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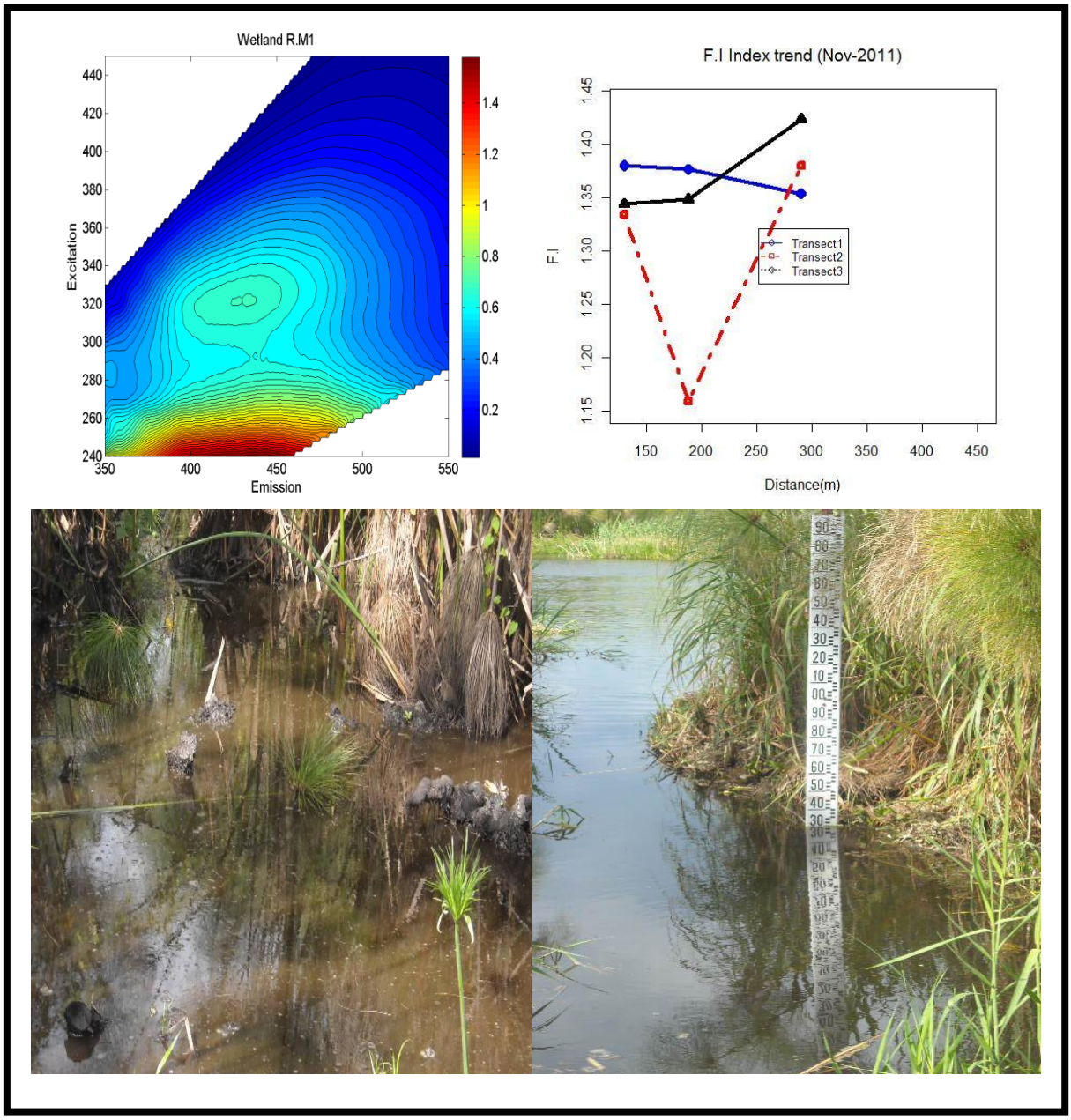

Nature and sources of dissolved organic carbon in the lower Mara River, Tanzania

Novati Philipo Kessy

MSc Thesis ES12.26
April 2012

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Master of Science Thesis
by

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This research is done for the partial fulfilment of requirements for the Master of Science degree at the UNESCO-IHE Institute for Water Education, Delft, the Netherlands

Delft
April 2012

The findings, interpretations and conclusions expressed in this study do neither necessarily reflect the views of the UNESCO-IHE Institute for Water Education, nor of the individual members of the MSc committee, nor of their respective employers.

Dedicated to my family, mother, wife, brothers, daughters and sons plus all nieces and nephews for their unconditional love.

Abstract

The Mara River is a transboundary river of Kenya and Tanzania starts in Mau highlands forests drains alongside Masai Mara national parks in Kenya and Serengeti in Tanzania and eventually drains its water to Lake Victoria. Environmental degradation through mining activities and planned dam construction is a challenge facing the basin. The overall objective of this study was to examine nature and sources of dissolved organic matter (DOM) in the lower Mara River in Tanzania. Specifically this study used, dissolved organic carbon (DOC), and dissolved organic nitrogen (DON) concentrations, as well as the optical properties of DOM, for comparisons in three different ecosystem types, including the main channel of the Mara River, three tributaries, and points in the papyrus wetland complex at the river mouth.

Three transects perpendicular to the flow of main river channel were created in the wetlands, while five sampling points were established in the main stem and four sampling points in the upstream tributaries of Tighite, Somonche and Tabora. Samples were collected twice in two periods which represented rainy and dry seasons. In addition, dissolved inorganic nutrients and other physical-chemical parameters were measured. Data were subjected to Shapiro and Bartlett for normality and Homogeneity tests respectively. Two way analyses of variances ANOVA was used to test significance difference between sampling periods and sites. Significant differences between sampling dates ($p<0.05$, $n=39$) were observed on DON, SUVA, Spectral slope, freshness index and coefficient. While lack of significance difference ($p>0.05$, $n=39$) were found on DOC, fluorescence index (FI) and protein peaks (T_{280}).

Higher FI values were observed in the main stem during January sampling (Wet period) as compared to November sampling (Dry period) suggesting microbial sources were originating from the soil and could be allochthonous despite higher FI values that were observed. Similar trend on DOC, DON, and FI were observed for both tributaries despite of different anthropogenic activities. Wetland transect have higher value DOC compared to the main river channel as well as upstream tributaries. DOM dynamics in wetland transects is governed by wet and dry cycle (Hydro period). This suggesting that during wet period the wetland transect connected to the main channel and exhibits relatively similar characteristics while during dry period the wetland is isolated from the main river channel.

Keywords: Nature and sources, Dissolved organic matter, dissolved organic carbon, fluorescence and absorbance.

Acknowledgements

I would like to take this opportunity to thank the un-ended lists of wonderful people and institutions who have provided physical and moral support, direction and assistance throughout the period of my study.

I would like to convey my sincere gratitude and thanks to my mentor **Dr. Gretchen.M.Gettel** for her Intellectual guidance, criticism, and corrections during the tenure of this study.

I also express my most sincere gratitude to **Dr. Anna Van Dam**. This work could not have been possible especially on data analysis without his help and support. His vast professional experience and advice about the fieldwork were the keys to collect the data for this study. Mwanza water quality laboratory is gratefully acknowledged for the use of laboratory facilities during nutrients analysis.

I would also like to express my sincerely thanks to NUFFIC for overall sponsoring of my masters study. Special thanks to **Dr. Michael McClain** coordinator of Mara flow projects for funding my research study in the lower Mara River. Last but not least, my employer, Ministry of water and irrigation for allowing me to undertake this study.

I thank my colleague **Jessica Salcedo**, for working together with me throughout the period of our study. Without her many things would not have been possible. I am also thankful to Madam **Clair Taylor**, whose lectures in English Academic Writing Course proved to be an excellent asset while writing this thesis.

I like to thank the Unesco-IHE laboratory staffs for helping with training and assistance in the laboratory

I finally thank my family, especially my wife Saida together with our children for their love, patience and understanding my long absence.

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List of symbols

List of abbreviations

BIX- biological-autochthonous index
CDOM - coloured dissolved organic carbon
DO - dissolved oxygen
DOC - dissolved organic matter
DOM - dissolved organic matter
DON - dissolved organic nitrogen
EC - electrical conductivity
EEM- excitation-emission matrix
FI - fluorescence index
GIS - Geographic Information System
GF/F -glass fibre filter
HIX - humification index
HQ - hydroquinone-like
IUCN - International Union for Conservation of Nature
NEP - net ecosystem production
POM - particulate organic matter
Q - Quinine-like
RI - redox index

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1 Background

1.1 Background

Organic matter plays a very important role in both terrestrial and aquatic life. Its concentration and composition both directly and indirectly influence biological processes (Aiken et al. 2011). Eutrophication of downstream waters has been reported and linked to excessive input of organic matter; however there are still gaps on understanding the sources of eutrophication. The current approaches only examined eutrophication as results of excessive inorganic nutrient inputs (mainly: nitrate, nitrite and phosphate) while ignoring the contribution of nutrient from organic matter particularly dissolved organic nitrogen (DON) after mineralisation (Ryther et al 1971). High input of dissolved organic matter in rivers and streams presents can present a challenge when it comes to drinking water supply. Several impacts related to dissolved organic matter has been reported, includes formation of disinfection by products (DPBs) that is major precursor to carcinogenic trihalomethanes (Imai. et al 2001) and it may enhance mobility of pesticides (Williams et al., 2000) and heavy metals (Li et al., 1997)

However, in riverine ecosystem dissolved organic matter plays a significant role. Literally it is believed to be the "stuff of life" as it sustains and supports life of heterotrophic organisms through provision of energy. Moreover, in aquatic ecosystem dissolved organic matter involved in various essential biogeochemical processes and chemical reactions such pH buffering, light attenuation, mobility and transport of trace metals and transformation of different compounds that may have effect in the system. Indeed, large amount of CO_2 out-gassing from inland waters was linked to organic matter processing. Typical amount range from 1000ppm to 12000ppm in rivers (Cole et al 2001) to more than 10000ppm in lakes and reservoirs (Sobek et al 2005)

Sources of DOM in inland and coastal waters are classified as either allochtonous or autochthonous. Allochtonous DOM is originated outside the ecosystem, mainly from the degradation of terrestrial plant matter, which is dissolved and transported through river systems and estuaries to the ocean or lake environment. Meanwhile, autochthonous DOM is results of exudation by aquatic plants both in littoral and pelagic zones, and their degradation is also important sources of DOM in natural waters (Nagata, 2002; Carlson, 2002). Bioavailability of organic matter in aquatic ecosystem is important when it comes to ecosystem sustenance, in water organic matter exists in two major forms; first organic matter can either be truly dissolved and second they can associate with colloids or bound to particles. The distinction between two forms of organic matter is based on the size of molecules that is done by filtration usually through 0.45µm filter (Aiken et al., 1993). Overlapping between the dissolved and particulate fractions is the colloidal fractions, which consists of suspended solids operationally considered as solutes (Morel and Gschwend, 1987)

In chemical composition both dissolved and particulate organic matter forms consists of complex heterogeneous mixture of aromatic and aliphatic hydrocarbons with higher and lower molecular weight compounds. The distinction between two is due to the fact that the later include the particulate organic carbon in the sediments. Due to organic matter

role in aquatic environment, it is important to study its dynamic in aquatic system and composition in various environmental compartments. This has been possible through spectroscopic analysis of optically active fraction of dissolved organic matter called coloured dissolved organic matter -CDOM (Stedmon et al., 2003). Two major DOM components that have been identified in natural waters and found to fluoresce are humic-like material and protein-like fractions (Coble 1996). The presence of humic and fluvic acids have been found to indicate of terrestrially origin dissolved organic matter while protein like compounds such as tyrosine and tryptophan indicate aquatic source dissolved organic matter (Mopper and Schultz, 1993). Humic and fluvic acids which are responsible for the yellowish-brown discoloration in water are considered to be the product of lignin and cellulose degradation (Thurman et al., 1985)

Regardless of the achievement made on the use coloured fractions of CDOM, still there is a lot to be done. The study of nature and environmental significance of organic matter in natural waters is hampered by its chemical complexity, and low concentration of dissolved organic matrix found in water (Thurman. 1985) limit our ability to define both dissolved organic matter composition and reactivity (Aiken et al., 1993). With the use of optically active fraction of DOM, a variety of so called simplest approaches has also been developed to supplement the study of dissolved organic matter, this approaches include determination of dissolved organic phosphorus (DOP), dissolved organic nitrogen (DON) and dissolved organic carbon (Quallis & Richardson, 2003)

1.2 Problem justification

This research study focused on the lower Mara River basin in Tanzania. The basin supports both wildlife (e.g. Masai-Mara and Serengeti national parks) and the livelihoods of more than 10 million people, through subsistence activities as well as through the tourist economy of the parks. The last two decades has seen an upsurge in population migration to the basin which comprised of mainly commercial and subsistence farmers and investors in the tourism sector (Gereta et al., 2002). This has come with increased demand for agricultural land, extraction of water for subsistence agriculture and domestic use, irrigation farming and discharge of domestic sewage to rivers and streams.

Soil erosion has resulted from farming activities in the MRB, and presents the greatest challenge to water quality (Mati 2005). Moreover, studies done by World Wildlife Fund/Global Water for Sustainability (WWF/GLOWS) between 2005 and 2007 have found that the Mau Forest Complex (MFC) which is located in the Kenyan side annually releases tons of sediments that contain nutrients and organic matter into the Mara River. Mara river basin (MRB) and its watershed are experiencing very high deforestation rates leading to reduced amount of water flowing in the river during the dry season and severe negative impacts on water quality from both sediments eroded from farms and discharge of untreated sewage. This poses a threat to the river's flow and quality and eventually diminishes the river's ability to continue providing year-round benefits to downstream users and ecosystems.

For example, in the lower Mara River Tanzanian side the river almost passes and bordered the great Serengeti national park, which is believed to be the back bone for tourism in Tanzania. However, massive migration of wildebeest from Serengeti Nation Park in Tanzania to Masai Mara national park in Kenya each year during dry seasons

has been linked and evidence to insufficient water to downstream ecosystem. Furthermore, the Mara waters passes and filtered in the connected papyrus wetlands before reach Lake Victoria, which is believed to be major supplier of freshwater to, among others, Tanzania, Kenya, and Uganda (UNEP 2002).

This research study focuses on characterizing DOM in the lower Mara River. Dissolved organic carbons (DOC), dissolved organic nitrogen (DON) were used to characterize DOM pool. The optical characteristics of DOM were used to determine quality and source (autochthonous and allochthonous), by using both fluorescence and absorption. Three ecosystem-types were studied, and included tributary streams, the main stem of the Mara River, and cross-sectional transects in papyrus wetlands.

1.3 Goal and objectives

The overall objective of this study was to characterize DOM concentration and quality in three different types of ecosystems in the Lower Mara River basin in a wet and dry period

1.4 Specific objectives

- ✓ To examine DOC, DON, and DOP concentration and determine spatial variability between the main channel, tributary streams, and wetlands in the lower Mara River.
- ✓ To determine dissolved organic matter sources by comparing optical characteristics between the main channel, tributary streams and the wetland
- ✓ To examine the relationships between DON as a component of DOM with inorganic nutrient availability

1.5 Research questions

- ✓ Do DOC, DON and DOP of the main channel, tributaries and the wetlands differ?
- ✓ Do the fluorescence properties of DOM in the upstream catchment differ from the Mara wetlands downstream?
- ✓ Are the main sources of DOM in the Mara catchment allochthonous or autochthonous?

2 Literature review

2.1 DOM Sources

Different types of OM both in dissolved and particulates are transported by rivers and streams. According to Raymond (2001) about $4x10^{14}$ grams of organic matter is exported to oceans and lakes via river and streams annually. The origin and sources of organic matters differ significantly. Literally organic matter has two sources; first, autochthonous DOM when it is produced within (in-situ production) the ecosystem and second, allochtonous when it is regenerated outside the system (Richardson et al., 2004).

In aquatic system in this case allochtonous originate from terrestrial ecosystem while autochthonous it is regenerated within the system. Generally, large part of allochthonous DOC is refractory and therefore physical chemically protected from microbial degradation. It has been hypothesized in various literatures that upon entrance into streams allochthonous DOC is photo-bleached and converted into low molecular weight compounds which can easily degraded by microbes.

Mostly, autochthonous DOM results from riverine metabolisms by primary producers; primarily algae and phytoplankton and autolysis of aquatic macrophytes as well as extracellular exudates (Fellman et al., 2010; Kowalczuk et al., 2010). On the other hands, allochtonous sources of organic matter to aquatic system are of terrestrial origin. For instance, in forested area leaves are the primary contributor of allochtonous input (Richardson et al., 2005), however, in some cases aquatic animal may also contributes substantially (Wipfli and Musslewhite, 2004)

2.2 The role of inland waters on carbon transformations

In contrary to old school of thought described by Leopold (1983) that rivers are just conduits linking terrestrial with aquatic ecosystem, rivers, streams and other inland waters are seems as important features in the landscape which transport, process and link the products of terrestrial ecosystem with aquatic and atmosphere.(Cole et al., 2007). Recently it has been revealed that bioactive element for instance discharged to the ocean by rivers is just a fraction of the amount that was entering in the rivers from the terrestrial ecosystems via soil respiration, leaching, chemical weathering and physical erosion (Aufdenkampe et al. 2011)

Some of the element like carbon and nitrogen is respired/ oxidized rather and eventually returned to the atmosphere in the form of carbon dioxide (CO_2) and di-nitrogen oxide respectively before reaching the oceans or is stored within river corridors as sedimentary organic carbon (OC) after erosion and transport from distant sites. Therefore taking into consideration the importance of this transformation it is clear that rivers and streams can affect carbon cycle at local and regional scale.

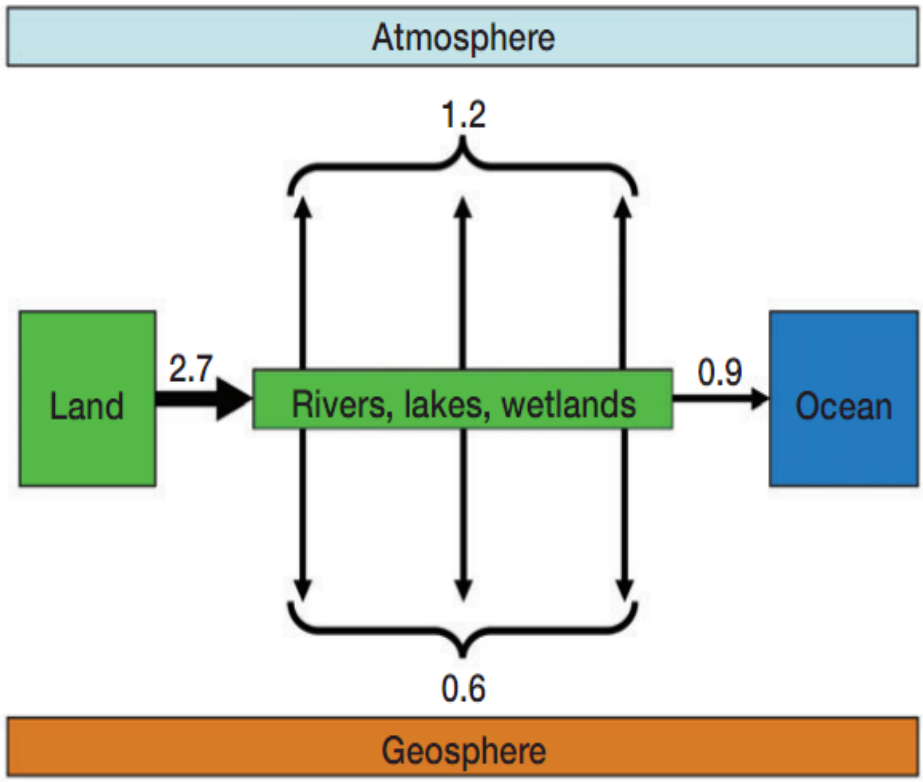


Figure 1: Roles of river in transformation of bioactive elements in Pg of C per year (Source: Aufdenkampe et al. 2011)

2.3 Processing and partitioning of organic matter in aquatic ecosystem

Streams are sites of organic matter cycling and habitat for biofilms, macroinvertebrates, fish and amphibians (Gomi, et al., 2002). These organisms process organic matter to gain energy for growth and reproduction. Thus organic carbon entering or produced in streams undergoes physical and chemical transformations (Abelho, 2001). It is in this line that leaves falling in streams in the form of POC are subjected to physical abrasion, microbial degradation and invertebrate fragmentation.

According to (Hieber and Gesner, 2002) this breakdown is a result of three processes: (i) Leaves start losing soluble organic and inorganic material shortly after immersion in water; (ii) they are thereafter colonized by a variety of aquatic microbes mainly consisting of fungi and bacteria which degrade complex organic compounds; and (iii) mechanical and invertebrate fragmentation follows microbial colonization.

Microbial softened leaves may also be fragmented and further abrased when redistributed by flow.

