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# Land use affects total dissolved nitrogen and nitrate concentrations in tropical montane streams in Kenya



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# HIGHLIGHTS

# GRAPHICAL ABSTRACT

- Few studies on surface water quality in tropical montane forest ecosystems.
- We studied effect of land use and topography on water quality in Mau Forest, Kenya.
- Strong land use effect on TDN and nitrate concentrations.
- Dissolved organic carbon and nitrogen controlled by catchment properties.



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# ABSTRACT

African tropical montane forests are facing fast and dynamic changes in land use. However, the impacts of these changes on stream water quality are understudied. This paper aims at assessing the effect of land use and physical catchment characteristics on stream water concentrations of dissolved organic carbon (DOC), total dissolved nitrogen (TDN), nitrate (NO<sub>3</sub>-N) and dissolved organic nitrogen (DON) in the Mau Forest, the largest tropical montane forest in Kenya. We conducted five synoptic stream water sampling campaigns at the outlets of 13–16 catchments dominated by either natural forest, smallholder agriculture or commercial tea and tree plantations. Our data show a strong effect of land use on TDN and NO<sub>3</sub>-N, with highest concentrations in stream water of catchments dominated by tea plantations ( $1.80 \pm 0.50$  and  $1.62 \pm 0.60$  mg N l<sup>-1</sup>, respectively), and lowest values in forested catchments ( $0.55 \pm 0.15$  and  $0.30 \pm 0.08$  mg N l<sup>-1</sup>, respectively). NO<sub>3</sub>-N concentration increased with stream temperature and specific discharge, but decreased with increasing catchment area. DOC concentrations increased with catchment area and precipitation and decreased with specific discharge, drainage density and topographic wetness index. Precipitation and specific discharge were also strong predictors for DON concentrations, with an additional small positive effect of tree cover. In summary, land use affects TDN and NO<sub>3</sub>-N

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Abbreviations: NF, natural forest; SHA, smallholder agriculture; TTP, tea and tree plantations; TWI, topographical wetness index.

concentrations in stream water in the Mau Forest region in Kenya, while DOC and DON were more related to hydrologic regimes and catchment properties. The importance of land use for  $NO_3$ -N and TDN concentrations emphasizes the risk of increased nitrogen export along hydrological pathways caused by intensified land use and conversion of land to agricultural uses, which might result in deterioration of drinking water quality and eutrophication in surface water in tropical Africa.

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#### 1. Introduction

Forests are widely recognized as playing an important role in regulating stream flow and water quality (Calder, 2002). However, the magnitude and direction of these effects are not well understood, because other factors contribute to solute concentrations in stream water. These factors include geomorphological catchment characteristics like geology, soil type and topography (Varanka et al., 2015), but also processes such as mixing of water of different geographical and hydrological sources (Bustillo et al., 2011), and inputs from precipitation (Billett and Cresser, 1996; Caine and Thurman, 1990). Hydrological flow paths (Boy et al., 2008; Hagedorn et al., 2000) and the transit time of water through a catchment regulate the chemical composition of water that enters the stream through sub-surface flow (Burns et al., 2003; Yamashita et al., 2014). During baseflow, stream water often originates from groundwater or deeper layers in the soil profile. The composition of water entering the stream will therefore most likely be determined by conditions in the soil, such as organic matter or inorganic nitrogen (N) contents, composition of the decomposer community, soil pH, moisture, temperature and the contact time between water and soil (Kalbitz et al., 2000). Furthermore, in-stream biogeochemical processes, such as N mineralisation and nitrification, respiration of organic material and uptake during (micro)biological processes further alter stream water chemistry (Neill et al., 2006).

In addition to the aforementioned natural factors, human activities may also have a large impact on water quality. Stream water chemistry can be altered directly through the addition of nutrients and pollutants to soils and water bodies, but also indirectly through land management practices that alter primary productivity, infiltration rates, flow paths, erosion of land surfaces, sediment deposition in streams or biogeochemical processes. Human activities can therefore have a detrimental effect on nutrient cycling and water quality, but also on stream ecological functioning (e.g. Kilonzo et al., 2014; Maloney and Weller, 2011).

Most of the research on stream water chemistry has been carried out in temperate zones, whereas much less is known about tropical regions, especially Africa. However, due to climatic and pedological differences, findings from temperate areas cannot simply be extrapolated to Africa. Moreover, in large parts of Africa land use and agricultural management practices, which are often characterised by low fertilizer use, differ markedly from temperate regions (Ometo et al., 2000). A particular ecosystem that has received less attention in hydrological research is the tropical montane forest (Bruijnzeel, 2001). Forests in this ecosystem are recognized for their high biodiversity and provision of ecosystem services such as clean drinking water (Martínez et al., 2009), and as important carbon sinks (Spracklen and Righelato, 2014). The geographical distribution of the tropical montane forest ecosystem is delimited by climate and elevation. Tropical montane forests are under threat through conversion to agriculture, as the generally cool and wet climate and fertile soils make such areas very attractive for agriculture. In spite of the regional importance of this ecosystem, the consequences of land use changes in tropical montane areas are still poorly understood.

