DRIVERS OF THE BIOGEOCHEMISTRY AND FUNCTIONING OF THE AFROMONTANE-SAVANNA MARA RIVER, KENYA

BY

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DECLARATION

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DEDICATION

I dedicate this work to my father and mother, the late Mr and Mrs Wanderi. Forever your spirit remains ingrained in my heart. You were and still are my eagle, “Nderi”.

ABSTRACT

In Afromontane-savanna rivers, data on the role of land use, stream size and large mammalian herbivores (LMH, both wildlife and livestock) and their interactions on nutrient cycling, dissolved organic matter (DOM) composition, and ecosystem metabolism are still limited. This study investigated the role of land use, stream size LMH and their interactions on the biogeochemistry of the Mara River, Kenya. Specifically, the influence of land-use change, stream order and density of LMH on water physico-chemical, quantity and composition (quality) of DOM and ecosystem metabolism in the river was investigated. A total of 82 sites were selected for sampling during the beginning of the dry season in January 2018 for nutrients, dissolved organic matter (DOM), and modelling of whole-stream/ ecosystem metabolism. Sites were grouped into five broad categories defined by land use and density of LMH: forested (19), agricultural (26), low-density livestock (15), high-density livestock (12), and wildlife (i.e., hippopotami- hippos) (10) sites. There were significant (PERMANOVA, $p<0.05$) spatial variations in water physico-chemical parameters, nutrients, DOM quantity, and measures of ecosystem metabolism among land uses and not among stream orders. Sites influenced by LMH had high electrical conductivity, temperature, and dissolved oxygen levels ($p<0.05$). LMH inputs had varied effects on nutrients, ammonium and DOC associated with hippos and high-density livestock streams ($p<0.05$). Total dissolved nitrogen (TDN) and nitrates were higher in agricultural sites and low livestock density streams than in the high livestock and hippo-influenced sites. Hippos and high-density livestock streams had high aromaticity and high molecular weight DOM ($p<0.05$). In contrast, low-density livestock and agricultural streams had photodegraded and low molecular weight DOM. The ratio of gross primary production (GPP) and ecosystem respiration (ER) was greater than one (GPP/ER >1) in low-density livestock and agriculture sites. At forested sites, the ratio was less than one, which is an indication of heterotrophic conditions. The findings of this study show that irrespective of their location on the fluvial continuum, LMH strongly influence the biogeochemistry of Afromontane-savanna rivers, which overrides the influence of stream size on the physico-chemical, DOM composition and ecosystem metabolism in the Mara River. Therefore, physico-chemical, DOM composition and ecosystem metabolism must be included in continuous monitoring for better management of LMH density in Mara River. In addition, pre-existing riverine models need to be updated to suit the Afrotropical savanna river functioning and biogeochemistry.

Keywords: *Large mammalian herbivores, land-use, dissolved organic matter, stream order, ecosystem metabolism*

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LIST OF ABBREVIATIONS

BIX:	Biological/Autochthonous index
BDOC:	Biodegradable dissolved organic matter
CDOC:	Chromophoric dissolved organic matter
DOC:	Dissolved organic carbon
DOM:	Dissolved organic matter
DON:	Dissolve organic nitrogen
EEM:	Excitation-emission Matrix
ER:	Ecosystem metabolism
FI:	Fluorescence index
GPP:	Gross primary production
HMW:	High-molecular-weight
HIX:	Humification index
Hs:	Humic substances
LMH:	Large mammalian herbivore (wildlife and livestock)
LMW:	Low-molecular-weight:
PARAFAC:	Parallel factor analysis
POC:	Particulate organic matter
SRP:	Soluble reactive phosphorous
TDN:	Total dissolved nitrogen
TSS:	Total suspended solids

LIST OF SYMBOLS

a_{254}	absorbance coefficient at 254 nm
a_{410}	absorbance coefficient at 410 nm
a_{254}/ a_{410}	absorbance coefficient ratio of 254 nm and 410 nm
C: N	carbon-nitrogen ratio
λ	wavelength
S	ultraviolet spectral slope
$SUVA_{254}$	specific ultraviolet absorbance at 254 nm
UV-Vis	ultraviolet-visible

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CHAPTER ONE

INTRODUCTION

1.1 Background information

Freshwater ecosystems are among the world’s most threatened aquatic habitat types (Dudgeon *et al*., 2006; Hering *et al*., 2006; Carpenter *et al*., 2011). This threat has been linked to the increasing human population (Tilman *et al*., 2011), which has resulted in land use and land cover change along the riparian areas of rivers to meet the increasing human demands for natural resources (Odada *et al*., 2009). In the years between 1990 to 2015, approximately 7.8 million hectares of native forest in the wet tropics were converted into agricultural land uses globally (Keenan *et al*., 2015). Similarly, in the Mara River basin, forest land in the catchment areas has been converted to settlements, grazing land, agriculture, and fuelwood harvest, among other human activities, so as to meet the increasing demand for food and shelter (Masese *et al*., 2014; Mngube *et al*., 2020). This decline in forest cover for livestock grazing and farmlands has also resulted in the reduction of the population of wild large mammalian herbivores (LMH) in the Mara River basin (Ogutu *et al*., 2011; Ogutu *et al.*, 2016).

Land use change along rivers affects river biogeochemistry and functioning (Kasangaki *et al*., 2008; Silva-Junior *et al*., 2014; Fuss *et al*., 2017). Ecosystem functioning is the process which controls ecosystem processes, such as energy and matter fluxes, nutrient cycling, organic matter decomposition and ecosystem metabolism (Gessner *et al*., 2002). Ecosystem functioning encompasses factors affecting all the characteristics of living things (respiration, movement, growth, et cetera) and how these characteristics affect their environment's physical and chemical conditions. In contrast, biogeochemistry is the interaction between the aquatic ecosystem's chemical, physical, biological, and geological processes. These interactions influence the distribution and cycling of nutrients and chemical components in aquatic ecosystems (Sandin and Solimini, 2009). Changes in ecosystem functioning and biogeochemistry in rivers because of land use change lead to increased nutrient concentrations, major ions, turbidity, temperature, sunlight, and shifts in DOM quality and quantity (Kasangaki *et al*., 2008; Silva-Junior *et al*., 2014; Fuss *et al*., 2017; Masese *et al.*, 2017). Changes in land use type along the riparian areas may result in changes in the supply and quality of trophic resources, macro-invertebrate diversity, and water quality (Carpenter *et al*., 2011; Hladyz *et al*., 2011), among other effects (Kasangaki *et al*., 2008; Silva-Junior *et al*., 2014).

Agricultural land use along rivers in Kenya, such as Nzoia, Nyando, and Mara, among others, has been associated with the increase in physico-chemical and nutrients due to agricultural-related activities such as tillage, use of fertilisers, pesticides, among others (Masese and McClain 2012; Achieng *et al.*, 2021; Wanderi *et al*., 2022). For example, in the Nyando River, an increase in nutrients, especially nitrates and phosphorous, was reported in agro-industrial influenced streams compared to forested streams (Raburu and Okeyo-Owuor, 2006; Onyando *et al*., 2013; Guya, 2019). The conversion of natural forest into agricultural land use can lead to a loss of 50–58% carbon due to reduced organic matter inputs through litterfalls, wood and root debris, among others, further leading to reduced dissolved organic matter quantity (Ahamed *et al.*, 2022). In the Nzoia

River, the decomposition rate of the leaf litter has been affected by agricultural land use (Kadeka *et al*., 2021). Agricultural land use may introduce exotic plants, consequently affecting the leaf litter quality thus affecting the organic matter decomposition rates (Tomanova *et al.*, 2008). In addition, agriculture activities may increase the production of autochthonous dissolved organic matter (biological autochthonous index ~ 0.8) that is of low molecular weight and highly biodegradable (Masese *et al.,* 2017). Agriculture practices such as the monoculture of *Eucalyptus* trees in riparian zones may also compromise the quality and quantity of leaf litter entering the rivers, affecting macroinvertebrates' functional and community structure. (Patrick, 2013; Cooper *et al.*, 2013; Silva-junior *et al.*, 2014).

In Afrotropical savanna rivers, LMH) both wildlife and livestock) are vital in linking terrestrial and aquatic ecosystems by transporting terrestrial nutrients and organic matter to aquatic ecosystems (Subalusky *et al*., 2015). LMH is an adult mammal weighing more than 5 kg (Bourlière, 1975). The amount of organic matter mediated by the LMH may increase the primary production of grasslands (Frank *et al*., 1993), modifies the traits of vegetation cover along the riparian areas of rivers, and accelerates nutrient cycling (DÍaz *et al*., 2007). In addition, LMH inputs contribute a significant amount of organic matter in the form of dung, which influences the recipient system's nutrient cycling (Kitchell *et al*., 1999; Vanni, 2002), primary productivity (Marcarelli *et al*., 2011), and food structure and stability (Leroux & Loreau, 2008).

The LMH such as hippos, livestock, wildebeest, zebra, elephant, and buffalo can transfer substantial amounts of major ions and nutrients into rivers through direct defecation and urination during their migrations and watering (du Toit, 2003; Bond *et al*., 2014; Subalusky *et al*., 2017; Masese *et al*., 2020). Hippos, for instance, transfer dissolved silica from savanna grassland into the recipient rivers through egestion and excretion (Schoelynck *et al*., 2020), while cattle transfer ammonium-rich urine during excretion at watering points along the streams and rivers (Iteba *et al*., 2021). Similarly, LMH's inputs may also affect ecosystem metabolism, a measure of total stream primary productivity and ecosystem respiration (Tank *et al*., 2010).

The amount and composition or quality of resource subsidies contributed by the LMH to aquatic ecosystems depend on the species, population densities, feeding behaviour, and season (Bond *et al*., 2012; Bond *et al*., 2014; Masese *et al*., 2020). For instance, change in species composition along the riparian areas from large wildlife to livestock may induce shifts in the characteristics, quality, and quantity of organic matter, change in nutrient concentration and water quality (Masese *et al*., 2014; Masese *et al*., 2017), with likely effects on the structure and functioning of the river. Also, LMH's inputs may provide more labile allochthonous carbon sources, which may be assimilated by bacteria and other organisms to provide energy at the base of food webs (Vannote *et al*., 1980; Junk *et al*., 1989).

Productivity in streams and rivers is measured using metrics such as gross primary production (GPP), ecosystem respiration (ER), and net ecosystem production (NEP)

(Young *et al*., 2008). In most temperate streams, terrestrial organic matter, such as leaf litter, is a vital energy resource for food webs (Tank *et al*., 2010). Both LMH and land use types affect ecosystem metabolism in rivers by altering the rates of GPP, NEP, and ER. Agriculture land use is mainly characterised by a reduced canopy which increases the surface area for light absorption, thus increasing the rates of GPP. During the wet season, the rate of GPP is diminished, while ER rises due to high turbidity resulting from soil erosion along the agricultural areas, which reduces the amount of light reaching the streambed. On the other hand, LMH transfers organic matter into recipient rivers which may drive ER and GPP (Masese *et al*., 2020). In addition, an increase in organic matter accelerates microbial activities such as decomposition, which consumes oxygen, thus accelerating ER.

As stream size increases, the surface area increases, the transformation and absorption of nutrients increase and the transportation of nutrients further downstream and to the ocean. As a result, Litterfalls decrease with increasing stream order, while course particulate organic matter reduces with stream order (Cummin 1975, 1977; Vannote *et al*., 1980). Stream order affects organic matter processing (Cummin, 1975, 1977). However, other factors, such as the quality and quantity of organic matter and climate, may also affect it (Vannote *et al*., 1980; Webster & Meyer, 1997; Williams *et al.,* 2010). Stream size is also a good predictor of ecosystem metabolism, especially GPP (Vannote *et al*., 1980; Webster & Meyer, 1997). This is because gross primary production increases with increased stream size and reduces with canopy cover over the stream (Vannote *et al*., 1980; Webster & Meyer, 1997). However, in larger streams, factors such as increased turbidity may reduce sunlight insolation hence reducing rates of GPP (Vannote *et al*., 1980). In recent studies, however, stream size is a poor predictor of water quality (Wanderi *et al*., 2022) compared to land use. In addition, Coble *et al*. (2022) also reported that land use effects override the influence of stream order and seasonality in driving the dynamics of organic matter in rivers. Therefore, stream order and seasonality should not be used as the only predictors of nutrients, dissolved organic matter and ecosystem metabolism in streams and rivers. Instead, all these factors should be considered to provide conclusive results.

To understand the role of LMH and land uses in Afrotropical rivers, routine monitoring of physico-chemical parameters, nutrients, DOM (quality and quantity), and biogeochemical processes is crucial. The ecological integrity of the freshwater ecosystem has been monitored using physico-chemical parameters in various streams and rivers (American Public Health Association, 2005). Furthermore, analysis of physicochemical parameters has traditionally been widely used in assessing water quality as influenced by human-related activities (Karr and Chu, 1999; Cairns, 2003). But studies have emphasised the inclusion of functional measures, such as organic matter processing, including the composition of dissolved organic matter, and ecosystem metabolism to give conclusive results on anthropogenic effects, such as land use change, in rivers (Arman *et al*., 2019; Ferreira *et al.*, 2020; Ruaro *et al.*, 2020).

Studies on dissolved organic matter characterisation and ecosystem metabolism for freshwater biomonitoring have gained interest in recent freshwater studies (Jaffé *et al*., 2008; Ferreira *et al.*, 2020). However, DOM characterisation and assessment of ecosystem metabolism in freshwater ecosystems have been widely investigated in temperate streams relative to tropical streams and rivers (Masese *et al*., 2017; Ferreira *et al.*, 2020). Hence, this has limited long-term or broad-scale research on the biochemical composition of DOM and ecosystem metabolism for comparative studies in Afrotropical freshwater ecosystems (Richardson *et al*., 2010).

In Afrotropical savanna rivers, LMH are very predominant, but their role in the structure and functioning of aquatic ecosystems is poorly understood. Therefore, this study investigated the impact of land use, LMH and stream size or order on physico-chemical parameters, DOM quantity and composition, and ecosystem metabolism in the Mara River system. In addition, this study aims at understanding interactions between land uses and stream size to determine which factors drive the biogeochemistry and functioning of the Mara River.

1.2 Statement of the problem and justification

1.2.1 Statement of the problem

Studies on the impacts of land use on biogeochemistry and river functioning of temperate rivers have been widely done; however, research in tropical regions is still scarce (Ferreira *et al*., 2020), especially concerning the role of LMH. Most researchers in the tropics have also associated agricultural land uses as the major driver affecting the river functions leading to calamities such as pollution, loss of habitat, and loss of biodiversity, among others (UNEP, 2016). While this represents most global rivers, LMH may mediate river functions compared to stream size and agricultural land use effects. In addition, the intensification of livestock is increasing faster in most countries compared to cropping systems (FAO, 2006), yet information on their role in driving biogeochemistry and the functions of rivers is also limited (Mateo-Sagasta, 2017; Masese *et al.,* 2020).

Riverine models such as the river continuum concept (RCC) emphasise the role of stream size in mediating the temperate river functions, but recent studies have found that land use as the driver of biogeochemical processes in rivers (Mwanamke *et al.,* 2019; Wanderi *et al.,* 2022; Coble *et al.,* 2022). For example, tropical rivers, such as the Mara River, are characterised by LMH, which is not covered in riverine models, yet their inputs and daily activities along the riparian areas affect the recipient river's functionality. In addition, Afrotropical savanna rivers' land use, such as grasslands and higher plants, are unique to these systems compared to temperate streams (Wanderi *et al.,* 2022). Hence, these river systems' functioning may deviate from other rivers in temperate areas. Limited studies have also focused on the combined influences of agriculture, LMH, land use, and stream order/size on the physical-chemical variables, dissolved organic matter and ecosystem metabolism in streams and rivers.

Furthermore, studies on the characterisation of dissolved organic matter and ecosystem metabolism are challenging, coupled with a lack of facilities, the high cost of mini dot-sensors, and benthos-torch, among others (Ferreira *et al*., 2020), which have further limited information on these themes, hence need for innovative approaches in conducting such studies through collaborative research.

1.2.1 Justification for the study

Land use affects water quality (Giri *et al.,* 2016; Ayuyo, 2021; Dalu *et al..,* 2022; Wanderi *et al.,* 2022), dissolved organic matter dynamics (Liu *et al*., 2019; Coble *et al.*, 2022), and ecosystem metabolism (Silva-Junior *et al.,* 2016; Fuss *et al*., 2017; Masese *et al*., 2017). Agricultural land use is the most researched, and it has been related to a negative effect on water quality and dissolved organic matter (Wilson et al., 2009; Griffiths *et al.,* 2013; Graeber *et al*.,2015; Fuss *et al.,* 2017; Masese et al., 2017), and nutrient regimes shifts affecting ecosystem metabolism (Fuss *et al.,* 2017), increased nutrient concentration (especially nitrates and ammonium) (Mateo-Sagasta *et al*., 2017; Jacobs *et al.,* 2017; Mwanamke *et al.,* 2019). These studies have proved the overriding effect of land use on river function compared to other factors, such as stream size.

Early riverine models such as the river continuum concept (RCC; Vannote *et al*., 1980) emphasised the importance of allochthonous carbon sources from mainly higher plants than C4 (savanna grasses) and instream production. However, in large rivers such as the Amazon River, floodplains are essential sources of nutrients and dissolved organic matter (Junk *et al*. 1989). Similarly, the Mara River has large populations of both livestock, wild LMH, and savanna grasslands (C3 plants), and the river is highly seasonality in terms of its flow regime. The presence of LMH affects the river's biogeochemistry and functioning through its interaction with the recipient river during its movement, feeding, trampling, egestion and excretion (Stears *et al.,* 2018; Masese *et al*., 2020).

Freshwater ecosystems provide habitat, and large aquatic mammalian herbivores, such as hippos, use their riparian areas for grazing. Hippos live in lakes, rivers, and other western, eastern, and southern African wetlands, with an estimated population of between 125,000 and 148,000 (Lewison & Oliver, 2008). Hippo feed during the night and spend the rest of the day in the water. Therefore, they spend more time in the water, approximately 50% of the time, than most LMH, thus transferring a significant amount of nutrients and dissolved organic matter from savanna landscapes into the recipient freshwater ecosystems (Subalusky *et al*., 2015; Doughty *et al*., 2018). The hippo's inputs are rich in carbon and nutrients, with most studies showing that these nutrients are an essential source of food for aquatic organisms either directly or through microbial and stimulated primary production (Masese *et al*., 2015, 2018; McCaluely *et al*., 2015; Masese *et al*., 2022).

According to Schoelynck *et al*. (2020), hippos influence the Mara River's silicon cycle by providing silicon-rich organic matter, which they obtain from feeding on silica-rich C3 savanna grasses. Silica is a building block for diatoms in freshwater ecosystems, and the diatoms community forms an essential base for food webs in many aquatic ecosystems (Stenger-Kovács *et al.*,2022). Silica cycling and concentration influence primary production and ecosystem metabolism in streams and rivers (Schoelynck *et al*., 2020). Both livestock and hippo populations can be detrimental to savanna grasslands; for instance, an increase in the hippo populations increases their daily food requirements, which could subsequently lead to an increase in organic matter inputs in the recipient rivers and streams. An increase in organic matter in rivers and streams is detrimental to water quality and may even lower oxygen levels in water (Stears *et al*., 2018; Dutton *et al*., 2018, 2021).

The livestock population is also associated with increased nutrient and organic matter, affecting water quality (Thornton, 1971; Fleischner, 1994). Livestock input to the recipient river contributes to low molecular weight organic matter, which is bioavailable for organisms (Masese *et al.,* 2017; 2018; 2020). This organic matter is decomposed or directly used by the primary producer, thus promoting primary production. Therefore, an increase in primary production increases GPP and even abnormal algal biomass production, which may cause eutrophication when livestock input increases in larger quantities (Masese *et al*., 2022). Increased livestock populations also lead to increased soil erosion which is washed into the rivers, leading to increased water turbidity, which is detrimental to aquatic organisms. Therefore, properly managing livestock and hippos' population densities is crucial in maintaining the structure and functioning of the Mara River (Vavra, 2005).

Understanding the role of LMH in driving nutrients, physical and chemical parameters, dissolved organic matter, and ecosystem metabolism in streams and rivers is paramount for adequate water resources management. This can be achieved by incorporating frequent monitoring of nutrients, dissolved organic matter, and ecosystem metabolism. In addition, this will help fill the knowledge gaps, especially in the Afrotropical savanna rivers, where this information is still limited. In addition, filling knowledge gaps on the role of LMH in driving ecosystem metabolism, organic matter processing, geomorphology, and nutrient cycling in savanna rivers which are not well represented (Masese *et al*., 2020).

Therefore, this study aimed to understand the role of LMH in the Mara River. This study hypothesises that the livestock population is increasing and may replace the hippo population or compete with hippos for food and water. Hence, agriculture and forested land uses were used to better compare these dynamics. The data in this study will provide current information for LMH management, sustainable agriculture, and land use management for water quality through LMH density control. In addition, dissolved organic matter characterisation will improve the understanding of the role of savanna rivers in carbon and nutrient cycling before transportation to lakes and the ocean. Further, this will help us understand the role of the savanna rivers in outgassing carbon dioxide and other greenhouse gases into the atmosphere. In Kenya, this study will also improve the monitoring of the influence of land use change and LMH (including grazing) on water quality, which is essential in policy development, freshwater restoration, wildlife protection, and conservation of water resources.

1.3 Study objectives

1.3.1 General objective

The general objective is to determine the influence of land use change and stream order on the biogeochemistry and functioning of the Mara River in Kenya.

1.3.2 Specific objectives

1. To determine the influence of the large mammalian herbivores and land use on the physico-chemical of the Mara River.
2. To determine the influence of large mammalian herbivores, stream size and land use on DOM concentration and composition in the Mara River.
3. To determine the influence of the large mammalian herbivores land use and stream size on the ecosystem metabolism (GPP and ER) in the Mara River.
4. To investigate the interactions between stream size, large mammalian herbivores density, and land uses on the physiochemistry, DOM composition, and ecosystem metabolism in the Mara River.

1.3.4 Hypotheses

H_o There is no influence of large mammalian herbivores and land use on the physico-chemical of the Mara River.

H_o There is no influence of large mammalian herbivores and land use on dissolved organic matter composition and concentration in the Mara River.

H_o There is no influence of large mammalian herbivores and land use on ecosystem metabolism in the Mara River.

H_o Large mammalian herbivore's density, and not stream order, influence the physico-chemical, DOM composition, and ecosystem metabolism in the Mara River.

CHAPTER TWO

LITERATURE REVIEW

2.1 Influence of land use and large mammalian herbivores on water quality in rivers

Water quality consists the gamut of biological, physical and chemical characteristics that define its usability for different purposes (Karr, 1999). Water quality parameters determine whether the water is clean and safe for drinking, industrial, recreation and agricultural purposes (Giri & Qiu, 2016). Water quality plays a pivot in all aspects of living organisms and thus has attracted attention from a broad range of scientists, researchers, and water resource managers (Giri and Qiu, 2016). The United Nations General Assembly in July 2016 declared access to clean and safe water for human consumption as a human right (UN, 2016), because of the multiple stressors on fresh water from pollution, mainly from land use change, agriculture, urbanisation and industrialisation. Therefore, there is a need for water quality monitoring using cost-effective tools, especially in Afro-tropical streams and rivers, to ensure clean water safety requirements are met (Achieng *et al.*, 2021).

Catchment areas strongly influence the condition of the rivers, and therefore rivers are a good predictor of the status of their riparian area (Hynes, 1975; Karr, 1999; Williamson *et al*., 2008). Hence, water quality in streams and rivers has been used broadly to provide information on hydrological and biogeochemical processes in the catchment areas they drain. Therefore, it is assumed that the catchment influences water quality more in the headwater than downstream because in the headwaters there is a strong linkage between the terrestrial and fluvial domain (Vannote *et al*., 1980; Lambert *et al*., 2010). However, the contribution of catchments and headwater streams is critical to river basins' physical and biogeochemical characteristics, particularly concerning carbon, nitrogen, and associated element transfer and transformation (Cole *et al.,* 2007; Aufdenkampe *et al.*, 2011).

Land use change from natural vegetation (forest) to other land uses (e.g., agriculture or grazing) is a significant cause of degradation of water quality, biodiversity loss and ecological integrity loss in streams and rivers (Allan, 2004; Vörösmarty *et al*., 2010; Brauns *et al*., 2022). Land use changes affect the structure and functioning of the river mainly through changes in runoff and soil erosional processes, organic matter processes, the contribution of nutrients and major ions inputs (Dudgeon *et al.,* 2006; Petrone, 2010; Tank *et al.,* 2010; Fugère *et al*., 2018). Water quality in aquatic ecosystems is closely correlated with the riparian land use type and proportion (Tong & Chen, 2002; Hwang *et al*., 2016). For instance, an increase in the proportion of agriculture along the riparian area is associated with an increase in major ions, salinity, electrical conductivity, suspended solids, and nutrients (Minaya *et al*., 2013; Kilonzo *et al*., 2014). However, despite these catchment-scale land use influences, some studies have shown that the effect proportion of land use is not only the factor which drives water quality in aquatic ecosystems but rather the use and size of the riparian area (Minaya *et al*., 2013; Hilary *et al*., 2021; Kadeka *et al*., 2021).

Agricultural land use is also associated with negative impacts on the ecological condition of Afrotropical rivers due to increased concentrations of nutrients, such as total nitrogen, nitrite and total carbon and sediments (Minaya *et al.*, 2013; Masese *et al.,* 2014; 2017; Fugère *et al.*, 2018; Dalu *et al.,* 2019). Furthermore, irrigation farms along the rivers causes water abstraction and excessive water withdrawals, which may change the rivers' natural flow regimes and discharge. In addition, untreated water from irrigation may also cause rivers may also pollute water.

The influence of large mammalian herbivores (LMH), both wildlife and livestock, are increasingly recognized for playing a major role in determining the structure and functioning of streams and rivers (Masese *et al.*, 2020). Livestock use of streams and rivers increase river turbidity and nutrients through defecation and excretion at water points and crossing along the rivers (Subalusky *et al.*, 2015; Dutton *et al.*, 2018; Masese *et al.*, 2017; Iteba *et al.*, 2021). During dry seasons reduced discharge promotes the accumulation of ammonia, an increase in the concentration of solutes, and reduced dissolved oxygen levels (Dutton *et al.*, 2021; Wanderi *et al.,* 2022). Livestock and large wildlife grazing may negatively affect water quality and the ecological integrity of rivers through loading organic matter, dissolved organic carbon (DOC), soluble reactive phosphorous (SRP), and carbon-to-nitrogen ratio (C: N) (Dutton *et al.*, 2018; Iteba *et al.*, 2022). During LMH's movement and trampling, the river bank may lose its stability, further increasing soil erosion and turbidity and sediments rich in major ions such as dissolved silica.

Studies on water quality determinants at spatial and temporal space in Afromontame-savanna rivers are minimal (Wanderi *et al.,* 2022). Despite this, changes in water quality in Afromontame-savanna rivers can occur at short spatial and temporal scales due to the highly heterogeneous nature of the landscapes caused by rapid changes in the amount of rainfall, elevation, vegetation type, and geology. Usually, the uplands are characterised by higher amounts of rain and relatively cooler temperature supporting the broadleaf tropical vegetation, while the lowlands are characterised by much drier conditions, shallow soils and sparse vegetation and is rich in grasslands as well as shrublands (Tamooh *et al*., 2012; Abrantes *et al*., 2013; Aich *et al*., 2014; Englmaier *et al*., 2020).

Unlike other biomes, Afromontane-savanna rivers also present a unique situation where land use features vary both altitudinally and longitudinally from the headwaters. Specifically, rivers are postulated to exhibit a change in physical (temperature, organic matter) and chemical factors from upstream to downstream (Vannote *et al*., 1980; Downing *et al*., 2012; Creed *et al*., 2015), however different patterns have been observed and reported in African savanna rivers (Masese & McClain, 2012; Masese *et al.*, 2015; 2022). The LMH's abundance and biomass in African savanna landscapes also show a physical gradient, with a low abundance in forested uplands and a high abundance in savanna grasslands in the lowlands. Rivers that drain these landscapes have a close relationship with terrestrial ecosystems due to the vectoring role of livestock and large wildlife in transferring large amounts of organic matter and nutrients at water points and crossing streams and rivers. (Subalusky *et al.,* 2015; Iteba *et al.,* 2021).

As new frontiers of land use change, African savanna landscapes are also emerging because of human and livestock migration from upstream which is more productive and densely populated lands, to marginalised less populated areas. Hence more dramatic land cover changes in humid upstream and drier savanna lowlands, with mid-elevation areas remaining instead natural. Thus, according to Vannote *et al.* (1980), postulated changes from upstream-downstream gradients may not apply to these river systems, especially rivers draining savanna landscapes. Furthermore, Savanna rivers are seasonal with highly variable flow regimes characterised by dry seasons with cessation of flow and during the wet seasons of flash floods (McClain *et al*., 2014). Therefore, these characteristics of Afromontane-savanna rivers present intriguing scenarios for understanding the interactions among different land uses as drivers of water quality in savanna rivers, and the Mara River represents all these factors to be investigated.

2.2 Dissolved organic matter in rivers

In rivers, organic matter is composed of dissolved organic matter (DOM), particulate organic matter (POM), and colloidal organic carbon (COC) (Aiken *et al*., 2014). Dissolved organic matter (DOM) is that part of organic matter that can pass through a 0.45 µm pore filter (Aiken *et al*., 2014). Therefore, in rivers, DOM forms the most significant proportion of the organic matter pool (Wetzel, 1992). Dissolved organic matter in rivers can either originate from terrestrial sources, commonly referred to as allochthonous DOM sources (Weyhenmeyer *et al*., 2012; Drake *et al.,* 2018), or from within an aquatic ecosystem (Lapierre and Frenette, 2009; Massicotte & Frenette, 2017;

Lutz *et al*., 2012; Drake *et al.,* 2018). Autochthonous DOM sources are formed through primary production by autotrophic biofilms, phytoplankton, macrophytes, and bacteria (Bertilsson & Jones, 2003; Tank *et al*., 2010; Pollard & Ducklow, 2011).

The autochthonous dissolved organic matter comprises low molecular weight substances with fewer aromatic rings, high proteins, and other extra-cellular material. Therefore, bacteria quickly degrade it and thus are considered more labile (Azam & Cho 1987; Farjalla *et al.,* 2009). Allochthonous DOM enters the fluvial systems as leaf litter, wood, and leaching plant nutrients from the surrounding riparian systems (Webster *et al*., 1997; Cawley *et al*., 2012). As such, it is usually carbon-rich and nutrient-poor with structurally complex molecules and thus considered more refractory to bacterial growth (Lean, 1998; Miller & Mcknight, 2010; Graeber *et al*., 2012). In addition, allochthonous fractions of dissolved organic matter may increase their lability with age (Mccallister & Paul, 2012).

2.2.1 The structure of dissolved organic matter

Dissolved organic matter constitutes numerous elements, mainly nitrogen (N), phosphorous (P), carbon (C), oxygen (O), sulfur (S), and hydrogen (H) (Hartnett, 2018). These elements react to form a complex mixture of substances such as humic, fluvic, and organic compounds such as dissolved organic carbon (DOC), dissolved organic phosphorus (DOP), and dissolved organic nitrogen (DON) (Hartnett, 2018). These complex mixtures are essential building blocks and energy sources for all aquatic and terrestrial organisms. The variable proportions of DOM also constitute humic substances, macromolecular hydrophilic acids, low-molecular-weight (LMW), and high-molecular-weight (HMW) compounds (Aitkenhead-Peterson *et al*., 2003). In addition, DOM contains carbohydrates, amino acids, lipids, and proteins. The chemical structure of DOM is made of carboxyl–rich alicyclic molecules (CRAM), heteropolysaccharides, hydroxyl, heterocyclic, aliphatic compounds, and an aromatic group, among others (Lam *et al*., 2007).

Humic substances are the largest fraction of fluorescent DOM and usually consist of lignin, tannins, polyphenols, and melanin (Fellman *et al*., 2010) and are obtained from biogeochemical disintegration of plant material by biogeochemical processes taking place both in terrestrial and aquatic ecosystems (Hudson *et al*., 2007). Humic substances are classified into fluvic and humic acids based on their solubility in water at different pH. The ratio of fulvic to humic acids is generally 10: 1 in low-coloured surface waters, 5:1 in highly-coloured surface waters, and 1: 3 in most interstitial soil solutions (Malcolm, 1993). Humic acids are a mixture of weak aliphatic carbon chains, and aromatic, carbon rings organic acids, which are soluble at a pH higher than two. Fluvic acids are a yellow, moderate molecular weight organic acid fraction of aquatic humic substances that are soluble at all pH values (Aiken, 1985) and made of mixtures of weak aliphatic and aromatic organic acids (Hudson *et al*., 2007). Fluvic acid is the most dominant humic DOM in natural waters than fluvic acid due to microbial degradation of plant and animal materials with a molecular structure made of mainly aliphatic and a carboxyl group. In addition, fulvic acid molecules can easily enter plant roots, stems, and leaves due to their small size. (Pettit, 2000).

DOM fractions can also be classified based on their molecular weight, which ranges from 100 to 100,000 dalton. High-molecular-weight fractions are depleted in nitrogen and phosphorous than carbon (Neff *et al*., 2002). The characterisation of HMW indicates that it is composed of high carbohydrates such as polysaccharides and humic substances with lower percentages of lipids and proteins (Neff *et al*., 2002). In addition, they are made of complex structure molecules such as humic and fulvic acids, making them less biodegradable (Graeber *et al*., 2012). Extracellularly released low-molecular-weight DOM from algal cultures is mainly composed of one or more of the following compounds: monomeric sugars, carboxylic acids, amino acids, and alditols with fewer aromatic rings (Jalliffier-Merlon *et al*., 1991) thus regarded as more labile.

2.2.2 Importance of dissolved organic matter in aquatic ecosystems

Dissolved organic matter is oxidised to release nutrients such as carbon and nitrogen, which supply nutrients to aquatic organisms (Giling *et al*., 2014). It can also be transported downstream to lakes and estuaries, thus allowing energy transportation from one system to another. In addition, DOM influences the metabolism and growth of bacteria (Benner, 2003). For instance, high molecular weight (HMW) DOM fuels high rates of bacterial metabolism, while LMW DOM supports high bacterial growth efficiencies (Bertilsson & Jones, 2003). Finally, DOM with multiple aromatic rings acts as an electron shuttle in redox reactions, thus significantly regulating ecosystem functions such as nutrient cycling and respiration (Cory & McKnight, 2005).

Flocculated DOM may contain essential micronutrients (i.e., calcium and magnesium), which provides primary food resources for macroinvertebrates in aquatic ecosystems (Aiken *et al*., 2014). Furthermore, during summer, DOM is metabolised in temperate regions to provide nutrients that drive gross primary production (Stepanauskas *et al*., 1999; Korth *et al*., 2012). As a result, stream DOM respiration plays a considerably high role in CO_2 evasion into the atmosphere (Battin *et al*., 2008; Raymond *et al*., 2013). Thus, the concentration of DOM can be quantified to indicate whether a river is a carbon source or a carbon sink, which is then related to the role of the aquatic ecosystem in climate change and global warming (Battin *et al*., 2008; Raymond *et al*., 2013).

Aquatic ecosystems act as carbon sources when allochthonous sources exceed autochthonous sources (Liu *et al*., 2019). Through decomposition, the organic nutrients, especially nitrogen and carbon, are transformed back to the inorganic form, making the system more heterotrophic, thus outgassing carbon back to the atmosphere in the form of CO_2 (Duarte & Prairie, 2005; Battin *et al*., 2008; Liu *et al*., 2019). During autochthonous DOM synthesis, autotrophic organisms use mainly carbon and nitrogen to form organic compounds. Therefore, using more carbon by autotrophic organisms makes freshwater ecosystems carbon sinks. DOM quality and quantity influence the ecological functioning of aquatic ecosystems (Wallace *et al*., 1997). Thus, DOM concentration and composition may be used to assess streams' ecological integrity in line with other tools, such as whole-stream or ecosystem metabolism, litter decomposition and composition of macroinvertebrate functional feeding groups (Ferreira *et al*., 2020). Furthermore, DOM may provide information on the level of human disturbances to water quality (Yu *et al*., 2015b; Fuss *et al*., 2017; Liu *et al*., 2019) since it can bind with heavy metals or aid in transporting pollutants from upstream to downstream or from surface water to groundwater (Kalbitz *et al*., 2003).

Chromorphic DOM protects aquatic organisms from UV radiation. However, it can also limit primary production by reducing the depth of the photic zone when the concentration of highly coloured humic molecules is high (Lean, 1998). Chromophoric DOM (CDOM) is the fraction of DOM that absorbs solar radiation reaching the earth’s surface (~65%, (Blough *et al*., 1993). Chromophoric DOM is vital in attenuating destructive UV rays, such as UV-B, which are detrimental to aquatic organisms such as plants and coral reefs (Williamson & Zagarese, 1994; Leu *et al.,* 2009). UV-B light is responsible for coral bleaching, low bacterioplankton growth due to changes in DNA structure, and low primary production due to inhibition of nutrient absorption (Leu *et al*., 2007). Dissolved organic matter regulates UV and visible light absorption (Nelson & Siegel, 2013). In lentic systems, DOM absorbs solar radiation within the water column's upper zone, which alters heat distribution and promotes thermal stratification (Jones & Bryan, 1998). Reduced photic zones and enhanced stratification impact almost every aspect of the ecosystem, including primary production, nutrient availability, oxygen distribution, and trophic structure (Jones & Bryan, 1998). Therefore, DOM is a crucial component in rivers in predicting aquatic ecosystems' functioning and ecological integrity under different stressors.

2.2.3 Dynamics of dissolved organic matter in rivers

The relative proportion of allochthonous and autochthonous organic matter in rivers is steady and independent of time (Vannote *et al*., 1980). Small streams in the headwater of major rivers are more influenced by the allochthonous DOM/DOC originating from terrestrial ecosystems (Vannote *et al*., 1980). In contrast, streams, mid-sized streams, and large rivers are more influenced by autochthonous sources of organic matter (Larson *et al*., 2007). The latter is attributed to reduced terrestrial inputs, higher water residence time, increased surface area, and reduced canopy cover for sunlight absorption, thus, high primary production (Larson *et al*., 2007). Allochthonous organic matter enters the aquatic ecosystem through sorption, adsorption, leaching, and flooding. (Webster & Meyer, 1997) while the photosynthetic process contributes to autochthonous organic sources (Vannote *et al*., 1980; Masese *et al*., 2017). The organic matter flows downstream, but their concentration and contribution to stream metabolism differ from one point to another, affected by factors such as the lability of the DOM. The processing of DOM changes its composition downstream with an increase in recalcitrant fractions as more labile fractions take part in biogeochemical processes first (Fellman *et al*., 2014). Thus, DOM is at its highest diversity and concentration upstream in contrast to midstream sections of rivers. Due to the aforementioned labile DOM removal, it is at lower diversity in midstream and downstream sections of the rivers.

The microbial activities upstream influence the DOM quality and quantity transported downstream (Vannote *et al*., 1980; Benner, 2003). High molecular weight and reactive DOM molecules characterise the upstream, while the refractory DOM is more prevalent downstream (Vannote *et al*., 1980; Thorp, 2002), but this state can change in disturbed freshwater ecosystems and Afrotropical rivers. Thus, based on this scenario, rivers are classified into either a passive pipe or reactor of DOM based on their ability to retain or transform DOM (Battin *et al*., 2008; Raymond *et al*., 2016; Casas- Ruiz *et al*., 2017). However, this is highly dependent on ecological conditions, land uses, and the hydrological properties of the aquatic ecosystem (Casas- Ruiz *et al*., 2017), which this study aims at investigating.