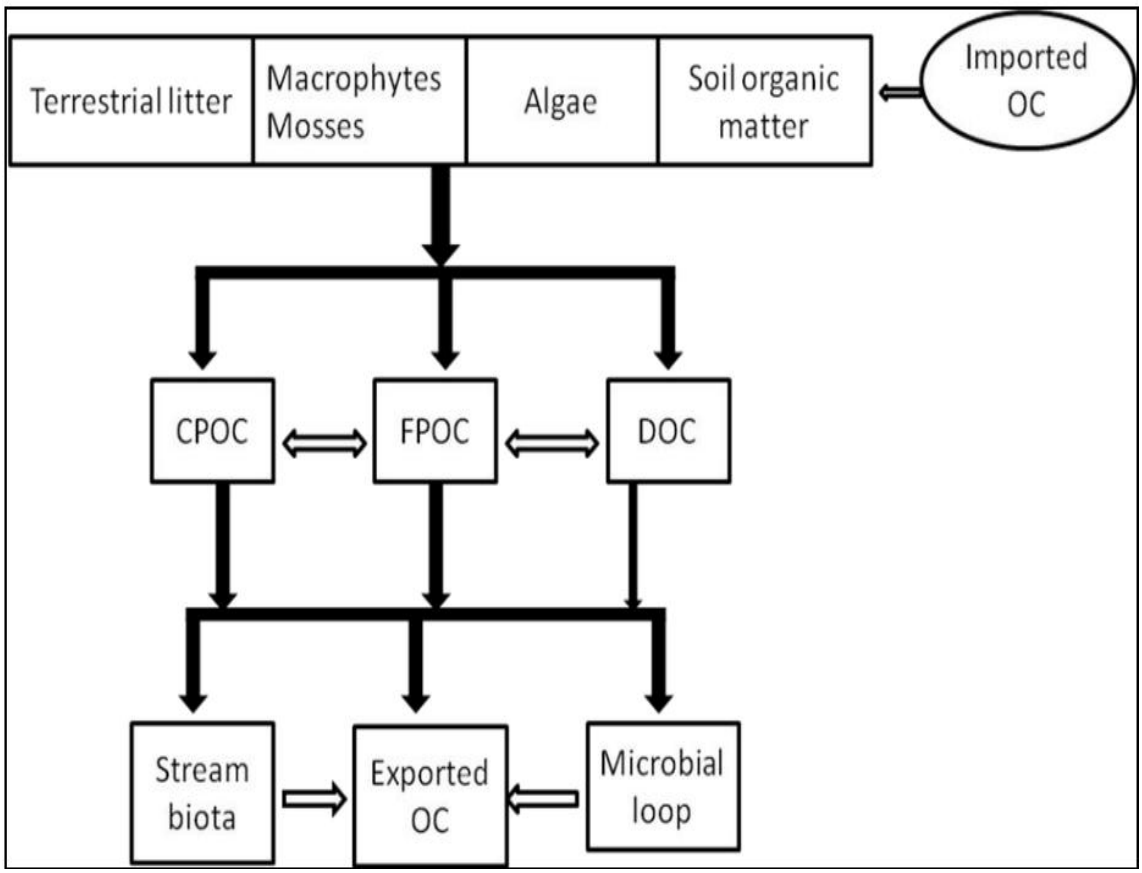


Figure 2: Simplified conceptual carbon fluxes in a streams ecosystem
(**Source:** Allan, 1995)

2.4 Importance of DOM in ecology

Dissolved organic matter is attracting the attention of ecologists due to its effects on the physical, chemical, and biological properties of freshwater systems (Gergel et al. 2002). By attenuation of solar radiation for example, Chromophoric DOC which includes humic fractions is known to provide sunscreen to microscopic flora and fauna within the aquatic ecosystems (Morris 1997; Schindler 1997), but it may also reduce primary productivity by decreasing transparency in an aquatic ecosystem. Fluvic and humic acids of DOM have been reported to influence the acid–base chemistry of freshwaters (Stephenson 1988); they can also act as electron shuttle, contributing to energy transfer via hyporheic exchange in aquatic system (Miller et al 2006). This in turn affects the cycling of metals like mercury, copper and aluminium, thereby influencing the amount of trace metals found in aquatic organisms. DOM can also support bacterial secondary production and influence the availability of some forms of labile phosphorus to phytoplankton. Phytoplankton releases a large portion of its cell material to the open water as extracellular DOM (Cole et al 2001).

DOM pool is colourless and is composed primarily of carbohydrates and amino acids that are immediately metabolized by bacteria. Aquatic macrophytes within the littoral zone can also secrete DOM, but the decomposition of these labile form of DOM which is believed to fuel the food webs aquatic ecosystem is often very rapid, may happen within about 48hours, and these compounds therefore constitute only a small proportion of DOM in natural waters (Gergel et al. 2002).

Opposed to these autochthonous DOM sources, allochthonous DOM can enter the stream through various pathways from the terrestrial environment: precipitation, leaching or decomposition. Productive wetlands can produce massive amounts of coloured DOM made up of fulvic and humic acids. These forms of DOM are considered as products of the degradation of lignin and cellulose (Engstrom 1987). Part of DOM in natural freshwaters is composed by these coloured fractions of allochthonous compounds. Coloured DOM can therefore be used as an indicator of organic loading in streams and terrestrial processing and a high degree of variability is seen across different ecosystems. Although most DOM is natural in origin, concentrations and major characteristics including molecular composition are therefore largely a function of catchment landscape features (Bernardes et al. 2004).

The loss of organic carbon from terrestrial ecosystems through respiration and its burial in inland waters has been identified as an important redistribution of carbon sinks and climate change mitigation strategies (Battin et al. 2009).
Streams and rivers have been identified as important sites for respiration of terrestrially derived organic carbon (Kaplan et al. 2008; Battin et al. 2009), which has led to the shift from the traditional view of these systems as mere conduits of organic matter from the continents to the oceans (Cole 2007). Though previous studies have confirmed that streams, rivers and estuaries produce remarkable amounts of CO_2 out gassing to the atmosphere, a better understanding of the mechanisms by which fluvial ecosystems achieve this high metabolic performance based on relatively persistent terrestrial and soil organic matter is still lacking (Battin et al. 2009).

2.5 DOM Characterization

In the aquatic environment dissolved organic matter (DOM) is a mixture of compounds with different structures and a wide range of molecular weight (Seredynska et al., 2007) Characterization of these compounds to understand their role in ecosystem function is important (Baker et al., 2004). Some of these compounds have been identified in natural water and their composition constitutes of carbohydrates, amino acids, hydrocarbons, phenol acids and humic substances (Paula, 1996). These compounds arises from different processes mainly the chemical and microbial degradation of animal and plant materials (Thurman, 1985).

Humic substances (Humic and fluvic acids) are known to comprise a high percentage of DOM (Friedrich et al., 1997); various literatures suggest that it result to yellowish-brown especially when DOC concentration is high. These fractions of dissolved organic matter have optical properties that facilitates absorption of visible light and ultraviolet light (Paula G 1996) as well as fluorescence emission when there is excitation. In some cases absorption and excitation are followed by fluorescence, this occur when an exited electron in an atom loose energy in form of light when returns to original energy level. The intensity of fluorescence light produced after excitation depends on the amount of compounds present in that particular sample. In brief, optical property of OM both absorption and fluorescence have been extensively studied in various aquatic environment to examine the source and transformation of organic matter

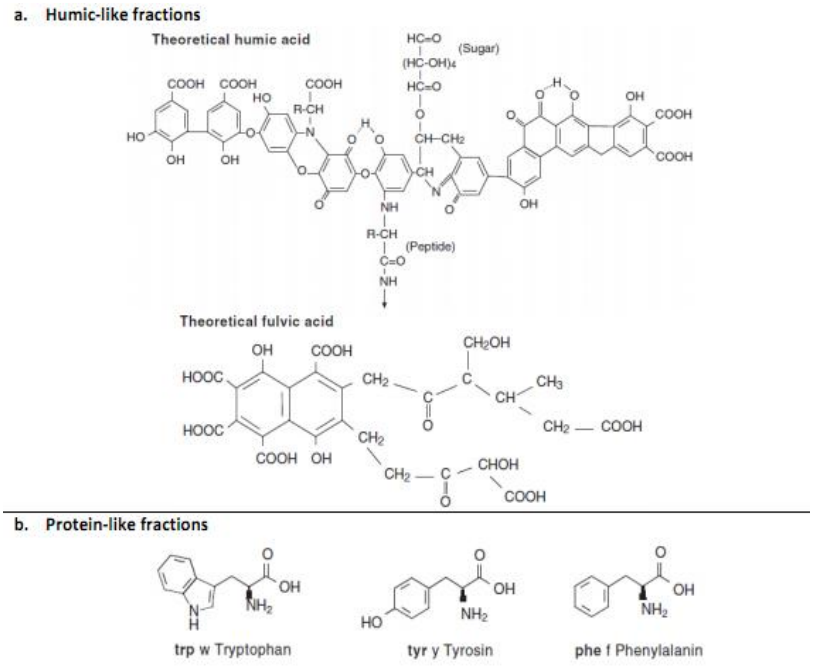


Figure 3: DOM structure showing humic, fluvic acid and protein like fractions components (**Source:** Adopted from Hudson *et al*., 2007)

2.5.1 Spectroscopy technique

In recent years the need for organic matter characterisation among different disciplines has increased tremendously. Water supply engineers for examples requires a proper understanding on the amount and chemical composition of DOC in order to decide proper treatment procedures to be undertaken. Various works has been done to study DOC and a good relationship has been established between the absorbance properties of natural waters and DOC concentration due to the broad variety of chromophores that can be found in the DOM pool.

Moreover, several indices has been discovered and currently used to provide information regarding DOM absorbance spectrum and reactivity of DOM. The indices includes absorption coefficient at various wavelength (eg λ=254, λ=340), spectra slopes (Stedmon et al. 2001), slope ratio (Helms, et al 2008) and SUVA at 254nm (Weishaar 2003). The achievements were made possible through the use of UV-Vis Spectroscopy; this is a technique for measuring absorbance of water or any other environmental samples at a specified wavelength. Absorbance property of DOM has been used for identifying functional groups in a molecule, because the bonds responsible for the absorption of UV-Vis radiation are related to specific absorption wavelengths. (Skoog.1985).The absorbance spectrum of DOM can be modelled using equation as described by Stedmon et al 2001

$$a_{\lambda} = a_{\lambda o} e^{s(\lambda o - \lambda),}$$

Where a_{λ} is Naperian absorption coefficient of a certain wavelength, aλo is absorption coefficient at a reference wavelength (commonly 400nm), and S is spectra slope coefficient describing the shape of absorbance curve (Stedmon et al., 2001)

Spectra slope (S) values have been used to indicate the presence of humic acids, lower spectra slope have been observed for terrestrial derived DOM sources and higher value to autochthonous derived DOM.

Helms et al (2008) proposed the spectra slope ratio (SR), which is a dimensionless ratio of the shorter wavelength region (275-295nm) divided by the slope of the longer wavelength region (350-400nm) as an improvement to spectra slope (S) proposed by Stedmon et al., (2001). The slope ratio (SR) has been strongly inversely correlated to the average molecular weight of DOM (Helms. 2008)

The Specific Ultraviolet Absorbance (SUVA254) as mentioned earlier is an index which can be computed by ratio of absorbance coefficient of water sample at a wavelength of 254nm in inverse meters (m-1) divided by dissolved organic carbon concentration in milligram per litre (Weishaar, 2003)

As alternatives to other approaches SUVA254 index has been suggested to be useful tool for determining aromaticity in natural water. The efficacy of the index has been tested and compared of with isotope techniques (^{13}C NMR) by Weishaar 2003 and many studies have verified that SUVA is an excellent proxy for aromatic content of DOM (Cory et al. 2007)

Index	Formular	Description	References
Specific UV absorbance at 254 nm (SUVA254)	Ratio of UV absorbance at 254 nm and DOC concentration	Indicator of aromaticity	Weishaar (2003)
Absorbance coefficient at 340 nm	UV absorbance measured at 340nm	Related to DOC concentration and CDOM	Baker and Spencer (2004)
Absorbance coefficient at 410 nm	UV absorbance measured at 410 nm	Related to DOC concentration and CDOM	Baker and Spencer (2004)
Absorption coefficient ratio (a_{254}/a_{410})	Ratio of a_{254} and a_{410}	Indicator of molecular weight and aromaticity	Baker et al., (2008)
Spectral slope (S)	refer formular	Related to the ratio of fulvic and humic acids	Bricaud et al., (1981)
Slope ratio (S_R)	Ratio of slope at higher wavelength to slope at lower wavelength	Related to molecular weight of DOM	Helms(2008)

Table 1: Indices used in characterisation of DOM (**Source**: Modified from Luzio. 2011 unpublished)

2.5.2 Fluorescence and Excitation emission matrix (EEM)

Recently, advancement in technology has made possible to use fluorescence characteristics of dissolved organic matter (DOM) to generate the excitation-emission matrix (EEMs) within 1 to 20 minutes time interval. In this part focus will be made on explaining fluorescence property of DOM and how EEM is produced. DOM molecules have a unique property, when exposed to light energy absorbs and later emits energy in form of light at different wavelengths. The absorption of light is due to the presence of chromophores structure within DOM molecules while fluorescence is through fluorophores structures (Mopper et al., 1996)

Ideally, when molecules in compound light energy it absorbs light and the electrons get excited and moves from lower energy level (Ground state-S_0) to higher energy level (S1). The extent of excitation is the one that determine the absorption wavelength of that molecules

In the course of relaxation of the molecules, the electrons loss (emission) energy in form of light and fall/return to lower energy level. The so called fluoro-spectroscopy methods have made use of the emitted light. The aim has been to measure the amount of light that is emitted (fluorescence) when the electron falls from higher to lower energy by the use of special detector. The emitted /fluorescence and excited/absorbed light are then arranged in the form of matrix (EEM) which provides information signals related to chemical composition, origin and processing of organic compound (Fellman et al., 2010)

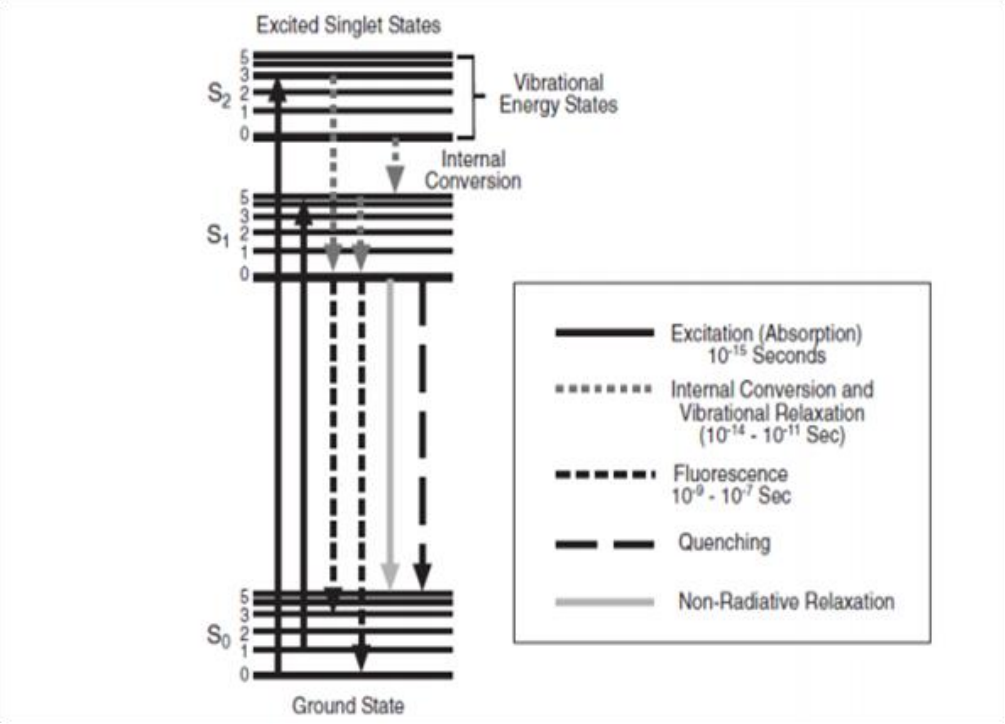


Figure 4: Shows mechanisms of excitation and emission of electrons (Source: Hudson et al., 2007)

An EEMs typically covers a range of excitation and emission wavelengths from ~ 200nm (short wavelength UV) through to ~550 nm (visible blue-green light) (Baker and Spencer 2004). Depending on the types and composition of fluorophores, characteristics and the intensity may vary significantly (Coble, 1996).
Fluorophores data can indicate the chemical properties of dissolved organic matter and distinguish its originality, for example terrestrial from microbial origin. According to Coble, 1996, there are five (5) major EEM peaks corresponding to different constituents of DOM. Peak A and C correspond to humic like, peak M correspond to marine humic like B correspond to protein like Tyrosine and peak T correspond to protein like Tryptophan (Coble, 1996). These peaks have been the basis for fluorescence comparisons in numerous studies over the years (Fellman et al. , 2010)

Peak name	Excitation Wavelength (nm)	Emission Wavelength (nm)	Type
A	250-260	380-480	Humic-like
C	330-350	420-480	Humic-like
B	225-237	309-321	Protein-like (Tyrosine)
	270-280	300-320	
T	225-237	340-381	Protein-like (Tryptophan)
	270-280	320-350	

Table 2: Freshwater aquatic fluorophores and their corresponding excitation-emission wavelength (**Source:** Coble, 1996)

Parameter	Description	References
Fluorescence index (FI)	Determine source of DOM, which is either: microbial (high FI ,1.8, derived from extracellular release and leachate from bacteria and algae) or terrestrially derived (low FI ,1.2, terrestrial plant and soil organic matter).	McKnight et al 2001 McKnight 2005
Freshness index (α: β)	Indicator of the contribution of recently produced DOM, where b represents more recently derived DOM and a represents more decomposed DOM.	Parlanti et al 2000
Humification index (HIX)	Indicator of humic substance content or extent of humification. The HIX is based on the idea that the emission spectra of fluorescing molecules will shift toward longer wavelengths (due to lower H:C ratios) as humification of DOM proceeds. Higher values indicate an increasing degree of humification.	Zsolnay et al 1996
Redox index (RI)	Oxidation state of DOM fluorescence.	Miller et al.2006

Table 3: Showing Indices used to quantify the fluorescence properties of DOM (Modified from Fellman et al., 2010)

3 Materials and Methods

3.1 Site description

The following table summarise sampling stations, their descriptions and abbreviation as used in this study.

Site name	Description	Abbreviation
Main stem		
TS Bridge	The most upstream sampling station in the main stem river, it is downstram to Tobora stream confluence, sampling point was established upstream the Bridge to reduce the effluence from the bridge	TS
Mara mine	The has nothing to do with mining, indeed the station is far from the mining of golg, this station station established at the mining pump house	MM
Wetland upstream	Sampling station in the main channel at the wetland, this was assumed to represent the most upstream point of the wetland as it was difficult to access the most upstream due to payrus blockage	WU
Wetland middle	Sampling point at the main river channel in the wetlands, to finf fishermen is usually the case at this point	WM
Wetland river mouth	The site is about 10km downstream to Kirumi bridge This site was assumed to represent the most downstream site, and the samples was colected about 1km from the lake to reduce the effluence from lake	RM
Tributaries		
Tighite upstream	The site is almost out side the mining activities therefore it was assumed to represent relative pristine characteristics of tighite catchment. The sample was collected at the upstream the bridge	TU
Tighite downstream	The site is downstream to Mining company and was assumed again to cointained signals as a results of mining activities	TD
Tabora	The site was established at the bridge, the catchment is free from mining activities and on Serengeti side so was assumed to be relatively prestine acompared to Tighite.	TB
Somoche	In the past the stream used to be seasonal, but recently it used to flow throughout, also the stream was assumed to present pristine conditions compared to Tighite.	SM

The trans-boundary Mara basin covers 13,834 km^2 and is located roughly between longitudes 33^{0}47' E and 35^{0}47'E and latitudes 0^{0}38' S and 1^{0}52' S. The upper 65% of the area (8,941 km2) is in Kenya, while the remaining lower portion is in Tanzania (Figure: 6). The 395 km long Mara River system has for a long time been considered as one of the most endangered river draining into Lake Victoria (Mati 2005).

The river also forms part of the upper catchments of the Nile basin. The altitudes range from 2,932 m at its source in the Mau Escarpment to 1,134 m on Lake Victoria. The main perennial tributaries in the upstream catchment Kenyan side are the Amala and the Nyangores, which drain from the western Mau escarpment. On the Tanzanian side, Rivers *Tabora, Somonche* and *Tighite* drain the basin.

Rainfall varies with altitude with mean annual rainfall ranging from 1,000-1,750 mm in the Mau Escarpment, 900-1,000 mm in the middle rangelands to 700–850 mm in the lower Loita hills and around Musoma. Rainfall seasons are bi-modal (Figure: 5), falling between April and September, and again between November-December (Mutie et al 2000).

