, environment and the long term plan for environmental conservation.

(iii) Poor agriculture practices along the rivers are among the major sources of water quality changes. This calls us to institutionalize the proper rules and regulations guiding the proper conservation of riverine environment

(iv) Pollution of Themi River has been mostly being contributed by poor performance of the sewerage treatment system of the Arusha City at Lemara. A need to adopt new technologies for waste water treatments is important since in the current world the nature and type of industrial, agricultural and domestic wastes have changed due to change in science and technology.

(v) It has been noted that during the dry season Nduruma River experiences seasonal drying of the flood plain from July to March due to over abstraction for other uses. This has endangered the aquatic lives of several creatures in several years. Further studies on the best irrigation technology to minimize the current excessive water loss and unplanned runoff associated with furrow irrigation practices should be carried out to evaluate its efficiency towards water economy and where possible to find alternative water sources for the same purpose.

(vi) Rehabilitation of the deforested riparian environment is necessary to provide a good buffer zone for rivers which will act as filters for oxygen demanding wastes seeping into rivers and reduce the runoff from rain water.

(vii) There is a great need to study the chemo-dynamics of waste waters in Temi River soon after it is discharged into the river and assess its socioeconomic and health implications to the floodplain part and societies depending on them.

(viii) Studies on the fates of various horticultural activities and their residues along the Nduruma River and their impact to the natural hydro-geochemistry of this river need to be carried out.

(ix) Modeling the point sources, trends and patterns of fluoride pollution on the slopes of Mount Meru is necessary for assessing the effects that may occur to the society.

(x) Lastly, follow-up study on fluoride trends and water quality status in the studied riverine environment is necessary in order to establish a permanent mapping on those trends.

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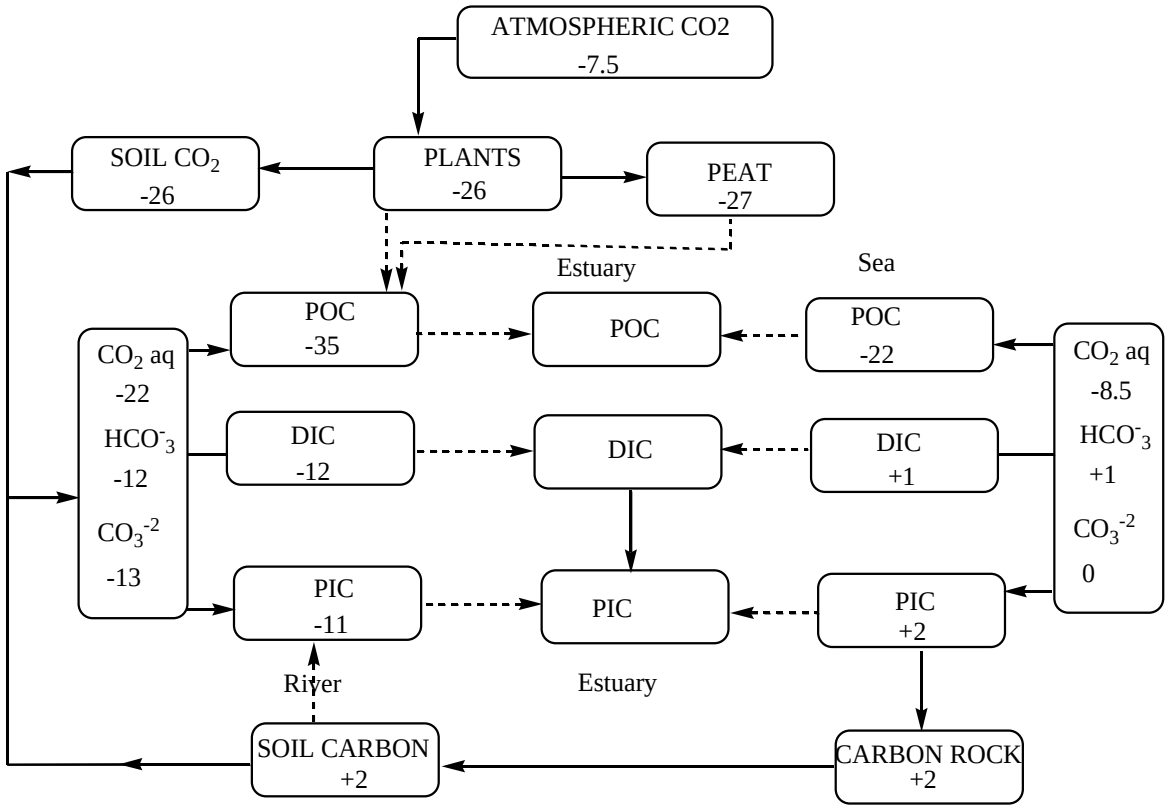
APPENDICES

Appendix 1: Categories of water hardness

Scale(mg/L)	0-60	61-120	61-120	>120
Category/Hardness	Soft	Moderate hard	Hard	Very hard

Source: (World Health Organization(WHO), 1996)

Appendix 2: Schematic diagram showing the sources of dissolved inorganic carbon (DIC), suspended particulate organic carbon (POC) and particulate inorganic carbon (PIC) in rivers and estuaries



Mook et al. (1974) and Mook (1986)

Note: Full lines with arrows indicate chemical and isotopic formation processes, dashed lines refer merely to transport and mixing. The numbers are representative average $\delta^{13}C$ values (‰), of which the realistic ranges and deviations are discussed in the literature.

