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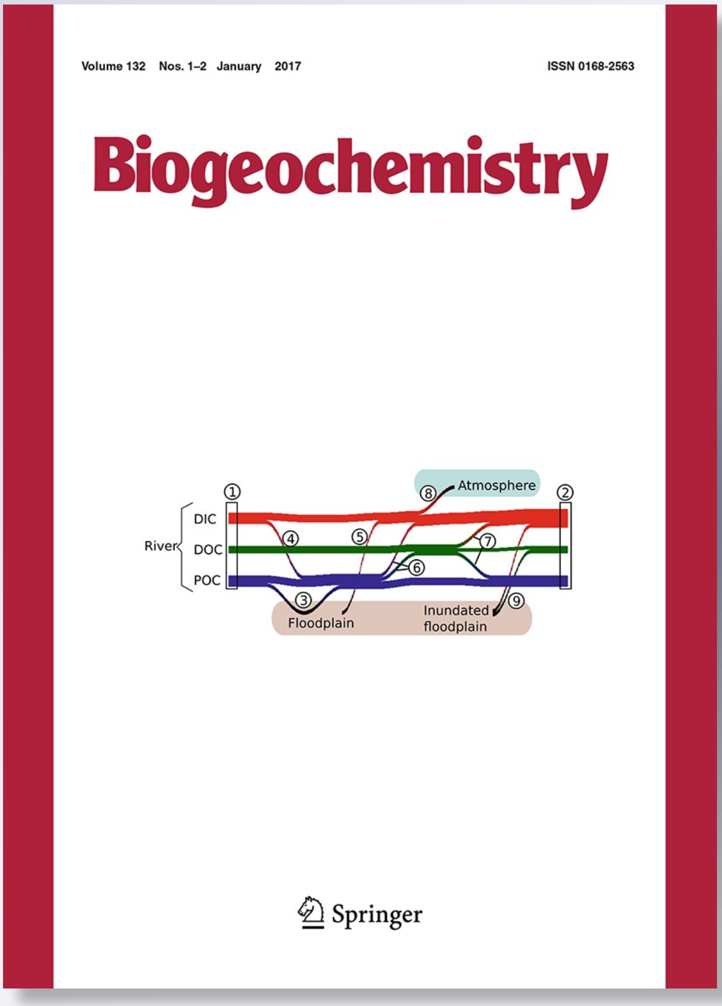
Biogeochemistry
An International Journal

ISSN 0168-2563
Volume 132
Combined 1-2

Biogeochemistry (2017) 132:1-22
DOI 10.1007/s10533-016-0269-6



Springer

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Influence of catchment land use and seasonality on dissolved organic matter composition and ecosystem metabolism in headwater streams of a Kenyan river

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Received: 7 January 2016 / Accepted: 24 October 2016 / Published online: 9 December 2016

Abstract Headwater streams influence the biogeochemical characteristics of large rivers and play important roles in regional and global carbon budgets. The combined effects of seasonality and land use change on the biogeochemistry of headwater streams, however, are not well understood. In this study we assessed the influence of catchment land use and seasonality on the composition of dissolved organic matter (DOM) and ecosystem metabolism in headwater streams of a Kenyan river. Fifty sites in 34 streams draining a gradient of catchment land use from 100% natural forest to 100% agriculture were sampled to determine temporal and spatial variation in DOM composition. Gross primary production (GPP) and ecosystem respiration (ER) were determined in 10 streams draining primarily forest or agricultural catchments. Absorbance and fluorescence spectrophotometry of DOM reflected notable shifts in composition along the land use gradient and with season. During the dry season, forest streams contained higher molecular weight and terrestrially derived DOM, whereas agricultural streams were dominated by autochthonous production and low molecular weight DOM. During the rainy season, aromaticity and high molecular weight DOM increased in agricultural streams, coinciding with seasonal erosion of soils and inputs of organic matter from farmlands. Most of the streams were heterotrophic. However, GPP and ER were generally greater in agricultural streams, driven by higher dissolved nutrient (mainly TDN) concentrations, light availability (open canopy) and temperature compared with forest streams. There were correlations between freshly and autochthonously produced DOM, GPP and ER during both the dry and wet seasons. This is one of the few studies to link land-use with organic carbon dynamics and DOM composition. Measures of ecosystem metabolism in these streams help to affirm the role of tropical streams and rivers as important components of the global carbon cycle and demonstrate that even semi-intensive, smallholder agriculture can have measurable effects on riverine ecosystem functioning.

Keywords Carbon cycling · DOM composition · Land use change · Whole-stream metabolism · Tropical streams

Responsible Editor: Jacques C. Finlay.

Electronic supplementary material The online version of this article (doi:10.1007/s10533-016-0269-6) contains supplementary material, which is available to authorized users.

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Introduction

Agricultural development and the loss of natural forests is a widespread global phenomenon that has diverse effects on streams and rivers (Allan 2004; Carpenter et al. 2011). Conversion of natural forest into agriculture has been linked to biodiversity loss and modification of ecosystem processes, such ecosystem metabolism, carbon and nutrient cycling in streams and rivers (Lepori et al. 2005; Gücker et al. 2009; Silva-Junior et al. 2014). While land use change, and specifically conversion of forest land to agriculture and pasture, seems to be stabilizing in many parts of the temperate world, it is still expanding in many parts of the tropics (Lambin et al. 2001; FAO 2010). This is the case in Africa, where increasing food demand amid the growing human population are expected to lead to cropland expansion and intensification in the coming years (Tilman et al. 2011; McClain 2013). Although limited, studies in tropical African headwater streams have linked agricultural land use with reduced canopy cover, increased water temperature, nutrients, and sediments, and reduced inputs of plant litter and standing stocks of organic matter (Magana 2001; Chapman and Chapman 2003; Masese et al. 2014a, b). These changes at both the catchment and reach scales are likely to affect the concentration and composition of DOM and stream ecosystem metabolism, which provide an integral measure of both carbon flux and overall ecosystem structure and function (Mulholland et al. 2001; Gücker et al. 2009; Tank et al. 2010; Bernot et al. 2010). While there have been notable recent studies on the biogeochemistry and C cycling in medium to large African rivers (Bouillon et al. 2009, 2012; Spencer et al. 2012; Borges et al. 2015; Teodoru et al. 2015), studies of the mechanisms that control the biogeochemistry and fluvial metabolism in tropical African headwater streams are very limited.

Ecosystem metabolism is an integrative measure of the processing of organic matter (i.e., production and respiration), and many studies have investigated both rates and controls in streams and rivers. Although drivers and responses are largely stream specific, the main factors that influence stream ecosystem metabolism include light availability, temperature, nutrients, organic matter quantity and quality, and hydrologic conditions (Elwood et al. 1981; Hill et al. 1995; Mulholland et al. 2001; Griffiths et al. 2013), and these proximal factors are influenced by distal controls such as catchment land use, soil, vegetation, and climate (Bernot et al. 2010). However, much of our understanding of carbon dynamics in streams and rivers is based on studies of temperate biomes, with the tropical biomes clearly underrepresented in available data (Battin et al. 2008). This is disproportionate considering that tropical rivers are responsible for larger fluxes of greenhouse gases to the atmosphere than their temperate counterparts (Aufdenkampe et al. 2011; Rasera et al. 2013; Borges et al. 2015), and at the same time transport >60% of the global riverine carbon (Ludwig et al. 1996; Schlünz and Schneider 2000). In order to more fully understand the role of river systems in C cycling and effects on global and region carbon budgets, additional data are needed for tropical systems.

The importance of DOM in the understanding of carbon dynamics (Battin et al. 2008; Tank et al. 2010) has led to many studies on the links between catchment land use and DOM quality in streams. While the influence of agricultural land use on fluvial DOM quality is unequivocal (Stanley et al. 2012), specific properties of DOM vary. For instance, streams draining agricultural catchments have been found to have both elevated levels of microbially derived and structurally less complex DOM (Wilson and Xenopoulos 2009; Williams et al. 2010) and elevated levels of structurally complex and aromatic DOM (Graeber et al. 2012) as compared with forested streams. These apparently divergent findings suggest that the proportion of agricultural land within a catchment alone is unlikely to explain patterns in DOM composition in recipient streams. Land use history, soil type, tillage practice or technique, catchment topography, climate and alterations to hydrological residence times and flow paths, in addition to the uptake rates and provenance to metabolism of the different pools of DOM, all have the potential to influence DOM composition in streams (Ogle et al. 2005; Ewing et al. 2006; Stanley et al. 2012). These changes in DOM composition have the further potential to impact stream metabolism (Cammack et al. 2004; Barrón et al. 2014; Halbedel et al. 2013).

In this study, we determined the spatial variation in DOM concentration and composition among 34 streams draining different proportions of forest and agricultural land in the headwaters of the Mara River basin, Kenya. Due to the strong temporal flow variations in the study area, we also examined seasonal variation in DOM concentration and composition at 10 streams (5 forest and 5 agricultural) during the dry and wet seasons. The same sites were also used for direct measurements of whole-stream metabolism [gross primary production (GPP) and ecosystem respiration (ER)]. We investigated possible relationships between DOM composition and ecosystem metabolism in the 10 streams. We predicted that (H1) streams draining agricultural catchments have higher proportions of autochthonously derived DOM than streams draining forest, and we hypothesized that (H2) agricultural streams have higher rates of ecosystem metabolism as a result of increased nutrient concentrations and reduced canopy cover. Finally, we hypothesized that, (H3) because DOM composition influences bioavailability for metabolism and, reciprocally, ecosystem metabolism affects DOM composition, such dependencies should lead to relationships between measures of ecosystem metabolism and DOM composition in streams.