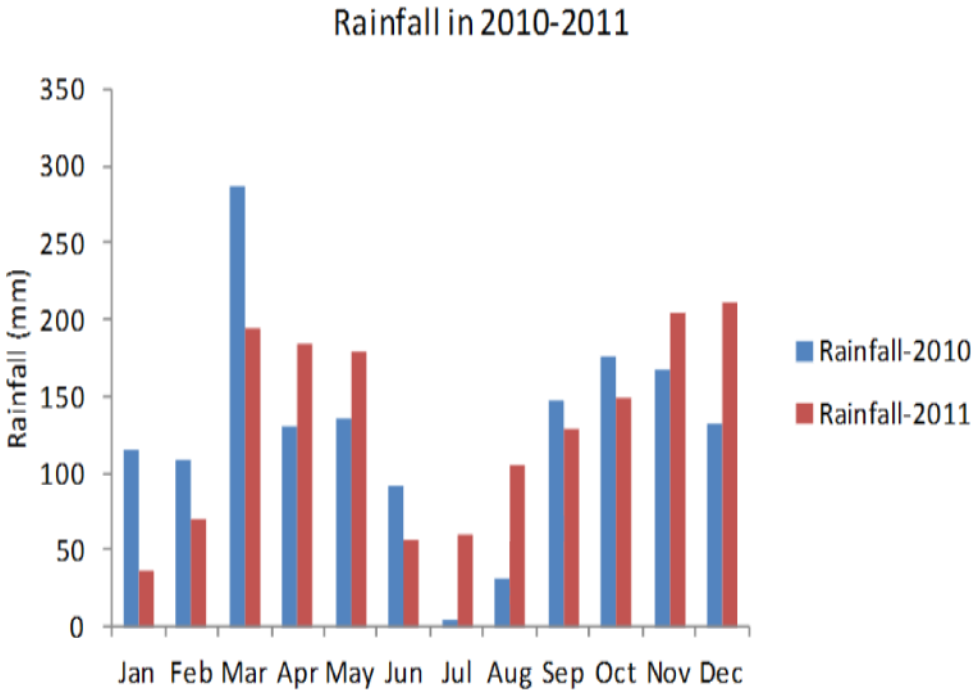


Figure 5: Rainfall trends in lower Mara sub-basin (**Source:** LVBWO, 2011)

3.2 Sampling

To accomplish the objectives of this study eighteen (18) sampling sites were established, five from the main Mara River, four from upstream tributaries of Tighite, Tabora and Somonche and nine from transects (Figure: 6). With the exceptional of Tighite stream where two sampling sites were established to cover the upstream and downstream of Tighite sub-catchment, only one sampling site was established in Tabora and Somonche sub-catchments and this is due to the physical in-accessibility of the upstream part of the stream.

Also to capture the DOM quality signal of the three tributaries to the main stem, two sampling sites were established at the main stem, one station was established at about 2 km downstream to Tabora-Mara confluence and the other site was established at about 5 km downstream to Somonche-Mara confluence (Figure: 6). Site could not be established in the main stem at the confluence with Tighite or downstream due to physical inaccessibility of the area. However, during sampling at the wetlands, one site was established at the far most to the upstream. Moreover, to observe the effect and contribution of the wetlands to the main stem three transects were established at the lower Mara wetland just upstream to Kirumi Bridge with three sampling sites at each transect and three sampling sites at the main stem within the wetland.

3.3 Mara river basin

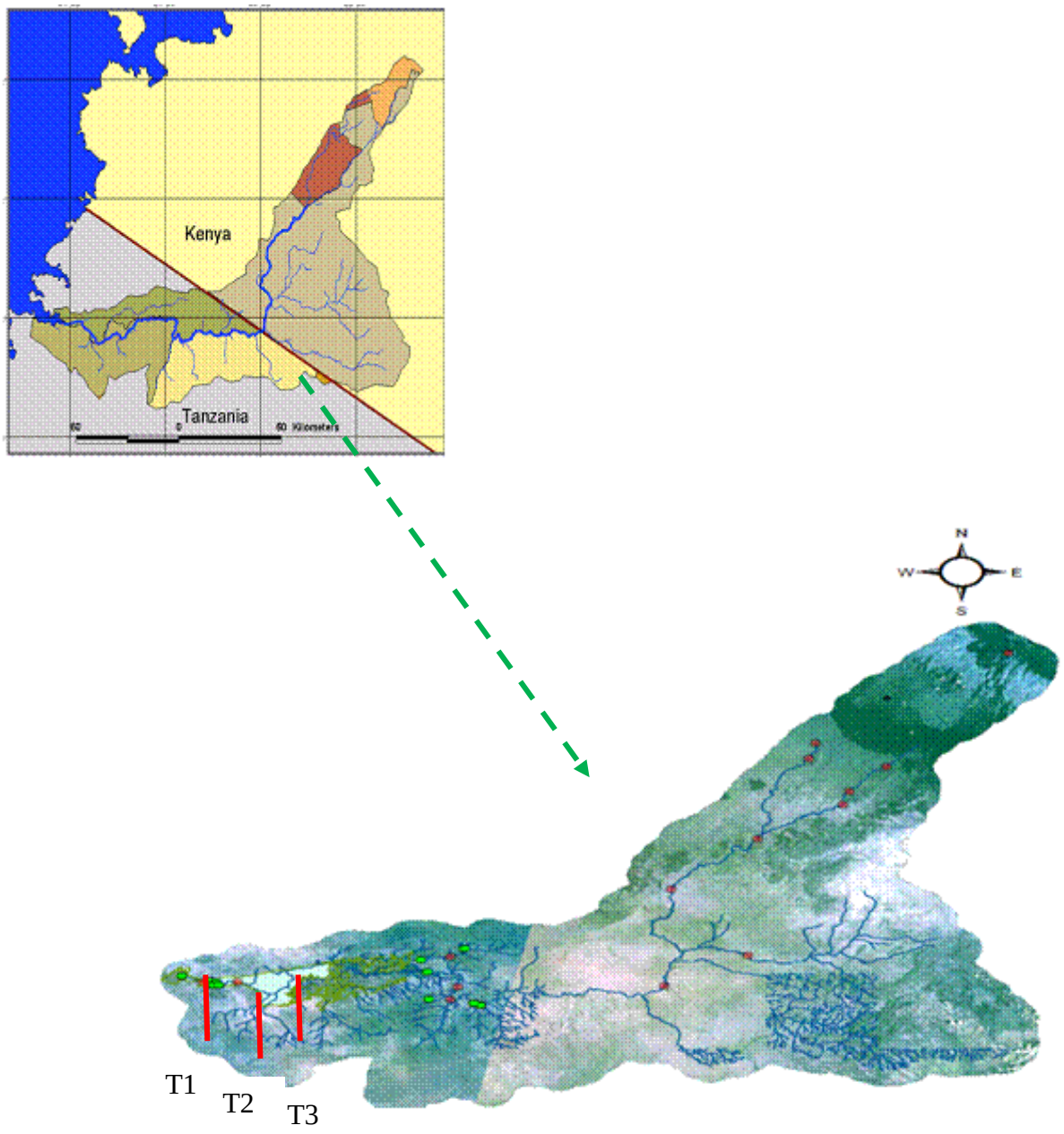


Figure 6: Mara basin water quality sampling network. The red lines are presenting three transects established at the Mara wetland. The distance between transect is about 5km

3.4 Sample collection and storage

Water samples were collected in two rounds; the 1st round was on 29th November, 2011 and 2nd round on 3rdJanuary, 2012. November sampling was assumed to represent dry period, this is due to the fact that was done just at the begging of autumn season. Meanwhile, January sampling was assumed to represent the wet-period as the sampling was done in at the middle of autumn season. Grab water samples in the wetlands and tributaries were collected at depth about 50cm. At each sampling site, dissolved oxygen (DO), Electrical conductivity (EC), pH, and temperature were recorded on site (Figure 7) using MAJI-meter (WAG-WE5100).

Water samples for nutrients were stored in acid-washed plastic bottles. Samples for fluorescence excitation emission matrix(FEEM) and DOC were filtered on site using pre-combusted (550^0C for 5hrs) whatman GF/F filters and acidified to pH <2 with sulphuric acid as described by Kaushal&Lewis (2003). Low pH has been used elsewhere by Edward et al. (1983), although it has shown that variation in pH can alter the EEMs of DOM (Mobed et al. (1996, Spencer et al 2004). The samples were stored in an amber glass bottles (120mL), which were combusted at 550^0C to remove inorganic carbon contamination. Samples were stored in cooler box ready for transportation to Mwanza laboratory for analysis and further storage for analysis at UNESCO-IHE, Delft, the Netherlands.

Figure 7: In situ physical chemical measurements at Mara mine station (Tanzania)

3.5 Analytical measurement

3.5.1 Nutrients measurements

Analysis of nutrients was done in Mwanza water quality laboratory-Tanzania (Figure 8) by photometric measurement, using Hitach spectrophotometer (HITACH U-2001). Total dissolved nitrogen (TDN) and nitrate (NO_3) were analyzed at 420nm following sodium salycilate method as described by Scheiner (1974), while ammonium (NH_4^+) was computed from ammonia concentration measured using Phenate method as described in American Public Health Association (APHA 2002).

DON was calculated by subtracting nitrate and ammonium concentration from total dissolved nitrogen ([DON] = [TDN]-[NO3]-[NH4]). Total dissolved phosphorus (TDP) and reactive phosphorus (Orthophosphate $P0_4^{3-}$) were measured at a wavelength of 880nm as per Ascorbic acid method and dissolved organic phosphorus was mathematically computed by subtracting phosphate concentration from total dissolved phosphorus [DOP] = [TDP]-[PO4].

Figure 8: Nutrients analysis at Mwanza laboratory -Tanzania. Laboratory quality assurance procedures were properly followed to assure the quality of data. This include the use of control standards and blanks samples

3.5.2 DOC concentration

DOC concentration was measured at UNESCO-IHE laboratory using Shimadzu TOC-V CPN analyzer which uses high temperature of 720^0C for combustion. The DOC and TDN concentration obtained were used to calculate carbon and nitrogen ratio (C: N) of the DOM. Prior to analysis, refrigerated DOC water samples were acclimatized to room temperature.

3.5.3 Absorbance of DOM

Measurements of absorbance were performed in 10-cm quartz cuvette using the UV-VIS (Ultraviolet-visible) spectrophotometer Shimadzu UV 2500.
The samples were stored at 4 °C and were first acclimatized to room temperature. Absorbance scans were done over a range of 220 to 550 nm at1.0 nm increments and Milli-Q water served as the blank. The optical density (absorbance) obtained was transformed to indices and coefficient in order to be interpreted. The absorbance was log (base 10) transformed and absorption coefficients were calculated as:

$a_\lambda = 2.303 * (A_\lambda / L)$

Where
a_λ = is the wavelength-specific absorption coefficient in nm m^{-1} computed from wavelength-specific absorbance A_λ and cuvette path length L measured in meters.
The absorbance coefficient was used to calculate SUVA which is specific Ultraviolet absorbance at 254 nanometer wavelength normalized with DOC concentration.

$SUVA_{254} = a_{254} / [DOC]$

Where

$SUVA_{254}$ is the specific absorption at 254 nm computed from a_{254} , the absorption coefficient at 254 nm, and [DOC], the concentration of dissolved organic carbon in mg C/ L

The coefficient was also used to calculate the spectral slopes and slope ratios according to Stedmon et al, 2001 and Helms, 2008 respectively.

$a_\lambda = a_{\lambda o} e^{S(\lambda o - \lambda)}$

Where,

"a" is absorbance coefficients, "S" slope and "λ" is wavelengths

From the above relationships Slope ratio (S_R) was calculated as a ratio of wavelength at lower wavelengths to that of higher wavelengths (Helms, 2008)

$$S_R = \frac{\text{Slope (275-295)}}{\text{Slope (350-450)}}$$

3.5.4 Excitation measurement (Fluorescence)

Fluorescence excitation emission matrices (FEEM's) were obtained using a spectrofluorometer Horiba Jobin Yvon Fluoromax 3. Measurements were performed in a 1 cm quartz cuvette and using the water Raman peak of Milli-Q water at Ex=370 nm as reference. Samples that were preserved at 4°C were acclimatised to room temperature. Spectra were collected at excitation wavelengths ranging from 240nm to 550 nm at 5 nm increments.

Emission scans were performed with 2 nm increments at wavelengths between 350 and 600 nm. The Fluorescence Spectrophotometer was set at a scan speed of 12 000 nm per minute and a response time of 0.25 s. Raw data thus obtained was processed to eliminate inner filter effects, Raman scatter peaks (McKnight, et al., 2001). Lamp performance was evaluated prior to analysis, and the background photo detector spectral corrections were taken care of during data collection using appropriate instrument settings. Corrected fluorescence intensities are expressed in Raman units. FEEM data processing which includes blank subtraction and inner filter correction was done using MATLAB software.

4 Statistical Analysis

Water quality data obtained after chemical analysis were subjected to different statistical tests. Selection of tests was done based on characteristic of data. Shapiro-Wilk and Q-Q plots test were used to test the data for normal distribution, while Bartlett test was used for variances homogeneity. Five percent (α=0.05) probability level was used to test for the level of significance between parameters.

Two way analysis of variance (ANOVA) was used to test for the significance difference between mainstream and transects on nutrients (NO_3, TDN, C: N) concentration, while Kruskal-Wallis test was used as a non parametric test for DOC, SUVA, and absorbance coefficients. All afore mentioned statistical tests were carried out using R-software (Version: 1.12.2).

5 Results

5.1 Assessing bulk dissolved organic matter

5.1.1 Variation of dissolved organic carbon (DOC)

Results from ANOVA showed no significant difference ($p=0.70$, $n=39$) observed on DOC concentration on samples collected from different sites in the basin in two sampling periods (Table 5). In November 2011, DOC concentration in the mainstream (Figure 9) showed decrease trend from upstream to the mouth. The highest DOC value of 25.62 mg C/L was observed in the upstream point of TS bridge, while the lowest DOC value of 6.02 mg C/L was observed in the river mouth point (RM) in the wetland. This contrasts with the results in January 2012, which showed increase in DOC concentration from 5.76 mg C/L in TS Bridge to 72.96 mg C/L in river mouth (RM). The results of the two-way analysis of variance (ANOVA) that compared the value of DOC concentration of the Mara main stem with date (November~Dry & January~wet) showed significant difference ($p<0.05$, $n=10$)

Four sampling sites from three upstream tributaries which represent different environmental pressure were grouped and tested for significant difference in DOC concentration. Tighite upstream and downstream represent mining and urbanisation pressures while Tabora and Somonche represent extensive agriculture and overgrazing. No significant difference ($p=0.87$, $n=4$) were observed on samples collected in Tighite upstream and downstream during November and January. Meanwhile Tabora and Somonche also showed insignificant differences ($p=0.99$, $n=4$).

Dissolved organic carbon in all three wetland transects during sampling period of January 2012 showed decline in concentration (Figure 9) from the upslope to the main channel. In transect -I, which was more downstream, DOC decreased from the upslope to the main river channel. For example, DOC value decreased from 13.1mgC/L to 9.3mgC/L, transect-II from 13.6mgC/L to 8.5mgC/L and in transect-III from 17.mgC/L to 7.1mgC/L (Figure 9).

DOC concentration in November along the transects showed a non-uniform trend that is difficult to explain (Figure 9). Regardless of the observed trends, highly significant differences ($p<0.01$, $n=21$) were found in samples collected between two sampling periods of November 2011(Dry period) and January 2012(Wet period).

There was no significant difference ($p=0.13$, $n=14$) observed on DOC concentration on samples collected in the three wetland transects as well as five established site at the Mara main stream during dry sampling period (November), however highly significant difference ($p<0.01$, $n=17$) were found during dry sampling period (January)

Analysis Of Variance table

Response:	DOC					
	Df	Sum Sq	Mean Sq	F value	Pr(>F)	
Date	1	41.7	41.7	0.147	0.7039	
Sites	3	1754	584.7	2.0597	0.1252	
Dates: Sites	2	8221.3	4110.6	14.4817	3.32E-05	***
Residuals	32	9083.2	283.8			

*** Highly significant

Table 5: Analysis of variance table for DOC concentration

5.1.2 Variation of dissolved organic nitrogen

Results from ANOVA showed highly significant difference in DON concentration from samples collected between different sites ($p<0.01$, $n=39$) as well as between two sampling dates ($p<0.01$, $n=39$) of November (Dry period) and January (Wet period). Specifically, DON in the main stem decreased in both sampling period of November, 2011 and January, 2012. During November sampling for example, DON concentration decreased from 0.87 mg N/L in Tarime-Serengeti bridge (Figure 10) which is the most upstream site to 0.12 mg N/L in the river mouth (RM) which is the most downstream site almost to the lake, while in the January sampling the DON value decreased from 0.74mgN/L to 0.05mgN/L in the river mouth station. However, no significant differences ($p= 0.99$, $n= 10$) were found on samples collected in the main stem between two sampling dates

The upstream watersheds of the lower Mara tributaries drain landscapes that are very different in nature (soil geology), and especially in land use, than the basin of the main-stem river, and thus, water from tributaries could alter the water characteristics and water quality of the main river as it flows towards the lake. Highly significant difference ($p<0.01$, $n=9$) in dissolved organic nitrogen were found between the upstream tributaries and the main stem in both two sampling period of November and January.

In both sampling periods, results of dissolved organic nitrogen (DON) in transects showed a decrease in concentration with distance from the mainland to main river channel (Figure 10). For example, in transect-I DON decreased from 2.0 mg N/L to 0.09 mg N/L, transect-II from 1.28mg N/L to 0.20 mg N/L and transect-III from 0.75mg N/L to 0.18mgN/L from the site near the mainland to the sampling point proximity to the main river channel respectively. Nevertheless, there was no significant difference ($p=0.57$, $n=21$) found in dissolved organic nitrogen (DON) concentration between two sampling periods of November and January.

Samples collected from Mara main stream and three established transect during November and January were analyzed and tested for differences in dissolved organic nitrogen (DON) concentration. Highly significant difference ($p<0.01$, $n=14$) in November sampling. However during January sampling no significant difference ($p=0.99$, $n=17$) were observed.

Analysis of variance table

Response:	DON					
	Df	Sum sq	Mean Sq	F value	Pr(>F)	
Dates	1	1.7379	1.73795	9.6601	0.003934	**
Sites	3	9.3417	3.11391	17.3082	7.38E-07	***
Dates: Sites	2	0.1453	0.07265	0.4038	0.671136	
Residuals	32	5.7571	0.17991			

Table 6: Analysis of variance table for DON concentration

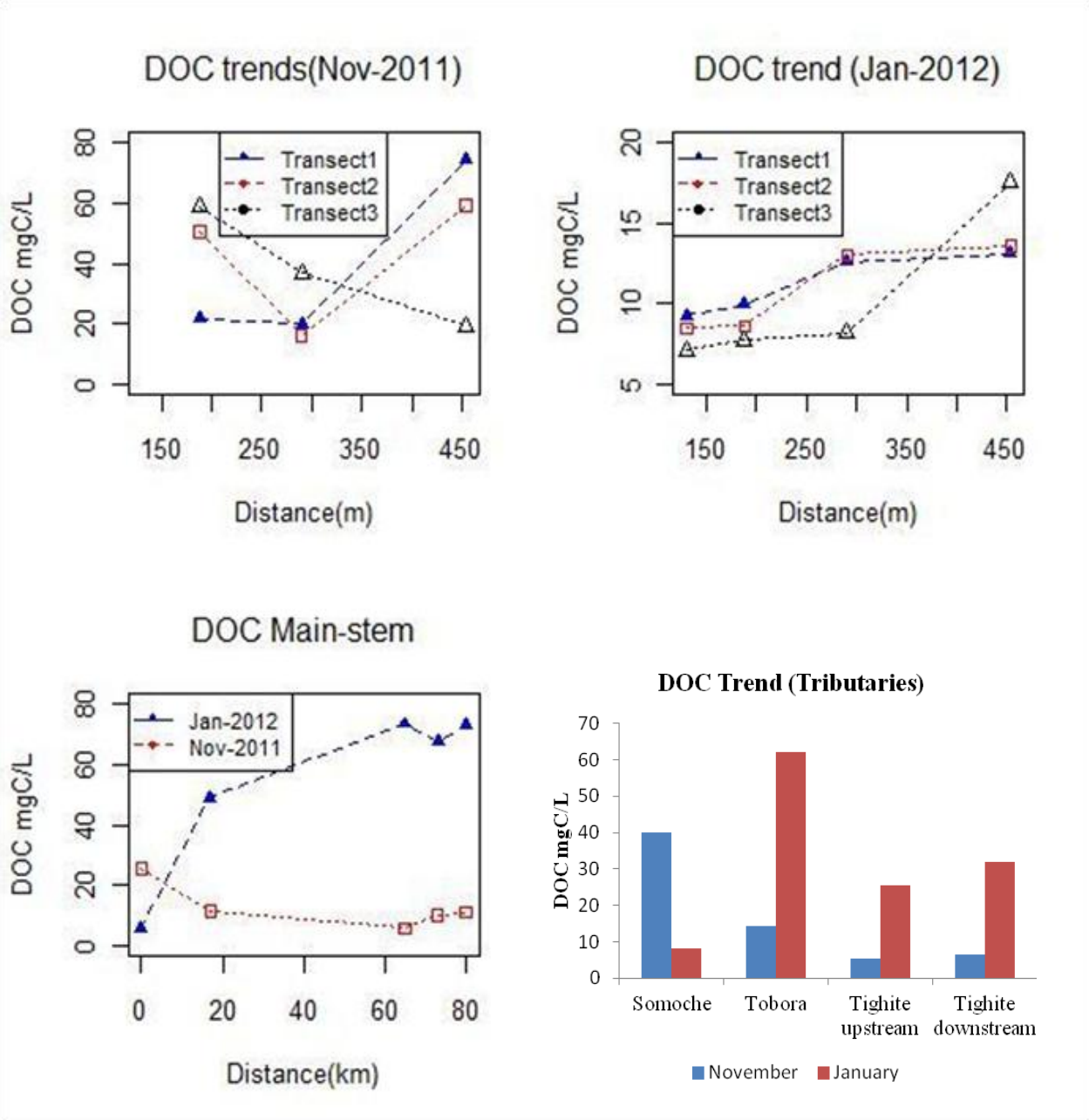


Figure 9: Dissolved organic carbon trends. Anova results showed significant differences ($p<0.05$, $n=39$) on samples collected between two sampling periods of November (Dry period) and January (Wet period).However, no significant differences ($p=0.70$, $n=39$) were observed on samples collected at different sites in the transect wetlands, tributaries and the main stem between two sampling periods of November and January.