Appendix 3: Standard methods for water measurements

Parameters	unit	Instrument	Analytical methods
pH	numeric	HANNA Multiparameter HI 9828	TZS 861-Electrometric method
Temperature	^{o}C	HANNA Multiparameter HI 9828	TZS 861-Electrometric method
DO	mg/L	HANNA Multiparameter HI 9828	Electrometric method
EC	µS/cm	HANNA Multiparameter HI 9828	Electrometric method
TDS	mg/L	HANNA Multiparameter HI 9828	TZS 861-Electrometric method
Turbidity	NTU	HANNA Turbidimeter HI 93703, 2100Q01	APHA 2130B-Nephelometric method
FC	CFU/100mL	Filtration unit & incubator	ISO 6222-Membrane filtration method
COD	mg/L	COD and Multiparameter photometer HI 83099	TZS 861-Dichromate Digestion Method
TSS	mg/L	Analytical balance, filtration unit & Oven	TZS 661Gravimetric method
Fluoride	mg/L	Ion selective electrode meter	APHA 4110-Ion selective electrode method
Hardness	mg/L	Titrimetric Methods	861 Titrimetric method
Nitrate	mg/L	HACH DR 2800	APHA 4110-Cadmium reduction method
Alkalinity	mg/L	HANNA, HI 755	APHA 4110-Alkalinity Checker
CDOM	RFU	TURNER Cyclops-7	APHA 4110-Cadmium reduction method
BOD_5	mg/L	BOD and Multiparameter photometer HI 83099	TZS 861-Dichromate Digestion Method
TP (as P)	mg/L	HACH DR 2800	TZS 861 Colorimetric Ascorbic Acid Method

(TBS, 2014; Baird & Bridgewater, 2017)

Appendix 4: Physico chemical, nutrients and biological data for Themi River during wet and dry seasons in 2015