Methods

Study area

The study was conducted in mid-elevation (1900–2300 m a.s.l.) streams draining the western slopes of the Mau Escarpment, which forms part of the Kenyan Rift Valley. The streams form the headwaters of the Mara River, which flows to Lake Victoria. The river drains the extensive tropical moist broadleaf Mau Forest Complex (MFC) that is a major source of many rivers in western Kenya (Fig. 1). Substantial parts of the MFC have been encroached and cleared, and in the upper Mara River Basin, 32% of the forest was cut between the years 1973 and 2000 (Mati et al. 2008). However, some intact forest blocks remain as part of forest reserves and national parks. People living in the adjoining areas are mainly involved in semi-intensive smallholder agriculture, characterized by cash crops (mainly tea), food crops (mainly maize, beans, and potatoes), and animal husbandry. Farming is not mechanized but fertilizer use is common. On most farms, riparian corridors have been maintained, but native vegetation along agriculture streams has been cleared and replaced by exotics, mainly *Eucalyptus* species. A number of small towns are spread out in the agricultural areas and none have a sewerage system for handling human waste. People in towns and rural settlements use toilets, and some are very close to waterways. Thus there is a potential of leakages to streams and rivers, especially during the wet season.

Climate of the area is relatively cool and seasonal with annual precipitation ranging from 1000 to 2000 mm. Dry conditions occur between two wet seasons (March–May and October–December), which are periods for the long and short rains, respectively. Spatially, rainfall in the catchment increases with elevation, with higher rains on the Mau Escarpment. During the dry season shedding of leaves is higher as compared with the rainy season (Magana 2001), and some tree species shed all their leaves (FOM pers. obser.). This phenological characteristic leads to openings of the canopy over streams. Consequently, intensity of insolation in streams is higher and of longer duration during the dry season.

Sampling design

To capture spatial variability in organic matter characteristics, nutrient concentrations and water physicochemistry, samples were collected from 50 sites spanning 34 different streams from December 2011–January 2012. Sites were located in streams draining a gradient of catchment land use from 100% forest to 100% agriculture and classified into three broad land use categories (AGR, FOR and MIX) depending on the proportions of forest and agriculture land uses. Based on the Digital Elevation Model of Kenya (90 m by 90 m) produced using data from the Shuttle Radar Topography Mission, catchments were delineated and the area of each land use category upstream of each sampling site was calculated. Forest sites (FOR, $n = 19$) and agricultural sites (AGR, $n = 17$) drained catchments with the percentage of catchment land use >60% for forest and agriculture, respectively. Both natural and plantation forests were categorized under forest land use (FOR), but the proportion of plantation forestry in FOR sites was much smaller, <1%. The third category of sites, mixed (MIX, $n = 14$) sites, did not meet the catchment land use criteria for FOR or AGR sites. Data collected from the 50 sites constituted the synoptic dataset used to explore relationships of catchment land use with water quality and organic matter characteristics in AGR, MIX and FOR streams. In addition, a metabolism data set was collected to

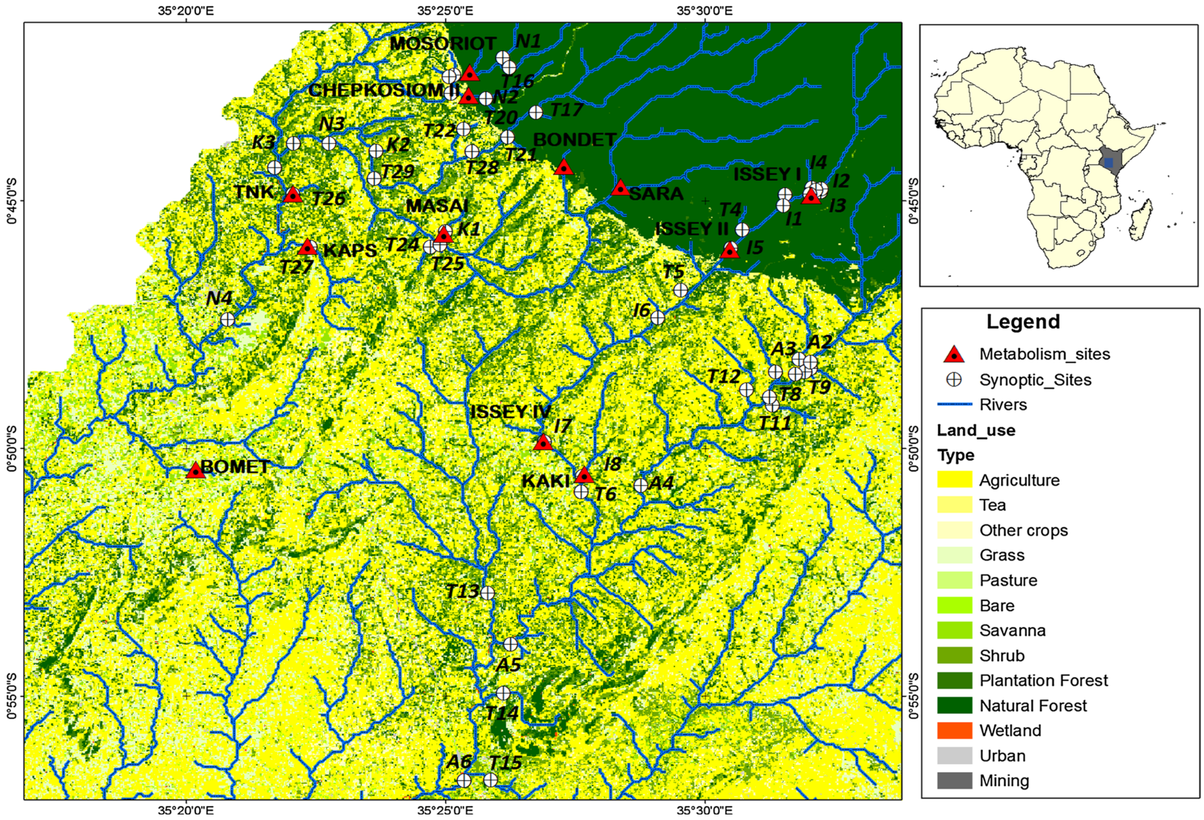

Fig. 1 Location of sample sites for metabolism and synoptic data sets in the upper Mara River basin, Kenya

compare whole-stream ecosystem metabolism and its links to DOM composition. Measurements were conducted on 10 streams (5 AGR and 5 FOR) during the wet (November–December 2011) and dry (January–March 2012) seasons.

Physical and chemical variables

At the synoptic and metabolism sites, pH, dissolved oxygen (DO), temperature and electrical conductivity were measured *in situ* using a YSI multi-probe water quality meter (556 MPS, Yellow Springs Instruments, Ohio, USA). Turbidity was measured using a portable Hach turbidity meter (Hach Company, 2100P ISO Turbidimeter, USA). Water samples were collected from the thalweg using acid washed HDPE bottles for analysis of nutrients, major anions and cations, dissolved organic carbon (DOC) and particulate organic matter (POM). For total suspended solids (TSS) and POM, water samples were filtered immediately through pre-weighed and pre-combusted (450 °C for 4 h) GF/F filters (Whatman International Ltd., Maidstone, England). All samples were stored in a cooler and frozen within 10 h of sampling until analysis. Water samples for DOM characterization were filtered on-site using pre-combusted GF/F filters into 30 ml amber glass bottles. Prior to sampling for DOM characterization, bottles were cleaned with 0.1 M HCl, soaked overnight in distilled water and then combusted (450 °C, 4 h). For the synoptic dataset, triplicate ($n = 3$) samples were taken at each site. For the metabolism dataset, triplicate samples were taken from upstream and downstream of each study reach. Samples were transported in a cooler before being frozen. Freezing of samples was necessary because of the time required for transport to the laboratory in Delft, the Netherlands. However, freezing has been shown to reduce specific ultraviolet absorbance (SUVA) and DOC concentration (Fellman et al. 2008). Short-term cold storage in a refrigerator has similar effects as single freezing and thawing (Hudson et al. 2009), hence stronger long-term effects of cold storage were avoided by freezing and thawing the samples only once and processing them identically. We therefore assume that this impacted all samples similarly and minimally.

Ecosystem metabolism

Whole-stream GPP and ER were determined using the upstream–downstream diurnal dissolved oxygen (DO) change technique (Marzolf et al. 1994; Young and Huryn 1998) in a 100 m study reach in five agricultural and five forest streams (Table 1) during the wet and dry seasons. We measured DO and temperature every 5–20 min using Hydrolab sondes (MS5 equipped with luminescent dissolved oxygen sensors (Hach Hydromet) at upstream and downstream stations over a 24-h period. Sondes were deployed in the thalweg of each stream, with sensors in the middle of the water column. At the end of the 24-h period, we placed the sondes together at 1 station for 30 min. If the sondes did not read the same value post-deployment, we corrected the data assuming a linear drift in calibration over the period of measurement, except in cases of severe probe malfunction, in which case we discarded the data. Elevation and temperature data were used to calculate saturation concentrations of DO (Colt 2012). Discharge and aeration rate (k min^{-1}) were measured from changes in dissolved propane concentration during steady-state injection of propane and a conservative tracer (Cl^-) (Genereux and Hemond 1992; Young and Huryn 1998; Webster and Valett 2006). At steady-state conditions, triplicate water samples were collected at five sampling sites corresponding to 5 (upstream station), 25, 50, 75 and 100 m (downstream station) from the propane and Cl^- injection point which was located 5 m upstream of the first sampling station to allow for effective mixing of propane and tracer with stream water. In addition, stream water conductance was measured (YSI multi-probe meter) at all sampling points during steady-state conditions and later used for metabolism calculations. Gas samples were then collected from the five sites and later analyzed for propane using gas chromatography. The aeration rate for propane was determined from the first-order rate constant of propane concentration decrease with increasing distance from the first to the fifth sampling sites after correcting for dilution in cases of discharge increase along the reach as determined by the conservative tracer. The aeration rate of propane was converted to oxygen using a factor of 1.39 (Rathbun et al. 1978).

