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The effects of agricultural land use on nutrients stoichiometry at River Nzoia headwaters in Kenya

Thesis submitted for the award of the Master of Science in Limnology and Wetlands Management

By

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Dedication

To my dearest mum; Daisy Mbuya Gachoni who has always committed herself in supporting me to achieve my career dreams and to Almighty God who has given me strength all through.

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Affidavit:

(i) This Master thesis comprises only my original work towards the attainment of the Masters of Science Degree in Limnology and Wetlands Management, except where indicated.

(ii) I give my solemn word that I have compiled this work solely and without external help, have not utilized any sources outside those permitted and that the sources used have been given verbatim or quoted textually in the places indicated.

This work was done under the guidance of Hein, Thomas, Univ.Prof. Dr. and Weigelhofer, Gabriele, Mag. Dr, my mentors in the institute of hydrogiology, BOKU University- Vienna, Austria.

Sign: . Date: 03/04/2020

NGARI NJAGI SAMUEL

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List of abbreviations and acronyms

AFDW	Ash Free Dry Weight
ANOVA	Analysis of variance
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
GPS	Global Positioning System
NEMA	National Environment Management Authority of Kenya
NH_4^+	Ammonium
NO_2^-	Nitrites
NO_3^-	Nitrates
OM	Organic Matter
SRP	Soluble Reactive Phosphorous
$SUVA_{254}$	Specific ultraviolet absorbance at 254nm wavelength
TN	Total Nitrogen
TP	Total Phosphorous
TSS	Total Suspended Solids
UNEP	United Nations Environment Program
POM	Particulate Organic Matter
P_{tot}	Total Phosphorous for the soils or Stream sediments
P_{org_labile}	Labile fraction of the Organic Phosphorous
Porg_tot	Total Organic Phosphorous for the soils and Stream sediments
P_{inorg}	Inorganic fraction of phosphorous for the soils and Stream sediments

The effects of agricultural land use on the nutrient's stoichiometry at the headwater tributaries of River Nzoia in Kenya.

Abstract.

Land use change in the headwater streams influences their water quality as well as their surrounding terrestrial environment. The conversion of forested land into cropland not only alters the organic matter delivery into streams but also affects the levels of soils and stream sediments nutrients. In this study, we evaluated the effects of agricultural land use on the soils, stream sediments and water nutrients levels on the Mount Elgon headwaters of River Nzoia during the high flows. Four up-stream sites with less agricultural influence were compared to six downstream agriculturally extensive sites. From the water N:P analysis, N was the limiting nutrient in the up-stream sites that were characterized by forest while P was the limiting nutrient in the downstream characterized by agricultural land use. $SUVA_{254}$ analysis showed an increasing Dissolved Organic Carbon aromaticity to the downstream. The average $\delta^{13}C$ of the soils in the up-stream sites was lower than those in the downstream, denoting a significant(p<0.05) effect of C4 crops on the soil carbon. The soils C/N was negatively corelated (Pearson, p<0.01) with P_{tot} and it increased from the upstream to downstream due to agriculture. All nutrients increased in the water column from upstream but were all within the Kenyan recommended standards for domestic water source. TSS levels both in upstream and downstream were beyond the set standards. Soils should be well managed to prevent fertility loss from the agricultural headwater's catchments.

Keywords: $SUVA_{254}$ Aromaticity Nutrients Agriculture Headwaters Catchment Fertility

1.0 Introduction

Land use change from forest into crop land is a key driver of nutrient influx and it has a tremendous and broader consequence on the aquatic systems. It results in soil erosion, reduction of stream canopy cover alongside increase in synthetic or organic fertilizer usage which not only reduces the habitat biodiversity and complexity, but also affects nutrients cycling (Goyette et, al. 2018), self-purification of streams (Stutter et, al., 2018) and organic matter dynamics (Tank et, al., 2010).

Carbon (C), Nitrogen (N) and Phosphorous (P) are essential macronutrients needed by all primary producers in many ecosystems. Globally, these macronutrients influx have been linked to freshwater systems degradation (Peters & Meybeck, 2000; Lotze et, al. 2006). In East Africa, their excess supply to Lake Victoria is evidenced by eutrophication (Lindensschmidt et. al., 1998) with a consequence of lake colonization by invasive species and biodiversity reduction (Oberholster et, al., 2010; Njiru et. al., 2008).

As reported by Redfield, 1958, Carbon and Nitrogen cycling relationships are crucial biogeochemical links in the biosphere. Increase in atmospheric CO_2 can lead into increased carbon fixation by photosynthesis and increased C: N in the terrestrial primary producers (Bosatta & Ågren 1991). Mineralization rate of OM in soil is affected by the C:N thus influencing the availability of these nutrients for uptake.

The changes of stream water C:N:P ratio along the river continuum occur majorly from assimilation, metabolism, burial or atmospheric exchange (Maranger et al., 2018). The catchment attributes that interplay to influence these processes includes the land cover (Wilson & Xenopaulos, 2009), soil properties (Autio et al. 2016), the residence time (Lambert et al. 2014) and nutrients availability which are all directly affected by land use change.

The effects of land use change on the streams is more severe in the tropical areas than in the temperate (Hartemink et al., 2008). This is as a result of rapid mineralization of tropical organic soils and high erodibility of soils by surface runoffs (Grip et al., 2004). The surface runoff is an event that is seasonal and its influenced by land use and climate (Singh et al., 2004). Tropical catchments experience both extreme wet and dry seasons in which rainfall is a result of the oscillation of the ICZ (Hedo et al., 2017).

The expansive land use in upper stream reaches mainly influences the chemistry of the larger rivers downstream, while the effects of local land uses in the catchments can be noted within the small streams in the catchment (Buck et al., 2004). The study of catchment's nutrients during the dry seasons with low flows in streams can be used to describe ambient water quality which persist in a longer time of the year (Brodie & Mitchell, 2005), whereas during a rainy seasons with high flow events, it can be used to estimate the catchment pollutants (Likens, 2001). Thus, this study is aimed at quantifying the amount of pollutants entering the streams through runoffs as a result of land use change.

1.1 Literature review

1.1.1 Main sources and composition of Dissolved Organic Carbon (DOC)

DOC is a crucial biogeochemical element in streams. It is involved in microbial processing water pH buffering, nutrients precipitation and dissolution processes. It is principally derived from allochthonous sources which include riparian soils and terrestrial leaf litter (Fiebig et al. 1990; Kaplan and Newbold 1993) and autochthonous sources such as stream algae and other aquatic plants. The quantity and quality of leaf litter depends on season, catchment and riparian condition (Wantzen et al., 2008). As human disturbance increases from the pristine forested stream conditions, a shift in the type of OM is observed to be derived more from algal or bacterial than plant and soil (Wilson and Xenopoulos, 2009; Lambert et al., 2017).

Quantifying DOC concentrations is important, but more important is to characterize its Aromaticity which influences its reactivity with oxidants (Li et al., 2000; Westahoff et al., 2003). The aromaticity of DOC determines how it reacts with other elements such as nitrogen during nitrification and denitrification processes (Zehr and Ward 2002, Vivanco and Austin, 2011). More also, it characterizes the OM that supports aquatic food web, mobilizes and transports pollutants and attenuates lights in the water column (Hansen et. al., 2016).

DOC concentrations and composition is influenced by two main processes; biodegradation and photodegradation (Del Vecchio and Blough. 2002; Hansen et. al., 2016). Biodegradation of DOC occurs both on photic and aphotic zones and leads into rapid losing of low molecular weight aliphatic materials which are labile (Wetzel et al. 1995) while it can also result into high molecular weight productions (humic acids) by heterotrophs (Stepanauskas et al. 2005).

The effects of DOC deficiency on nitrogen cycling and its different sources has been studied. (Xu et, al. 2015) observed that DOC deficiency inhibited the sequestration of N thereby increasing its transfer of nitrates downstream. A study by (Stutter et al., 2018) reported that agricultural runoff increases humic substances that does not balance C: N:P ratio within the stream whereas riparian wetlands and forest contributes to less humic DOC with little N and P inputs that rebalances the ratio (Stutter et al., 2018).

DOC chemical characteristic can be well predicted by Specific UV absorbance (SUVA) on a spectrophotometric wavelength at 254nm. This fraction estimates the aromaticity of humic substances in the DOC (Weishar et. al., 2003) which influences cycling of other nutrients. It can be computed by dividing UV absorbance at 254nm by the DOC concentration measured in milligrams per liter (mg/L).

1.1.2 C/N and δ^{13}C

The soils organic matter C/N relates to processes such as mineralization and immobilization of nitrogen. Moreover, C/N ratio in aquatic systems can reveal some character of the organic matter sources. The C/N ratio of 4 to 10 is attributed to phytoplanktonic and algal sources while that of 14-20 and above is attributed to vascular plants sources (Meyers &Teranes, 2001). The difference in this ratio is as a result of presence of cellulose in the vascular plants and its absence in algae. The $\delta^{13}C$ signatures are distinct in C3 and C4 plants. According to O'Leary, 1988, the organic matter resulting from atmospheric CO_2 ($\delta^{13}C$= -7‰) fixation by C_3 terrestrial plants has an average $\delta^{13}C$ of −27‰ (PDB), while that from C_4 pathway have an average of -14‰ (PDB). in combination with the C/N ratios can be used to determine the type of plants contributing to organic carbon in a system.

1.1.3 Nitrogen sources and transformation.

Nitrogen is a major component of amino acids; the building blocks of protein. Plants requires Nitrogen for their growth and survival. The inorganic forms of N include gaseous (N_2, N_2O, NH_3) and dissolved (NH_4^+, NO_2^-, NO_3^-) forms. NH_4^+ and NO_3^- are the most reactive forms of N. Its transformation into its major forms (Organic and inorganic) in the soils and streams is influenced by both biotic and abiotic factors (Dodds & Whiles, 2010). The major pathways of its transformation include: N_2 fixation, NH_4^+ desorption and adsorption, anaerobic NH_4^+ oxidation, dissimilatory reduction of NO_3^- into NH_4^+, volatization of NH_3 and it can be temporarily removed from water through assimilation by algae and macrophytes or permanently released to the atmosphere through denitrification. The main form of inorganic N that is assimilated by heterotrophs, plant and microbes is NH_4^+.The heterotrophs requires amino acids in order to digest protein. These amino acids are products of NH_4^+ which is also excreted by heterotrophs when it is in excess in their bodies.

1.1.4 Phosphorous sources and cycling

P in aquatic systems occurs naturally or through anthropogenic input. Natural inputs occur as a result of weathering process of rocks and soil parent materials in the catchment with low human activities or by remineralization of organic matter from dead plants or animals in the riparian and within the aquatic system. The anthropogenic sources can either be point source or diffuse source. Point sources entails a specific point of input such as wastewater and industry outlets. The diffuse sources entail non-specific input within a catchment and occur during storm events as either surface or (and) sub-surface runoff. Agriculture is the main diffuse source of P (Galloway et at., 2004; Elser et al. 2007;). The natural sources contribute very little amount of P compared to the anthropogenic sources (McDowell et al., 2002; Goyette et al., 2018). P input from point and diffuse sources within the catchment can be accumulated at various points along the longitudinal stretch of a stream such as soils, riparian, stream sediments and biomass. This P can be recycled and remobilized into the water systems as SRP for decades even centuries (McDowell et al., 2002).

The biogeochemical cycling of P in rivers is very complex. It is dependent on reactivity of soils and sediments, hydrology and weather conditions (House, 2003). The main processes by which P is removed from the water column in streams is by assimilation by autotrophs and burial into the sediments. The size of the sediments influences its P buffering capacity. The smaller the size, the higher the buffering capacity and vice versa. The Low flow in streams facilitates efficient P retention while during high flow, less retention and biogeochemical processes occur (Withers and Jarvie 2008).