Themi River

Point	F^-_W	F^-_D	FC_W	FC_D	Turbi_W	Turbi_D	NO_3^-_W	NO_3^-_D	TP_W	TP_D	BOD_W	BOD_D	DO_W	DO_D	TDS_W	TDS_D	T_W	T_D	pH_W	pH_D
Te 1	1.02 ± 0.01	1.60 ±0.01	500 ± 100	300 ± 100	BDL	0.01 ±0.01	0.23 ± 0.02	25.00 ± 1.30	0.06 ± 0.02	0.18 ± 0.04	1.00 ± 0.31	BDL	10.10 ± 1.86	9.16 ± 0.92	88.00 ± 11.82	41.00 ± 2.93	15.56 ± 1.72	14.95 ± 0.49	7.89 ± 0.46	7.79 ± 0.32
Te 2	1.40 ±0.15	1.87 ± 0.20	600 ± 120	300 ± 160	BDL	1.85 ± 0.21	14.20 ± 0.42	25.00 ± 2.10	0.06 ± 0.02	0.18 ±0.04	1.00 ± 0.57	BDL	9.63 ± 1.44	8.95 ± 2.10	97.00 ± 4.81	91.00 ± 7.91	16.54 ± 1.92	20.15 ± 1.99	8.05 ± 0.21	7.84 ± 0.52
Te 3	1.19 ± 0.19	1.83 ±0.32	900 ± 260	600 ± 170	BDL	1.13 ± 0.21	9.10 ± 0.31	17.50 ± 2.41	0.07 ±0.02	0.22 ± 0.11	11.00 ± 0.99	5.00 ± 1.03	8.90 ± 1.92	7.21 ± 0.84	97.00 ± 2.95	102.00 ±11.92	17.02 ± 0.42	24.46 ±01.95	8.07 ± 0.62	8.12 ± 0.31
Te 4	0.61 ± 0.16	0.94 ± 0.21	500 ± 230	300 ± 110	BDL	0.01 ± 0.01	2.60 ± 0.52	21.60 ± 3.93	0.05± 0.02	0.15 ± 0.02	7.00 ± 1.04	3.00 ± 0.93	9.04 ± 1.42	7.51 ± 1.14	99.00 ± 7.03	108.00 ± 14.72	20.00 ± 0.93	21.71 ± 1.77	8.01 ±0.21	7.94 ± 0.41
Te 5	1.26 ± 0.20	1.83 ± 0.72	2000 ± 140	1100 ± 120	6.81 ± 1.38	0.06 ±0.02	3.30 ± 1.20	12.50 ± 1.42	0.07 ± 0.01	0.22 ± 0.04	17.00 ± 3.84	5.00 ± 0.88	8.70 ± 1.33	7.46 ± 1.93	101.00 ± 9.17	114.00 ± 11.21	15.77 ± 0.49	24.40 ± 1,94	7.54 ± 0.44	8.52. ± 0.48
Te 6	1.41 ± 0.13	2.15 ± 0.22	7100 ± 160	4800 ± 410	6.32 ± 1.32	0.02 ± 0.01	2.50 ± 0.09	15.00 ± 2.47	0.05 ± 0.03	0.16 ± 0.01	22.00 ± 2.91	4.00 ± 0.58	8.40 ± 1.22	7.48 ± 1.31	102.00 ± 5.92	131.00 ± 6.24	17.81 ± 0.49	20.94 ± 2.82	7.58 ± 0.71	8.60 ±0.99
Te 7	1.54 ±0.03	2.68 ±0.02	3100 ± 210	2000 ± 290	5.20 ± 0.89	0.04 ± 0.01	1.83 ± 0.45	40.00 ± 2.43	0.13 ± 0.15	0.41 ±0.02	18.00 ± 0.72	9.33 ± 3.18	8.60 ± 1.41	6.99 ± 1.38	103.00 ± 10.48	147.00 ± 11.41	19.30 ± 1.17	26.17 ± 1.93	7.52 ± 0.18	9.00 ± 0.94
Te 8	1.36 ± 0.14	3.38 ± 0.58	2300 ± 200	800 ± 120	9.48 ± 0.24	0.02 ± 0.01	2.90 ± 0.42	15.00 ± 2.52	0.14 ± 0.02	0.43 ± 0.02	23.00 ± 2.93	8.00 ± 0.85	8.13 ± 1.93	7.13 ± 1.33	108.00 ± 12.92	153.00 ± 10.39	19.06 ± 1.83	25.09 ± 3.71	7.32 ±0.52	9.70 ± 0.55
Te 9	1.36 ± 0.19	1.96 ± 0.29	900 ± 210	400 ± 140	1.72 ± 0.73	0.04± 0.02	2.42 ± 0.41	BDL	0.04 ± 0.02	0.04 ± 0.22	2.30 ± 0.52	0.40 ± 0.28	9.05 ± 0.49	7.82 ± 0.60	102.00 ± 5.81	141.00 ± 9.17	15.04 ± 1.79	14.95 ± 1.94	7.71 ± 0.73	8.14 ± 0.38
Te 10	1.02 ± 0.03	1.27 ± 0.44	7800 ± 130	1200 ± 130	0.59 ± 0.58	1.73 ± 0.20	97.40 ± 1.33	60.00 ± 2.41	4.16 ±0.99	4.74 ± 0.36	34.00 ± 4.62	24.67 ± 4.29	7.91 ± 0.33	4.20 ±2.11	351.00 ± 17.33	563.00 ± 91.58	14.95 ± 0.69	15.36 ± 1.09	7.47 ± 0.59	7.78 ± 0.52
Te 11	1.37 ±0.30	2.01 ± 0.31	8300 ± 3200	1700 ± 260	11.59 ±0.27	1.45 ± 0.83	81.70 ± 7.15	92.50 ± 9.36	2.46 ± 0.31	2.91 ±0.27	16.00 ± 2.44	15.33± 2.27	8.88 ± 0.47	6.18 ± 0.28	390.00 ± 28.81	656.00 ± 72.05	17.97 ± 0.55	21.21 ± 1.36	7.47 ± 0.17	9.01 ± 0.69
Te 12	1.27 ±0.07	1.39 ± 0.37	10200± 1720	1900 ±180	4.60 ± 1.84	0.22 ± 0.03	12.50 ± 4.36	180.00 ±14.06	1.70 ±0.52	1.99 ± 0.95	19.00 ±3.91	12.67 ± 2.91	8.51 ± 1.33	6.44 ± 0.31	400.00 ±97.00	698.00 ± 55.92	15.07 ±1.04	15.87 ± 1.38	7.80 ± 0.22	7.37 ± 0.30

Note: All concentration values are in mg/l except for turbidity (NTU), FC (FCU/100ml sample), T (°C) and pH is unitless. W - Wet, D – Dry, ± σ.

Appendix 5: Physico chemical, nutrients and biological data for Nduruma River during wet and dry seasons in 2015