2.2.4 Dissolved organic matter quantification and characterisations in rivers

A comprehensive understanding of the influence of land use on DOM processing and its role in ecosystem processes in streams and rivers is still limited (Williams *et al*., 2016). Furthermore, land use affects the composition and concentration of the DOM and overall affects the ecosystem biogeochemistry and functioning (Fuss *et al.*, 2017) as land use controls factors such as light, water flow, and nutrient availability (Hunt *et al*., 2012). Therefore, DOM is an essential metric in understanding river health alongside commonly used metrics such as nutrients analysis, and physico-chemical parameters, among others (Williams *et al*., 2016). Furthermore, dissolved organic matter quality or composition has recently gained interest in monitoring assessment as previous studies where litter bag experiments have been widely done to understand DOM decomposition rates under different land use stressors (Ferreira *et al*., 2022). Although decomposition rates of organic matter provide a proxy of organic matter dynamics in ecosystem functioning, characterisation of DOM quality and quantity offers a better understanding of DOM impacts on water quality, community structure, and transportation of toxic pollutants, among other human stressors.

In freshwater systems, DOM optical properties are used to determine dissolved organic matter compositional variations using an excitation-emission matrix (EEM), UV-Vis fluorescence spectroscopy, and parallel factor (PARAFAC) analysis. (Coble, 1996; Baker, 2008; Stedmon *et al.*, 2003; Cory & McKnight, 2005). The optical properties of DOM are reflected by the proxies S_R and $SUVA_{254}$, with DOM having high molecular weight and aromaticity characterised by gentle spectral slopes (low S_R) and a high $SUVA_{254}$, respectively (Weishaar *et al.*, 2003; Helms *et al*., 2008). Besides that, EEM provides indices for distinguishing DOM sources. The fluorescence index (FI), humification index (HIX), and freshness index (β: α) are among these indices (McKnight *et al.,* 2001; Cory and McKnight, 2005; Helms *et al.*, 2008; Yamashita *et al.*, 2010). The FI indicates the relative contribution of microbial-derived organic matter versus terrestrial-derived organic matter in the DOM pool, with lower values indicating allochthonous (watershed) sources and higher values indicating autochthonous (in-stream) sources (McKnight *et al.,* 2001). The HIX values range from 0 to 1, with increasing values indicating increased humification, aromatic content, and molecular complexity. Finally, the β:α ratio is the index of recently produced autochthonous DOM, with lower values corresponding to recalcitrant allochthonous DOM (Parlanti *et al.*, 2000; Huguet *et al.*, 2009).

Excitation-emission-matrix fluorescence can further be decomposed using parallel factor (PARAFAC) analysis, a three-way multivariate statistical method, to provide information on their underlying fluorescent components (Stedmon *et al.*, 2003). These components are mainly used to provide information on organic matter sources. In addition, size exclusion chromatography (SEC) is also another method that is used to distinguish DOM into size fractions of bio-polymers, building blocks, humic substances of high molecular weight versus low molecular weight, carbon versus nitrogen, and humic verse non-humic substances (Perminova *et al.*, 2004). Finally, stable isotopes (isotope ratio mass spectrometers [IRMS]) may also be used to distinguish DOM sources based on their carbon and nitrogen signature and DOC concentration in freshwater (Barber et al., 2017).

Most studies that have applied dissolved organic matter quantification and quality determination using the above methods are mainly found in the temperate regions, with fewer studies located in the tropics (i.e., the Amazon River, Zambezi River, River Tana, Congo River, Mara River). Furthermore, most of these studies primarily focus on the impacts of land use (agriculture) on headwater, with minimal studies on the influence of LMH on DOM dynamics along the longitudinal trends, which is also paramount for the better management of freshwater systems.

2.2.5 Influence of land use and large mammalian herbivores on dissolved organic matter in rivers

Forests provide a buffer to rivers and streams and contribute significantly to allochthonous DOM sources, forming an important base for the food webs. Likewise, grasslands and other natural C4 grasses provide allochthonous DOM sources. However, with the current global land use change along the riparian regions, dominated mainly by croplands, livestock, and urban, alteration in legacies provided by native plants and animals may affect the DOM quality and quantity. For example, replacing forests with agricultural land may shift DOM quality as DOM originating from agricultural lands is characterised by rich weakly-humified DOM with high protein content and is more biodegradable than afforested allochthonous DOM (Naden *et al*., 2010; Graeber *et al.*, 2012).

Although this DOM quality seems to differ straightforward with land use, other factors such as stream metabolism, climate, nutrients concentration, and availability of light may affect shifts of DOM in streams through selective consumption of labile DOM in rivers leaving behind only the refractory high molecular weight DOM (Masese *et al*., 2017). For example, in the tropics, during rainy seasons, agricultural rivers are rich in high molecular weight DOM of terrestrial origin (Graeber *et al*., 2012; Masese *et al*., 2017), and hence increased turbidity due to high concentration of chromophoric DOM (Reche *et al.*, 1998; Biers *et al.*, 2007). Further, this may affect the water quality of agricultural streams, which may be unfit for direct consumption by humans.

Aromaticity is mainly a property of recalcitrant DOM, and low SR (indices for high molecular weight DOM) is mainly associated with headwater rivers compared to pasture and wetland rivers (Mulholland, 2002). However, terrestrial-derived humic-like DOM of high structural complex DOM substances is also abundant in some agricultural and headwater streams (Graeber *et al.*, 2012). This may be related to agriculture-related activities such as tillage which then increase soil disturbances and erosion, thus elevating the terrestrial DOM. In addition, headwaters are strongly linked with the terrestrial (Alexander *et al.*, 2007); hence it receives a lot of terrestrial inputs, which are then transferred downstream.

Agricultural land use may also affect riparian ecosystems through activities such as clearance of land cover and introducing of exotic plants and reservoirs, affecting the quality and quantity of DOM in streams. For example, in Amazon watersheds, replacing native trees with reservoirs shifted DOM composition from complex high molecular weight materials to low molecular weight DOM substances (Dalmagro *et al.,*2019). Similarly, the plantation of exotic tree species along agricultural rivers for rehabilitation may increase leaf litter concentrations, but this leaf litter may be of poor quality and not readily available for microbial activities (Tomanova *et al.*, 2008). For example, C4 grasses from sugarcane farming also introduce DOM of poor quality, made of tough lignin that is not easily degradable, limiting food for community organisms such as shredders (Masese & McClain, 2012). Similarly, an increase in the plantation of exotic plants in agriculture headwater streams increases the concentration of leaf litter materials from trees and the surrounding terrestrial environment (Omengo, 2010).

In addition, agriculture activities may induce shifts in the DOM carbon-to-nitrogen ratio (C: N). For example, increased productivity due to increased canopy cover in agricultural streams leads to microbial production of high degradable DOM of a low C: N ratio (Ohno *et al.,* 2010). Similarly, agriculture streams have been found to contain two times higher concentrations of DOC% than forested streams, i.e., 5.7 ± 3.7% and 2.1 ± 1.3% (p <

0.001), respectively (Heinz *et al.,* 2015). Further DON-rich substances may be elevated by agricultural activities such as tillage which accelerates the progressive degradation of high molecular weight DOM substances rich in protein materials (Ohno *et al.*, 2010). Furthermore, agriculture activities such as utilising nitrogen-rich fertiliser may also promote increased low molecular weight DOM rich in protein substances, hence increased DON% concentrations (Accoe *et al*., 2002).

Therefore, land use change significantly increases in agricultural land use induces a shift in DOM composition towards low molecular weight (low S_R), high photodegradable (high $SUVA_{254}$), freshly produced microbial, bioavailable DOM (high β: α) DOM (Parlanti *et al.,* 2000; Huguet *et al.,* 2009). Furthermore, enhanced bioavailability and lability in agriculture streams have increased eutrophication and even hypoxia levels (Glibert *et al.,* 2006; Conley *et al.,* 2009). Many studies have been done on the influence of agriculture on DOM composition at spatial and temporal scales (Dalzell *et al*., 2007; Petrone *et al.,* 2011; Graeber *et al*., 2012, Graeber *et al*., 2015; Heinz *et al*., 2015). However, limited studies have reported on the influence of riparian zones (e.g., the presence and absence of livestock and large mammalian wildlife) (Masese *et al*., 2017; Ledesma *et al*., 2018; Dalmagro *et al*., 2019; Werner *et al*., 2019).

Dissolved organic matter transport through the surface and sub-surface flowpaths, direct litterfall from riparian vegetation, and instream organic matter production are the primary sources of organic matter in streams and rivers (Naiman & Rogers, 1997). On the other hand, animal movement can actively transmit organic matter into the river via excretion and urination into recipient systems (Naiman & Rogers, 1997; Bond *et al.,* 2012). Therefore, through the movement, animals create a strong relationship between the limits of the terrestrial and river systems (Kitchell *et al.,* 1979; Vanni, 2002; Subalusky *et al.*, 2015). The role of large animals in savanna ecosystems is particularly noteworthy because, among tropical systems, it is most pronounced in Africa, but their impacts on dissolved organic matter in recipient rivers are not well understood due to limited research.

The impact of LMH organic matter subsidies in recipient rivers is determined by the quality, quantity, timing, and duration of LMH inputs at the recipient river (Richardson *et al*., 2010; Marcarelli *et al*., 2011). The role of large animals in savanna ecosystems is particularly noteworthy because it is most pronounced in Africa among other tropical systems. LMH can alter the quantity of dissolved organic matter by reducing the amount of leaf litter and altering the quality of leaf litter. Trees are an essential source of coarse particulate organic matter in rivers, and activities by LMH, such as movements, influence organic matter quantity. For example, elephants in Botswana have been associated with the reduction of tree density and alteration of tree species composition in riparian zones during feeding and movements (Rutina & Moe, 2014).

In addition, large wildlife has pronounced geomorphological and biogeochemical impacts on river ecosystems in Kenya, where many megafaunas remain, including significant transport of allochthonous inputs in the middle and lower river reaches (Masese *et al*., 2015; Subalusky *et al*., 2018). For example, hippos transport DOM input rich in C4 grasses from terrestrial to the recipient river daily (Subalusky *et al*., 2018; Masese *et al*., 2022). One hippo, for instance, can transport up to 9 metric tonnes of organic matter (wet weight) into the recipient rivers (Subalusky *et al*., 2018) compared to cattle which contribute a low amount of organic matter inputs, which is only an equivalent of 1% organic matter contributed by one hippo in Kenyan rivers (Masese *et al.,* 2020). Therefore, hippos are imperative vectors of organic matter in rivers and other freshwater ecosystems where they are found. Similarly, LMH are direct sources of C4 allochthonous sources to the aquatic organism. During the Wildebeest migration in Mara River, carcasses from the dead wildebeest are important allochthonous sources for macro-invertebrates (Masese *et al.,* 2015).

The quality of the dissolved organic matter varies with species of LMH. The quality of dissolved organic matter affects the decomposition rates, bioavailability to the aquatic organisms, community structures, and the production of instream autochthonous inputs. For example, hippo dung decomposes over 80 days (Subalusky *et al.*, 2018), and this was comparable to poor quality leaf litter decomposition rate at the headwaters (Newcomer *et al.*, 2012). This is because the hippo stomach retains more nutrients, realising inputs of low nutrients and more carbon. However, Hippo input is also comparable to cattle input which is richer in nitrogen and other nutrients (Iteba *et al.*, 2021); hence depending on animal species, their contribution to quality organic matter varies. In addition, hippo grazes during the night along streams and rivers and spends the daytime wallowing in water, releasing tonnes of faecal materials (McCauley *et al*., 2015). On the other hand, livestock interacts with streams and rivers during specific occasions, feeding, watering, and migrating; hence they contribute lower amounts of organic matter and nutrients to streams and rivers (Masese *et al*., 2020; Iteba *et al*., 2021).

Livestock, including cattle, sheep, and goats, has mainly replaced native animal biomass and vegetation biomass in many landscapes (Hempson *et al.,* 2017). As a result, livestock can have pronounced ecological effects on aquatic ecosystems, and their legacies may differ from the animals they have replaced (Emery- Butcher *et al.,* 2020). During watering and crossings at water bodies, livestock increase bioturbation and nutrients through egestion, thus alleviating the production of microbial and freshly produced autochthonous DOM (Masese *et al.,* 2020). Livestock may also have legacy effects on aquatic ecosystems by reducing the vegetation cover along the riparian landscape (Dutton *et al.,* 2018), which may promote the growth of invasive vegetation species, overall affecting the quality and quantity of dissolved organic matter. Still, information on the hippo, livestock and other LMH on dissolved organic matter quality and its significance in functioning in large tropical rivers are not well understood (e.g., Mosepele *et al.,* 2009; Masese *et al.,* 2020).

2.3 Ecosystem metabolism in rivers

Riverine ecosystem metabolism measures primary production and ecosystem respiration (Hauer & Lamberti, 2011). It is estimated by measuring the total organic carbon produced and consumed in the river (Williamson *et al*., 2008). Organic carbon is formed through the photosynthesis process, during which carbon (IV) Oxide (CO_2) is used, and oxygen (O_2) is released (Williamson *et al*., 2008). The gross primary production (GPP) and ecosystem respiration (ER) are the two main metrics used to measure ecosystem metabolism in streams and rivers. Gross primary productivity is defined as the rate at which energy is accumulated. At the same time, ER measures the respiration rates of aquatic life (i.e., fish, invertebrates, algae, aquatic plants, and microbes) (Young *et al*., 2008). ER can also be defined as the total consumption of organic matter in an ecosystem via aerobic respiration (Hoellein *et al*., 2013).

In all ecosystems, the energy flow in food webs starts from sunlight, where the plants or autotrophic organisms fix the sun's energy to form an organic compound. The basic equation for photosynthesis by autotrophic organisms is:

$$6CO_2+12H_2O+Light \Rightarrow 6O_2+C_6H_{12}O_6+6H_2O \qquad \text{(eqt.1)}$$

During this process, the energy produced may be lost through internal respiration in the autotroph (Ra), and the retained energy may be incorporated as biomass. The retained energy is referred to as Net Productivity (NPP). GPP is the sum of the NPP and respiration (Ra). It is the process by which all organisms obtain vital energy from various reduced-carbon compounds (del Giorgio 2005). Respiration represents the largest sink of organic matter in the biosphere.

$$GPP = NPP + Ra \qquad \text{(eqt.2)}$$

Odum (1956) defined the first concept of measuring GPP in flowing water by measuring daily changes in dissolved oxygen concentration. This concept assumes that the rate of change in dissolved oxygen concentration (dC/dt, g/m^3) is the function of photosynthesis

(P g/m^2/hr.), respiration (R), gas exchange with the atmosphere (k, [day -1]), and accrual of groundwater (A).

$$\Delta DO = f(P + R + k + A). \qquad \text{(Eqt.3)}$$

GPP, ER and NEP are ecosystem metabolism parameters that estimate an ecosystem's productivity, that is, freshwater ecosystems' heterotrophy or autotrophy state (Williamson *et al*., 2008). A system is said to be autotrophic when GPP is greater than ER; that is, it acts as a carbon sink, and the net ecosystem productivity (NEP) is greater than zero (NEP > 0). On the other hand, when an ecosystem is heterotrophic, ER is greater than GPP and NEP < 0. It acts as a carbon source. The estimated productivity in streams and rivers is also defined by the ratio between primary production and ecosystem respiration (P: R). If the P: R > 1, the river is said to be heterotrophic and vice versa. Net ecosystem productivity (NEP) is the difference between GPP and ER.

2.3.1 Effect of land use on ecosystem metabolism

Measuring ecosystem metabolism in streams and rivers has recently become important in understanding ecological integrity because it is sensitive to multiple land-use stressors (Silva-Junior, 2016; Jankowski *et al*., 2020). Agricultural and urban land uses are the most common stressors affecting ecosystem metabolism in streams and rivers (Young *et al*., 2008). Primary production occurs at the base of the aquatic food web; thus, it determines the trophic position of biotic components in a freshwater ecosystem. In addition, understanding ecosystem metabolism is an essential factor in carbon dynamics in freshwater ecosystems. In a review by Silva-Junior, (2016), agricultural land uses affect both gross primary production and ecosystem metabolism, with more influence on gross primary production.

The main land use factors influencing ecosystem metabolism in streams and rivers are light, temperature, nutrients, quality of dissolved organic matter and turbidity (Silva-Junior, 2016). An increase in nutrients from fertilisers used in agricultural land use, especially total dissolved nitrogen and soluble reactive phosphorous, is highly correlated with an increase in gross primary production (Mulholland *et al*., 2001). Seasonality influences rates of GPP and ER, especially in tropical streams and rivers, where ecosystem metabolism increase or decrease depending on the prevailing hydrological conditions (Masese *et al*., 2017). Heavy tropical rainfall is associated with erosion and flooding, increasing river turbidity in agricultural streams, lowering primary production and increasing ecosystem respiration (Masese *et al*., 2017).

Also, an increase in temperature, especially during summer or dry conditions, increases leaf litter decompositions in agricultural land, increasing ecosystem respiration (Demars *et al*., 2011; Masese *et al*., 2014). Riparian vegetation is an important biogeochemical filter which retains nutrients and soils, thus providing resilience to ecosystems during high flows/ rains (Hill, 1996). Therefore, deforestation along streams and rivers reduces stream resilience and canopy cover. Reduced canopy cover increases surface areas for sunlight and, eventually, mean water temperature, which promotes GPP (Masese *et al*., 2016). Some authors have also argued that agroforestry may affect ecosystem metabolism by changing the quantity and quality of litter (Griffith *et al*., 2013; Masese *et al*., 2017).

For example, agroforestry may introduce tree species whose leaf litter are not readily biodegradable or palatable to decomposers, affecting ecosystem metabolism (Masese *et al*., 2016). In the Mara River, the introduction of eucalyptus trees has been associated with increased GPP, and ER was suppressed by eucalyptus leachate (Tsisiche, 2018). In traditional agroforestry, such as growing rice and fruits along stream riparian areas, GPP was minimally affected due to an increase in canopy cover (Carlson *et al*., 2014).

Vegetation type may or may not affect ecosystem metabolisms, and in Mara River, studies have shown that savanna grasses, C4 plants, play a significant role in ecosystem processes and food webs compared to the higher plants (Marwick *et al*., 2014; Masese *et al.*, 2022). Savanna grasses are a silicon source for phytoplankton and diatom growth, forming essential components of primary productivity. Contrarily, in the prairie system, which is also characterised by grasslands, ecosystem metabolism is less affected by canopy cover than in River Mara (Wiley *et al*., 1990, Young and Huryn, 1996).

Ecosystem metabolism varies across different streams and rivers in the world. For example, in headwater desert streams, GPP is usually higher because of the increase in temperature compared to forested streams (Fisher *et al*., 1982, Mulholland *et al*., 2001). While in undisturbed tropical streams such as Puerto Rico, ecosystem respiration is higher regardless of an increase in light, and an increase in respiration was from the hyporheic zone, which can contribute up to 50% of total ecosystem respiration (Mulholland *et al*., 2001). In Afrotropical rivers, the application of ecosystem metabolism is still limited, thus, hindering the understanding of how ecosystem metabolism affects its function. Masese *et al.*, 2017 used ecosystem metabolism to assess the impacts of change in forested land use on agricultural land use, and the results showed that agricultural land use increased primary production during dry seasons and increased respiration during the dry seasons due to increasing in turbidity and reduced sunlight.

In conclusion, riverine ecosystem metabolism is a good indicator of ecosystem functioning and integrity because it is sensitive to land-use changes in the catchment's streams and rivers (Bott & Newbold, 2013; Gücker *et al*., 2009). Silva-Junior, 2016 found out that several studies on ecosystem metabolism were higher, in fact, five times higher, in temperate than in tropical streams. To have conclusive data on factors affecting ecosystem metabolism in tropical streams and rivers, especially in the Afrotropic, long-term studies are needed to address limited studies on this biome (Ferreira *et al*., 2020).

2.3.2 Influence of large mammalian herbivores on ecosystem metabolism

Early models of riverine ecosystem functioning show that primary production changes from upstream to downstream. These models emphasized natural factors affecting ecosystem metabolisms, such as a change in light, temperature, stream size, and coarse particulate matter (Vannote *et al*.,1980). Hence early models failed to include other factors, such as the presence of savanna vegetation and LMH in the tropical streams, which are also important drivers of ecosystem metabolism (e.g., Masese *et al*., 2018, 2020).

In Afrotropical savanna landscapes, LMH interact intimately with streams and rivers and, hence, are important components that drive ecosystem functioning (Leroux & Loreau, 2008). In addition, LMH includes wildlife and livestock, which interact with the rivers in different ways through the mediation of organic matter and nutrients (Polis *et al*., 1997; Paetzold *et al*., 2007). For example, in the Okavango River in Botswana, elephants, an important keystone species in ecosystems, are known to create dams along the river (Mosepele *et al*., 2009). This damming along the streams may increase temperature and siltation, increasing ecosystem respiration. Also, damming may interfere with substrate stability, further limiting primary production.

Bison and wildebeest also affect nutrient dynamics in temperate and tropical areas (Wenger *et al*., 2019; Subalusky *et al*., 2020). Most of the research has focused on livestock, with limited research focusing on wildlife (Ferreira. *et al*., 2020). Nevertheless, wildlife plays a critical role in ecosystem processes such as nutrient cycling and organic matter processing (Subalusky *et al*., 2015; Dulton *et al*., 2018; Stears *et al*., 2018). An increase in nutrients and more diverse DOC concentration from the wildlife and livestock inputs may promote high levels of gross primary production (Masese *et al*., 2020), while an increase in organic matter inputs may promote ecosystem respiration (ER) thus the ecosystem metabolism (Mulholland *et al*., 2001; Bernot *et al*., 2010; Masese *et al*., 2017). The annual mass drowning of LMH in the Assininobe River in Canada (Wenger *et al*., 2019) and the Mara River in Kenya/Tanzania (Subalusky *et al*., 2020) contributes to phosphorous loading in both rivers. In the Assiniboine River, bison contribute ~50% of total phosphorous loading (Wenger *et al*., 2019; Subalusky *et al*., 2020). Total phosphorous affects GPP through the promotion of algal biomass production hence stream productivity

Research focusing on the impact of LMH on ecosystem metabolism is limited. This has further been compounded by less research in tropical compared to temperate regions (Gücker *et al.*, 2009; Bott & Newbold, 2013; Silva-Junior, 2016; Ferreira *et al.*, 2020). Therefore, research on the comparative roles of large wildlife (such as hippos) and livestock on water quality and ecosystem processes is fundamental to understanding the Afrotropical River processes (Masese *et al.,* 2020). Therefore, more research to provide comparative information is significant for properly managing aquatic ecosystems under the influence of overgrazing and loss of biodiversity (for example, hippos).

2.4 Influence of stream size on nutrients, dissolved organic matter, and ecosystem metabolism in rivers

2.4.1 Influence of stream size on nutrients

The importance of stream size in nutrient dynamics has gained interest over the years (Alexander *et al.,* 2007), but recently some other reports argue that other factors (anthropogenic) rather than stream size may affect the export of nutrients in rivers and streams (Doyle, 2005; Wollheim *et al*., 2006; Mwanake *et al.,* 2019; Coble *et al.,* 2022). In rivers, nutrients continuously move from upstream to downstream in a spiral manner (Vannote *et al*., 1980; Ensign and Doyle, 2006; Webster, 2007). According to Alexander *et al*. (2000) and Peterson *et al*. (2001), the transfer of nutrients downstream depends on stream size, where streams and rivers control nutrient dynamics. On the other hand, other researchers argue that large rivers are relatively important in nutrient movement compared to smaller streams (Seitzinger *et al*., 2002; Mwanake *et al.*, 2019). Physical water quality parameters such as oxygen and turbidity deteriorate longitudinally as stream size increases (Masese & McClain, 2012).

Large streams are more turbid because of the increase in the fine particulate matter than smaller ones which in most cases are made of coarse particulate matter (Vannote *et al.*, 1980). Similarly, this increase in turbidity lowers oxygen concentration due to low productivity, increasing ecosystem respiration (Masese & McClain, 2012). Temperature increases with the increase in stream size. An increase in stream size increases the surface area for temperature absorption; furthermore, as the stream increases, canopy cover decreases (Shivoga *et al.*, 2007). A decrease in canopy cover in large streams also increases surface area for light absorption, further promoting increased algae biomass (Masese *et al*., 2009; Raburu *et al*., 2009).

Longitudinal trends of nutrients and major cations are not well predicted in the river continuum concept as it is highly dependent on geology, discharge, and land use along the riparian areas, among others; furthermore, RCC is more applicable to pristine rivers and streams. For example, in the Lake Victoria River basin, total phosphorous and total nitrogen increased with stream orders, although this was more related to the increase in human activities as stream size/order increased (Masese & McClain, 2012). Contrarily, it has also been urged that small-sized rivers have a long residence time, retaining more major ions such as phosphorous than larger rivers (Stachelek *et al.,* 2019). Also, small streams are a hotspot for nutrient processing compared to high-order streams (Alexander *et al.,* 2007). The longitudinal trends in physico-chemical parameters and nutrients change from upstream to downstream are not straightforward because they are highly variable with changes in other factors such as land use change, seasonality, hydrology and geology (Mwanake *et al.,* 2019; Coble *et al.,* 2022; Wanderi *et al*., 2022)

2.4.2 Influence of stream size on dissolved organic matter

The river continuum concept RCC has been widely used in understanding rivers' organic matter dynamics until recently when other models, such as the Pulse Shunt hypothesis, were developed to expand on the inefficiency of RCC (Raymond *et al.,* 2016). This model emphasizes the influence of hydrological patterns on dissolved organic matter evolution transformation in rivers. Although stream hydrology, such as the size of the stream, runoff, baseflow, floods, drainage area, and snowmelt affect the DOM composition, residence time, and characteristics (Dawson *et al*., 2008; Jaffé *et al.,* 2008a) flooding, DOM interaction with the small stream is low because of the reduced residence time and increased transient storage of DOM. Although this stream size effect may be overridden by the flow base effect, during flooding, the river may act as a passive corridor for DOM since there may be less or no interaction of DOM with river biota (Fasching *et al*., 2016). Influence stream order on the dissolved organic matter is poorly understood across the entire flow regime.

In temperate, small streams (stream order 1-3) have low dissolved organic matter concentration of less aromatic (specific ultraviolet absorbance at 254 nm (SUVA254)), more autochthonous (fluorescence index), and more recently produced (β/α) compared to large streams (Coble *et al.*, 2022). Autochthony and production of recently produced DOM are intriguing because, in most studies, headwater streams are mainly driven by light and temperature hence their heterotrophic nature. For example, studies have shown that land use influences dissolved organic matter as opposed to stream order and seasons in temperate streams, while stream order influences dissolved organic matter composition during winter (Coble *et al.*, 2022). Conversely, in tropical headwater streams, both seasonality and stream size affect DOM such that during droughts, instream production of autochthonous DOM increases due to the decrease in surface transportation, increase in transient storage, and water residence time (Spencer *et al*., 2010).

Lamprey River's first-order stream was associated with lower molecular weight (S_R) and less humification (HIX) than high-order streams. However, the fourth-order streams behaved similarly to first-order streams hence introducing patchiness across the longitudinal gradient, which could be explained by other factors rather than stream size/order (Ferreira-Martins *et al.*, 2021). Based on these findings on the impacts of stream order on dissolved organic matter, stream size/order effect is dependent on other factors to drive the functionality of dissolved organic matter in rivers. Stream size does not directly influence dissolved quantity and quality; rather, it is compounded by other confounding effects. This, therefore, necessitates more research under this theme to get more information to improve our understanding of dissolved organic matter functionality in rivers.

2.4.3 Influence of stream size on ecosystem metabolism

The river continuum concept has been used to predict stream size effect on longitudinal trends of ecosystem metabolism from lower order streams to higher stream orders. Lower stream orders are heterotrophic in nature due to smaller size and increased canopy cover, which limits light absorption for primary production (Vannote *et al.*, 1980). As the river continues to flow from low order stream to mid-streams autotrophic increases because of the increase in stream size (Acuña *et al*., 2004), light intensity, temperature and nutrient concentrations ((Mulholland *et al.*, 2001). Further, as stream size increases, higher stream orders become more heterotrophic due to increased fine particulate matter from upstream and new tributaries joining the river, increasing turbidity and limiting primary production (Webster & Benfield, 1986). The heterotrophic nature downstream is promoted by a decrease in stream depth, limiting light absorption for primary production (Vannote *et al.*, 1980).

Some studies agree with Vannote *et al.* (1980), where gross primary production and ecosystem metabolism are more influenced by larger rivers (5th-7th order) compared to small-sized streams (Lamberti & Steinman, 1997; Chen, 2013). However, this is not the case with most rivers across the world where stream size and other factors drive ecosystem metabolism, such as water temperature due to climate change, which may promote catabolic processes and thus increase ecosystem respiration in mid-size rivers

(Chen, 2013). Most streams in tropical, subtropical and temperate regions have also confirmed that most mid-stream does not reach a maximum value of one ratio of production verse respiration (P: R>1) because of latitude and stream size effect. P: R ratio was greater in higher stream orders and higher latitudes than in lower stream orders and lower latitudes (Young & Huryn, 2011). In addition, larger streams are more stable, with high retention time, which promotes the growth of algae biomass as opposed to the smaller streams, increasing gross primary production (Uehlinger *et al.,* 2002). In tropical rivers such as the lower Tana River, similar results were observed where productivity increased downstream and was more influenced by increased temperature and resident time as stream size increased (Tamooh *et al.,* 2013).

This counter-intuitive observation of high productivity in the turbid river has also been reported for some large temperate rivers, such as the Mississippi (Kendall *et al.,* 2001; Delong and Thorp, 2006). Several studies have therefore argued that other factors correlated with stream order, such as riparian vegetation and channel morphology, actually drive the longitudinal shifts in ecosystem metabolism described by the RCC and that these should be considered rather than stream order (Wiley *et al.,* 1990; Young and Huryn, 1996).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

The research was carried out in Kenya's Mara River catchment area. East Africa's Mara River is located between latitudes 0°21'S and 1°54'S and longitudes 33°42'E and 35°54'E (Mati *et al*., 2008). The Mara River Basin (MRB) is shared between Kenya (65%) and Tanzania (35%), with a surface area of 13,835 km^2. The Mara River originates from Enapuiyapui Swamp in the eastern Mau Escarpment in Kenya at an altitude of 2,932m above sea level (asl). It drains its water into Lake Victoria at an altitude of about 1,134 m asl (Mati *et al*., 2008). The Nyangores and Amala rivers are perennial tributaries of the Mara River that drain the Mau Forest, East Africa's most extensive tropical moist broadleaf forest. The two tributaries join to form the Mara River mainstem in the lowlands (Fig. 1). In the middle reaches, several seasonal tributaries, including the Talek, Olare Orok, Ntiakntiak, Molibany, and the Sand, drain the semi-arid livestock grazing lands and wildlife conservancies outside the Maasai Mara National Reserve (MMNR) in Kenya.

Annual rainfall in the MRB varies from about 2,000 mm in the highlands to around 1000 mm in the lowlands (Jackson & McCarter, 1994). January to March is typically dry, while March-July and October-November are wet periods known as the long and short rains, respectively. The Kalenjin ethnic group lives on the highlands, while the Maasai pastoralists occupy Kenya's middle and lower portions of the basin. The MRB hosts substantial numbers of livestock, but densities differ across the catchment as the Kalenjin have diversified to crop farming and husbandry of small herds of improved cattle breeds. The Maasai are traditional pastoralists whose culture revolves around large herds of cattle that are the mainstay of their livelihoods and economy (Lamprey and Reid, 2004). Agricultural expansion is ongoing across the basin, including in the semi-arid grasslands and shrublands in areas adjoining the conservancies and the MMNR (Lamprey and Reid, 2004; Mati *et al*., 2008).

The middle reaches of the Mara River and its tributaries within the MMNR host >4,000 hippos (Kanga *et al*., 2011), which graze in savanna grasslands at night and rest in or near the river during the day, transferring ~36,000 kg of organic matter in the form of dung per day from the terrestrial to the aquatic domain (Subalusky *et al*., 2015). In the same region, Maasai pastoralists graze nearly 200,000 cattle and large numbers of goats and sheep in communal lands adjoining the MMNR and utilize rivers as watering points (Lamprey and Reid, 2004; Ogutu *et al*., 2016; Veldhuis *et al*., 2019). By virtue of their large numbers, livestock (mainly cattle) also transfer a significant amount of dissolved organic matter and nutrients into the Mara River and its tributaries, although the per capita input of cattle is much lower compared to that of hippos (Masese *et al*., 2020; Iteba *et al*., 2021). In the Mara River landscape, communal conservancies outside the Masaai Mara National Reserve serve as grazing land where livestock and wildlife co-exist (Kanga *et al*., 2013). This distribution results in a displacement pattern with hippo areas inside the reserve, mixed hippo and livestock (mainly cattle) areas in the conservancies, and only livestock grazing areas outside the conservancies (Kanga *et al*., 2013).

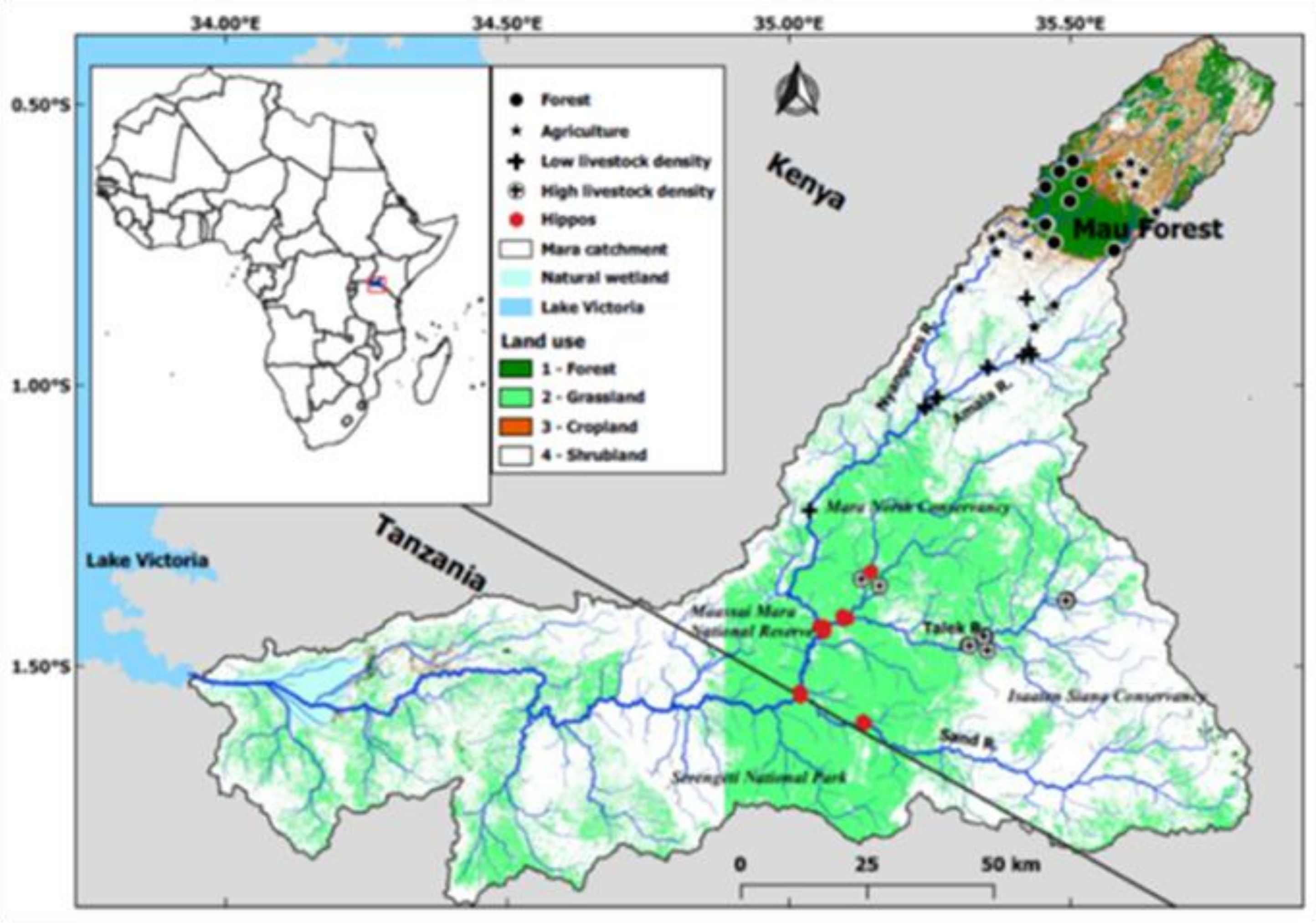


Figure1, Location of sampling sites for nutrients, DOM and ecosystem metabolism in the lower Mara River basin, Kenya

3.2 Study design

A total of 80 sites were selected in the Mara River basin for sampling during the beginning of the dry season in January 2018. All sites were sampled only once unless specified otherwise. The high number of sites enabled space for time substitution as many sizes were sampled in different orders or sizes of streams ranging from smallest stream order one (the smallest) to the largest stream order 7 (the Mara River mainstem). In most cases, we sampled at confluences, i.e., working in both upstream tributaries and a third downstream mainstem site after effectively mixing water from the two tributaries. Sites were selected depending on the influences of catchment scale (mainly land use) and reach scale (human activities, cattle and wildlife disturbances). Sampling sites were then grouped into five (5) broad regions or categories depending on these influences: forested (19), agricultural (26), low-density livestock (15), high-density livestock (12), and wildlife (i.e., hippos; 10) sites. Forested sites had C3 vegetation dominating the catchment and riparian areas and were used as a reference for land use and LMH influences. Agricultural sites were in farming areas (crop cultivation), although most farmers in the area also own low numbers (<20 per km^2) of livestock (mainly cattle). The low-density livestock sites were also in agricultural areas but had a higher density of livestock (20-50 per km^2) than agricultural sites. The high-density livestock sites were located in conservancies outside the MMNR where the only land use activity is grazing large herds of cattle (>100 heads per km^2), goats and sheep (shoats). However, wildlife, such as zebra, wildebeest, and other herbivores (but rarely hippos), also occur in these areas. Finally, hippo sites were located on the Mara River mainstem and tributaries in the

MMNR downstream of river sections inhabited by large populations of hippos (Kanga *et al*., 2011). The catchments area was delineated, and the area of each site category upstream to downstream of each sampling site was calculated using the Digital Elevation Model of Kenya (90m by 90m) produced using data from the Shuttle Radar Topography Mission. Based on delineation, sampling sites were classified into percentage forest, agriculture, and grasslands.

3.3 Field sampling for river characteristics and stream size

Water depth was measured at each site, and sampling reaches using a meter rule at >50 points were randomly selected along the reach to calculate average depth. Using a mechanical velocity meter, water velocity was also measured at >50 randomly located points. The flow meter was first calibrated to allow the number of revolutions/counts to be converted to stream velocity. The flow meter was then placed in the river and removed after ten seconds, and the number of counts was recorded. A stopwatch was set at 10 seconds intervals to count the number of revolutions which was then converted to velocity (m/s) using an equation supplied by the manufacturer. Average water depth, water velocity and width in the study reach were used to calculate discharge using the following formula;

$$\text{Total discharge} = \sum(\text{Area } 1 \times \text{Velocty}) + (\text{Area } n \times \text{velocity } n)$$

At each site, *in situ* physicochemical parameters that included pH, electrical conductivity, dissolved oxygen (DO) concentration, temperature, salinity and turbidity were measured using a WTW Multiprobe 3320 (pH320, OxiCal-SL, Cond340i; Weilheim, Germany).