The carbon (C) and nitrogen (N) cycles are closely linked to the hydrological cycle with stream water DOC concentrations strongly related to discharge patterns (Goller et al., 2006; Hope et al., 1994; Raymond and Oh, 2007) and flow paths (Boy et al., 2008; Wilson and Xenopoulos, 2008). The transport and export of nitrogen is similarly controlled by hydrology (Mitchell, 2001). Because land use change can alter hydrological processes, e.g. through reduction in mean transit time after conversion from forest to grassland (Roa-García and Weiler, 2010), or changes in soil hydrological properties such as infiltration (Owuor et al., 2016) which might result in an increased contribution of overland flow to stream flow (Chaves et al., 2008; Neill et al., 2011), land use changes can increase nutrient export or reduce concentrations through dilution.

Deforestation and land use change are considered important human drivers of changes in stream water chemistry with significant alterations observed after conversion from forest to agriculture or pastures in the Central Amazon, including elevated nitrate (NO<sub>3</sub>-N) loads (Williams et al., 1997; Williams and Melack, 1997) or increased turbidity as a consequence of accelerated soil erosion in the Eastern Amazon (Figueiredo et al., 2010) and India (Singh and Mishra, 2014). Other evidence suggests that large-scale (>66-75%) deforestation causes higher total dissolved nitrogen (TDN) concentrations in the dry season in the Amazon due to loss of nutrient retention capacity of the soil and direct inputs from cattle and humans, especially around urban areas (Biggs et al., 2004). A 1-year field study in a tropical rain forest in western Kenya found that dissolved organic carbon (DOC) exports rose by 153% after conversion to agriculture due to mobilization of organic C originally stored in the forest topsoil (Recha et al., 2013). Studies, mainly conducted in the northern hemisphere, confirm that streams from catchments with a high percentage of agricultural land or wetlands have higher DOC concentrations than streams from forested catchments (e.g. Glendell and Brazier, 2014; Graeber et al., 2012b; Singh et al., 2015).

Despite the evidence that land use plays a role in regulating concentrations of dissolved C and N, there is no agreement on the importance of land use compared to other catchment characteristics such as topography. Oni et al. (2014) observed very different patterns in DOC concentrations and loadings in two similar catchments, indicating complex interactions of seasonality and land use on DOC concentrations. Neff et al. (2013) demonstrated that elevation and topography influences NO<sub>3</sub>-N concentrations in the Great Smoky Mountains, USA, through increased rates of acid deposition, precipitation, base cation leaching and increased occurrence of steeper slopes with less well-developed soils at higher elevation (Neff et al., 2013). Elevation changes are also linked to changes in temperature, which can affect the composition and activity of the soil microbial community and rates of mineralisation and primary productivity (Monteith et al., 2015; Nottingham et al., 2015). In addition, soil types play an important role in controlling concentrations of N and DOC (Wohlfart et al., 2012). Many studies conclude that there is no single controlling variable and in most cases stream water chemistry is a result of a combination of factors such as topography, land cover, geochemical reactivity, climate and catchment area (Chuman et al., 2013; Rothwell et al., 2010).

This study focuses on the Mau Forest Complex, which is the largest remaining indigenous tropical montane forest area in Kenya. The forests are classified as Afromontane mixed forest dominated by a *Tabernaemontana – Allophylus – Drypetes* forest formation at lower altitude (Kinyanjui, 2010), changing into montane bamboo forest above 2300 m elevation (Edwards and Blackie, 1979). The Mau Forest Complex is the headwater area for twelve major rivers in western Kenya and is an important source of freshwater for approximately 5 million people living downstream (UNEP et al., 2008). The area is also highly suitable for agriculture due to the high annual rainfall and well-drained

deep soils (Krhoda, 1988). Consequently, 25% of the forest was converted to agriculture between 1973 and 2013 (Swart, 2016) and it is believed to have led to significant decrease in water quality through increased nutrient and sediment loads (Kilonzo et al., 2014; Nyairo et al., 2015), but thorough scientific evidence is lacking. Therefore, this study aims to estimate and explain the influence of land use, physicochemical and physical catchment characteristics, such as elevation, drainage density and topographical wetness index (TWI) on stream water chemistry in the Mau Forest Complex.

# 2. Methods

# 2.1. Study area

The study was located in the headwater area of the Sondu River, which originates in the South-West block of the Mau Forest Complex and drains into Lake Victoria. The South-West Mau is under human pressure through forest excisions, encroachment of smallholder farms into the forest, illegal logging, charcoal burning and poaching (Government of Kenya, 2009; Olang and Kundu, 2011). Large parts of the forest have been converted to smallholder agriculture in the past decades (Baldyga et al., 2008), while commercial tea plantations were established in the area in the first half of the 20th century (Binge, 1962). The sampling sites selected for this study fall within the Chemosit River basin with an area of 1023 km<sup>2</sup>, a sub-basin of the Sondu basin (Fig. 1a). Elevation ranges from 2932 m on top of the Mau Escarpment to 1717 m at the outlet of the catchment. The geology in the area originates from the early Miocene (Edwards and Blackie, 1979), with phonolites dominating in the lower part of the catchment, and phonolitic nephelinites in the upper part (Binge, 1962; Woolley, 2001). A variety of Tertiary tuffs are found on the highest part of the Mau Escarpment (Jennings, 1971).

The temperature in the study area is relatively constant throughout the year with a mean of 15.7 °C at 2081 m elevation between 1990 and



**Fig. 1.** Maps of the study area in the South-West Mau, Kenya, showing (a) elevation (SRTM digital elevation model 30 m resolution; USGS, 2000), and (b) land use classification based on LandSat imagery from 2013 (Swart, 2016). Precipitation gauges, sampling sites and catchments within the Chemosit basin are indicated on both maps. Labels refer to the sampling site and corresponding land use: NF = natural forest, SHA = smallholder agriculture and TTP = tea and tree plantations.