Nduruma River																		
Point	**F^-_W**	**F^-_D**	**FC_W**	**FC_D**	**Turbi_W**	**Turbi_D**	**NO_3^-_W**	**NO_3^-_D**	**TP_W**	**TP_D**	**BOD_W**	**BOD_D**	**DO_W**	**DO_D**	**TDS_W**	**TDS_D**	**T_W**	**T_D**	**pH_W**	**pH_D**
N1	2.01 ± 0.31	2.94 ± 0.17	1700 ±220	1100 ± 150	BDL	BDL	6.30 ± 0.83	0.18 ± 0.04	0.38 ±0.19	0.02 ± 0.01	9.00 ±0.47	25.00 ±0.29	5.38 ±0.71	7.54 ± 0.33	95.00 ±2.71	106.00 ± 9.46	12.21 ±1.35	12.01 ± 0.06	7.88 ±1.27	8.11 ± 0.99
N2	2.81 ± 0.36	2.22 ± 0.31	2100 ± 120	1200 ± 200	BDL	BDL	4.90 ± 0.53	0.70 ± 0.22	0.22 ± 0.18	0.29 ± 0.20	17.00 ± 0.32	29.00 ± 4.94	5.90 ± 0.83	6.29 ± 0.21	101.00 ± 4.85	116.00 ± 2.73	14.42 ±1.94	14.7 ± 1.32	7.93 ± 0.68	8.00 ± 0.49
N3	1.60 ± 0.42	1.78 ± 0.53	5900 ± 170	4000 ± 150	2.38 ± 0.37	BDL	44.00 ± 0.67	2.34 ± 0.67	0.12 ± 0.07	0.54 ± 0.12	23.00 ± 9.42	7.00 ± 6.22	4.90 ± 0.21	8.22 ± 0.31	83.00 ± 5.39	81.00 ± 6.83	16.62 ± 0.92	17.40 ± 1.31	6.40 ± 0.48	7.63 ± 0.01
N4	1.13 ± 0.21	1.34 ± 0.42	1000 ± 30	700 ± 110	BDL	BDL	5.00 ± 0.88	0.07 ± 0.02	0.39 ± 0.36	0.42 ± 0.02	15.00 ± 3.57	15.00 ± 2.03	7.20 ± 0.43	7.80 ± 0.12	76.00 ± 8.93	84.00 ± 2.63	16.56 ± 1.93	17.34 ± 1.21	7.67 ± 0.23	7.59 ± 0.29
N5	1.39 ± 0.31	1.69 ± 0.25	2300 ± 260	1800 ± 40	0.80 ± 0.18	0.01 ± 0.01	60.00 ± 0.72	73.80 ± 2.68	0.16 ± 0.07	0.41 ± 0.22	14.10 ± 1.05	13.00 ± 8.52	8.54 ± 0.28	7.93 ± 0.52	80.00 ± 9.70	105.00 ± 2.83	16.90 ± 0.93	19.21 ± 1.94	7.71 ± 0.38	7.40 ± 0.08
N6	2.16 ± 0.01	2.90 ± 0.05	4700 ± 660	3400 ± 635	2.13 ± 0.52	1.80 ± 0.20	5.80 ± 0.69	0.26 ± 0.03	0.77 ± 0.39	0.51 ± 0.21	18.00 ± 4.19	20.00 ± 2.17	5.38 ± 0.55	7.67 ± 0.14	80.00 ± 20.51	121.00 ± 2.72	17.91 ± 1.98	22.00 ± 0.99	7.80 ± 0.17	9.90 ± 0.01
N7	0.92 ± 0.16	1.02 ± 0.02	900 ± 60	600 ± 90	BDL	BDL	5.30 ± 0.33	0.01 ± 0.02	0.46 ± 0.11	0.36 ± 0.06	21.00 ± 0.99	9.00 ± 2.42	5.24 ± 0.17	8.16 ± 0.11	97.00 ± 29.29	100.00 ± 1.94	17.20 ± 0.92	17.18 ± 0.39	7.90 ± 0.19	8.06 ± 0.29
N8	1.59 ± 0.16	2.68 ± 0.57	4400 ± 95	3700 ± 80	1.89 ± 0.33	0.65 ± 0.31	7.10 ± 0.41	0.05 ± 0.02	0.66 ± 0.42	0.59 ± 0.31	18.00 ± 4.29	17.00 ± 1.55	5.70 ± 0.32	7.78 ± 0.31	89.00 ± 7.41	120.00 ± 36.92	18.51 ± 1.04	22.11 ± 0.69	7.91 ± 0.69	8.16 ± 0.48
N9	1.59 ± 0.26	2.16 ± 0.53	9000 ± 70	600 ± 20	2.86 ± 0.18	BDL	41.30 ± 0.21	0.02 ± 0.01	0.26 ± 0.16	0.35 ± 0.05	18.00 ± 2.18	14.00 ± 2.51	7.20 ± 0.12	7.81 ± 0.31	71.00 ± 28.72	132.00 ± 16.93	17.40 ± 0.93	19.25 ± 1.04	8.12 ± 0.37	7.84 ± 0.49
N10	1.67 ± 0.21	2.43 ± 0.22	1100 ± 30	500 ± 410	3.31 ± 0.52	BDL	40.00 ± 0.52	0.04 ± 0.01	0.29 ± 0.21	0.21 ± 0.17	15.00 ± 0.89	20.00 ± 8.37	7.80 ± 0.17	7.65 ± 0.11	104.00 ± 25.92	147.00 ± 31.94	20.48 ± 0.04	24.32 ± 0.07	8.15 ± 0.29	8.40 ± 0.99
N11	1.82 ± 0.61	2.65 ± 0.52	9700 ± 90	900 ± 80	1.40 ± 0.31	1.26 ± 0.22	39.40 ± 0.84	0.02 ± 0.01	0.45 ± 0.36	0.64 ± 0.51	9.00 ± 0.58	26.00 ± 9.29	9.24 ± 0.50	6.44 ± 0.42	108.00 ± 17.92	154.00 ± 17.42	18.34 ± 1.82	18.34 ± 0.97	8.01 ± 0.59	8.26 ± 0.39
N12	1.71 ±0.83	2.45 ±0.82	11000 ± 630	1100 ±95	3.73 ± 0.68	1.73 ± 0.28	50.20 ± 2.83	0.01 ± 0.01	0.74 ± 0.21	0.92 ±0.33	9.00 ± 2.71	31.00 ± 2.49	10.58 ± 0.19	6.16 ±0.94	104.00 ± 7.42	148.00 ±21.96	19.92 ± 1.03	19.86 ±1.00	9.04 ± 0.39	9.4 ±0.03

Note: All concentration values are in mg/l except for turbidity (NTU), FC (FCU/100ml sample), T (°C) and pH is unitless. W - Wet, D – Dry, ± σ.