The river distance from the source (RDS) was calculated for each site by square-rooting the drainage area (Rasmussen *et al.,* 2009) as a measure of stream order or linear dimension of the watershed (Masese *et al.,* 2020). Data on livestock (goat, sheep, cattle and donkeys) and wildlife data (hippos and ungulates) were obtained from the Ministry of Agriculture and Livestock Production reports (KNBS-IHBS, 2007; KNBS-LS, 2009; KNBS, 2016, 2018), Development Plans for Bomet and Narok Districts (Plan, 2007, 2008) and any other relevant published and unpublished report (Ottichilo *et al.,* 2000; Lamprey and Reid, 2004; Kanga *et al.,* 2011; Kiambi *et al.,* 2012; Ogutu *et al.,* 2016). Densities for hippo was expressed as the number of individual hippos per river (km) and those for livestock as livestock in the catchment area of the sampling site of the river per km^2 (Masese *et al.*, 2020).

3.4 Field sampling of water physico-chemical parameters and dissolved organic matter

At each site, the sampling bucket, syringes, filter holders, and filtration unit were well-rinsed using the river water before use. Water samples for nutrients and major ions were then collected from the river using a bucket from the thalweg, a well-mixed and flowing section of the river. Finally, the filtration process was done using filter holders and syringes into respective well-labelled vials indicating sites, nutrients and ions. The samples were triplicated for all solutes and filtrates, including orthophosphate (PO_4), silica, cations, labile carbohydrates, ammonium (NH_4^+), DOC and major ions.

The filtration process was done using disposable GF/0.2 filters. The filtrate was then stored in 24ml white bottles for phosphorous, 0.2 ml epi tubes for anions, 15 ml tubes for cations and ammonium, and glass vials for DOC composition. Yellow disposable GF/0.45was used for silica, LC-OCD aqualog, and dissolved organic carbon, where the filtrate was stored in 15ml, 20 ml glass, and 15 ml long glass for respective nutrients. The samples were then stored in a cooler box under 4ºC temperature. Water samples for DOM characterization were filtered on-site using pre-combusted (450 °C, 4h) GF/F filters into 30 ml amber glass bottles. Before sampling for DOM characterization, bottles were cleaned with 0.1M HCl, soaked overnight in distilled water, and then combusted. Samples containing cations and NH_4^+ were acidified using HCl to prevent further oxidation and grazing by bacteria that would affect DOM quality and quantity.

3.5 Field sampling and laboratory analysis for total suspended solids and particulate organic matter

Water samples for total suspended solids (TSS) were collected and filtered through pre-combusted (450 °C for 4 h) and pre-weighed GF/F (0.7 µm, 47 mm diameter) filters (Whatman International Ltd., Maidstone, England); see plat 1. Samples were then stored in a cooler box at 4 ºC until analysis in the laboratory. In the lab, the GF/F filter holding suspended matter was dried at (60 °C) for 48h until constant weight and re-weighed using an analytical balance (0.1 g). The weight of the dried GF/F filters was subtracted from the initial pre-combusted weight to obtain the total suspended solids (TSS). The dried filters were then ashed at 500°C for 4h and re-weighed to determine particulate organic matter (POM), which was calibrated by obtaining the difference between TSS and ash-free-dry weight (APHA, 1998).

Plate 1: Water sample collection for nutrients and dissolved organic matter. Water filtration for analysis of dissolved organic matter and nutrients (a and b), collection of water samples (c), filtration for total suspended solids (d), high livestock density sites in Mara River, Kenya (e), and *in situ* measurement of physio-chemical in the Mara River, Kenya (f). Photo Credit; Elizabeth Wanderi, Frank Masese, and Ole Keshe Evans.

3.6 Analytical analysis for nutrients and major ions

A Shimadzu TOC-V CPN with a coupled total nitrogen analyzer unit (TNM-1) at the Leibniz-Institute for Freshwater Fisheries and Inland waters (IGB), Berlin, Germany, was used to analyse total dissolved nitrogen (TDN) and dissolved organic carbon (DOC) levels. The water sample for DOC was oxidized at a high temperature in the presence of high-temperature catalytic oxidation-HTCO to remove carbon IV oxide, which was measured through infrared absorption. Oxidative combustion-chemo luminescence was used for TN.

Standard colourimetric methods determined NO_3^- and NH_4^+ concentrations (APHA, 1998). Major anions NO_3^-, Cl^- and SO_4-^{2} were determined using a Dionex ICS-1000 ion chromatograph equipped with an AS-DV autosampler, and the major cations; aluminium (Al^{3+}), Boron (B), calcium (Ca^{2+}), ferrous iron (Fe^{2+}) potassium (K^+), magnesium, (Mg^{2+}), manganese (Mn^{2+}), sodium (Na^+), phosphide (P^{3+}), Sulphide(S^{2+}) and dissolved silica (DSi). NH_4^+ was determined using an ICP-MS at the IGB laboratory.

3.7 Analytical analysis for optical properties of dissolved organic matter

Absorption spectra (200–600 nm) of DOM were measured on a UV-2501 PC UV/VIS spectrophotometer (Shimadzu, Duisburg, Germany) using a 1 cm quartz cuvette. Before analysis, samples were brought to room temperature. MilliQ-Water was used as a blank. Absorption coefficients were determined following $\lambda = 2.303\ A(\lambda)/1$ where $A(\lambda)$ is the absorption coefficient at wavelength λ (in nm), and l is the cuvette path length (m). The scans calculated several optical properties of DOM, where the absorption coefficient ratio a_{254}/a410 was calculated as an indicator of molecular weight and aromaticity (Baker *et al*., 2008). A commonly used ratio of absorption coefficients *E*2:*E*3 (a_{250}: a_{365}) was calculated to provide further information about DOM aromaticity and molecular weight (Peuravuori & Pihlaja, 1997; Helms *et al*., 2008). The spectra slope ratio (SR) was computed as the ratio of the short wavelength slope ($S_{275–295}$) and the long wavelength slope ($S_{350–400}$). SR and $S_{275–295}$ are inversely correlated with the average molecular weight of DOM and are associated with photodegradation (Helms *et al*., 2008).

The fluorescence of DOM was measured with a FluoroMax spectro-fluorometer (HORIBA Scientific, Longjumeau, France). Samples were measured at room temperature 20–25°C, and the fluorescence spectra scans were corrected for instrument bias using specific files supplied by the manufacturer. Fluorescence scans were collected at 10 nm increments over an excitation range from 220 to 450 nm and an emission range from 350 to 600 nm at 2 nm increments (Cory *et al*., 2010). Several corrections were performed in the EEM scan data, following the procedure of Cory and McKnight (2005); first, to remove the effects of Raman and Rayleigh scattering, the subtraction of the MilliQ water EEMs from each sample EEM was done, and this was followed by inner filter correction (Kothawala *et al*., 2014), which is caused by macromolecules, especially in turbid water samples, that scatter light (Lakowicz, 2006). Finally, emission intensities were normalized to the area under the water Raman peak (excitation 350 nm).

The processing of EEMs was done using Parallel factor analysis (PARAFAC) in R-statistical software, according to Murphy *et al*. (2013), and yielded three indices: fluorescence index (FI) (McKnight *et al.*, 2001); freshness index (β: α) (Wilson and Xenopoulos 2009) and autochthonous biological index (BIX) (Huguet *et al*., 2009). The FI typically ranges from ∼ 1.2 to ∼ 2 and indicates DOM origin by distinguishing allochthonous sources from microbial sources. Low values (FI = ∼1.2) are characteristic of terrestrial higher-plant sources of DOM, and high values (FI = ∼1.8) indicate microbial sources of DOM (Cory & McKnight, 2005; Jaffé *et al*., 2008b). The freshness index (β: α) indicates the proportion of recently produced DOM relative to more decomposed DOM (Wilson & Xenopoulos, 2009). High values (>1) of β: α indicate that DOM is primarily of autochthonous origin, and values <0.6 indicate primarily allochthonous origin (Huguet *et al*., 2009). The biological autochthonous index (BIX) is a measure of autochthonous biological activity, with higher values >0.8 indicating a higher contribution of recently produced autochthonous DOM (i.e., biological activity or aquatic microbial origin). In contrast, lower values indicate less autochthonous DOM (Huguet *et al*., 2009). The humification index (HIX) is a proxy of the humification status of DOM, and higher values indicate a high degree of humification (Fellman *et al*., 2010).

3.8 The measure of algal biomass and ecosystem metabolism

Biomass of benthic algae was quantified on rocks and sediments using the BenthoTorch fluorometer (BG36700-V, bbe Moldaenke GmbH, Schwentinental, Germany). The BenthoTorch is a deployable pulse-amplitude-modulated spectrofluorimetric tool that uses predefined algorithms to instantaneously identify the chlorophyll-*a* (Chl-*a*) fluorescence signal of benthic algae and primary producers such as diatoms, cyanobacteria and green algae (Carpentier *et al*., 2013). This instrument emits light pulses at 470, 525, 610, and 700 nm and records the Chl-*a* response at 690 nm (Kahlert & McKie, 2014). I placed the BenthoTorch on benthic substrates (both stones and sediments) with care taken to avoid physical disturbance of the biofilm and light entering the algal surface area of excitation, see plate 2 (Kaylor *et al.*, 2018). The sampled area where the beam of light excited Chl-a measured 1 cm^2. Ten seconds of exposure provides Chl-a concentrations in diatoms, cyanobacteria, and green algae, and the fluorescence algorithm calculates the proportion of each group (Catherine *et al*., 2012). The instrument is delivered calibrated using algal cultures to reduce variation by at least three readings for each measurement and averaged them, as suggested by the manufacturer (bbe Moldaenke, http://www.bbemoldaenke.de/chlorophyll/benthotorch).

3.8.1 *In situ* measurement of ecosystem metabolism

At each site, dissolved oxygen concentration (DO) and the water temperature were recorded at 1-min intervals for 24 hrs using MiniDOT loggers (Optode Technology, PME, Vista, California). In addition, photosynthetically active radiation (PAR, 400–700 nm) was recorded with HOBO Pendant Temperature/Light Data Loggers (UA-002-64; Onset, Bourne, Massachusetts). Using the one-station method, these variables were used to model gross primary production (GPP) and ecosystem respiration (ER) for each sampling site (Plate 1).

Plate 2: Collecting water samples for nutrients, major ions, and *in situ* ecosystem metabolism and algal biomass measurements. Photo credits; Elizabeth Wanderi and Frank Masese

3.9 Data analysis

3.9.1 Modelling ecosystem metabolism

Whole-stream ecosystem metabolism was estimated by modelling the two components, gross primary production (GPP) and ecosystem respiration (ER), following Fuss *et al*. (2017) by fitting a differential equation model (Van de Bogert *et al*., 2007; Hotchkiss & Hall, 2014) to diel dissolved oxygen (DO) concentration measured at a single site (Odum, 1956; Marzolf *et al.*, 1998). The model simulates temporal changes in DO concentration (*d*DO/d*t*) as the result of parameterized GPP, ER and reaeration (RF, equation 1):

$$\frac{d\mathrm{DO}}{dt} = (\mathrm{GPP} - \mathrm{ER} + \mathrm{RF}) \times \frac{1}{z} \tag{1}$$

where GPP adds DO to the water by photosynthesis; ER consumes DO, and RF is the gas exchange at the water-air interface. GPP (g O_2 m^{-2} min^{-1}) was modelled with light saturation (Uehlinger *et al.*, 2000) as:

$$\mathrm{GPP} = \frac{\mathrm{PAR}}{\mathrm{P_1} + \mathrm{P_2} + \mathrm{PAR}} \tag{2}$$

where PAR (photosynthetically active radiation, W m^{-2}) is the observed, instantaneous PAR. P_1 (W min g^{-1} O_2) is the inverse of the slope of a photosynthesis–irradiance curve at a low light intensity, and P_2 (m2 min g^{-1} O_2) is the inverse maximum photosynthesis rate. Daily GPP (GPP24, g O_2 m^{-2} day^{-1}) was integrated from P1, P2, the light record, and the time step Δt between light measurements:

$$\mathrm{GPP24} = \sum_{t=t_0}^{t\ end} \frac{PAR_t}{P_1 + P_2 + PAR_t} \times \Delta t \tag{3}$$

Since ER (g O_2 m^{-2} min^{-1}) is a strongly temperature-dependent process (Kirschbaum, 1995), it was modelled with the van't Hoff–Arrhenius equation (Parkhill & Gulliver, 1999):

$$\mathrm{ER} = \frac{\mathrm{ER_{20}}}{(24 \times 60)} \times \theta^{(T-20)} \tag{4}$$

where $ER24_{20}$ (g O_2 m^{-2} day^{-1}) is the daily rate of ER standardized to 20 °C, T (°C) is the observed, time-specific ambient stream temperature, and θ (theta) is the temperature dependence on respiration. Because different authors have used different values of θ (e.g., Demars *et al.*, 2015), and my modelling efforts were unsuccessful with the commonly used value of 1.045, I decided to model this value. To investigate ER at *in situ* temperature, I translated $ER24_{20}$ to $ER24_{insitu}$ (g O_2 m^{-2} day^{-1}) using recorded *in situ* temperature measurements T (°C) for every time interval Δt:

$$\mathrm{ER24}_{insitu} = \sum_{t=t_0}^{t\,end} \frac{ER_{20}}{(24\times 60)} \times 1.1085^{(T_t-20)} \times \Delta t \qquad (5)$$

The reaeration flux RF (g O_2 m^{-2} min^{-1}) was computed as

$$\mathrm{RF} = k \times \mathrm{DO}_{\mathrm{deficit}} \qquad (6)$$

where k is the temperature-dependent vertical gas exchange velocity (m min^{-1}) and $DO_{deficit}$ (g m^{-3}) is the difference between the observed DO concentration (DO) to DO at 100% saturation (DO_{Sat}): $\mathrm{DO}_{\mathrm{deficit}} = \mathrm{DO}_{\mathrm{Sat}} - \mathrm{DO}$ (7)

DO_{Sat} was calculated from observed, time-specific ambient stream temperature and atmospheric pressure (Benson & Krause Jr, 1984). The vertical gas exchange velocity k (m min^{-1}) is related to the reaeration coefficient K (min^{-1}) by multiplication with depth (m) (Marzolf *et al.*, 1998; Raymond *et al.*, 2012). The reaeration coefficient used was also modelled. Temperature dependence of gas exchange was calculated according to Elmore (1961) and Bott (1996):

$$K_T = \mathrm{K}_{20} \times 1.024^{T-20} \qquad (8)$$

where K_T and K_{20} are reaeration coefficients at ambient stream temperature T and at 20 °C, respectively. For model fitting, the time derivative $d\mathrm{DO}/dt$ of equation (1) was approximated by differences in $\Delta\mathrm{DO}/\Delta t$ across the observed time intervals, and a discretized time series of

DO was predicted using observed, time-specific temperature and light conditions, barometric pressure and a chosen parameter set P1, P2, $ER24_{20}$ and K_{20} (Fuss *et al.*, 2017; Hotchkiss & Hall, 2014; Van de Bogert *et al*., 2007):

$$\mathrm{DO}_{t+1} = \mathrm{DO}_t + (\mathrm{GPP}_t - \mathrm{ER}_t + \mathrm{RF}_t) \times \Delta t \times \frac{1}{z} \qquad (9)$$

DO_{t+1} (g O_2 m^{-3}) was computed from DO_t and GPP, ER and RF were computed from temperature and light conditions at the previous time point t. Δt, the time interval between t and t + 1, is needed to scale up the minute-specific rates accordingly and is chosen in agreement with the observed time series. Equation (9) was obtained by forwarding differencing or Eulerian integration of equation (1) (Soetaert & Herman, 2009). A first observed DO measurement is used as a starting value (DO_{t0}), from which all subsequent DO_t values are computed. To fit P1, P2, $ER24_{20,}$ and K_{20} to empirical data, I used equation (9) in an inverse modelling approach that repeatedly models a DO time series with updated parameter values and minimizes the sum of squared residuals of the modelled to the observed DO time series. The modelled *k* was used to derive $K_{20,}$ which was then used as a starting value to reliably model P1, P2, $ER24_{20,}$ and K_{20} using a four-parameter model. For temperature dependency of ERI used a commonly used theta value of 1.072 (Sand-Jensen *et al.*, 2013; Demars *et al*., 2015).

Several checks were done to ensure that all sites' metabolism parameters were successfully modelled. First, I used *nlm* in the metabolism FIT function to minimize the negative log-likelihood between measured and modelled DO values. Low values (< -100) of the sum of squared residuals for each model were considered indicative of a successful and constrained fit. Secondly, model fits (graphs) were inspected to confirm that the modelled DO values perfectly or closely matched measured DO values. Finally, the modelled outputs for GPP and ER were inspected to make sure that they made sense. For instance, cases where GPP values were negative or ER values were zero or positive were discarded.

3.9.2 Statistical analysis

The differences in water physico-chemical variables, DOM composition, and ecosystem metabolism among study regions defined by livestock density and land use (forest, agriculture, low livestock density, high livestock density, and hippos) and stream size/ stream order (stream orders 1 to 7), with regions and stream orders as main factors and regions × stream order interactions were analysed using two-way analysis of variance (ANOVA). Post hoc Tukey’s Honestly Significant Difference (HSD) multiple comparisons of means test was then used to assess the statistically significant differences between pairs of group means. Tables and bar graphs were then used to represent mean data of physico-chemical variables, DOM composition, and ecosystem metabolism.

Principal Component Analysis (PCA) was used to reduce the dimensionality of the physico-chemical, DOM composition, and components and correlates of ecosystem metabolism data. Two PCAs were used to describe water quality, DOM composition, and ecosystem metabolism. PCAs were statistically tested by permutational analysis of variance (PERMANOVA) based on Bray-Curtis dissimilarity matrices (Anderson *et al.*, 2001; McArdle & Anderson, 2001). In all the permutational tests, statistical significance was determined by 999 permutations. Before statistical analyses, data were quintile-quintile to meet assumptions for parametric tests. Descriptive statistics, biplots, tables and graphs were used to represent physicochemical parameters, DOM quantity and quality, ecosystem metabolism parameters, algal biomass and ecosystem metabolism parameters (GPP, ER and NEP).

Given our unbalanced study design and the lack of spatial independence between some study reaches that fall within the same river system or sub-catchment (Figure 1), Linear mixed models were used to inspect the drivers of ecosystem metabolism (GPP and ER) (Pinheiro & Bates, 2000; Zuur *et al*., 2009). This approach allowed me to account for spatial autocorrelation by including stream or sampling sites as a random effect. Given the many numbers of water physico-chemical variables, Principal component analysis (PCA) was used to collapse the dimensionality of the physico-chemical data by collapsing the variables into individual PCs. Then the PC scores were used as predictor variables (i.e., fixed effects) in the GPP and ER linear mixed models. The proportion of agricultural land cover within the study sites' drainage area (%AGR) was not included in the PCA because I was interested in representing the proximal drivers of stream metabolism. This variable provides an integrated measure of land-use influences on land stream metabolism (Allan, 2004). Instead, %AGR was included as a separate predictor variable. I used Kaiser's criterion (i.e., factors with scores [1) to establish the number of PC to extract and include in the linear mixed models.

Next, I used the variables' loadings on each axis to determine the characteristics represented by each PC. Based on Kaiser's criterion, we retained the scores of PC1, PC2 and PC2 to use as fixed effects. Based on the interpretation of the PCA results, the full model of GPP and ER included PC1, PC2 and PC3, and regions and %AGR as fixed effects. First, models were fitted using the restricted maximum-likelihood (REML) approach (Zuur *et al*., 2009) using the *nlme* R package (Pinheiro *et al*., 2016; R Development Core Team, 2020). Then, the deviations from the analysis assumptions were inspected using model diagnostic plots

(Pinheiro & Bates, 2000). Second, the variance function in both GPP and ER models was included to account for variance heterogeneity (Pinheiro & Bates, 2000; Zuur *et al*., 2009). Third, the most parsimonious fixed effect structure was determined by comparing nested models using the maximum-likelihood test and Akaike's Information Criterion. Finally, I re-fitted the best GPP and ER models with REML and re-inspected model diagnostic plots (Zuur *et al*., 2009).

To assess relationships, including longitudinal trends, between measures of ecosystem metabolism and changes in stream size (RDS) and the density of LMH, generalized additive models were used (GAMs) (Wood, 2017), which incorporate smooth functions that are more flexible in modelling nonlinear relationships (Hastie & Tibshirani, 1990). GAMs were selected over more commonly used linear regression techniques because patterns were hypothesized to be nonlinear. GAMs were built using penalized cubic regression splines with degrees of freedom automatically identified based on the generalized cross-validation score (GCV). GAMs were fitted using the R-package *mgcv* (Wood & Wood, 2015). All statistical analyses were performed in R 4.0.2 (R Core Team, 2020).

CHAPTER FOUR

RESULTS

4.1 Influence of land use and LMH on physiochemistry, major ions and nutrients of the Mara River

4.1.1. Water physiochemistry

In this study, the sites were categorized into four site categories/region forest (FOR), agriculture (AGR), low livestock density (LLIV), high livestock density (HLIV) and hippo sites (HIPP). Livestock and wildlife sites were further grouped under large mammalian herbivore sites (LMH). The stream order, width, depth and discharge differed significantly among the land use types and large mammalian sites. For example, the HIPP sites had the highest number of stream orders, with deeper and broader channels hence high discharge, with a mean value of 6.40±1.65, 15.84±9.87m, and 0.47±0.37m^3/s respectively, compared to AGR sites whose mean value for stream order, width, depth and discharge were; 3.65±1.62, 7.08±6.06m, 0.21±0.09, and 0.35±0.55m^3/s ($p<0.05$)

Overall, the density of LMH increased with stream size (stream order), stream depth and percentage of grasslands in the catchment areas of the sampling sites (Table 1). As the proportion of the grassland increases, the LMH density (individuals/km^2) increased, with FOR sites having a lower LMH density (9.26±4.04) compared to HIPP sites having the highest LMH density of (101.6±22.07). The percentage of the forest was high in FOR (64.74±2.46) and low in LLIV (25.37±15.43) and HIPP (26.97±8.47) sites. The percentage of agriculture was high in LLIV (63.51±23.91) and AGR (56.13±22.19), and it decreased in both HLIV and HIPP sites (table 1). The mean percentage for grasslands was high in both

HLIV (59.11±9.88) and HIPP (54.24±6.39) and low in FOR (5.62±5.24) and AGR (8.79±7.59) sites.

The pH did not respond to land use type or LMH density (One-way ANOVA, F = 0.7, p = 0.59; Table 1). There was a highly significant influence of land uses and LMH on mean water temperature, dissolved oxygen concentration, electrical conductivity and salinity ($p < 0.05$; Table 2). The mean temperature ranged from 15.8±1.8°C at FOR sites to 23.9±2.2 °C at AGR sites. The lowest electrical conductivity was reported in FOR sites at 74.1±29.4 µS/cm, and the highest value was recorded at HIPP sites at 325.0±178.7 µS/cm. DO was highest in FOR and AGR sites compared to LMH sites (Table 1). FOR streams recorded the highest oxygen values of 7.75±0.39 mg/L, while HIPPO sites recorded the lowest mean values of 4.01±1.07 mg/L. AGRI sites recorded the highest concentration of salinity (26.0±0.1 mg/L), and HIPPO sites recorded the lowest value (10.0±0.2 mg/L).

Particulate organic matter (POM), total suspended solids and (TSS) differed significantly among the land use ($p < 0.05$). AGR and FOR sites recorded lower POM, TSS and %POM values than the high-density LMH sites (HLIV and HIPP). The HIPP sites had the highest POM, TSS, and %POM given by mean values of 554.7±251.5 mg/L, 3737.5±285.3 mg/L and 63.6±17.6 %, respectively. In contrast, AGR sites recorded the lowest concentration of POM, TSS, and %POM, given by mean values of 81.2±84.9 mg/L, 261.8±59.2 mg/L and 29.7±15.2%, respectively

Table 1: Characteristics of the sampling sites across the site categories in Mara River, River, during the study period.

Site characteristics	FOR	AGR	LLIV	HLIV	HIPP	F - value	p-value
Stream order	4.00±1.53^{a}	3.65±1.62^{a}	4.80±1.86^{a}	4.00±2.00^{a}	6.40±1.65^{b}	5.3	<0.001*
Width (m)	7.87±4.95^{b}	7.08±6.06^{b}	8.73±5.81^{b}	6.61±3.50^{b}	15.84±9.87^{a}	5.1	<0.001*
Depth (m)	0.20±0.13^{b}	0.21±0.09^{b}	0.23±0.16^{b}	0.16±0.08^{b}	0.47±0.37^{a}	5.5	<0.001*
Discharge (m^3/s)	0.23±0.20^{b}	0.35±0.55^{b}	0.48±0.55^{b}	0.30±0.61^{b}	17.43±26.89^{a}	7.6	<0.001*
LMH Density (individuals/ km^2)	9.26±4.05^{a}	28.00±16.76^{b}	44.80±17.66^{b}	99.58±16.63^{c}	101.6±22.07^{c}	100.2	<0.001*
% Forest	64.74±28.46^{a}	38.18±22.47^{b}	25.37±15.43^{b}	38.06±10.89^{b}	26.97±8.47^{b}	9.9	<0.001*
% Agriculture	32.14±27.96^{b}	56.13±22.19^{a}	63.51±23.93^{a}	19.20±0.45^{c}	22.39±17.25^{bc}	20.5	<0.001*
% Grasslands	5.62±5.24^{c}	8.79±7.59^{c}	16.54±13.85^{b}	59.11±9.88^{a}	54.24±6.39^{a}	117.6	<0.001*
pH (units)	7.63±0.32^{a}	7.62±0.31^{a}	7.72±0.17^{a}	7.61±0.09^{a}	7.56±0.24^{a}	0.71	0.592
Temperature (^{0} C)	15.81±1.79^{c}	18.48±3.17^{b}	20.31±2.48^{b}	23.74±2.06^{a}	23.94±2.24^{a}	27.9	<0.001*
DO (mg/L)	7.75±0.39^{a}	6.98±1.09^{b}	6.34±0.85^{b}	4.39±0.96^{a}	4.01±1.07^{a}	7.3	<0.001*
EC (µS/cm)	74.13±29.44^{b}	103.23±50.00^{b}	260.30±128.90^{a}	309.00±172.80^{a}	325.00±178.70^{a}	18.1^{b}	<0.001*
Salinity (mg/L)	19±0.05^{a}	26±0.07^{b}	15±0.17^{c}	12±0.16^{d}	10±0.16^{e}	15.0	<0.001
POM (mg/L)	247.56±145.2^{a}	81.20±84.8^{c}	262.11±249.2^{a}	349.40±295.30^{a}	554.74±251.5^{b}	11.01	<0.001*
TSS (mg/L)	161.12±125.10^{a}	261.78±591.20^{b}	378.07±383.30^{c}	3986.76±3752.30^{c}	3737.45±2856.30^{c}	16.66	<0.001*
%POM in TSS	56.63±29.5^{a}	29.72±15.2^{b}	45.01±21.4^{a}	54.74±24.5^{a}	63.62±17.6^{a}	6.49	<0.001*

***Means that do not share a letter (superscript) are significantly different, Tukey posthoc tests**

p-values marked with asterisks are significantly different among site categories at *$p<0.05$

Abbreviations for (Site categories; FOR = forested, AGR = Agricultural, LLIV = low livestock density, HLIV = high-density livestock and HIPP = Hippo sites).

4.1.2. Major ions

Aluminium (Al^{3+}) and manganese (Mn^{2+}) concentrations did not differ among land use and LMH density (Table 2; *$p>0.05$*). Boron (B^{3+}), calcium (Ca^{2+}), ferrous iron (Fe^{2+}), potassium (K^+), magnesium (Mg^{2+}), sodium (Na^+), phosphorous (P^{3+}), Sulphur (S^{2+}), and dissolved silica (Dsi) were significantly different among all the land-use sites (*$p<0.05$*, table 2).

HLV sites had the highest concentrations of most of the major anions and cations (B^{3+}, Ca^{2+}, Na^+, and S^{2+}), while FOR sites had the lowest concentrations (*$p<0.05$*). DSi concentration ranged from the lowest concentration of 14.6±5.7 mg/L at HLIV sites to the highest concentration of 18.9±6.1 mg/L at AGR sites (*$p<0.05$*). FOR sites were characterized by a high concentration of Fe^{2+} (0.16±0.07 mg/L), while the AGR sites had the lowest values of 0.01±0.06 mg/L. LLV had the highest values of K^+ (11.9±5.6 mg/L) compared to FOR sites with the lowest concentration (4.7±2.6 mg/L). On the other hand, the concentration of Na^+ increased with an increase in LMH density, with HIPP sites recording the highest concentration (35.3±23.0 mg/L) while AGRI and FOR sites recorded the lowest concentrations (*$p<0.05$*).

4.1.3. Nutrients

Land use and LMH density had a significant influence on the concentrations of dissolved organic carbon (DOC mg/L), ammonium (NH_4^+ μg/L), soluble reactive phosphorus (SRP μg/L), total dissolved nitrogen (TDN mg/L), and nitrates (NO_3^- mg/L) (One-way ANOVA, $p < 0.05$; Table 3). The concentrations of nitrites (NO_2^- μg/L) did not respond to land use or LMH density ($p = 0.28$; Table 3). LMH sites recorded the highest concentration of (DOC, mg/L), ammonium (NH_4^+, μg/L), and soluble reactive phosphorus (SRP, μg/L).

HLIV, LLIV, and HIPP sites recorded the highest mean values of6.84±1.59 mg/L, 6.39±2.93 mg/L, and 5.82 mg/L, respectively. The HLIV (47.0±34.4 mg/L) and HIPP (43.6±37.3 mg/L) sites had the highest concentrations of SRP, while FOR (12.9±14.6 mg/L) and AGR (11.2±10.3) sites had the lowest concentrations ($p<0.05$). High NH_4^+ was recorded at HIPP sites (531.9±471.5 µg/L), and the lowest concentrations were recorded at FOR sites (24.0±19.9 µg/L) ($p<0.05$). Interestingly, NH_4^+ behaved differently from other species of nitrogen (N) by having the highest concentrations in high-density LMH sites (HLIV and HIPP), where low DO concentrations were occasionally reported in the hypoxic hippo pools ($p<0.05$).

Concentrations of TDN (1.3±0.8 mg/L) and NO_3^- (1.0±0.4 mg/L) were highest in low livestock density (LLIV) sites ($p<0.05$). HLV recorded the lowest concentrations of NO_3^- (0.4±0.4 mg/L), while FOR recorded the lowest values of TDN (0.8±0.5 mg/L). TDN and ammonium were always high in all land use except for FOR sites.

Table 2; Means (±SD) of major ions across the five different site categories in Mara River during the study period.

Major ions	**FOR**	**AGR**	**LLIV**	**HLIV**	**HIPP**	**F - value**	***p*-value**
Al^{3+} (mg/L)	0.05±0.03^{a}	0.04±0.04^{a}	0.03±0.05^{a}	0.07±0.07^{b}	0.04±0.04^{a}	1.09	0.373
B^{3+} (mg/L)	0.01±0.01^{a}	0.01±0.01^{a}	0.02±0.01^{a}	0.03±0.02^{b}	0.02±0.01^{a}	13.22	<0.001*
Ca^{2+} (mg/L)	3.82±2.04^{a}	4.72±2.40^{a}	11.36±5.38^{b}	21.96±19.29^{b}	16.94±11.41^{b}	12.00	<0.001*
Fe^{2+} (mg/L)	0.16±0.07^{b}	0.01±0.06^{a}	0.04±0.04^{a}	0.04±0.06^{a}	0.03±0.03^{a}	15.90	<0.001*
K^{+} (mg/L)	4.75±2.61^{a}	6.11±2.86^{a}	11.93±5.63^{b}	11.01±3.07^{b}	11.44±5.04^{b}	13.05	<0.001*
Mg^{2+} (mg/L)	1.04±0.56^{b}	1.23±0.52^{b}	1.82±0.86^{a}	2.42±1.25^{a}	2.20±1.46^{a}	7.08	<0.001*
Mn^{2+} (mg/L)	0.03±0.02^{a}	0.07±0.06^{a}	0.04±0.04^{a}	0.31±0.93^{a}	0.04±0.06^{a}	1.36	0.261
Na^{+} (mg/L)	5.81±1.80^{a}	9.74±5.39^{a}	29.89±18.23^{b}	39.31±28.07^{b}	35.29±22.98^{b}	15.15	<0.001*
P^{3+} (mg/L)	0.01±0.02^{a}	0.01±0.01^{a}	0.03±0.03^{a}	0.05±0.03^{b}	0.05±0.04^{b}	10.17	<0.001*
S^{2+} (mg/L)	0.59±0.24^{a}	0.81±0.57^{a}	4.55±3.34^{a}	11.39±9.12^{b}	9.90±7.39^{b}	18.30	<0.001*
DSi (mg/L)	15.97±3.77^{a}	18.88±6.07^{b}	14.02±4.25^{a}	14.57±5.62^{a}	15.47±4.25^{a}	2.93	0.035*

***Means that do not share a letter (superscript) are significantly different, Tukey posthoc tests**

p-values marked with asterisks are significantly different among site categories at *p<0.05

Abbreviations for (Site categories; FOR = forested, AGR = Agricultural, LLIV = low livestock density, HLIV = high-density livestock and HIPP = Hippo sites)

Table 3: Means (±SD) of nutrients across the five site categories or regions in the Mara River basin during the study period.

Variables	**FOR**	**AGR**	**LLIV**	**HLIV**	**HIPP**	**F - value**	***p*-value**
DOC (mg/L)	2.76±1.88^{a}	2.77±1.26^{a}	6.39±2.93^{b}	6.84±1.59^{b}	5.82±2.51^{b}	17.00	<0.001*
NH_4^+ (µg/L)	24.02±19.87^{a}	63.08±69.59^{b}	75.17±54.27^{b}	424.2±531.88^{c}	531.88±471.57^{c}	7.56	<0.001*
SRP (µg/L)	12.93±14.55^{a}	11.19±10.30^{a}	28.43±22.22^{a}	46.95±34.41^{b}	43.64±37.31^{b}	8.44	<0.001*
TDN (mg/L)	0.78±0.51^{b}	1.12±0.60^{a}	1.26±0.83^{a}	0.81±0.56^{b}	1.06±0.59^{a}	1.78	<0.001*
NO_3^- (mg/L)	0.58±0.27^{a}	0.84±0.40^{a}	0.95±0.38^{a}	0.38±0.35^{b}	0.67±0.54^{a}	4.97	<.001*
NO_2^- (µg/L)	161.12±34^{a}	179.42±321.19^{a}	235.95±552.75^{a}	2.17±0.25^{a}	2.09±0.45^{a}	1.31	0.283

***Means that do not share a letter (superscript) are significantly different, Tukey posthoc tests**

p-values marked with asterisks are significantly different among site categories at *$p<0.05$

Abbreviations for (Site categories; FOR = forested, AGR = Agricultural, LLIV = low livestock density, HLIV = high-density livestock and HIPP = Hippo sites)

4.2 Influence of land use and LMH on dissolved organic matter (DOM) composition and concentration in Mara River

4.2.1 Excitation-emission matrix (EEM) fluorescence spectroscopy of DOM in Mara River

Following PARAFAC analysis, fluorescence EEMs were very dissimilar and occurred over a wide range of excitation (ca. 250−450 nm) and emission (ca. 270−600 nm) wavelengths (Figures 2, Table 4). The PARAFAC model consisted of six components (C1–C6) whose fluorophores were compared with the literature (Table 4 and Table). The position and spectral shape of the six components are shown in Figure 2. In the dataset, fluorescence components were characterized by humic, reduced humic, and protein-like substances. The humic-like components were one and two (C1 and C2), reduced humic-like components were C3 and C4, and protein-like components were C5 and C6 (Table 7). The C5 component was characterized by tryptophan, a microbially produced DOM, compared to the C6, whose DOM constitute a more degraded tyrosine-like protein.

The intensities of the various DOM components differed across land uses significantly, with all components (C1-C6) having high intensities in LLIV and HLIV streams as compared to the FOR streams ($p<0.05$). The UVA humic-like component of lower molecular weight (C1) DOM substances was high in HLIV land use sites (1.15±0.15) compared to FOR land use sites 0.42±0.26.

Similarly, UVC humic-like, fluvic-acid components (C2) had higher intensities in LLIV (1.79±0.94) and HLIV (1.72±0.32) sites as compared to FOR streams (0.57±0.31) and

AGR sites (0.81±0.40). A similar trend was observed in reduced-humic components (C3 and C4) and protein and tyrosine-like DOM substances (C5). In components C3, C4, and C5, LLIV had the highest intensities of values; 0.61±0.30, 0.44±0.22, and 0.30±0.11, respectively, while lower intensities were observed in FOR land use sites with values of 0.22±0.15, 0.14±0.09, and 0.17±0.09, respectively. LLIV, AGR, and HLIV sites recorded the highest C5 intensities as follows; 0.30±0.11, 0.25±0.11, and 0.24±0.04 respectively, while FOR had the lowest intensity of 0.17±0.09. The HLIV sites had a high concentration of C6 (0.28±0.12), followed by the LLIV sites (0.15±0.13), and the lowest values were recorded at FOR sites (0.11±0.07).