Logistical constraints prevented determination of k by propane injection during the wet season, so instead the energy dissipation model of Tsivoglou and Neal (1976) was used; which showed a better relationship with aeration rates estimated by propane injection during the dry season (Pearson correlation, $p < 0.05$, $r = 0.89$, $n = 10$) than all other equations given by Genereux and Hemond (1992) and Melching and Flores (1999). We used the equation published by Elmore and West (1961) as modified by Bott (2006) to correct k for temperature.

The change in dissolved oxygen concentration between upstream and downstream stations (ΔDO) was calculated based on the oxygen saturation deficit or excess within the study reach and corrected for aeration (k) following Marzolf et al. (1994) and Bernot et al. (2010):

$$\Delta\mathrm{DO} = \frac{\mathrm{C_{ds}} - \mathrm{C_{us}}}{\Delta\mathrm{t} - (\mathrm{K_{02}} \times \mathrm{D})} \times \mathrm{z}$$

where (ΔDO) is $\mathrm{g\ O_2\ m^{-2}\ min^{-1}}$, $\mathrm{C_{us}}$ is the $\mathrm{O_2}$ concentration at the upstream site ($\mathrm{g\ O_2\ m^{-3}}$), $\mathrm{C_{ds}}$ is the $\mathrm{O_2}$ concentration at the downstream site, Δt (min) is the water travel time between the upstream and downstream sites; $\mathrm{K_{O_2}}$ is the temperature-corrected gas aeration rate of $\mathrm{O_2}$ ($\mathrm{min^{-1}}$) corrected for water temperature, D is the saturation deficit or excess, which is the difference between the measured DO concentration and the concentration at 100% saturation during the time interval for measured stream temperature and atmospheric pressure, and z is mean stream depth (m). Water travel time (Δt) between the upstream and downstream stations were determined using a conservative tracer (Cl^-) according to Webster and Valett (2006), and used to determine the logging intervals for dissolved oxygen. This was to ensure that the logging intervals used at a given site (range 5–20 min) were shorter than the water travel time. For all sites, the travel time was much higher than the logging interval (range 5–20 min) used to allow for detectable differences in DO between the upstream (0 m) and downstream sites (100 m). During the dry season the travel time ranged from 28 min (Issey I) to 141 min (Bomet), and in the wet season it ranged from 24 min (Issey I) to 62 min (Bomet). ER was estimated from net DO change at night and the linearly extrapolated rate of ER during the day and were reported as negative values because of oxygen consumption. GPP was estimated as the difference

Table 1 Location, drainage area (DA), which is the total area of upstream catchment draining to a site, stream order and physical characteristics of metabolism streams in agriculture and forest catchments in the upper Mara River basin, Kenya

Site	Season	Latitude (S)	Longitude (E)	DA (Ha)	Stream order	Gradient (mm^{-1})	% FOR	% AGR	*k* (min^{-1}) (measured)	*K* (min^{-1}) (calculated)	Discharge (L/S)	Wetted width (m)	Depth (m)	% canopy cover	Temperature (°C)
Issey I[a]	Dry	0°44′48.8″	35°32′07.7″	2320	2nd	0.015	99.8	0.2	34.9	35.4	64.4	3.1	0.17	55	12.9
	Wet									39.6	187.6	3.4	0.28	70	14.9
Issey II[a]	Dry	0°49′47.1″	35°26′53.1″	3198	3rd	0.019	99.9	0.1	29.6	32.0	71.8	4.1	0.15	35	16.0
	Wet									44.9	119.9	4.8	0.16	40	15.3
Bondet[a]	Dry	0°44′27.7″	35°27′15.0″	207	1st	0.038	90.1	9.9	29.4	29.9	3.1	2.4	0.09	70	14.4
	Wet									39.6	58.6	2.5	0.22	85	14.3
Mosoriot[a]	Dry	0°42′18.2″	35°25′28.8″	455	1st	0.025	100.0	0.0	4.1	13.1	2.65	1.8	0.08	70	13.1
	Wet									19.5	22.2	2.3	0.12	90	14.2
Sara[a]	Dry	0°44′41.1″	35°28′24.9″	996	1st	0.021	99.9	0.1	28.3	24.8	18.2	1.7	0.15	70	14.1
	Wet									27.73	57.7	1.9	0.19	75	14.3
Masai[c]	Dry	0°45′36.6″	35°25′0.3″	202	1st	0.022	24.2	75.6	30.9	47.2	6.7	2.0	0.08	40	16.6
Issey IV[b]	Wet	0°46′50.7″	35°26′55.1″	5985	3rd	0.018	57.2	42.0		45.4	116.8	3.7	0.27	50	17.6
Kaps	Dry	0°44′46.9″	35°22′06.7″	236	1st	0.025	18.2	79.9	37.0	39.3	21.7	1.8	0.18	35	19.1
	Wet									43.6	62.8	2.2	0.15	40	18.2
Bomet	Dry	0°47′47.9″	35°20′05.5″	1398	2nd	0.022	5.1	71.6	2.0	3.7	2.7	1.6	0.15	35	17.6
	Wet									25.9	189.6	2.1	0.29	40	17.8
Kaki	Dry	0°50′34.6″	35°27′35.1″	698	1st	0.021	11.1	87.7	3.5	9.2	3.5	1.2	0.11	25	18.8
	Wet									14.8	54.9	1.9	0.15	30	18.3
TNK	Dry	0°45′53.7″	35°22′20.1″	1270	2nd	0.021	28.5	71.1	51.6	63.4	13.6	1.5	0.09	45	18.1
	Wet									39.5	116.5	1.7	0.28	50	18.6

k (measured and corrected for water temperature) was determined from propane injections only during the dry season, while *k* (calculated) was determined using the energy dissipation model (Tsivoglou and Neal 1976) during both the dry and wet seasons. Discharge, wetted width, depth and % canopy cover values are means calculated from transects throughout the study reach during both the dry and wet seasons. Temperature values are means of logged data (Hydrolab, MS5 sondes) from upstream and downstream stations during the 24-h metabolism period. % FOR is per cent catchment land use under forest, and % AGR is per cent of catchment land use under agriculture

[a] Identifies forest streams, [b] sampled during the wet and [c] sampled during the dry season only

between net DO production rates during the day and linearly extrapolated ER during the day and are reported as positive values (Reichert et al. 2009). GPP and ER were used to calculate net ecosystem production (NEP), which reflects the balance between autotrophic and heterotrophic processes in an ecosystem, as the difference between GPP and ER (i.e., NEP = GPP − ER). The ratio of GPP/ER was also calculated as a measure of heterotrophy (GPP/ER < 1) or autotrophy (GPP/ER > 1) (Odum 1956).

A number of physical, chemical and biological characteristics were determined at each study reach to establish relationships with stream metabolism. Canopy cover was estimated visually and expressed as a percentage. Stream width, depth and water velocity were measured at 11 transects located along each reach, and discharge was estimated using the velocity-area method. Known volumes of water were filtered through 0.7 µm pore-sized GF/F filters for water column chlorophyll *a* determination. In addition, samples from each major benthic substrate type were collected for benthic chlorophyll *a* determination. For hard surfaces (e.g. cobbles), a recorded area of substrate was scrubbed for biofilm and the slurry filtered through a 0.7 µm GF/F filters. For soft sediments (gravel, sand and silt), a fixed area of the top 20 mm of substrate was removed using a cut-off 60 ml syringe. All chlorophyll *a* samples were wrapped in aluminum foil to prevent exposure to light, transported on ice and stored frozen in the laboratory until analysis. Triplicate samples of coarse particulate organic matter (CPOM) were collected from pools, riffles and runs by kicking a standard 1 m^2 of stream bottom using a kick net (mesh size 1 mm). The standing crop of detrital fine benthic organic matter (FBOM) was determined according to Mulholland et al. (2000). An open-ended bucket was placed in the stream and sediments vigorously agitated to a depth of about 10 cm. The slurry was subsampled using 500 ml HDPE bottles. Because of logistical constraints, comprehensive data on particulate organic matter quantity and instream characteristics were collected only during the dry season.

Laboratory analyses

Water samples were filtered in the laboratory before analysis. Total dissolve phosphorus (TDP) and soluble reactive phosphorus (SRP) were determined using standard colorimetric methods, while TSS and POM were determined gravimetrically (APHA 1998). DOC and total dissolved nitrogen (TDN) concentrations were determined using a Shimadzu TOC-V-CPN with a coupled total nitrogen analyzer (TNM-1) and used to calculate C:N ratio. Dissolved organic nitrogen (DON) was calculated by subtracting the inorganic nitrogen (NO_3^- and NH_4^+) from TDN. Chlorophyll *a* was extracted by 90% ethanol and concentrations determined spectrophotometrically (APHA 1998). Major anions NO_3^-, Cl^- and SO_4^{2-} were determined using a Dionex ICS-1000 ion chromatograph equipped with an AS-DV auto sampler, and the major cations Na^+, K^+, Ca^{2+}, Mg^{2+}, dissolved silicates (DSi) and NH_4^+ using an ICP-MS. CPOM samples were sorted to remove visible invertebrates and inorganic materials and dried at 68 °C for 48 h to a constant mass. The mass of different CPOM fractions—leaves, sticks, seeds and flowers—were weighed separately using a Sartorius balance (precision 0.1 mg). The FBOM samples were dried (68 °C), weighed, combusted (500 °C) and reweighed to determine ash-free dry weight. CPOM and FBOM biomass were expressed per unit area sampled.