Appendix 6: Physico chemical, nutrients and biological data for Tengeru River during wet and dry seasons in 2015

Tengeru River																	
Point	**FC_W**	**FC_D**	**Turbi_W**	**Turbi_D**	**NO_3^-_W**	**NO_3^-_D**	**TP_W**	**TP_D**	**BOD_W**	**BOD_D**	**DO_W**	**DO_D**	**TDS_W**	**TDS_D**	**T_W**	**T_D**	**pH_W**	**pH_D**
T1	1300 ±70	1200 ± 300	BDL	BDL	2.50 ± 0.20	3.08 ± 0.27	0.19 ± 0.02	0.31 ± 0.02	BDL	0.20 ± 0.09	9.37 ± 1.29	7.74 ± 2.19	37.00 ± 3.96	42.00 ± 12.03	15.00 ± 0.01	14.00 ± 0.02	7.13 ± 0.22	7.33 ± 0.25
T2	2100 ± 100	1600 ± 450	0.06 ± 0.20	BDL	1.40 ± 0.12	1.72 ± 0.17	0.10 ± 0.02	0.16 ± 0.07	3.00 ± 0.50	5.00 ± 1.03	9.34 ± 2.93	7.20 ± 2.42	77.00 ± 9.42	93.00 ± 11.72	16.47 ± 1.92	14.83 ± 0.94	7.19 ± 0.63	7.23 ± 0.16
T3	2000 ± 60	1300 ± 270	BDL	BDL	6.90 ± 0.26	8.49 ± 0.42	0.25 ± 0.01	0.41 ± 0.03	13.00 ± 0.30	14.00 ± 2.72	9.19 ± 1.83	7.28 ± 3.12	58.00 ± 19.52	97.00 ± 16.02	17.39 ± 0.52	18.40 ± 0.53	7.28 ± 0.73	7.88 ± 0.52
T4	1900 ± 100	1400 ± 320	BDL	BDL	1.60 ± 0.71	1.97 ± 0.18	0.18 ± 0.12	0.29 ± 0.10	10.00 ± 0.52	12.67 ± 1.62	9.29 ± 2.46	7.21 ± 3.21	77.00 ± 39.21	76.00 ± 9.32	16.47 ± 0.92	17.04 ± 1.27	7.19 ± 0.52	7.50 ± 0.11
T5	2000 ± 70	1200 ± 300	BDL	BDL	3.80 ± 0.24	4.67 ± 0.82	0.07 ± 0.02	0.12 ± 0.09	10.00 ± 1.72	12.67 ± 1.52	9.28 ± 1.32	8.38 ± 1.33	84.00 ± 26.42	94.00 ± 28.31	15.60 ± 1.53	16.40 ± 0.53	7.34 ± 0.62	7.62 ± 0.43
T6	1500 ± 630	200 ± 30	BDL	BDL	2.60 ± 0.16	3.20 ± 0.41	0.14 ± 0.06	0.23 ± 0.05	14.00 ± 2.73	3.33 ± 0.95	9.28 ± 1.22	7.76 ± 0.99	80.00 ± 15.71	96.00 ± 13.62	17.74 ± 1.33	18.81 ± 0.96	7.31 ± 0.52	7.92 ± 0.12
T7	2400 ± 710	1700 ± 410	BDL	BDL	3.20 ± 0.16	3.94 ± 0.18	0.20 ± 0.01	0.33 ± 0.14	16.00 ± 5.41	4.00 ± 0.52	8.67 ± 3.18	7.45 ± 0.92	82.00 ± 17.29	95.00 ± 11.62	16.55 ± 0.62	17.07 ± 0.52	7.36 ± 0.72	7.38 ± 0.52
T8	1400 ± 390	400 ±70	BDL	BDL	3.80 ± 0.51	4.67 ± 1.41	0.14 ± 0.02	0.23 ± 0.10	19.00 ± 9.42	11.25 ± 0.83	8.11 ± 0.99	6.84 ± 1.29	84.00 ± 18.27	98.00 ± 15.23	16.61 ± 0.83	18.46 ± 1.42	7.42 ± 0.62	7.92 ± 0.99
T9	1900 ± 510	700 ± 70	7.37 ± 1.02	BDL	1.06 ± 0.39	1.30 ± 0.32	0.09 ± 0.02	0.15 ± 0.05	31.00 ± 7.61	19.38 ± 3.62	6.56 ± 2.1	6.98 ± 0.20	85.00 ± 27.62	93.00 ± 3.72	16.77 ± 0.99	18.97 ± 1.92	7.12 ± 0.11	7.83 ± 0.42
T10	2700 ± 320	1900 ± 120	8.03 ± 0.92	BDL	0.80 ± 0.21	0.98 ± 0.18	0.08 ± 0.03	0.14 ± 0.02	18.00 ± 7.23	17.50 ± 3.21	8.15 ± 2.1	7.45 ± 2.1	87.00 ± 12.72	98.00 ±13.22	16.94 ± 0.57	19.34 ± 0.58	7.51 ± 0.62	8.06 ± 0.72
T11	2100 ± 270	1400 ± 210	10.47 ± 1.27	BDL	2.50 ± 0.44	3.08 ± 0.99	0.13 ± 0.02	0.21 ± 0.02	14.00 ± 4.52	11.00 ± 3.71	9.18 ± 0.31	7.45 ± 0.99	101.00 ± 19.32	123.00 ± 14.32	17.53 ± 0.39	18.05 ± 0.63	7.58 ± 0.43	8.03 ± 0.50