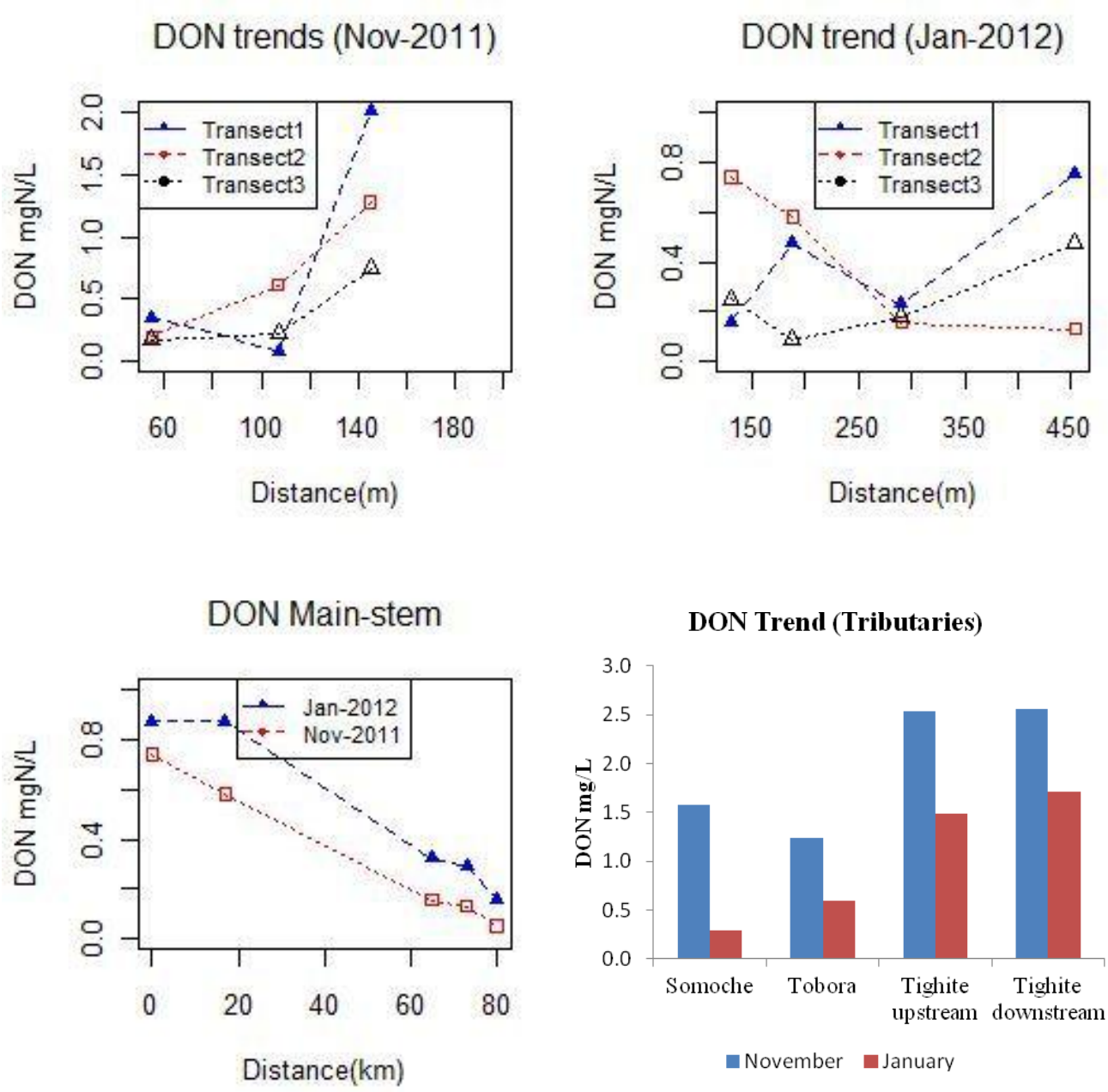


Figure 10: Dissolved organic nitrogen trends. The main effect after Anova showed significant difference ($p<0.01$, $n=39$) was observed between two sampling periods. Moreover, significant results ($p<0.05$, $n=39$) were also observed on samples collected at different sites in the main stem and transect wetlands.

5.2 Assessment of organic matter quality (Absorbance)

5.2.1 Variation of specific ultraviolet absorbance (SUVA)

The value of SUVA in main stem in November sampling showed a sharp increase from 1.65$Lmg^{-1}m^{-1}$ near the TS Bridge to 10.28 L $mg^{-1}m^{-1}$ in Mara mine station, while during January sampling the value of SUVA decreased from the same sampling points (Figure 12). The SUVA value decreased from 5.77$Lmg^{-1}m^{-1}$ in TS Bridge to 0.87$Lmg^{-1}m^{-1}$ in the Mara mine station. The decrease and increase in SUVA value would imply the aromaticity dynamics between two stations of TS Bridge and Mara mine.

Uniform SUVA values were found in the three sampling stations in the main channel of the wetland area. Meanwhile, the value of SUVA observed during November sampling was almost ten times higher than the value of SUVA observed during January sampling.

With regard to upstream tributaries, higher values of SUVA were found during November sampling compared to January sampling. Tighite upstream site had relatively higher SUVA compared to other tributaries, while Somonche showed the lowest SUVA value. Significance differences ($p<0.05$, $n=8$) in SUVA values were found in samples collected from Tighite upstream and downstream between November and January sampling.

In November, SUVA showed less uniformity between the wetland transects points than in January. SUVA was lower at the highest point near the mainland, increased in the middle of the wetland, and decreased near the main channel (Figure: 12). The value for SUVA three wetlands transect during November sampling showed non-uniform trends between three sampling points within each transect. For example, the minimum and maximum SUVA values of 1.5 $Lmg^{-1}m^{-1}$ and 8.6 $Lmg^{-1}m^{-1}$ were observed in transect-II during November and January sampling respectively.

In addition, the flow pattern in the wetlands could have effect on sampling and eventually affects the whole results, during sampling time the wetland was overflow following high rainfall in the upstream catchments and basin as whole. No significant difference ($p=0.99$, $n=21$) were found in transects between November and January sampling. Moreover, regardless of different SUVA values in both transects and the main stem, there was no significant differences ($p=0.98$, $n=17$) observed between two sampling periods

Analysis of Variance Table

Response:	SUVA					
	Df	Sum Sq	Mean Sq	F value	Pr(>F)	
Dates	1	46.833	46.833	10.3326	0.002982	**
Sites	3	161.971	53.99	11.9117	2.12E-05	***
Date: Sites	2	23.036	11.518	2.5412	0.094561	.
Residuals	32	145.042	4.533			

Table 7: Showing the main result of SUVA after two way analysis of variance

5.2.2 Variation of absorbance coefficient at 340nm

Highly significant difference ($p<0.001$, n=39) observed on absorbance coefficient (a_{340}) on samples collected from two sampling periods. However, there was marginally significant difference ($p=0.058$, n=39) in absorbance coefficient on samples collected from different sites (Table 7); specifically, in November 2011, absorbance coefficient in the mainstream (Figure 13) showed decrease trend. The highest coefficient value of 44.9 m^{-1} was observed in the upstream point of Mara mine (MM), while, the lowest coefficient value of 33.9 m^{-1} was observed in the river mouth point (RM) in the wetland. This trend is consistency with the results in January 2012, which also showed slight decrease in coefficient from 27.9 m^{-1} in Mara mine to 21.1 m^{-1} in river mouth (RM).

No significant difference ($p=0.87$, n=4) were observed in absorbance coefficient on samples collected in Tighite upstream and downstream during November and January. Meanwhile Tabora and Somonche also showed insignificant results ($p=0.89$, n=4)

Absorbance coefficient in all three wetland transects during sampling period of November 2011 showed decline in trend (Figure 13) from the upslope to the main channel. In transect -I, which was more downstream a_{340} decreased from the sampling sites closer to the mainland to that near the main river channel. For example, a_{340} value in transect-I decreased from 196 m^{-1} to 53.4m^{-1}, transect-II from 140 m^{-1} to 51.1 m^{-1} and in transect-III from 91.2 m^{-1} to 77.4 m^{-1} (Figure 13).

a_{340} value in January sampling showed trend with that observed in November sampling. Regardless of the observed trends, highly significant differences ($p<0.01$, n=21) were found in samples collected between two sampling periods of November 2011(Dry period) and January 2012(Wet period). There was no significant difference ($p=0.13$, n=14) observed a_{340} value on samples collected in the three wetland transects as well as five established site at the Mara main stream during dry sampling period (November), however highly significant difference ($p<0.05$, n=17) were found during dry sampling period (January)

Analysis of Variance Table

Response:	a_{340}					
	Df	Sum Sq	Mean Sq	F value	Pr(>F)	
Date	1	14451.4	14451.4	20.8531	6.97E-05	***
Sites	3	5716.9	1905.6	2.7498	0.05884	.
Date: Sites	2	4058.1	2029.1	2.9279	0.06796	.
Residuals	32	22176.2	693			

Table 8: Analysis of variance table for absorbance coefficient at a wavelength of 340 nm

5.2.3 Spectral slope and slope ratio (S_R) variation

The results after two-way ANOVA showed highly significant difference ($p<0.05$, $n=39$) on spectral slope ratio (SR) from samples collected from different sites within the lower Mara catchment. However, there was no significant difference ($p=0.55$, $n=39$) in slope ratio for samples collected from different sampling periods (Table 8)

However, specifically for the samples collected in the mainstream the result after post hoc test showed significant difference ($p<0.05$) in two sampling periods. In November 2011, slope ratio in the mainstream (Figure 14) showed an increase in trend longitudinally to downstream. The lowest SR value of 0.04 was observed in the upstream point of TS bridge, while, the highest SR value of 0.426 was observed in the river mouth point (RM) in the wetland. This trend is consistency with the results in January 2012, which also showed also increase in SR from 0.11 in TS Bridge to 0.33 in river mouth (RM).

The results from post hoc test after ANOVA showed No significant difference ($p=0.99$, $n=4$) on SR from samples collected in Tighite upstream and downstream during November and January.

SR in three wetlands transects during sampling period of November 2011 showed decline in trend (Figure 8) from the upslope to the main channel. In transect-I, which was more downstream SR decreased from the sampling sites closer to the mainland to that near the main river channel. For example, SR value in transects-I decreased from 0.62 to 0.55, transect-II from 0.63 to 0.51 and in transect-III from 0.52 to 0.38 (Figure 8). SR value in January sampling showed trend with that observed in November sampling. Regardless of the difference observed in trends, there was no significant differences ($p=0.99$, $n=21$) found on samples collected from wetlands transects between two sampling periods of November 2011(Dry period) and January 2012(Wet period).

Analysis of Variance Table

Response: S_R					
	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Date	1	0.00639	0.006391	0.3538	0.5562
Sites	3	0.88422	0.294742	16.3157	1.302e-06 ***
Date: Sites	2	0.01221	0.006103	0.3379	0.7158
Residuals	32	0.57808	0.018065		

Table 9: Analysis of variance table for the spectral slope ratio obtained as a ratio of spectral slope at lower wavelengths to spectral slope at higher wavelengths.

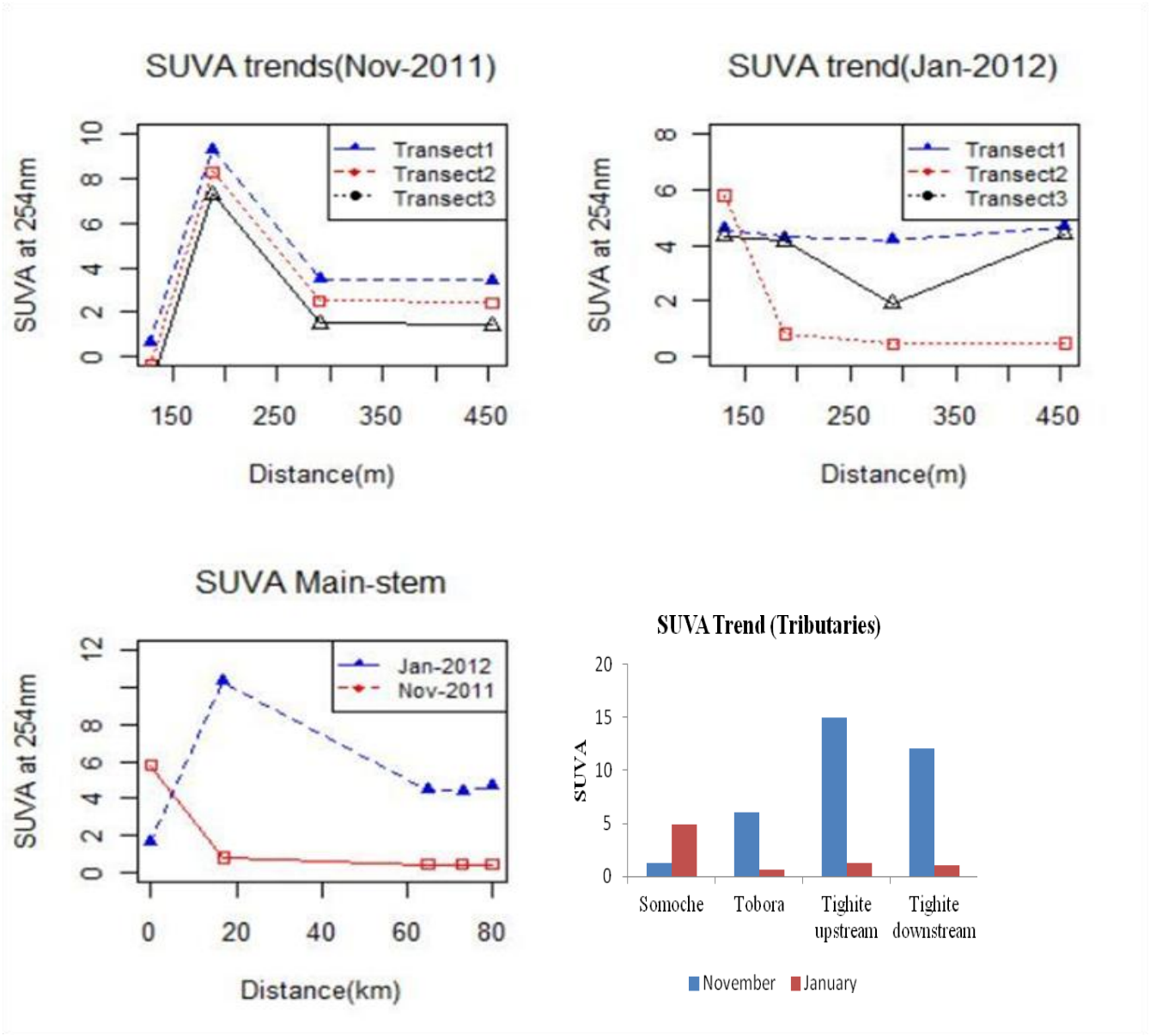


Figure 12: Showing trend of SUVA values for selected sites in the mainstream, wetlands transect and upstream tributaries. The main results after Anova (Table 9) showed significant differences ($p<0.05$, $n=39$) on samples collected between two sampling dates of November and January. Also highly significant difference ($p<0.002$, $n=39$) were observed on samples collected at different sites. However, after post *hoc* test, there was no significant difference ($p=0.2$, $n=10$) observed on samples collected in the main-stem in two periods of November and January.

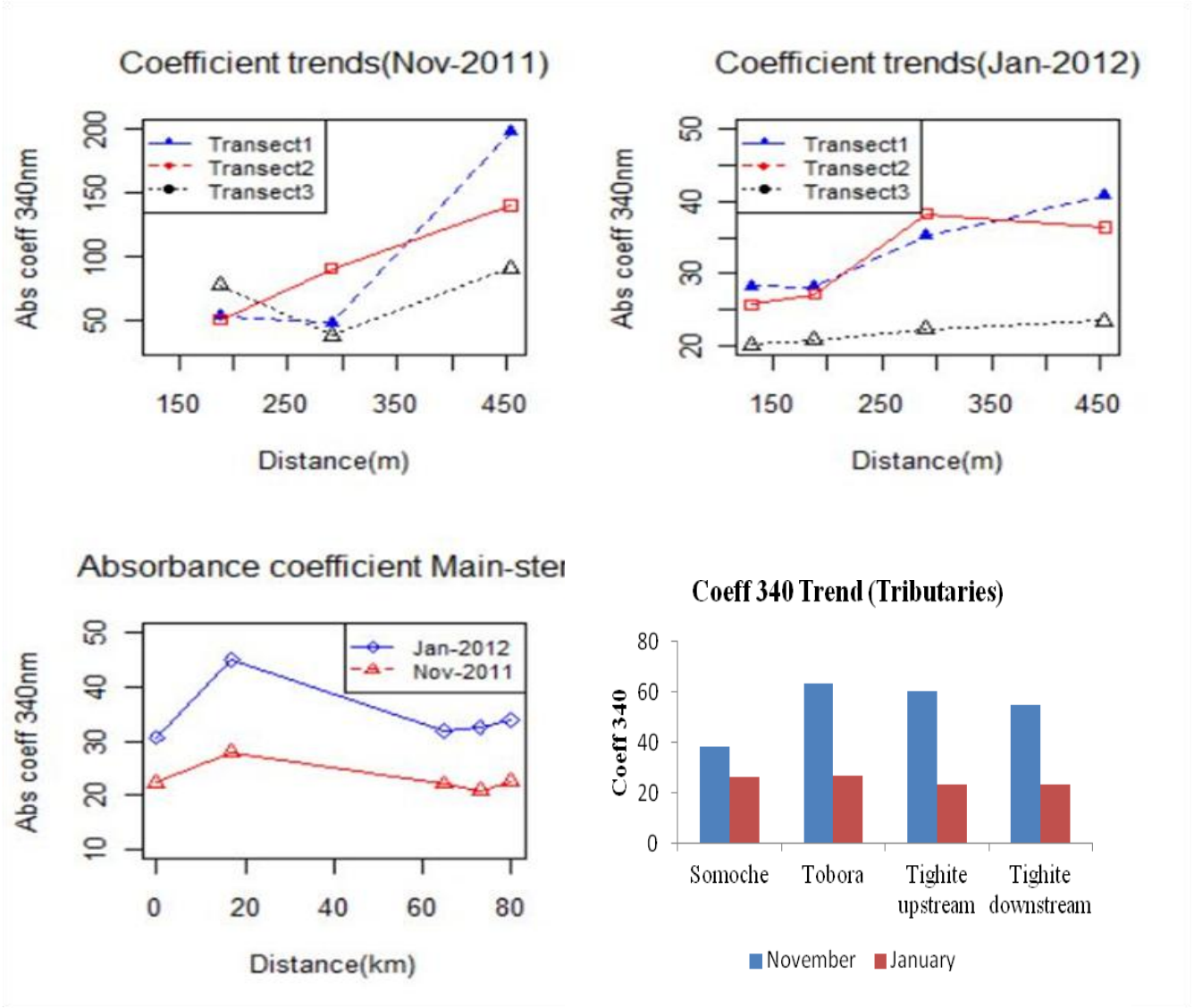


Figure 13: Absorbance coefficient of selected sites in the lower Mara catchment. Absorbance coefficient at 340 nanometer wavelength has been found to have positive correlation with DOC and proposed to be used as proxy to DOC concentration (Spenser, 2004). The results after Anova test showed significant difference ($p<0.01$, $n=39$) in absorbance coefficient for samples collected between November and January. However, marginal significant results ($p=0.058$, $n=39$) were found on samples collected at different sites in the in the Mara catchment.