P has been classified into its operational analysis method as SRP (soluble reactive phosphorous) and TP (Total phosphorous). The sediments P sequential extraction by (Psenner et al., 1984) classifies it according to its mobility and immobility from the sediments. P_{inorg} is comprised of SRP extraction from milli-Q (Labile inorganic P), NaOH (Aluminum bound P) and HCL (calcium bound inorganic P), while P_{tot} involves digestion using H_2SO_4. The difference in P_{tot} and P_{inorg} is the $P_{org\_tot.}$

1.1.5 Primary productivity limitation

Primary productivity of aquatic ecosystems is depended on nutrients availability, light and other physical-chemical parameters. When light is not limiting, primary production is controlled by the availability of nutrients majorly being Nitrogen and Phosphorous (Vitousek & Howarth 1991; Elser et al. 2007). Nutrients limitation for biomass varies with region. In the temperate, (Europe), P has been documented to be the main limiting nutrient in aquatic systems (Langan et al., 1999; Fillipelli, 2008). This has been attributed largely to industrialization and usage of N fertilizers for cropping. In the tropics, N has been documented to be limiting in a lake in Brazil (Feresin et al., 2010), African streams (Mosisch et al., 2001; Dudgeon, 2011) and 75% of streams in South-eastern Queensland (Udy & Dennison, 2005).

N is said to be the limiting nutrient when the molar N:P is less than 10 while P is limiting when the molar N:P is greater than 20 (Lohman et al. 1991; Thomas et al., 2003; Sedimentserson et al., 2009).A C:N and a C:P greater than 8.3 and 129 respectively infers to P limitation(Healey 1978) . However, these ratios might be of less importance in determining the limiting nutrients if the nutrients are present in very high or very low levels (Bowman et al. 2005). N is most likely to be limiting when its supply into the aquatic system is low or when the anthropogenic P supply is high (Koch et al. 2004).

Major biological and chemical processes within the streams depend temperature (Dudgeon, 2011). Autotrophic and heterotrophic productivity, Organic matter metabolism, Nitrogen sequestration, atmospheric oxygen and carbon exchange are among the main processes affected by temperature. Temperature variation in stream mainly occur as a result of altitude change as well as presence or absence of canopy cover. Light affects mainly photosynthesis process while pH and specific electric conductivity can influence the microbial processes and communities.

1.2 Justification statement

The fate of stream nutrients from the origin to their recipient bodies has been documented. Streams are not simply passive pipes for nutrients i.e C, N and P but rather, they are active reactors (Maranger et al., 2018). The streams internal processing of these nutrients along the way determines their fate. They are either lost through atmospheric flux, biotic uptake and sediment burial, or(and) are exported down to the recipient bodies (Likens, 2001; McDowell et al., 2002).Their abundance over the last 200+years has been on a significant increase due to land use change, agricultural industrialization and population growth (Galloway et al. 2004; Wilson & Xenopaulos, 2009). Land conversion from forest to agricultural land has immense influence on the microbial processing of organic matter and nutrients loading into the freshwater systems. Increasing usage of organic and chemically synthesized nitrogenous fertilizers and phosphate rocks in the farms end up increasing nutrients into the streams through runoffs (Galloway et at., 2004).

(UNEP 2004) approximated a 38% east African forest land conversion into cropland and grazing land by the year 2035. Mt Elgon forest has already experienced rapid conversion into crop land to the extent of encroaching the protected area, (Mugagga et al., 2012). This conversion is coupled by increased soil erosion susceptibility due to overgrazing, maximum tillage and the steep inclination of the landscape (Semalulu et. al, 2015).

There has been an increasing need to understand the nutrients dynamics within the tropic's freshwater ecosystems (Brunet et al., 2009; Bouillon et al., 2014). Several studies have been conducted on R. Nzoia watershed. Point sources of nutrients pollution has been researched

(Achoka., 1998; Adams and Simiyu., 2009; Nadir et. al., 2019) with a lesser focus on diffuse nutrient's dynamics at the Mt Elgon headwater catchment. Thus, there is need to carry out a comprehensive study on the influence of land use change on the nutrients stoichiometry in this catchment headwater systems of R. Nzoia.

1.3 Objectives and research questions.

The purpose of our study was to examine whether and how increased agricultural land use in the downstream reaches affected the water, soil and stream sediments chemistry by comparing it to up-stream forested reaches. In order to achieve this, we came up with the following objectives:

i. To assess average water nutrients concentrations in the headwater's tributaries of R. Nzoia on Mt. Elgon catchment during high water level.
ii. To assess the variation of Organic matter in the TSS of R. Nzoia headwaters tributaries on Mt. Elgon catchment during the high-water level.
iii. To assess the P fractions and C/N ratios in the soils and stream sediments of R. Nzoia headwaters tributaries on Mt. Elgon catchment.
iv. To assess the POM and $\delta^{13}C$ ratios in the soils and stream sediments of R. Nzoia headwaters tributaries on Mt. Elgon catchment.

Our study was guided by couple of specific questions that aided in achieving our objectives. The first question was how agricultural land use changed the nutrient supply and potential nutrient limitations in the water column alongside effects on $SUVA_{254}$. The second question was how the change affected the nutrients concentration as well as how it influenced the $\delta^{13}C$ of the soil and stream sediments. Our final question was how the soil and stream sediments POM changed as a result of agricultural land use.

1.4 Hypothesis

I. Nutrient concentrations, DOC concentrations as well as $SUVA_{254}$ and N:P ratios in the water column and in the sediments increase from the forested reach to the agricultural reaches.
II. POM in soil decreases from the forested to the agricultural land use.
III. POM in sediments increases from the forested reach to the agricultural reach of the streams.
IV. C/N ratio decrease in both soils and sediment from forest to agricultural streams reaches.

2.0 Materials and methods

2.1 Study site

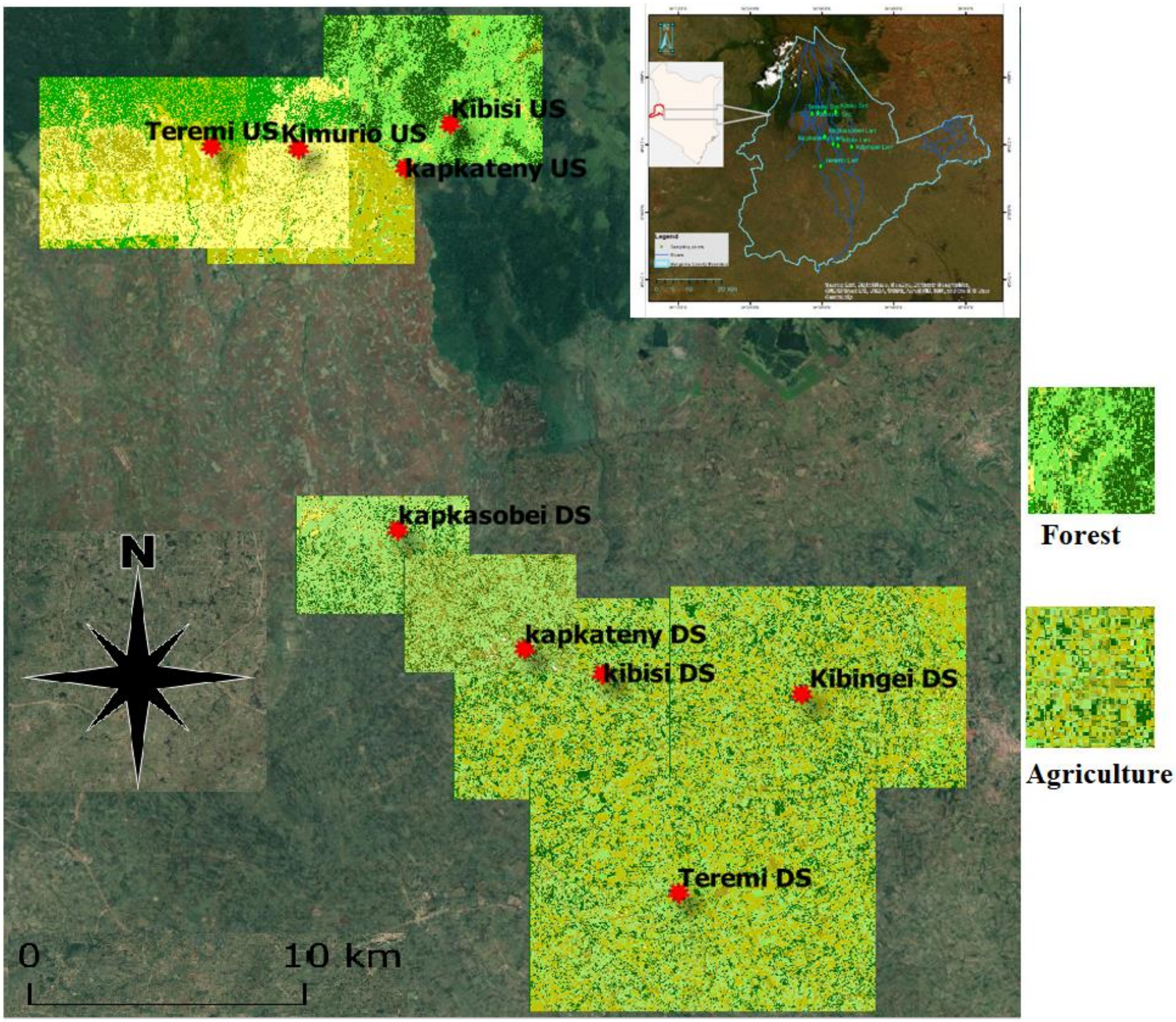

Figure 1 showing the land use at the sampling sites within Bungoma county, Kenya

The study area is within Bungoma county administrative boundaries and sampling sites located on the steep slopes of the extinct volcanic Mt Elgon that has a height of 4321m above sea level. The forest covered an area of 78.025 ha when it was gazzetted as a forest reserve in the year 1932, however, several incisions have been made in the recent years converting it into settlement, cropland and grazing land (Hitimana et al., 2004). The sampling sites lie within the moist montane forests that is characterized by both closed and open canopy and occur between altitude 1500–2450 m above sea level.

R. Nzoia has its origin from Mt Elgon and Cherengani hills and drains its water into L. Victoria. The Mt. Elgon catchment is among the main water sources for domestic and industrial use in Kenya with an average rainfall of 1400-1800 mm and the temperature ranging from 14^{o}C to 24^{o}C depending on the altitude and season (Musau and Luedeling 2015). The area experiences two main rain seasons per annum (Hitimana et al., 2004). Short rain period of October, November and December and Long rain period occurring in April, May, June and July

The soils in the forests are well drained friable clay derived from volcanic rock while the cultivated soils are poorly drained loam soil that range from reddish brown to black colour (Ongugo et al., 2002).The agricultural areas are subdivided into small units ranging from 1 to 2 acres with main crops cultivation being maize and beans and keeping of cattle, goats and sheep (Ongugo et al., 2002). The county has a population density of 552 km^{-2} with 70% of the population practicing agriculture as their main economic activity (KBS, 2019)

Arc- GIS version 10.5 in combination with Google earth was used to extract the study area. The sampling streams shape file was digitized from close examination of images on google earth pro imagery version of 12/13/2015

2.2 Sampling design

The sampling was done on the Mt. Elgon catchment R.Nzoia tributaries as shown in figure 1 during the short rain period of November 2019. Sampling during a rain season, enabled us to capture the diffuse effects of run off from the agricultural land. The runoffs carry most of the pollutants from the catchment, thus it enabled us to quantify the influence of agricultural land use on the aquatic system.