Optical properties of DOM

Absorption spectra (200–600 nm) of DOM were measured on a UV-2501 PC UV/VIS spectrophotometer (Shimadzu, Duisburg, Germany) using a 1 cm quartz cuvette. Prior to analysis, samples were brought to room temperature. MilliQ-Water was used as a blank. Absorption coefficients were determined following $\lambda = 2.303\ A(\lambda)/1$ where $A(\lambda)$ is the absorption coefficient at wavelength λ (in nm) and l the cuvette path length (m). A number of optical properties of DOM were calculated from the scans. The absorption coefficient ratio a_{254}/a_{410} was calculated as an indicator of molecular weight and aromaticity (Baker et al. 2008). We calculated a commonly used ratio of absorption coefficients E_2:E_3 (a_{250}:a_{365}) to provide further information about DOM aromaticity and molecular weight (Peuravuori and Pihlaja 1997; Helms et al. 2008). The spectra slope ratio (S_R) was computed as the ratio of the short wavelength slope ($S_{275–295}$) and the long wavelength slope ($S_{350–400}$). Both S_R and $S_{275–295}$ are inversely correlated with average molecular weight of DOM and are associated with photodegradation (Helms et al. 2008).

Fluorescence of DOM was measured with a FluoroMax-3 spectro-fluorometer (Jobin Yvon [now HORIBA Scientific], Longjumeau, France).Excitation-emission matrices (EEMs)were obtained by a 3D-scan of fluorescence over an excitation range of 220–450 nm (at 10 nm increments)and at an emission range of 350–600 nm(at 2 nm increments) using methods outlined in Cory et al. (2010).To correct for instrument bias related to wavelength-dependent efficiencies, instrument specific files supplied by the manufacturer were applied. Normalized blank EEMs were subtracted from each sample EEM to eliminate effects of Raman and Rayleigh scattering. EEMs were also corrected for inner-filter effects and normalized to Raman units (in nm^{-1}, Raman peak area of the blank at 350 nm excitation). The processing of EEMs was done in MATLAB 8.2 (Mathworks, MATLAB 2013) and yielded three fluorescence indices: fluorescence index (FI) (McKnight et al. 2001); freshness index (β:α) (Wilson and Xenopoulos 2009) and biological autochthonous index (BIX) (Huguet et al. 2009). The FI provides information on DOM origin, distinguishing terrestrially derived DOM (FI $\sim$ 1.3) from microbially derived DOM (FI $\sim$ 1.8) (McKnight et al. 2001). β:α indicates the proportion of recently produced DOM relative to more decomposed DOM (Wilson and Xenopoulos 2009). β:α values >1 indicate that DOM is primarily of autochthonous origin and values <0.6 indicate primarily allochthonous origin (Huguet et al. 2009). The biological autochthonous index (BIX) estimates autochthonous biological activity with values higher than 0.8 indicating freshly released and autochthonously produced DOM whereas lower values indicate less autochthonous DOM (Huguet et al. 2009).

Statistical analysis

Except for GPP and ER, all data were transformed using natural-log transformations before analysis. For the synoptic dataset, one-way analysis-of variance (ANOVA) was used to test for differences in water quality variables, optical properties of DOM and its concentration among land uses followed by *post hoc* Tukey's Honestly Significant Difference (HSD) multiple comparisons of means. Principal component analysis (PCA) was used to summarize variation in physico-chemical variables and optical properties of DOM among land uses. Similarly, for the metabolism data set, PCA was used to condense and summarize data that were grouped into four multivariate data sets: (i) water physico-chemistry including conservative ions and nutrients (but excluding all carbon-related information); (ii) all absorbance and fluorescence indices (optical properties) describing the composition of DOM; (iii) all data related to organic matter quantity (both dissolved and particulate), including TSS and canopy cover; and (iv) measures of stream size (catchment area, discharge, depth, wetted and flowing width).

Partial least squares projection to latent structures (PLS) was performed to define which environmental factors were more influential on ecosystem metabolism. PLS is an extension of multiple regression analysis which is now widely used in ecological studies (Carrascal et al. 2009; Smith and Cox 2014). In PLS the effects of linear combinations of several predictors on a response variable (or multiple response variables) are analyzed (Frank and Friedman 1993). PLS is especially useful when (1) the number of predictor variables is similar to or higher than the number of observations (i.e. overfitting) and/or (2) predictors are highly correlated (i.e. there is strong collinearity) (Carrascal et al. 2009). We followed the methods outlined by Carrascal et al. (2009) and retained only those factors that explained >5% of the original variation in the response variable. Consequently, we retained the first and second components, which explained more than 90% of original variance in the response variables. We gathered from each simulation the explanatory capacity (R^2) of each component as well as the weight of each predictor within each component, which helped us to understand the latent factors defined by each component. The sum of the R^2 of the first four components gave us the total explanatory capacity of the PLS models. A cross validation statistical test (Eriksson et al. 1995) was performed to select the number of significant components, which provides Q^2 (i.e. the cross-validated R^2). We also used the variable importance for the projection (VIP) to determine the importance of each X-variable taking into account the amount of Y-variance explained by each latent variable (Wold 1995). The variables with VIP values higher than 1 are considered the most relevant with strong predictive power and values higher than 0.7 are considered important (Eriksson et al. 1999; Lepori et al. 2005). The most relevant and most important variables were subsequently used as factors controlling GPP and ER in stepwise multiple linear regressions (MLR) to determine their relative influences. For GPP, factors considered in MLR during the dry and wet seasons were TDN, temperature, % canopy cover, % AGR land use, TSS and SRP. For ER, factors considered during the dry and wet seasons were CPOM, TDN and temperature, while POM, FBOM and TSS were included in the dry season only and % canopy cover, SRP and % AGR land use were included during the wet season only (refer to Fig. 4). We used correlation analysis to examine relationships and potential linkages between components of metabolism (GPP and ER) and optical indices of DOM and the first four PC-axes (principal components) derived from PCA ordinations of the DOM composition indices (absorbance and fluorescence indices). Separate correlations were performed for each season (dry and wet). Mann-Whitney U tests were used to test for differences in GPP and ER between seasons and land uses. Statistical analyses and graphs were done in STATISTICA (Version 7, StatSoft, Tulsa, Oklahoma) and SigmaPlot Version 12.0 (Systat Software, San Jose, CA).

Results

Water quality and DOM composition for different land uses

Synoptic dataset

Clear differences in physico-chemistry and DOM composition in the studied streams were observed in relation to land use (Supplementary Information). While agricultural (AGR) and forest (FOR) streams showed differences in physico-chemistry and DOM composition, for some variables mixed (MIX) streams were not always distinct from AGR and FOR (Table 2). Following PCA ordinations to establish relationships between land use, water quality and DOM composition (Fig. 2), Factor 1 (PCA-axis 1) accounted for most variation (49%) in water quality. Higher concentrations of nutrients (SRP, TDN and NO_3^-) and conservative ions (Cl^-, SO_4^{2-}) were associated with AGR streams (Fig. 2a). Land use related variation in DOM composition was visible along the first and second PCA-axes (Factors 1 and 2) with most FOR and AGR streams separated along PCA-axis 1 (44%) and MIX streams lying intermediate (Fig. 2b). The separation was not however, complete along PCA-axis 2, implying that despite the catchment land use influences, reach-scale influences also affected some DOM properties. Most AGR sites were associated with higher proportions of recently produced (β:α), photodegraded (S_R) and microbially derived (FI) DOM (Table 2). Some forest streams were associated with autochthonously (BIX) produced DOM, but these were wider with an open canopy.

Metabolism dataset

Among the metabolism sites, most AGR sites were also associated with higher electrical conductivity, temperature and concentrations of dissolved nutrients (NO_3^- and NH_4^+) and major ions (Cl^-, Ca^{2+}, Mg^{2+} and SO_4^{2-}) (Fig. 3a, d) as in the synoptic data set. Land use influenced changes in organic matter quantity along the first PCA-axis (OM-PC1, Fig. 3b). On the second PCA-axis (OM-PC2) most sites were also separated according to land use with four of the five AGR sites and three of the five FOR sites separated along this axis. AGR sites were associated with higher concentrations of DOC, benthic and water column chlorophyll *a*, TSS and lower C:N ratio. FOR sites were associated with higher standing stocks of CPOM, canopy cover, proportion of carbon (OM) in TSS (% POM) and C:N ratio. There were no clear distinctions between stream size characteristics for AGR and FOR streams (Fig. 3e). Land use-associated variation of DOM composition was visible along the first PCA-axis (DOM-PC1) during the dry season (Fig. 3c). Two FOR streams, which were also the widest (see Table 1 for details), were associated with autochthonous DOM (BIX), while the rest were associated with higher molecular weight of DOM (a_{310}/a_{410}, E2:E3). AGR sites were associated with photodegraded (S_R) and recently produced DOM (β:α). Trends were unclear during the wet season as PCA failed to identify land use-linked influences on DOM composition for many of the sites (Fig. 3f). Both AGR and FOR streams had a mixture of DOM sources with both lower ($E2$:$E3$ and S_R) and higher molecular weight DOM (a_{254}/a_{410}).