1996 (Ekirapa and Shitakha, 1996). Daily minimum temperatures lie between 8 and 9 °C throughout the year, while the daily maximum temperature ranges from 21 °C in July to 25 °C in March (Stephens et al., 1992). The area experiences a bi-modal rainfall pattern, with the long rains occurring from April to July and the short rains from October to December. Mean annual precipitation between 1905 and 2014 was 1988  $\pm$  328 mm, with highest rainfall generally occurring in April and May during the long rains (>250 mm per month) and lowest in January and February during the dry season (<75 mm per month).

The Chemosit basin is dominated by three land use types: (a) natural forest (NF), (b) smallholder agriculture (SHA) and (c) commercial tea and tree plantations (TTP; Fig. 1b). The natural forest is located between 1930 and 2470 m elevation. The eastern part of the forest, bordering an area of smallholder agriculture, is degraded through human encroachment. In total, >25% of the forest cover in the South-West Mau was lost since the 1990s (Kinyanjui, 2010), although forest cover is slowly increasing after eviction of settlers from this area in 2005 and 2006 (Chacha, 2015). However, illegal activities such as logging, charcoal burning and grazing are still ongoing. The area of the forest neighbouring the tea plantations in the west is less degraded (Bewernick, 2016), although the mentioned human activities also affect the forest on that side.

On the north eastern side of the forest, smallholder agriculture is prevalent, mainly consisting of small farms of up to 2 ha. People practice subsistence farming, growing maize, beans, cabbage and potatoes, interspersed with grazing areas and *Eucalyptus* spp. or *Cypress* spp. woodlots. Farmers apply up to 50 kg N ha<sup>-1</sup>, depending on the crops they grow, although this can increase to  $100-120 \text{ kg N ha}^{-1}$  at smallholder farms where tea is grown. Riparian zones are often severely degraded, due to cultivation up to the river bank and access to the river for fetching water, washing clothes and bathing as well as watering livestock, predominantly cattle. In several places the natural bamboo vegetation in the riparian zone is replaced by small *Eucalyptus* plantations.

At a low altitude (<2100 m), an area of approx. 20,000 ha is covered by commercial tea plantations, some of which fall within the study catchment. Within this area, the commercial tea fields are alternated with Eucalyptus and Cypress plantations with an average ratio of 3:1 (tea:tree plantation). Riparian zones of up to 30 m distance from the river are maintained within the tea estates and consist of native vegetation. Aerial application of fertilizer in pellet form is carried out two to three times per year, with annual application rates of 150-250 kg N ha<sup>-1</sup> depending on the soil fertility status of individual tea fields. Manure is applied manually on fields within the commercial estates where certified-organic tea is grown. Land use change occurs within commercial tea plantations, whereby tea fields are replaced by Eucalyptus and vice versa, depending on soil conditions. The area of commercial tea production is surrounded by smallholder farms, where tea is grown on small fields of <1 ha in addition to the common food crops.

#### 2.2. Sites selection and sampling campaigns

Sampling sites were selected based on land use and accessibility. Initially thirteen sites were selected: five in the smallholder area (SHA1–5), five in the natural forest (NF1–5) and three within the commercial tea and tree plantations (TTP1–3; Fig. 1), covering a broad range of catchment sizes (4–103 km<sup>2</sup>). Three sites were added in 2016: SHA2 and SHA3 were combined to form SHA7 after the confluence of the streams draining SHA2 and SHA3, and NF2 and NF3 to form NF6 to increase the number of sites with a catchment size > 40 km<sup>2</sup>. SHA6 was selected to include a smallholder catchment with size <10 km. No additional suitable and accessible TTP catchments could be identified within the study area.

In total five snapshot sampling campaigns were conducted during periods of baseflow, which coincided with the dry season: on 9–10, 12–13 and 23–24 February 2015, 16–17 February 2016 and 5–6

March 2016, with each campaign taking two days. Opportunities for sampling were limited, because a period of stable flow is required for the sampling (Grayson et al., 1997). Daily and highly localised rainfall hinders sampling in periods other than the dry season, because it could result in sampling during rising or falling limbs of the hydrograph, reducing the comparability of the samples. Rainfall events were more frequent in the dry season of 2016 than in the dry season of 2015, further limiting the number of sampling campaigns. In February 2015, the 13 initially selected sites were sampled, while in 2016 all 16 sites were sampled. The route along sampling sites differed between 2015 and 2016 to avoid bias of sampling time. However, in both years all TTP catchments were sampled during the afternoon, whereas NF and SHA catchments were sampled in the morning and afternoon.

During all sampling campaigns, discharge was measured using the salt dilution method, whereby a known quantity of table salt (NaCl) mixed in a bucket with stream water was instantaneously released in the river (Moore, 2004). Electrical conductivity (EC) was measured downstream at a 1-second interval, using a handheld data logger (Multi 3420, WTW Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, Germany) equipped with an EC probe (TetraCon 925-3, WTW Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, Germany). The sensor also measured stream water temperature. The resulting time-concentration curve was used to calculate discharge (Moore, 2004). The quantity of salt and distance between salt release and EC measurement (20–100 m) was determined on site based on visually estimated discharge to ensure proper mixing of the salt with stream water. Specific discharge was calculated using the equation:

$$Q_s = \frac{Q_m}{A} * 864 \tag{1}$$

where  $Q_s$  is specific discharge in m<sup>3</sup> ha<sup>-1</sup> day<sup>-1</sup>,  $Q_m$  is the measured discharge in m<sup>3</sup> s<sup>-1</sup> and A is the catchment area in km<sup>2</sup>. A factor of 864 was included to convert the units from m<sup>3</sup> km<sup>-2</sup> s<sup>-1</sup> to m<sup>3</sup> ha<sup>-1</sup> day<sup>-1</sup>.