Four sampling sites were selected in the forested agriculture transition areas on Mt. Elgon, R. Nzoia tributaries outside the protected area of Mt Elgon national reserve while 5 sites were selected on the lower stream agriculturally extensive point. The sampling points selection was based on the stream order and on their accessibility. Efforts were made to sample both upper and lower sites of same streams; however, due to inaccessibility of the agricultural lower section of Kimurio stream, alternative first order streams were sampled i.e Kibingei and kapkasobei. The name of the sampled streams, their GPS coordinates and their altitude are listed on table 1.11

Table 1 The sampling sites, their GPS coordinates and altitude

S/No.	Stream sampling points	GPS coordinates	Altitude(m) ASL
1.	Teremi up-stream	00° 54’ 34”N, 34° 35’ 58” E	2388m
2.	Kimurio up-stream	00° 53’ 28.8”N, 34° 35’ 21.2” E	2239m
3.	Kapkateny up-stream	00° 53’ 45.28”N, 34° 35’ 56.28” E	2293m
4.	Kibisi Up-stream	00° 54’ 10”N, 34° 37’ 03” E	2298m
5.	Kapkasobei down-stream	00° 49’ 28.50”N, 34° 36’ 28.0” E	1881m
6.	Kapkateny down-stream	00° 48’ 51.9”N, 34° 37’ 27.5” E	1660m
7.	Kibisi down-stream	00° 47’ 50”N, 34° 38’ 44”E	1624m
8.	Kibingei down-stream	00° 47’ 37.23”N, 34° 40’ 53.40” E	1633m
9.	Teremi down-stream	00^{o}45'18.23"N, 34.39'33.83"E	1535m

2.2.1 Physico-chemical parameters and water samples collection.

The sample collection was guided by UNEP, 1996 on recommendation for water and sediments sampling. Physico-chemical parameters including pH, dissolved oxygen (DO), DO saturation, temperature and electrical conductivity were measured *in situ* using a HACH 40d Multi- meter probe.

The samples in the field were placed in a cooler box and then placed in a fridge under $4^{o}C$ temperature upon arrival in the Laboratory. Water samples for nutrients analysis were collected at the water surface at a depth of between 15cm and 20cm into 300ml acid washed plastic vials. Four (4) samples in a replicate of three (3) per site were collected. 100ml to 200ml of each sample was filtered immediately upon arrival in the laboratory using a vacuum filter pump and Whatman GF/F of 0.7µm that had been pre-combusted at $500^{o}C$ for two hours. The filtrate and the remaining sample was stored in the fridge for nutrients analysis. Water sampling was done once per week involving four sampling expeditions in the month of November. Three (3) water samples per site in a replicate of three (3) for DOC/DOM analysis were collected alongside the nutrients water samples. Their filtration was done in the field using syringe hand filter device and pre-combusted

GF/F Whatman filter (combustion at 500°C for 2 hours). The samples were subjected to spectrophotometric readings at 254 nm upon arrival to Egerton Laboratories. One of the three samples per site in triplicates was transported to Wassercluster, lunz am see Austria, in an iced cooler box for DOC/DOM analysis using the Spectrophotometer Fluorescence Device.

2.2.2 Soil samples

A longitudinal stretch of 20m along the stream with accessible right bank and left bank was selected at every sampling point for both forest and agricultural land use. Samples were collected at an approximate diagonal distance of 10 to 20 meters from riverbank. Three samples per site were collected in replicates of ten; (five replicates from the right bank and 5 others from the left bank of the stream). Stainless steel scoop was used for surface soil sampling to depths of approximately 7 cm below ground surface where conditions were generally soft and non-indurated. A 4mm sieve was used to ensure uniform soil grain collection. The samples were transported in an icebox to the Egerton Laboratory for further analysis. The most dominant land use activity/ (agricultural activity) at each sampling site was recorded in the field notebook.

2.2.3 Stream sediments samples

At every sampling site, a 20m stretch of the stream was estimated and 3 stream sediments samples collected in replicates of 5 by use of a stainless-steel scoop and sieved using a 4mm sieve to ensure grain size uniformity. The samples collection was random across the 20m stretch. They were then placed in a prelabeled polythene sampling bags and transported in a cooler box to the Egerton Laboratory for further analysis.

2.3 Water Sample analysis

2.3.1 SRP and TP

SRP was analyzed spectrophotometrically in accordance to (APHA, 2004) method. The samples absorbances were read using a GENESIS 10uv scanning spectrophotometer calibrated to the wavelength of 885nm. The TP was measured from the unfiltered samples by digesting and reducing the forms of phosphorus present in the water into the free orthophosphate form (SRP) using 0.5m $K_2S_2O_8$ in an autoclave at a temperature of 120°C and 1.2 atm for 1hr 30min and then determining the concentrations through the SRP procedure describe above.

2.3.2 NO_3^- and TN

Sodium-salicylate method described by (Vosset &Basset 1989), was used to analyze the nitrates concentration. The photometric absorbances at wavelength 420nm were taken using GENESIS 10uv scanning spectrophotometer. The TN was determined by persulphate oxidation method described by (Koroleff, 1983) where all nitrogenous compounds were oxidized into nitrates in an autoclave at 110^oC for 1 hour. Absorbances at 220 and 275 nm against distilled water were determined on a GENESIS 10uv scanning spectrophotometer and the TN (as mg NO_3-N/L) calculated using the following formula:

$$\text{mg } NO_3^- \text{-N/L} = \frac{\mu g\ NO_3 \text{ - } N \text{ in 50 mL endvolume}}{mL \text{ sample}}$$

2.3.3 NO_2

NO_2 was analysed using standard method described by (APHA, 1998) involving Sulfanilamide and N-Naphthyl-(1) - ethylendiamin-dihydrochlorid. GENESIS 10uv scanning spectrophotometer was used in taking photometric readings at a wavelength of 543nm, calibration being done against the milli-Q.

2.3.4 NH_4^+

The standard analytical procedure by (APHA 1995) was used to analyze for ammonium nitrogen and the photometric absorbances at 655nm wavelength were taken using a GENESIS 10uv scanning spectrophotometer.

2.3.5 Dissolved organic carbon and TSS

TSS for all the water samples was determined in accordance to (APHA 1995) analytical standards

Molecules that comprise DOC in water samples have their average absorptivity at 254 nm photometric readings (Traina et al., 1990; Weishar et al., 2003). It is for this reason that DOC samples in Egerton University were subjected to photometric readings at 254nm using GENESIS 10uv scanning spectrophotometer. The DOC in milligrams per liter was determined using Shimadzu TOC-L (Total Organic Carbon Analyzer) at wassercluster lunz am see.

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2.4 Soil and sediments analysis

2.4.1 POM

All Soil and sediment samples were dried in an oven for 24 hours at 75^{o}C. Sub-samples were made, weighed and placed in a Kiln for 2hrs at 500^{o}C. After cooling, the combusted samples were weighed and the POM calculated as a percentage of weight loss using the following equation POM= ((W1-W2)/W1)*100 where W1 is weight after muffling in an oven, W2 is the weight after combusting in a kiln.

2.4.2 Sequential P extraction

Sequential P extraction involved characterizing the different forms of P in terms of the solubility of Porg and Pinorg as outlined by (Psennar et al., 1984 and Lukkari et al. 2007). This enabled us to determine the potentially mobile or immobile P in the soils and sediments at the two land uses.

The organic P (Pinorg) was determined by weighing 1-2g of the dried samples and adding 25ml of milli-Q. They were then placed on a shaker for 2hours after which they were centrifuged at 3000 RPM at a temperature of 12^{o}C for 15minutes. The resulting supernatant was slowly decanted into a separate uncontaminated tube for SRP determination.

A 25ml of 0.5M NaOH was then be added to the residue and then placed on a shaker for 24hours after which they were centrifuged at 3000 RPM at a temperature of 12^{o}C for 15minutes. The supernatant was decanted into uncontaminated tubes before rinsing the sediments with 25ml of milli-Q, centrifuging it and adding it to the supernatants and placing it in a fridge for SRP determination.

The TP from the NaOH supernatant was determined by diluting the NaOH supernatant 20 folds and autoclaving it for 1 hour before analyzing the TP in form of SRP. The remaining sediments after NaOH extraction were added with 25ml of 0.5M HCL and following the same procedure as that of NaOH SRP extraction.

The TP was determined by combusting the grinded samples in a furnace at 500^{o}C for 2 hours. 0.1g to 0.2g was weighed and 10ml of 0.5M H_2SO_4 added before placing it in a microwave for digestion for one hour. The resulting supernatant was diluted accordingly, and TP analyzed in form of SRP.

The SRP was analyzed using the continuous flow analyzer (CFA) that uses the automated ascorbic acid reduction. It operates by reacting orthophosphate with molybdate in acidic conditions and subsequently reducing it using Potassium antimony tartrate as a catalyst that increases its sensitivity. The resulting molybdenum blue complex is then measured photometrically at 880nm wavelength.

The P fractions in the soils were calculated as follows; P_{inorg} was calculated by summation of SRP from Milli-Q extraction, SRP from HCl extraction and SRP from NaOH extraction. P_{org} labile was calculated as the difference between the TP and SRP from NaOH extraction. P_{tot} was the total P from the H_2SO_4 digestion while Porg_tot was calculated as the difference between the P_{tot} and the P_{inorg}.

The C/N samples were dried at Egerton University laboratories in an oven for 24 hours at a temperature of 75°C. They were grinded at wassercluster Lunz am see and then acidified using 0.5M HCL to moderate the organic carbon. They were then subjected to a Thermo Fisher elemental analyzer Flash 2000- HT PLUS for total carbon and Nitrogen determination and then to the Delta V advantage isotope ratio mass spectrometer (EA-IRMS). Low organic soil standards were used for the analysis

2.5 Land use analysis

Land use analysis was achieved by use of Q-GIS version 3.8 madeira equipped with LUC plugins for remote sensing. Saga GIS was used for band extraction and classification while the images were downloaded from landsat and sentinel 3(students account). Raster layer extraction, digitization(vectorization) and analysis per micro pixel class was by use of Q-GIS. The visual output of the area analysis was per 1km radius per site. The output categorized the land use and vegetation cover in terms of Forests, Shrub vegetation, agriculture crop land, agriculture bare land and housing. The forest and shrub vegetation were summed together and reported as forest while agricultural crop land and agricultural bare land was also summed and reported as agriculture. Sites with 69%+ of forest and a 60%+ canopy cover were regarded to be under forest land use while those with 70%+ cropland was regarded to be under agricultural land use

2.6 Statistical analysis

Shapiro-Wilk normality test was done for all the sediments and water nutrients data using IBM SPSS statistics version 26 (USA) software. Where necessary, some variables were LN transformed in order to meet the statistical equality of variance and normality assumption. Variables that were not normally distributed were subjected to Kruskal Wallis non-parametric test. The parametric variables were subjected to one-way ANOVA with the stream sampling point (either up-stream or downstream) being selected as the factor for the general land use comparison. Streams were selected as a factor for the interstream nutrients comparison and Tukey HSD was selected for the post hoc analysis. A significant level of $P < 0.05$ was adopted throughout the analysis unless where stipulated otherwise. Pearson's method was used to carry out correlation analysis for the soils, stream sediments and water nutrients properties.

In order to determine the possible limiting aspects of water N:P, the N was derived from the summation of the molar mass of NO_2- ,NO_3^- and NH_4^+ while the P was the measure of SRP molar mass. The C was from the DOC in mg/L converted to its equivalent molar.

The $SUVA_{254}$ was computed in accordance to (Weishar et al., 2003) by dividing the Absorbances at 254nm measured using 1cm cuvette with the DOC in mg/L multiplied by 100.

3.0 Results

The GIS land use analysis showed that the up-stream sites were covered by 69 to 99% forest and vegetation while those in the Downstream had 40 to 60% (Fig. 2). However, the Kapkateny upstream site was more encroached by agriculture with about 40%. The canopy cover was higher (60 to 90%) in the up-stream than Downstream sites (20 to 40%).