Whole-stream metabolism

Except for one agricultural stream (Kaki) during the dry season, all other streams were heterotrophic with

Table 2 Land use affects stream water nutrients, conservative ion concentrations and optical properties of DOM and organic matter

	Land use mean ± SD			Statistics	
	FOR	MIX	AGR	F	p
DOC (mg/L)	1.7 ± 0.4^{a}	1.1 ± 0.4^{a}	1.4 ± 0.7^{a}	3.0	0.0642
TDN (mg/L)	1.2 ± 0.5^{a}	1.7 ± 1.2^{a}	6.6 ± 2.6^{b}	44.3	<0.0001*
DON (mg/L)	0.2 ± 0.1^{a}	0.2 ± 0.2^{a}	0.5 ± 0.2^{b}	8.8	0.0009*
Dissolved C:N	10.2 ± 4.0^{a}	8.5 ± 6.9^{a}	4.0 ± 2.6^{b}	9.3	0.0007*
SRP (mg/L)	0.09 ± 0.10^{a}	0.33 ± 0.28^{b}	0.30 ± 0.42^{b}	16.3	0.0001*
TDP (mg/L)	0.15 ± 0.06^{a}	0.36 ± 0.01^{b}	0.41 ± 0.01^{b}	3.4	0.0238*
Chloride (mg/L)	3.2 ± 0.7^{a}	2.7 ± 0.7^{a}	6.3 ± 3.4^{b}	11.5	0.0002*
NO_3^- (mg/L)	1.0 ± 0.4^{a}	1.5 ± 1.1^{a}	6.1 ± 2.6^{b}	46.1	0.0000*
SO_4^{-2} (mg/L)	2.6 ± 0.2^{a}	1.8 ± 0.6^{b}	4.6 ± 3.3^{a}	7.0	0.0031*
NH_4^+ (mg/L)	0.02 ± 0.01^{a}	0.02 ± 0.01^{a}	0.04 ± 0.03^{b}	6.2	0.0053*
FBOM (g/m^2)	515 ± 570^{a}	629 ± 709^{a}	1203 ± 1090^{a}	2.3	0.0813
CPOM (g/m^2)	145.6 ± 13.6^{a}	169.1 ± 19.2^{b}	233.0 ± 14.4^{b}	8.4	0.0410*
Water column chlorophyll *a* (μg/L)	6.1 ± 6.5^{a}	9.8 ± 7.1^{a}	37.5 ± 21.1^{a}	3.9	0.0303*
Benthic chlorophyll a (μg/m^2)	2.7 ± 1.5^{a}	14.3 ± 4.8^{a}	17.5 ± 11.1^{b}	7.7	0.0031*
TSS (mg/L)	36.6 ± 20.5^{a}	173.5 ± 14.6^{b}	254.9 ± 74.1^{b}	20.21	0.0001*
% carbon in TSS	13.2 ± 4.2^{a}	8.7 ± 6.4^{ab}	4.1 ± 3.2^{a}	7.6	0.0023
a_{254}/a_{410}	6.2 ± 4.9^{a}	5.3 ± 0.5^{ab}	4.9 ± 0.8^{b}	7.2	0.0027*
FI	1.3 ± 0.14^{a}	1.5 ± 0.06^{b}	1.8 ± 0.07^{c}	16.3	0.0002*
$\beta{:}\alpha$	0.4 ± 0.3^{a}	0.9 ± 0.1^{b}	0.8 ± 0.1^{b}	8.9	0.0009*
BIX	0.7 ± 0.1^{a}	0.8 ± 0.3^{ab}	0.9 ± 0.1^{b}	7.1	0.0029*
S_R	1.2 ± 0.1^{a}	1.3 ± 0.1^{a,b}	1.4 ± 0.2^{b}	8.9	0.0009*
$S_{275\text{–}295}$	0.013 ± 0.001^{a}	0.013 ± 0.001^{a}	0.014 ± 0.001^{a}	1.8	0.1828
$E_2{:}E_3$	3.8 ± 0.2^{a}	3.7 ± 0.4^{a}	4.0 ± 0.4^{a}	3.0	0.0640

Mean (±SD) physico-chemical water quality variables and optical properties of dissolved organic matter and its concentration, carbon to nitrogen (C:N) ratio, organic matter standing stocks and chlorophyll *a* concentrations for three catchment land use categories mixed (MIX, n = 14), forest (FOR, n = 19) and agriculture (AGR, n = 17) in the upper Mara River basin, Kenya. Statistics of one-way analysis of variance (ANOVA) results among three land use categories are presented together with post hoc Tukey's HSD comparisons among means. Similar superscripts among means indicate lack of significant differences between land uses at $p < 0.05$. Model degrees of freedom (df) = 2 and residual df = 31

Dissolved C:N was calculated as (DOC/12,000)/(TDN/14,000). FBOM, water column chlorophyll a and benthic chlorophyll a data were collected mainly from metabolism sites used for metabolism measurements. CPOM data were obtained during the dry season only

* Significant differences at $p < 0.05$, one-way ANOVA

negative NEP values during both dry and wet seasons (Table 3). GPP values were greater in AGR streams than in FOR streams during the dry (Mann-Whitney U= 0.000, $p = 0.008$) and wet (Mann-Whitney U= 0.000, $p = 0.008$) seasons, but ER did not differ between the two land uses. In FOR streams, GPP ranged from 0.1 to 1.13 and 0.1 to 1.7 g O_2 m^{-2} day^{-1} during the wet and dry seasons, respectively (Table 3). Comparatively in AGR streams, GPP in AGR streams ranged from 2.3 to 11.5 and 3.6 to 11.7 g O_2 m^{-2} day^{-1} during the wet and dry seasons, respectively Notably there were no overlaps in GPP between FOR and AGR streams; dry and wet season GPP in all FOR streams were lower than the lowest GPP in an AGR stream. The same AGR site (Bomet) recorded the highest GPP and ER during the wet (11.5 and −17.4 O_2 m^{-2} day^{-1}, respectively) and dry (11.7 and −20.2 g O_2 m^{-2} day^{-1}, respectively) seasons.

The ER rates were highly variable among streams within similar catchment land uses. ER ranged from −1.04 to −8.70 and −4.52 to −13.66 g O_2 m^{-2} day^{-1} at FOR streams during the wet and dry seasons,

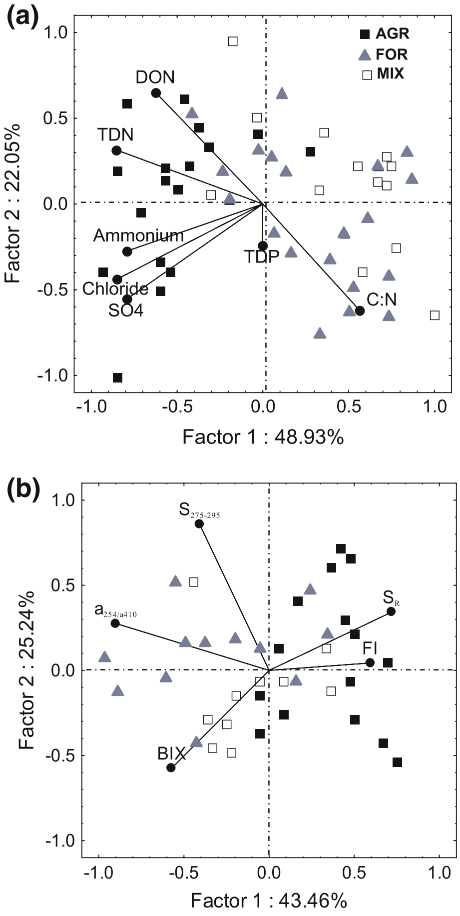

Fig. 2 Principal component analysis (PCA) of water quality and DOM composition of the synoptic data set, **a** shows scores and loadings for the land uses based on water quality ($n = 50$), and **b** shows the scores and loadings for the land uses based on the optical properties of DOM ($n = 37$). Variation explained by each PC-axis, (Factor 1 and 2) is indicated by the regression coefficient (R^2) which is expressed as a percentage

respectively. In AGR streams ER ranged from −5.08 to −17.39 and −4.82 to −20.16 g O_2 m^{-2} day^{-1} during the wet and dry season, respectively.

There were no significant differences in NEP between forest and agriculture land uses during the dry (Mann-Whitney U= 12.5, $p = 0.189$) and wet (Mann-Whitney U= 9.0, $p = 0.548$) seasons. During the wet season, NEP in forested streams ranged from −7.61 to −0.91 g O_2 m^{-2} day^{-1} (P/R range: 0.09–0.17), while NEP in agricultural streams ranged from −6.69 to −1.37 g O_2 m^{-2} day^{-1} (P/R range: 0.17–0.73). During the dry season NEP in forested streams ranged from −12.02 to −2.86 g O_2 m^{-2} day^{-1} (P/R range: 0.02–0.37) while in agricultural streams the range was from −8.47 to 0.84 g O_2 m^{-2} day^{-1} (P/R range: 0.51–1.17).

The first two components of the PLS analysis explained more than 80% of the original variance in the response variables (GPP and ER) during the dry and wet seasons (Table 4). For all analyses, the first component accounted for a major proportion (>70%) of the explained variance, while the second component accounted for a marginal, but significant proportion (>5%). The meaning of the components can be interpreted considering the weights attained by the variables. The addition of the squares of the weights within each component sums to one, so the contribution of each predictor variable to the meaning of each component can be easily estimated. Component 1 mainly associated GPP with higher nutrient concentrations (mainly TDN), % agricultural land use in the catchment and open canopy cover. These predictor variables are proxies for land use differences between forest and agriculture in the study area. These three variables alone retain 68.5% ($0.604^2 + 0.433^2 + -0.363^2$) of the information content of the first component explaining GPP during the dry season and 52.5% during the wet season (Fig. 4). For ER, Component 1 was associated with higher standing stocks of CPOM, nutrient concentrations (TDN and SRP) and open canopy cover. CPOM standing stocks and TDN concentrations alone accounted for 87.3% ($0.717^2 + 0.599^2$) of the information content of the first component during the dry season, whereas concentrations of TDN, canopy cover and CPOM standing stocks accounted for 53.9% of the information ($0.454^2 + 0.411^2 + 0.405^2$, respectively) during the wet season. CPOM standing stocks and TDN concentrations were the relevant and important variables explaining ER during the dry season while TDN concentration and canopy cover were the important variables during the wet season (Fig. 4).

Stepwise multiple regression models linked TDN and amount of canopy cover to GPP, while TDN and organic matter biomass (CPOM and/ or FBOM) were linked to ER during both the dry and wet seasons (Table 5). In addition, the proportion of catchment area under agriculture and temperature were key drivers of GPP and ER, respectively, during the dry season. During the wet season, other key factors influencing GPP and ER were TSS and % canopy cover, respectively (Table 5).