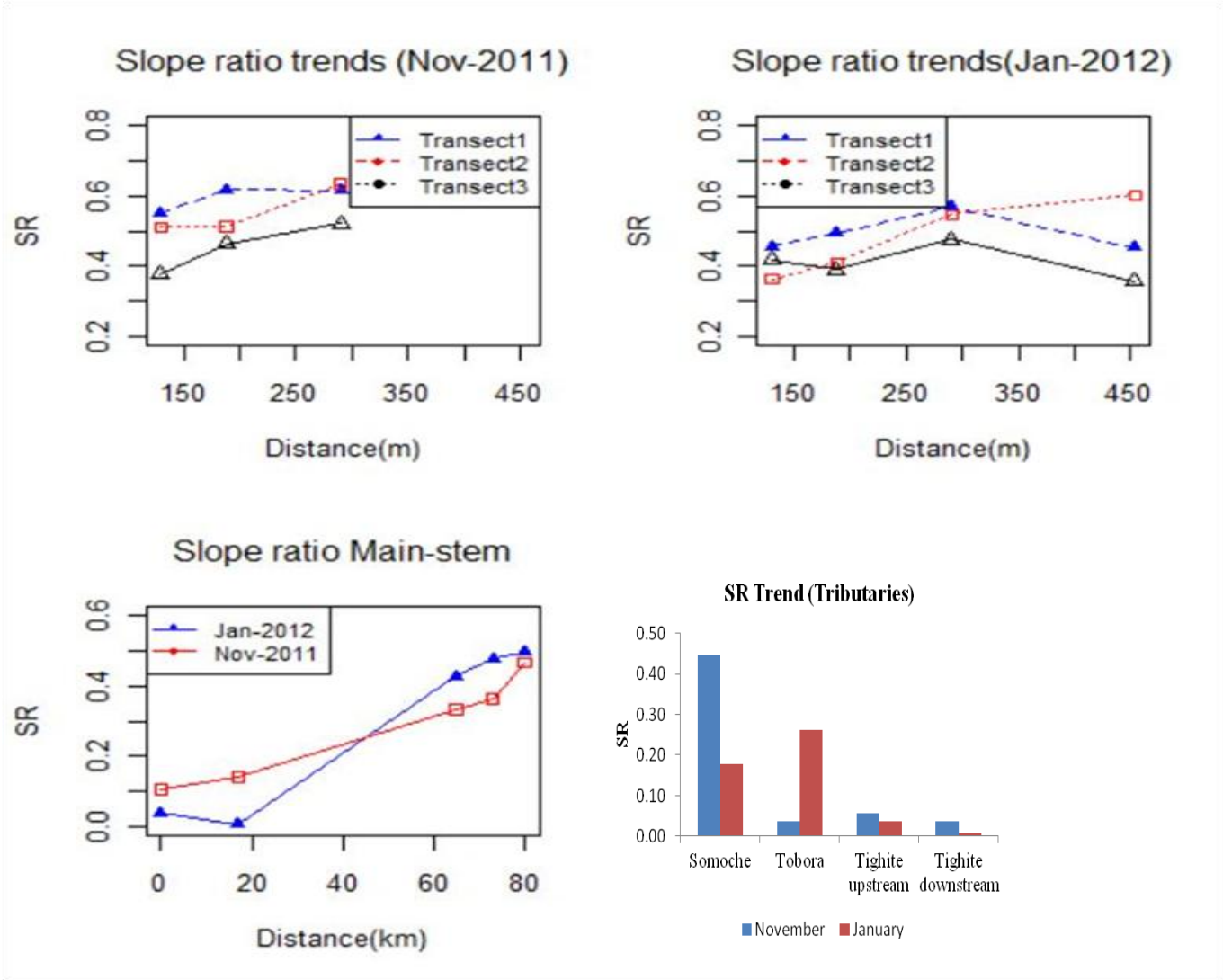


Figure 14: Slope ratio in the main Mara stream and transects during November-January sampling periods. Insignificant results (p>O.05, n=39) were observed on samples collected in the main stem between November and January. There was highly significant difference (p<0.05, n=39) in spectral slope ratio for samples collected in Main stem and wetland transects between the two sampling periods

5.3 Assessment of organic matter quality (Fluorescence)

5.3.1 Variation in fluorescence index along the main stem and wetlands transects

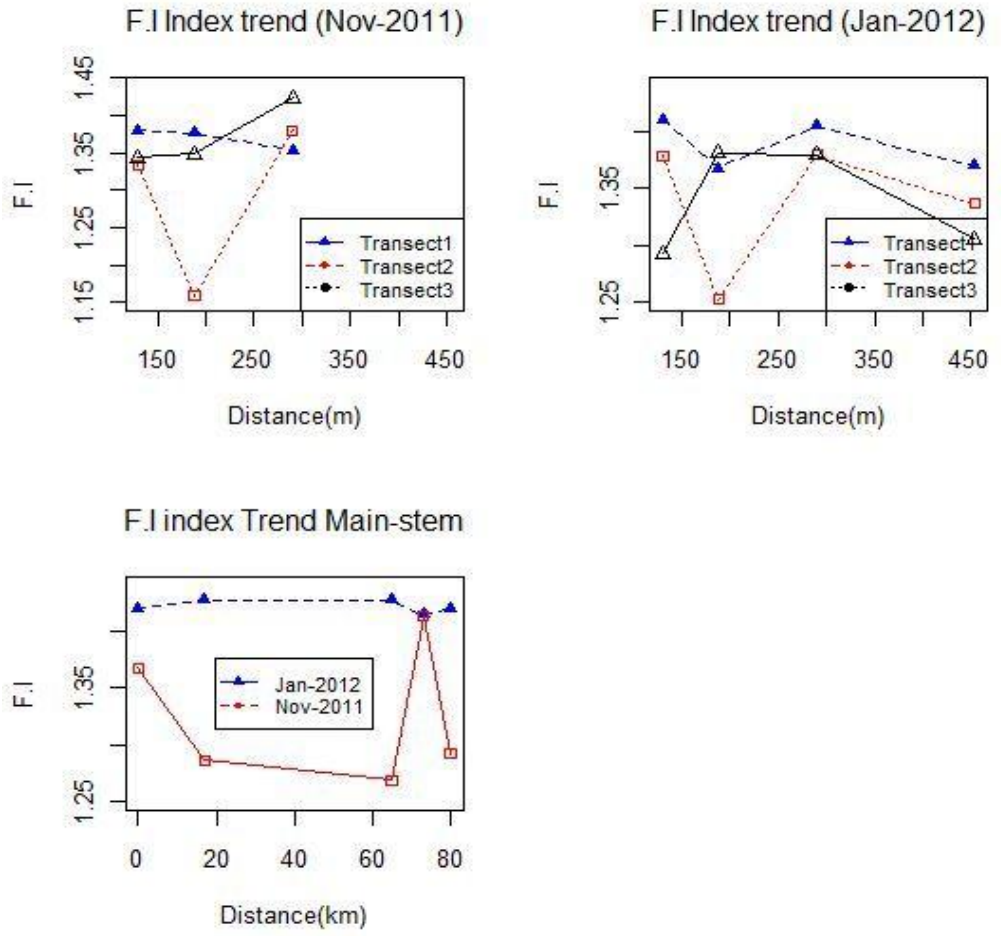


Figure15: Showing longitudinal variation of fluorescence index (F.I) along Mara main stem and down slope along the wetlands transects. Higher F.I would indicate more autochthonous (Microbial derived) DOC while lower F.I would indicate allochtonous (Terrestrial derived) DOC (McKnight, 2005). Almost uniform FI values were observed along Mara main stem, from the upstream sampling point (TS Bridge) to the river mouth point (RM) in both sampling date. However, during January sampling F.I values were higher compared to November sampling. F.I values in wetlands transect were uniform and almost constant in both sampling dates. No significant difference ($p=0.56$ $n=39$) on F.I values were found between two sampling periods. Moreover, insignificant results ($p=0.77$, $n=39$) were found for sites comparisons

5.3.2 Variation of Tryptophan peak index (T_{280}) along the main stem and wetlands transects

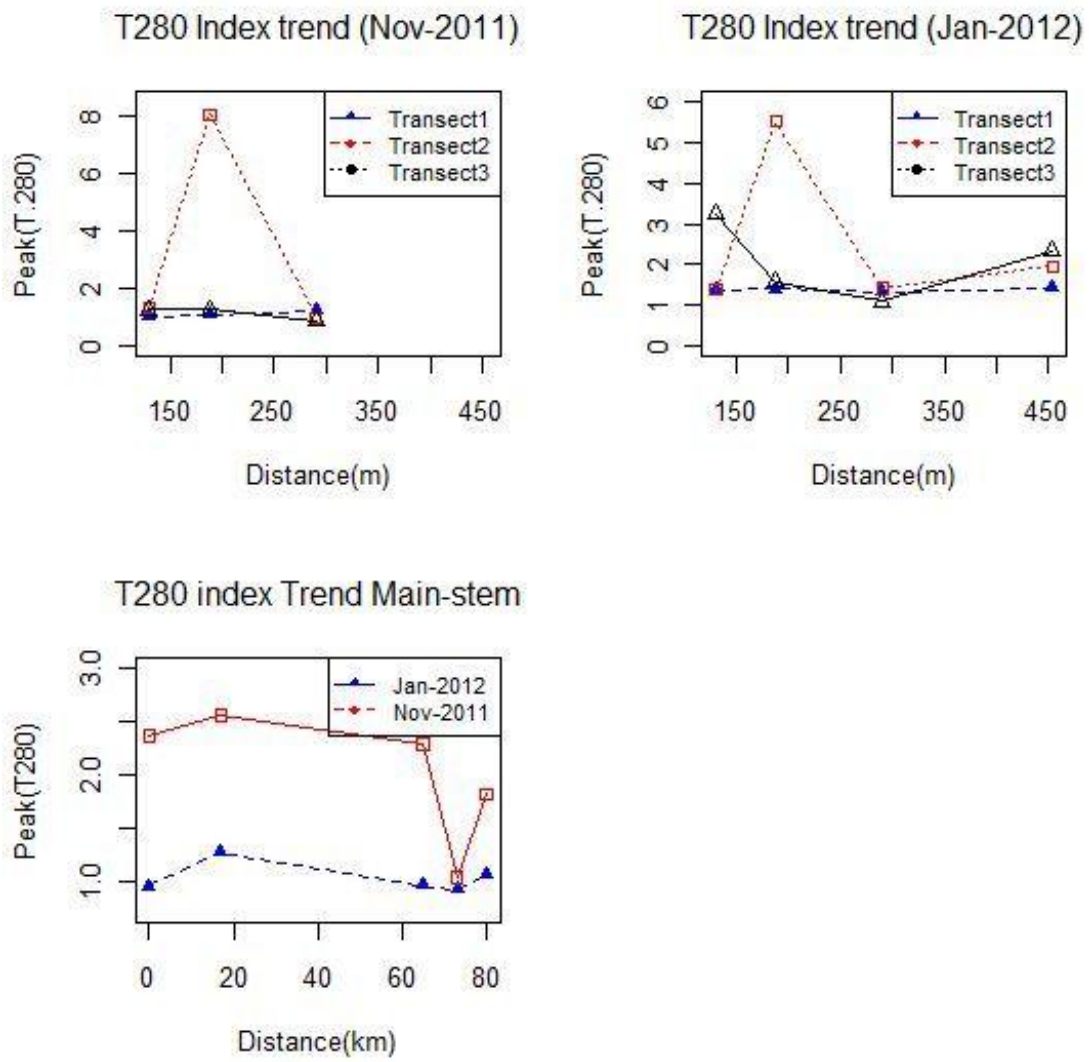


Figure 16: Variation of protein peaks (T_{280}) longitudinal along the Mara main stem and down slope along transects wetland. Uniform protein peak index values were observed along the Mara main stem. However, in January sampling the values of protein peak were higher than that of November sampling. With exception to transect-II, the values of protein peak were almost constant down slope to the main river channel. No significant difference ($p=0.84$, $n=39$) were found on samples collected between two sampling dates of November and January. Insignificant ($p=0.73$, $n=39$) results were also observed on samples collected at different sites

5.3.3 Variation of freshness index (β: α) along the main stem and wetlands transects

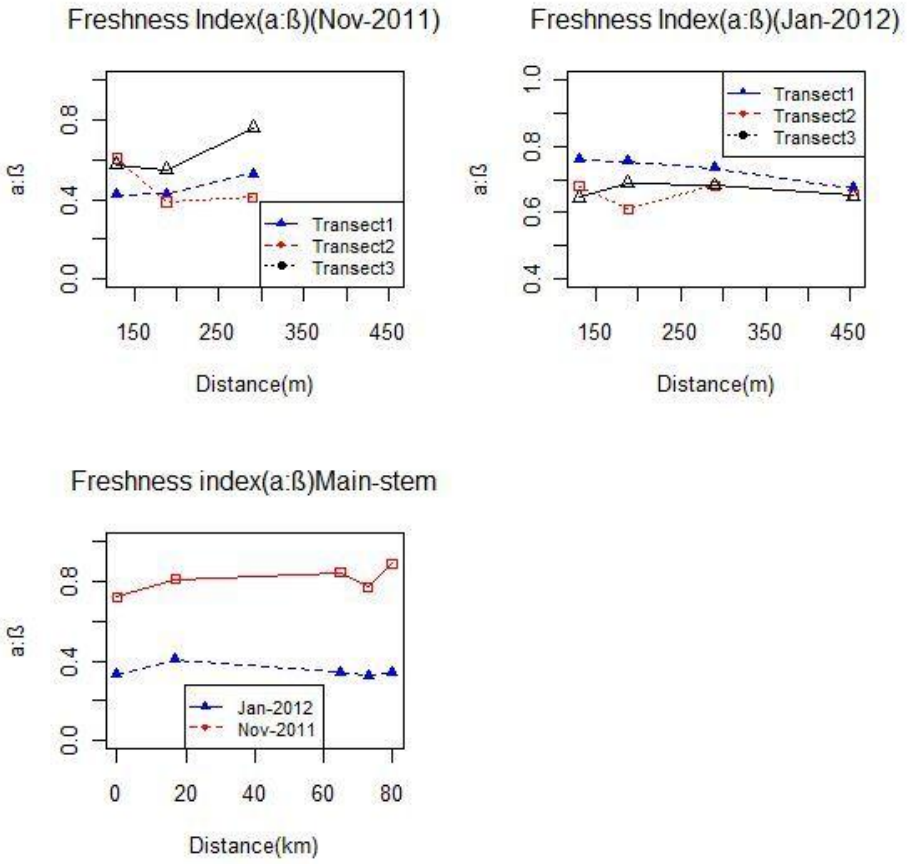


Figure 17: Variation of freshness index (β: α) in the main stem and down slope wetland transects. Freshness index is as a ratio of recently produced DOC (β) to more decomposed (α) (Parlant et al 2000), for both sampling periods of November and January uniform β: α trend were observed longitudinally along the main stem from the upstream sampling point TS bridge to the river mouth. However, contrasts to January sampling, November sampling had higher fresh values. Constant freshness index values were observed in wetland transects in both sampling dates. Highly significant different ($p<0.001$, $n=39$) observed on samples collected from two different sampling dates, while insignificant results ($p=0.15$, $n=39$) were found on samples collected at different sites

5.3.4 Variation of biological index (BIX) along the main stem and wetlands transects

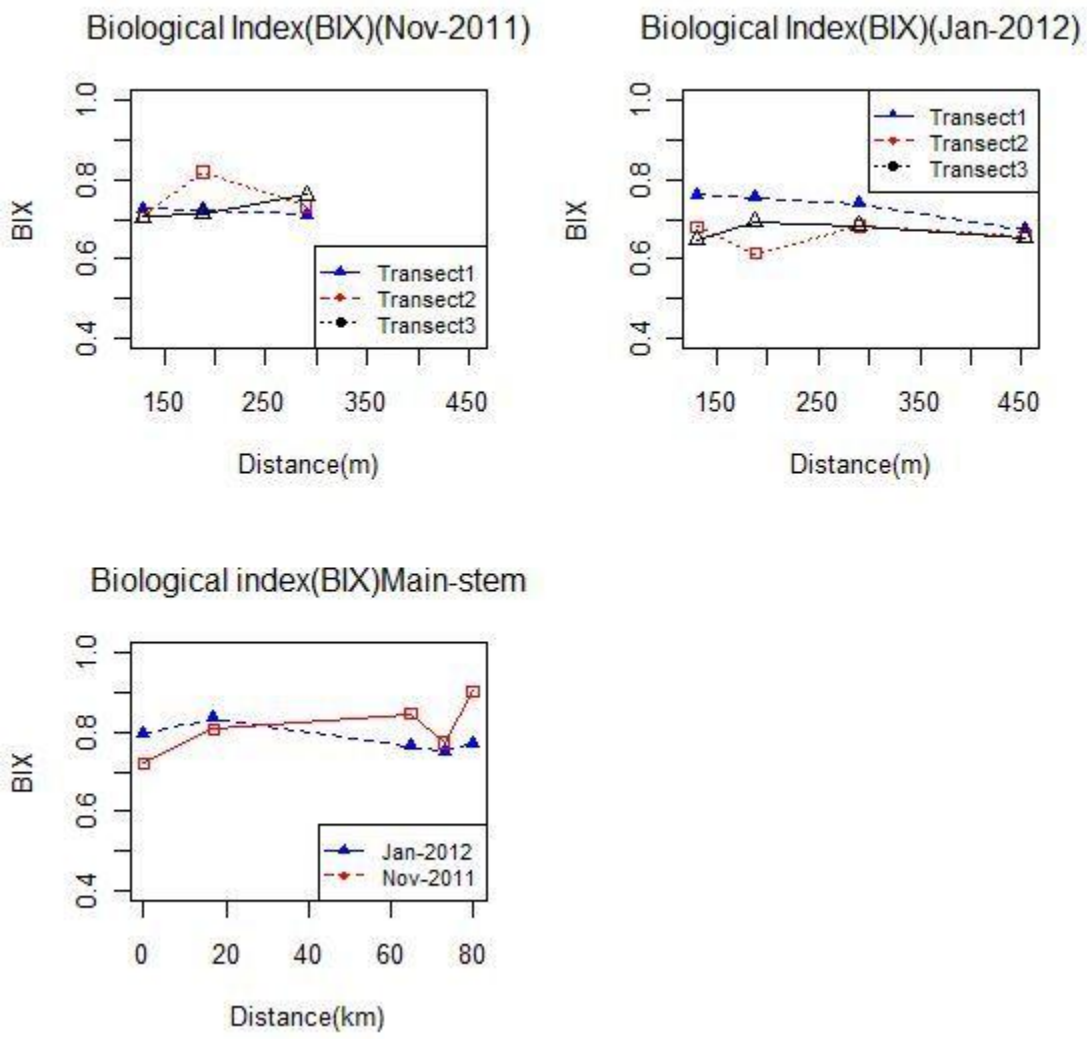


Figure 18: Showing variation of biological index (BIX) along the main stem and down slope the wetland transects.BIX is an indicator of relative contribution of autochthonous DOC to DOC pool. An increase in BIX is related to an increase in the concentration in the β fluorophores. Significant results ($p<0.001$, $n=39$) of BIX index were observed on samples collected at different sites. No significant difference ($p=0.21$, $n=39$) were found in two sampling two dates. Uniform BIX values were observed in the main stem and wetlands transects in two sampling dates.

6 Discussion

6.1 DOC and DON concentration dynamics at different sites and sampling periods

Both quantity and quality of dissolved organic carbon (DOC) in the Mara catchment was dynamic, and this was perhaps due to the fact that DOC concentration was responding to hydrological conditions. November was the start of autumn period in the region, therefore during sampling there was little rainfall compared to January sampling, which was almost the mid-session of the autumn period. The reasons for high concentration of DOC were assumed to be caused by leaching and erosion after heavy storms in the upstream catchments. Storms have been reported in previous studies to be important driver of DOC availability in streams and rivers (Boyer et al 2000). Degrading plant and soil material rich in humic content as well as breakdown products of bacteria would be delivered from the landscape to the water column and eventually increase DOC concentration. However, these results contrast the idea that rainy water dilution would reduce DOC concentration (Lu et al 2003). Other possible factors that could affect DOC concentration are in situ processing for example degradation by mineralization (Cory et al 2007), photo degradation reaction by light (Spenser et al 2007).

In November, longitudinal variation in DOC concentration was observed along the main stem. Upstream sites had slight higher DOC concentration than the point in the river mouth. This result is parallels the observed values of DON concentration, which also showed higher DON values in upstream sites as compared to downstream sites in the river mouth (Figure 10). One of reason for the decline in DOC in the main stem could be due to loss of carbon in the form of CO_2 as a result of heterotrophic respiration (Aufdenkampe et al 2011). It could also be dilution, as tributaries and groundwater sources low in DOC and DON enter the main channel (reference). In addition to that abiotic sorption could also remove substantial amount of DOC from the water column (McDowell, 1985, McKnight, 2002).

The longitudinal gradient in November contrasted the pattern observed in January. In January, the DOC concentration increased longitudinally from the upstream sampling point to the RM, and this was opposite the pattern observed in DON, which showed decline longitudinally to the RM. The reasons for the increase in DOC could be due to the fact that after storms river discharge increased dramatically and perhaps this would affect the residence time and reduce time for microbes to mineralize DOM, while increasing the delivery of C-rich terrestrial organic matter to the river channel.

There was no difference in DOC concentration between the wetland transects and the main-channel sites during the wetland. However, DOC concentration was higher in the wetland transects than the main stem during both sampling periods. This could be a result of isolation and connectivity during the wet and dry seasons. During the rainy seasons, the hydrological connectivity between water and landscapes usually increased; hence isolated water pools would be left in the wetlands transects during the transition period, that pools would have more DOC concentration from leached plants (papyrus) as compared to water from the main channel.