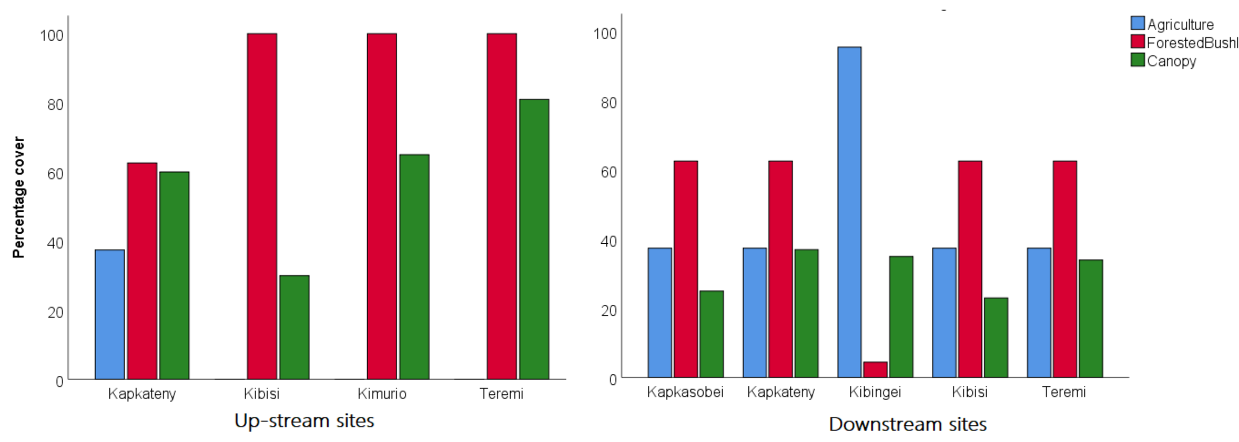

Figure 2 The percentage cover of agriculture, forest and stream canopy, at the upstream and downstream sampling sites

3.1 inter-stream specific results

The results are hereby presented comparing the different streams at the two sampling sites locations. First comparison is at the upstream then the downstream sites.

3.1.1 Up-stream

3.1.1 (a) Physico-chemical and nutrients properties of water

As it is illustrated in Table 2, the one-way ANOVA showed that the mean EC levels varied significantly ($F_{4,49}$= 47.67, p<0.05) cross the up-stream sites. Tukey HSD test revealed that Kibisi mean E.C was different from the rest of the sites. There was no significant difference across the sites in either range or mean levels of pH, DO saturation and TSS (ANOVA, p<0.05, n=42). Most streams had a mean temperature range of 14.9^{o}C to 16^{o}C except Kibisi (13.3^{o}C). Similarly, Kibisi's mean DO (8.82±0.61mg/L) differed from the rest of streams whose DO ranged from 6.5 to 7mg/L (ANOVA, p<0.05, n=42). The mean discharge differed across all the four up-stream sites with Kibisi having the highest (1.42±0.01m^3s^{-1}) while Kapkateny having the lowest (0.37±0.10m^3s^{-1}).

Table 2 The mean values and standard deviation (stdev) for physico-chemical properties of water at the upstream site.

Stream	Land use	n	Temp °C	stdev	pH	E.C µS/cm	stdev	DOmg/l	stdev	TSSmg/L	stdev	OM	stdev
Teremi	Forest	n= 9	14.97	2.37	6.66-7.89	48.06	9.87	6.86	0.45	27.61	21.72	67.90	6.89
Kibisi	Forest	n= 9	13.25	0.76	7.55-7.67	72.57	0.62	8.83	0.61	38.13	17.40	54.61	20.35
Kapkateny	Forest	n= 12	15.74	0.46	6.80-7.65	54.45	2.59	6.69	0.07	41.42	11.49	55.97	45.98
Kimurio	Forest	n= 12	16.02	0.65	6.76-7.66	53.17	2.54	6.65	0.16	37.50	8.05	50.40	12.87

There was no significant difference (ANOVA, $p<0.05$, n=42) in mean levels of NH_4, NO_3, NO_2 and DOC across the four up-stream sampling sites illustrated on table 3. Kimurio had the highest mean ammonium NH_4 (26.51± 22.70µg/L) while Kapkateny had the lowest (23.94±19.83 µg/L). The mean NO_3, NO_2 and DOC levels across the streams were generally very low.

Table 3 The mean values and standard deviation for NH_4, NO_3, NO_2 and DOC of water at the upstream sites

Stream	Land use	n	NH4µg/L	stdev	NO3mg/L	stdev	NO2µg/L	stdev	DOCmg/L	stdev
Teremi	Forest	n= 12	26.00	22.39	0.01	0.00	1.05	0.60	1.04	0.19
Kibisi	Forest	n= 9	26.36	14.03	0.04	0.05	0.84	0.09	1.19	0.05
Kapkateny	Forest	n= 12	23.94	19.83	0.03	0.05	1.23	0.84	0.96	0.16
Kimurio	Forest	n= 12	26.51	22.70	0.01	0.02	0.81	0.35	1.03	0.08

The mean Total phosphorous (TP), Soluble reactive phosphorous (SRP) and Total Nitrogen (TN) levels differed significantly (ANOVA, $p<0.05$, n=45) across the up-stream sites (Table 4). Kibisi had the highest mean TP (0.09±0.02mg/L), SRP (34.75±0.02µg/L) and TN (1.80±0.26mg/L) levels while Teremi had the lowest mean TP (0.05±0.01mg/L), Kapkateny had lowest SRP (15.37±3.24 µg/L) and Kimurio had the lowest TN (1.13±0.69).

Table 4 The mean values and standard deviation for TP, SRP, and TN in water at the upstream sites

Stream	Land use	n	TPmg/L	Stdev	SRPµg/L	stdev	TNmg/L	stdev
Teremi	Forest	n= 12	0.05	0.01	19.44	3.17	1.16	0.71
Kibisi	Forest	n= 9	0.09	0.02	34.75	11.27	1.80	0.26
Kapkateny	Forest	n= 12	0.08	0.01	15.37	3.24	1.17	0.78
Kimurio	Forest	n= 12	0.08	0.01	20.18	3.19	1.13	0.69

There was no significant difference (ANOVA, $p<0.05$, n=45) in the mean N:P, and C: N across all the up-stream sites (Table 5). C:P differed (ANOVA, $p<0.05$, n=45) across all the up-stream sites.

The mean N:P was highest at Kapkateny (12.8±13.7) whereas the rest of the streams had an average of about 8.1. Teremi had the highest C:N (56.9±69) while Kapkateny had the highest C:P(110.2±39.3).

Table 5 The mean values and standard deviation for N:P, C:N and C:P in water at the up-stream sites

Stream	**Land use**	**n**	**N:P**	**stdev**	**C:N**	**stdev**	**C:P**	**stdev**
Teremi	Forest	n=12	7.22	5.93	56.97	69.96	84.73	19.03
Kibisi	Forest	n=9	8.11	2.70	36.91	1.77	55.24	5.87
Kapkateny	Forest	n=12	12.88	13.73	28.03	23.39	110.24	39.31
Kimurio	Forest	n=12	8.76	7.09	21.18	17.85	90.35	17.36

3.1.1 (b)Soil and stream sediment P, C:N, $\delta^{13}C$

The mean $\delta^{13}C$ and C/N in the soils differed significantly (ANOVA, $p<0.05$, n=24) across the up-stream sites whereas no significant difference (ANOVA, $p<0.05$, n=24) was observed for $\delta^{15}N$ (Table 6). Kibisi had the highest mean of soils' $\delta^{13}C$ (-17.26±0.09), $\delta^{15}N$(10.07±0.20) and C/N (10.83±0.40) while Kapkateny had the lowest $\delta^{13}C$ (-20.73± 0.11) and C/N(8.99±0.65).The mean percentage Particulate organic matter(POM) in soils across the streams ranged from 23% to 29% except for Kibisi (15%).

Table 6 The mean values and standard deviation for $\delta^{13}C$, $\delta^{15}N$, C/N and Percentage POM of soils at the up-stream sites. The superscripts letters denote the Tukey HSD analysis for sites with significant (p<0.05) differences: a=Teremi, b= Kibisi, c= Kapkateny and d= Kimurio

Stream	**Land use**	**n**	**$\delta^{13}C$**	**stdev**	**$\delta^{15}N$**	**stdev**	**C/N**	**stdev**	**POM (n)**	**%POM**	**stdev**
Teremi[a]	Forest	6	-19.85	1.24[b]	9.27	1.02	10.25	0.27[c]	30	29.14	10.10[b]
Kibisi[b]	Forest	6	-17.26	0.09[ac]	10.07	0.20	10.83	0.40[cd]	30	15.23	10.17[acd]
Kapkateny[c]	Forest	6	-20.73	0.11[bd]	9.83	0.39	8.99	0.65[abd]	30	23.49	11.26[b]
Kimurio[d]	Forest	6	-18.22	2.37[b]	8.65	1.62	9.77	0.41[bc]	30	24.58	10.31[b]

There was no significant difference (ANOVA, $p<0.05$, n=24) across streams' Soils P_{tot}, P_{inorg} and P_{org_tot} fractions (Table 7). The mean soil P_{tot} and mean P_{inorg} were highest at Kimurio (1672.75±363.63 and 355.83±57.94 respectively). Kibisi had the lowest mean P_{tot} (1080.23±301.11mg/kg) while Kapkateny had the lowest P_{inorg}. The $P_{org-labile}$ differed significantly (ANOVA, $p<0.05$, n=24) across the up-stream sites. It ranged from 37.5 mg/kg at Kibisi to 511 mg/kg at Teremi. The P_{org_tot} was approximately triple higher than P_{inorg} across all the forest sites

Table 7 The mean values and standard deviation for Total phosphorous (P_{tot}), Inorganic phosphorous (Pinorg), Total organic phosphorous (P_{org_tot}) and Labile organic phosphorous ($P_{org-labile}$) of soils at the upstream sites. The superscripts letters on the stdev denote the Tukey HSD analysis for streams with significant (p<0.05) differences: a=Teremi, b= Kibisi, c= Kapkateny and d= Kimurio

Stream	Land use	n	P_{tot}	Stdev	P_{inorg}	stdev	P_{org_tot}	stdev	P_{org_labile}	Stdev
Teremi[a]	Forest	n= 6	1667.45	564.20[b]	311.39	80.02	1356.06	508.63	511.16	202.19[bc]
Kibisi[b]	Forest	n= 6	1080.23	301.11	323.09	113.19	757.14	369.08	37.53	11.90[acc]
Kapkateny[c]	Forest	n= 6	1487.40	353.58	262.88	9.30	1224.52	348.35	270.58	60.20[ab]
Kimurio[d]	Forest	n= 6	1672.75	363.63	355.83	57.94	1316.92	318.51	351.93	53.94[b]

From the stream sediments analysis (Table 8), $\delta^{13}C$ differed significantly (ANOVA, *p*<0.05, n=12) across the up-stream sites. It ranged from (-20.36±0.07) at Kapkateny to (-18.17±0.31) at Kibisi. A significant difference in C/N was observed across the up-stream sites. It was highest at Teremi 13.26±1.00 and lowest at Kimurio (9.73±0.16). Kimurio had the highest %POM (14±9%) in the stream sediments while Kapkateny had the lowest (4±1%).