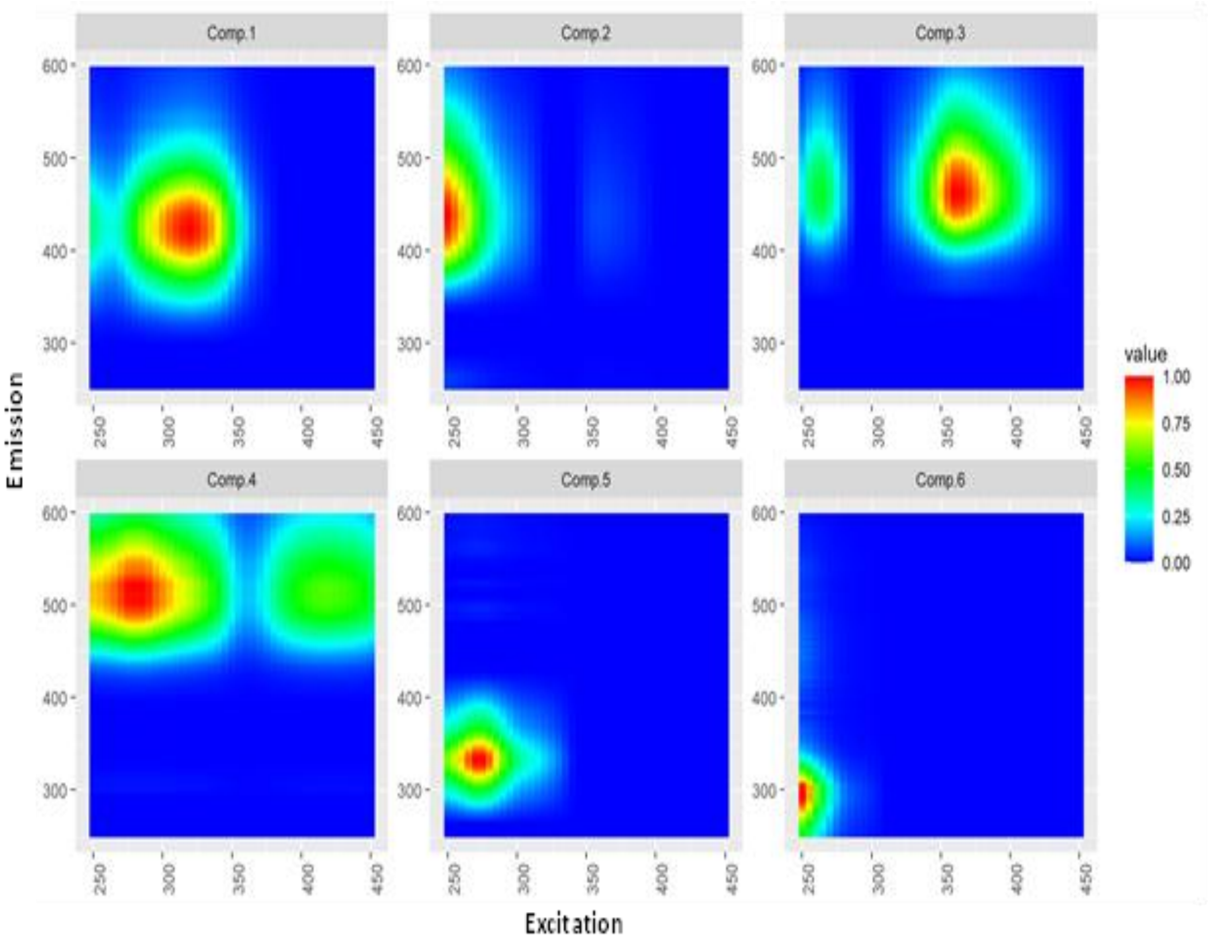


Figure 2: Observed excitation and emission wavelengths for maximum fluorescence of the 6 PARAFAC components identified in Mara River during the study period.

Table 4: Fluorescent components of DOM as identified by parallel factor analysis (PARAFAC).

PARAFAC component (this study)	Excitation maximum (nm)	Emission maximum (nm)	Name of PARAFAC component (previous studies)	Probable sources*	Description
C1	<250, 250	428-444	C[Ca, Cb, Cd], M[Cd], β[P], 1[SMa], 4[SMb], 1[Ma], 11[CMK], 1[MS]	T, A, M	UVA humic-like component. Low molecular weight, biological activity, widespread
C2	<250, 250	436-456	A[Ca,Cb], A[Cb], α[P], 4[MS]	T	UVC humic-like, fulvic acid component.
C3	256-262 (366-378)	446-472	A[C, Cd], C[CA, Cd], α[P], 6[MS]	T	UVC humic-like + UVA humic-like component reduced humic, widespread.
C4	<250, 250	516-530 (500-550)	4[CMK], 2[MS]	T, M	Hydroquinone-like component. Reduced humic-like component
C5	270-276	320-332	B[Ca], δ[P], 8[CMK], 6[SMa], 7[SMb], 5[SMB], 7[Ma], 6[Mb], 4[CK], 3[MS]	T, A, M	Protein- and tryptophan-like components, microbial-produced, widespread
C6	254	302	B[Cb,Cd], T[Cd], γ[P], 13[CMK], 4[SMa], 8[SMb], 1[Ma], 7[Mb], 7[MS]	T, A, M	Protein- and tyrosine-like components may indicate more degraded peptide material

NB: [a]Value in parentheses is secondary maximum. See the text for a discussion of probable origins. T, terrestrial plant or soil organic matter; A, autochthonous production; M, microbial processing. [Ca] Coble, Green, Blough, and Gagosian (1990); [cb]Coble (1996); [cd]Coble, Del Castillo, and Avril (1998); [P]Parlanti *et al*. (2000); [SMa]C. A. Stedmon and Markager (2005b); [SMb]C. A. Stedmon and Markager (2005a); [Ma]K. R. Murphy, Stedmon, Waite, and Ruiz (2008); [Mb]K. M. Murphy, K. R. *et al*. (2011); [CMK]Cory and McKnight (2005); [SMB]C. A. Stedmon, Markager, and Bro (2003); [CK]Cory and Kaplan (2012), [MS](Masese *et al*., 2020).

Table 5: Intensities of the 6 PARAFAC components (C1-C6) across different site categories in the Mara River during the study period.

Components	FOR	AGR	LLIV	HLIV	F – value	p-value
C1	0.42 ± 0.26^{a}	0.54 ± 0.27^{a}	1.25 ± 0.63^{b}	1.15 ± 0.15^{a}	17.14	<0.001*
C2	0.57 ± 0.31^{a}	0.81 ± 0.40^{a}	1.79 ± 0.94^{b}	1.72 ± 0.13^{b}	17.38	<0.001*
C3	0.22 ± 0.15^{a}	0.26 ± 0.13^{a}	0.61 ± 0.30^{b}	0.51 ± 0.07^{b}	14.84	<0.001*
C4	0.14 ± 0.09^{a}	0.17 ± 0.08^{a}	0.44 ± 0.22^{b}	0.40 ± 0.06^{b}	19.72	<0.001*
C5	0.17 ± 0.09^{b}	0.25 ± 0.11^{a}	0.30 ± 0.11^{a}	0.24 ± 0.04^{a}	4.11	<0.01*
C6	0.11 ± 0.07^{a}	0.14 ± 0.09^{a}	0.15 ± 0.13^{a}	0.28 ± 0.12^{a}	3.43	0.027*

***Means that do not share a letter (superscript) are significantly different, Tukey posthoc tests**

p-values marked with asterisks are significantly different among site categories at *$p<0.05$

Abbreviations for (Site categories; FOR = forested, AGR = Agricultural, LLIV = low livestock density, HLIV = high-density livestock and HIPP = Hippo sites).

4.2.2 DOM absorbance and fluorescence indices in the Mara River

DOM composition was determined using various fluorescence and absorption indices. Because of logistical constraints, fluorescence and absorbance index were calculated for 63 sites spanning all the regions except hippos (HIPP), i.e., FOR, AGR, HLIV, and LLIV sites. In the LLIV and HLIV density, there was a higher concentration of photodegradable DOM, the spectral slope (S_R) ratio, as opposed to AGR and FOR sites ($p>0.05$, Table 6). The S_R concentration varied from 0.9±0.1 in FOR to 1.2±0.1 in livestock regions (HLIV and LLIV). E_4:E_6 ratio, which is an indicator of molecular weight and aromaticity, $SUVA_{254,}$ and fluorescence index (FIX) did not significantly differ among the site categories ($p>0.05$, Table 6). On the other hand, the freshness index (β:α), fluorescence index (FIX), humification index (HIX), and a_{255}/a_{365} were statistically different among the land uses ($p<0.05$; Table 6).

FOR streams were characterized by a low molecular weight of lower aromaticity DOM (a_{255}/a_{365}; 3.8±0.3), while HLIV sites were associated with high molecular weight and aromatic DOM (4.9±0.8; Table 6). Humification (HIX) increased with the change in land use and increased livestock density. The LLIV and HLIV sites recorded high HIX values associated with humified plant material (Table 6), with HLV and LLV sites having a mean value of 0.86±0.01 respectively, while FOR had a mean value of 0.80±0.01 (Table 6). Recently produced autochthonous DOM (β:α) was higher in AGR regions (0.6±0.02) and LLIV (0.62±0.02), while HLIV and regions recorded the lowest levels of 0.59±0.02 and 0.61±0.02 respectively.

Table 6: Means (±SD) of fluorescence and absorbances indices of dissolved organic matter composition across different site categories in the Mara River, Kenya.

Optical properties	FOR	AGR	LLIV	HLIV	*F* – value	*p*-value
S_R	0.92±0.05a	0.96±0.10a	1.19±0.14b	1.16±0.14b	25.66	<0.001*
E4:E6	2.91±0.34^{a}	5.85±12.60^{a}	2.66±0.44^{a}	3.21±0.22^{a}	0.68	0.578
a_{255}: a_{365}	3.78±0.32^{a}	3.71±0.45^{a}	3.92±0.58^{a}	4.88±0.78^{b}	7.36	<0.001*
SUVA$_{254}$	4.32±0.68^{a}	4.58±1.26^{a}	4.79±1.63^{a}	4.51±1.33^{a}	0.41	0.753
FIX	1.47±0.02^{a}	1.49±0.03^{a}	1.48±0.04^{a}	1.46±0.02^{a}	1.48	0.235
HIX	0.80±0.05^{b}	0.81±0.06^{b}	0.86±0.04^{a}	0.86±0.01^{a}	4.35	0.012*
β: α	0.61±0.02^{b}	0.64±0.02^{a}	0.62±0.03^{a}	0.59±0.02^{b}	7.41	<0.001*

***Means that do not share a letter (superscript) are significantly different, Tukey posthoc tests**

p-values marked with asterisks are significantly different among site categories at *$p<0.05$

Abbreviations for (Site categories; FOR = forested, AGR = Agricultural, LLIV = low livestock density, HLIV = high-density livestock and HIPP = Hippo sites).

4.2.3 Size exclusion chromatography of DOM quality and quantity in Mara River

The dissolved organic matter (DOM) with high molecular weight substances characterized HIPP and HLV stream sites, while LLIV sites were rich in low molecular weight substances (Table 7). HMWS were rich in nitrogen or carbon components. There was a statistical difference between HMWS-C ($p<0.05$), while HMWS-N was not statistically different ($p>0.05$). LMH sites had DOM rich in high molecular weight substances (HMWS-C) as opposed to AGR and FOR sites. The HIPP sites are characterized by HMW DOM substances rich in carbon (1.17±0.78) as opposed to LLIV sites with HMW DOM rich in nitrogen (0.24±0.07; Table 7).

The LLIV sites were also characterized with high values of Humic-like carbon DOM (4.12±2.17) as opposed to HIPP (0.52±0.91), AGR (2.07±1.18) and FOR (2.08±1.68). Similarly, LLIV was also rich in low molecular weight substances rich in carbon (LMWS-C=1.01±0.47) compared to other sites, FOR, AGR, and HIPP.

SUVA humic DOM was also pronounced in HIPP and FOR streams with a mean concentration of 4.81±0.28 and 4.45±0.40, respectively, compared to HLIV sites at 4.26±0.56. Similarly, SUVA (ges) was also high in the HIPP sites (4.28±0.28) compared to other sites FOR, AGRI, LLIV and HLIV. The livestock sites (LLIV and HLIV) were characterized by a high concentration of BDOC, CDOC, and DOC compared to FOR and AGR. The LLIV has the highest values of BDOC (6.38±2.88) and CDOC (5.99±2.62), while HLIV has high mean DOC concentrations (6.84±1.59)

Table 7: Means (±SD) for DOM indices of DOM based on size-exclusion chromatography LC-OCD-OND across different site categories in the Mara River, Kenya

DOM Characteristics	FOR	AGR	LLIV	HLIV	HIPP	F – value	p-value
HMWS_C	0.27±0.12^{a}	0.36±0.18^{a}	0.68±0.52^{a}	1.23±0.75^{b}	1.17±0.78^{b}	13.45	<0.001*
HMWS_N	0.05±0.33^{a}	0.05±0.02^{a}	0.17±0.41^{a}	0.06±0.04^{a}	0.03±.01^{a}	1.51	0.217
Humic-like_C	2.08±1.68^{a}	2.07±1.18^{a}	4.12±2.17^{b}	1.14±1.65^{c}	0.52±0.91^{d}	9.90	<0.001*
Humic-like_N	0.10±.0.08^{a}	0.11±0.06^{a}	0.21±.0.13^{b}	0.24±0.07^{b}	0.22±0.10^{b}	10.07	<0.001*
LMWS_C	0.61±0.55^{a}	0.60±0.34^{a}	1.01±0.47^{b}	0.89±.0.27^{b}	0.73±0.28^{c}	3.20	0.022*
SUVA (humics)	4.45±0.40^{a}	4.38±0.26^{a}	4.43±0.31^{a}	4.26±0.56^{a}	4.81±0.28^{b}	3.49	0.013*
SUVA (ges)	3.34±0.80^{a}	3.24±0.54^{a}	3.40±0.48^{a}	3.75±0.53^{b}	4.28±0.37^{b}	6.68	<0.001*
BDOC	3.24±2.16^{a}	3.26±1.61^{a}	6.38±2.88^{b}	5.76±2.08^{b}	5.16±2.33^{b}	7.81	<0.001*
CDOC	2.96±2.03^{a}	3.03±1.45^{a}	5.99±2.62^{b}	5.28±1.86^{b}	4.75±2.09^{c}	8.31	<0.001*
DOC (mg/L)	2.76±1.88^{a}	2.77±1.26^{a}	6.39±2.93^{b}	6.84±1.59^{b}	5.82±2.51^{c}	17.00	<0.001*

***Means that do not share a letter (superscript a-d) are significantly different, Tukey posthoc tests**

***p-values marked with asterisks are significantly different among site categories at p<0.05Abbreviations for (Site categories; FOR = forested, AGR = Agricultural, LLIV = low livestock density, HLIV = high-density livestock and HIPP = Hippo sites).**

4.3 Influence of land use and LMH on whole stream ecosystem metabolism in Mara River

Ecosystem metabolism was measured at 38 sites in the study area, which fall into forested (FOR), agricultural (AGR), low livestock density (LLIV), and high livestock density (HLIV) sites. Metrics used to measure ecosystem metabolism include; gross primary production (GPP), ecosystem respiration (ER), GPP: ER ratio and net ecosystem production (NEP) and biomass of algae (measured using a BenthoTorch) as a measure of the primary output. There were no significant differences between site categories in the biomass of green algae, cyanobacteria and total algal biomass. However, there was a significant difference (*p*<0.05) in the biomass of diatoms across land use and LMH (Table 8 and figure 3).

The biomass of diatoms was highest in FOR (0.38±0.20 $\mu g/cm^3$) and AGR (0.30±0.17) as compared to HLIV (0.05±0.01 $\mu g/cm^2$). As a result, the gross primary production recorded for 24 hours (GPP_{24} gO_2m^2/day) was lower in FOR sites with a mean of 0.88±0.96 g O_2 m^{-2} day^{-1} (Table 8 and figure 3). However, the GPP_{24} rates were high in AGR and LLIV sites with mean values of 2.08±0.81g O_2 m^{-2} day^{-1} and 2.69±0.82 g O_2 m^{-2} day^{-1}, respectively. Similarly, ER_{24} rates were high in HLV had the highest rates (-4.56±1.62 g O_2 m^{-2} day^{-1}), followed by the AGR site with mean values of (2.07±0.96 g O_2 m^{-2} day^{-1}) (Table 11, figure 6).

Table 8: Means (±SD) of measures of ecosystem metabolism and the algal biomass at different algal components among different site categories in the Mara River basin, Kenya, during the sampling period.

Measures of metabolism	**FOR**	**AGR**	**LLIV**	**HLIV**	**F – value**	***p-value***
Cyanobacteria biomass (µg/cm^2)	0.68±0.28^{a}	0.57±0.31^{a}	0.45±0.32^{a}	0.52±0.05^{a}	0.51	0.684
Green-algae biomass (µg/cm^2)	0.08±0.11^{a}	0.07±0.09^{a}	0.01±0.01^{a}	0.01±0.00^{a}	1.39	0.263
Diatoms biomass (µg/cm^2)	0.38±0.20^{a}	0.30±0.17^{a}	0.16±0.19^{b}	0.05±0.01^{c}	2.98	0.042*
Total-algae biomass (µg/cm^2)	1.08±0.46^{a}	0.94±0.45^{a}	0.62±0.43^{a}	0.58±0.04^{a}	1.75	0.189
GPP$_{24}$ (g O$_2$ m^{-2} day^{-1})	0.88±0.58^{a}	2.08±0.81^{b}	2.69±0.82^{c}	1.34±0.81^{c}	7.88	<0.001*
ER$_{24}$ (g O$_2$ m^{-2} day^{-1})	-1.83±0.86^{a}	-2.07±0.96^{a}	-1.62±0.63^{a}	-4.56±1.62^{b}	7.90	<0.001*
GPP: ER	0.53±0.31^{a}	1.17±0.60^{b}	1.84±0.74^{b}	0.54±0.18^{a}	7.61	<0.001*
NEP (g O$_2$ m^{-2} day^{-1})	-0.8±0.96^{a}	0.01±0.83^{b}	1.07±0.92^{b}	-2.21±1.55^{a}	11.42	<0.001*

***Means that do not share a letter (superscript) are significantly different, Tukey posthoc tests**

p-values marked with asterisks are significantly different among site categories at *p<0.05

Abbreviations for (Site categories; FOR = forested, AGR = Agricultural, LLIV = low livestock density, HLIV = high-density livestock and HIPP = Hippo sites).

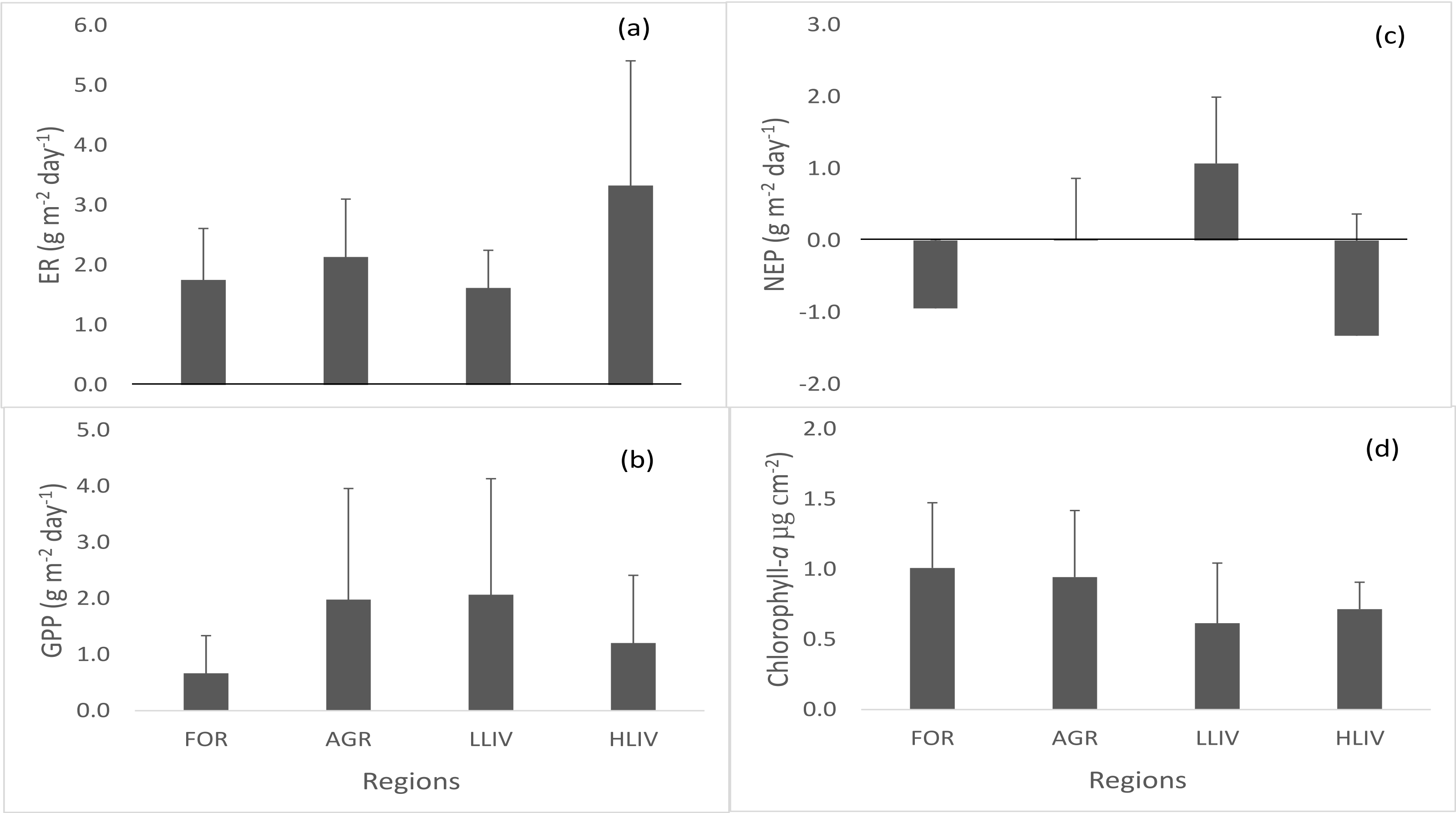


Figure 3: The ecosystem metabolism and algae composition across site categories and stream order in the Mara River basin.

Therefore given GPP and ER values, the AGR and LLIV streams were autotrophic (GPP: ER>1), while FOR and HLIV were heterotrophic (GPP: ER<1). Similarly, both AGR and LLIV streams were carbon sinks (NEP>0), while FOR and HLIV streams were carbon sources (NEP<0) (Figure 3).

4.4 Influence of stream size, physico-chemical, dissolved organic matter and ecosystem metabolism in Mara River

4.4.1 Influence of stream size on physico-chemical of Mara River

Width, depth, and velocity increased from low-order streams (1-3) to high-order streams (4-7), and so was the discharge (m^3/s), which is obtained from the calculation of these three parameters (width, depth and velocity), see table 9. Low-order streams (1-3) had the lowest discharge, ranging from 0.02±0.02m^3/s to 0.1±0.1m^3/s in an increasing trend. As the river further flowed midstream (4-6), the river discharge increased, and stream order 5 recorded the highest mean (0.9±0.9 m^3/s) than stream orders 4 and 6. The stream discharged further peaked downstream at mean values of 13.4±24.5 m^3/s (stream order 7).

River distance from the source responded with longitudinal gradient, upstream to downstream, with the highest mean values recorded at stream orders one and two (3.5±1.2) and highest values recorded at stream order 7 (54.9±15.1). There was no significant increase in forest and agriculture percentage cover across the stream orders, from low order to high order stream ($p>005$).

There were, however, significant differences in the percentage of grasslands across the stream order, though the trend from upstream to downstream was unclear. For example, stream order 4 had the lowest grassland percentage (11.2±19.3) compared to stream orders 1 and 2. (18.5±26.0). Conversely, the higher stream order had the most extensive grassland percentage cover (50.4±13.7) than the lower and midstream orders. The proportion of grassland affected the density of LMH, with a similar observation also reported in LMH density. Stream order 4 had the lowest LMH density, 24.0±24.0 individual/km^{2,} while stream order 7 recorded the highest LMH density, 100.9±24.2 individual/km^2.

Stream size did not influence the concentration of DO ($p > 0.05$, Table 9). However, there were significant differences in mean pH, water temperature, electrical conductivity and salinity ($p < 0.05$; Table 9). The pH responded to changes in the longitudinal gradient of the river (One-way ANOVA, $F = 6.6$, $p<0.5$; Table 9). Stream orders 1 and 2 had the lowest pH (7.5±0.02), while stream order 6 had the highest pH (7.9±0.3). However, there was a drop in pH at the large stream order 7 (7.6±0.2). The temperature and electrical conductivity varied among the stream order with increasing trends from upstream to downstream, although stream order 5 behaved differently as expected. The lowest temperature was recorded in the 1 and 2 stream order (17.8±3.8°C), while stream order 7 had the highest mean values (24.1±2.1°C).

The lowest electrical conductivity was recorded in stream order 5 (96.4±77.8 µS/cm), with stream order 7 recording the highest values (3,091.6±3,369.8 µS/cm). The total suspended solids (TSS) differed significantly among stream orders ($p < 0.05$), with stream orders 5 and 6 recording the lowest mean values of 197±.257.6mg/L and 375.8±. 862.7mg/L, respectively compared to stream order 7, whose values were significantly higher (3091.6±. 3,369.8 mg/L). However, this was not the case with the percentage of POM (%POM) in TSS ($p > 0.05$).

4.4.2 Influence of stream size on major ions of Mara River

The mean values for ferrous iron (Fe^{2+}), aluminium (Al^{3+}), Boron (B^{3+}), calcium (Ca^{2+}), potassium (K^{+}), magnesium (Mg^{2+}), manganese (Mn^{2+}), phosphorous (P^{3+}) and dissolved silica (DSi) concentration were not significantly different among all the stream order sites ($p > 0.05$, Table 10). Sodium (Na^{+}) and sulphur (S^{2+}) concentration changed along the longitudinal gradient (stream sizes), but there was no clear trend with an increase in stream order/size ($p>0.05$). Na^{+} and S^{2+} were highest in stream order 7 and lowest in stream order 6 (Table 10). Even though stream size affected the concentration of major ions, the effect was not longitudinal and was mainly linked to the density of LMH (Figure 4)

4.4.3 Influence of stream size on nutrients of Mara River

In this study, mean nutrients for all the nutrients, DOC, NO_3^-, NO_2^-, NH_4^+ and TDN, did not vary among the stream orders (stream order 1-7). See table 11.

Table 9: Means (±SD) of physical-chemical parameters across the stream order (1 and 2 - 7) in Mara River, Kenya, during the study period.

	Stream orders							
Site characteristics	**1 and 2**	**3**	**4**	**5**	**6**	**7**	**F - value**	***p*-value**
Width (m)	2.1±1.1^{a}	4.0±2.1^{b}	5.6±2.9^{c}	12.8±2.8^{d}	13.5±2.9^{e}	15.2±6.2^{f}	42.3	<0.001*
Depth (m)	0.1±0.04^{a}	0.2±0.1^{a}	0.2±0.1^{a}	0.3±0.1^{b}	0.3±0.13^{b}	0.4±0.4^{b}	6.5	<0.01*
Velocity (s)	0.2±0.1^{a}	0.2±0.2^{a}	0.2±0.1^{a}	0.3±0.2^{b}	0.2±0.1^{a}	0.8±1.1^{c}	4.0	<0.01*
Discharge (m^{3}/s)	0.02±0.02^{a}	0.1±0.1^{b}	0.2±0.2^{c}	0.9±0.9^{d}	0.8±0.6^{e}	13.4±24.5^{f}	3.9	<0.01*
RDS	3.5±1.2^{a}	7.2±1.4^{b}	11.1±19.3^{c}	20.0±5.52^{d}	27.8±6.71^{e}	54.9±15.1^{f}	99.3	<0.001*
%Forest	34.6±34.2^{a}	41.8±29.0^{a}	54.9±29.4^{a}	48.2±17.7^{a}	40.2±11.9^{a}	31.4±13.3^{a}	1.4	0.245
%Agriculture	49.1±41.6^{a}	38.1±37.1^{a}	36.6±27.1^{a}	40.0±23.3^{a}	48.9±16.2^{a}	17.9±15.2^{a}	2.2	0.067
%Grasslands	18.5±26.0^{a}	22.0±25.1^{b}	11.2±15.4^{c}	14.7±22.0^{d}	15.3±12.0^{e}	50.4±13.7^{f}	6.6	<0.01*
LMH density (individuals/ km^{2})	40.5±38.0^{a}	42.4.2^{b}	24.0±24.0^{c}	24.7±34.2^{c}	36.5±20.2^{d}	100.9±24.2^{e}	10.9	<0.001*
DO (mg/L)	6.9±1.0^{a}	7.18±1.4^{a}	6.7±1.3^{a}	7.6±0.5^{a}	7.3±0.6^{a}	7.7±0.9^{a}	1.6	0.162
pH	7.5±0.2^{a}	7.5±0.3^{a}	7.6±0.2^{b}	7.7±0.1^{c}	7.9±0.3^{c}	7.6±0.2^{b}	6.6	<0.01*
Temperature (^{0} C)	17.8±3.8^{a}	18.6±4.4^{b}	19.1±3.0^{c}	17.7±2.6^{a}	20.0±2.7^{d}	24.1±2.1^{e}	6.5	<0.01*
EC (µS/cm)	155.4±101.2^{a}	162.9±132.7^{b}	169.0±162.2^{c}	96.4±77.8^{d}	144.2±105.0^{a}	352.9±184.4^{e}	5.5	<0.01*
Salinity (mg/L)	0.1±0.1^{a}	0.1±0.1^{a}	0.1±0.1^{a}	0.1±0.0^{b}	0.1±0.1^{a}	0.2±0.1^{a}	3.1	<0.01*
TSS (mg/L)	738.1±1604.3^{d}	1333.2±2666.4^{e}	1144.5±3033.5^{e}	197.6±257.6^{a}	375.8±862.7^{c}	3091.6±3369.8^{b}	2.7	0.03*
%POM in TSS	37.3±23.3^{a}	46.6±20.4^{a}	46.0±21.5^{a}	57.3±33.6^{a}	49.2±28.7^{a}	55.7±20.8^{a}	1.1	0.39

NB: RDS = the square root of drainage are in km^{2}

***Means that do not share a letter (superscript) are significantly different, Tukey posthoc tests**

Table 10; Means (±SD) of major ions variables across the five different stream orders in Mara River during the study period.

Major ions	**1 and 2**	**3**	**4**	**5**	**6**	**7**	**F – value**	**p-value**
Al^{3+} (mg/L)	0.05±0.07^{a}	0.05±0.04^{a}	0.04±0.03^{a}	0.03±0.02^{a}	0.05±0.04^{a}	0.04±0.04^{a}	0.31	0.911
B^{3+} (mg/L)	0.01±0.01^{a}	0.01±0.01^{a}	0.02±0.02^{a}	0.01±0.01^{a}	0.01±0.01^{a}	0.02±0.01^{a}	1.47	0.213
Ca^{2+} (mg/L)	6.75±3.99^{a}	10.50±10.57^{a}	13.09±22.61^{a}	6.40±8.98^{a}	6.64±4.42^{a}	15.89±9.07^{a}	1.80	0.125
Fe^{2+} (mg/L)	0.08±0.07^{a}	0.11±0.10^{a}	0.09±0.08^{a}	0.08±0.06^{a}	0.10±0.07^{a}	0.03±0.03^{b}	2.33	0.051
K^{+} (mg/L)	8.99±4.52^{a}	8.51±4.88^{a}	8.46±6.57^{a}	5.42±4.43^{a}	6.60±3.35^{a}	10.66±4.65^{a}	1.77	0.133
Mg^{2+} (mg/L)	1.47±0.70^{a}	1.78±1.33^{a}	1.34±0.94^{a}	1.19±1.00^{a}	1.37±0.65^{a}	2.17±1.11^{a}	1.65	0.165
Mn^{2+} (mg/L)	0.06±0.05^{a}	0.25±0.76^{a}	0.04±0.04^{a}	0.03±0.02^{a}	0.03±0.03^{a}	0.04±0.04^{a}	0.92	0.471
Na^{+} (mg/L)	15.66±13.87^{a}	16.57±16.00^{a}	22.35±27.20^{a}	15.85±25.65^{a}	14.58±13.30^{a}	37.83±25.01^{b}	2.87	0.028*
P^{3+} (mg/L)	0.04±0.03^{a}	0.03±0.04^{a}	0.02±0.02^{a}	0.01±0.02^{a}	0.02±0.02^{a}	0.04±0.01^{a}	1.32	0.262
S^{2+} (mg/L)	2.94±5.98^{a}	2.83±3.94^{a}	3.71±6.04^{a}	3.30±7.56^{a}	2.28±3.26^{a}	10.59±8.04^{b}	4.21	<.001*
DSi (mg/L)	19.41±7.66^{c}	16.17±5.39^{b}	17.42±5.32^{b}	14.91±3.33^{a}	13.73±2.76^{a}	16.34±3.70^{b}	2.33	0.053

***Means that do not share a letter (superscript) are significantly different, Tukey posthoc tests**

p-values marked with asterisks are significantly different among site categories at *$p<0.05$

Table 11: Means (±SD) of concentrations of dissolved organic carbon (DOC) and nutrients across different stream orders (1 and 2 - 7) in Mara River during the study period.

Variables	**2**	**3**	**4**	**5**	**6**	**7**	**F - value**	***p*-value**
DOC (mg/L)	4.43±2.48^a	5.29±3.77^a	4.42±3.30^a	2.71±1.58^a	3.54±1.57^a	5.24±1.77^a	1.67	0.156
NO_3^- (mg/L)	0.85±0.43^a	0.74±0.40^a	0.83±0.59^a	0.48±0.20^a	0.67±0.31^a	0.64±0.47^a	1.06	0.394
NO_2^- (μg/L)	42.30±152.23^a	96.86±260.09^a	375.35±706.49^a	218.74±288.35^a	190.64±332.12^a	2.08±0.40^a	1.92	0.102
NH_4^+ (μg/L)	128.01±113.24^a	287.36±514.19^a	154.47±387.06^a	30.57±51.34^a	59.45±81.25^a	173.69±221.35^a	1.37	0.245
TDN (mg/L)	1.02±0.44^a	1.17±0.61^a	1.36±1.17^a	0.73±0.37^a	0.92±0.48^a	0.82±0.55^a	1.49	0.207

***Means that do not share a letter (superscript) are significantly different, Tukey posthoc tests**

p-values marked with asterisks are significantly different among site categories at *$p<0.05$

4.4.4 Influence of stream size on DOM quality and quantity of Mara River

There was no significant difference in intensities of the 6-PARAFAC components (C1-C6) and optical properties for dissolved organic matter (DOM) among the stream order ($p>0.05$). See appendix I. However, based on size-exclusion chromatography, LC-OCD-OND humic-like-C AND SUVA (ges) differed significantly among the stream orders ($p<0.05$, table 12). Humic-like-C was high in lower stream order 1 to 3, 3.16±2.03, 2.29±1.94, and 2.80±2.62 respectively, and at its lowest values in higher stream order 7 (0.54±0.90) although high values of humic-like-C substances were also observed in larger stream order 6 (2.21±1.30). SUVA (ges) ranged from 2.97±0.95 (stream order 5) to 4.10±0.52 (stream order 7), an indication of no longitudinal trends (upstream to downstream effect). Low-stream and high-stream orders had high concentrations of SUVA (ges) except for some mid-stream orders (Table 12).

4.4.5 Influence of stream size on DOM

Table 12: Means (±SD) for DOM indices of DOM based on size-exclusion chromatography LC-OCD-OND across different site categories in the Mara River, Kenya

DOM characteristics	2	3	4	5	6	7	F - value	p-value
HMWS_C	0.51±0.33^a	0.76±0.81^a	0.71±0.82^a	0.41±0.45^a	0.39±0.30^a	0.97±0.50^a	2.14	0.07
HMWS_N	0.17±0.41a	0.05±0.04a	0.06±0.05a	0.04±0.02a	0.05±0.01a	0.03±0.01a	1.20	0.32
Humic-like_C	3.16±2.03^a	2.29±1.94^b	2.80±2.62^b	1.18±0.66^c	2.21±1.30^b	0.54±0.90^d	4.03	0.00*
Humic-like_N	0.18±0.11^a	0.18±0.13^a	0.15±0.14^a	0.09±0.06^a	0.13±0.08^a	0.18±0.06^a	1.49	0.20
LMWS_C	0.77±0.26^a	0.81±0.42^a	0.77±0.68^a	0.89±0.78^a	0.60±0.35a	0.69±0.21^a	0.70	0.62
SUVA (humics)	4.51±0.36^a	4.38±0.32^a	4.42±0.33^a	4.38±0.32^a	4.37±0.39^a	4.59±0.54^a	0.76	0.58
SUVA (ges)	3.32±0.60^a	3.45±0.55^a	3.46±0.65^a	2.97±0.95^b	3.49±0.57^a	4.10±0.52^c	3.81	0.00*
BDOC	5.00±2.24a	4.99±2.91a	5.16±4.23a	3.07±1.52a	3.59±1.75a	4.35±1.33a	1.38	0.24
CDOC	4.59±2.19a	4.64±2.70a	4.72±3.80a	2.84±1.32a	3.37±1.56a	4.02±1.23a	1.31	0.27
DOC	4.43±2.48^a	5.29±3.77^a	4.42±3.30^a	2.71±1.58^a	3.54±1.57^a	5.24±1.77^a	1.67	0.15

***Means that do not share a letter (superscript a-d) are significantly different, Tukey posthoc tests**

***p-values marked with asterisks significantly differ among site categories at $p<0$.**

4.4.6 Influence of stream order on whole stream ecosystem metabolism

Cyanobacteria, total algae, GPP_{24}, and GPP: ER differed among the stream orders, although the trends were not clear longitudinal (table 13, figure 6). On the other hand, green algae, diatoms, ER24 and NEP did not differ significantly among stream orders ($p>0.05$, table 12, figure 6). Cyanobacteria showed increasing trends from lower stream order 1 and 2 and peaked at stream order 7, with the values ranging from 0.38±0.20 $\mu g/cm^2$ to 0.76±0.38$\mu g/cm^2$ (see table 12). First, cyanobacteria were more pronounced in stream order 6 (0.26±0.21 µg/cm2) than in stream order 7 (0.26±0.21 $\mu g/cm^2$). Then a drastic drop was observed from stream order 6 to stream order 7. Similar trends were also observed in total algae biomass.

Mean total-algae increased from stream order (1 and 2 to 6) with mean values of 0.59±0.38 $\mu g/cm^2$, 0.84±0.32 $\mu g/cm^2$, 0.95±0.38 $\mu g/cm^2$, 1.18±0.30 $\mu g/cm^2$, 1.17±0.53 $\mu g/cm^2$, 0.34±0.19 $\mu g/cm^2$ respectively and rapidly declined in stream order 7 (0.34±0.19 $\mu g/cm^2$). The highest value of GPP_{24} was 3.12±1.07 g O2 m^{-2} day^{-1} in stream order 7, while the lowest value was recorded in stream order 5 (0.67±0.42 O2 m^{-2} day^{-1}). GPP: ER ratio ranged from 0.45 O_2 m^{-2} day^{-1} (stream order 7) and 1.56±0.88 O_2 m^{-2} day^{-}1 (stream order 4). Most streams were autotrophic (GPP: ER>1), including stream orders 3, 4,6 and 7. Heterotrophic streams were low-order streams 1 and 2 and stream order 5.

Table 13: Means (±SD) of parameters of ecosystem metabolism and the algal biomass among stream orders in the Mara River basin during the study period.