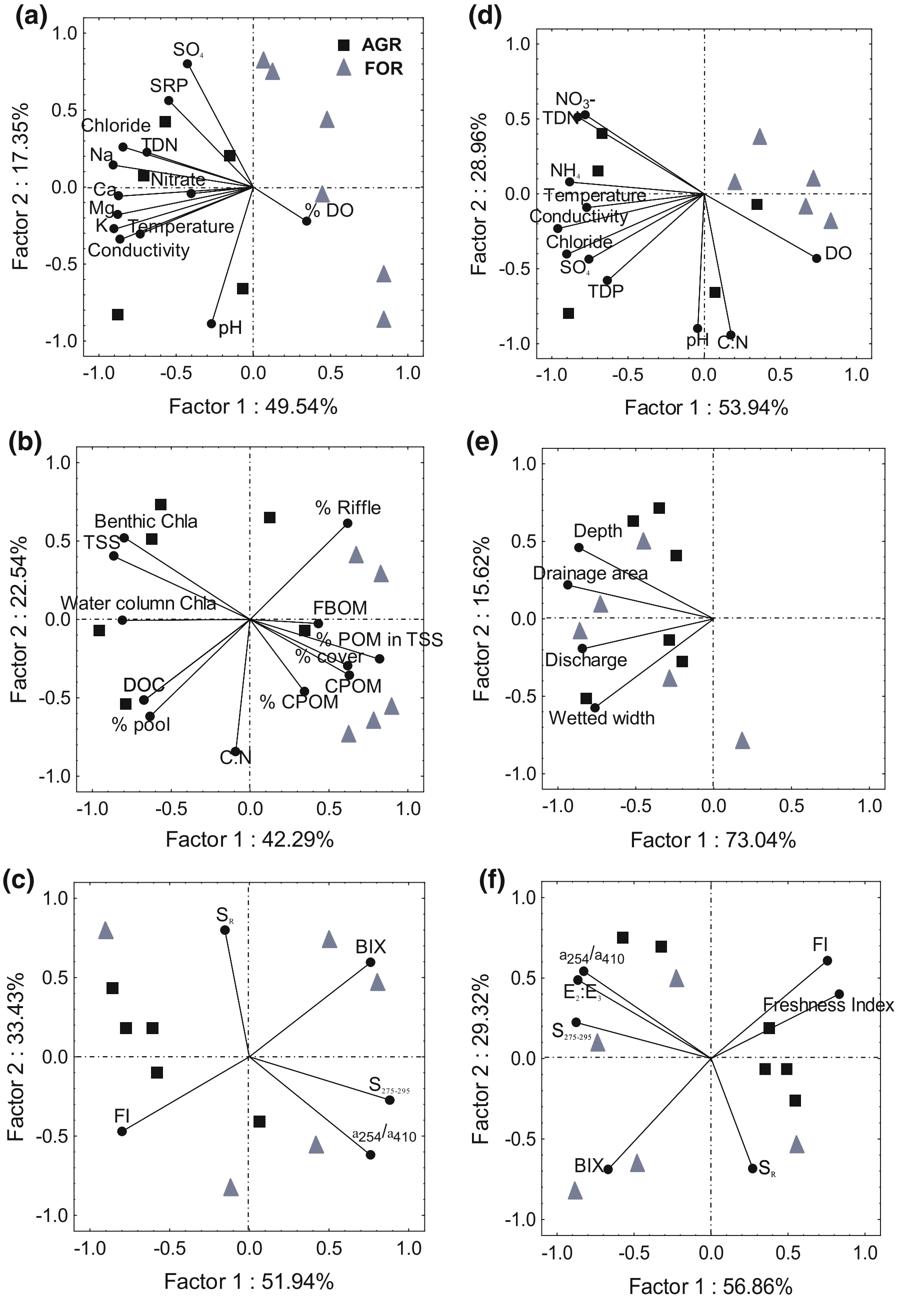

Fig. 3 Separation of land use influences in PCA on the metabolism data set based on **a**, **d** water physico-chemistry, including major ions and nutrients, **b** measures of organic matter quantity, **e** stream size variables, and **c**, **f** optical properties of dissolved organic matter, during the dry (**a**–**c**, **e**) and wet (**d**, **f**) seasons. Variation explained by each PC-axis (Factors 1 and 2) is indicated by the regression coefficient (R^2) which is expressed as a percentage. *F index* freshness index (also β:α), *FI* fluorescence index

Relationships between metabolism and DOM composition

GPP had a significant positive correlation with ER ($r = 0.81$, $p < 0.001$, $n = 20$). Similarly, there were significant relationships between GPP and ER and indices of DOM composition (Table 6). GPP rates were positively correlated with fluorescence index (FI) and freshness index (β:α) during the dry and wet seasons (correlation $r > 0.50$, $p < 0.05$, $n = 10$). In addition, GPP rates were positively correlated with DOM-PC1 ($r = 0.82$, $p < 0.05$, $n = 10$) and negatively related with DOM-PC2 ($r = -0.82$, $p < 0.05$, $n = 10$) during the dry season. DOM-PC 1 and DOM-

Table 3 Dry and wet season gross primary production (GPP), ecosystem respiration (ER) and net ecosystem production (NEP) in streams draining agriculture and forest catchments in the upper Mara River basin, Kenya; streams were sampled only during the $^{\#}$wet and *dry seasons, respectively

		Wet season				Dry season			
Site	Land use type	GPP (g O_2 m^{-2} day^{-1})	ER (g O_2 m^{-2} day^{-1})	NEP (g O_2 m^{-2} day^{-1})	GPP/ER	GPP (g O_2 m^{-2} day^{-1})	ER (g O_2 m^{-2} day^{-1})	NEP (g O_2 m^{-2} day^{-1})	GPP/ER
Issey I	Forest	1.1	−8.7	−7.6	0.2	1.6	−13.7	−12.0	0.1
Issey II	Forest	0.3	−2.7	−2.4	0.1	1.3	−7.1	−5. 8	0.2
Bondet	Forest	0.2	−2.0	−1.8	0.1	0.1	−8.1	−7.9	0.02
Mosoriot	Forest	0.1	−1.0	−0.9	0.1	1.5	−7.7	−6.3	0.2
Sara	Forest	0.7	−4.1	−3.4	0.2	1.7	−4.5	−2.9	0.4
Issey IV$^{\#}$	Agriculture	2.3	−8.0	−6.7	0.2	–	–	–	
Masai*	Agriculture	–	–	–		3.6	−7.1	−3.4	0.5
Kips	Agriculture	2.8	−6.1	−3.3	0.5	6.7	−9.5	−2.9	0.7
Bomet	Agriculture	11.5	−17.4	−5.9	0.7	11.7	−20.2	−8.5	0.6
Kaki	Agriculture	9.3	−15.3	−5.9	0.6	5.7	−4.8	0.8	1.2
TNK	Agriculture	3.7	−5.1	−1.4	0.7	7.1	−12.9	−5.8	0.6

Table 4 Results of the partial least squares regression analysis (PLS) carried out with gross primary production (GPP) and ecosystem respiration (ER) (response variables) as the components of whole-stream ecosystem metabolism and predictor variables describing the physico-chemical characteristics of the studied streams

	PLSR weighted components			
	Dry season		Wet season	
	Component 1	Component 2	Component 1	Component 2
Gross primary production				
Discharge (L/S)	−0.119	0.189	0.072	0.139
Wetted width (m)	−0.109	0.032	−0.175	−0.176
% AGR land use	**0.433**	0.354	0.370	−0.176
Temperature (°C)	0.324	−0.186	0.357	−0.373
% canopy cover	−0.363	**0.414**	**−0.422**	−0.120
TDN (mg/L)	**0.604**	**0.578**	**0.469**	0.211
SRP (mg/L)	0.045	−0.134	**0.416**	0.149
TSS mg/L	0.303	−0.302	0.236	**−0.495**
R^2Y	0.800	0.123	0.934	0.051
Q^2	0.407	−0.614	0.816	0.124
Ecosystem respiration				
Discharge (L/S)	0.034	0.140	0.188	−0.397
Flowing width (m)	0.003	0.098	−0.061	0.266
Arcsine % AGR	0.042	−0.226	0.296	**0.548**
Temperature (°C)	0.181	**−0.526**	0.311	−0.355
% canopy cover	−0.145	−0.023	**0.411**	0.040
TDN (mg/L)	**0.599**	0.021	**0.454**	0.105
SRP (mg/L)	0.116	**−0.437**	0.346	0.190
TSS mg/L	0.100	−0.327	0.275	−0.176
FBOM (g/m^2)	0.165	**0.519**	−0.198	**0.450**
CPOM (g/m^2)	**0.717**	0.111	**0.405**	−0.104
POM (mg/L)	0.197	0.251	0.053	−0.229
R^2Y	0.735	0.118	0.841	0.071
Q^2	0.123	−0.042	0.744	−0.184

Components 1–2: weights of each variable in the first two PLS components. R^2Y: proportion of the variance in the response variables accounted for by each component of the PLS. All predictor variables were log-transformed before inclusion in the models. PLS weights whose squares are larger than 0.16 are shown in bold type. Each component in the table was significant

PC2 are principal components derived from PCA ordinations of the DOM composition indices. DOM-PC1 was associated with low molecular weight, freshly produced and autochthonous DOM, as indicated by its strong positive correlation with the fluorescence index ($r = 0.77$, $p < 0.05$). On the other hand, DOM-PC2 was negatively correlated with freshness index ($\beta{:}\alpha$, $r = -0.84$, $p < 0.05$). During the wet season GPP and ER were correlated with DOM-PC2 ($r = 0.65$, $p < 0.05$, $n = 10$ and $r = 0.73$, $p < 0.05$, $n = 10$, respectively). DOM-PC2 was positively related to FI ($r = 0.86$, $p < 0.05$) indicating that this PC-axis was associated with autochthonous produced DOM. In addition, both GPP and ER were correlated with the short wavelength slope ($S_{275-295}$), which is indicative of low molecular weight DOM.

Discussion

Effects of land use on DOM composition

We report notable shifts in DOM composition and ecosystem metabolism with catchment land use and we interpret these differences to reflect shifts in DOM composition resulting from conversion of forest land to agricultural land. The land use influence was also expressed through water physico-chemistry with major ions, suspended solids and dissolved nutrients recording higher concentrations in agricultural streams (Fig. 2a).