Stream water samples were filtered using a syringe and 0.45 µm polypropylene filter (Whatman Puradisc 25 syringe filter, GE Healthcare, Little Chalfont, UK or KX syringe filter, Kinesis Ltd., St. Neods, UK) and stored in clean 125 ml HDPE bottles with screw cap. The samples were immediately stored in a cooler box with ice and frozen on return from the field. All samples were analysed in the lab of Justus Liebig University Giessen, Germany for DOC and TDN (TOC cube, Elementar Analysensysteme GmbH, Hanau, Germany), as well as NO<sub>3</sub>-N (ICS-2000, Dionex, Sunnyvale CA, USA). Dissolved organic nitrogen (DON) was estimated by subtracting NO<sub>3</sub>-N from TDN, assuming that NO<sub>3</sub>-N was the dominant form of dissolved inorganic N. Four sites were sampled four times during baseflow and samples were analysed for both ammonium (NH<sub>4</sub>-N) and NO<sub>3</sub>-N. NH<sub>4</sub>-N concentrations were found to be negligible, probably due to missing point source pollution or any intensive farming activities. In 4 out of 77 samples, measured NO<sub>3</sub>-N values exceeded the TDN values, which is a common problem with this method of DON estimation when the DIN:TDN ratio is high (Graeber et al., 2012a). In these cases, DON concentrations were set to zero. In addition, two values for NO<sub>3</sub>-N were discarded based on improbability of the values compared to other results and identification as outliers by Grubbs' test (p < 0.05). For NF6 and SHA7, which are both combinations of two smaller catchments, parameters for campaigns 1–3 were estimated by combining the data from NF2 and NF3, and SHA2 and SHA3, respectively. The data obtained during campaigns 4–5 confirmed that this is a reasonable estimate.

#### 2.3. Explanatory variables

Data on stream water temperature and specific discharge were collected during the field campaigns as described above. Precipitation in the six weeks before each sampling campaign was calculated using precipitation data recorded at 10-minute intervals using six tipping buckets (Theodor Friedrichs, Schenefeld, Germany) and two weather stations (Decagon Devices, Meter Group, Pullman WA, USA) within the Chemosit basin (Fig. 1). Total precipitation for each catchment was estimated by weighing the data from each station using Thiessen polygons.

Data on catchment characteristics (Table 1) were collected from GIS sources. The categorical variable *land use* was obtained from a land use classification analysis for the Mau Forest complex, using LandSat imagery from 2013 (Swart, 2016). Tree cover was calculated from a raster dataset on forest cover in the area in 2016 and includes primary and secondary forest, shady forest in mountain ridges and tree plantations (Bewernick, 2016). The 30 m resolution of the LandSat imagery was not sufficient to map single trees or small woodlots on farms.

All data on topography and drainage network were derived from a 30 m SRTM digital elevation model (USGS, 2000). Elevation data was obtained directly from the SRTM DEM. Catchments were delineated using the Spatial Analyst toolbox in ArcMap 10.2 (Environmental Systems Research Institute, Inc. (ESRI), Redlands, California, USA). These were used to calculate catchment area and drainage density for each catchment. SAGA GIS (Conrad et al., 2015) was used to delineate the stream network and to calculate Topographical Wetness Index (TWI). TWI is an index developed for the prediction of wetness patterns within a catchment, based on upslope contributing area  $\alpha$  and slope tan  $\beta$  derived from commercially available topographic data (Beven and Kirkby, 1979; Rodhe and Seibert, 1999):

$$TWI = \frac{\alpha}{\tan(\beta)}$$
(2)

Both  $\alpha$  and tan( $\beta$ ) were derived directly from the DEM and used to calculate TWI with the Topographical Wetness Index module in SAGA GIS. The results were then normalised to range from 0 to 1.

### 2.4. Statistical analysis

All variables were tested for normality using Q-Q plots and the Shapiro-Wilk test (p < 0.05). DOC, TDN, NO<sub>3</sub>-N concentrations, specific discharge, precipitation and tree cover showed a significant deviation and were therefore log-transformed.

ANOVA and Tukey's HSD test were applied to test for significant differences (p < 0.05) in stream water concentrations for catchments with different land use. SHA3–5 were excluded from the analysis because of the different underlying geology. Pearson's correlation coefficients were calculated to identify the strength and direction of

Table 1

Characteristics of the 16 snapshot sampling catchments in the South-West Mau, Kenya. Dominant land use and percentage tree cover were derived from 2013 and 2016 LandSat imagery, respectively. Mean elevation, area, drainage density and Topographical Wetness Index were calculated from SRTM DEM with 30 m resolution (USGS, 2000).