Measures of metabolism	**2**	**3**	**4**	**5**	**6**	**7**	**F - value**	***p*-value**
Cyanobacteria biomass (µg/cm^2)	0.38±0.20^b	0.48±0.18^b	0.70±0.28^c	0.75±0.14^c	0.76±0.38^c	0.26±0.21^a	3.97	0.01*
Green-algae biomass (µg/cm^2)	0.02±0.04^a	0.04±0.04^a	0.07±0.10^a	0.11±0.15^a	0.07±0.07^a	0.00±0.01a	1.25	0.31
Diatoms biomass (µg/cm^2)	0.19±0.20^a	0.33±0.16^a	0.18±0.11^a	0.32±0.11^a	0.35±0.25^a	0.08±0.05^a	1.83	0.14
Total-algae biomass (µg/cm^2)	0.59±0.38^a	0.84±0.32^a	0.95±0.38^a	1.18±0.30^b	1.17±0.53^b	0.34±0.19^a	3.76	0.01*
GPP$_{24}$ (g O$_2$ m^{-2} day^{-1})	2.20±0.95^a	1.93±0.45^a	2.25±0.96^a	0.67±0.42^b	2.07±0.93^a	3.12±1.07^a	4.01	0.01*
ER$_{24}$ (g O$_2$ m^{-2} day^{-1})	2.67±0.83^a	1.85±0.78^a	1.52±0.55^a	1.82±0.84^a	1.79±1.51^a	3.17±2.50^a	1.56	0.20
GPP: ER	0.82±0.28^a	1.28±0.71^b	1.56±0.88^b	0.45±0.31^a	1.50±0.73^b	1.54±1.06^b	2.88	0.03*

***Means that do not share a letter (superscript a-d) are significantly different, Tukey posthoc tests**

***p-values marked with asterisks are significantly different among site categories at $p<0.05$**

4.5 Interaction between stream size and LMH on physico-chemical, nutrients, DOM and ecosystem metabolism Mara River

4.5.1 Interaction between land use and stream order on physico-chemical, major ion and nutrients

There were significant differences in water physico-chemical among regions (PERMANOVA F =5.8, df = 4, p = 010) and among different stream sizes (PERMANOVA F =3.1, df = 5, p = 0.010). Stream size interaction with the river's physical-chemical parameters showed no difference. The PCA summarized water physico-chemical and nutrient differences among regions and stream sizes (Figure 4). We used the first two PCA axes to explain the study area's variation in water quality physico-chemical. The first PCA Axis 1 (PC1) and second PCA Axis 2 (PC 2) explained >45% of the total variation in water physico-chemical variables and nutrients among the different regions defined by land use and livestock and wildlife (mainly hippos) densities.PC 1 explained 34.3% of the total variance in the water physico-chemical dataset, while PC 2 explained 11.2% (Figure 4).

The PC 1 separated sites largely according to regions or the density of LMH (both livestock and wildlife), with sites with livestock and hippos (LLIV, HLIV, and HIPP) associated with higher concentrations of major ions (Na^{+}, P^{3+}, S^{2+}, Ca^{2+} and Mg^{2+}) and DOC and higher values of electrical conductivity and water temperature (Figure 4). The PC 1 can therefore be defined as the water chemistry gradient.

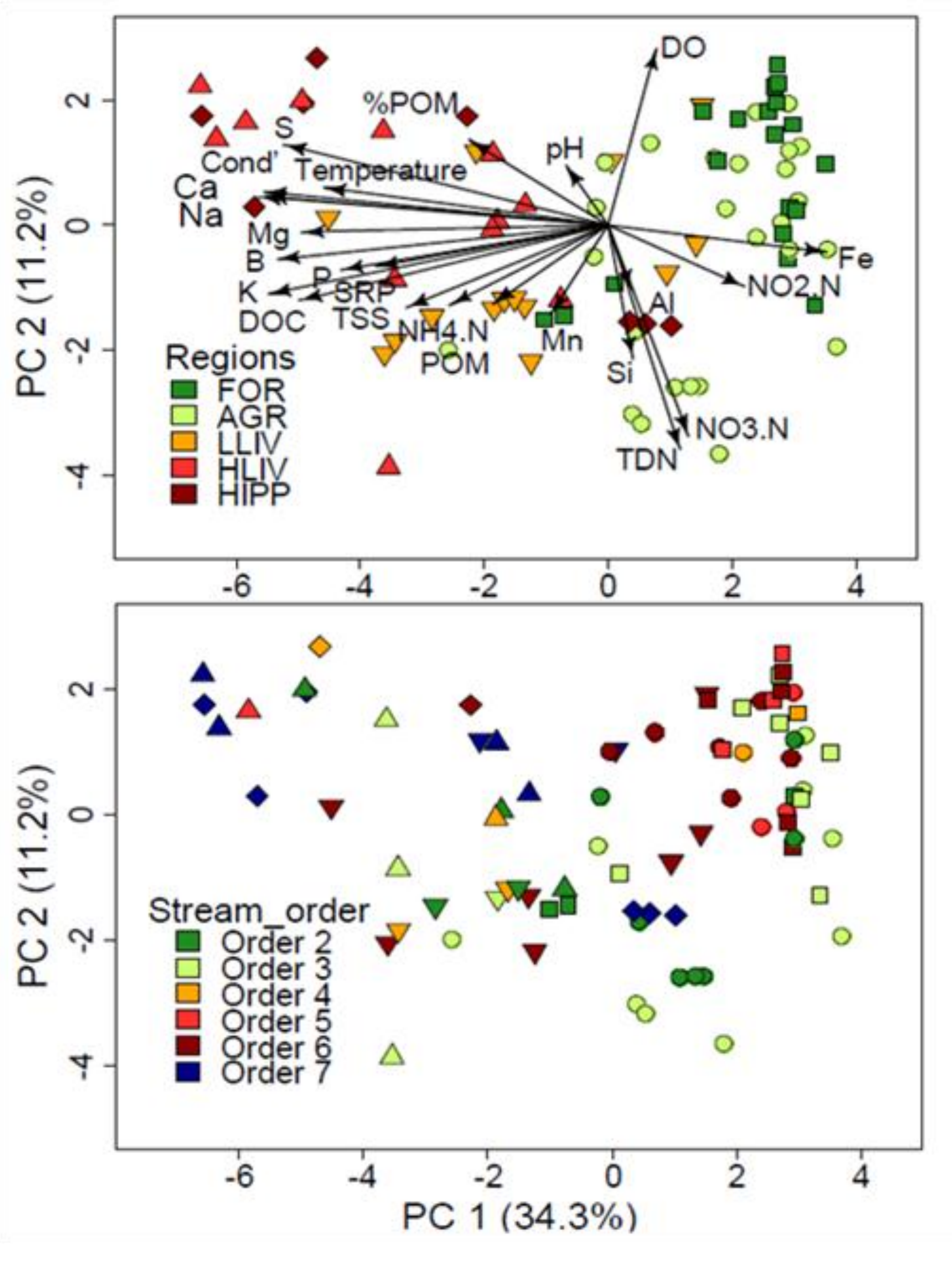


Figure 4: PCA biplot for water physico-chemical variables and nutrients across the Mara River's site categories (top panel) and stream size/order (bottom panel) during the study period.

The second PCA axis (PC 2) separated sites according to land use, with sites in agricultural areas (AGR) recording higher concentrations of dissolved nitrogen (nitrates and TDN) and DSi, as opposed to sites in forested areas (FOR). FOR streamrecorded high concentrations of DO and ferrous iron (Fe^{2+}) Figure 4). Surprisingly, sites with high densities of livestock and wildlife (hippo sites) recorded low amounts of dissolved nitrogen (except ammonium), although they recorded high DOC and SRP concentrations. Therefore, the second PCA Axis (PC 2) can be defined as the nutrient concentration gradient.

4.5.2 Interaction between land use and stream order on DOM composition based on fluorescence and absorbance indices

The PCA summarized relationships in DOM composition among the different regions or site categories (Figure 5). There were significant differences in absorbance and fluorescence indices of DOM composition among regions (PERMANOVA F = 7.9, df = 3, p = 010) but not among different stream sizes (PERMANOVA F =1.5, df = 5, p = 0.110), and there were no significant regions X stream size interactions (PERMANOVA F =1.3, df = 9, p = 0.180) (Figure 5).

The first and second PC components explained nearly 60% of the total variation in DOM composition, as explained by the absorbance and fluorescence indices (Figure 5). The PCA (PC 1) axis explained 41.6% of the total variance in dataset e, while the second PCA axis (PC 2) explained 18.3%. The PC 1 separated sites depending on land use or regions with livestock-influenced sites (LLIV and HLIV) associated with DOC with the highest amount of high molecular weight substances and rich in aromatic structures and humic substances indicative of leaching from plant material in cattle dung. Similarly, DOC from cattle dung at the livestock-influenced sites was more fluorescent and humic than DOC in FOR and AGR sites, which, by contrast, had seemingly fresher and autochthonously produced DOC with relatively low amounts of humic substances (Figure 5).

The second PCA axis (PC 2) defined the autochthony/ autochthony gradient with agricultural and low-density livestock sites recording high concentrations of freshly produced autochthonously DOM (autochthony). In contrast, high-density livestock (HLIV) sites and some forested (FOR) and low-density livestock sites (LLIV) recorded microbially produced and allochthonous DOM (Figure 4). Stream order had no clear effect on DOM composition (Figure 5).

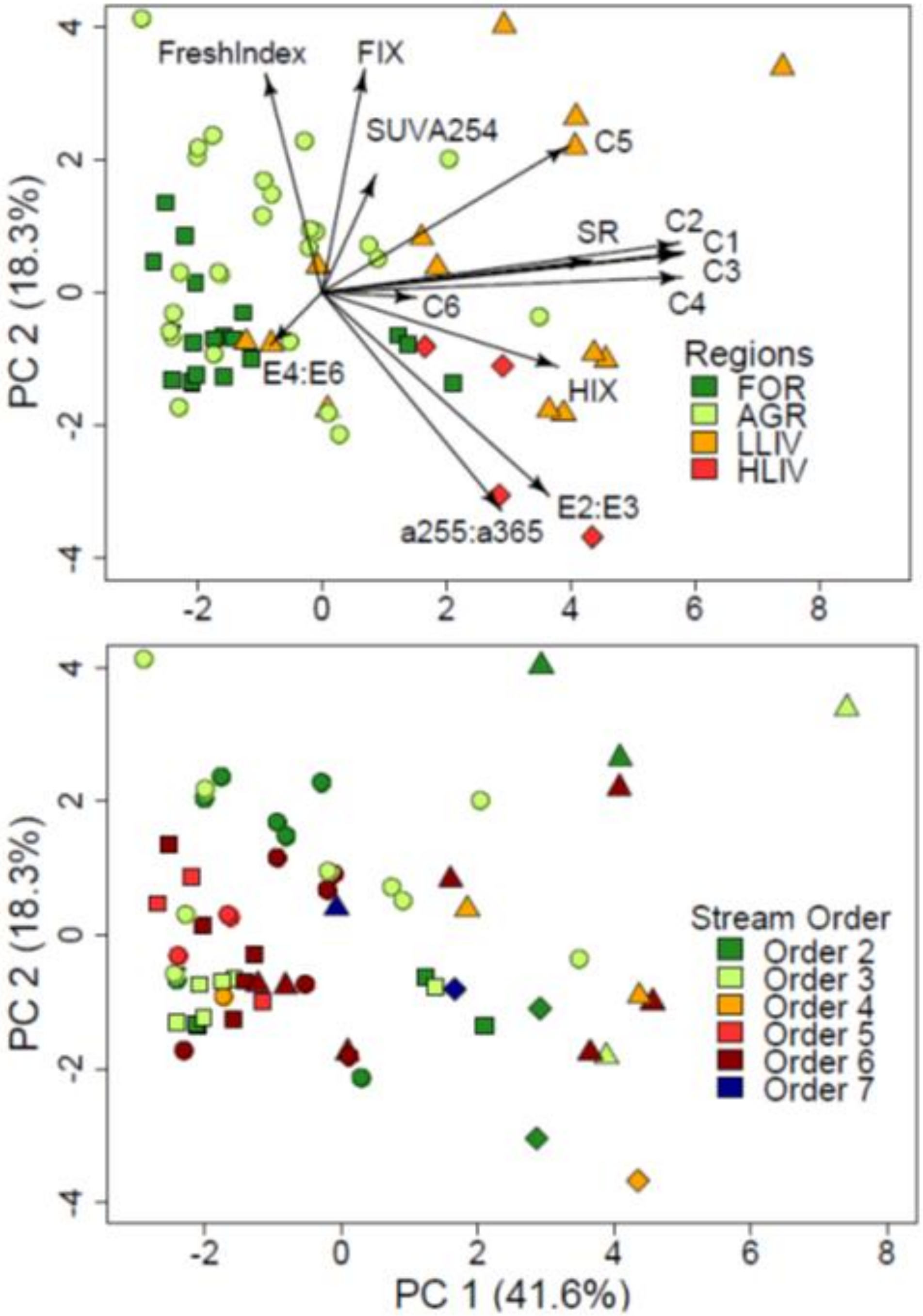


Figure 5: PCA biplot for DOM composition based on fluorescence and absorbance indices for 63 site categories and stream width in the Mara River, Kenya.

NB; The top panel displays loadings for regions, and the bottom panel shows loadings for stream size (stream orders)

4.5.3 Interaction between land use and stream order on DOM composition based on LC-OCD-OND

There were significant differences in DOM composition defined by size-exclusion chromatography (SEC) among regions (PERMANOVA *F* =8.3, *df* = 3, *p* < 001) and among different stream sizes (PERMANOVA *F* =4.3, *df* = 5, *p* = 0.010) (Figure 6). However, there were no significant regions X stream size interactions (PERMANOVA *F* =1.5, *df* = 9, *p* = 0.070). The PCA summarized relationships among LC-OCD-OND indices of DOM composition among the different regions and stream sizes (Figure 6). The first and second PCA components explained nearly more than 73% of the total variation in DOM composition as defined by LC-OCD-OND properties.

PCA (PC 1) axis explained 44.7% of the total dataset variance, while the second PCA axis (PC 2) explained 28.4%. The PC 1 separated sites largely according to regions, and sites with high livestock density (HLIV) and inhabited by hippos (HIPP) recorded DOM with high molecular weight substances (HMWS) and aromaticity (SUVA) as opposed to sites in forested and agricultural areas (FOR and AGR). The second PCA axis (PC 2) separated AGR and LLIV sites from the rest of the LMH high-density HLIV and HIPP sites, suggesting these two groups of sites had different DOM compositions. The HLIV and HIPP sites were associated with high molecular weight substances with high C: N. In contrast, AGR and LLIV sites were associated with low molecular weight DOM possibly of autochthonous origin. The Second PCA (figure 6) can therefore be defined as the autochthony/ autochthony gradient with some forested and low-density livestock sites recording high concentrations of humic substances (HS) and low molecular weight substances (LMWS), respectively

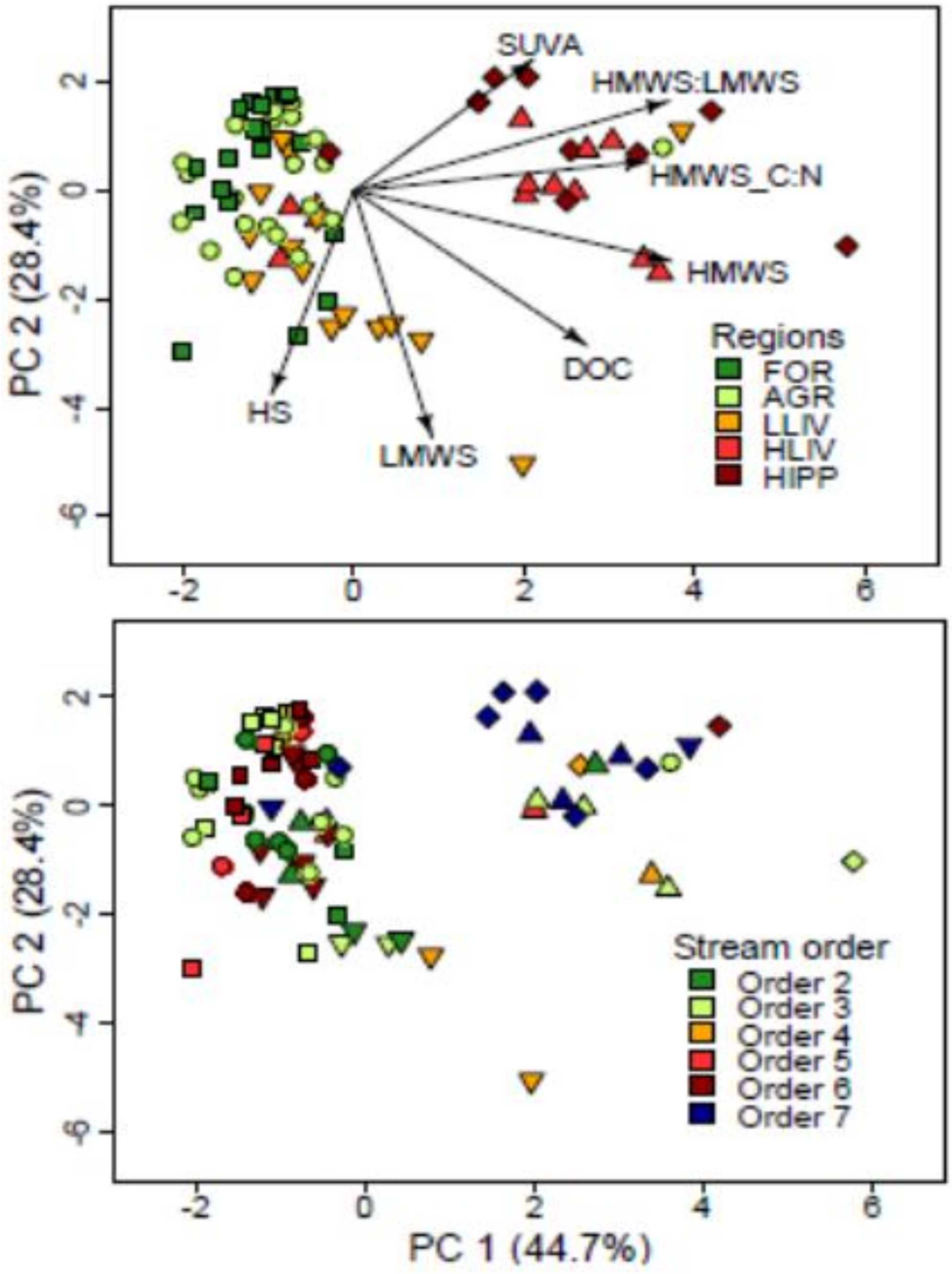


Figure 6: PCA biplot for DOM composition based on LC-OCD-OND in the Mara River basin. **The top panel displays loadings for regions, and the bottom panel shows loadings for stream width (stream orders).**

4.5.4 Interaction between land use and stream order on DOM in Mara River

Cyanobacteria, total algae, GPP_{24}, and GPP: ER differed among the stream orders, although the trends were not clear longitudinal (table 13, figure 7). There were significant differences in algal biomass and ecosystem metabolism (GPP, ER and NEP) among regions in the study area (PERMANOVA F =1.9, df = 3, p = 0.05) and among different stream sizes (PERMANOVA F =2.7, df = 5, p = 0.02) (Figure 7). However, there were no significant region X stream size interactions in algal biomass and ecosystem metabolism (PERMANOVA F=1.3, df = 4, p = 0.260).

The PCA summarized measures of ecosystem metabolism, algal composition, and biomass among the different regions and stream sizes (Figure 7). The first and second PC components explained nearly 70% of the total variation in ecosystem metabolism, algal composition, and biomass. PCA (PC 1) axis explained the most significant variation (39.0%) of the total variance in the dataset, while the second PCA axis (PC 2) explained 31.6%.

The PC 1 separated sites largely according to regions, and forested and agricultural sites (FOR and AGR) recorded high algal biomass. In contrast, livestock and hippo sites recorded high GPP and ER rates. The second PCA axis (PC 2) also separated sites according to the regions with high livestock density and FOR, recording higher ER rates. Streams with low livestock density weres= associated with GPP: ER and GPP. Some agricultural sites also recorded high rates of GPP and NEP (Figure 6).

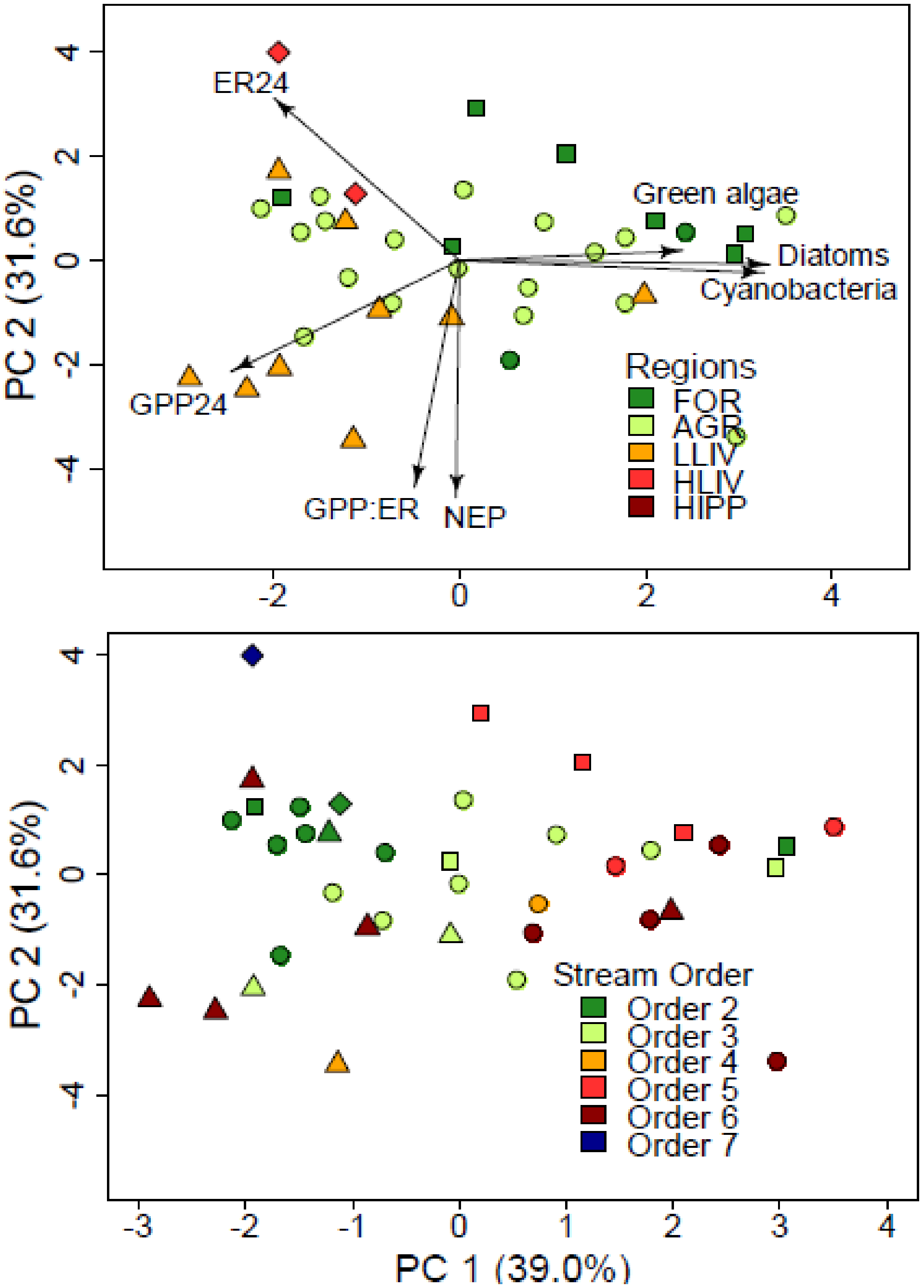


Figure 7 PCA biplot for measuring ecosystem metabolism (GPP: ER: NEP, and algae composition, across FOR, AGRI, LLIV AND HLIV regions and interaction between regions and stream order in the Mara River basin during the study period.

4.6 Interaction between stream size, land use and LMH on physico-chemical and ecosystem metabolism in Mara River

The PCA on physico-chemical variables yielded three PCs that explained > 73% of the variance in the dataset (Table 14). The loadings of the variables on each of the different axes showed that PC1 was represented by stream order, light intensity (PAR) and stream width, which is also a measure of stream size. The PC2 was represented by nutrients SRP and TSS, while PC3 was represented by TDN (Table 14). The results of generalized linear mixed models for measures of ecosystem metabolism (GPP, ER and NEP) are presented in Table 15.

Region or site categories, which by extension represent the influence of LMH density and land use, strongly influenced GPP, NEP and algal biomass. In contrast, %AGR strongly influenced ER and algal biomass (Table 15). In addition, the two nutrient PCs (PC2 and PC3) significantly influenced GPP, NEP and algal biomass. There were significant relationships between the PC scores from the PCA on physico-chemical variables (PC1, PC2 and PC3) and measures of ecosystem metabolism and algal biomass (Figure 8). PC1 was positively associated with algal biomass (Figure 8d), while PC2 was negatively associated with ER (Figure 8a). PC3 was positively correlated with GPP (Figure 8b) and NEP (Figure 7c).

Table 14. Loading on variables in different PCs in the PCA of the physico-chemical data.

	PC1	PC2	PC3
Variance explained (%)	32.7	26.1	14.7
Stream order	**0.59**	-0.07	0.18
TDN	-0.15	0.21	**0.86**
SRP	-0.05	**0.66**	0.04
TSS	0.04	**0.63**	-0.34
PAR	**0.39**	0.04	-0.25
Stream width	**0.56**	-0.12	0.13
Temperature	**0.40**	0.32	0.15

Table 15: The study period results of generalized linear mixed-effects models (GLMM) for ecosystem metabolism and total chlorophyll-a/ algal biomass/concentration (µg cm^2) in Mara River.

	GPP$_{24}$	**ER$_{24}$**	**NEP**	**Total Chl-a**
Fixed effects	β **(SE)**t-value	β **(SE)**t-value	β **(SE)**t-value	β **(SE)**t-value
Intercept	-0.19(0.94)-0.20	0.06(0.17)0.33	1.55(1.12)1.38	2.00(0.39)5.09***
Region	0.68(0.29)2.38*	-0.01(0.07)-0.17	-0.73(0.34)-2.13*	-0.25(0.12)-2.07*
Percent AGR	0.04(0.02)1.02	-0.001(0.003)-2.39*	-0.04(0.02)-1.74	-0.02(0.01)-2.21*
PC2/ PC3	-0.99(0.57)-2.2*	0.17(0.20)2.56*	1.27(0.67)1.98*	0.56(0.24)2.37*
Region × Percent AGR	-0.01(0.01)-2.01*	0.002(0.001)1.31	0.02(0.01)2.47*	0.004(0.003)1.30
Region × PC2/PC3	0.30(0.19)1.59	-0.02(0.05)-0.45	-0.49(0.23)-2.19*	-0.09(0.08)-1.17
Percent AGR × PC2/PC3	-0.003(0.01)-0.19	0.007(0.0041.81	-0.01(0.02)-0.79	-0.01(0.01)-0.98
Region × Percent AGR × PC2/PC3	0.001(0.005)0.27	-0.003(0.001)-2.63*	0.01(0.01)0.96	0.001(0.02)0.06
Random effects	**SD**	**SD**	**SD**	**SD**
Stream (intercept)	0.88	0.18	1.05	0.18
Residuals	0.33	0.07	0.39	0.07
$R^2_{\text{GLMM(m)}}$	0.42	0.54	0.31	0.54
$R^2_{\text{GLMM(c)}}$	0.93	0.94	0.91	0.94

The marginal R^2 (GLMM[m]; fixed effects only) and the conditional R^2 (GLMM[c]; fixed and random effects) represent the proportion variance explained by each model. SE = standard error; SD = standard deviation; Significance of t-values:
*P < 0.05, **P < 0.01, ***P < 0.001

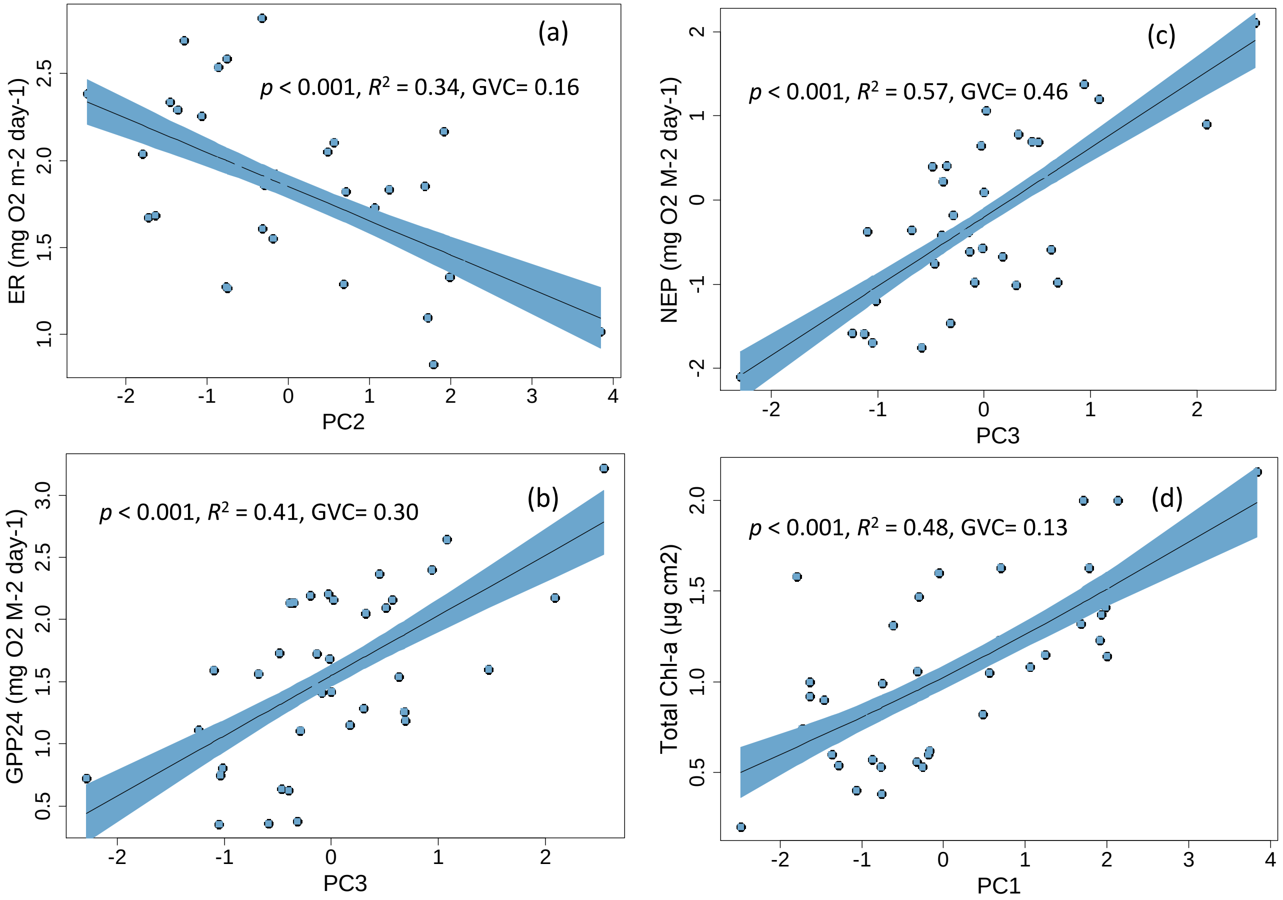


Figure 8: Relationships between PCA scores of physico-chemical variables (P1, PC2 and PC3) and measures of ecosystem metabolism (ER, GPP and NEP) and algal biomass in the Mara River during the study period.

4.6.1 Large mammalian herbivores and not stream size affect ecosystem metabolism in the Mara River

LMH density significantly influenced the measures of ecosystem metabolism (GPP, ER and GPP: ER) more than stream size. GPP (Figure 9a) and ER (Figure 9b) responded to an increase in LMH density, although at high densities, GPP was negatively influenced by LMH. Longitudinal trends in measures of metabolism showed that only ER significantly responded to changes in stream size measured by RDS (Figure 9e). The rest of the measures (GPP and GPP: ER) did not respond to changes in stream size. Similarly, algal biomass positively responded to an increase in stream density, but in large rivers, algal production was reduced (Figure 10b, table 12). Although not significant, algal biomass was negatively influenced by LMH density (Figure 10a). NEP did not respond to either stream size or LMH densities.

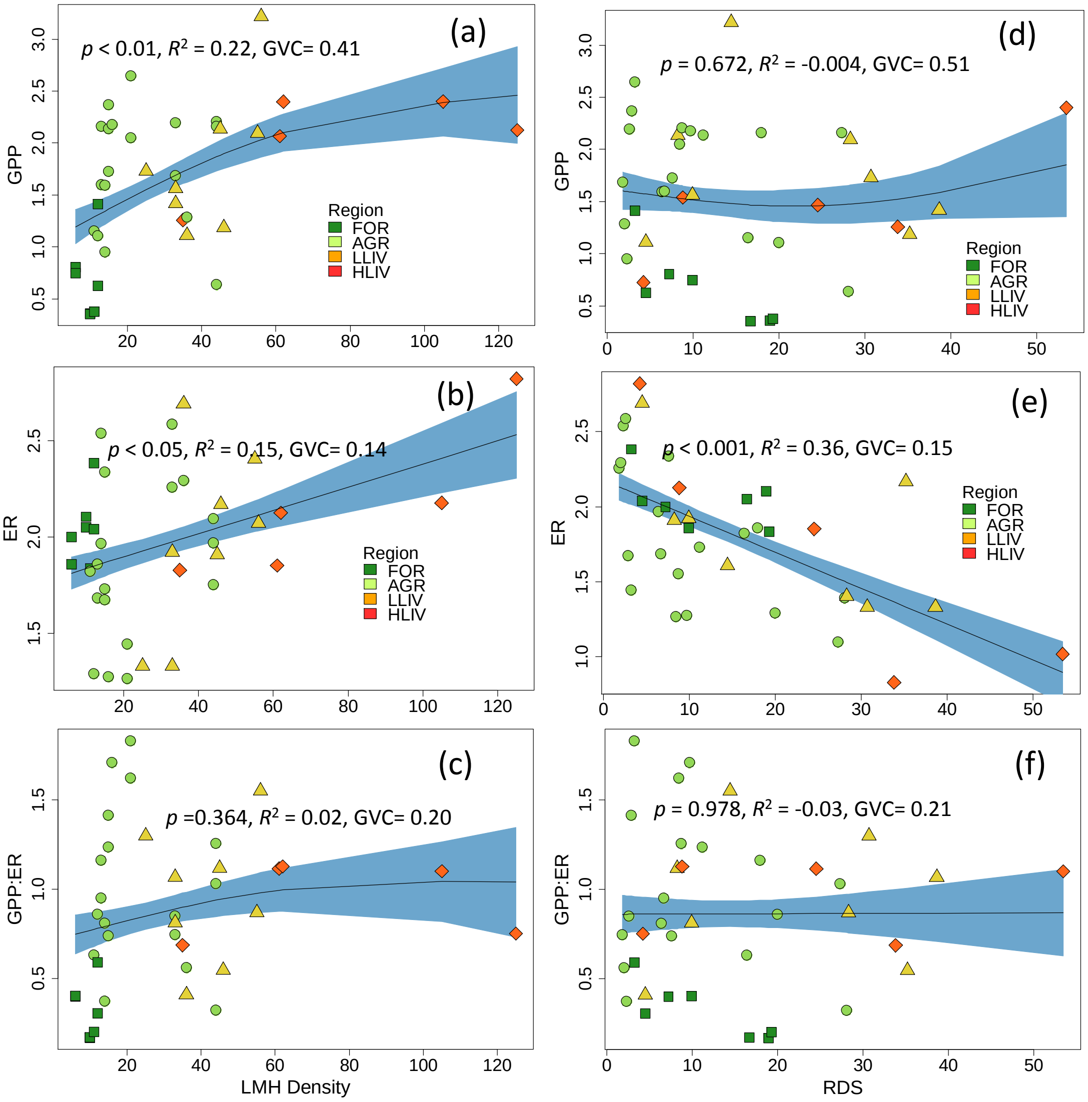


Figure 9. Relationships between measures of ecosystem metabolism (GPP, ER and GPP: ER) and LMH density and stream size (RDS) in Mara River during the sampling period.

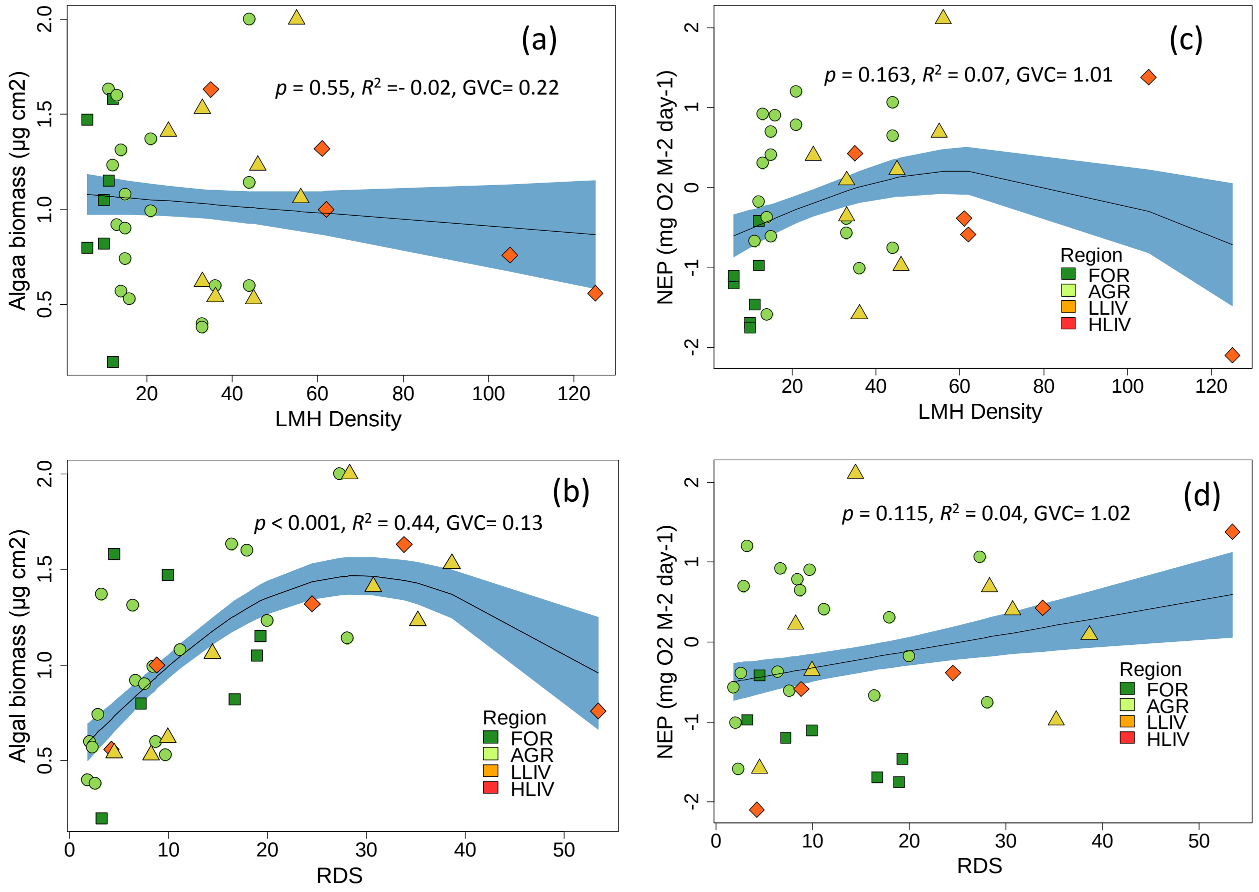


Figure 10. Relationships between algal biomass and net ecosystem production (NEP) and LMH density and stream size (RDS) in Mara River during the study period.

CHAPTER FIVE

DISCUSSION

5.1 The influence of land use and LMH inputs on the physico-chemical of the Mara River

The Mara River is an Afrotropical savanna river characterized by different land use and land cover types, including natural forests in the headwaters, mixed farmlands and livestock grazing in the mid-reaches and savanna grasslands and shrublands in the lower reaches. This land use gradient and land cover are also mirrored by large mammalian herbivores (LMH), whose density increases from the uplands to the lowlands (forested to grassland areas). This study sought to determine the interaction between land use change, stream size and LMH density on water physico-chemical, DOM composition and ecosystem metabolism in the Mara River. The findings show that LMH density diminishes stream size's role in influencing the Mara River's biogeochemistry compared to land use change (forest, agriculture, livestock and large wildlife).