No significant differences were observed in DOC concentration in the upstream tributary sites. This result was in contrast to our hypothesis given the fact that the tributaries varied with respect to anthropogenic impacts. Tighite for example is facing pressures from both large scales mining that used several of chemicals like cyanide for gold purification as well as small mining which use mercury for gold extraction. In addition to mining pressure the Tighite sub-catchment also receives rapid urbanisation due to ongoing population growth. On the other hand, Tabora and Somonche sub-catchments are facing pressure main from over-grazing and extensive agriculture. Regardless of different in environmental degradation pressures

Significant differences ($p<0.01$, $n=39$) in DON concentration were observed between two sampling periods of November and January as well as between sampling sites. DON decreased significantly in both sampling periods of November 2011 and January 2012. The observed decrease in DON concentration trends especially longitudinally in the main river stream was hypothesized in various aquatic reviews. One of the reasons for the decline could be due to the fact that the labile form of DON fractions would be utilized by heterotrophic organism for synthesis (anabolism) processes (Carpenter et al 2005). Also river spiraling concepts describes cycling of organic matter and how they are incorporated into the biomass and predicted changes in DOM composition to downstream waters.

In November sampling the value of DON concentration decline down the slope to the main river channel, this is contrary to the value of DON observed during January sampling which showed non-uniform trends. As you approach the main river channel the soil is more saturated with water, this favors the establishment of anaerobic condition to the soil due to consumption of the remaining oxygen in water by microbes. Miller et al 2006 used redox index (RI) to explain moves from the wetlands to the mainstream and DON was rapidly mineralized and ammonium for the decrease of DON concentration in wetlands, observed shift of redox index as water was oxidized and converted to nitrates. Mineralization of DOM under oxygen condition is approximately three times higher than under anaerobic condition. (DeBusk et al 1998)

6.2 SUVA dynamics at different sites and sampling periods

Highly significant SUVA values were found on samples collected at two sampling periods of November and January. However, lack of significant results were observed on samples collected at different sampling sites in the main stem, tributaries and the transect wetlands. On both dates the results of SUVA in the main stem decreased longitudinally from TS Bridge to RM sampling points. Nevertheless, January samples had relatively higher SUVA values than November samples. This supports our idea that more of allochthonous DOM entered into the river during rain period. The decrease of SUVA value along the main stem could indicate decrease in aromaticity with distance. This result is consistence to that reported by Lu et al 2003 in Everglades that followed the similar trend. Higher input of SUVA from upstream tributaries and transect wetland could influence photosynthesis especially for benthic primary producers (Aiken et al 2011)

Uniform SUVA values were observed in two sampling points in all three wetland transects during November sampling. However there was overshoot of SUVA value in the sampling point closer to the main river channel. This was observed in all transects. Two reasons were assumed to be the cause of the overshoot. In transect I there was papyrus harvesting which is usually the case in Mara wetlands. Harvesting exposed the wetland to sunlight and eventually increases photo-degradation of DOM and release of nutrient and carbon. Also temperature has been mentioned to accelerate mineralization in the wetlands.

6.3 FI index dynamics at different sites and sampling periods

No significant result on FI values were observed on samples collected at different sampling periods of November and January as well as at different sampling sites (Figure 15). During both sampling dates the value of FI observed in the main stem were almost uniform, from the upstream sampling point of TS bridge to the river mouth point (RM). However, FI values during January sampling were higher than that observed in November sampling. Higher FI value would indicate more of autochthonous (Microbial derived) DOM, while lower FI value would indicate terrestrial-allochtonous derived DOM (McKnight 2005). The argument was on the shift of FI values between two sampling periods of November and January. Shift of FI values would imply dynamics on DOM sources between November and January. The reason for the shift was assumed to be due to high input of DOM form the soil by erosion after rain. This is due to the fact that in some system organic matter pools can be dominated by bacteria cells (Cotner et al 2004) which are well known to exhibit intrinsic fluorescence from tryptophan, tyrosine and phenylalanine residuals associated with proteins.

The results of FI on samples collected in the transects wetland lack significant differences. With exception to transect II that showed bigger variation from the point near to the landscape to that closer to the main river channel, transect I and transect III appeared almost uniform down slope to the main channel. The results of transect II contradicted to that observed in protein peaks-T_{280} (figure 16). Literary, the lower value of FI observed in transect II at the middle section point would implies more of allochtonous production at this point (McKnight 2005), this observation supposed to be reflected by lower value of protein peaks that was not the case. However, from the observation made after Excitation spectral (Figure 19) the middle section of transect II(T_2P_2) confirmed to have to more of humic-like substances and no protein peaks was difficult to be observed.

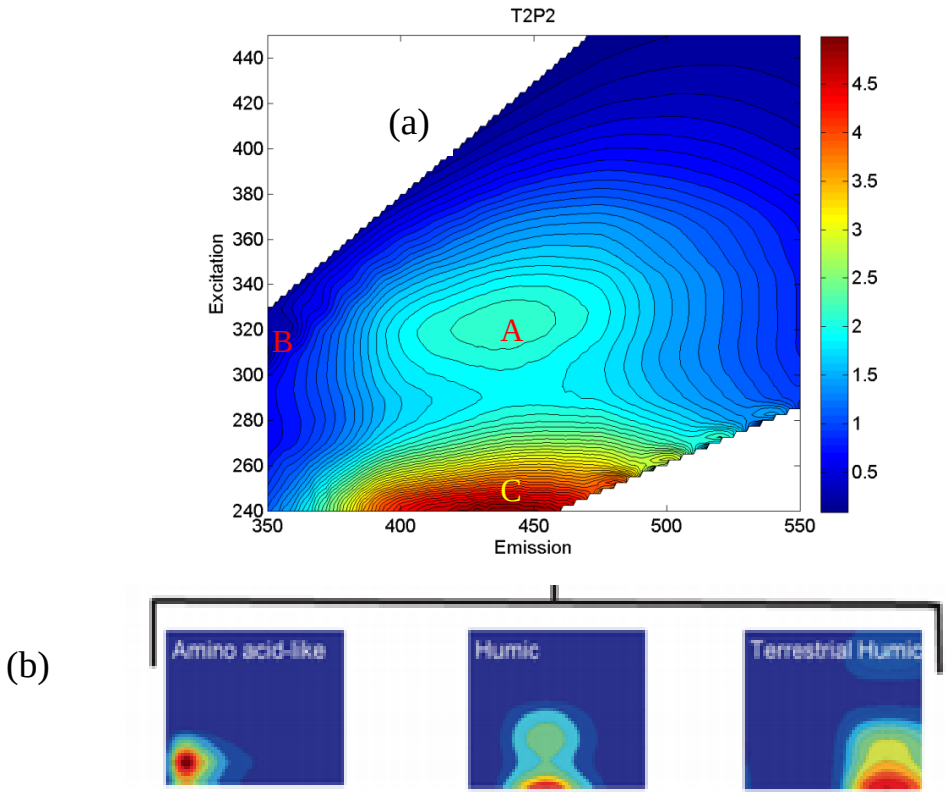


Figure 19: (a) Showing DOC fluorescence spectra and its corresponding humic-like peaks (A, B&C) obtained from the transect-II in the middle section (T_2P_2); the spectral was collected over a range of excitation wavelength where the color is proportional to the intensity of fluorescence. (b) Showing the standard fluorescence spectral from International Humic substances Society (IHSS)

7 Conclusions and recommendations

7.1 Conclusions

From this research that was dealing with nature and sources of dissolved organic carbon (DOC) in the lower Mara River Tanzania, following conclusions were drawn:

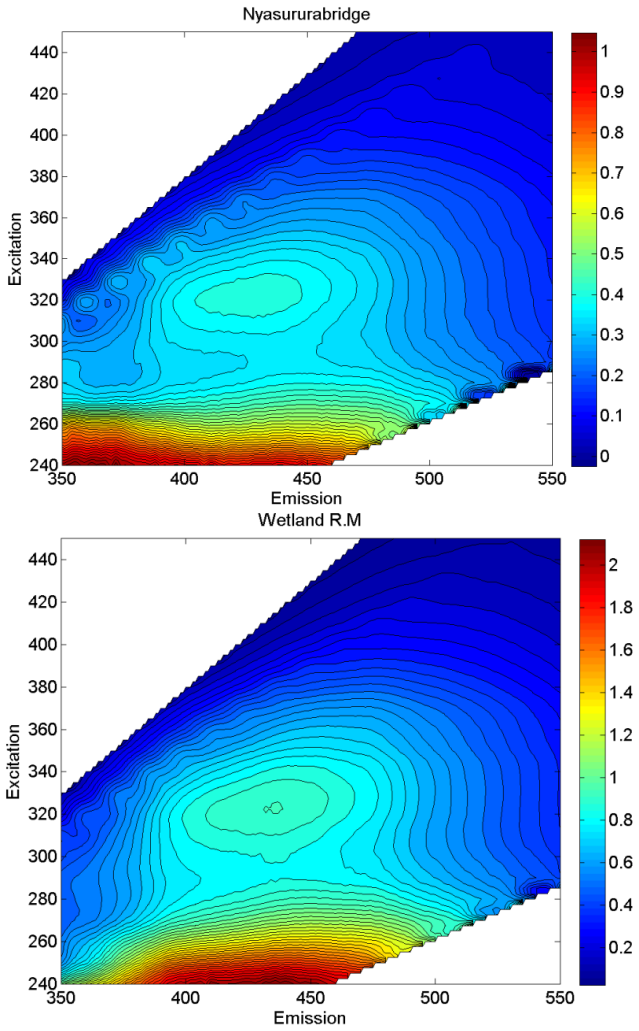
- ✓ DOC concentrations were higher in January (wet season) than in November (dry season) in the main stem of the Mara, indicating that allochthonous sources of DOM perhaps would entered the river through increased connectivity with terrestrial and wetland sources.
- ✓ Longitudinal patterns in DON concentration in the main stem also showed opposite patterns in January and November. For example, in January DON decreased from upstream to downstream indicating a relative increase in carbon rich terrestrial sources.
- ✓ High fluorescence index values were observed during the wet season suggesting that microbial sources of DOM would be originated from the soil and perhaps could be allochthonous despite high FI values.
- ✓ Despite the fact that upstream catchments experienced different anthropogenic pressures, similar trend was observed for both tributaries. However, Tighite tributary had relatively higher SUVA and DON values compared to Somonche and Tabora
- ✓ Wetland transects have higher value DOC and DON compared to the main river channel. The water quality fluctuation (dynamics) in both wetlands and main channel could be governed by wet and dry cycle (Hydro period). This could be due to the fact that during wet period the wetland usually connected to the main channel and exhibits relatively similar characteristics while during dry period the wetland is in isolated to the main river channel.

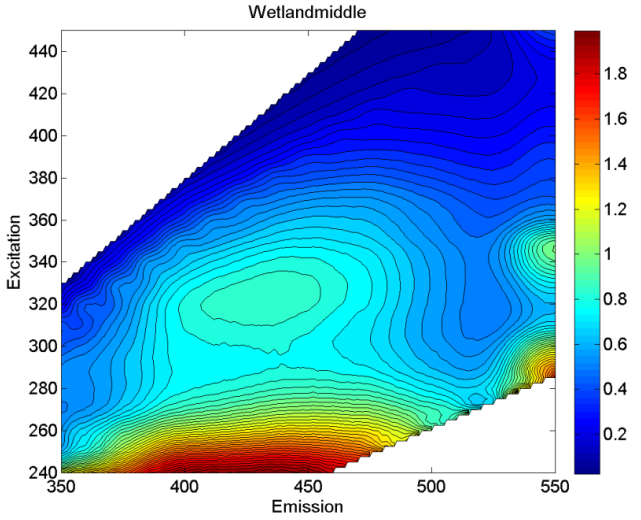
7.2 Recommendations

- ✓ Future studies on Mara River should focus on isotopic identification to explore the contribution of DOM as a result of erosion from upstream catchments
- ✓ Understanding DOM sources and dynamics requires detailed study of other factors that affect its availability for example hydrology, soil types and land uses.
- ✓ Scientific decisions needs statistical analysis that would require year rounds data representing different environmental conditions (Example, Dry period and wet period), therefore there is a needs of combining various studies done on the Mara catchments and come up with integrated decision and scientific conclusion.

8 Appendices

Annex 1: Excitation emission matrix (EEM's) for November sampling.

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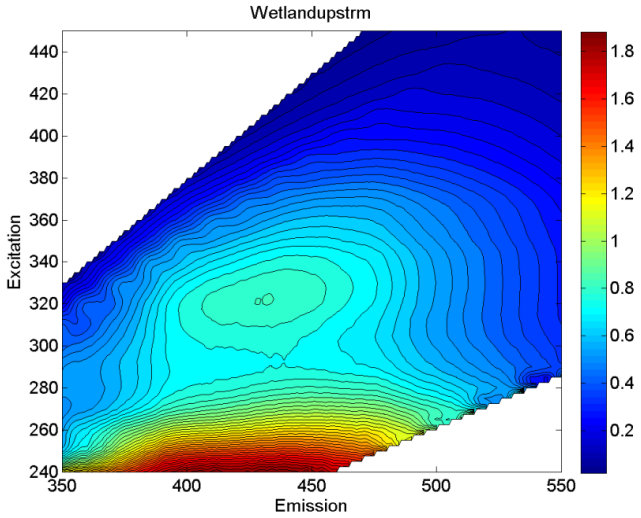
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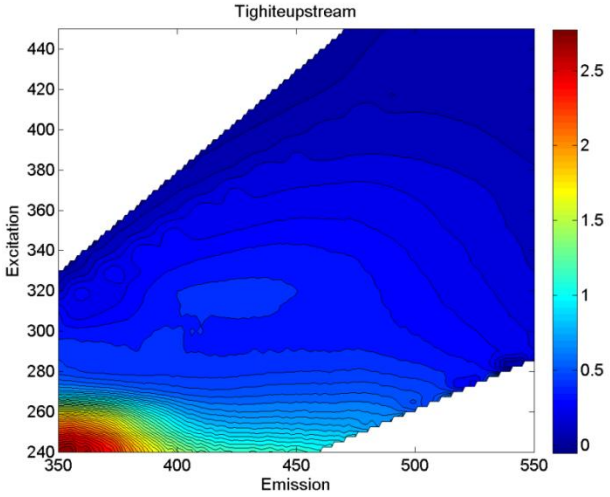
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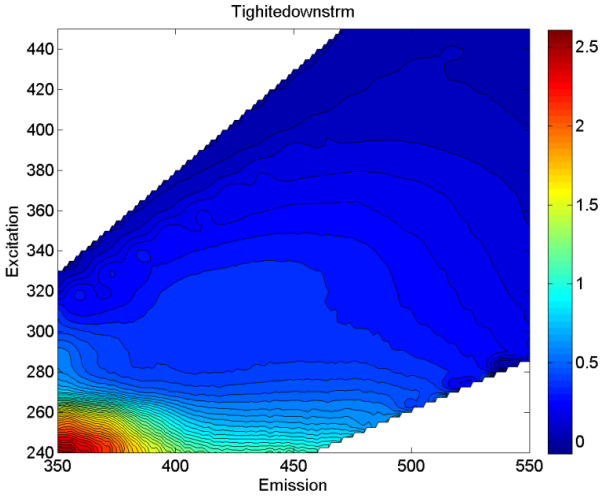
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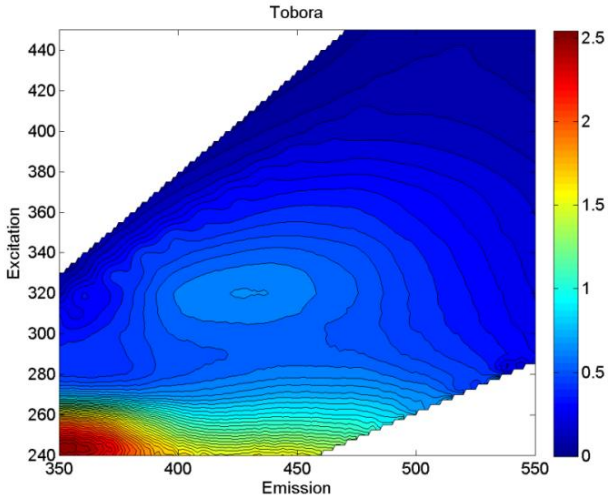
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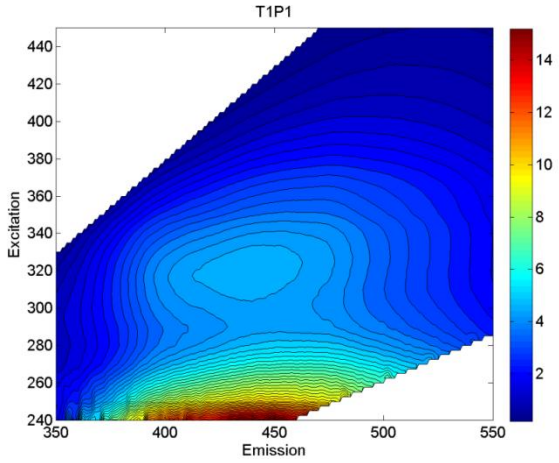
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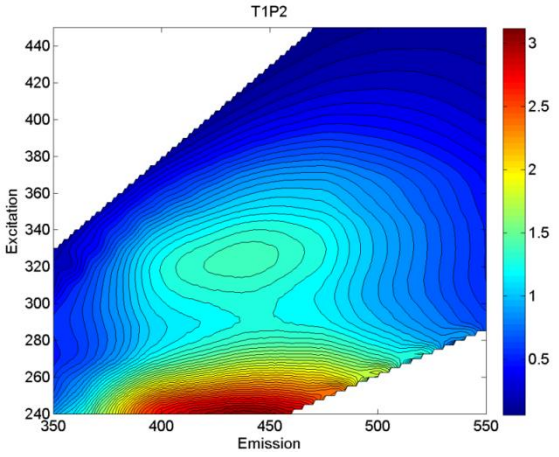
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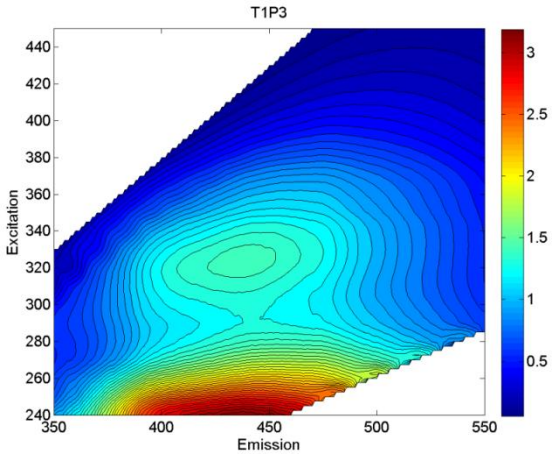
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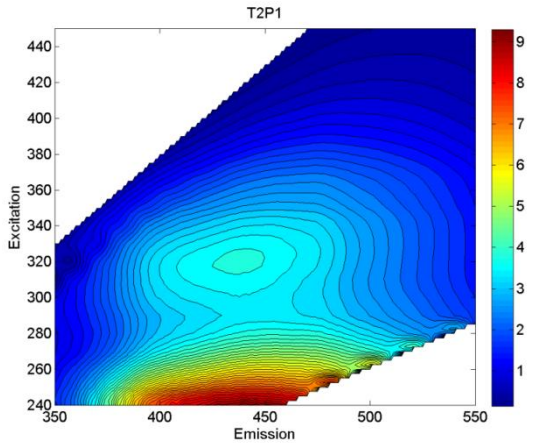
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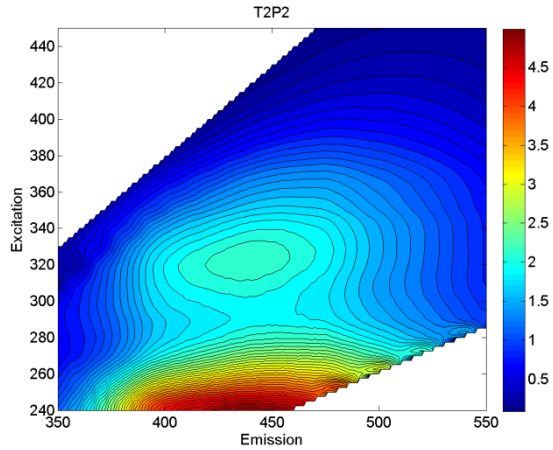
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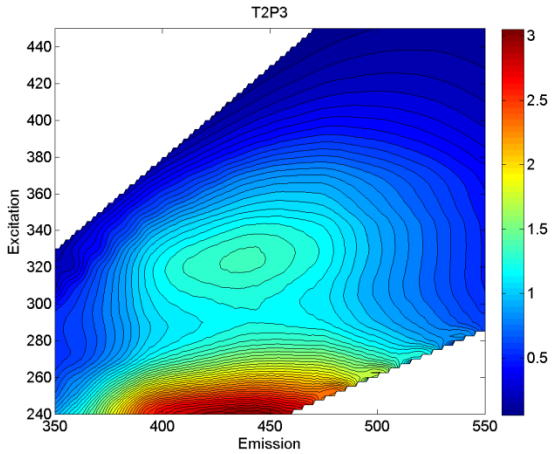
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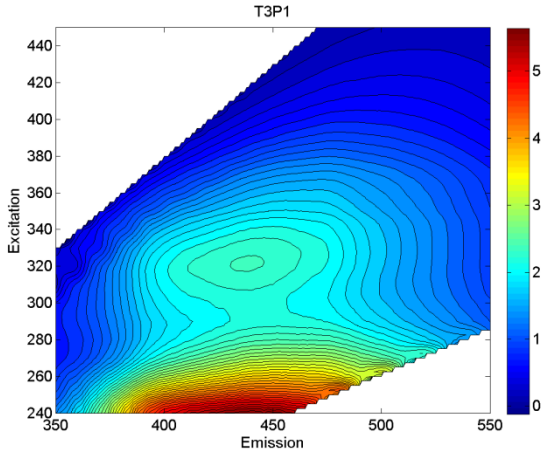
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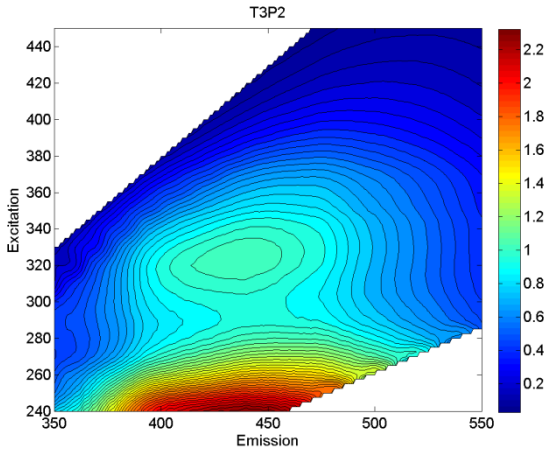
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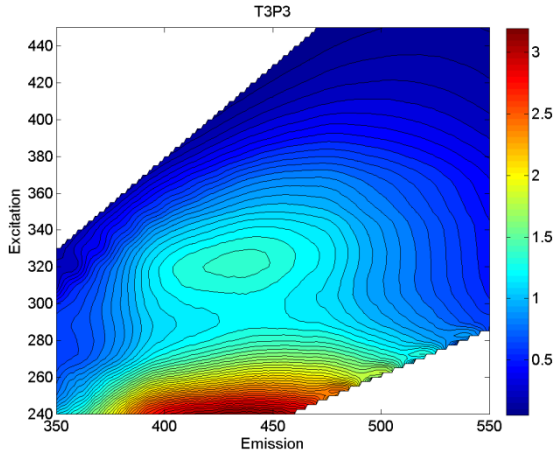
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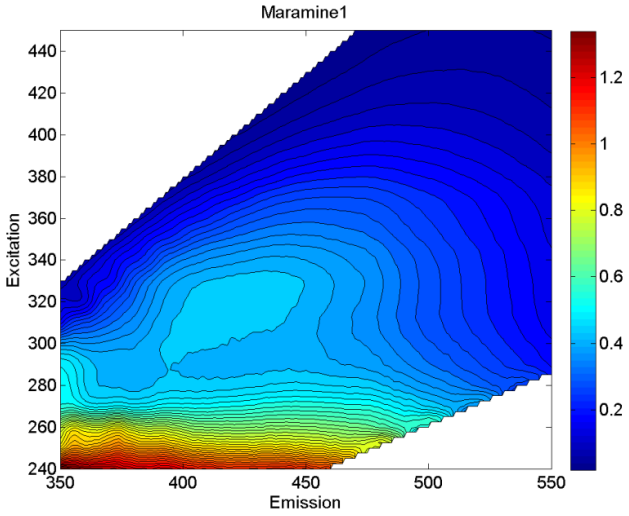
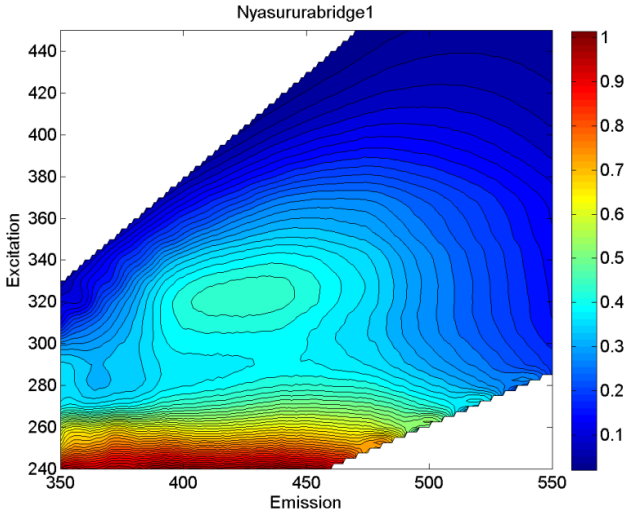
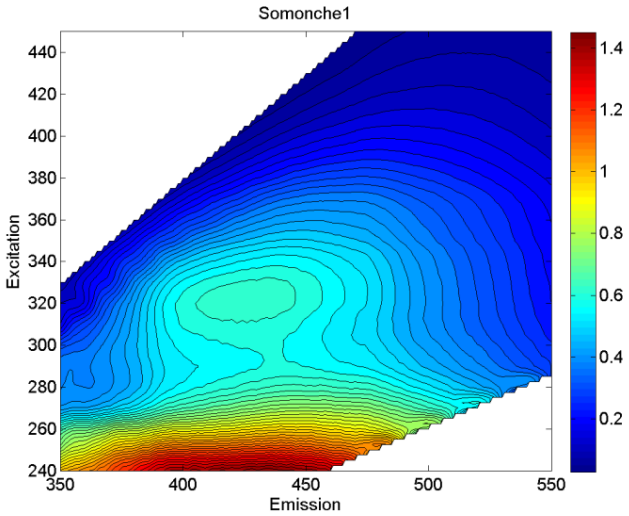
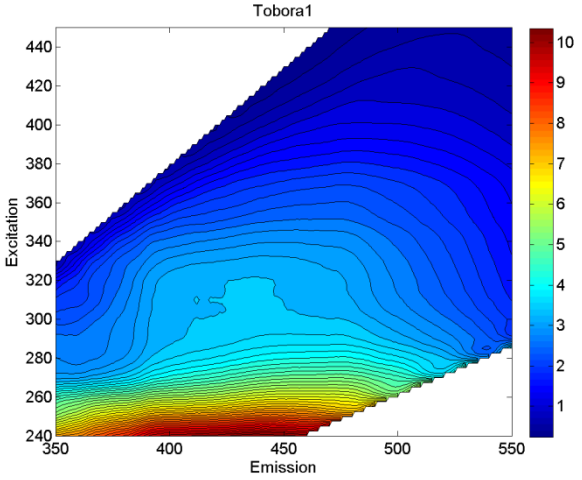
Annex 2: EEMs for January sampling