T12	7900 ± 920	6200 ± 710	33.90 ± 2.18	11.98 ± 1.25	18.40 ± 0.53	22.63 ± 1.52	0.17 ± 0.02	0.28 ± 0.04	10.00 ± 0.92	8.00 ± 2.17	8.99 ±2.31	8.02 ± 2.19	146.00 ± 11.72	172.00 ± 8.42	18.67 ±1.53	20.15 ± 0.52	7.52 ± 0.25	8.14 ± 0.52
T13	1400 ± 270	1100 ± 200	2.72 ± 0.36	BDL	1.20 ± 0.19	1.48 ± 0.30	0.11 ± 0.02	0.18 ± 0.01	11.00 ± 1.74	5.63 ± 0.38	9.23 ±3.19	6.66 ± 0.25	102.00 ± 9.41	117.00 ± 9.48	18.71 ± 0.02	19.89 ± 1.03	7.32 ± 0.22	7.96 ± 0.32
T14	6100 ± 800	300 ± 40	14.04 ± 2.10	0.86 ± 0.26	10.30 ± 1.85	12.67 ± 2.71	0.16 ± 0.02	0.26 ± 0.02	15.00 ± 2.55	4.00 ± 1.52	8.76 ± 2.1	7.94 ± 0.95	260.00 ± 57.29	243.00 ± 12.52	18.67 ± 1.04	19.50 ± 1.56	7.40 ± 0.11	8.34 ± 0.55
T15	6900 ± 810	600 ± 30	5.71 ± 0.27	1.16 ± 0.14	12.70 ± 1.63	15.62 ± 0.99	0.29 ± 0.05	0.48 ± 0.03	17.00 ± 0.84	4.00 ± 3.22	8.31 ± 3.21	7.56 ± 0.24	195.00 ± 13.82	181.00 ± 26.41	18.81 ± 1.84	19.35 ± 1.00	7.41 ± 0.73	7.94 ± 0.42
T16	4100 ± 390	3800 ± 310	8.16 ± 0.72	3.08 ± 0.12	14.70 ± 1.92	18.08 ± 0.62	0.15 ± 0.01	0.25 ± 0.05	6.40 ± 0.29	7.00 ± 2.10	9.29 ± 1.32	7.63 ± 1.33	200.00 ± 18.93	197.00 ± 19.53	18.66 ± 0.99	17.01 ± 1.74	7.44 ± 0.52	8.59 ± 0.21
T17	4700 ± 990	800 ± 190	16.15 ± 0.99	1.27 ± 0.62	1.90 ± 0.35	2.34 ± 0.52	0.25 ± 0.04	0.42 ± 0.32	16.00 ± 1.53	5.63 ± 3.11	8.56 ± 1.42	7.60 ± 1.62	110.00 ± 27.03	181.00 ± 16.42	18.32 ± 0.52	16.05 ± 0.99	7.47 ± 0.11	7.75 ± 0.32
T18	1600 ± 200	1300 ± 320	27.39 ± 0.44	1.42 ± 0.18	16.32 ± 0.93	20.07 ± 4.72	0.19 ± 0.02	0.32 ± 0.03	44.90 ± 9.52	31.00 ± 6.72	6.45 ± 1.37	7.91 ± 1.62	129.00 ± 13.62	131.00 ± 18.43	18.52 ± 1.03	18.50 ± 0.53	7.30 ± 0.52	8.05 ± 0.21
T19	9800 ± 1020	9 ± 3	19.27 ± 1.04	16.92 ± 0.44	2.70 ± 0.31	3.32 ± 0.77	0.22 ± 0.02	0.36 ± 0.01	12.00 ± 0.52	4.00 ± 1.42	9.23 ± 1.32	8.25 ± 1.42	125.00 ± 28.52	174.00 ± 19.53	18.27 ± 1.94	16.65 ± 0.56	7.21 ± 0.22	8.51 ± 0.32
T20	7900 ± 710	2100 ± 50	32.80 ± 3.15	12.44 ± 0.92	10.40 ± 0.22	12.79 ± 7.21	0.24 ± 0.02	0.40 ± 0.28	14.00 ± 1.99	3.00 ± 0.32	9.17 ± 3.25	8.24 ± 1.93	127.00 ± 8.52	174.00 ± 25.38	18.24 ± 1.63	19.49 ±0.53	7.40 ± 0.31	7.92 ± 0.22
T21	11500 ± 1600	1400 ± 240	16.02 ± 1.92	8.98 ± 0.79	10.10 ± 0.83	12.42 ± 2.47	0.24 ± 0.02	0.40 ± 0.33	25.00 ± 3.52	3.00 ± 0.62	7.85 ± 3.12	7.21 ± 0.93	81.00 ± 21.23	185.00 ± 15.33	18.29 ±0.93	21.00 ± 0.04	7.34 ± 0.94	8.10 ± 0.33

Note: All concentration values are in mg/l except for turbidity (NTU), FC (FCU/100ml sample), T (°C) and pH is unitless. W - Wet, D – Dry, ±σ.