Hippos and HLV were found in sites with deeper depth, broader width and high discharge, a characteristic of larger rivers. Therefore, River Mara is an essential habitat for wildlife, especially semi-aquatic wildlife such as hippos. Hippos spend most of their day wallowing and excreting their input during the day in the river. In addition, hippos depend on savanna grasslands as their source of food, and they spend a lot of time feeding on savanna grasslands at night. Hence hippos play an essential role in transferring organic matter inputs from the terrestrial ecosystem to aquatic ecosystems (Subalusky *et al*., 2015; Dutton *et al*., 2018; Subalusky and Post, 2019). This observation agrees with the study done by Clarke (1953) and Field (1970), who reported that hippos prefer sites where they can lie half-immersed in the water and where it is comfortable for their young ones to breastfeed. Also, Olivier and Laurie (1974) reported that hippos prefer sites with a considerable amount of water levels, which agrees with our studies. In addition, livestock depends on the Mara River for water and food. They also spent significant time drinking water from the river while feeding and defecting into it (Iteba *et al.,* 2021). Hence livestock plays a vital role in Mara River's biogeochemistry and functioning.

LMH population density increased with the percentage of grasslands in the catchments of the sampling sites. Forest and grassland cover across catchment areas has decreased due to the increasing human activities, especially agriculture, human settlements and livestock grazing, to meet the growing human demands for food and shelter (GoK, 2009; Mati *et al*., 2008; NEMA, 2013). Replacement of forest cover and grasslands with other land uses (e.g., agriculture and settlements) leads to displacement and reduction of native LMH numbers (Doughty *et al*., 2013; Ogutu *et al*., 2016; Veldhuis *et al*., 2019). This scenario concurs with this study, where agriculture and livestock sites have less forest cover and reduced hippo populations.

An increase in LMH densities is associated with an increase in temperature, electrical conductivity, and salinity and a decrease in oxygen level. The LMH sites were located in streams with less forest cover (refer to table 1). Reduced forest cover led to the increased surface area for temperature absorptions, hence high temperature. Decreased oxygen level is related to increased oxygen level, which explains the low oxygen levels in LMH sites. Also, the low oxygen concentration is due to increased organic matter decomposition rates and leaching, which utilizes a lot of oxygen (Masese *et al*., 2020). The FOR sites were expected to have high DO concentrations because FOR land use has fewer human stressors and LMH densities. Agriculture land use during our studies was related to high dissolved oxygen, contrary to most studies where agriculture has been reported as the primary contributor to water pollution (Woodward *et al.,* 2012; Leip *et al.,* 2015).

Both increased temperature and reduced canopy cover in agricultural land use accelerate the primary production rate, thus increasing oxygen production (Dawson *et al*., 2016; Masese *et al*., 2017). Although this interaction seems straightforward, other water quality parameters, such as increased turbidity and stream hydrology, may affect primary productivity, lowering oxygen levels; for example, this was observed in high livestock sites (low dissolved oxygen) compared to low-livestock sites (high dissolved oxygen)

High mineralization in the Mara River has been associated with some streams, positively increasing the electrical conductivity and salinity (Kilonzo *et al.,* 2014). The electrical conductivity during the study was above 70 µS/cm for undisturbed sites (Lubanga *et al.,* 2021), indicating that change from forested to agriculture and LMH significantly compromises the water quality. Although, an increase in electrical conductivity and salinity could also be associated with the increase in major ions from LMH inputs. Conductivity and salinity varied greatly among study sites, and these results concur with Pond *et al*. (2008). Conductivity and salinity are often used as a surrogate for low water quality and are correlated with urban and agricultural development (Dow and Zampella, 2000). Significantly elevated electrical conductivity can also indicate an alteration in the concentration of solutes, especially major ions, and an increase in water temperature. Changes in electrical conductivity and salinity can also be linked to geology and hydrology as streams and rivers draining semi-arid lands record high levels of solutes due to evaporation and leaching of erodible soils common in semi-arid landscapes (McLennan, 1993). These processes are exacerbated by livestock activity in semi-arid lands, as high densities can cause overgrazing and soil erosion during storm events hence degradation of solutes.

Land use change leads to increased runoff, which can cause flash flooding, sedimentation of streams and rivers, and supra-reduced baseflows during droughts (Bruijnzeel, 2004). For example, an increase in the density of LMH, especially livestock and hippos, is bound to increase TSS and % POM in TSS because LMH transfers large amounts of organic matter into the river in the form of dung during egestion in water (Subalusky *et al.*, 2015; Iteba *et al.*, 2021). Hippos and livestock are also linked to increased input of sediments in rivers because of their trampling activity and bioturbation when watering in and/or crossing rivers (livestock) or resting in water (hippos) (Bond *et al*., 2014; Dutton *et al*., 2018). In the Mara River basin, cattle footpaths in the upper reaches and hippo trails in the savanna grasslands are visible features along the fluvial network. These paths leading to the river (e.g., Jacobs *et al*., 2017; Kroese *et al*., 2018) direct run-off, often laden with sediments and organic matter, from grazing areas into the river. The role of livestock in driving physical parameters is even more pronounced during dry seasons when the numbers visiting watering points can be high due to increased metabolic requirements for water during dry weather conditions (Iteba *et al*., 2021).

Livestock is also a vector of nutrients (carbon, nitrogen, phosphorous and potassium) and organic matter in streams and rivers (DOC and DOM) (Subalusky *et al*., 2015; Subalusky and Post, 2019; Masese *et al*., 2020; Iteba *et al*., 2021) and this was evident in this study where nutrient and organic matter concentration increased with an increase in LMH density. Land-use change influenced major ions except for aluminium (Al^{+}) and manganese (Mn^{2+}). Hippos-influenced sites (HIPP) and HLIV sites where high concentrations of major ions such as Ca^{2+}, K^{+}, P^{3-} and Na^{+} were recorded, possibly from the dung rich in these nutrients (Bond *et al.,* 2014; Masese *et al*., 2020). HLIV had the most significant influence on the major ions (B^{3+}, Ca^{2+}, Na^{+}, K^{3+} and Mg^{2+}) in the river compared to LLIV and HIPP sites. This implies that although LMH plays a significant role as a vector for both nutrients and organic matter (Subalusky *et al.,* 2015; Subalusky and Post, 2019; Masese *et al.,* 2020; Iteba *et al.,* 2021), its impact on ionic chemistry of the river varied with LMH species and population density. Therefore, replacing hippos with livestock may shift the dynamics of nutrients and major ions in streams and rivers.

Forested land use had a higher concentration of ferrous iron than the other land-use types, which could be mainly associated with the high concentration of humic substances (HS) in forested sites. Iron is bound primarily to humic substances and dissolves easily in oxygen-rich water (Shapiro, 1964). Therefore, in LMH, low iron concentration was due to an increase in oxygen concentration, which increased iron uptake. Silica is the most abundant element in the lithosphere, and its primary source is mainly chemical weathering (Exley, 1998). Silica is an essential element for diatom growth, and changes in silica dynamics may promote the formation of toxic cyanobacteria in freshwater ecosystems (Bootsma *et al.,* 2003). In Lake Victoria, for instance, an increase in toxic bacteria has been highly associated with anthropogenic impacts on silica balance (Cockerton *et al.,* 2015). In the Mara River, hippos transport savanna silica-rich grasses from the terrestrial to the water through excretion (Schoelynck *et al.,* 2020). Contrary to previous findings (Schoelynck *et al.,* 2020), dissolved silica did not differ significantly among land uses, mainly hippo verse other land uses sites.

High nutrient concentrations in LMH sites may be due to an increase in the ungulate population along the rivers as they seek water and food. Furthermore, LMH migrates to rivers during dry seasons (Valeix *et al*., 2007, Bond *et al*., 2012), and as a result, high-density HLIV sites had high concentrations of DOC and SRP as compared to other sites. The high ammonia concentrations in these sites are related to hippo and livestock excretion (Iteba *et al.*, 2021), which accumulates in the river because of prevailing anoxic or hypoxic conditions that do not favour nitrification (Dutton *et al*., 2020). Indeed, nitrate concentration was very low in the high-density LMH sites, especially in the pools receiving high inputs of dung from both hippo and livestock defecation. On the other hand, in these pools, ammonium concentrations were always high.

Cattle dung supplies nutrients that are more easily mineralized and leached in the water than hippo dung, whose larger particles sizes are heavier and it tend to settle faster at the bottom of the river than livestock dung (Dawson *et al*., 2016; Dutton *et al*., 2020; Masese *et al*., 2020). Hippo dung also decomposes slowly, which may cause nutrient limitation as opposed to livestock dung which is mineralized and leached faster in the water, thus elevating the concentration of DOC and limiting nutrients (N and P) for primary production. This result agrees with other studies in Mara River, where a high concentration of DOC and nutrients was recorded in high-density livestock sites or treatments compared to other sites or treatments (Masese *et al.*, 2020; Wanderi *et al.*, 2022).

5.2 Influence of land use and LMH on DOM concentration and composition

Variations in DOM composition can be used to establish the water quality status and the type of land use surrounding the river (Ferreira *et al.*, 2020). In most studies, DOM characterization has been used to classify the DOM sources as either autochthonous or allochthonous and their bioavailability for biogeochemical processes (Jaffe *et al.*, 2008; Rhymes *et al.*, 2015). Changes in land use from forestry to cropland and livestock grazing significantly influenced DOM concentration and quality, and this finding concurs with studies done by Masese *et al.* (2017) and Shang *et al*. (2018). Forests and wetlands are rich in high aromatic, high molecular weight (HMW) DOM, which is rich in humic substances (Lutz *et al.*, 2012), concurred with this study's results. According to Parr *et al*. (2015), agricultural land use is associated with highly photodegradable protein-like components, which agrees with this study's findings. Agricultural land use was also associated with protein and tryptophan-like components, indicating microbially driven DOM (Wilson and Xenopoulos, 2009; Williams *et al*., 2010; Graeber *et al*., 2015).

While much has been done on the impact of AGRI land use on DOM quality and quantity (Ferreira *et al*., 2020), fewer studies have examined the effects of LMH (Masese *et al.*, 2020). Because of the transfer of large amounts of plant material from terrestrial to aquatic ecosystems in the form of dung, LMH is more likely to increase HMWS, BDOC, DOC, and CDOC in aquatic ecosystems as opposed to agricultural activities. Both low-livestock and high-livestock density sites had a DOM rich in hydroquinone-like components associated with reduced humic-like molecules potentially of terrigenous plant material.

A total of six PARAFAC components (C1 – C6) were identified in my study (Table 7). All PARAFAC components identified in my dataset have previously been found in water in the Mara River basin (Masese *et al*., 2017; 2020), and the most widespread among them were C5 and C6 (Table 5). Out of these, C1, C3, C5, and C6 are among the most commonly observed components in DOM in surface waters (Murphy *et al*., 2013). The components were used to distinguish the sources of DOM in the Mara River, distinguishing between the dominance of terrestrial verse microbial DOM and the presence or predominance of humic-like, reduced humic, and protein-like molecules in DOM. Components C1 and C2 were characteristic of humic-like substances, while less humified DOM substances were described by C4 and C6. Similarly, C5 and C6 components were associated with protein-like and tyrosine-dominated DOM (Dawson *et al*., 2008; Jaffé *et al*., 2008, and Kothawala *et al*., 2014).

The C1 and C4 components were more prominent in livestock sites. Components C1 and C4 were located in the fluorescence region that usually defines the ubiquitous humic-like Peaks C and A, respectively, in surface waters (Coble, 1996) and are related to high molecular weight humic substances of terrestrial origin (Fellman *et al*., 2010). On the other hand, low livestock density sites had a higher concentration of C4 resistant to photodegradation (Stedmon & Markager, 2003). Also, protein-like C5 and C6 spectra were characteristics of low livestock density sites and agricultural land use sites which also resembled the DOM of tryptophan and tyrosine-free amino acids originating from autochthonous products and microbial processes, and this concurs with Cory &

McKnight, (2005) and Fellman *et al*., (2010). Low livestock density drove autochthony gradient, while high livestock sites promote heterotrophy by providing input rich in high molecular dissolved organic matter.

C6 had both a primary excitation peak (ca 250−270 nm) and a secondary excitation peak (340−420 nm), which according to Wu et al. (2003), are associated with a large molecular size and hydrophobic compounds. C6 is also rich in protein-like components (Cory & McKnight, 2005; Fellman *et al*., 2010), and in this study, they were mainly associated with livestock sites compared to forest and agricultural areas, and its concentration is likely to increase with the increase in livestock density (table 10). Increased livestock density could also promote elevated C1 and C2, indicators of reduced humified DOM, which again could be attributed to an increase in soil disturbances during trampling

Livestock and hippo use of riparian areas is often detrimental to riparian vegetation (Kanga *et al.*, 2013), which opens streams and rivers to increased sunlight insolation and photodegradation of DOM. Photodegradation affects the reactivity and bioavailability of DOM to microbial organisms and ecosystem processes (Mopper and Schultz 1993; Moran and Zepp 1997). For instance, photodegradation can alter DOM from a larger molecular size into a smaller labile DOM efficiently utilized by microbiota (Helms *et al*., 2008; Mccallister & Paul, 2012, Masese *et al*., 2017). Similarly, photodegradation can promote the provenance of refractory HMW DOM, making it more available for ecosystem processes (Obernosterer *et al*. 1999). In the high livestock density and hippo sites, an increase in photodegradable low molecular weight (LMW) DOM was likely formed through the microbial loop enhanced by elevated temperature and sunlight due to reducing canopy cover (Helms *et al*., 2008; Jaffé *et al*., 2014).

The freshness index was used as an indicator of the autochthonous production of DOM (Wilson and Xenopoulos, 2009). In this study, the freshness index ranged from 0.59 to 0.61, and agriculture and low livestock density sites had the highest values, suggesting that they were the most metabolically active and productive in producing fresh autochthonous DOM. This concentration is more associated with freshly produced allochthonous sources than autochthonous sources, and it contradicts the previous study in the Mara River, where in AGR streams freshness index was greater than one (Masese *et al*., 2017). E_4:E_6 ratio is used to infer differences in the proportion of humic and fulvic acids (Spencer *et al.*, 2007; Moody *et al.*, 2013), $SUVA_{254}$, a strong indicator for aromaticity and fluorescence index (FIX), an index of DOM sources (Weishaar *et al.*, 2003), were not shifted by land use changes. The humification index (HIX) was used as a proxy for humic substances and is directly correlated to DOM dominated by high molecular (HMW) substances (Ohno, 2002). In this study, high livestock density (HLIV) sites recorded higher levels of HIX than other sites, indicating that livestock is associated with increases in high molecular weight DOM in surface waters.

Size-exclusion chromatography (SEC) was also used to characterize DOM into different molecular sizes and /or weight fractions and bioavailability (Huber *et al*., 2011). There were significant differences in DOM composition defined by SEC among regions. The results show that hippos contribute to DOM dominated by HMW substances rich in carbon, while livestock DOM is richer in nitrogen. Inputs from hippos are mainly made of C4 grasses made of undigested materials because of their long digestive systems that are efficient in extracting nutrients from ingesta, leading to high ratios of carbon relative to nutrients N and P (Iteba *et al*., 2021; Masese *et al*., 2020). On the other hand, as ruminants, cattle have efficient digestive systems that produce dung with smaller particle sizes, enhancing leaching and remineralising nutrients, leading to high inputs of N and P relative to C. As a result of these differences, livestock sites (mainly HLIV) and hippo sites (HIPP) had notable differences in the composition of their DOM (Masese *et al.*, 2015).

5.3 Influence of land use and LMH on ecosystem metabolism

The sum of gross primary production (GPP) and ecosystem respiration (ER) is known as ecosystem metabolism (Williamson *et al*., 2008). In rivers, ecosystem metabolism is defined by GPP and ER ratio (P: R). The values of GPP among the different land uses were within the mean range values 0.10–4.6 g O_2/m^2 /day found in other tropical studies (Mulholland *et al.,* 2001; Ortiz-Zayas *et al.,* 2005; Gücker *et al.,* 2009; Hunt *et al.,* 2012). However, the measure of ecosystem metabolism and algal biomass differed among land uses. For example, forested streams were characterized by higher diatom biomass than high livestock-density streams, and this could be due to increased ammonium concentration in livestock sites that hindered primary production. On the other hand, high diatom biomass in agricultural streams could be associated with increased dissolved silica, TDN and nitrates from fertilisers used during farming. Furthermore, this study was done during the dry season, so high diatoms biomass was a substitute for low terrestrial inputs from the surrounding, which are mainly baseflow dependent.

In agricultural (AGR) and low livestock density (LLIV) streams, GPP was greater than one, indicating that a change in land use from forestry to other services (agriculture and grazing) in the riparian promoted autotrophy more than heterotrophy (Vannote *et al*., 1980; Marcarelli *et al*. 2011). Moreover, increased GPP rates in agricultural and livestock streams were facilitated by a reduced canopy and increased light availability, which can be a limiting factor for primary production. These results agree with Vannote *et al*. (1980), Masese *et al.* (2017), Fuß *et al.* (2017), and Masese *et al*. (2020), who stated that GPP is influenced by land use change which modifies light intensity. Land use change and human activities, especially livestock grazing, can alter biogeochemical and ecological processes in low and high-order streams (Minaya *et al*., 2013; Mwanake *et al*., 2019; Masese *et al*., 2022). Similarly, reach-scale influences, such as watering of livestock, laundry washing and water abstractions by people and related disturbances abound along many rivers in the region, leading to localized effects that can have a strong influence on ecosystem processes (Mathooko, 2001; Yillia *et al*., 2008; Masese *et al*., 2009; Kroese *et al*., 2020).

ER was high in both HLIV and FOR sites, resulting from increased input of organic matter by livestock defecation. In freshwaters, heterotrophic respiration is highly subsidized by terrestrial organic matter, so ecosystem respiration can significantly exceed gross GPP (Cole *et al*. 1994; Battin *et al*. 2008). In addition, livestock density may increase suspended solids and organic matter, increasing turbidity. Increased turbidity reduces the surface area for light absorption hence promoting high ER. Also, increased organic matter from LMH excretion and egestion may promote microbial decompositions, further elevating ecosystem respiration (Masese *et al*., 2020). In FOR, it was expected that the ER would be higher due to the large canopy cover and increase in allochthonous input from the riparian streams.

In this study, FOR sites and HLV were heterotrophic with NEP values less than zero (NEP < 0), which is a common characteristic of most forested streams (Vannote *et al*., 1980). Forested streams also rely on riparian areas for their energy sources (table 7 and table 6). However, in some cases, especially during the dry season, reduced litters lead to increased insolation of water and the benthos and, hence, elevated primary production and algal biomass (Spencer *et al*., 2010; Masese *et al*., 2017). An increase in livestock density leads to overgrazing, soil degradation, and the mobilization of nutrients from the riparian regions to rivers and streams. Livestock inputs to the recipient streams could have increased in the decomposition process hence an increase in ecosystem respiration and reduced NEP<0. Therefore, during the dry seasons, FOR and HLV in Mara River were carbon sinks, while AGRI and LLIV streams were carbon sinks. Hence LMH affects carbon emissions from streams and rivers.

5.4 Influence of stream size on the physiochemistry, nutrients DOM composition, and ecosystem metabolism in the Mara River.

5.4.1 Influence of stream size on physiochemistry and nutrients

As Mara River flow from the upstream to downstream, water depth, breadth and discharge also increase. This is representative of most global rivers in more pristine rivers (Vannote *et l.*, 1980). There was a significant change in stream depth, width, velocity, and discharge longitudinally from stream order one to seven, which concurs with (Mwanake et al., 2019). According to *Mwanake et al.* (2019), the mean values of depth ranged from 0.01 to 0.49 m, which were close to this study result (Table 9). The average discharge of Mara River has been reported to be close to 0.77 m^3/s, which peaks at 16.28 m^3/s in Nyangores river (Mwanake *et al*., 2019). Relatively similar results were obtained in this study, where the mean discharge values ranged from 0.02±0.02 to 13.4±24.5 (Table 9).

Mara River is also characterized by grasslands and forest cover (Ayuyo, 2021) and their distribution from upstream to downstream is not dependent on the stream size/stream order. For example, Midstream (stream 6) had reduced savanna grassland and forest coverage, with high agriculture percentage coverage indicating land use changes. In the Mara Basin, grassland has been modified and covered with other lands due to the increasing human population and human-related activities (Mango *et al.*, 2011).

Change in the stream along the gradient didn't affect the dissolved oxygen level, which concurs with Mwanake *et al.* (2019). However, stream size affected stream pH, temperature, electrical conductivity, salinity and total suspended solids, although the differences among the stream order were not straightforward as postulated by the river continuum concept (Vannote *et al.* 1980). Although some of our results on electrical conductivity and temperature disagree with Mwanake *et al.* (2019), who reported that stream order had no influence on these two variables. The higher streams in Mara River are mainly LMH influenced hence the increase in their organic matter inputs rich in a high concentration of pH, temperature, electrical conductivity, total suspended solids, and total suspended solids as aforementioned.

High levels of Na^+ and S^{2+} in high-stream order were reported, which could also be linked to high LMH density. LMH density increased with the increase in stream order (Table 9).

Furthermore, increased major ions have increased human activity (Kaushal *et al.,* 2017). In this study, besides the stream size effect, an increase in livestock and hippos could have accelerated weathering and anthropogenic salts used in livestock farming, hence high levels of Na^+ and S^{2+}.

Stream size had no effect on the nutrient dynamic of River Mara, and this concurs with Wanderi *et al.* (2022) and Mwanake *et al*. (2019). Although some findings on nutrients such as dissolved organic carbon disagree with Mwanake *et al.* (2019), who reported significant changes in dissolved organic carbon with mean values ranging from 2.67±0.21((stream order 1) to 4.43±0.37 (stream order 3). However, despite the disparity between the finding of this study's results and that of Mwanake *et al*. (2019), DOC concentration was at its highest at stream order 3, and the change from upstream to downstream was not clear in both studies. Therefore, these results could indicate that rather than stream size, other factors, such as land use, affects the nutrient of the Mara River.

5.4.2 Influence of stream size on DOM concentration and composition

The RCC predicts that the diversity of DOM peaks in 1st-order streams as ground waters with low DOM molecular diversity surface and extract organic molecules from detritus. Still, diversity diminishes approximately 2-fold in 2nd-order streams and 3-fold in 5th-order streams, with little change through 11th-order streams as heterotrophic microbial activity removes labile compounds from downstream transport (Vannote *et al*. 1980). However, in this study, DOM quality and quantity did not vary among stream orders, and there were no clear trends, indicating that other factors, such as land use had more influence. This was in contrast to findings of longitudinal increases in intensities of DOM quality factors such as FI and BIX in other rivers (Begum *et al*., 2017; Begum *et al.*, 2019). Although, humic-carbon substances reduced with an increase in stream size.

5.4.3 Influence of stream size on ecosystem metabolism

Many attributes, such as GPP and NEP, are postulated to have a linear or nonlinear response from low-order to high-order streams (Vannote *et al.,* 1980). However, several measures of ecosystem metabolism that did not respond to changes in stream size agreed with the diminished role of stream size. (Figure 9). This result contradicts a study by Naiman and Sedell (1980), who reported that ecosystem metabolism did not change with stream order. Small and large streams had low concentrations of cyanobacteria and total algae biomass, which could be attributed to increased canopy in the headwaters. In the large streams increase in LMH inputs could have resulted in increased turbidity, limiting algae and cyanobacteria growth. In small streams, lower nutrients could have resulted in a decrease in cyanobacteria and total algae biomass compared to mid-stream, which could be on receiving end of nutrients from either agriculture or large mammalian herbivores (livestock). High nutrient concentrations correlate with increased algal and cyanobacteria (Lohman *et al*. 1991). Furthermore, algae biomass is associated with ample light availability, stable hydraulic conditions, and high nutrient levels in freshwater aquatic ecosystems (Dodds and Gudder 1992).

5.5 The interaction between land use, LMH and stream order on the physiochemistry, nutrients, major ions, DOM composition, and ecosystem metabolism in Mara River

The influence of land use change on river functionality depends on interactions among physical, chemical, and biological conditions on spatial and temporal scales (Ponette-González *et al.,* 2010a, 2010b; Uriarte *et al*., 2011). However, the interaction of seasonality and land use change effects on the measure of ecosystem metabolism is poorly understood (Masese *et al.*, 2017). Notwithstanding, the interaction between LMH and stream order effects on physiochemistry, DOM composition, and ecosystem metabolism of the Afromontane savanna river has not been done. This study reports an interaction between land use, LMH, and stream size on physiochemistry and ecosystem metabolism ($p>0.05$). Land use and LMH influenced TSS, SRP, and TDN, while stream order controlled light intensity and stream width, and their interaction influenced ecosystem metabolism.

5.5.1 Drivers of ecosystem metabolism

Algae biomass, GPP and NEP were strongly influenced by land use and LMH in the Mara River. Drivers of ecosystem metabolism and algal biomass were found to be stream order, width, TSS, light intensity, and nutrients (TDN and SRP). This result concurs with Masese *et al.* (2017) and Fuss *et al.* (2017). In addition, studies in Queensland and Puerto Rico reported that GPP was influenced by the availability of nutrients (Mosisch *et al.*, 2001; Mulholland *et al.*, 2001). SRP and TDN had high levels in both AGRI and LMH sites, promoting ER, NEP and ER. However, the percentage of agriculture strongly influenced ecosystem respiration and algal biomass production. Increased algal biomass due to the increased percentage of agriculture could be attributed to elevated levels of TDN from using nitrogenous fertilisers on the farm.

Although stream order affected algal biomass and ecosystem metabolism, LMH density had more influence on the measure of stream metabolism. An increase in LMH density increased ER and GPP, although, at higher densities, GPP was reduced. Increased ER could be attributed to increasing organic matter input by LMH, which increased ammonium, turbidity and decomposition. In addition, increased GPP results from the mediation of LMH input rich in SRP boosted primary production. Compared to GPP: ER, and GPP, ER responded to changes in stream order. Hence only ER as a measure of ecosystem metabolism agrees with the riverine continuum concept, RCC (Vannote *et al.*, 1980)

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Like any other system, the functioning of riverine ecosystems is driven by energy, hydrology, and geology, which have been captured in early ecosystem structure and functioning models. These models include the riverine continuum concept (RCC) and river productivity model (RPM), among others (Vannote *et al*., 1990; Thorp and Delong, 1994, 2002). While these models have been widely applied in most rivers and streams worldwide, their applicability in the Afrotropical-savanna rivers is still questionable. Furthermore, Afrotropical-savanna rivers are characterized by the presence of large numbers of LMH, and their role in driving river ecosystem functioning is not well represented in the existing models. Therefore, this study sought to understand the role of LMH as a vector of nutrients and organic matter that drive the biogeochemistry of these rivers.

This study shows that high LMH density increased Ca^{2+}, P^{3-}, Na^{+}, Mg^{2+}, temperature, conductivity, DOC, SRP, and NH_4^+ in streams and rivers. These parameters were more elevated in hippo sites than in livestock sites. Also, LMH influenced the concentrations of nutrients in the Mara River, where hippos increased ammonium levels, while high livestock density increased dissolved organic carbon, total dissolved nitrogen and nitrates. A previous study in the Mara associated hippos as a source of biogenic silica in the river (Schoelynck *et al.*, 2019). However, this was not the case in this study, as high silica levels were more associated with agricultural sites. LMH-influenced sites had a high concentration of soluble reactive phosphorous and dissolved organic carbon, while agriculture sites were mainly associated with a high concentration of nitrates and total dissolved nitrogen. High livestock sites and hippos had increased ammonium concentration, indicating anoxic and hypoxic conditions with low oxygen concentrations. In addition, livestock and hippos were essential sources of coarse particulate matter in the form of dung, increasing the total suspended solids. Increased turbidity and increased nutrients and organic matter levels reduce water quality and lead to forming anoxic and hypoxic zones that are reservoirs for ammonia. Forest sites had a high DO and Fe^{2+} than all the other sites. Stream size or order had little to no effect on the physical, chemical, and biogeochemical parameters.

LMH is a vector of organic matter in the Mara River, affecting the quantity and quality of dissolved organic matter (DOM). LMH are sources of high molecular weight substances of terrestrial origin. An increase in livestock density further promoted the formation of high molecular substances that are less biodegradable and photodegradable. Low livestock density and agricultural streams were also important sources of autochthonous DOM, which were more labile and thus an important source of energy for microbiota and other consumers. In addition, both HLV and HIPP sites were rich in aromatic DOM substances, but the concentration of nitrogen to carbon differed. Hippos-mediated aromatic DOM is rich in carbon, while livestock-mediated DOM is rich in nitrogen.

LMH were critical drivers of ecosystem metabolism in the river. Agriculture and low livestock density were carbon sinks (NEP>0), while forested and high livestock sites were carbon sources (NEP<0). Therefore, livestock density increases ecosystem respiration, which is linked to increased organic matter inputs and negatively influences GPP.

In summary, LMH and land use strongly influenced physico-chemical, ecosystem metabolism, DOM composition, and concentration of major solutes (ions) in the Mara River. Thus, LMH density and land use, and not stream order, had more influence on the physico-chemical, DOM composition, and ecosystem metabolism of Afromontane-savanna rivers, which has not been captured in existing models of river ecosystem functioning. TSS, TDN, SRP, stream size, stream order, LMH density, and agriculture percentage interactions were vital drivers of ecosystem metabolism in the Mara River. Although LMH density had more influence than stream order on ecosystem metabolism.

6.2 Recommendations

A change in land use from forest to agriculture or an increase in livestock and hippo density can be detrimental to water quality. Therefore, the LMH population should be monitored and managed to prevent future water quality degradation of the Mara River, primarily streams with high livestock and hippo populations. Also, the government should put in place policies which prevent encroachment of the riparian areas by human activities. Land use changes to agriculture activities are likely to introduce nutrients rich in silica, nitrates and total dissolved nitrogen, which may accelerate the growth of algae and other aquatic plants. In addition, agriculture activities may also introduce bioavailable nutrients that promote autotrophy in streams and rivers. Therefore, a lack of proper agriculture management may be detrimental to streams and rivers as these nutrients may promote eutrophication. Hence, agricultural activities along the riparian areas of rivers should be done sustainably.

This study shows that LMH influences Mara River ecosystem functions, including nutrient cycling, DOM dynamics, and ecosystem metabolism. These ecosystem functions are critical drivers of riverine food webs, global biogeochemical cycles, water quality for humans and animals, and the general ecosystem integrity of streams and rivers. Therefore, this study recommends the development of riverine models that incorporate the influence of LMH and agricultural land uses in Afrotropical savanna rivers. Notwithstanding, the presence of LMH and semi-arid savanna grasslands strongly influences the biogeochemistry of the Afrotropical savanna rivers. Development of Afrotropical savanna rivers can be achieved through long-term studies on DOM quality, quantity, and ecosystem metabolism.

REFERENCES

Abrantes, K. G., Barnett, A., Marwick, T. R., & Bouillon, S. (2013). Importance of terrestrial subsidies for estuarine food webs in contrasting East African catchments. *Ecosphere, 4*(1), 1-33.

Accoe, F., Boeckx, P., Cleemput, O. V., Hofman, G., Zhang, Y., Li, R. H., & Guanxiong, C. (2002). Evolution of the δ13C signature related to total carbon contents and carbon decomposition rate constants in a soil profile under grassland. *Rapid Communications in Mass Spectrometry, 16*(23), 2184-2189.

Achieng, A. O., Masese, F. O., Coffey, T. J., Raburu, P. O., Agembe, S. W., Febria, C. M., & Kaunda-Arara, B. (2021). Assessment of the ecological health of Afrotropical rivers using fish assemblages: A case study of selected rivers in the Lake Victoria Basin, Kenya. *Frontiers in Water, 2*, 620704.

Acuña, V., Giorgi, A., Muñoz, I., Uehlinger, U. R. S., & Sabater, S. (2004). Flow extremes and benthic organic matter shape the metabolism of a headwater Mediterranean stream. *Freshwater Biology*, *49*(7), 960-971.

Ahmed, I. U., Assefa, D., & Godbold, D. L. (2022). Land-Use Change Depletes Quantity and Quality of Soil Organic Matter Fractions in Ethiopian Highlands. *Forests, 13*(1), 69.

Aich, V., Liersch, S., Vetter, T., Huang, S., Tecklenburg, J., Hoffmann, P., ... & Hattermann, F. F. (2014). Comparing impacts of climate change on streamflow in four large African river basins. Hydrology and *Earth System Sciences, 18*(4), 1305-1321.E

Aiken, G. R. (1985). Humic Substances in Soil, Sediment, and Water. Wiley, New York.

Aiken, G. R., Spencer, R. G., Striegl, R. G., Schuster, P. F., & Raymond, P. A. (2014). Influences of glacier melt and permafrost thaw on the age of dissolved organic carbon in the Yukon River basin. lobal *Biogeochemical Cycles, 28,* 525–537.

Aitkenhead-Peterson, J. A., McDowell, W. H., & Neff, J. C. (2003). Sources, production, and regulation of allochthonous dissolved organic matter inputs to surface waters. In *Aquatic ecosystems* (pp. 25-70). Academic Press.

Alexander, R. B., Elliott, A. H., Shankar, U., & McBride, G. B. (2002). Estimating the sources and transport of nutrients in the Waikato River Basin, New Zealand. *Water resources research, 38*(12), 4-1.

Alexander, R. B., Smith, R. A., & Schwarz, G. E. (2000). Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. *Nature*, *403*(6771), 758-761.

Allan, J. D. (2004). Influence of land use and landscape setting on the ecological status of rivers. *Limnetica*, *23*(3-4), 187-197.

American Public Health Association. (1998). *APHA Advocates' Handbook: A Guide for Effective Public Health Advocacy*. The Association.

Anderson, M. J., & Walsh, D. C. (2013). PERMANOVA, ANOSIM, and the Mantel test in the face of heterogeneous dispersions: what null hypothesis are you testing? *Ecological monographs*, *83*(4), 557-574.

APHA (American Public Health Association). (1998). Standard Methods for the Examination of Water and Wastewater (20th edit). Washing-ton, DC. American Public Health Association, *American Water Works Association*, Water Environment Federation.

Arman, N. Z., Salmiati, S., Said, M. I. M., and Aris, A. (2019). Development of macroinvertebrate-based multimetric index and establishment of biocriteria for river health assessment in Malaysia. *Ecological Indicators*, 104, 449–458. doi: 10.1016/j.ecolind.2019.04.060

Aufdenkampe, A. K., Mayorga, E., Raymond, P. A., Melack, J. M., Doney, S. C., Alin, S. R., ... & Yoo, K. (2011). Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. *Frontiers in Ecology and the Environment*, *9*(1), 53-60.

Ayuyo, I. O. (2021). *Impact of Land Cover, Land Use and Climate Change on the Hydrological Regimes of the Mara River Basin* (Doctoral dissertation, University of Nairobi).

Azam, F., & Cho, B. C. (1987). Bacterial utilization of organic matter in the sea. In M. Fletcher, T. Gray, & J. Jones (Eds.), *Ecology of Microbial Communities* (pp. 261–281). Cambridge: Cambridge University Press.

Baker, A., Bolton, L., Newson, M., & Spencer, R. (2008). Spectrophotometric properties of surface water dissolved organic matter in an afforested upland peat catchment. *Hydrological Processes, 22*, 2325–2336.

Barber, A., Sirois, M., Chaillou, G., & Gélinas, Y. (2017). Stable isotope analysis of dissolved organic carbon in Canada's eastern coastal waters. *Limnology and Oceanography, 62*(S1), S71-S84.

Battin, T. J., Kaplan, L. A., Findlay, S., Hopkinson, C. S., Marti, E., Packman, A. I., … Sabater, F. (2008). Biophysical controls on organic carbon fluxes in fluvial networks. *Nature Geoscience, 1*, 95–100.

Begum, M. S., Jin, H., Jang, I., Lee, J. M., Oh, H. B., & Park, J. H. (2017). Optical and molecular-level characterization of fluvial organic matter biodegradation in a highly urbanized river system. *Biogeosciences Discussions*, 1-37.

Begum, M. S., Jang, I., Lee, J. M., Oh, H. B., Jin, H., & Park, J. H. (2019). Synergistic effects of urban tributary mixing on dissolved organic matter biodegradation in an impounded river system. *Science of the total environment, 676*, 105-119.

Benner, R. (2003). Molecular indicators of the bioavailability of dissolved organic matter. In *Aquatic ecosystems* (pp. 121-137). Academic Press.

Bernot, M. J., Sobota, D. J., Hall Jr, R. O., Mulholland, P. J., Dodds, W. K., Webster, J. R., ... & Wilson, K. Y. M. (2010). Inter‐ regional comparison of land‐ use effects on stream metabolism. *Freshwater Biology, 55*(9), 1874-1890.

Bertilsson, S., & Jones Jr, J. B. (2003). Supply of dissolved organic matter to aquatic ecosystems: autochthonous sources. In *Aquatic ecosystems* (pp. 3-24). Academic Press.

Biers, E. J., Zepp, R. G., & Moran, M. A. (2007). The role of nitrogen in chromophoric and fluorescent dissolved organic matter formation. *Marine Chemistry, 103*(1-2), 46-60.

Blough, N. V., & Del Vecchio, R. (2002). Chromophoric DOM in the coastal environment. In D. A. Hansell & C. A. Carlson (Eds.), *Biogeochemistry of marine dissolved organic matter*. Academic (pp. 509–546).

Blough, N. V., Zafiriou, O. C., & Bonilla, J. (1993). Optical absorption spectra of waters from the Orinoco River outflow: Terrestrial input of colored organic matter to the Caribbean*. Journal of Geophysical Research Oceans, 98,* 2271 – 2278.

Bond, T. A., Sear, D., & Edwards, M. (2012). Temperature-driven River utilisation and preferential defecation by cattle in an English chalk stream. *Livestock Science*, *146*(1), 59-66.

Bond, T., Sear, D., & Sykes, T. (2014). Estimating the contribution of in-stream cattle faeces deposits to nutrient loading in an English Chalk stream. *Agricultural water management, 131*, 156-162.

Bootsma, H. A., Hecky, R. E., Johnson, T. C., Kling, H. J., & Mwita, J. (2003). Inputs, outputs, and internal cycling of silica in a large, tropical lake. *Journal of Great Lakes Research, 29*, 121-138.

Bott, T. L. (1996). Primary productivity and community respiration. *Methods in Stream Ecology*, 533-556.

Bott, T. L., & Newbold, J. D. (2013). Ecosystem metabolism and nutrient uptake in Peruvian headwater streams. *International Review of Hydrobiology*, *98*(3), 117-131.

Bourlière, F. (1975). Mammals, small and large: the ecological implications of size. *Small mammals: their productivity and population dynamics. Cambridge University Press, Cambridge*, 1-8.

Brauns, M., Allen, D. C., Boëchat, I. G., Cross, W. F., Ferreira, V., Graeber, D., Patrick, C. J., Peipoch, M., von Schiller, D., & Gücker, B. (2022). A global synthesis of human impacts on the multifunctionality of streams and rivers. *Global Change Biology*, *28*(16), 4783–4793. https://doi.org/10.1111/gcb.16210

Bruijnzeel LA. (2004). Hydrological functions of tropical forests: not seeing the soil for the trees? *Agriculture, Ecosystems and Environment 104*: 185–228

Cairns, J.Jr. (2003). Biotic Community Response to Stress. In Biological Response Signatures: *Indicator Patterns Using Aquatic Communities* (Simon, T.P., ed.): pp. 13-20. Boca Raton, CRC Press.