Site	Coordinates <sup>a</sup>	oordinates <sup>a</sup>		Tree cover	Mean elevation	Mean elevation Area		Topographical Wetness Index
	Longitude	Latitude		%	m	km <sup>2</sup>	$\rm km \ km^{-2}$	
NF1	35° 18′ 32.939″ E	0° 27′ 48.286″ S	NF	99.00	2177	35.9	1.652	0.176
NF2	35° 23′ 2.220″ E	0° 32′ 45.474″ S	NF	95.23	2200	9.7	1.515	0.181
NF3	35° 23′ 2.374″ E	0° 32′ 46.352″ S	NF	97.76	2269	36.2	1.793	0.181
NF4	35° 23′ 33.598″ E	0° 34′ 15.531″ S	NF	98.89	2254	17.8	1.657	0.177
NF5	35° 23′ 34.575″ E	0° 35′ 2.451″ S	NF	97.80	2222	9.5	1.737	0.166
NF6	35° 22′ 57.998″ E	0° 32′ 47.376″ S	NF	97.13	2254	46.0	1.772	0.181
SHA1	35° 28′ 31.454″ E	0° 24′ 3.797″ S	SHA	9.29	2524	27.2	1.467	0.194
SHA2	35° 29′ 22.864″ E	0° 25′ 32.442″ S	SHA	5.26	2536	26.7	1.640	0.200
SHA3	35° 29′ 26.687″ E	0° 25′ 33.112″ S	SHA	2.69	2602	48.7	1.577	0.199
SHA4	35° 31′ 26.721″ E	0° 25′ 58.857″ S	SHA	3.98	2606	49.9	1.583	0.197
SHA5	35° 31′ 24.400″ E	0° 26′ 12.150″ S	SHA	1.68	2651	103.7	1.645	0.209
SHA6	35° 28′ 9.278″ E	0° 23′ 9.573″ S	SHA	4.77	2445	7.7	1.429	0.194
SHA7	35° 29′ 17.812″ E	0° 25′ 37.110″ S	SHA	3.73	2574	77.8	1.639	0.199
TTP1	35° 13′ 15.216″ E	0° 28′ 37.699″ S	TTP	34.10	1953	33.3	1.667	0.196
TTP2	35° 14′ 23.210″ E	0° 29′ 19.548″ S	TTP	34.20	1949	5.3	1.679	0.197
TTP3	35° 15′ 30.753″ E	0° 33′ 18.911″ S	TTP	17.28	1992	4.3	1.605	0.189

<sup>a</sup> WGS 1984 UTM Zone 36S.

 $^{\rm b}$  NF = natural forest, SHA = smallholder agriculture, TTP = tea and tree plantations.

significant relationships (p < 0.05) between the dependent and explanatory variables.

Stepwise-forward linear regression was used to quantify the effect of all continuous explanatory variables on water quality. Tree cover (%) was included in the analysis as a proxy for the categorical variable *land use*. To avoid overfitting the model, variables with p > 0.01 were excluded from the model as having no significant influence on the water quality parameter. The Variance Inflation Factor (VIF) was used to assess multicollinearity between variables included in the model. A variable was considered highly collinear if the VIF > 10 (O'Brien, 2007) and was consequently excluded from the model. We report adjusted  $R^2$  as a measure of explanatory power of each model. All statistics were carried out with R 3.2.1 (R Core Team, 2015).

# 3. Results

#### 3.1. Stream water chemistry across catchments

Highest stream water electrical conductivity (EC) values were observed in the catchments dominated by smallholder agriculture (SHA), followed by commercial tea and tree plantations (TTP) and the natural forest (NF; Table 2; p < 0.01). Stream temperature varied between 12.0 and 21.7 °C, with the lowest temperatures recorded in the morning around 7 a.m. and a highest around 2 p.m. Stream water temperatures in the NF catchments were significantly lower (p < 0.01) than in the TTP catchments. However, temperatures in NF and SHA as well as in SHA and TTP did not differ significantly (p = 0.219 and p = 0.354, respectively).

Specific discharge was lower for SHA catchments than for NF and TTP catchments (p < 0.001). Overall, baseflow specific discharge values were lower during the campaigns of 2015, with a mean of 2.07  $\pm$  1.15 m<sup>3</sup> ha<sup>-1</sup> day<sup>-1</sup> in 2015 compared to 5.84  $\pm$  4.50 m<sup>3</sup> ha<sup>-1</sup> day<sup>-1</sup> in 2016. This is most likely due to more rainfall in the period preceding the samplings campaigns in 2016.

The TTP catchments were characterised by the highest stream water TDN and NO<sub>3</sub>-N concentrations (Fig. 2). Minimum values in the three TTP catchments were up to 4 times higher than the maximum values in all other catchments (Table 2). NF catchments showed the lowest stream water TDN and NO<sub>3</sub>-N concentrations. Concentrations of both solutes also differed between catchments dominated by the three different land uses (p < 0.001). Conversely, DOC concentrations in the TTP catchments (Fig. 2; Table 2). DON concentrations were similar across all catchments (p = 0.738).

# Table 2

Stream water chemistry for all sites sampled in February 2015 and February/March 2016 (n = 5 for all sites, except SHA6 with n = 2) in the South-West Mau, Kenya. Range is presented for concentrations of dissolved organic carbon (DOC), total dissolved nitrogen (TDN), nitrate (NO<sub>3</sub>–N), dissolved organic nitrogen (DON), electrical conductivity (EC), stream temperature and specific discharge. Mean  $\pm$  SD of these variables is given in parentheses for all sampling sites of the same land use. Different superscripts for the means of each parameter indicate significant differences (p < 0.05) between sites grouped by land use (NF = natural forest, SHA = smallholder agriculture, TTP = tea and tree plantations). The total amount of precipitation was calculated for a period of six weeks preceding each sampling campaign (1–5).