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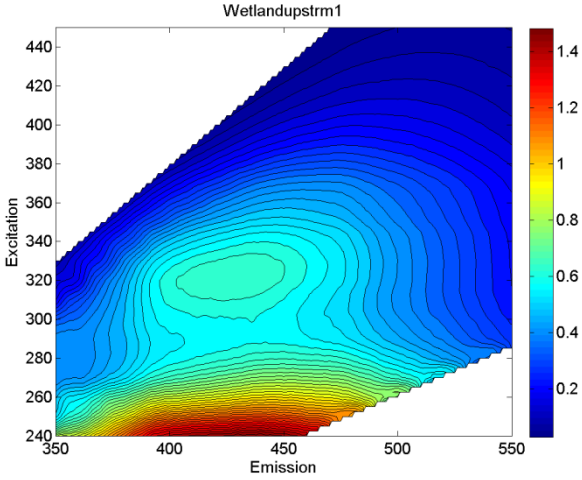
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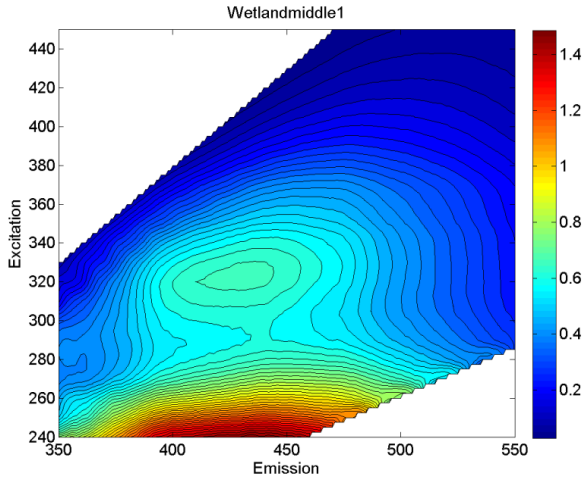
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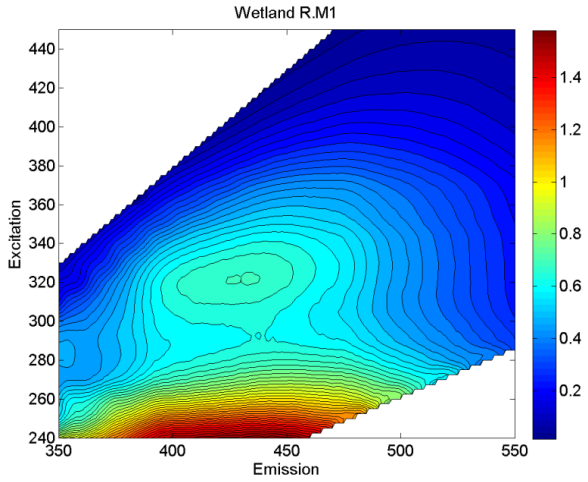
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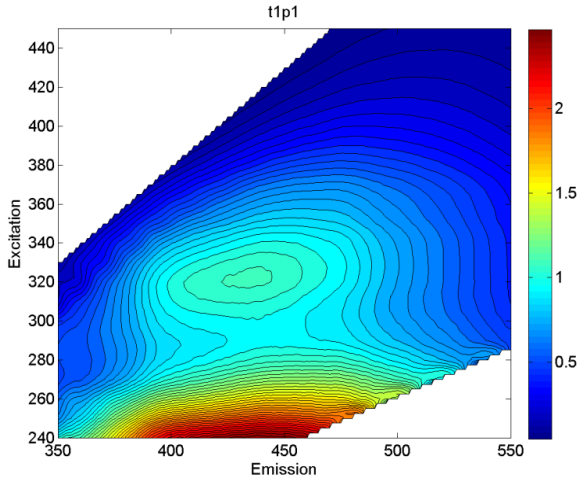
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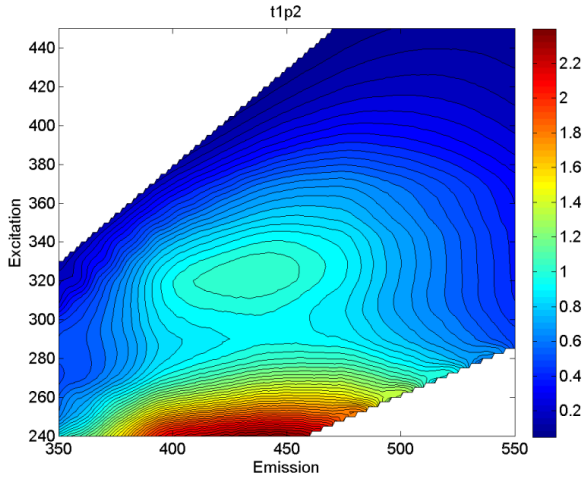
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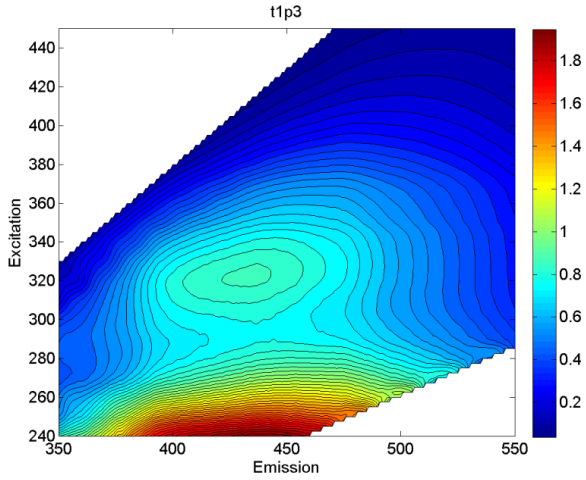
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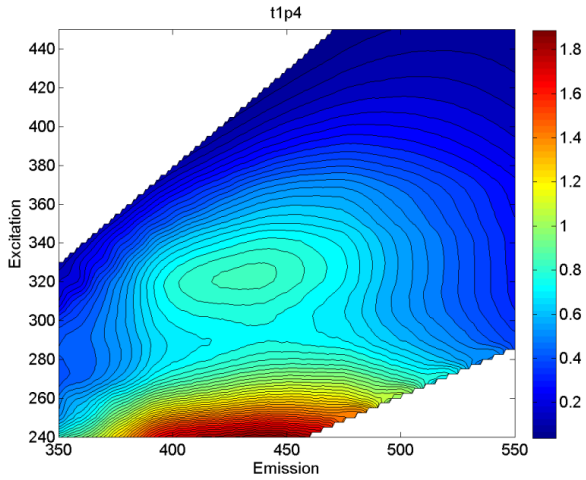
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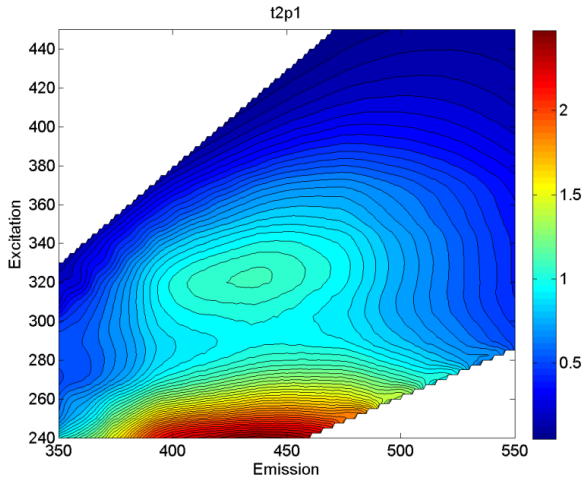
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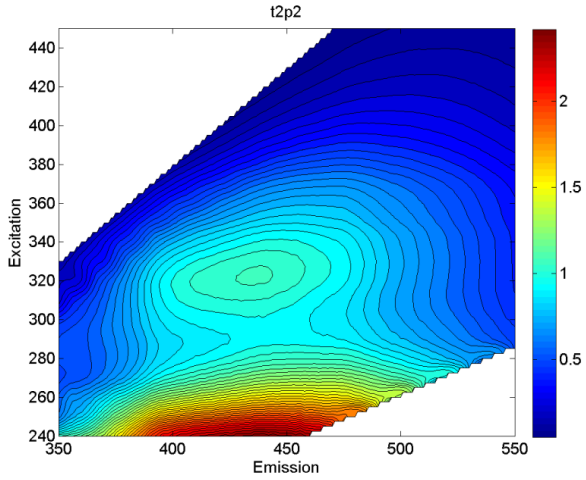
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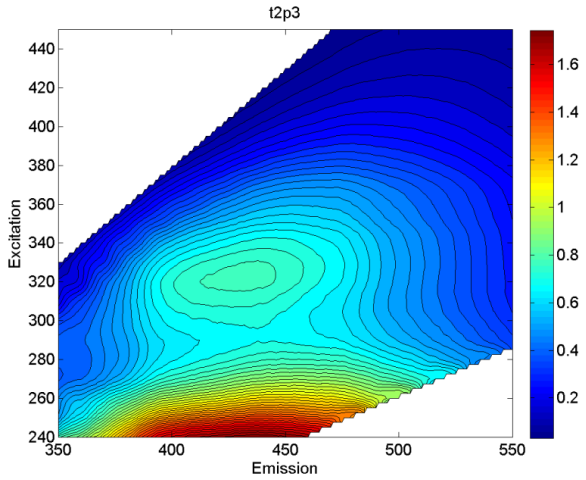
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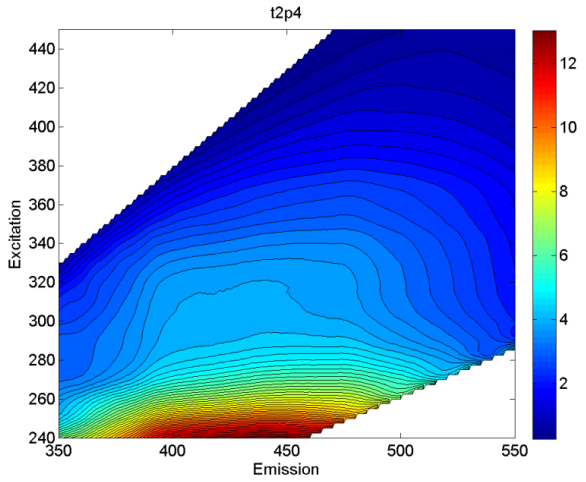
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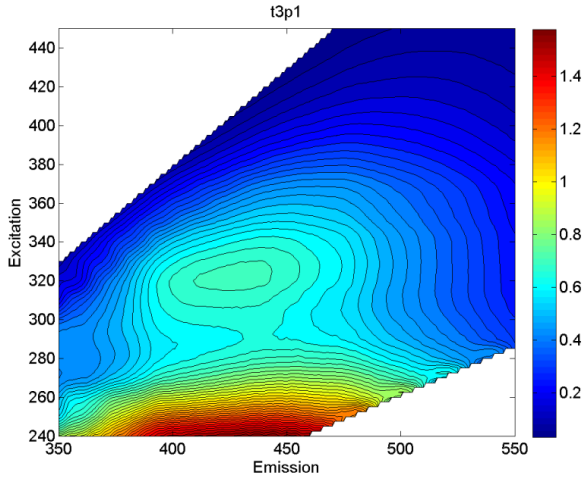
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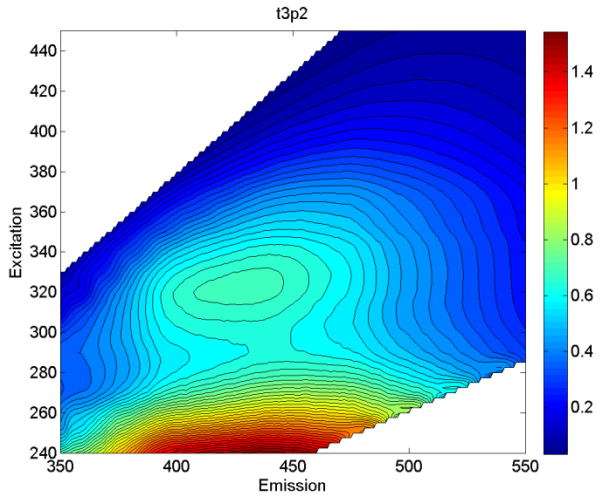
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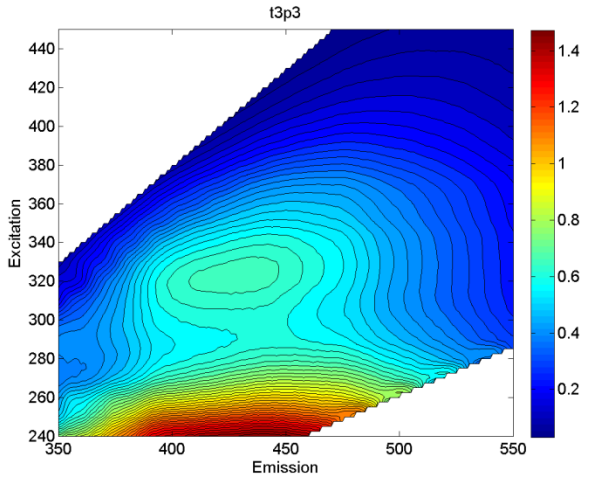
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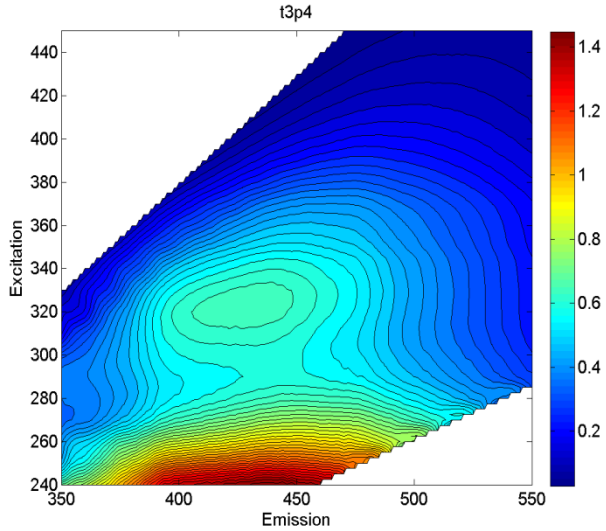
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Annex3: Physical chemical characteristics of water in selected sites of lower Mara River**.**