Carlson, K. M., Curran, L. M., Ponette- González, A. G., Ratnasari, D., Lisnawati, N., Purwanto, Y., ... & Raymond, P. A. (2014). Influence of watershed- climate interactions on stream temperature, sediment yield, and metabolism along a land use intensity gradient in Indonesian Borneo. *Journal of Geophysical Research: Biogeosciences*, *119*(6), 1110-1128.

Carpenter, S., Stanley, E. H., & Vander, Z. M. (2011). State of the world’s freshwater ecosystems: physical, chemical, and biological changes. *Annual Review Environmental Resource, 36*, 75–99. https://doi.org/10.1146/annurev-environ-021810-094524

Carpentier, C., Dahlhaus, A., van de Giesen, N., & Maršálek, B. (2013). The influence of hard substratum reflection and calibration profiles on in situ fluorescence measurements of benthic microalgal biomass. *Environmental Science: Processes & Impacts*, *15*(4), 783-793.

Casas- Ruiz, J. P., Catalán, N., Gómez- Gener, L., von Schiller, D., Obrador, B., Kothawala, D. N., ... & Marcé, R. (2017). A tale of pipes and reactors: Controls on the in- stream dynamics of dissolved organic matter in rivers. *Limnology and Oceanography*, *62*(S1), S85-S94.

Catherine, A., Escoffier, N., Belhocine, A., Nasri, A. B., Hamlaoui, S., Yéprémian, C., ... & Troussellier, M. (2012). On the use of the FluoroProbe®, a phytoplankton quantification method based on fluorescence excitation spectra for large-scale surveys of lakes and reservoirs. *Water Research*, *46*(6), 1771-1784.

Cawley, K. M., Wolski, P., Mladenov, N., & Jaffé, R. (2012). Dissolved organic matter biogeochemistry along a transect of the Okavango Delta, Botswana. *Wetlands*, *32*(3), 475-486.

Chen, W., Zheng, X., Chen, Q., Wolf, B., Butterbach-Bahl, K., Brüggemann, N., & Lin, S. (2013). Effects of increasing precipitation and nitrogen deposition on CH4 and N2O fluxes and ecosystem respiration in a degraded steppe in Inner Mongolia, China. *Geoderma*, *192*, 335-340.

Clarke, J. R. (1953). The Hippopotamus in Gambia, West Africa. *Journal of Mammalogy*, *34*(3), 299-315.

Coble, P. G. (1996). Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. *Marine chemistry*, *51*(4), 325-346.

Coble, P. G. (2007). Marine optical biogeochemistry: the chemistry of ocean color. *Chemical reviews*, *107*(2), 402-418.

Cockerton, H. E., Street-Perrott, F. A., Barker, P. A., Leng, M. J., Sloane, H. J., & Ficken, K. J. (2015). Orbital forcing of glacial/interglacial variations in chemical weathering and silicon cycling within the upper White Nile basin, East Africa: stable-isotope and biomarker evidence from Lakes Victoria and Edward. *Quaternary science reviews*, *130*, 57-71.

Cole, J. J., Caraco, N. F., Kling, G. W., & Kratz, T. K. (1994). Carbon dioxide supersaturation in the surface waters of lakes. *Science*, *265*(5178), 1568-1570.

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Melack, J. (2007). Plumbing the Global Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget. *Ecosystems, 10,* 172–185. https://doi.org/10.1007/s10021-006-9013-8

Conley, D. J., Paerl, H. W., Howarth, R. W., Boesch, D. F., Seitzinger, S. P., Havens, K. E., ... & Likens, G. E. (2009). Controlling eutrophication: nitrogen and phosphorus. *Science, 323*(5917), 1014-1015.

Cooper, S. D., Lake, P. S., Sabater, S., Melack, J. M., & Sabo, J. L. (2013). The effects of landuse changes on streams and rivers in mediterranean climates. *Hydrobiologia, 719*(1), 383425.

Cory, R. M., McNeill, K., Cotner, J. P., Amado, A., Percell, J. M., & Marchall, G. A. (2010). Singlet oxygen in the coupled photochemical and biochemical oxidation of dissolved organic matter. *Environment Science Technology, 44,* 3683–3689.

Cory, R., & McKnight, D. (2005). Fluorescence Spectroscopy Reveals Ubiquitous Presence of Oxidized and Reduced Quinones in Dissolved Organic Matter. *Environmental Science & Technology, 39*, 8142–8149.

Creed, I. F., McKnight, D. M., Pellerin, B. A., Green, M. B., Bergamaschi, B. A., Aiken, G. R., ... & Stackpoole, S. M. (2015). The river as a chemostat: fresh perspectives on dissolved organic matter flowing down the river continuum. *Canadian Journal of Fisheries and Aquatic Sciences, 72*(8), 1272-1285.

Cummins, K. W. (1975). *Ecology of running waters; theory and practice* (No. CONF-7505119-1). Michigan State Univ., Hickory Corners (USA). WK Kellogg Biological Station.

Cummins, K. W. (1977). From headwater streams to rivers. *American Biology Teacher;(United States), 39*.

Dalmagro, H. J., Lathuillière, M. J., Sallo, F. D. S., Guerreiro, M. F., Pinto Jr, O. B., de Arruda, P. H., ... & Johnson, M. S. (2019). Streams with Riparian Forest buffers versus impoundments differ in discharge and DOM characteristics for pasture catchments in Southern Amazonia. *Water, 11*(2), 390.

Dalu, T., Mwedzi, T., Wasserman, R. J., Madzivanzira, T. C., Nhiwatiwa, T., & Cuthbert, R. N. (2022). Land use effects on water quality, habitat, and macroinvertebrate and diatom communities in African highland streams. *Science of The Total Environment, 846*, 157346.

Dalzell, B. J., Filley, T. R., & Harbor, J. M. (2007). The role of hydrology in annual organic carbon loads and terrestrial organic matter export from a midwestern agricultural watershed. *Geochimica et cosmochimica acta, 71*(6), 1448-1462.

Dawson, J., Pillay, D., Roberts, P. J., & Perissinotto, R. (2016). Declines in benthic macroinvertebrate community metrics and microphytobenthic biomass in an estuarine lake following enrichment by hippo dung. *Scientific Reports*, *6*(1), 1-8.

Dawson, J., Soulsby, C., Tetzlaft, D., Hrachowitz, M., Dunn, S., & I., M. (2008). Influence of hydrology and seasonality on DOC exports from three contrasting upland catchments. *Biogeochemistry, 90*, 93–113.

del Giorgio, P. A., & Williams, P. L. B. (2005). The global significance of respiration in aquatic ecosystems: from single cells to the biosphere. *Respiration in aquatic ecosystems*, *1*.

Delong, M. D., & Thorp, J. H. (2006). Significance of instream autotrophs in trophic dynamics of the Upper Mississippi River. *Oecologia, 147*(1), 76-85.

Demars, B. O., Russell Manson, J., Olafsson, J. S., Gislason, G. M., Gudmundsdottir, R., Woodward, G. U. Y., ... & Friberg, N. (2011). Temperature and the metabolic balance of streams. *Freshwater Biology, 56*(6), 1106-1121.

Demars, B. O., Thompson, J., & Manson, J. R. (2015). Stream metabolism and the open diel oxygen method: Principles, practice, and perspectives. *Limnology and Oceanography: Methods, 13*(7), 356-374.

DÍaz, S., Lavorel, S., McIntyre, S. U. E., Falczuk, V., Casanoves, F., Milchunas, D. G., ... & Campbell, B. D. (2007). Plant trait responses to grazing–a global synthesis. *Global Change Biology*, *13*(2), 313-341.

Dodds, W. K., & Gudder, D. A. (1992). The ecology of Cladophora. *Journal of Phycology, 28*(4), 415-427.

Doughty, C. E., Wolf, A., & Malhi, Y. (2013). The impact of large animal extinctions on nutrient fluxes in early river valley civilizations. *Ecosphere*, *4*(12), 1-17.

Downing, J. A., Cole, J. J., Duarte, C. M., Middelburg, J. J., Melack, J. M., Prairie, Y. T., ... & Tranvik, L. J. (2012). Global abundance and size distribution of streams and rivers. *Inland waters, 2*(4), 229-236.

Doyle, M. C., & Lynch, D. D. (2005). *Sediment Oxygen Demand in Lake Ewauna and the Klamath River, Oregon, June 2003*. US Geological Survey.

Drake, T. W., Wickland, K. P., Spencer, R. G., McKnight, D. M., & Striegl, R. G. (2015). Ancient low–molecular-weight organic acids in permafrost fuel rapid carbon dioxide production upon thaw. *Proceedings of the National Academy of Sciences, 112*(45), 13946-13951.

Duarte, C. M., & Prairie, Y. T. (2005). Prevalence of heterotrophy and atmospheric CO2 emissions from aquatic ecosystems. *Ecosystems, 8*, 862–870.

Dudgeon, D. (2010). Prospects for sustaining freshwater biodiversity in the 21st century: linking ecosystem structure and function. *Current Opinion in Environmental Sustainability*, *2*(5-6), 422-430.

Dudgeon, D., Arthington, A. H., Gessner, M. O., Kawabata, Z., Knowler, D. J., Lêvêque, C., … Sullivan, C. A. (2006). Freshwater biodiversity: importance, threats, status and conservation challenges. *Biological Reviews, 81*, 161–182.

du Toit, J. T. (2003). Large herbivores and savanna heterogeneity. *The Kruger experience: Ecology and management of savanna heterogeneity*, 292-309.

Dutton, C. L., Subalusky, A. L., Hamilton, S. K., Rosi, E. J., & Post, D. M. (2018). Organic matter loading by hippopotami causes subsidy overload resulting in downstream hypoxia and fish kills. *Nature Communications, 9*(1), 1-10.

Dutton, C. L., Subalusky, A.L., Hamilton, S.K., Bayer, E.C., Njoroge, L., Rosi, E.J., Post, D.M., (2021). Alternative Biogeochemical States of River Pools Mediated by Hippo Use and Flow Variability. *Ecosystems*, *24*, 284-300.

Elmore, H. (1961). Effects of water temperature on stream sanitation. *Journal of the Sanitary Engineering Division* 87(6), 59-71.

Emery- Butcher, H. E., Beatty, S. J., & Robson, B. J. (2020). The impacts of invasive ecosystem engineers in freshwaters: A review. *Freshwater Biology*, *65*(5), 999-1015.

Englmaier, G. K., Hayes, D. S., Meulenbroek, P., Terefe, Y., Lakew, A., Tesfaye, G., ... & Graf, W. (2020). Longitudinal river zonation in the tropics: examples of fish and caddisflies from the endorheic Awash River, Ethiopia. *Hydrobiologia*, *847*(19), 4063-4090.

Ensign, S. H., & Doyle, M. W. (2006). Nutrient spiraling in streams and river networks. Journal of Geophysical Research: *Biogeosciences*, *111*(G4).

Exley, C. (2003). A biogeochemical cycle for aluminium? Journal of Inorganic *Biochemistry*, *97*(1), 1-7.

FAO. (2006). Livestock’s long shadow. Rome, Food and Agriculture Organization of the United Nations (FAO)

Farjalla, V. F., Marinho, C. C., Faria, B. M., Amado, A. M., Esteves, F. D. A., Bozelli, R. L., & Giroldo, D. (2009). Synergy of fresh and accumulated organic matter to bacterial growth. *Microbial ecology*, *57*(4), 657-666.

Fasching, C., Ulseth, A. J., Schelker, J., Steniczka, G., & Battin, T. J. (2016). Hydrology controls dissolved organic matter export and composition in an Alpine stream and its hyporheic zone. *Limnology and Oceanography.*, *61*, 558–571.

Federation, W. E., & Aph Association. (2005). Standard methods for the examination of water and wastewater. *American Public Health Association (APHA): Washington, DC, USA*, *21*.

Fellman, J. B., Hood, E., & Spencer, R. G. M. (2010). Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review. *Limnology and Oceanography, 55*(6), 2452–2462.

Fellman, J., Spencer, R. G. M., Raymond, P. A., Pettit, N. E., Skrzypek, G., Hernes, P. J., & Grierson, P. F. (2014). Dissolved organic carbon Landscape, biolability decreases along with its modernization in fluvial networks in an ancient. *Ecology*, *95*, 2622–2632.

Ferreira, V., Elosegi, A., D. Tiegs, S., von Schiller, D., & Young, R. (2020). Organic matter decomposition and ecosystem metabolism as tools to assess the functional integrity of streams and rivers–a systematic review. *Water, 12*(12), 3523.

Field, C. R., & Laws, R. M. (1970). The distribution of the larger herbivores in the Queen Elizabeth National Park, Uganda. *Journal of applied ecology*, 273-294.

Fierro, P., Bertrán, C., Tapia, J., Hauenstein, E., Peña-Cortés, F., Vergara, C., ... & Vargas-Chacoff, L. (2017). Effects of local land-use on riparian vegetation, water quality, and the functional organization of macroinvertebrate assemblages. *Science of the Total Environment, 609*, 724-734.

Fisher, T. R., Peele, E. R., Ammerman, J. W., & Harding Jr, L. W. (1992). Nutrient limitation of phytoplankton in Chesapeake Bay. *Marine Ecology Progress Series*, 51-63.

Fleischner, T. L. (1994). Ecological costs of livestock grazing in western North America. *Conservation Biology, 8(*3), 629-644.

Frank, D. A., & McNaughton, S. J. (1993). Evidence for the promotion of aboveground grassland production by native large herbivores in Yellowstone National Park. *Oecologia, 96*(2), 157-161.

Fugère, V., Jacobsen, D., Finestone, E. H., & Chapman, L. J. (2018). Ecosystem structure and function of afrotropical streams with contrasting land use. *Freshwater Biology, 63*(12), 1498-1513.

Fuss, T., Behounek, B., Ulseth, A. J., & Singer, G. A. (2017). Land use controls stream ecosystem metabolism by shifting dissolved organic matter and nutrient regimes. *Freshwater Biology, 62(*3), 582-599. doi: 10.1111/fwb.12887

Gessner, M. O., & Chauvet, E. (2002). A case for using litter breakdown to assess functional stream integrity. *Ecological applications, 12(*2), 498-510.

Giling, D. P., Grace, M. R., Thomson, J. R., Mac Nally, R., & Thompson, R. M. (2014). Effect of Native Vegetation Loss on Stream Ecosystem Processes: Dissolved

Organic Matter Composition and Export in Agricultural Landscapes. *Ecosystems, 17*, 82–95.

Giri, S., & Qiu, Z. (2016). Understanding the relationship of land uses and water quality in Twenty First Century: A review. *Journal of Environmental Management, 173*, 41-48.

Glibert, P. M., & Burkholder, J. M. (2006). The complex relationships between increases in fertilization of the earth, coastal eutrophication and proliferation of harmful algal blooms. In *Ecology of harmful algae* (pp. 341-354). Springer, Berlin, Heidelberg.

Godsey, S. E., Hartmann, J., & Kirchner, J. W. (2019). Catchment chemostasis revisited: Water quality responds differently to variations in weather and climate. *Hydrological Processes, 33*(24), 3056-3069.

Government of Kenya (GoK), (2009). Report of the government's task force on the conservation of the Mau Forest complex. Government of Kenya (GoK), Nairobi.

Graeber, D., Gelbrecht, J., Pusch, M. T., Anlanger, C., & von Schiller, D. (2012). Agriculture has changed the amount and composition of dissolved organic matter in Central European headwater streams. *Science of the Total Environment, 438*, 435–446.

Graeber, D., Goyenola, G., Meerhoff, M., Zwirnmann, E., Ovesen, N. B., Glendell, M., ... & Kronvang, B. (2015). Interacting effects of climate and agriculture on fluvial

DOM in temperate and subtropical catchments. *Hydrology and Earth System Sciences, 19*(5), 2377-2394.

Greathouse, E. A., Pringle, C. M., McDowell, W. H., & Holmquist, J. G. (2006). Indirect upstream effects of dams: consequences of migratory consumer extirpation in Puerto Rico. *Ecological Applications, 16*(1), 339-352.

Griffiths, N. A., Tank, J. L., Royer, T. V., Roley, S. S., Rosi-Marshall, E. J., Whiles, M. R., ... & Johnson, L. T. (2013). Agricultural land use alters the seasonality and magnitude of stream metabolism. *Limnology and Oceanography, 58*(4), 1513-1529.

Gücker, B., Boechat, I.G. and Giani, A (2009). Impacts of agricultural land use on ecosystem structure and whole- stream metabolism of tropical Cerrado streams. *Freshwater Biology, 54*(10), 2069-2085. http://dx.doi.org/10.1111/j.1365-2427.2008.02069.x

Guya, F. J. (2019). Intrinsic and extrinsic sources of phosphorus loading into the Nyando River, Kenya. *Lakes & Reservoirs: Research & Management, 24(*4), 362-371.

Hartnett, H. (2018). Dissolved organic matter (DOM). In *Encyclopedia of Earth Sciences Series* (pp. 375-378). Springer Netherlands.

Hastie, T.J., Tibshirani, R.J., (1990). Generalized additive models, CRC press.

Hauer, F.R. and Lamberti, G.A., (2011). *Methods in stream ecology*. New York: Academic Press.

Heinz, M., Graeber, D., Zak, D., Zwirnmann, E., Gelbrecht, J., & Pusch, M. T. (2015). Comparison of organic matter composition in agricultural versus forest affected headwaters with special emphasis on organic nitrogen. *Environmental cience & technology*, *49*(4), 2081-2090.

Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., & Mopper, K. (2008). Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnology and Oceanography, 53*, 955–969.

Hempson, G. P., Archibald, S., & Bond, W. J. (2017). The consequences of replacing wildlife with livestock in Africa. *Scientific reports, 7*(1), 1-10.

Hering, D., Feld, C. K., Moog, O., & Ofenböck, T. (2006). Cook book for the development of a Multimetric Index for biological condition of aquatic ecosystems: experiences from the European AQEM and STAR projects and related initiatives. In *The ecological status of European rivers: Evaluation and intercalibration of assessment methods* (pp. 311-324). Springer, Dordrecht.

Hilary, B., Chris, B., North, B. E., Maria, A. Z. A., Lucia, A. Z. S., Alberto, Q. G. C., ... & Andrew, W. (2021). Riparian buffer length is more influential than width on river water quality: A case study in southern Costa Rica. *Journal of Environmental Management*, *286*, 112132.

Hladyz, S., Åbjörnsson, K., Chauvet, E., Dobson, M., Elosegi, A., Ferreira, V., ... & Woodward, G. (2011). Stream ecosystem functioning in an agricultural landscape:

the importance of terrestrial–aquatic linkages. In *Advances in ecological research* (Vol. 44, pp. 211-276). Academic Press.

Hoellein, T. J., Bruesewitz, D. A., & Richardson, D. C. (2013). Revisiting Odum (1956): A synthesis of aquatic ecosystem metabolism. *Limnology and Oceanography, 58*(6), 2089-2100.

Hotchkiss, E. R., & Hall, R. O. (2014). High rates of daytime respiration in three streams: Use of delta O-18(O2) and O-2 to model diel ecosystem metabolism. *Limnology and Oceanography, 59*(3), 798-810. doi: 10.4319/lo.2014.59.3.0798

Huber, S. A., Balz, A., Abert, M., & Pronk, W. (2011). Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography–organic carbon detection–organic nitrogen detection (LC-OCD-OND). *Water Research*, *45*(2), 879-885.

Hudson, N., Baker, A., & Reynolds, D. (2007). Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters—a review. *River research and applications*, *23*(6), 631-649.

Huguet, A., Vacher, L., Relexans, S., Saubusse, S., Froidefond, J. M., & Parlanti, E. (2009). Properties of fluorescent dissolved organic matter in the Gironde estuary. *Organic Geochemistry, 40*, 706–719. http://dx.doi.org/10.1016/j.orggeochem.2009.03.002

Hunt, R. J., Jardine, T. D., Hamilton, S. K., & Bunn, S. E. (2012). Temporal and spatial variation in ecosystem metabolism and food web carbon transfer in a wet-dry tropical river. *Freshwater Biology*, *57*, 435–450.

Hwang, S. A., Hwang, S. J., Park, S. R., & Lee, S. W. (2016). Examining the relationships between watershed urban land use and stream water quality using linear and generalized additive models. *Water, 8*(4), 155.

Hynes, H. B. N. (1975). The stream and its valley: With 4 figures and 2 tables in the text. *Internationale Vereinigung für theoretische und angewandte Limnologie: Verhandlungen*, *19*(1), 1-15.

Iteba, J. O., Hein, T., Singer, G. A., & Masese, F. O. (2021). Livestock as vectors of organic matter and nutrient loading in aquatic ecosystems in African savannas. *PLOS One, 16*(9), e0257076.

Jackson, A. J. H., & McCarter, P. S. (1994). A Profile of the Mau Forest Complex. *KEFCON, Nairobi*.

Jacobs, S. R., Breuer, L., Butterbach-Bahl, K., Pelster, D. E., & Rufino, M. C. (2017). Land use affects total dissolved nitrogen and nitrate concentrations in tropical montane streams in Kenya. *Science of the Total Environment, 603*, 519-532.

Jaffé, R., McKnight, D. M., Maie, N., Cory, R. M., McDowell, W. H., & Campbell, J. L. (2008). Spatial and temporal variations in DOM composition in ecosystems: The importance of long-term monitoring of optical properties. *Journal of Geophysical Research Biogeochemestry*, *113*, G04032. https://doi.org/10.1029/2008JG000683

Jaffé, R., McKnight, D., Maie, N., Cory, R., McDowell, W. H., & Campbell, J. L. (2008b). Spatial and temporal variations in DOM composition in ecosystems: The importance of long-term monitoring of optical properties. *Journal of Geophysical Research*: B*iogeosciences*, 113.

Jaffé, R., Cawley, K. M., & Yamashita, Y. (2014). Applications of excitation emission matrix fluorescence with parallel factor analysis (EEM-PARAFAC) in assessing environmental dynamics of natural dissolved organic matter (DOM) in aquatic environments: a review. *Advances in the physicochemical characterization of dissolved organic matter: impact on natural and engineered systems*, 27-73.

Jalliffier-Merlon, E., Marty, J. C., Denant, V., & Saliot, A. (1991). Phytoplankton sources of volatile aldehydes in the river Rhone estuary. *Estuarine Coastal and Shelf Science, 32*, 463–482.

Jankowski, K. J., Mejia, F. H., Blaszczak, J. R., & Holtgrieve, G. W. (2021). Aquatic ecosystem metabolism as a tool in environmental management. *Wiley Interdisciplinary Reviews: Water*, *8*(4), e1521. https://doi.orge1521. 10.1002/wat2.1521

Jones, M. N., & Bryan, N. D. (1998). Colloidal properties of humic substances. *Advances in Colloid and Interface Science*, *78*(1), 1-48.

Junk, W. J., Bayley, P. B., & Sparks, R. E. (1989). The flood pulse concept in river-floodplain systems. *Canadian Special Publication of Fisheries and Aquatic Sciences*, *106*(1), 110-127.

Kadeka, E. C., Masese, F. O., Lusega, D. M., Sitati, A., Kondowe, B. N., & Chirwa, E. R. (2021). No Difference in Instream Decomposition Among Upland Agricultural and Forested Streams in Kenya. *Frontiers in Environmental Science*, 610.

Kahlert, M., & McKie, B. G. (2014). Comparing new and conventional methods to estimate benthic algal biomass and composition in freshwaters. *Environmental Science: Processes & Impacts, 16*(11), 2627-2634.

Kalbitz, K., Schmerwitz, J., Schwesig, D., & Matzner, E. (2003). Biodegradation of soil-derived dissolved organic matter as related to its properties. *Geoderma, 113*(3), 273–291.

Kanga, E. M., Ogutu, J. O., Olff, H., & Santema, P. (2011). Population trend and distribution of the Vulnerable common hippopotamus Hippopotamus amphibius in the Mara Region of Kenya. *Oryx, 45*(1), 20-27.

Kanga, E. M., Ogutu, J. O., Piepho, H. P., & Olff, H. (2013). Hippopotamus and livestock grazing: influences on riparian vegetation and facilitation of other herbivores in the Mara Region of Kenya. *Landscape and Ecological Engineering, 9*(1), 47-58.

Karr, J. R., & Chu, E. W. (1999). *Restoring life in running waters*. Island press.

Kasangaki, A., Chapman, L. J., & Balirwa, J. (2008). Land use and the ecology of benthic macroinvertebrate assemblages of high-altitude rainforest streams in Uganda. *Freshwater Biology, 53*, 681–697. https://doi.org/10.1111/j.1365-2427.2007.01925.xS

Kaushal, S. S., Duan, S., Doody, T. R., Haq, S., Smith, R. M., Johnson, T. A. N., ... & Stack, W. P. (2017). Human-accelerated weathering increases salinization, major ions, and alkalinization in fresh water across land use. *Applied Geochemistry*, *83*, 121-135.

Kaylor, M. J., Argerich, A., White, S. M., VerWey, B. J., & Arismendi, I. (2018). A cautionary tale for in situ fluorometric measurement of stream chlorophyll a: influences of light and periphyton biomass. *Freshwater Science*, *37*(2), 287-295.

Keenan, R. J., Reams, G. A., Achard, F., de Freitas, J. V., Grainger, A., & Lindquist, E. (2015). Dynamics of global forest area: Results from the FAO Global Forest Resources Assessment 2015. *Forest Ecology and Management*, *352*, 9-20.

Kendall, C., Silva, S. R., & Kelly, V. J. (2001). Carbon and nitrogen isotopic compositions of particulate organic matter in four large river systems across the United States. *Hydrological processes*, *15*(7), 1301-1346.

Kiambi, S., Kuloba, B., Kenana, L., Muteti, D., & Mwenda, E. (2012). Wet season aerial count of large herbivores in masai mara national reserve and the adjacent community areas (June 2010). *Narok: Mara Research Station, Kenya Wildlife Service*.

Kilonzo, F., Masese, F. O., Van Griensven, A., Bauwens, W., Obando, J., & Lens, P. N. (2014). Spatial–temporal variability in water quality and macro-invertebrate assemblages in the Upper Mara River basin, Kenya. *Physics and Chemistry of the Earth, Parts A/B/C*, *67*, 93-104.

Kirschbaum, M. U. (1995). The temperature dependence of soil organic matter decomposition, and the effect of global warming on soil organic C storage. *Soil Biology and Biochemistry, 27*(6), 753-760.

Kitchell, J. F., O’Neill, R. V., Webb, D., Gallepp, G. W., Bartell, S. M., Koonce, J. F., & et al. (1979). Consumer regulation of nutrient cycling. *BioScience, 29,* 28–34.

Kitchell, J. F., Schindler, D. E., Herwig, B. R., Post, D. M., Olson, M. H., & M., O. (1999). Nutrient cycling at the landscape scale: the role of diel foraging migrations by geese at the Bosque del Apache National Wildlife Refuge, New Mexico. *Limnology and Oceanography, 44*, 828–836.

KNBS-LS. (2009). *Livestock population by type and district. Nairobi: Census* Kenya National Bureau of Statistics

KNBS. KNBS (2016). *Livestock statistics*. Kenya National Bureau of Statistics.

KNBS (2018). *Economic Survey 2018*. Kenya National Bureau of Statistics

Korth, F., Deutsch, B., Liskow, I., & Voss, M. (2012). Uptake of dissolved organic nitrogen by size-fractionated plankton along a salinity gradient from the North Sea to the Baltic Sea. *Biogeochemistry, 111*(1), 347-360.

Kothawala, D. N., Stedmon, C. A., Müller, R. A., Weyhenmeyer, G. A., Köhler, S. J., & Stanvik, L. J. (2014). Controls of dissolved organic matter quality: evidence from a large scale boreal 646 lake survey. *Global Change Biology, 20*, 1101–1114.

Lakowicz, J. R. (Ed.). (2006). *Principles of fluorescence spectroscopy*. Boston, MA: springer US.

Lam, B., Baer, A., Alaee, M., Lefebvre, B., Moser, A., & Simpson, A. J. (2007). Major structural components in freshwater dissolved organic matter. *Environmental Science & Technology, 41*(24), 8240–8247.

Lambert, T., Pierson-Wickmann, A. C., Gruau, G., Thibault, J. N., & Jaffrezic, A. (2011). Carbon isotopes as tracers of dissolved organic carbon sources and water pathways in headwater catchments. *Journal of Hydrology, 402*(3-4), 228-238.

Lamprey RH, Reid RS. (2004). Expansion of human settlement in Kenya's Maasai Mara: what future for pastoralism and wildlife? *Journal of Biogeography 31*(6): 997–1032.

Lapierre, J. F., & Frenette, J. J. (2009). Effects of macrophytes and terrestrial inputs on fluorescent dissolved organic matter in a large river system. *Aquatic Sciences, 71*(1), 15-24.

Larson, J. H., Frost, P. C., Zheng, Z., Johnston, C. A., Bridgham, S. D., Lodge, D. M., & Lamberti, G. A. (2007). Effects of upstream lakes on dissolved organic matter in streams. *Limnology and Oceanography, 52*–60.

Lean, D. (1998). Attenuation of solar radiation in humic waters. In *Aquatic humic substances* (pp. 109-124). Springer, Berlin, Heidelberg.

Ledesma, J. L. J., Kothawala, D. N., Bastviken, P., Maehder, S., Grabs, T., & Futter, M. N. (2018). Stream dissolved organic matter composition reflects the riparian zone, not upslope soils in boreal forest headwaters. *Water Resources Research*, *54*(6), 3896-3912.

Leip, A., Billen, G., Garnier, J., Grizzetti, B., Lassaletta, L., Reis, S., ... & Westhoek, H. (2015). Impacts of European livestock production: nitrogen, sulphur, phosphorus and greenhouse gas emissions, land-use, water eutrophication and biodiversity. *Environmental Research Letters*, *10*(11), 115004.

Leroux, S. J., & Loreau, M. (2008). Subsidy hypothesis and strength of trophic cascades across ecosystems. *Ecology Letters*, *11*, 1147–1156.

Leu, E., Falk-Petersen, S., & Hessen, D. O. (2007). Ultraviolet radiation negatively affects growth but not food quality of artic diatoms. *Limnology and Oceanography, 52*, 787 – 797.

Lewison, R., & Oliver, W. (2008). Hippopotamus Amphibius. *The IUCN Red List of Threatened Species 2014.*

Liu, Qi; Jiang, Yuan; Tian, Yulu; Hou, Zhaojiang; He, Kejian; Fu, Lan; Xu, Hui (2019). Impact of land use on the DOM composition in different seasons in a subtropical river flowing through a region undergoing rapid urbanization. *Journal of Cleaner Production, 212*, 1224–1231. doi: 10.1016/j.jclepro.2018.12.030

Lohman, K., Jones, J. R., & Baysinger-Daniel, C. (1991). Experimental evidence for nitrogen limitation in a northern Ozark stream. *Journal of the North American Benthological Society, 10*(1), 14-23.

Lutz, B. D., Bernhardt, E. S., Roberts, B. J., Cory, R. M., & Mulholland, P. J. (2012). Distinguishing dynamics of dissolved organic matter components in a forested stream using kinetic enrichments. *Limnology and Oceanography*, *57*(1), 76-89.

McCauley, D. J., Dawson, T. E., Power, M. E., Finlay, J. C., Ogada, M., Gower, D. B., ... & Brashares, J. S. (2015). Carbon stable isotopes suggest that hippopotamus-vectored nutrients subsidize aquatic consumers in an East African river. *Ecosphere, 6*(4), 1-11.

Malcolm, R. L. (1993). Concentration and composition of dissolved organic carbon in soils, streams, and groundwaters. *Organic Substances in Soil and Water: Natural Constituents and Their Influences on Contaminant Behavior,* 19-30.

Mamun, M., & An, K. G. (2020). Stream health assessment using chemical and biological multi-metric models and their relationships with fish trophic and tolerance indicators. *Ecological Indicators*, *111*, 106055. doi: 10.1016/j.ecolind.2019.106055

Mango, L. M., Melesse, A. M., McClain, M. E., Gann, D., & Setegn, S. (2011). Land use and climate change impacts on the hydrology of the upper Mara River Basin, Kenya: results of a modeling study to support better resource management. *Hydrology and earth system sciences*, *15*(7), 2245-2258.

Marcarelli, A. M., Baxter, C. V., Mineau, M. M., & Hall Jr, R. O. (2011). Quantity and quality: unifying food web and ecosystem perspectives on the role of resource subsidies in freshwaters. *Ecology, 92*(6), 1215-1225.

Marwick, T. R., Tamooh, F., Ogwoka, B., Teodoru, C., Borges, A. V., Darchambeau, F., & Bouillon, S. (2014). Dynamic seasonal nitrogen cycling in response to anthropogenic N loading in a tropical catchment, Athi–Galana–Sabaki River, Kenya. *Biogeosciences, 11*(2), 443-460.

Marzolf, E. R., Mulholland, P. J., & Steinman, A. D. (1998). Reply: improvements to the diurnal upstream-downstream dissolved oxygen change technique for determining whole-stream metabolism in small streams. *Canadian Journal of Fisheries and Aquatic Sciences, 55*(7), 1786-1787.

Masese, F. O., Muchiri, M., & Raburu, P. O. (2009). Macroinvertebrate assemblages as biological indicators of water quality in the Moiben River, Kenya. *African Journal of Aquatic Science, 34*(1), 15-26.

Masese, F. O., & McClain, M. E. (2012). Trophic resources and emergent food web attributes in rivers of the Lake Victoria Basin: a review with reference to anthropogenic influences. *Ecohydrology, 5*(6), 685-707.

Masese, Frank O., Nzula Kitaka, Julius Kipkemboi, Gretchen M. Gettel, Kenneth Irvine, and Michael E. McClain. "Litter processing and shredder distribution as indicators of riparian and catchment influences on ecological health of tropical streams." *Ecological Indicators* 46 (2014): 23-37.

Masese, F. O., Abrantes, K. G., Gettel, G. M., Bouillon, S., Irvine, K., & McClain, M. E. (2015). Are large herbivores vectors of terrestrial subsidies for riverine food webs?. *Ecosystems*, *18*(4), 686-706.

Masese, F. O., Salcedo-Borda, J. S., Gettel, G. M., Irvine, K., & McClain, M. E. (2017). Influence of catchment land use and seasonality on dissolved organic matter composition and ecosystem metabolism in headwater streams of a Kenyan river. *Biogeochemistry*, *132*(1), 1-22.

Masese, F. O., Abrantes, K. G., Gettel, G. M., Irvine, K., Bouillon, S., & McClain, M. E. (2018). Trophic structure of an African savanna river and organic matter inputs by large terrestrial herbivores: a stable isotope approach. *Freshwater Biology*, *63*(11), 1365-1380.

Masese, F. O., Kiplagat, M. J., González-Quijano, C. R., Subalusky, A. L., Dutton, C. L., Post, D. M., & Singer, G. A. (2020). Hippopotamus are distinct from domestic livestock in their resource subsidies to and effects on aquatic ecosystems. *Proceedings of the Royal Society B*, *287*(1926), 20193000.

Masese, F. O., Fuss, T., Bistarelli, L. T., Buchen-Tschiskale, C., & Singer, G. (2022). Large herbivorous wildlife and livestock differentially influence the relative importance of different sources of energy for riverine food webs. *Science of The Total Environment*, *828*, 154452.

Massicotte, P., Asmala, E., Stedmon, C., & Markager, S. (2017). Global distribution of dissolved organic matter along the aquatic continuum: Across rivers, lakes and oceans. *Science of the Total Environment, 609*, 180-191.

Mateo-Sagasta, J., Zadeh, S. M., Turral, H., & Burke, J. (2017). *Water pollution from agriculture: a global review*. Executive summary.

Mati, B. M., Mutie, S., Gadain, H., Home, P., & Mtalo, F. (2008). Impacts of land-use/cover changes on the hydrology of the transboundary Mara River, Kenya/Tanzania. *Lakes & Reservoirs: Research & Management, 13(*2), 169-177.

McArdle, B. H., & Anderson, M. J. (2001). Fitting multivariate models to community data: a comment on distance- based redundancy analysis. *Ecology, 82*(1), 290-297.

McCallister, S. L., & del Giorgio, P. A. (2012). Evidence for the respiration of ancient terrestrial organic C in northern temperate lakes and streams. *Proceedings of the National Academy of Sciences*, *109*(42), 16963-16968.

McCauley, D. J., Dawson, T. E., Power, M. E., Finlay, J. C., Ogada, M., Gower, D. B., ... & Brashares, J. S. (2015). Carbon stable isotopes suggest that hippopotamus-vectored nutrients subsidize aquatic consumers in an East African river. *Ecosphere, 6*(4), 1-11.

McClain, M. E., Subalusky, A. L., Anderson, E. P., Dessu, S. B., Melesse, A. M., Ndomba, P. M., ... & Mligo, C. (2014). Comparing flow regime, channel hydraulics, and biological communities to infer flow–ecology relationships in the

Mara River of Kenya and Tanzania. *Hydrological Sciences Journal, 59(*3-4), 801-819.

McKnight, D., Boyer, E., Westerhoff, P., Doran, P., Kulbe, T., & Andersen, D. (2001). Characterization of Dissolved Organic Matter for Indication of Precursor Organic Material and Aromaticity. *Limnology and Oceanography, 46*(38–48).

McLennan, S. M. (1993). Weathering and global denudation. *The Journal of Geology*, *101*(2), 295-303.

Miller, M. P., & Mcknight, D. M. (2010). Comparison of seasonal changes in fluorescent dissolved organic matter among aquatic lake and stream sites in the Green Lakes Valley. *Journal of Geophysical Research*, 115.

Minaya, Veronica, Michael E. McClain, Otto Moog, Fred Omengo, and Gabriel A. Singer. "Scale-dependent effects of rural activities on benthic macroinvertebrates and physico-chemical characteristics in headwater streams of the Mara River, Kenya." *Ecological Indicators 32* (2013): 116-122.

Minshall, G. W., Petersen, R. C., Cummins, K. W., Bott, T. L., Sedell, J. R., Cushing, C. E., & Vannote, R. L. (1983). Interbiome comparison of stream ecosystem dynamics. *Ecological Monographs, 53,* 1–25.

Mngube, F. N., Kapiyo, R., Aboum, P., Anyona, D., & Dida, G. O. (2020). Subtle impacts of temperature and rainfall patterns on land cover change overtime and future projections in the Mara River Basin, Kenya. *Open Journal of Soil Science*, *10*(09), 327. doi: 10.4236/ojss.2020.109018

Moody, C. S., Worrall, F., Evans, C. D., & Jones, T. G. (2013). The rate of loss of dissolved organic carbon (DOC) through a catchment. *Journal of Hydrology*, *492*, 139-150.

Mopper, K., & Schultz, C. A. (1993). Fluorescence as a possible tool for studying the nature and water column distribution of DOC components. *Marine Chemistry, 41*(1-3), 229-238.

Moran, M. A., & Zepp, R. G. (1997). Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. *Limnology and Oceanography, 42*(6), 1307-1316.

Mosepele, K., Moyle, P. B., Merron, G. S., Purkey, D. R., & Mosepele, B. (2009). Fish, floods, and ecosystem engineers: aquatic conservation in the Okavango Delta, Botswana. *Bioscience, 59*(1), 53-64.

Mosisch, T. D., Bunn, S. E., & Davies, P. M. (2001). The relative importance of shading and nutrients on algal production in subtropical streams. *Freshwater biology*, *46*(9), 1269-1278.