Site	DOC	TDN	NO <sub>3</sub> -N	DON	EC	Stream temp.	Specific discharge	Precipitation						
	mg C l <sup>-1</sup>	mg N l <sup>-1</sup>	mg N l <sup>-1</sup>	mg N l <sup>-1</sup>	$\mu S \ cm^{-1}$	°C	$\mathrm{m}^3~\mathrm{ha}^{-1}~\mathrm{day}^{-1}$	mm						
								1	2	3	4	5		
NF1	1.66-3.21	0.50-0.90	0.36-0.40	0.11-0.52	30.1-44.0	13.1-21.7	2.41-8.20	6.2	5.8	56.6	297.5	79.6		
NF2	1.29-1.72	0.51-0.81	0.29-0.43	0.10-0.50	25.6-37.8	12.0-17.2	2.04-12.72	6.4	6.0	58.2	278.2	73.2		
NF3	0.82-1.51	0.32-0.64	0.18-0.26	0.06-0.46	28.7-45.2	12.9-17.1	2.53-10.37	4.3	3.7	41.1	214.6	54.1		
NF4	1.12-1.60	0.35-0.47	0.21-0.31	0.07-0.25	26.1-35.3	13.0-16.6	2.00-11.55	4.8	4.3	45.2	229.9	58.7		
NF5	1.34-1.84	0.47-0.58	0.27-0.43	0.11-0.29	28.1-41.3	12.9-18.6	1.35-11.67	7.6	6.9	70.5	278.2	73.2		
NF6	1.00-1.75	0.37-0.68	0.21-0.31	0.09-0.46	28.2-43.7	12.7-15.7	2.52-11.07	3.6	3.3	32.4	228.1	58.1		
NF	$(1.53 \pm 0.43)^{a}$	$(0.55 \pm 0.15)^{a}$	$(0.30 \pm 0.08)^{a}$	$(0.26 \pm 0.16)^{a}$	$(34.7 \pm 5.7)^{a}$	$(15.1 \pm 2.4)^{a}$	$(4.81 \pm 3.41)^{a}$							
SHA1	1.44-1.86	0.76-0.98	0.39-0.87	0.10-0.42	51.6-72.4	12.5-18.2	1.52-4.60	3.3	3.1	12.6	146.1	38.7		
SHA2	1.44-2.05	0.76-0.96	0.54-0.79	0.04-0.42	55.8-66.9	15.1-19.5	0.93-2.73	2.8	2.6	13.6	150.3	39.9		
SHA3	1.42-2.54	0.74-1.10	0.44-0.67	0.08-0.50	64.9-96.2	16.6-18.6	0.65-1.51	1.8	1.8	8.8	152.9	43.3		
SHA4	1.77-3.06	0.74-0.98	0.36-0.92	0.06-0.38	66.9-83.8	14.3-19.9	0.36-1.11	2.2	2.1	8.7	150.2	42.3		
SHA5	2.94-3.72	0.54-0.67	0.19-0.55	0.12-0.37	98.6-135.8	12.3-21.5	0.41-0.84	1.5	1.5	6.5	153.1	44.5		
SHA6	1.26-1.44	0.69-0.79	0.58-0.73	0.06-0.11	36.5-37.7	12.1-12.6	3.51-5.78	3.6	3.3	18.6	149.4	37.1		
SHA7	1.50-2.77	0.80-1.04	0.57-0.71	0.16-0.46	60.5-84.6	14.5-20.2	0.75-1.98	2.2	2.1	11.0	152.6	42.1		
SHA	$(2.09 \pm 0.65)^{a}$	$(0.82 \pm 0.13)^{b}$	$(0.57 \pm 0.17)^{\rm b}$	$(0.24 \pm 0.14)^{a}$	$(76.1 \pm 24.4)^{b}$	$(16.6 \pm 2.6)^{ab}$	$(1.41 \pm 1.25)^{b}$							
TTP1	0.73-1.02	1.48-1.74	1.14-1.71	0.00-0.35	38.2-41.7	16.3-17.3	3.38-16.56	4.0	3.9	43.8	275.6	93.9		
TTP2	0.80-1.58	1.17-1.74	0.94-1.74	0.00-0.32	37.3-39.5	12.2-18.0	3.01-15.06	4.3	4.3	29.3	254.4	97.5		
TTP3	0.80-1.48	1.97-2.91	1.66-3.07	0.00-0.34	46.3-48.9	18.0-20.4	2.26-9.66	10.2	10.1	39.8	201.8	86.0		
TTP	$(1.00\pm0.25)^{b}$	$(1.80\pm0.50)^{c}$	$(1.62\pm0.60)^{c}$	$(0.20\pm0.15)^a$	$(41.8 \pm 4.4)^{c}$	$(17.4 \pm 1.8)^{b}$	$(6.04 \pm 4.47)^{a}$							



**Fig. 2.** Comparison of (a) dissolved organic carbon (DOC), (b) total dissolved nitrogen (TDN), (c) nitrate ( $NO_3-N$ ) and (d) dissolved organic nitrogen (DON) concentrations between the three land use types (NF = natural forest, SHA = smallholder agriculture, TTP = tea and tree plantations) based on data collected in the South-West Mau, Kenya, in February 2015 and February/March 2016. The thick line represents the median and the box the inter quartile range, while whiskers show the minimum and maximum values. Different letters above the land uses in the box plot indicate a significantly different mean (p < 0.05).