FOR streams were associated with higher molecular weight and terrestrially derived DOM (Fig. 2b). However, there was a shift in DOM composition with

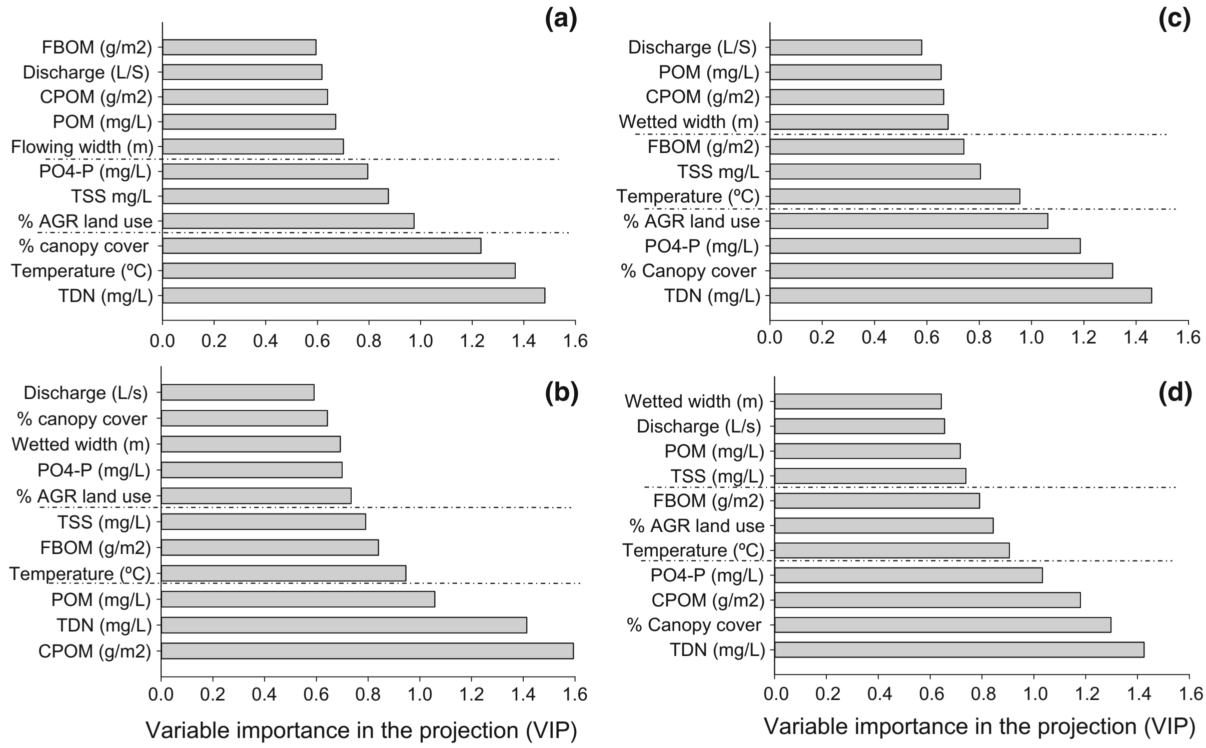

Fig. 4 Results of projection to latent structures (PLS) regression analysis showing ranked physico-chemical variable importance in the projection (VIP) at ten ecosystem metabolism experimental streams. **a** Dry season GPP, **b** dry season ER, **c** wet season GPP, **d** wet season ER. The *dashed lines* show cutoffs for variables that were most relevant (*lower panel*) and variables that were important (*middle panel*) in the analysis

land use change from forest to agriculture (Table 2) with FI and β:α values indicating increased autochthonous production and microbially derived DOM in AGR and MIX streams (Fellman et al. 2010; Huguet et al. 2009; Wilson and Xenopoulos 2009). Increased autochthonous DOM production in AGR and MIX streams was further supported by BIX, where values >0.8 in MIX and AGR streams were indicative of predominantly fresher and autochthonous DOM (Huguet et al. 2009). Predominance of low molecular weight DOM in AGR streams was further supported by low a_{254}/a_{410} values (Baker et al. 2008). This shift in DOM character with land use change from forest to agriculture was probably driven by the higher concentrations of nutrients (mainly dissolved fractions of nitrogen) in AGR streams (Table 2) which probably increased the microbial biomass. Given that increased nitrogen concentrations have been linked to both increased microbial production and release of chromophoric DOM (Reche et al. 1998; Biers et al. 2007), the higher concentrations of dissolved nitrogen in AGR streams probably caused an increase in autochthonous and microbially derived DOM. Similar to our findings, a number of studies have reported increased levels of microbially derived and autochthonous DOM in agricultural streams (Wilson and Xenopoulos 2009; Williams et al. 2010; Graeber et al. 2015).

Although higher nutrient concentrations could explain the predominance of microbially derived and autochthonous DOM in AGR streams, other land use related factors potentially played a role. For instance, canopy cover is one of the major drivers of primary production in these streams (details below), and this could have contributed to the increased autochthonous character of DOM in AGR streams, which had a slightly more open canpoy compared with FOR streams (Table 1). Additionally, higher S_R values were reported in AGR streams and this can be interpreted to be evidence of photodegradation (Helms

Table 5 Results of stepwise multiple linear regression for important variables driving gross primary production (GPP), ecosystem respiration (ER) and net ecosystem production (NEP) as identified from PLS analysis ($n = 10$ for each analysis)

Dependent variable	Independent variable	Parameter estimate (SE)	R^2	Prob. > F
Dry season				
GPP	Intercept	−2.743 (0.765)		
	TDN	2.827 (0.425)	0.754	<0.001
	% Canopy cover	−2.716 (0.764)	0.058	0.012
	% AGR land use	0.723 (0.264)	0.051	0.034
	Full model		0.863	<0.001
ER	Intercept	10.757 (0.871)		
	CPOM	5.374 (0.478)	0.761	<0.001
	TDN	2.699 (0.654)	0.013	0.009
	Temperature	0.721 (0.227)	0.005	0.025
	Full model		0.779	<0.002
NEP	Intercept	8.661 (0.816)		
	TDN	12.549 (0.458)	0.689	<0.001
	% Canopy cover	4.877 (0.609)	0.057	<0.001
	Full model		0.746	<0.001
Wet season				
GPP	Intercept	25.145 (3.630)		
	% Canopy cover	−3.846 (0.780)	0.631	0.002
	TSS	−3.316 (0.582)	0.154	0.013
	TDN	2.832 (1.163)	0.092	0.049
	Full model		0.877	<0.001
ER	Intercept	23.661 (13.419)		
	TDN	17.425 (3.196)	0.686	<0.001
	% Canopy cover	11.273 (2.081)	0.096	<0.001
	FBOM	7.010 (2.351)	0.026	0.002
	Full model		0.808	0.002
NEP	Intercept	−58.912 (9.598)		
	% Canopy cover	12.062 (2.286)	0.559	<0.001
	TDN	5.275 (1.681)	0.258	0.016
	Full model		0.817	0.003

Criterion for entry into the model was $p = 0.05$

et al. 2008), which we did not directly measure but could result from water exposure to sunlight as a result of the open canopy.

Effect of seasonality on DOM composition

Seasonal and reach-scale influences on DOM composition were notable. DOM composition in AGR streams responded more to seasonal changes in rainfall than FOR streams. AGR streams were dominated by fresher, autochthonously produced and low molecular weight DOM during the dry season. However, there was a slight increase in the proportions of higher molecular DOM during the wet season, with sites not completely separating according to land use along PCA-axes (Fig. 2b and 3f). High molecular weight DOM in AGR streams during the wet season can be explained by erosion of soils in cultivated areas which eventually leads to leaching of inert pools of DOM, thereby increasing the input of higher molecular weight DOM to stream water (Ogle et al. 2005; Graeber et al. 2012). Land use effects on TSS were stronger than on POM (Table 2), suggesting increased soil erosion in the agriculture-dominated catchments as has been reported in previous studies in the area (Defersha et al. 2012; Kilonzo et al. 2014).

Although seasonal rainfall patterns and erosion were drivers of variability in the composition of DOM

Table 6 Correlation analysis among optical properties of dissolved organic matter (DOM) and gross primary production (GPP, g O_2 m^{-2} day^{-1}) and ecosystem respiration (ER, g O_2 m^{-2} day^{-1}) by season

DOM optical properties	Dry season		Wet season	
	GPP	ER	GPP	ER
FI	**0.73**	0.28	**0.69**	**0.70**
β:α	**0.74**	0.12	**0.53**	0.02
BIX	**0.56**	0.11	0.22	−0.02
a_{254}/a_{410}	−0.16	0.19	0.37	0.33
S_R	−0.16	0.03	0.13	−0.02
$S_{275–295}$	−0.17	**0.59**	**0.52**	**0.48**
E_2:E_3	−0.20	0.18	**0.45**	0.35
DOM PC1	**0.82**	0.34	−0.28	−0.31
DOM PC2	**−0.82**	−0.33	**0.65**	**0.73**
DOM PC3	0.15	0.35	−0.35	−0.08
DOM PC4	−0.21	0.02	0.24	0.24

DOM PC1–4 are the first four PC-axes derived from principal component analysis (PCA) ordinations of DOM composition data. For details on optical indices see text. Bold face correlation values are significant at $p < 0.05$

in both AGR and FOR streams in the study area, other factors might have contributed to the character of DOM. Specifically, the slightly open canopy in FOR streams during the dry seasons potentially influenced DOM composition through an increase in water temperature and light availability, and by extension increased primary production. Evidence of increased autochthonous production of DOM in both AGR and FOR streams during the dry season is captured by a lack of clear separation of sites according to land use and DOM composition (Fig. 3c).