Table 8 The mean values and standard deviation for $\delta^{13}C$, $\delta^{15}N$, C/N and Percentage organic matter (POM) of the stream sediments at the up-stream sites. The superscripts letters on the stdev denote the Tukey HSD analysis for sites with significant (p<0.05) differences: a=Teremi, b= Kibisi, c= Kapkateny and d= Kimurio

Stream	Land use	n	$\delta^{13}C$	Stdev	$\delta^{15}N$	stdev	C/N	stdev	%POM (n)	%POM	Stdev
Teremi[a]	Forest	3	-20.21	0.12[b]	7.48	1.06[bcd]	13.26	1.00[bcd]	15	8.58	2.76[d]
Kibisi[b]	Forest	3	-20.36	0.07[abc]	9.81	0.09[a]	9.90	0.06[a]	15	11.04	3.12[c]
Kapkateny[c]	Forest	3	-19.87	0.07[bd]	9.34	0.41[a]	10.03	0.49[a]	15	4.14	1.14[bd]
Kimurio[d]	Forest	3	-18.17	0.31[cd]	9.65	0.41[a]	9.73	0.16[a]	15	14.27	9.17[ac]

As illustrated in Table 9, no significant difference (ANOVA, *p*<0.05, n=12) across all the up-stream sites in the mean levels of the P_{org_labile} and P_{org_tot} fractions of the stream sediments. The P_{org_tot} was higher than the P_{inorg} across all the sites. The $P_{org-labile}$ average levels ranged from 0.00 at Teremi to 74.58±69.64 at Kapkateny. The mean P_{tot} was highest at Kimurio (2098.33±343.92) and lowest at Kapkateny (1300.951±206.71. The average $\delta^{13}C$ differed significantly (ANOVA, *p*<0.05, n=12) across the streams. It ranged from (-20.36±0.07) at Kapkateny to Kibisi (-18.17±0.31).

Table 9 The mean values and standard deviation for P_{tot}, Pinorg, P_{org_tot} and $P_{org-labile}$ of instream sediments at the upstream sites. The superscripts letters on the stdev denote the Tukey HSD analysis for sites with significant (p<0.05) differences: a=Teremi, b= Kibisi, c= Kapkateny and d= Kimurio

Stream	Land use	n	P_{tot}	Stdev	P_{inorg}	stdev	P_{org_tot}	stdev	P_{org_labile}	Stdev
Teremi[a]	Forest	n= 3	1661.47	225.16	728.88	72.85[bc]	932.59	275.98	0.00	0.00
Kibisi[b]	Forest	n= 3	1363.63	150.60	339.79	4.14	1023.84	146.45	58.82	1.85
Kapkateny[c]	Forest	n= 3	1300.95	206.71[d]	400.74	106.41[a]	900.21	193.56	74.58	69.64
Kimurio[d]	Forest	n= 3	2098.33	343.92[c]	581.71	35.81[a]	1516.61	308.41	56.81	20.64

3.1.2 Downstream

3.1.2 (a) Physico-chemical and nutrients properties of water

As illustrated in Table 10, the mean levels of water E.C differed significantly (ANOVA, $p<0.05$, n=54) across all the downstream sites except for Kibisi and Kapkasobei. Kibingei had the highest mean EC (196.23±6.32µS/cm) and pH range (7.45-8.44) while Kapkateny had the lowest mean E.C(100.60±29.39 µS/cm) and Teremi had the lowest pH range (7.09 – 7.59). The mean DO range from 6.2±0.1mg/L at Kapkasobei to 6.81±0.35mg/L at Kibisi. Kapkasobei had the highest mean temperatures (21.98±0.98) whereas Kapkateny had the lowest (18.73±2.62). The mean discharge was highest at Teremi (3.64±0.78m^3s^{-1})), two times higher than the rest of the downstream sites.

Table 10 The mean values and standard deviation (stdev) for physico-chemical properties of water at the downstream sites.

Stream	Land use	n	Temp °C	stdev	pH	E.C µS/cm	stdev	DOmg/l	stdev	TSSmg/L	stdev	OM	stdev
Teremi	Agriculture	n= 9	19.44	0.78	7.09-7.53	103.93	4.83	6.56	0.12	248.89	54.46	20.30	3.39
Kibisi	Agriculture	n=12	18.77	2.03	7.51-8.28	141.31	7.54	6.81	0.35	117.92	35.72	30.38	15.19
Kapkateny	Agriculture	n=12	18.73	2.62	7.27-8.40	100.60	29.39	6.75	0.27	196.67	67.53	28.29	6.62
Kapkasobei	Agriculture	n= 9	21.99	0.98	7.25-8.03	141.90	29.07	6.28	0.11	80.56	24.55	27.49	6.63
Kibingei	Agriculture	n=12	19.28	2.22	7.45-8.44	196.23	6.32	6.78	0.41	185.28	44.01	27.72	5.21

The mean levels of NH_4, and NO_3, were highest at Kapkasobei amounting to 30.55±25.11µg/L and 1.24±0.37mg/L respectively (Table 11.) Teremi had the lowest NH_4 (23.71±15.16µg/L) and NO_3 (0.37±0.06mg/L). The mean DOC was highest at Teremi (1.82±0.23mg/L) and lowest at Kapkasobei (1.45±0.22). No significant difference (ANOVA, $p<0.05$, n=54) was observed in the mean levels of NH_4 across all the downstream sites unlike those of NO_3, NO_2, and DOC. Kapkasobei had a double level of NO_3 compared to the rest of downstream sites.

Table 11 The mean values and standard deviation for NH_4, NO_3, NO_2 and DOC of water at the downstream sites

Stream	Land use	n	NH4µg/L	stdev	NO3mg/L	stdev	NO2µg/L	stdev	DOCmg/L	stdev
Teremi	Agriculture	n= 9	23.71	15.16	0.37	0.06	5.33	1.05	1.82	0.23
Kibisi	Agriculture	n=12	28.94	18.65	0.42	0.15	4.83	2.11	1.31	0.19
Kapkateny	Agriculture	n=12	30.48	19.29	0.56	0.13	7.95	4.36	1.36	0.21
Kapkasobei	Agriculture	n= 9	40.55	25.11	1.24	0.37	5.39	1.18	1.13	0.11
Kibingei	Agriculture	n=12	27.66	19.40	0.55	0.19	4.76	1.062	1.45	0.22

The mean levels of TP, SRP and TN differed significantly (ANOVA, $p<0.05$, n=54) across the downstream sites (Table 12.). TP was highest at Teremi (0.20±0.03mg/L) and lowest at Kapkasobei (0.09±0.02mg/L) while TN was highest at Kapkasobei (2.20±0.49mg/L) and lowest at Kibisi (1.29±0.62mg/L). The mean SRP ranged from 16.29µg/L at Kapkateny to 38.33±7.64µg/L at Kibingei.

Table 12 The mean values and standard deviation for TP, SRP, and TN in water at the upstream sites

Stream	Land use	n	TPmg/L	Stdev	SRPµg/L	stdev	TNmg/L	stdev
Teremi	Agriculture	n= 9	0.20	0.03	20.30	4.14	1.39	0.74
Kibisi	Agriculture	n=12	0.14	0.04	27.50	5.16	1.29	0.62
Kapkateny	Agriculture	n=12	0.17	0.07	16.29	8.14	1.49	0.74
Kapkasobei	Agriculture	n= 9	0.09	0.02	18.33	7.66	2.20	0.49
Kibingei	Agriculture	n=12	0.20	0.07	38.33	7.64	1.57	0.64

As illustrated on Table 13, The mean levels of N:P, C:N and C:P differed significantly (ANOVA, $p<0.05$, n=54) across the downstream sites. Kapkasobei had the highest N:P (147.1±94.9) and the lowest C:N (0.49±0.6).The mean C:P levels at Kapkateny were double those of other streams.

Table 13 The mean values and standard deviation for N:P, C:N and C:P in water at the downstream sites

Stream	Land use	n	N:P	stdev	C:N	stdev	C:P	stdev
Teremi	Agriculture	n=9	36.58	9.60	4.58	0.50	158.07	48.32
Kibisi	Agriculture	n=12	29.66	9.93	3.59	2.75	82.38	23.98
Kapkateny	Agriculture	n=12	94.91	72.91	2.34	0.97	270.29	284.28
Kapkasobei	Agriculture	n=9	147.10	94.92	0.49	0.75	131.20	48.35
Kibingei	Agriculture	n=12	25.98	6.23	3.21	2.32	66.28	17.76

3.1.2 (b)Soil and stream sediments P, C:N, $\delta^{13}C$.

A significant difference was observed across the downstream soil $\delta^{13}C$ (ANOVA, $p<0.05$, n=42) and the percentage POM (ANOVA, $p<0.05$, n=140) (Table 14). No significant difference (ANOVA, $p<0.05$, n=42) was observed in the mean C/N across all the downstream sites. The mean $\delta^{13}C$was highest at Teremi (-14.55±1.87) and lowest at Kibingei (-18.15±1.14) whereas the C/N was highest at Kapkateny (13.08±1.23) and lowest at Kibisi (10.68±0.46). The mean percentage soil POM was generally low across all the sites.

Table 14 The mean values and standard deviation for δ13C, δ15N, C/N and Percentage organic matter (POM) of the soils at the downstream sites. The superscripts letters on the stdev denote the Tukey HSD analysis for sites with significant (p<0.05) differences: e=Teremi, f= Kibisi, g= Kapkateny, h= Kapkasobei and i= Kibingei

Stream	Land use	n	$\delta^{13}C$	stdev	$\delta^{15}N$	stdev	C/N	stdev	POM (n)	%POM	stdev
Teremi^{e}	Agriculture	6	-14.55	1.87^{gh}	11.82	0.67^{g}	11.09	0.80	20	9.04	3.81
Kibisi^{f}	Agriculture	6	-16.06	0.47^{i}	11.47	0.57	10.68	0.46	30	6.49	3.35
Kapkateny^{g}	Agriculture	6	-17.50	0.19^{e}	10.77	0.44^{e}	13.08	1.23	30	9.00	4.14^{h}
Kapkasobei^{h}	Agriculture	6	-16.67	0.81^{e}	11.38	0.36	11.58	0.63	30	10.60	2.68^{fi}
Kibingei^{i}	Agriculture	6	-18.15	1.14^{ef}	11.12	0.53	11.21	0.56	30	7.87	4.63^{h}

The P fractions in the soil varied significantly (ANOVA, $p<0.05$, n=42) across the downstream sites (Table 15.). Both mean P_{tot} and P_{inorg} were highest at Kibingei (1474.08±137.56; 311.54±25.61mg/kg) and lowest at Teremi (497.53±54.60; 75.22±26.98mg/kg) respectively while the P_{org_tot} was highest at Kibingei (1162.54±129.12mg/kg) and lowest at Kapkateny (389.97±202.07mg/kg).

Table 15 The mean values and standard deviation for P_{tot}, Pinorg, P_{org_tot} and $P_{org-labile}$ of soils at the downstream sites. The superscripts letters on the stdev denote the Tukey HSD analysis for sites with significant (p<0.05) differences: e=Teremi, f= Kibisi, g= Kapkateny, h=Kapkasobei and i= Kibingei

Stream	Land use	n	P_{tot} mg/kg	Stdev	P_{inorg} mg/kg	stdev	P_{org_tot} mg/kg	stdev	P_{org_labile}mg/kg	Stdev
Teremi^{c}	Agriculture	n= 6	497.53	54.60^{fhi}	75.22	26.98^{gfhi}	422.30	35.87^{hi}	31.44	25.96^{ghi}
Kibisi^{f}	Agriculture	n= 6	821.76	99.49^{ci}	186.47	38.76^{chi}	635.29	79.41^{i}	34.28	39.07^{ghi}
Kapkateny^{g}	Agriculture	n= 6	541.79	245.09^{hi}	151.81	76.37^{chi}	389.97	202.07^{hi}	86.08	10.12^{cf}
Kapkasobei^{h}	Agriculture	n= 6	1085.97	227.22^{ci}	284.71	26.63^{cfh}	801.26	243.06^{cfi}	118.85	24.63^{cf}
Kibingei^{i}	Agriculture	n= 6	1474.08	137.56^{cfgh}	311.54	25.61^{cfg}	1162.54	129.12^{cfgh}	116.84	17.40^{cf}

As it is illustrated on Table 16, the stream sediments' $\delta^{13}C$ and C/N differed significantly (ANOVA, $p<0.05$, n=15) across the downstream sites unlike the percentage POM. The highest mean $\delta^{13}C$ was at Teremi (-15.55±0.21) and lowest at Kibingei (-17.52±0.24) while the mean percentage POM was highest at Kapkateny (7.26±8.24%) and lowest at Kapkasobei (2.16±1.23%). The mean C/N ranged from 9.1±0.6 at Kibisi to 11.8±0.2 at Kapkasobei.