Appendix 7: Physico-chemical, nutrients and biological data for Maji ya Chai River during wet and dry seasons in 2015

	Maji ya Chai																
Point	**FC_W**	**FC_D**	**Turbi_W**	**Turbi_D**	**NO_3^-_W**	**NO_3^-_D**	**TP_W**	**TP_D**	**BOD_W**	**BOD_D**	**DO_W**	**DO_D**	**TDS_W**	**TDS_D**	**T_W**	**T_D**	**pH_W**	**pH_D**
M1	4300 ± 170	5500 ± 1040	BDL	2.31 ± 0.22	15.90 ±1.38	22.26 ± 0.33	0.40 ±0.07	0.66 ± 0.14	6.00 ± 0.90	12.00 ± 0.79	5.44 ±0.34	7.41 ± 1.33	490.00 ± 17.92	472.00 ± 89.26	19.48 ± 0.12	19.48 ±0.53	8.60± 0.14	8.56 ± 0.92
M2	4800 ± 600	6000 ± 940	BDL	4.61 ± 0.94	16.50 ± 1.71	23.10 ± 0.41	0.51 ± 0.26	0.75 ± 0.24	41.00 ± 2.53	77.00 ± 11.09	0.54 ± 0.19	0.10 ± 0.02	566.00 ± 91.04	813.00 ± 49.41	17.00 ± 0.61	19.64 ± 0.02	8.49 ± 0.69	9.60 ± 1.03
M3	5200 ± 910	6900 ± 1510	BDL	0.67 ± 0.26	7.20 ± 0.94	10.08 ± 2.51	0.49 ± 0.14	0.81 ± 0.20	11.00 ± 2.79	10.67 ± 3.61	5.32 ± 0.99	7.81 ± 0.94	415.00 ± 72.04	466.00 ± 70.00	17.76 ± 0.37	20.15 ± 1.78	8.33 ± 0.52	8.31 ± 0.52
M4	5500 ± 1020	4300 ± 710	BDL	3.24 ± 0.13	3.10 ± 0.47	4.34 ± 0.99	0.47 ± 0.21	0.79 ± 0.51	2.00 ± 0.37	17.00 ± 1.71	8.87 ± 1.72	6.00 ± 1.02	422.00 ± 85.71	448.00 ± 92.05	17.83 ± 0.84	21.20 ± 0.99	8.52 ± 0.61	8.54 ± 0.62
M5	5900 ± 970	1900 ± 200	BDL	BDL	5.40 ± 0.26	7.56 ± 0.90	0.40 ± 0.13	0.64 ± 0.17	5.00 ± 0.22	14.38 ± 3.64	8.75 ± 0.92	7.03 ± 2.03	395.00 ± 27.41	497.00 ± 75.94	18.67 ± 0.59	17.37 ± 1.25	7.39 ± 0.65	7.91 ± 0.52
M6	6100 ± 1740	400 ± 50	361.60 ±19.04	71.46 ± 5.74	1.60 ± 0.13	2.24 ± 0.13	0.28 ± 0.09	0.46 ± 0.16	3.00 ± 0.71	7.00 ± 1.60	8.85 ± 1.77	7.89 ± 0.85	458.00 ± 57.92	586.00 ± 92.07	18.30 ± 0.94	20.38 ± 1.56	7.55 ± 0.78	8.38 ± 0.78
M7	6900± 1620	300 ± 40	BDL	BDL	5.80 ±0.95	8.12 ±0.97	0.05 ± 0.03	0.08 ±0.02	19.00 ±1.77	3.00± 0.61	2.62 ±0.92	7.97 ±0.83	594.00± 85.94	861.00± 93.57	18.83± 0.37	21.44 ± 0.73	7.37 ± 0.16	8.69± 0.47

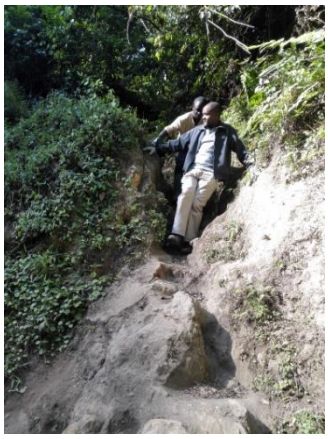
Note: All concentration values are in mg/l except for turbidity (NTU), FC (FCU/100ml sample), T (°C) and pH is unitless. W - Wet, D – Dry, ± σ