Date	Longitudes	Latatitudes	a_{340}	SR	SUVA	FI	T280	α:β	BIX	DOC	DON	C/N	NH4	NO3	TDN	PO4	TDP	DOP
11-Nov	E034028.4146	S01035.4255	38.23	0.448	1.29	1.42	1.14	0.40	0.75	40	1.58	26	0.15	0.07	1.8	0.1	0.2	0.06
11-Nov	E034036.3851	S01036.5397	63.1	0.037	6.06	1.19	8.13	0.38	0.81	14	1.24	11	0.17	0.06	1.47	0.1	0.1	0.03
11-Nov	E034028.4146	S01027.5043	60.11	0.056	14.94	1.33	1.03	0.32	0.81	5.4	2.53	2.4	0	0.09	2.62	0.1	0.1	0.05
11-Nov	E034028.4146	S01027.5043	55.04	0.038	12.06	1.35	1.02	0.33	0.76	6.4	2.56	2.8	0.02	0.12	2.7	0.1	0.1	0.02
11-Nov	E034035.5594	S01036.1974	30.63	0.040	1.65	1.42	0.95	0.33	0.79	26	0.66	34	0.13	0.08	0.87	0.1	0.1	0.02
11-Nov	E034029.1228	S01029.8451	44.91	0.009	10.28	1.43	1.27	0.41	0.83	12	0.67	8	0.11	0.09	0.87	0.2	0.2	0.01
11-Nov	E034000.5342	S01032.0042	31.78	0.494	4.50	1.43	0.96	0.34	0.76	6	0.28	38	0	0.03	0.32	0	0	0.01
11-Nov	E033059.7885	S01031.8216	32.47	0.477	4.43	1.41	0.93	0.33	0.75	10	0.26	45	0	0.03	0.29	0	0	0.01
11-Nov	E033057.6365	S01031.3875	33.85	0.426	4.68	1.42	1.05	0.34	0.77	11	0.12	87	0	0.03	0.16	0	0	0.01
11-Nov	E033059.6940	S01038.4880	53.43	0.547	3.83	1.38	1.05	0.43	0.73	22	0.35	63	0.01	0.05	0.4	0	0	0.01
11-Nov	E033059.6837	S01032.5150	48.59	0.616	3.82	1.38	1.09	0.43	0.72	20	0.09	144	0.01	0.06	0.16	0	0	0
11-Nov	E033059.6693	S01032.6272	196.4	0.615	4.18	1.35	1.24	0.53	0.71	74	2	36	0.14	0.24	2.38	0.4	0.6	0.13
11-Nov	E 034000.1074	S 01032.5450	51.13	0.511	1.59	1.33	1.32	0.60	0.71	50	0.2	235	0.01	0.04	0.25	0	0	0.02
11-Nov	E 034059.1083	S 01032.5599	90.74	0.513	8.66	1.16	8.02	0.39	0.82	16	0.61	27	0.01	0.09	0.71	0.1	0.1	0.03
11-Nov	E034000.1055	S01032.6056	139.8	0.633	3.77	1.38	1.01	0.41	0.73	59	1.28	48	0.01	0.14	1.43	0.2	0.2	0.05
11-Nov	E 034000.8319	S 01032.4582	77.38	0.379	1.53	1.34	1.29	0.57	0.71	59	0.18	321	0	0.03	0.21	0	0.1	0.01
11-Nov	E 034000.8326	S 01032.4731	38.46	0.463	1.59	1.35	1.29	0.55	0.71	37	0.23	167	0.01	0.02	0.26	0.1	0.1	0.02
11-Nov	E034000.8270	S01032.4975	91.2	0.522	7.27	1.42	0.88	0.76	0.76	19	0.75	26	0.03	0.1	0.88	0.1	0.1	0.05
12-Jan	E034028.4146	S01035.4255	26.25	0.179	4.86	1.42	0.94	0.76	0.76	8.3	0.29	10	0.62	0.07	0.97	0.2	0.2	0.02
12-Jan	E034036.3851	S01036.5397	26.71	0.262	0.61	1.42	0.90	0.75	0.75	62	0.6	46	0.84	0.14	1.58	0.2	0.2	-0.01
12-Jan	E034028.4146	S01027.5043	23.26	0.036	1.27	1.41	1.05	0.76	0.76	25	1.49	15	0.23	0.24	1.96	0.1	0.1	0.04
12-Jan	E034028.4146	S01027.5043	23.49	0.006	1.04	1.17	0.15	0.80	0.92	32	1.71	17	0.3	0.25	2.26	0.1	0.1	0.02
12-Jan	E034035.5594	S01036.1974	22.34	0.11	5.77	1.37	2.36	0.72	0.72	5.8	0.74	5.9	0.3	0.09	1.13	0	0.1	0.02
12-Jan	E034029.1228	S01029.8451	27.87	0.14	0.83	1.29	2.55	0.81	0.81	49	0.58	58	0.29	0.12	0.99	0.1	0.1	0.04
12-Jan	E034000.5342	S01032.0042	22.11	0.46	0.47	1.27	2.28	0.84	0.84	73	0.16	197	0.26	0.02	0.43	0.1	0.1	0.02
12-Jan	E033059.7885	S01031.8216	20.96	0.36	0.49	1.41	1.03	0.77	0.77	67	0.13	209	0.22	0.02	0.37	0.1	0.1	0.02
12-Jan	E033057.6365	S01031.3875	22.57	0.33	0.47	1.29	1.82	0.89	0.90	73	0.05	372	0.15	0.02	0.23	0.1	0.1	0.03
12-Jan	E033059.6939	S01038.4879	28.33	0.46	4.58	1.41	1.39	0.76	0.76	9.3	0.16	33	0.14	0.02	0.33	0	0.1	0.03
12-Jan	E033059.6940	S01038.4880	28.1	0.49	4.28	1.37	1.41	0.75	0.75	10	0.47	20	0.11	0.02	0.59	0.1	0.1	0.03
12-Jan	E033059.6837	S01032.5150	35.24	0.57	4.20	1.40	1.33	0.73	0.74	13	0.23	38	0.11	0.04	0.38	0.1	0.1	0.03
12-Jan	E033059.6693	S01032.6272	40.76	0.45	4.63	1.37	1.44	0.67	0.67	13	0.75	16	0.15	0.04	0.94	0.2	0.2	0.05
12-Jan	E 034000.1073	S 01032.5449	25.79	0.36	4.55	1.38	1.38	0.68	0.68	8.5	0.02	64	0.11	0.03	0.16	0.1	0.1	0.03
12-Jan	E 034000.1074	S 01032.5450	27.18	0.41	4.76	1.25	5.49	0.61	0.61	8.6	0.23	27	0.13	0.01	0.37	0.1	0.1	0.04
12-Jan	E 034059.1083	S 01032.5599	38.23	0.55	4.39	1.38	1.42	0.68	0.68	13	0.39	28	0.11	0.04	0.54	0.1	0.1	0.03
12-Jan	E034000.1055	S01032.6056	36.39	0.60	4.05	1.34	1.96	0.65	0.66	14	0.3	36	0.1	0.03	0.44	0.1	0.1	0.04
12-Jan	E 034000.8318	S 01032.4581	20.27	0.42	4.33	1.29	3.22	0.65	0.65	7.1	0.25	24	0.08	0.01	0.34	0.1	0.1	0.03
12-Jan	E 034000.8319	S 01032.4582	20.96	0.39	4.15	1.38	1.59	0.69	0.69	7.8	0.09	43	0.1	0.02	0.21	0.1	0.1	0.03
12-Jan	E 034000.8326	S 01032.4731	22.34	0.48	1.89	1.38	1.11	0.68	0.68	8.2	0.18	63	0.13	0.02	0.32	0.1	0.1	0.04
12-Jan	E034000.8270	S01032.4975	23.49	0.36	4.37	1.31	2.32	0.65	0.65	18	0.47	16	0.12	0.02	0.61	0.1	0.1	0.04

9 References

Abelho M (2001) from litterfall to breakdown in streams. The Scientific World 1:658- 680

Aiken, G., and Leenheer, J. (1993) Isolation and chemical characterization of dissolved and colloidal organic matter. Chemistry and Ecology, 8, 135–151.

Aiken, G. R., Gilmour, C. C., Krabbenhoft D. P., and Orem W. (2011). Dissolved Organic matter in the Florida Everglades: Implications for ecosystem restoration. Critical Reviews in Environmental Science and Technology 41: S1, 217–248.

Allan JD (1995) Stream ecology: Structure and function of running waters Chapman & Hall, London

Aufdenkampe AK, Hedges JI, Richey JE, Krusche AV, L lerena CA. 2001. Sorptive fractionation of dissolved organic nitrogen and amino acids onto fine sediments within the Amazon Basin. Limnol Oceanogr 46:1921–35

Baghoth, S. A., S. K. Sharma, et al. (2011). "Tracking natural organic matter (NOM) in a drinking water treatment plant using fluorescence–emission matrices and PARAFAC." Water Research 45(2): 797-809.

Baker A. Spectrophotometric discrimination of river dissolved organic matter. Hydrological Processes (2002b) 16:3203-3213.

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

Baker A, Inverarity R. Protein-like fluorescence intensity as a possible tool for determining river water quality. Hydrological Processes (2004) 18:2927-2945.

Baker A, Inverarity R, Charlton M, Richmond S. Detecting river pollution using fluorescence spectrophotometry: case studies from the Ouseburn, NE England. Environmental Pollution (2003) 124:57-70.

Baker, A. and R. G. M. Spencer (2004). "Characterization of dissolved organic matter from source to sea using fluorescence and absorbance spectroscopy." Science of The Total Environment 333(1-3): 217-232.

Badr E-SA, Achterberg EP, Tappin AD, Hill SJ, Braungardt CB (2003) Determination of dissolved organic nitrogen in natural waters using high-temperature catalytic oxidation. TrAC Trends in Analytical Chemistry 22: 819-827

Battin TJ, Kaplan LA, Findlay S, Hopkinson CS, Marti E, Packman AI, Newbold JD, Sabater F (2008) Biophysical controls on organic carbon fluxes in fluvial networks. Nature Geosci 1: 95-100

Battin TJ, Tranvik LJ, Luyssaert S, Kaplan LA, Aufdenkampe AK, Richter A. The boundless carbon cycle. Nat. Geosci. Nature Geoscience (2009) 2:598-600.

Boyer EW, Hornberger GM, Bencala KE et al (2000) Effects of asynchronous snowmelt on flushing of dissolved organic carbon: a mixing model approach. Hydrol Process 14:3291–3308

Carpenter SR, Cole JJ, PaceML et al (2005) Ecosystems subsidies: terrestrial support of aquatic food webs from ^{13}C addition to contrasting lakes. Ecology 86:2737–2750. doi:10.1890/04-1282

Chin, Y.-P.; Aiken,G.;Danielson, K. Environ. Sci. Technol. 1997, 31, 1630 -1635.

Coble GP (1996) Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. Marine Chemistry 51: 325-346

Coble PG, Green SA, Blough NV, Gagosian RB. Characterization of dissolved organic matter in the Black Sea by fluorescence spectroscopy. Nature (1990) 348:432-435.

Cole J, Prairie Y, Caraco N, McDowell W, Tranvik L, Striegl R, Duarte C, Kortelainen P, Downing J, Middelburg J, Melack J (2007) Plumbing the Global Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget. Ecosystems 10: 172-185

Cotner JB, Biddanda BA, Makino W et al (2004) Organic carbon biogeochemistry of Lake Superior. Aquat Ecosyst Health 7:451–464

Cory, R.M.;McKnight,D.M. Fluorescence spectroscopy revealsubiquitous presence of oxidized and reduced quinones in dissolved organicmatter. Environ. Sci. Tecnol. 2005, 39, 81428149.

Debusk WF, Reddy KR (2005) Litter Decomposition and Nutrient Dynamics in a Phosphorus Enriched Everglades Marsh. Biogeochemistry 75: 217-240 DOI 10.1007/s10533-004-7113

Engstrom, D. R. (1987). "Influence of Vegetation and Hydrology on the Humus Budgets of Labrador Lakes." Can. J. Fish. Aquat. Sci. 44(7) 1306-1314

Fellman JB, D'Amore DV, Edwards RT, White D. Seasonal changes in the chemical quality and biodegradability of dissolved organic matter exported from soils to streams in coastal temperate rainforest watersheds. Biogeochemistry (2009) 95:2-3.

Fellman JB, Hood E, Spencer RGM. Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review. Limnology and oceanography. (2010) 55:2452.

Findlay, S. E. G., and Sinsabaugh, R. L. (Eds.). (2003). Aquatic ecosystems: Interac tivity of dissolved organic matter. Academic Press, San Diego, CA.

Gomi T, Siddle RC, Richardson SJ (2002) Understanding processes and downstream linkages of headwater systems. Bioscience 52: 905-916

Helms RJ, Stubbins A, Ritchie DJ, Minor CE (2008) Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. Limnol Oceanogr 53: 955-969

Henderson, R. K., A. Baker, et al. (2009). "Fluorescence as a potential monitoring tool for recycled water systems: A review." Water Research 43(4): 863-881.

Hudson, N., A. Baker, et al. (2008). "Can fluorescence spectrometry be used as a surrogate for the Biochemical Oxygen Demand (BOD) test in water quality assessment? An example from South West England." Science of The Total Environment 391(1): 149-158.

Hernes, P. J. (2009). Utilizing chromophoric dissolved organic matter measure-ments to derive export and reactivity of dissolved organic carbon exported to the Arctic Ocean: A case study of the Yukon River, Alaska. Journal of Geophysical Research,36,L06401.doi:10.1029/2008GL036831

Integrated Water Quality/ Limnology Study for Lake Victoria; Consultant Technical Report LVEMP/COWI, (2001). Dar-es-salaam-Tanzania.

Keeny, D.R. 1973. The Nitrogen Cycle in Sediment-Water Systems. Journal Environ. Quality 2(1):15-29.

Kowalczuk P, Cooper WJ, Durako MJ, Kahn AE, Gonsior M, Young H. Characterization of dissolved organic matter fluorescence in the South Atlantic Bight with use of PARAFAC model: Relationships between fluorescence and its components, absorption coefficients and organic carbon concentrations. Marine Chemistry (2010) 118:22-36.

Kraus, T. E. C., Bergamaschi, B. A., Hernes, P. J., Spencer, R. G. M., Stepanauskas, R., Kendall, C., Losee, R. F., and Fujii, R. (2008). Assessing the contribution of wetlands and subsided islands to dissolved organic matter and disinfection by product precursors in the Sacramento-San Joaquin River Delta: A geochemical approach. Organic Geochemistry, 39, 1302–1318

Lean, D. (1998). Attenuation of solar radiation in humic waters. In D. O. Hessen and L. J. Tranvik (Eds.), Aquatic humic substances: Ecology and biogeochemistry. Ecological studies (Vol. 133, pp. 109–124). Springer-Verlag, Berlin.

Lee, G, E., Bentley and R. Amundson. 1969. Effect of Marshes on Water Quality. University of Wisconsin, Madison.

Li, C.-W.; Benjamin, M.M.; Korshin, G. V. Environ. Sci. Technol.2000, 34, 2570 -2575.

Mati, M. B., S. Mutie, et al. (2005). Land Use Changes in the Transboundary Mara Basin: A Threat to Pristine Wildlife Sanctuaries in East Africa. 8th International River Symposium. Brisbane.

McKnight, D. M., and Aiken, G. R. (1998). Sources and age of aquatic humic substances. In D. Hessen and L. J. Tranvik (Ed.), Aquatic humic substances: Ecology and biogeochemistry. Ecological studies (pp. 9–40). Springer, New York.

McKnight MD, Boyer WE, Wasterhoff KP, Doran TP, Kulbe T, Andersen TD (2001) Spectrofluorometric characterisation of dissolved organic matter for indication of precursor organic material and aromaticity. Limnol Oceanogr 46: 38-48

Miller, C. M., Gilmour, C. C., Heyes, A., and Mason, R. P. (2007). Influence of dissolved organic matter on the complexation of Hg under sulfidic conditions.Environmental and Toxicological Chemistry, 26, 624–633.

Miller MP, McKnight DM, Cory RM et al (2006) Hyporheic exchange and fulvic acid redox reactions in an alpine stream. Environ Sci Technol 40:5943–5949

Mobed, J. J.; Hemmingsen, S. L.; Autry, J. L.; McGown, L. B.Fluorescence characterization of IHSS humic substances: Totalluminescence spectrawith absorbance correction. Environ. Sci.Technol. 1996, 30, 3061 3065.

Mopper, K.; Schultz, C. A. Fluorescence as a possible tool forstudying the nature of water column distribution of DOC components. Mar. Chem. 1993, 41, 229 238.

Morel, F. M. M., and Gschwend, P. M. (1987). The role of colloids in the partitioning of solutes in natural waters. In W. Stumm (Ed.), Aquatic surface chemistry (pp. 405–422). Wiley,New York.

Nichols, D. 1983. Capacity of Natural Wetlands to Remove Nutrients from Wastewater. Jour. Of Water Poll. Control Fed. 55(5):495.

Nixon, S.W., 1995. Coastal marine eutrophication: a definition, social causes, and future concerns. Ophelia 41:199-219.

Orem, William, Gilmour, Cynthia, Axelrad, Donald, Krabbenhoft, David, Scheidt, Daniel, Kalla, Peter, McCormick, Paul, Gabriel, Mark and Aiken, George (2011) 'Sulfur in the South Florida Ecosystem: Distribution, Sources, Biogeochemistry, Impacts, and Management for Restoration', Critical Reviews in Environmental Science and Technology, 41: 6, 24 288

Owen, D. M., G L Amy, Z K Chowdhury, R Paode, G McCoy, K Viscosil (1995). "NOM Characterization and Treatability." AWWA 87 (1): 46-63.

Parlanti E, Wörz 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

Paula G, C. (1996). "Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy." Marine Chemistry 51(4): 325-346.

Pisani, O., Y. Yamashita, et al. (2011). "Photo-dissolution of flocculent, detrital material in aquatic environments: Contributions to the dissolved organic matter pool." Water Research 45(13): 3836-3844.

Qualls, R. G., and Richardson, C. J. (2003). Factors controlling concentration, export and decomposition of dissolved organic nutrients in the Everglades, Florida. Biogeochemistry, 62, 197–229.

Qualls, R. G., and Richardson, C. J. (2008a). Carbon cycling and dissolved organicmatter export in the northern Everglades. In C. J. Richardson (Ed.), The Everglades experiments: Lessons for ecosystem restoration. Ecological studies (pp.351–374). Springer, New York.

Raymond, P. A. and J. E. Bauer (2001). "Use of 14C and 13C natural abundances for evaluating riverine, estuarine, and coastal DOC and POC sources and cycling: a review and synthesis." Organic Geochemistry 32(4): 469-485.

Reddy, M. M., and Aiken, G. R. (2001). Fulvic acid-sulfide ion competition for mer-cury ion binding in the Florida Everglades. Water, Air, and Soil Pollution, 132,89–10

Richardson, T. L., G. A. Jackson, et al. (2004). "Carbon fluxes through food webs of the eastern equatorial Pacific: an inverse approach." Deep Sea Research Part I: Oceanographic Research Papers 51(9): 1245-1274.

Richardson SJ, Bilby ER, Bondar AC (2005) Organic matter dynamics in small streams of the Pacific Northwest. Journal of the American Water Resources Association 41: 921-934

Seredyńska-Sobecka, B., A. Baker, et al. (2007). "Characterisation of colloidal and particulate organic carbon in freshwaters by thermal fluorescence quenching."

Skoog DA. Principles of instrumental analysis. W. (1985) Philadelphia: Saunders College.

Spencer RGM, Pellerin BA, Bergamaschi BA et al (2007) Diurnal variability in riverine dissolvedorganic matter composition determined by in situ optical measurement in the San Joaquin

River (California, USA). Hydrol Process 21:3181–3189. doi:10.1002/hyp. 6887

Stedmon CA, Markager S, Bro R (2003) Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. Marine Chemistry 82:239-254

Stedmon, C. A.; Markager, S.; Kaas, H. Optical properties and signatures of chromophoric dissolved organic matter (CDOM) in Danish coastal waters. Estuarine, Coastal Shelf Sci. 2000, 51,267 -278.

Steinman DA, Lamberti AG, Leavitt RP (2007) Biomass and pigments of benthic algae. In: Hauer FR, Lamberti AG (eds) Methods in stream ecology.

Thurman EM (1985) Developments in biogeochemistry: organic geochemistry of natural waters Martinus Nijhoff and Dr W. Junk Publishers

Twardowski MS, Boss E, Sullivan JM, Donaghay PL (2004) Modeling the spectral shape of absorption by chromophoric dissolved organic matter. Marine Chemistry 89: 69-88

Wang, Y., Hsieh, Y. P., Landing, W. M., Choi, Y. H., Salters, V., and Campbell, D.(2002). Chemical and carbon isotopic evidence for the source and fate of dissolved organic matter in the northern Everglades. Biogeochemistry, 61, 269–289.

Weishaar JL, Aiken RG, Bergamaschi BA, Fram MS, Fujii R, Mopper K (2003) Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ Sci Technol 37: 4702-4708

Wetzel, R. G. (2001). Limnology: Lake and river systems (3rd ed.). Academic Press, Orlando,FL.

Wipfli M, Musslewhite J (2004) Density of red alder (Alnus rubra) in headwaters influences invertebrate and detritus subsidies to downstream fish habitats in Alaska. Hydrobiologia 520: 153-163

Woelki, G., S. Friedrich, et al. (1997). "HPLC fractionation and structural dynamics of humic acids." Fresenius' Journal of Analytical Chemistry 357(5): 548-5