Table 16 The mean values and standard deviation for $\delta^{13}C$, δ15N, C/N and Percentage organic matter (POM) of the stream sediments at the downstream sites. The superscripts letters on the stdev denote the Tukey HSD analysis for sites with significant (p<0.05) differences: e=Teremi, f= Kibisi, g= Kapkateny, h= Kapkasobei and i= Kibingei

Stream	Land use	n	$\delta^{13}C$	Stdev	$\delta^{15}N$	stdev	C/N	stdev	%POM (n)	%POM	Stdev
Teremi[e]	Agriculture	3	-15.55	0.21^{fghi}	12.11	0.37	11.05	0.31^{f}	10	5.39	2.03
Kibisi[f]	Agriculture	3	-16.59	0.26^{ei}	14.92	2.50	9.09	0.55^{eghi}	15	2.34	1.23^{g}
Kapkateny[g]	Agriculture	3	-16.73	0.20^{ei}	11.59	0.14	11.07	0.40^{f}	15	7.26	8.24^{hf}
Kapkasobei[h]	Agriculture	3	-16.45	0.08^{ei}	14.60	1.04	11.81	1.19^{f}	15	2.16	1.23^{g}
Kibingei[i]	Agriculture	3	-17.52	0.24^{efgh}	12.89	0.49	11.06	0.35^{f}	15	3.37	1.46

The Stream sediments P fractions had no significant difference (ANOVA, $p<0.05$, n=15) across all the downstream sites except for the P_{org_labile} (Table 17.). The mean P_{org_labile} was highest at Kapkateny (45.42±7.18) and lowest at Kibingei (0.65±1.14) whereas the mean P_{tot} and P_{inorg} were highest at Teremi (1097.26±370.79; 402.59±68.78mg/kg) and lowest at Kapkasobei (458.49±171.54; 73.93±21.30mg/kg) respectively.

Table 17 The mean values and standard deviation for P_{tot}, Pinorg, P_{org_tot} and $P_{org-labile}$ of instream sediments at the downstream sites. The superscripts letters on the stdev denote the Tukey HSD analysis for sites with significant (p<0.05) differences: e=Teremi, f= Kibisi, g= Kapkateny, h=Kapkasobei and i= Kibingei

Stream	Land use	n	P_{tot}	Stdev	P_{inorg}	stdev	P_{org_tot}	stdev	P_{org_labile}	Stdev
Teremi[e]	Agriculture	n= 3	1097.26	370.79	402.59	68.78	694.66	421.27	5.94	5.27^{g}
Kibisi[f]	Agriculture	n= 3	862.70	413.86	182.36	60.76	677.82	328.42	6.77	11.73^{g}
Kapkateny[g]	Agriculture	n= 3	860.19	380.79	206.29	11.51	656.40	425.37	45.42	7.18^{efhi}
Kapkasobei[h]	Agriculture	n= 3	458.49	171.54	73.93	21.30	384.55	170.34	15.82	9.46^{g}
Kibingei[i]	Agriculture	n= 3	1083.38	100.80	357.37	265.32	726.00	329.47	0.65	1.14^{g}

3.2 Comparison of the upstream and downstream sites

3.2.1 Physico-chemical and nutrients properties of water

As illustrated on table 10, a positive correlation (*P*<0.01) was observed between the specific E.C and SRP, NO_3, DOC, pH, Temperature, TSS and N:P while negatively correlating with C:P (P<0.01) and C:N (*P*<0.05). The pH was positively correlated (*P*<0.01) to TP, NO_2, NO_3, NH_4, Temperature, TSS and N:P and negatively correlated (*P*<0.01) to C: P.

Table 18 The Pearson correlation analysis for the water physico-chemical properties, nutrients levels and ratios.

Elements	Correlation	TP	NO_2	NO_3	NH_4	DOC	EC	PH	D.O	TEMP	Disch	TSS	TN:TP	C:TP	C:TN	N:P
TP	Pearson Cor	1														
	N	99														
NO_2	Pearson Cor	.48**	1													
	N	99	99													
NO_3	Pearson Cor	.33**	.57**	1												
	N	99	99	99												
NH_4	Pearson Cor	.21*	.01	.35**	1											
	N	99	99	99	99											
DOC	Pearson Cor	.45**	.53**	.19	-.17	1										
	N	69	69	69	69	69										
EC	Pearson Cor	.57**	.50**	.59**	.06	.43**	1									
	N	93	93	93	93	69	93									
PH	Pearson Cor	.58**	.37**	.41**	.43**	-.032	.54**	1								
	N	93	93	93	93	69	93	93								
D.O	Pearson Cor	-.03	-.08	-.38**	-.26*	.06	-.10	.00	1							
	N	93	93	93	93	69	93	93	93							
TEMPERATURE	Pearson Cor	.50**	.43**	.78**	.36**	.24*	.62**	.47**	-.63**	1						
	N	93	93	93	93	69	93	93	93	93						
DISCHARGE	Pearson Cor	.48**	.21*	-.02	-.01	.59**	.20	.08	.06	.20	1					
	N	93	93	93	93	69	93	93	93	93	93					
TSS	Pearson Cor	.88**	.60**	.43**	.13	.62**	.55**	.41**	-.17	.60**	.55**	1				
	N	99	99	99	99	69	93	93	93	93	93	99				
C:P	Pearson Cor	-.78**	-.26*	-.37**	-.22	-.09	-.40**	-.35**	.01	-.48**	-.33**	-.63**	.57**	1		
	N	69	69	69	69	69	69	69	69	69	69	69	69	69		
C:N	Pearson Cor	-.25*	-.24*	-.28*	-.23	-.27*	-.25*	-.16	-.218	-.07	-.19	-.20	-.43**	.14	1	
	N	69	69	69	69	69	69	69	69	69	69	69	69	69	69	
N:P	Pearson Cor	.202*	.511**	.708**	.403**	.049	.234*	.398**	-.236*	.519**	-.112	.268**	.041	-.230	-.210	1
	N	99	99	99	99	69	93	93	93	93	93	99	99	69	69	99

*. Cor is significant at the 0.05 level (2-tailed).

**. Cor is significant at the 0.01 level (2-tailed).

The pH in the up-stream sites ranged from 7.16 to 7.39 while that of the downstream sites ranged from 7.59 to 7.70. Other physico-chemical properties including Discharge, EC, temperature and TSS increased significantly (ANOVA, $p < 0.05$, n=99) from the up-stream (Forest) to the downstream (Agriculture) sites as illustrated on Figure 3.

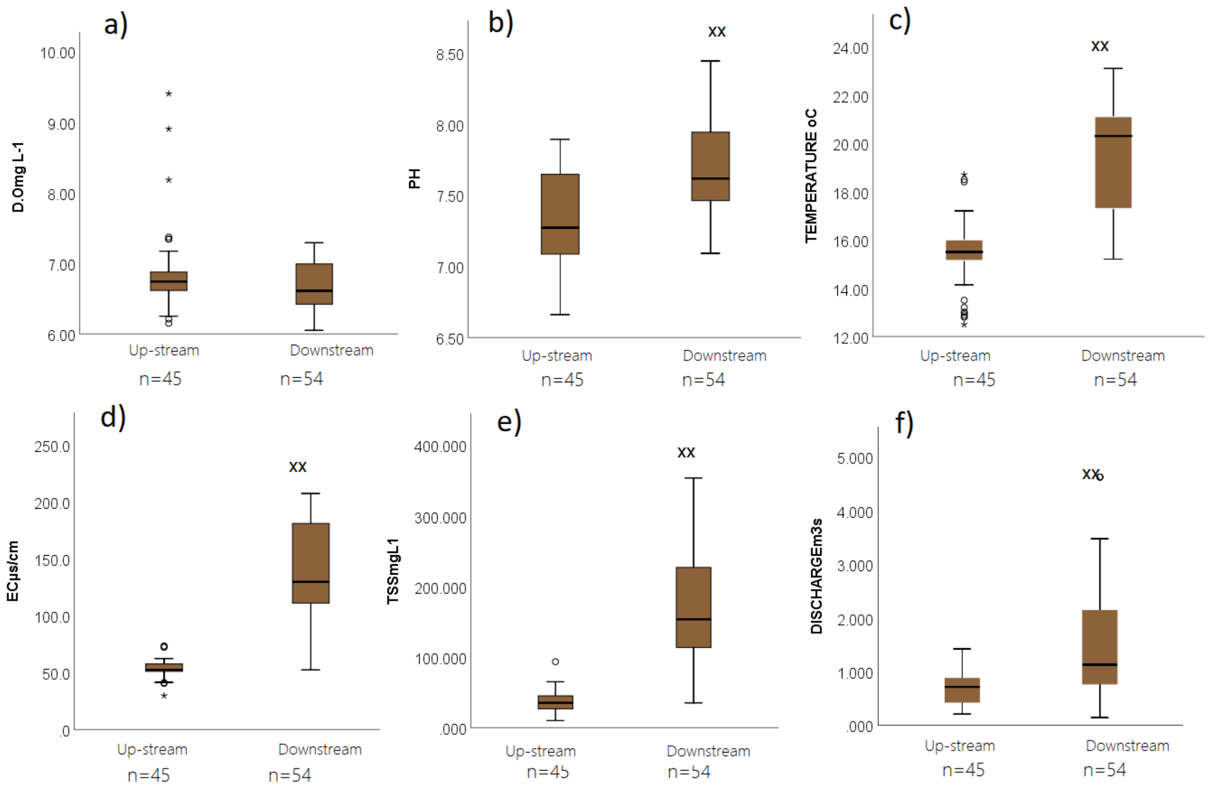

Figure 3 Boxplot showing the variation of physico-chemical properties of water from the forest to the agricultural land use. a) Dissolved oxygen in mg/L, b)pH, c) Temperature ºC, d) Electrical Conductivity µS/cm, e) Total suspended solids mg/L, f) Discharge m^3s^{-1}.The “**XX” sign** denotes that the physico-chemical property is significantly different (p<0.05) between the two land uses

A significant (ANOVA, p<0.05, n=99) increase in mean DOC, $SUVA_{254}$, TN, NO_2, NO_3 and TP from up-stream to downstream was observed (Table 19). There was no significant difference (ANOVA, p<0.05, n=99) in NH_4 and SRP a. The C:N:P in water showed a significant difference (ANOVA, p<0.05, n=99) between the up-stream and the downstream sites. Also, other ratios; C:P, and C:N significantly (ANOVA, p<0.05, n=99) decreased from the up-stream to the downstream sites. Moreover, the C:N:P ratios indicated N limitation in the upstream sites while the downstream sites were P limited.