## 3.2. Correlation between variables

DOC concentrations showed a negative correlation with specific discharge and tree cover (%) (Table 3), a strong positive correlation with elevation and area, and a weak positive correlation with TWI. Significant correlations between the explanatory variables and TDN and NO<sub>3</sub>-N were similar in direction and magnitude, except for catchment area, which was correlated only with NO<sub>3</sub>-N. This similarity can be explained by the high correlation between TDN and NO<sub>3</sub>-N (r = 0.894; p < 0.001). The strongest correlation was found between TWI and both TDN and NO<sub>3</sub>-N. DON was only significantly correlated to specific discharge and precipitation.

# 3.3. Explaining stream water chemistry

A model including area, precipitation in the six weeks before the sampling campaign, specific discharge, TWI and drainage density explained 70.3% of the variation in DOC concentrations (p < 0.001; Table 4). The most important variables were catchment area and specific discharge, which together explained 59.1% of the variance (Fig. 3).

Elevation and tree cover were both included in the models predicting TDN and NO<sub>3</sub>-N concentrations in stream water. Whereas these are the only selected variables for TDN, explaining 78.2% of TDN variation (p < 0.001), stream water temperature, area and specific discharge were also included in the model for NO<sub>3</sub>-N. However, elevation and tree cover were also the most important variables for NO<sub>3</sub>-N, explaining 12.5 and 47.3% of the variation, respectively. Precipitation, specific discharge and tree cover explained 53.1% of variation in DON concentrations (p < 0.001), but the contributions of tree cover (3.6%) and specific discharge (4.8%) are very small compared to precipitation (46.7%).

### 4. Discussion

#### 4.1. Variation in DOC

The DOC concentrations in our natural forest (NF) and smallholder (SHA) catchments are similar to those found in the tropical montane forests in the Aberdare Mountains in central Kenya (Bouillon et al., 2009), the forest and agricultural areas in the Transmara block of the Mau Forest Compex (Masese et al., 2017), and in the tropical rain forest and catchments dominated by maize cultivation in western Kenya (Recha et al., 2013; Table 5).

Despite the similarity with values found in other Kenyan case studies, DOC concentrations in our forest catchments  $(1.53 \pm 0.43 \text{ mg l}^{-1})$ were lower than those measured in small headwater catchments in a tropical montane forest in Ecuador (Goller et al., 2006), and in Peru (Saunders et al., 2006; Table 5). This difference could be related to sampling conditions, since our values represent baseflow, while the concentrations reported by Goller et al. (2006) and by Saunders et al. (2006) represented different flow conditions throughout the year. Similar to our study, Goller et al. (2006) found that stream water DOC concentrations were positively related to rainfall, potentially through flushing of soluble organic compounds from the organic layer, which can explain the higher values found in their study. Furthermore, the catchments in our study were on average > 10 times larger, suggesting a longer transit time and therefore a higher possibility for sorption of DOC to soil particles before reaching the stream, resulting in lower stream concentrations. However, this contradicts the results of our multiple regression analysis, which showed a strong positive effect of catchment area.

The negative effect of discharge on DOC in our study cannot be attributed to dilution by rainfall, because sampling was carried out during baseflow. The effect observed here most likely reflects land use, because the lowest specific discharge was found in the SHA catchments, which exhibit the highest DOC concentrations, whereas higher specific discharge and lower DOC concentrations were found in the TTP catchments. Reduced infiltration rates were observed in croplands (40.5  $\pm$  21.5 cm h<sup>-1</sup>), pastures (13.8  $\pm$  14.6 cm h<sup>-1</sup>) as well as commercial tea plantations (43.3  $\pm$  29.2 cm h<sup>-1</sup>) compared to natural forest (76.1  $\pm$  50.0 cm h<sup>-1</sup>) in our study area (Owuor et al., in review), which could result in lower specific discharge during baseflow, due to decreased replenishment of groundwater during the wet season. Furthermore, the SHA catchments received on average 52.9  $\pm$  15.7% and 57.0  $\pm$  11.7% less precipitation in the six weeks before each sampling campaign than NF and TTP catchments, respectively.

Despite the significant negative correlation between DOC concentrations and tree cover, only the commercial tea and tree plantation (TTP) catchments had significantly lower DOC concentrations (p < 0.05). Most of the biomass produced in the TTP catchments is harvested (both tea and timber) and is therefore not available for decomposition and eventual export as DOC in the streams, which could explain lower DOC concentrations in the TTP catchments. However, a catchment dominated by an agro-forestry cacao plantation in northeast Brazil showed higher DOC concentrations (4.1 mg  $l^{-1}$ ) compared to tropical sub-montane forest (2.6 mg l<sup>-1</sup>) during baseflow (Da Costa et al., 2017). Also Brazilian catchments dominated by sugar cane production exhibited higher DOC concentrations (2.23–3.44 mg  $l^{-1}$ ) than catchments with natural Cerrado savannah or Eucalyptus plantations  $(1.38-1.71 \text{ mg } l^{-1})$  (Da Silva et al., 2007). This could be due to soil management practices such as ploughing or harvesting that stimulate mobilization of the organic C pool in the soil (Nosrati et al., 2012). Less shading of streams in the SHA catchments due to degraded riparian vegetation could lead to increased in-stream productivity as an effect of higher light-availability for primary producers. Furthermore, the SHA catchments receive manure inputs due to livestock watering, whereas this is not the case in the NF and TTP catchments. Direct inputs from livestock drinking from the streams or disturbance of river banks and stream bed sediment through human and animal activity could have resulted in higher DOC concentrations in the SHA catchments during baseflow.