Mulholland, P. J., Fellows, C. S., Tank, J. L., Grimm, N. B., Webster, J. R., Hamilton, S. K., ... & Peterson, B. J. (2001). Inter- biome comparison of factors controlling stream metabolism. *Freshwater biology*, *46*(11), 1503-1517.

Mulholland, P. J., Tank, J. L., Webster, J. R., Bowden, W. B., Dodds, W. K., Gregory, S. V., ... & Wollheim, W. M. (2002). Can uptake length in streams be determined by nutrient addition experiments? Results from an interbiome comparison study. *Journal of the North American Benthological Society*, *21*(4), 544-560.

Mulholland, P, J., Dodds, W. K., Webster, J. R., Tank, J. L., Ashkenas, L. R., … Wilson, K. Y. (2010). Inter-regional comparison of land-use effects on stream metabolism. *Freshwater Biology, 55*, 1874–1890.

Murphy, K. R., Stedmon, C. A., Graeber, D., & Bro, R. (2013). Fluorescence spectroscopy and multi-way techniques. PARAFAC. *Analytical Methods, 5*(23), 6557-6566.

Mwanake, R. M., Gettel, G. M., Aho, K. S., Namwaya, D. W., Masese, F. O., Butterbach- Bahl, K., & Raymond, P. A. (2019). Land use, not stream order, controls N2O concentration and flux in the upper Mara River basin, Kenya. Journal of Geophysical Research: *Biogeosciences, 124*(11), 3491-3506.

Naden, P. S., Old, G. H., Eliot-Laize, C., Granger, S. J., Hawkins, J. M. B., Bol, R., & et al. (2010). Assessment of natural fluorescence as a tracer of diffuse agricultural pollution from slurry spreading on intensely-farmed grasslands. *Water Research, 44*, 1701–1712.

Naiman, R. J., & Rogers, K. H. (1997). Large animals and system level characteristics in river corridors. *BioScience, 47*, 521–529.

Naiman, R. J., & Sedell, J. R. (1980). Relationships between metabolic parameters and stream order in Oregon. *Canadian Journal of Fisheries and Aquatic Sciences, 37*(5), 834-847.

National Environment Management Authority (NEMA)., (2013). *Mau Complex at a glance- Report*. National Environment Management Authority, Nairobi, Kenya.

Nelson, N. B., & Siegel, D. A. (2013). The global distribution and dynamics of chromophoric dissolve organic matter. *Annual Review of Marine Science, 5*, 447–476.

Newcomer, T. A., Kaushal, S. S., Mayer, P. M., Shields, A. R., Canuel, E. A., Groffman, P. M., & Gold, A. J. (2012). Influence of natural and novel organic carbon sources on denitrification in forest, degraded urban, and restored streams. *Ecological Monographs, 82*(4), 449-466.

Obernosterer, I., & Benner, R. (2004). Competition between biological and photochemical processes in the mineralization of dissolved organic carbon. *Limnology and Oceanography, 49*(1), 117-124.

Odada, E., Ochola, W., & Olago, D. (2009). Drivers of ecosystem change and their impacts on human wellbeing in Lake Victoria basin. *African Journal of Ecology, 47*, 46–54.

Odum, H. T. (1956). Primary production in flowing waters 1. *Limnology and oceanography, 1*(2), 102-117.

Ogutu, J. O., Owen- Smith, N., Piepho, H. P., & Said, M. Y. (2011). Continuing wildlife population declines and range contraction in the Mara region of Kenya during 1977–2009. *Journal of Zoology, 285*(2), 99-109.

Ogutu, J. O., Piepho, H. P., Said, M. Y., Ojwang, G. O., Njino, L. W., Kifugo, S. C., & Wargute, P. W. (2016). Extreme wildlife declines and concurrent increase in livestock numbers in Kenya: What are the causes?. *PloS one*, *11*(9), e0163249.

Ohno, T. (2002). Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter. *Environmental science & technology, 36*(4), 742-746.

Ohno, T., He, Z., Sleighter, R. L., Honeycutt, C. W., & Hatcher, P. G. (2010). Ultrahigh resolution mass spectrometry and indicator species analysis to identify marker components of soil-and plant biomass-derived organic matter fractions. *Environmental science & technology, 44*(22), 8594-8600.

Olivier, R. C. D., & Laurie, W. A. (1974). Habitat utilization by hippopotamus in the Mara River. African *Journal of Ecology, 12*(4), 249-271.

Omengo, O. F. (2010). *Carbon cycling in the Mara River system-influence and land use and location in the fluvial network on organic matter processing and CO2-production.*[Thesis Master of Science, UNESCO-IHE Institute for Water Education, Delft]. Delft : UNESCO-IHE Institute for Water Education.

Onyando, Z. A., Shivoga, W. A., Lung'ayia, H., Ochieno, D. W., Agevi, H., & Kigen, C. (2013). The influence of land use on nutrient regime in a tropical stream. *Elixir Pollution,2013*(64), 19290-19294.

Pacheco, F. S., Ometto, J. P. H. B., Gomes, L., Tosto, K., Miranda, M., Loverde-Oliveira, S., ... & Cox, C. (2021). Nutrient balance and use efficiency in agricultural lands in the Vermelho River watershed, Upper Pantanal, Brazil. Journal of Geophysical Research: *Biogeosciences, 126*(3), e2020JG005673

Pacheco, J. P., Aznarez, C., Levi, E. E., Baattrup-Pedersen, A., & Jeppesen, E. (2022). Periphyton responses to nitrogen decline and warming in eutrophic shallow lake mesocosms. *Hydrobiologia, 849*(17), 3889-3904.

Paetzold, A., Lee, M., & Post, D. M. (2008). Marine resource flows to terrestrial arthropod predators on a temperate island: the role of subsidies between systems of similar productivity. *Oecologia, 157*(4), 653-659.

Parkhill, K. L., & Gulliver, J. S. (1999). Modeling the effect of light on whole-stream respiration. *Ecological Modelling, 117*(2-3), 333-342.

Parkhill, K. L., & Gulliver, J. S. (2002). Effect of inorganic sediment on whole-stream productivity. *Hydrobiologia, 472*(1), 5-17.

Parlanti, E., Worz, K., Geoffroy, L., & Lamotte, M. (2000). Dissolved organic matter fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs. *Organic Geochemistry, 31*, 1765–1781.

Parr, T. B., Cronan, C., Ohno, T., Findlay, G. E., Smith, C. M., & Simon, K. S. (2015). Urbanization changes the composition and bioavailability of dissolved organic matter in headwater streams. *Limnology and Oceanography, 60*, 885–900.

Patrick, C. J. (2013). The effect of shredder community composition on the production and quality of fine particulate organic matter. The effect of shredder community composition on the production and quality of fine particulate organic matter. *Freshwater Science, 32*(3):10261035

Perminova, I. V., Frimmel, F. H., Kudryavtsev, A. V., Kulikova, N. A., Abbt-Braun, G., Hesse, S., & Petrosyan, V. S. (2003). Molecular weight characteristics of humic substances from different environments as determined by size exclusion chromatography and their statistical evaluation. *Environmental Science & Technology, 37*(11), 2477-2485.

Peterson, B. J., Wollheim, W. M., Mulholland, P. J., Webster, J. R., Meyer, J. L., Tank, J. L., ... & Morrall, D. D. (2001). Control of nitrogen export from watersheds by headwater streams. *Science*, *292*(5514), 86-90.

Petrone, K. C. (2010). Catchment export of carbon, nitrogen, and phosphorus across an agro- urban land use gradient, Swan- Canning River system, southwestern Australia. Journal of Geophysical Research: *Biogeosciences*, *115*(G1).

Pettit, R. (2000). Organic Matter, Humus, Humates, Humic Acid, Fulvic Acid and Humin: Their Importance in Soil Fertility and Plant Health. Pinheiro, J., & Bates, D. (2006). Mixed-effects models in S and S-PLUS. Springer science & business media.

Peuravuori, J., & Pihlaja, K. (1997). Molecular size distribution and spectroscopic properties of aquatic humic substances. *Analytica Chimica Acta, 337*(2), 133-149.

Pinheiro, J. C., & Bates, D. M. (2000). Linear mixed-effects models: basic concepts and examples. *Mixed-effects models in S and S-Plus*, 3-56.

Plan, D.D., (2007). *Effective management for sustainable economic growth and poverty reduction, Bomet District 2002-2008*.

Plan, D.D., (2008). *Effective management for sustainable economic growth and poverty reduction, Narok District 2002-2008.*

Polis, G. A., Anderson, W. B., & Holt, R. D. (1997). Toward an integration of landscape and food web ecology: the dynamics of spatially subsidized food webs. *Annual Review of Ecology and Systematics*, *28,* 289–316.

Pollard, P., & Ducklow, H. (2011). Ultrahigh bacterial production in a eutrophic subtropical Australian River: Does viral lysis short-circuit the microbial loop? *Limnology and Oceanography, 3*, 1115–1129.

Pond, G. J., Passmore, M. E., Borsuk, F. A., Reynolds, L., & Rose, C. J. (2008). Downstream effects of mountaintop coal mining: comparing biological conditions using family-and genus-level macroinvertebrate bioassessment tools. *Journal of the North American Benthological Society, 27*(3), 717-737.

Ponette-González, A. G., Weathers, K. C., & Curran, L. M. (2010a). Tropical land- cover change alters biogeochemical inputs to ecosystems in a Mexican montane landscape. *Ecological applications*, *20*(7), 1820-1837. doi:10.1890/09-1125.1.

Ponette-González, A. G., K. C. Weathers, and L. M. Curran (2010b), Water inputs across a tropical montane landscape in Veracruz, Mexico: Synergistic effects of land cover, rain and fog seasonality, and interannual precipitation variability. *Global Change Biology*, *16*(3), 946–963. doi:10.1111/j.1365-2486.2009.01985.x

R Core Team (2020) R: A Language and Environment for Statistical Computing. *R Foundation for Statistical Computing*, Vienna, Austria. https://www.r-project.org/ extensions in ecology with R (pp. 101-142). Springer, New York, NY.

Raburu, P. O., & Okeyo-Owuor, J. B. (2006). *Impact of agro-industrial activities on the water quality of River Nyando, Lake Victoria Basin, Kenya*. Rongo University (pp 307-314).

Raburu, P. O., Masese, F. O., & Mulanda, C. A. (2009). Macroinvertebrate Index of Biotic Integrity (M-IBI) for monitoring rivers in the upper catchment of Lake Victoria Basin, Kenya. *Aquatic Ecosystem Health & Management, 12*(2), 197-205.

Rasmussen, J. B., Trudeau, V., & Morinville, G. (2009). Estimating the scale of fish feeding movements in rivers using δ13C signature gradients. *Journal of animal ecology*, *78*(3), 674-685.

Raymond, P. A., Zappa, C. J., Butman, D., Bott, T. L., Potter, J., Mulholland, P., ... & Newbold, D. (2012). Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers. *Limnology and Oceanography: Fluids and Environments, 2*(1), 41-53.

Raymond, P. A., & et al. (2013). Global carbon dioxide emissions from inland waters. Nature, 503, 355–359. Raymond, P. A., J. E. Saiers, and W. V. Sobczak. (2016). Hydrological and biogeochemical controls on watershed dissolved organic matter transport: Pulse-shunt concept. *Ecology, 97*: 5– 16. doi:10.1890/14-1684

Raymond, P. A., Saiers, J. E., & Sobczak, W. V. (2016). Hydrological and biogeochemical controls on watershed dissolved organic matter transport: Pulse-shunt concept. *Ecology, 97*(1), 5-16.

Reche, I., Pace, M. L., & Cole, J. J. (1998). Interactions of photobleaching and inorganic nutrients in determining bacterial growth on colored dissolved organic carbon. *Microbial ecology, 36*(3), 270-280.

Rhymes, J., Jones, L., Lapworth, D. J., White, D., Fenner, N., McDonald, J. E., & Perkins, T. L. (2015). Using chemical, microbial and fluorescence techniques to understand contaminant sources and pathways to wetlands in a conservation site. *Science of the Total Environment, 511*, 703-710.

Richardson, J. S., Zhang, Y. X., & Marczak, L. B. (2010). Resource subsidies across the land-freshwater interface and responses in recipient communities. *River Research and Applications, 26*, 55–66.

Roach, K. A., Winemiller, K. O., & Davis III, S. E. (2014). Autochthonous production in shallow littoral zones of five floodplain rivers: effects of flow, turbidity and nutrients. *Freshwater Biology, 59*(6), 1278-1293.

Rodrigues, V., Estrany, J., Ranzini, M., de Cicco, V., Martín-Benito, J. M. T., Hedo, J., & Lucas-Borja, M. E. (2018). Effects of land use and seasonality on stream water quality in a small tropical catchment: The headwater of Córrego Água Limpa, São Paulo (Brazil). *Science of the Total Environment, 622*, 1553-1561.

Rodriguez-Avella, K. A., Baraer, M., Mark, B., McKenzie, J., & Somers, L. (2020). Comparing the performance of three methods to assess DOM dynamics within two distinct glacierized watersheds of the tropical Andes. *Environmental Pollution, 265*, 115052.

Ruaro, R., Gubiani, E. A., Hughes, R. M., & Mormul, R. P. (2020). Global trends and challenges in multimetric indices of biological condition. *Ecological Indicators, 110*, 105862.doi: 10.1016/j.ecolind.2019.105862

Rutina, L. P., & Moe, S. R. (2014). Elephant (Loxodonta africana) disturbance to riparian woodland: effects on tree-species richness, diversity and functional redundancy. *Ecosystems, 17*(8), 1384-1396.

Sandin, L., & Solimini, A. G. (2009). Freshwater ecosystem structure–function relationships: from theory to application. *Freshwater Biology, 54*(10), 2017-2024.

Sand-Jensen, K., Pedersen, N. L., & Sondergaard, M. (2007). Bacterial metabolism in small temperate streams under contemporary and future climates. *Freshwater Biology, 52*(12), 2340-2353. doi: doi:10.1111/j.1365-2427.2007.01852.x

Schoelynck, J., Subalusky, A. L., Struyf, E., Dutton, C. L., Unzué-Belmonte, D., Van de Vijver, B., Post, D. M., Rosi, E. J., Meire, P., & Frings, P. (2019). Hippos (Hippopotamus amphibius): The animal silicon pump. *Science Advances, 5*(5), eaav0395. https://doi.org/10.1126/sciadv.aav0395

Seitzinger, S. P., Mayorga, E., Bouwman, A. F., Kroeze, C., Beusen, A. H., Billen, G., ... & Harrison, J. A. (2010). Global river nutrient export: A scenario analysis of past and future trends. *Global Biogeochemical Cycles*, *24*(4).

Shang, P., Lu, Y., Du, Y., Jaffé, R., Findlay, R. H., & Wynn, A. (2018). Climatic and watershed controls of dissolved organic matter variation in streams across a gradient of agricultural land use. *Science of the Total Environment*, *612*, 1442-1453.

Shapiro, J. (1966). The relation of humic color to iron in natural waters: With 5 figures and 2 tables in the text. *Internationale Vereinigung für theoretische und angewandte Limnologie: Verhandlungen*, *16*(1), 477-484.

Shivoga, W. A., Muchiri, M., Kibichi, S., Odanga, J., Miller, S. N., Baldyga, T. J., ... & Gichaba, M. C. (2007). Influences of land use/cover on water quality in the upper and middle reaches of River Njoro, Kenya. Lakes & Reservoirs: *Research & Management*, *12*(2), 97-105.

Silva-Junior, E. F., Moulton, T. P., Boe¨chat, I. G., & Gu¨cker, B. (2014). Leaf decomposition and ecosystem metabolism as functional indicators of land use impacts on tropical streams. *Ecological Indicator*, *36*, 195–204.

Silva-Junior, E. F. D. (2016). Land use effects and stream metabolic rates: a review of ecosystem response. Acta *Limnologica Brasiliensia*, *28*.

Soetaert, K., & Middelburg, J. J. (2009). Modeling eutrophication and oligotrophication of shallow-water marine systems: the importance of sediments under stratified and well-mixed conditions. In *Eutrophication in Coastal Ecosystems* (pp. 239-254). Springer, Dordrecht.

Spencer, R. G., Pellerin, B. A., Bergamaschi, B. A., Downing, B. D., Kraus, T. E., Smart, D. R., ... & Hernes, P. J. (2007). Diurnal variability in riverine dissolved organic matter composition determined by in situ optical measurement in the San Joaquin River (California, USA). *Hydrological Processes: An International Journal*, *21*(23), 3181-3189.

Spencer, R. G. M., Hernes, P. J., Ruf, R., Baker, A., & Dy, R. Y. (2010). Temporal controls on dissolved organic matter and lignin biogeochemistry in a pristine tropical river, Democratic Republic of Congo. Journal of Geophysical Research: *Biogeosciences*, *115*(3). https://doi.org/10.1029/2009JG001180

Stachelek, J., Weng, W., Carey, C. C., Kemanian, A. R., Cobourn, K. M., Wagner, T., ... & Soranno, P. A. (2020). Granular measures of agricultural land use influence lake nitrogen and phosphorus differently at macroscales. *Ecological Applications*, *30*(8), e02187.

Stears, K., McCauley, D. J., Finlay, J. C., Mpemba, J., Warrington, I. T., Mutayoba, B. M., ... & Brashares, J. S. (2018). Effects of the hippopotamus on the chemistry and ecology of a changing watershed. *Proceedings of the National Academy of Sciences*, *115*(22), E5028-E5037.

Stedmon, C. A., Markager, S., & Bro, R. (2003). Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Marine*

Chemistry, 82(2339–254), 239–254. https://doi.org/10.1016/S0304-4203(03)00072-0

Stedmon, C. A., & Bro, R. (2008). Characterizing dissolved organic matter And, fluorescence with parallel factor analysis: a tutorial. *Limnology and Oceanography, 6*, 572–579.

Stenfert Kroese, J., Jacobs, S. R., Tych, W., Breuer, L., Quinton, J. N., & Rufino, M. C. (2020). Tropical montane forest conversion is a critical driver for sediment supply in East African catchments. *Water Resources Research, 56*(10), e2020WR027495.

Stenger-Kovács, C., Buczkó, K., Padisák, J., Selmeczy, G. B., Lengyel, E., & Tapolczai, K. (2022). Ecosystem services provided by freshwater and marine diatoms. *Hydrobiologia*, 1-27.

Stepanauskas, R., Leonardson, L., & Tranvik, L. J. (1999). Bioavailability of wetland-derived DON to freshwater and marine bacterioplankton. *Limnology and Oceanography, 44*, 1477–1485.

Strahler, A. N. (1952). Hypsometric (area-altitude) analysis of erosional topography. *Geological society of America bulletin, 63*(11), 1117-1142.

Strahler, A. N. (1957). Quantitative analysis of watershed geomorphology. *Eos, Transactions American Geophysical Union*, 38(6), 913-920.

Stream, W. (1990). Concepts and methods for assessing solute dynamics in stream ecosystems. *Journal of the North American Benthological Society, 9*, 95–119.

Stubbins, A., Lapierre, J. F., Berggren, M., Prairie, Y. T., Dittmar, T., & del Giorgio, P. A. (2014). What’s in an EEM? Molecular signatures associated with dissolved organic fluorescence in boreal Canada. *Environmental science & technology*, *48*(18), 10598-10606.

Subalusky, A., Dutton, C., Rosi-Marshall, E., & Post, D. (2015). The hippopotamus conveyor belt: Vectors of carbon and nutrients from terrestrial grasslands to aquatic systems in sub-Saharan Africa. *Freshwater Biology*, *60,* 512–525.

Subalusky, A. L., Dutton, C. L., Rosi, E. J., & Post, D. M. (2017). Annual mass drownings of the Serengeti wildebeest migration influence nutrient cycling and storage in the Mara River. *Proceedings of the National Academy of Sciences, 114*(29), 7647-7652.

Subalusky, A. L., Dutton, C. L., Njoroge, L., Rosi, E. J., & Post, D. M. (2018). Organic matter and nutrient inputs from large wildlife influence ecosystem function in the Mara River, Africa. *Ecology, 99*(11), 2558-2574.

Subalusky, A. L., Dutton, C. L., Njoroge, L., Rosi, E. J., & Post, D. M. (2018). Organic matter and nutrient inputs from large wildlife influence ecosystem function in the Mara River, Africa. *Ecology, 99*(11), 2558-2574.

Subalusky, A. L., & Post, D. M. (2019). Context dependency of animal resource subsidies. *Biological reviews, 94*(2), 517-538.

Subalusky, A. L., Dutton, C. L., Rosi, E. J., Puth, L. M., & Post, D. M. (2020). A river of bones: Wildebeest skeletons leave a legacy of mass mortality in the Mara River, Kenya. *Frontiers in Ecology and Evolution, 8*, 31.

Tamooh, F., Borges, A. V., Meysman, F. J. R., Van den Meersche, K., Dehairs, F., Merckx, R., & Bouillon, S. (2013). Dynamics of dissolved inorganic carbon and aquatic metabolism in the Tana River basin, Kenya. *Biogeosciences*, *10*(11), 6911-6928.

Tamooh, F., Van den Meersche, K., Meysman, F., Marwick, T. R., Borges, A. V., Merckx, R., ... & Bouillon, S. (2012). Distribution and origin of suspended matter and organic carbon pools in the Tana River Basin, Kenya. *Biogeosciences, 9*(8), 2905-2920.

Tank, J. L., Rosi-Marshall, E. J., Griffiths, N. A., Entrekin, S. A., & Stephen, M. L. (2010). A review of allochthonous organic matter dynamics and metabolism in streams*. Journal of the North American Benthological Society, 29*(1), 118-146.

Thompson, S. E., Basu, N. B., Lascurain Jr, J., Aubeneau, A., & Rao, P. S. C. (2011). Relative dominance of hydrologic versus biogeochemical factors on solute export across impact gradients. *Water resources research, 47*(10).

Thornton, D. D. (1971). The effect of complete removal of hippopotamus on grassland in the Queen Elizabeth National Park, Uganda. *African Journal of Ecology*, *9*(1), 47-55.

Thorp, J. H., & Delong, M. D. (2002). Dominance of autochthonous autotrophic carbon in food webs of heterotrophic rivers. *Oikos*, *96*(3), 543-550.\

Tilman, D., Balzer, C., Hill, J., & Befort, B. L. (2011). Global food demand and the sustainable intensification of agriculture. *Proceedings of the national academy of sciences*, *108*(50), 20260-20264.

Tomanova, S., Moya, N., & Oberdorff, T. (2008). Using macroinvertebrate biological traits for assessing biotic integrity of neotropical streams. *River research and applications*, *24*(9), 1230-1239.

Tong, S. T., & Chen, W. (2002). Modeling the relationship between land use and surface water quality. *Journal of Environmental Management, 66*(4), 377-393.

Tsisiche, A. R. (2018). *Effect of land use on ecosystem metabolism and decay rate of Eucalyptus saligna and Neuboutonia macrocalyx leaves in streams draining Upper Mara catchment, Kenya* (Doctoral dissertation, Egerton University). Egerton University.

Twesigye, C. K., Onywere, S. M., Getenga, Z. M., Mwakalila, S. S., & Nakiranda, J. K. (2011). The impact of land use activities on vegetation cover and water quality in the Lake Victoria watershed. *The Open Environmental Engineering Journal, 4*, 66-77 10.2174/1874829501104010066

Uehlinger, U. (2000). Resistance and resilience of ecosystem metabolism in a flood-prone river system. *Freshwater Biology, 45*(3), 319-332.

Uehlinger, U., Naegeli, M., & Fisher, S. G. (2002). A heterotrophic desert stream? The role of sediment stability. *Western North American Naturalist*, 466-473.

UNEP. (2016). *A snapshot of the world's water quality: towards a global assessment.* Nairobi, United Nations Environment Programme (UNEP).

Uriarte, M., Yackulic, C. B., Lim, Y., & Arce-Nazario, J. A. (2011). Influence of land use on water quality in a tropical landscape: a multi-scale analysis. *Landscape ecology*, *26*(8), 1151-1164. doi:10.1007/s10980-011-9642-y.

Valeix, M., Chammaille-Jammes, S. and Fritz, H. (2007). Interference competition and temporal niche shifts: elephants and herbivore communities at waterholes. *Oecologia 153*(3):739-748. doi:10.1007/s00442-007-0764-

Van de Bogert, M. C., Carpenter, S. R., Cole, J. J., & Pace, M. L. (2007). Assessing pelagic and benthic metabolism using free water measurements. *Limnology and Oceanography-Methods, 5*, 145-155. doi: DOI 10.4319/lom.2007.5.145

Vanni, M. J. (2002). Nutrient cycling by animals in freshwater ecosystems. *Annual Review of Ecology and Systematics, 341*-370.

Vannote, L. R., Minshall, W. G., Cummins, W. K., Sedell, R. J., & Cushing, E. C. (1980). River continuum concept. *Canadian Journal of Fisheries and Aquatic Sciences, 37*, 130–137.

Vavra, M. (2005). Livestock grazing and wildlife: developing compatibilities. *Rangeland Ecology & Management, 58*(2), 128-134.

Veldhuis, M.P., Ritchie, M.E., Ogutu, J.O., Morrison, T.A., Beale, C.M., Estes, A.B. Mwakilema, W., Ojwang, G.O., Parr C.L., Probert J. (2019). Cross-boundary human impacts compromise the Serengeti-Mara ecosystem. *Science 363*, 1424-1428.

Vörösmarty, C. J., McIntyre, P. B., Gessner, M. O., Dudgeon, D., Prusevich, A., Green, P., ... & Davies, P. M. (2010). Global threats to human water security and river biodiversity. *Nature, 467*(7315), 555-561. https://doi.org/10.1038/nature09440

Wallace, J. B., Eggert, S. L., Meyer, J. L., & Webster., J. R. (1997). Multiple trophic levels of a forest stream linked to terrestrial litter inputs. *Science, 277*, 102–104. https://doi.org/10.1126/science.277.5322.102

Wanderi, E. W., Gettel, G. M., Singer, G. A., & Masese, F. O. (2022). Drivers of water quality in Afromontane-savanna rivers. *Frontiers in Environmental Science, 1846*. **https://doi.org/10.3389/fenvs.2022.972153**

Webster, J. R. (2007). Spiraling down the river continuum: stream ecology and the U-shaped curve. Journal of the North American *Benthological Society, 26*(3), 375-389.

Webster, J. R., & Benfield, E. F. (1986). Vascular plant breakdown in freshwater ecosystems. *Annual Review of Ecology and Systematics*, 567-594.

Webster, J. R., & Meyer, J. L. (1997). Organic matter budgets for streams: a synthesis. *Journal of the North American Benthological Society*, *16*(1), 141-161.

Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., & Mopper, K. (2003). Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental Science & Technology, 37*, 4702–4708.

Wenger, S. J., Subalusky, A. L., & Freeman, M. C. (2019). The missing dead: The lost role of animal remains in nutrient cycling in North American Rivers. *Food Webs, 18*, e00106.

Werner, B. J., Musolff, A., Lechtenfeld, O. J., de Rooij, G. H., Oosterwoud, M. R., & Fleckenstein, J. H. (2019). High-frequency measurements explain quantity and quality of dissolved organic carbon mobilization in a headwater catchment. *Biogeosciences, 16*(22), 4497-4516.

Wetzel, R. G. (1992). Gradient-dominated ecosystems: Sources and regulatory functions of dissolved organic matter in freshwater ecosystems. *Hydrobiologia, 229*, 181–198.

Weyhenmeyer, G. A., Fröberg, M., Karltun, E., Khalili, M., Kothawala, D., Temnerud, J., & Tranvik, L. J. (2012). Selective decay of terrestrial organic carbon during transport from land to sea. *Global Change Biology, 18*(1), 349-355.

Wiley, M. J., Osborne, L. L., & Larimore, R. W. (1990). Longitudinal structure of an agricultural prairie river system and its relationship to current stream ecosystem theory. *Canadian Journal of Fisheries and Aquatic Sciences, 47*(2), 373-384.

Williams, C. J., Frost, P. C., Morales- Williams, A. M., Larson, J. H., Richardson, W. B., Chiandet, A. S., & Xenopoulos, M. A. (2016). Human activities cause distinct dissolved organic matter composition across freshwater ecosystems. *Global change biology*, *22*(2), 613-626. https://doi.org/10.1111/gcb.13094

Williams, C. J., Yamashita, Y., Wilson, H. F., Jaffe, R., & Xenopoulos, M. A. (2010). Unraveling the role of land use and microbial activity in shaping dissolved organic matter characteristics in stream ecosystems. *Limnology and Oceanography*, *55*, 1159–1171.

Williamson, C. E., & Zagarese, H. E. (1994). Impact of UV-B radiation on pelagic freshwater ecosystems.

Williamson, C. E., Dodds, W., Kratz, T. K., & Palmer, M. A. (2008). Lakes and streams as sentinels of environmental change in terrestrial and atmospheric processes. *Frontiers in Ecology and the Environment*, *6*(5), 247-254.

Wilson, H. F., & Xenopoulos, M. A. (2009). Effects of agricultural land use on the composition of fluvial dissolved organic matter. *Nature Geoscience*, *2*(1), 37-41.

Wollheim, W. M., & et al. (2001). Influence of stream size on ammonium and suspended particulate nitrogen processing. *Limnology and Oceanography*, *46*(1), 1–13.

Wood, S., & Wood, M. S. (2015). *Mixed GAM Computation Vehicle with Automatic Smoothness Estimation*. Package “mgcv.” R package version 1.29. R Cran, Vienna, Austria.

Wood, S. N. (2017). *Generalized additive models: An introduction with R 2 An Introduction with R. Generalized Additive Models*, 10, 9781315370279.

Woodward, G., Gessner, M. O., Giller, P. S., Gulis, V., Hladyz, S., Lecerf, A., ... & Chauvet, E. (2012). Continental-scale effects of nutrient pollution on stream ecosystem functioning. *Science, 336*(6087), 1438-1440.

Wu, Y., Zhang, J., Li, D. J., Wei, H., & Lu, R. X. (2003). Isotope variability of particulate organic matter at the PN section in the East China Sea. *Biogeochemistry, 65*(1), 31-49.

Xenopoulos, M. A., Downing, J. A., Kumar, M. D., Menden- Deuer, S., & Voss, M. (2017). Headwaters to oceans: Ecological and biogeochemical contrasts across the aquatic continuum. *Limnology and Oceanography, 62*(S1), S3-S14.

Yamashita, Y., Cory, R. M., Nishioka, J., Kuma, K., Tanoue, E., & Jaffé, R. (2010). Fluorescence characteristics of dissolved organic matter in the deep waters of the Okhotsk Sea and the northwestern North Pacific Ocean. *Deep Sea Research Part II: Topical Studies in Oceanography, 57*(16), 1478-1485.

Yillia, P. T., Kreuzinger, N., & Mathooko, J. M. (2008). The effect of in-stream activities on the Njoro River, Kenya. Part II: Microbial water quality. *Physics and Chemistry of the Earth, Parts A/B/C, 33*(8-13), 729-737.

Young, R. G., & Huryn, A. D. (1999). Effects of land use on stream metabolism and organic matter turnover. *Ecological Applications, 9*(4), 1359-1376.

Young, R. G., Matthaei, C. D., & Townsend, C. R. (2008). Organic matter breakdown and ecosystem metabolism: functional indicators for assessing river ecosystem health. Journal of the North American *Benthological Society*, *27*(3), 605-625.

Yu, H., Song, Y., Gao, H., Liu, L., Yao, L., & Peng, J. (2015). Applying fluorescence spectroscopy and multivariable analysis to characterize structural composition of dissolved organic matter and its correlation with water quality in an urban river. *Environmental Earth Sciences, 73*(9), 5163-5171.

Zampella, R. A., Procopio, N. A., Lathrop, R. G., & Dow, C. L. (2007). Relationship of Land- Use/Land- Cover Patterns and Surface- Water Quality in The Mullica River Basin 1. JAWRA *Journal of the American Water Resources Association, 43*(3), 594-604.

Zuur, A. F., Ieno, E. N., Walker, N. J., Saveliev, A. A., & Smith, G. M. (2009). *Mixed effects models and extensions in ecology with R* (Vol. 574). New York: Springer.

APPENDICES

Appendix I: Means (±SD) of DOM fluorescence and absorbances indices and intensities of the 6 PARAFAC components (C1-C6) across stream order 1-7 in the Mara River during the study period.

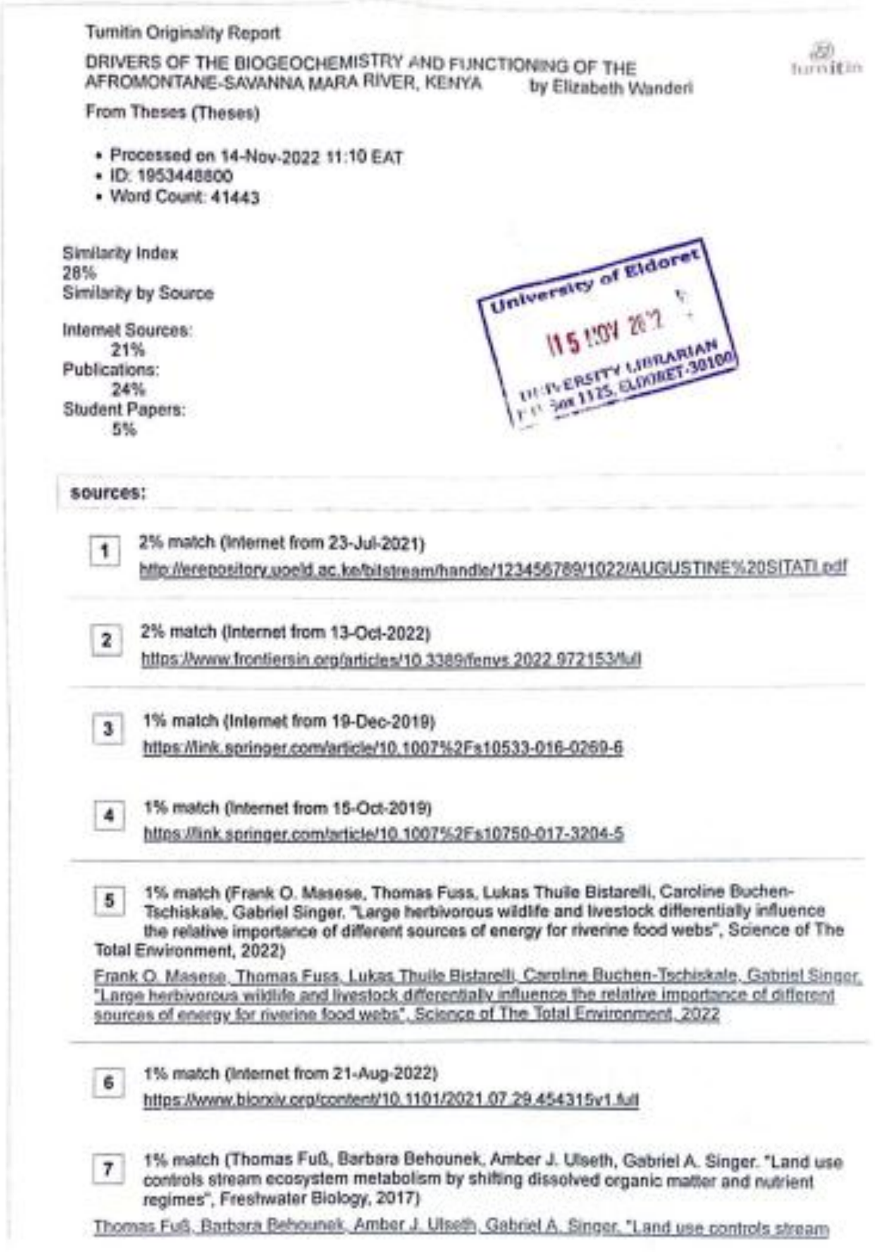
DOM Composition	**1&2**	**3**	**4**	**5**	**6**	**7**	**F - value**	***p*-value**
SR	1.02±0.15^b	0.98±0.15^a	0.98±0.14^a	0.92±0.06^a	1.02±0.14^b	1.19±0.17^b	2.31	0.06
E2:E3	3.96±0.59^a	4.19±0.81^a	4.04±0.22^a	3.80±0.23^a	4.03±0.39^a	4.31±0.52^a	0.74	0.60
E4:E6	3.09±0.38^a	2.92±0.43^a	2.94±0.32^a	3.08±0.40^a	7.70±16.58^a	2.61±0.48^a	0.76	0.58
a255: a365	3.78±0.56^a	4.02±0.77^a	3.79±0.27^a	3.59±0.23^a	3.82±0.47^a	4.09±0.53^a	0.82	0.54
SUVA254	4.72±1.62^a	4.38±0.89^a	4.52±0.66^a	4.79±0.78^a	4.60±1.55^a	4.11±0.86^a	0.28	0.92
FIX	1.49±0.04^a	1.49±0.04^a	1.48±0.03^a	1.47±0.02^a	1.47±0.02^a	1.48±0.01^a	1.46	0.22
HIX	0.84±0.04^a	0.81±0.08^a	0.81±0.07^a	0.80±0.04^a	0.81±0.04^a	0.88±0.04^a	1.67	0.16
Beta: Alpha	0.62±0.04^a	0.62±0.04^a	0.61±0.03^a	0.63±0.01^a	0.63±0.01^a	0.61±0.02^a	1.03	0.41

PARAFAC components	**1&2**	**3**	**4**	**5**	**6**	**7**	**F - value**	***p*-value**
C1	0.82 ± 0.45^{a}	0.72 ± 0.45^{a}	0.82 ± 0.84^{a}	0.33±0.07a	0.52 ± 0.30^{a}	1.11 ± 0.44^{a}	2.21	0.07
C2	1.11 ± 0.63^{a}	1.03 ± 0.61^{a}	1.15 ± 1.20^{a}	0.46 ± 0.09^{a}	0.82 ± 0.54^{a}	1.71 ± 0.71^{a}	2.11	0.08
C3	0.41 ± 0.22^{a}	0.35 ± 0.22^{a}	0.40 ± 0.39^{a}	0.16 ± 0.03^{b}	0.24 ± 0.14^{b}	0.52 ± 0.21^{a}	2.42	0.05
C4	0.26 ± 0.14^{a}	0.24 ± 0.16^{a}	0.27 ± 0.27^{a}	0.10 ± 0.02^{a}	0.18 ± 0.14^{a}	0.42 ± 0.20^{b}	2.43	0.05
C5	0.27 ± 0.13^{a}	0.26 ± 0.14^{a}	0.24 ± 0.13^{a}	0.16 ± 0.03^{b}	0.21 ± 0.07^{a}	0.25 ± 0.04^{a}	0.98	0.44
C6	0.15 ± 0.10^{a}	0.18 ± 0.16^{a}	0.14 ± 0.07^{a}	0.09 ± 0.04^{a}	0.13 ± 0.09^{a}	0.10 ± 0.06^{a}	0.78	0.57

***Means that do not share a letter (superscript) are significantly different, Tukey posthoc tests**

p-values marked with asterisks are significantly different among site categories at *p<0.05

Appendix IV: Similarity Report



Turnitin Originality Report

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Frank O. Masese, Thomas Fuss, Lukas Thuile Bistarelli, Caroline Buchen-Tschiskale, Gabriel Singer. "Large herbivorous wildlife and livestock differentially influence the relative importance of different sources of energy for riverine food webs", Science of The Total Environment, 2022

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