Ecosystem metabolism

The range of GPP and ER values in our streams (Table 3) is large and falls within ranges of rates reported from tropical and temperate biomes (Mulholland et al. 2001; Ortiz-Zayas et al. 2005; Fellows et al. 2006). Notably, GPP in FOR and AGR streams did not overlap, with greater rates recorded in AGR streams. This is indicative of a strong influence of catchment land use on primary production and carbon cycling in tropical African streams. Similarly, the range of ER in our forest streams encompassed forest streams in Puerto Rico (Ortiz-Zayas et al. 2005) and New Zealand (Young and Huryn 1999), and a number of streams draining mixed land uses in New York (Bott et al. 2006). For agricultural streams, our range for both the dry and wet seasons (Table 3) are similar to ranges obtained from continuous year-long measurements in an agricultural stream in mid-western United States (−0.9 to −34.8 g O_2 m^{-2} day^{-1}, Griffiths et al. 2013) and in a study of streams draining mixed land uses in tropical Australia (−0.1 to −23.4 g O_2 m^{-2} day^{-1}; Fellows et al. 2006). However, the highest ER rate was measured in Bomet stream which is influenced by nutrients and organic waste (sewage leakages) inputs from a town nearby (20,000 people without sewerage services). Compared with forest streams, agricultural streams were more metabolically active with greater GPP during both the dry and wet seasons. The lower nutrient levels and high canopy cover in forest streams can explain the comparatively lower rates; these are the major variables identified in PLS regression analysis as being important as drivers of GPP in the study area (Table 3 and Fig. 4). In contrast, canopy cover in agricultural streams was much reduced, ≤50% overall, and light availability and higher dissolved nitrogen concentration explained the greater GPP rates (Table 3). Higher nutrient concentrations in AGR streams were attributed to runoff from farms using nitrogenous fertilizers, inputs by livestock watering in streams, and leakages from toilets in human settlements. This is one of the few studies that link nutrients with metabolism in tropical streams. Most other comparative studies show a strong light/canopy effect, but weak nutrient effect (Bernot et al. 2010).

The significant positive correlation between GPP and ER suggest a coupling of the two processes as explained by the strong covariance and a slope near −1, but other factors also controlling variation are not accounted for by the relationship. For example, some percentage of the variation in ER would be explained by GPP, because a proportion of ER is autotrophic respiration (Griffiths et al. 2013). The other variation not explained by GPP is largely due to heterotrophic respiration, and may be explained by factors such as CPOM and FBOM (Table 4). Coupled GPP and ER in these streams are consistent with studies showing that significant amounts of GPP are respired, even though the amount respired varies significantly both spatially and temporally (Bunn et al. 1999; Griffiths et al. 2013; Hall and Beaulieu 2013). In our study, ER was consistently much greater than GPP, indicating a dominance of heterotrophy as expected in headwater streams (Vannote et al. 1980). GPP values were greater at AGR streams leading to the higher GPP/ ER values and suggesting a potential shift towards autotrophy. Similar shifts with land use change have been reported in both tropical and temperate biomes (Bunn et al. 1999; Young et al. 2008), although not in all studies (Young and Huryn 1999; Bernot et al. 2010).

Seasonality affected discharge differently, showing that longitudinal connectivity and terrestrial-aquatic hydrologic linkages are important and may explain differences in seasonality of GPP and ER among land uses. Greater GPP and ER were recorded during the dry compared with the wet season. Seasonal storms that trigger scour and deposition in streams can reduce metabolism rates (Griffiths et al. 2013). Increased turbidity during the wet season likely smothered streambeds and limited light availability for primary production. Even though conducted during short periods in the dry and wet seasons, the findings of this study show that GPP and ER in tropical streams can also change seasonally as in temperate streams in response to wet-dry conditions caused by rainfall variability.

Linkage between DOM composition and ecosystem metabolism

Land use driven shifts in DOM influence its availability for metabolism and, reciprocally, ecosystem metabolism (GPP and ER) can affect DOM composition via consumption or generation by primary producers (Halbedel et al. 2013; Barrón et al. 2014). We postulated that such dependencies should lead to relationships among measures of ecosystem metabolism and DOM. During the dry and wet seasons, GPP and ER were positively correlated with the fluorescence index and PCA-derived DOM-axes associated with freshly and autochthonously produced DOM (Table 5). Considering that the molecular composition of DOM influences its bioavailability to microbial communities (Sun et al. 1997; Fellman et al. 2009), the greater magnitude of ER in our AGR streams could have been driven by the lability and bioavailability of the predominantly fresher and low molecular weight DOM of autochthonous origin. Similar studies in streams have shown that low molecular-weight DOM actually leads to an increase in heterotrophic activity and further degradation of organic matter (Finlay et al. 2011; Matheson et al. 2012).

In forest streams, however, the low GPP and GPP/ ER values were evidence of heterotrophy and system dependence on allochthonous energy resources (Vannote et al. 1980). The higher ER values suggest that the predominantly high molecular DOM in FOR streams contributed to heterotrophic metabolism irrespective of its quality (Halbedel et al. 2013). However, this contribution of aromatic and high molecular weight DOM to metabolism is intriguing and calls for further discussion. It has been shown that DOM derived from fresh and senescent plant litter can be a readily available and rapidly utilized carbon source for heterotrophic bacteria (Kaplan and Bott 1983; Mann and Wetzel 1996; Cleveland et al. 2004), Thus, the predominance of aromatic and high molecular weight DOM in FOR streams can be attributed to selective consumption of highly labile, low-molecular-weight compounds leached from fresh litter, with remaining plant secondary compounds more resistant to microbial breakdown (Maie et al. 2006; Ortega-Retuerta et al. 2009).

The influence of DOM composition on ecosystem metabolism can likewise be reciprocal, whereby ecosystem metabolism affects DOM composition. One way that GPP can influence DOM composition is through the production of low molecular weight autochthonous DOM. Subsequently, GPP can positively influence microbial communities which prefer low molecular-weight DOM (Cleveland et al. 2004; Barrón et al. 2012), and this would lead to further processing of DOM (Bano et al. 1997). On the other hand, ER can influence DOM composition through selective consumption of labile and low molecular weight DOM leading to a predominance of aromatic and high molecular weight DOM in streams and rivers. Because DOM is a complex mixture that is continuously being produced, processed and consumed in streams and rivers, determination of its linkage with ecosystem metabolism is difficult. However, the findings of this and similar studies (Cammack et al. 2004; Barrón et al. 2014; Halbedel et al. 2013) suggest that this linkage is evident and its determination will lead to better constraining the controls and understanding the mechanisms of ecosystem functioning and energy flow in aquatic ecosystems.

Conclusions and broader implications

This study identified effects of land use on sources and composition of DOM and ecosystem metabolism in upland streams in the Mara River, Kenya. Both GPP and ER varied with land use, with greater values in agricultural streams driven by higher nutrient concentrations and light availability (open canopy cover). DOM composition tracked this variability; forest streams transported terrestrially derived DOM, whereas agricultural streams transported a mixture of DOM that was dominated by fresher and autochthonous DOM during the dry season. High molecular weight DOM was higher in AGR streams during the wet season, suggesting a predominance of terrestrially sourced DOM.

Inland waters are increasingly recognized as important sources of CO_2 to the atmosphere, with global emissions estimated at 2.1 Pg C yr^{-1} (Raymond et al. 2013). However, estimating fluxes of CO_2 and other greenhouse gases has faced a challenge of unrepresentative data sets especially from tropical biomes (Battin et al. 2008; Aufdenkampe et al. 2011; Borges et al. 2015). Our mean dry and wet season rates of net ecosystem production (-1.2 and -1.7 g C m^{-2} day^{-1}, respectively) are comparable with both a meta analysis of 65 streams by Battin et al. (2008, NEP $= -1.2$ g C m^{-2} day^{-1}) and mean daily NEP estimated from continuous year-long monitoring in Shatto Creek, and agricultural stream in the USA (NEP $= -1.9$ g C m^{-2} day^{-1}; Griffiths et al. 2013). Although our estimates may differ from mean annual rates of continuous monitoring because of seasonal and day-to-day variation in rates, the inclusion of our streams in future meta-analyses would provide representative and better constrained estimates of outgassing of CO_2 from streams. Land use change from forest to agriculture, however, has altered carbon processing and cycling in these streams with agricultural streams outgassing less CO_2 (-1.23 g C m^{-2} day^{-1}) than forest streams (-2.18 g C m^{-2} day^{-1}) during the dry season and more CO_2 (-1.46 g C m^{-2} day^{-1}) than forest streams (-1.01 g C m^{-2} day^{-1}) during the wet season.

By integrating the influence of land use and seasonality (wet vs dry) on GPP and ER, this study shows that periodic measurements conducted mainly during the dry season low flows when ecosystem metabolism may be high when compared with other seasons and, thus, cannot be relied upon to refine estimates used to calculate carbon fluxes from streams (Griffiths et al. 2013). The results also demonstrate a link between DOM composition and ecosystem metabolism in headwater tropical streams. Measures of ecosystem metabolism in these streams have helped complement the role of tropical streams and rivers as important components of the global carbon cycle and adds to our growing understanding of the effects of agriculture on riverine ecosystem functioning. In the broadest sense, our findings imply that changes in DOM composition as a result of land use change would result in changes in the patterns of aquatic microbial metabolism and, thus in altered aquatic ecosystem functioning, with likely consequences for food-web structure and carbon cycling.

Acknowledgements We are grateful to Lubanga Lunaligo and David Namwaya (University of Eldoret) who assisted during lab work and Phillip Sigilai, Robertson Marindany and Kimutai Kitur for assistance during field work. We appreciate the technical assistance offered by Fred Kruis, Ferdi Battes, Lyzette Robbemont, Frank Weigman and Berrend Lolkema during sample analyses at the UNESCO-IHE laboratory in Delft, The Netherlands. Comments from Jacques C. Finlay and four reviewers helped to improve this manuscript. This is a publication of the MaraFlows Project and was funded by the Dutch Ministry of Foreign Affairs through the UNESCO-IHE Partnership Research Fund (UPaRF).

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