Table 19 The mean values, standard deviation (Stdev) and One-way ANOVA analysis for the water nutrients levels and ratios variation between the up-steam and downstream sites. * denotes a significant difference (p<0.05)

Elements	Sampling site	n	Mean	Stdev	*F*	*p*
TPµg/L	Up-stream	45	76.49	22.79	68.89	.00*
	Downstream	54	165.60	68.89		
SRPµg/L	Up-stream	45	21.61	8.86	2.38	.12
	Downstream	54	24.69	10.62		
NO_2µg/L	Up-stream	45	.99	.57	134.90	.00*
	Downstream	54	5.68	2.65		
NO_3mg/L	Up-stream	45	.02	.043	125.23	.00*
	Downstream	54	.61	.35		
NH_4µg/L	Up-stream	45	25.66	19.74	1.23	.27
	Downstream	54	30.06	19.61		
DOC mg/L	Up-stream	30	1.03	0.16	51.86	.00*
	Downstream	39	1.40	0.28		
$SUVA_{254}$	Up-stream	30	4.85	1.80	43.32	.00*
	Downstream	39	7.90	1.69		
TNmg/L	Up-stream	45	1.28	.69	3.96	.04*
	Downstream	54	1.57	.70		
N:P	Up-stream	45	9.27	9.25	33.82	.00*
	Downstream	54	64.07	67.94		
C:N	Up-stream	30	35.54	42.58	8.41	.00*
	Downstream	39	2.98	2.03		
C:P	Up-stream	30	88.76	29.56	15.75	.00*
	Downstream	39	141.19	154.83		
OM%	Up-stream	45	57.39	28.87	53.06	.00*
	Downstream	54	27.16	9.04		

3.2.2 Soil and Stream sediments P fractions, POM, C: N and δ13C

As it is illustrated in Table 20, the soils P_{org_tot} correlated positively with P_{inorg} (p<0.01), P_{tot}(p<0.01) as well as inversely with C/N (P<0.01), $\delta^{13}C$ (p<0.01) and $\delta^{15}N$ (p<0.01).The stream sediments P_{org_tot} was positively correlated to its P_{inorg} (p <0.05) and P_{tot}(p <0.01) as well as inversely correlated to $\delta^{13}C$ (p <0.01) and $\delta^{15}N$ (p <0.01).

Table 20 The Pearson correlation analysis for the soil and stream sediments P fraction, C/N, δ^{13}Cs, and δ^{15}N.

Item			P_{org_tot}	P_{org_labile}	P_{inorg}	P_{tot}	C/N	$\delta^{13}C$	$\delta^{15}N$
Stream sediment	P_{org_tot}(mg/kg)	Pearson Cor	1						
		N	27						
	P_{org_labile}(mg/kg)	Pearson Cor	.22	1					
		N	27	27					
	P_{inorg}(mg/kg)	Pearson Cor	**.41***	-.05	1				
		N	27	27	27				
	P_{tot}(mg/kg)	Pearson Cor	**.92****	.14	**.72****	1			
		N	27	27	27	27			
	C/N	Pearson Cor	-.277	-.33	.271	-.09	1		
		N	27	27	27	27	27		
	$\delta^{13}C$	Pearson Cor	**-.54****	-.34	**-.66****	**-.69****	-.05	1	
		N	27	27	27	27	27	27	
	$\delta^{15}N$	Pearson Cor	**-.50****	-.30	**-.77****	**-.70****	-.20	**.78****	1
		N	27	27	27	27	27	27	27
Soil	P_{org_tot}(mg/kg)	Pearson Cor	1						
		N	54						
	P_{org_labile}(mg/kg)	Pearson Cor	.73**	1					
		N	54	54					
	P_{inorg}(mg/kg)	Pearson Cor	**.59****	**.49****	1				
		N	54	54	54				
	P_{tot}(mg/kg)	Pearson Cor	**.98****	**.73****	**.71****	1			
		N	54	54	54	54			
	C/N	Pearson Cor	**-.49****	**-.42****	-.268	**-.48****	1		
		N	54	54	54	54	54		
	$\delta^{13}C$	Pearson Cor	**-.41****	**-.49****	**-.34***	**-.43****	**.41****	1	
		N	54	54	54	54	54	54	
	$\delta^{15}N$	Pearson Cor	**-.48****	**-.55****	**-.51****	**-.52****	**.37****	**.45****	1
		N	54	54	54	54	54	54	54

*. Cor is significant at the 0.05 level (2-tailed).

**. Cor is significant at the 0.01 level (2-tailed).

A significant decline in mean levels of $P_{org\text{-}labile}$, $P_{org\text{-}tot}$, P_{inorg} and P_{tot} is observed from the forest to the agricultural land uses for both soils (ANOVA, $p<0.05$, n=54) and stream sediments(ANOVA, $p<0.05$, n=27) (Table 21). The C/N ratio of the soil increased significantly (ANOVA, $p<0.05$, n=54) from the forest to agriculture, whereas no significant difference (ANOVA, $p<0.05$, n=27) was observed for C/N in the stream sediments between the two land uses. The mean $\delta^{13}C$ and $\delta^{15}N$ for both soil and stream sediments increased significantly from Forest to the agricultural land use.

Table 21 The mean values, standard deviation (Stdev) and One-way ANOVA analysis for the mean P fractions levels and C/N ratios variation in soil and stream sediments between the Forest and Agricultural land use

Sediment type	Parameter	Sites	n	Mean	Stdev	F	*p*
Stream sediments	P_{org_tot}(mg/kg)	Up-stream	12	1068.63	344.02	11.81	.00
		Downstream	15	627.89	320.43		
	P_{org_labile}(mg/kg)	Up-stream	12	53.96	49.84	7.99	.00
		Downstream	15	14.92	17.85		
	P_{inorg}(mg/kg)	Up-stream	12	512.18	170.60	17.17	.00
		Downstream	15	244.51	163.71		
	P_{tot}(mg/kg)	Up-stream	12	1580.81	412.24	22.87	.00
		Downstream	15	872.40	357.23		
	C:N	Up-stream	12	10.73	1.60	.03	.86
		Downstream	15	10.82	1.089		
	$\delta^{13}C$	Up-stream	12	-19.65	.92	99.81	.00
		Downstream	15	-16.57	.67		
	$\delta^{15}N$	Up-stream	12	9.07	1.10	52.09	.00
		Downstream	15	13.22	1.72		
Soil	P_{org_tot}(mg/kg)	Up-stream	24	1163.66	440.62	21.46	.00
		Downstream	30	682.27	322.76		
	P_{org_labile}(mg/kg)	Up-stream	24	292.80	202.03	32.17	.00
		Downstream	30	77.50	45.48		
	P_{inorg}(mg/kg)	Up-stream	24	313.30	78.02	20.80	.00
		Downstream	30	201.95	97.05		
	P_{tot}(mg/kg)	Up-stream	24	1476.96	453.20	25.92	.00
		Downstream	30	884.23	401.44		
	C:N	Up-stream	24	9.96	.80	33.20	.00
		Downstream	30	11.53	1.11		
	$\delta^{13}C$	Up-stream	24	-19.01	1.86	26.32	.00
		Downstream	30	-16.59	1.60		
	$\delta^{15}N$	Up-stream	24	9.45	1.07	63.85	.00
		Downstream	30	11.31	.61		

The stream sediments had a significant (ANOVA, p<0.05, n=36) higher P_{inorg} than the soils while the $P_{org\text{-}labile}$ was higher in the soils than the stream sediments for both agricultural and forest land uses. Looking at the forest land use, the mean stream sediments C: N was higher than that of its soils while in the agricultural land use, soils had a higher mean C: N than the stream sediments.

Table 22 The mean values, standard deviation (Stdev) and One-way ANOVA analysis for the mean P fractions levels and C/N ratios variation between the Soil and stream sediments

Site Location	sediments type		N	Mean	Std. Deviation	F	*P*
Up-stream	P_{org_tot}	soil	24	1163.66	440.62	.42	.51
		Stream sediments	12	1068.63	344.02		
	P_{org_labile}	soil	24	292.80	202.03	16.06	.00*
		Stream sediments	12	53.96	49.84		
	P_{inorg}	soil	24	313.30	78.02	23.38	00*
		Stream sediments	12	512.18	170.60		
	P_{tot}	soil	24	1476.96	453.20	.44	51
		Stream sediments	12	1580.81	412.24		
	CN	soil	24	9.96	.80	3.64	.06
		Stream sediments	12	10.73	1.60		
	$\delta^{13}C$	soil	24	-19.01	1.86	1.23	.27
		Stream sediments	12	-19.65	.92		
	$\delta^{15}N$	soil	24	9.45	1.07	1.01	.00*
		Stream sediments	12	9.07	1.10		
Downstream	P_{org_tot}	soil	30	682.27	322.76	.28	.59
		Stream sediments	15	627.89	320.43		
	P_{org_labile}	soil	30	77.50	45.48	26.12	.00*
		Stream sediments	15	14.92	17.85		
	P_{inorg}	soil	30	201.95	97.05	1.20	.27
		Stream sediments	15	244.51	163.71		
	P_{tot}	soil	30	884.23	401.44	.00	.92
		Stream sediments	15	872.40	357.23		
	CN	soil	30	11.53	1.11	4.13	.04*
		Stream sediments	15	10.82	1.08		
	$\delta^{13}C$	soil	30	-16.59	1.60	.00	0.48
		Stream sediments	15	-16.57	.67		
	$\delta^{15}N$	soil	30	11.31	.61	29.89	00*
		Stream sediments	15	13.22	1.72		

The particulate organic matter (POM) both in soils and stream sediments decreased from the up-stream to the downstream sites. In soils, it decreased from 23± 11% to 8±3% while in stream sediments, it decreased from 9±6% to 4±4% as illustrated on Figure 3.

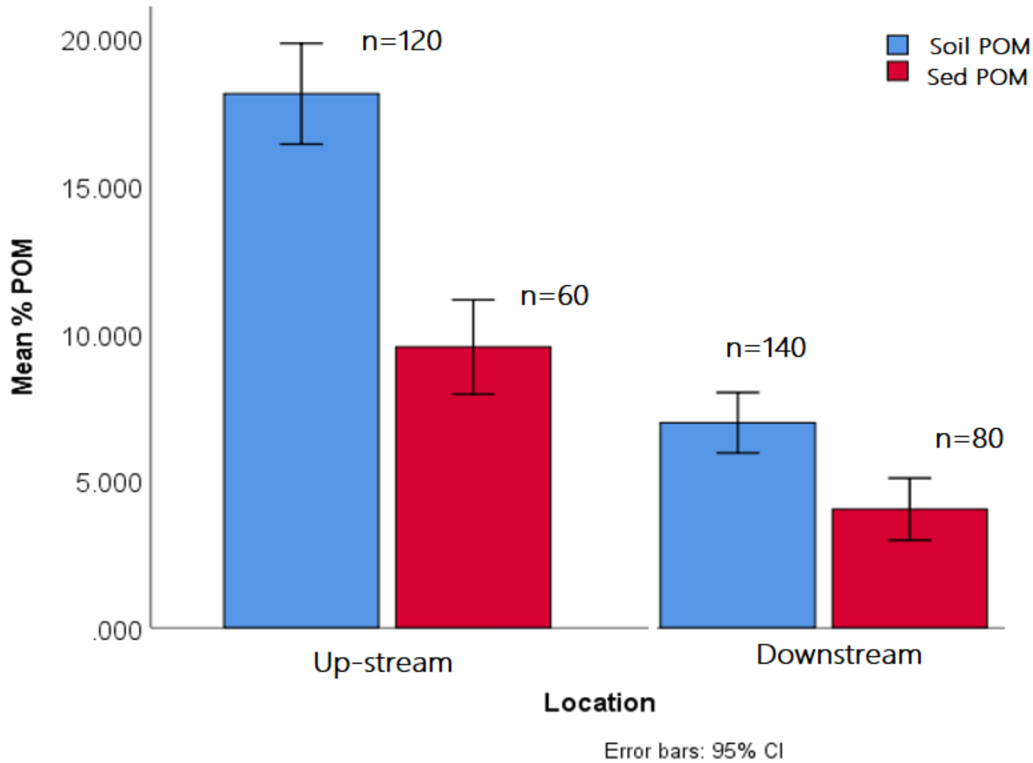

Figure 4 Bar graphs showing the mean percentages of Particulate organic matter variation in the soils and stream sediments for both the forest and agricultural land use.