Appendix 8: Some photos of sampling areas in rivers

Themi (Te10)

Kijenge (Te7)

Nduruma (N8)



Songota (N6)

Themi source (Te3)

Tengeru source (T1)

Maksoro (Maji ya Chai source M1)

Maji ya Chai (M5)

Appendix 9: Rocks used for laboratory experiments (a–c), particle size (d–g) and setup

(a) Whole rock

(b) Whole rock

(c) Whole rock

(d) Grounded rock

(e)0.35 mm

(f)1.5 mm

(g) 20 µm

(h) Experiment for F^- leaching setup

Appendix 10: Research Permit for Maji ya Chai River in ANP from TANAPA

TANZANIA NATIONAL PARKS
OFFICE OF THE DIRECTOR GENERAL
P.O. BOX 3134, ARUSHA - TANZANIA

Ref. No. TNP/HQ/E.20/08(B) Date 01/07/2015

The Nelson Mandela African Institution of Science and Technology (NM-AIST)
Water and Environmental Science and Engineering Department
P.O. Box 447,
ARUSHA

Attn: Jasper N. Ijumba

RE: PERMISSION FOR CONDUCTING RESEARCH SURVEY

This is in response to your letter with Ref. NM-AIST/P112/T.13/22 dated 23/06/2015 regarding the subject above.

I am pleased to inform you that permission is hereby granted for Mr. Aldo Kitalika, to conduct his research titled: **"Water quality dynamics on the slopes of Mount Meru rivers"**, and take water samples from Maji ya Chai River source in Arusha National Park, which is part of the student's partial fulfillment for PhD in Environmental Science and Engineering award, from 03rd July, 2015 to 02nd July, 2016.

The student is required to observe all Tanzania National Parks rules and regulations while in the park. Tanzania National Parks will not bear any of the costs of the researcher, and he is required to brief the CPW for Arusha about the project before starting data collection.

Yours sincerely,
TANZANIA NATIONAL PARKS

F. A. Lejora
For: **DIRECTOR GENERAL**

Copy:
1. CPW - Arusha National Park
2. Student - Mr. Aldo Kitalika.

Appendix 11: Request for Research Permit from WESE

THE NELSON MANDELA
AFRICAN INSTITUTION OF SCIENCE AND TECHNOLOGY
(NM-AIST)
WATER AND ENVIRONMENTAL SCIENCE AND ENGINEERING DEPARTMENT

)irect Line: +255 272555070
lobile Phone: +255 754296993
ax: +255 272555071
-mail: karoli.njau@nm-aist.ac.tz
)ur Ref: NM-AIST/P112/T.13/22

Tengeru
P.O. Box 447
Arusha

Website: www.nm-aist.ac.tz

Date: 23/06/2015

Chief Park Warden
Arusha National Park
ARUSHA

MR. ALDO KITALIKA

Reference is made to the subject above.

Kindly be informed that, Mr. Aldo Kitalika the bearer of this letter and whose name appears above is a *bonafide* student of the Nelson Mandela African Institution of Science and Technology with **Reg. No. P112/T.13)**. He is doing his research on water quality dynamics in rivers on the slopes of mount Meru. He wishes to take water samples from Maji ya chai River source and therefore, I am requesting you to accord him the necessary assistance to enable him to accomplish the task.

I am thanking you in advance,

Yours Sincerely,
Jasper N. Ijumba (PhD), Sen. Lecturer
Ag. HEAD OF DEPARTMENT

Appendix 12: Waybill for Waterloo University-Canada

ARCHIVE DOC
Do not attach to package!

XEP DHL

From: NELSON MANDELA- AIST
ALDO KITALIKA
MANDELA ROAD
P.O.BOX 447

ARUSHA, TANZANIA
TANZANIA

Tel/PH: +255767208366

Origin: ARK

To: UNIVERSITY OF WATERLOO
C/O RICHARD HEEMSKERRK,LAB MANAGER
ENVIRONMENTAL ISOTOPE LABORATORY DEPT.OF EARTH & ENVIRONMENTAL SCIENCE,200UNIVERSITY AVENUE

N2L 3G1 ONTARIO
CANADA

Tel/PH: +1(519)-888-4567

CA-YHM-GTW

Day: Time:

Account No.: CASHSPARK
Ref:

Shipment Weight: 6.00kg
Date: 2016-09-24

Pieces: 1

DHL standard Terms & Conditions apply. Warsaw Convention may also apply.
Shipment may be carried via intermediate stopping places DHL deems appropriate.

Content: WATER SAMPLE FOR LAB ANALYSIS

WAYBILL 97 8063 4006

Product : 8 EXPRESS EASY NON DOCUMENT
Services :
DTP Account No :
Insured Value :
Declared Value : 0.10 USD

Website: www.dhl.co.tz

TEL:255 22 219 4900

SHIPMENT CHARGES	277500
FUEL CHARGES	
INSURANCE	–
PACKAGING	
VAT-18%	
TOTAL CHARGES TZS	277500

PICKED UP BY REDE / NEEMA

Route No. AR00

Time 12:36:08 PM Date 9/24/2016

Sender Signature :

RESEARCH OUTPUTS

Research articles

Poster presentations