4.0 Discussion

A clear difference is observed between the up-stream and downstream sites. The upstream sites have less variation in terms of nutrients levels, organic matter content and isotopic ratios whereas the downstream had major variations of these elements. The level of anthropogenic disturbance varied across the sites with different cropping preferences and farm management practices. Nitrate is a good indicator of catchment disturbance in P-limited systems (Peiearls et al., 1991). P is easily adsorbed to the soils and sediments unlike Nitrate which is easily dissolved in water or lost to the atmosphere through the denitrification process. Among the up-stream sites, Kapkateny had been encroached more by agriculture than any other site and this was well evidenced by the moderately increased levels of NO_3 in water and the $\delta^{13}C$ in sediments. It was the only up-stream site that was not N limited. Teremi downstream on the other hand was the most agriculturally impacted with the lowest soil P_{tot}, highest $\delta^{13}C$ and with highest stream sediments P_{tot}. It was the furthest downstream site from the upstream, with the highest discharge, hence the higher impact.

All the downstream sites were characterized by higher levels of nutrients than the upstream sites. We compared the levels against those set by the Kenyan government agencies (KEBS, 2015) and we found that they were within the set standards for consumable drinking water sources except for TSS which exceeded by huge margin both in the upstream and downstream.

The %POM in soils of upstream and downstream sites are comparable to those by (Recha et al, 2013) of 17% to 7% respectively. The stream sediments POM was lower in the downstream sites similar to (Webster et al., 1995) and would be explained by the activity of microbes (Wilson and Xenopaulos 2009). Although the streams were different, and impacted by different anthropogenic agricultural drivers, a similar decreasing trend is observed in the POM content and an increasing $SUVA_{254}$ is observed towards downstream agriculture land use.

4.1 Effects of agriculture on water Quality

As it is documented by several other varying tropical catchments stream studies (Masese 2015; Hedo & Lucas, 2017; Masese et al., 2017), we found that the up-stream sites were characterized by low levels of dissolved nutrients, E.C , pH, temperatures and TSS that had minimal variations across the sites. A varying increase in these parameters was observed at downstream sites.

Temperature change can result from change in altitude, shading and insolation (Ohmura, 2012). The sampling sites were located within an altitude difference of 800m, thereby we assumed that temperature could not be resulting from altitude change. When a riparian forest is lost stream temperatures tend to increase due to loss of shade (Baxter et al., 2005). The low water temperatures in the forested sites can be explained by the high canopy cover by the natural riparian vegetation that shielded the streams from direct insolation. The agricultural sites had a lower canopy cover hence the higher water temperatures. Other studies ie; (Dugdale et al., 2018) in Europe reported a significant warming of stream water with open canopy while those with planted woodland remained cooler, similar as (Masese, 2015), who reported a significant increase in temperatures of tropical streams from a 100% Forest to a 100% agriculture land use.

Land use and vegetation cover influences the TSS in the stream water (Ahearn et al., 2005). The high TSS at downstream sites was attributed to the high fragmentation (Ongugo et al., 2002) and big proportions of bare soils. The decrease of organic matter composition of TSS from the forest to the agricultural sites was more likely due to the increased amount of eroded silts into the streams.

Streams that drain similar geological catchment are more likely to have similar E.C hence its variation is a likely indicator of anthropogenic impacts (Masese, 2015). Agricultural land use is associated with usage of synthetic fertilizers, pesticides and acaricides for livestock's which ends up into the streams during runoff events. This increases the water ionic concentrations which leads to the observed high E.C levels in the downstream sites.

Phosphorous occurs naturally from the weathering of soil materials. It is rapidly captured in form of SRP by primary producers in availability of other nutrients (wetzel, 2001). Upon death and lysis of phytoplankton, a portion of inorganic P (SRP) is restored into the water through mineralization process by microbes whereas the other is buried in the sediments as organic P (wetzel, 2001). The P reduction from the water column is not only limited to phytoplankton assimilation, but also through adsorption on calcium, iron and aluminum hydroxides (Dodds &Welch, 2000; Lukkari et al., 2007). The higher water TP levels in the downstream sites was as a result of increased discharge and the observed higher TSS. This is in line with observations made by (Markewitz et al., 2001 and Bucker et al., 2011) where water nutrients correlated with discharge. This study established that there was a general decline in the stream sediments P_{tot} from the upstream to downstream sites. Similarly, the soils in the agricultural land use were generally depleted of POM and P. We attributed this observation to the cropping and farm tillage. Besides, tillage has been shown to increase the microbial activity of mineralization and remobilization of POM (Luo et al., 2010;

Lambert et al., 2017). Literature has it that land use change or reduction of forest cover affects export of P (Harris, 2001). Usage of fertilizers increases levels of both water TP and SRP (Harris 2001). In our study, the water TP increased in the downstream but not in the form of (SRP). Thus, we conclude that the mineralized P from the agricultural land use end up in the streams through runoffs as observed elsewhere (Wilson & Xenopaulos 2009; Galloway et al., 2005).

Tropical agricultural soils are subjected to high N leaching through runoffs (Snyder, 1996). Although there was no significant difference in the mean TN and NH_4 levels between the two land uses, a clear difference was observed in the dissolved NO_3. The elevated NO_3 in the agricultural land use is likely resulting from manure and nitrogenous fertilizer usage that leaches with run offs and end up into the streams just like it is recorded for the temperate regions (King et al., 2013). This study concurs with (Lewis et al. 1995) who observed that tropical stream was inefficient in retaining inorganic nitrogen during rain events. Riparian buffer strips have been documented to effectively remobilizes and increases retention of NO_3 across the agricultural lands (Fiebig et al., 1990), however, cultivation at the study area was up to the riverbanks, thus the higher NO_3 into the streams. The NO_3 levels in the downstream are like those recorded by (Recha et al., 2013) in a similar land use at R. Yala headwaters.

The low molar N:P levels in the upstream sites suggest that the streams were N limited whereas the high N:P downstream sites suggest that P was the limiting nutrient. Although its reported by several studies that tropical freshwater systems are N limited (Vitousek & Howarth, 1991; Mosisch et al., 2001; Davies et al., 2008;), a recent study on a catchment scale has reported a substantial variation in relative inorganic N and P abundance and variation across tropics (Gücker et al., 2016), thereby suggesting that the nutrients limitation in tropics could be as variable as that of temperate. Our observed results in the downstream sites would be due to the N leaching from the agricultural lands through runoffs as it has been documented elsewhere (Snyder, 1996).

The observed DOC levels were like those recorded within tropics of 1.3mg/L from Yala headwaters streams in Western Kenya (Recha et al., 2013), from Gambia River draining a savanna grassland (Lesack et al.,1984) and also in temperate Spree river in Germany (Lewandowski & Nutzmann 2010). Lower levels have also been recorded in lower Yala River and in L.Victoria (Aloo, 2003). The $SUVA_{254}$ (DOC aromaticity) increased from the upstream to the downstream sites. It would be expected that the upstream would have a higher aromaticity due to the terrestrial forest aromatic materials input. As it is in the river continuum concept (Vannote et al., 1980), stream primary productivity increase with the decreasing canopy cover hence the DOC in the downstream would be derived more of autochthonous materials with a lower aromaticity. Our inverse results could be justified by the fact that the sampling for this study was carried out a month after the onset of rains, thus a higher likelihood that the higher molecular aromatic materials in the upstream had been washed away, similar to observation made by (Masese, 2015). Also, it has been documented that agricultural tillage facilitate mobilization of recalcitrant DOM which end up in the streams (Wilson & Xenopaulos, 2009; Graeber et al., 2012).

4.2 Effects of agriculture on Soil and stream sediments POM and nutrients

Soil particulate organic matter is an important component and determinant of nutrients in soils. It acts as a source energy for microbial communities that carry out mineralization process, availing nutrients for use by plants (lambert et al., 2017). The significant reduction in %POM composition in the soils from the forest to the agricultural land was largely due to the change in forest and vegetation cover. Models have shown that the impact of Forest conversion to agriculture leads to 25 to 30% reduction of POM (Haughton and Goodale, 2004). This decline can be attributed to one) the microbial community activity (Roth et al., 2011) that are known to increase with agricultural activities, and two) agricultural management practices (Chang et al., 2014), as maximum tillage exposes POM to both wind and water erosion thereby being lost into streams. The increment in levels of DOC, Nitrates and phosphates in the downstream could be attributed to mineralization process of POM in soils and stream sediments. In the long run, the reduced POM can have a consequence of reduced microbes that would affect not only soil fertility but also amount and quality of DOC in the surrounding water body (Compton and Boone, 2002).

Stream sediments POM constitute both allochthonous and autochthonous sources. Agricultural Land use in the headwaters increases the quantity of POM delivery to the downstream (Erin et al., 2018). However, there was a general decline in POM content of stream sediments from the up-stream forest in our study area. The deposition process is influenced by residence time and stream energy. Our downstream sites were characterized by high stream energy thereby hindering the deposition process. Moreover, the upstream soil POM was higher than that of downstream thus the low POM in the stream sediments indicates that the upstream soil is retained in the upstream section and not transported downstream; and that the downstream sediments consist mainly of the POM-depleted soil of the agricultural surroundings. This is evidenced from the stream sediments

$\delta^{13}C$ analysis. The soils and stream sediments $\delta^{13}C$ were similar in the upstream as well as downstream but a significance ($p<0.050$) difference was observed across the land use (Table 21&22).

The soil C:N influences the microbial growth and activities by providing energy to them. A C:N of 1 to 15 increases N mineralization while that above 35 increases N immobilization (Watson et al., 2002; Brust, 2019). Usage of organic fertilizers in agricultural land use have been documented to stimulate the microbial decomposition of Soil organic matter (Luo et al., 2010; Pisani et al., 2016) that should in turn result into lower soil C:N. Our study had a significant increase in soil C:N from the forest to the agricultural land. We argue that this increase was due to cropping of C_4 crop (*Zea mays)* whose impact was investigated using $\delta^{13}C$ where we found a significant impact of *zea mays* in the agricultural soils with a similar isotopic $\delta^{13}C$sign as that obtained by (O'leary 1988) of -11 ±4. Moreover, the shift in type of vegetation and trees could have influenced the C:N. The exotic trees such as *Eucalyptus globulus* were more in the agricultural land use and their N mineralization rate has been documented to be high (Shamahs et. al., 2003).

The P_{tot} decreased from the forest to the agricultural land use for both soils and stream sediments. Its decline in soil is arguably as a result of crops cultivation over time. More also, the decline in POM could have influenced its abundance. The stream sediments P_{tot} change is more likely to result from desorption as it is evidenced by increasing TP levels in the water column. P_{org_tot} constituted the highest percentage of $P_{tot;}$ both in the soils and stream sediments at both land uses. This can be explained by its high competitiveness against both decomposition and remineralization (Spohn, 2020). Recent studies have reported 8.8 times higher P_{org} (Spohn, 2020) in soils with a close link to the grain size of the soils.

There were no significant differences between the Soils and stream sediments C:N and P fractions both in the up-stream sites and the downstream sites. This was a clear indicator of land use influence on the stream sediments nutrients through increased erosion as observed by (Grip et al., 2004).

5.0 Conclusion

The study has established a huge impact of agriculture on both stream ecosystem and terrestrial surroundings. The streams ecosystems effects entailed the increase in the levels of nutrients in the water column thereby shifting the streams from N-limitation to P-limitation. On the other hand, it reduced soils POM leading to low water OM and low POM in the stream sediments.

With the current development in terms of growing populations and increasing agricultural subsidy by governments, more intensification of agriculture is expected in Africa with a severe impact on the aquatic ecosystems. We hereby propose creation of riparian buffers and sustainable management of farms such as use of terraces, minimum tillage and provision of farm extension services by the government to prevent soils erosion and protect streams. Moreover, more studies within the tropics in relation to microbial activities as a result of land use change are needed to facilitate evidence-based management of the lotic systems.

6.2 References

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