TWI was negatively correlated to DOC concentrations. High TWI values are indicative of shallow groundwater table and higher soil moisture (Rodhe and Seibert, 1999). Therefore, areas with high TWI can represent wetland areas that can act as source of DOC, since waterlogged or

Table 3

Significant Pearson's correlation coefficients (*p* < 0.05) for relationships between dissolved organic carbon (DOC), total dissolved nitrogen (TDN), nitrate (NO<sub>3</sub>-N) and dissolved organic nitrogen (DON) and the explanatory variables included in the analysis for all samples taken at the 16 sampling sites in the South-West Mau, Kenya, in February 2015 and February/March 2016.

n	n	Stream temp.	Specific discharge	Precipitation	Elevation	Area	Drainage density	Topographical Wetness Index	Tree cover
DOC 77 TDN 77 NO <sub>3</sub> -N 75 DON 75	77 77 75	n.s. 0.341** 0.419***	-0.589*** n.s. n.s. -0.389**	n.s. n.s. n.s.	0.727*** -0.359** -0.343**	0.641*** n.s. -0.287*	n.s. -0.275* -0.301**	0.263* 0.433*** 0.414***	-0.496*** -0.284* -0.296*

n.s. = not significant ( $p \ge 0.05$ ).

\* *p* < 0.05.

\*\* p < 0.01.

\*\*\* p < 0.001.

### Table 4

Coefficients and standardised beta coefficients (in parentheses) of significant variables (p < 0.01) included the multiple linear regression models for dissolved organic carbon (DOC), total dissolved nitrogen (TDN), nitrate (NO<sub>3</sub>-N) and dissolved organic nitrogen (DON) concentrations in stream water, based on data collected in the South-West Mau, Kenya, during five sampling campaigns in February 2015 and February/March 2016.

Variable	ln DOC	ln TDN	ln NO <sub>3</sub> -N	DON
Stream temperature			0.050***	
In Specific discharge	$-0.246^{***}$		(0.181) 0.293 <sup>***</sup> (0.326)	$-0.059^{**}$
In Precipitation	0.103***		()	-0.048***
Elevation	(0.459)	$-0.002^{***}$ (-1.221)	$-0.002^{***}$ (-0.826)	(-0.563)
Area	0.008***	()	-0.008***	
Drainage density	(0.607) -1.130 <sup>***</sup> (-0.274)		(-0.291)	
Topographical Wetness Index	-12.987***			
In Tree cover	(-0.396)	$-0.380^{***}$ (-1.178)	$-0.579^{***}$ (-1.245)	0.041 <sup>***</sup> (0.438)
Constant	4.353***	6.686***	5.903***	0.323***
Adj. R <sup>2</sup>	0.703	0.766	0.869	0.531
Overall model p	< 0.001	< 0.001	< 0.001	< 0.001
n	77	77	75	75

<sup>\*\*</sup> *p* < 0.01.

poorly drained soils are usually rich in DOC (Kalbitz et al., 2000). However, the negative relationship between TWI and DOC found here, contradicts the common finding that wetland areas significantly increase DOC concentrations in streams (Chapman et al., 2001; Monteith et al., 2015). The range of TWI values for all catchments was very narrow, which could also explain why the expected positive correlation was not found. Moreover, as water samples were taken during dry season, the effect of wetlands was potentially limited due to a lack of hydrological connectivity.

Because TWI is strongly negatively correlated to slope (r = -0.959, p < 0.05), it is also possible that the significant effect is caused by a positive effect of slope rather than a negative effect of TWI itself. Steeper slopes often promote overland flow, especially in managed catchments, which could be an important source of DOC in stream water. However, the range of mean slope values was small (7.43%–13.5%) and such effect would not be visible during baseflow.

Soil type and texture have been found to be relevant predictors of instream DOC concentrations. Billett et al. (2006) identified, for example, that soil C stocks are related to DOC concentrations in stream water, though the relationship is complex and does not hold in small catchments. Since stocks of soil organic carbon (SOC) were higher in forest soils compared to agricultural soils in neighbouring part of the Mau Forest (Were et al., 2016), this could explain the higher DOC concentrations in streams in the NF catchments than in TTP catchments. We also noticed that catchments with mollic Andosols as dominant soil type (SHA3-5) showed significantly higher DOC concentrations (p < 0.001) than the catchments dominated by humic Nitisols when controlling for land use. Both soil types, but especially Andosols, are characterised by high organic matter content. These soils also contain iron  $(Fe^{2+/3+})$  or aluminium  $(Al^{3+})$ , which strongly bind organic matter, making the organic matter difficult to mobilize. However, increased mobilization and loss of soil organic carbon from forest soils converted to agriculture is commonly found in Andosols (Covaleda et al., 2011; Were et al., 2013), which could lead to increased DOC concentrations in stream water. This implies a potential role of soil type or geology on stream water DOC concentrations. More data on soil organic matter content, C and N stocks are required to confirm this hypothesis, but this data was not available for our study area.

#### 4.2. Variation in dissolved nitrogen fractions

Total dissolved nitrogen (TDN) concentrations in the NF catchments were higher than found in tropical montane forest in Kenya (Masese et al., 2014) and Ecuador (Goller et al., 2006), whereas the values found in SHA and TTP catchments were lower than in agricultural areas in the Mara Basin, Kenya (Masese et al., 2017, 2014; Table 5). Conversely, nitrate (NO<sub>3</sub>-N) concentrations in smallholder areas in the Eastern Mau (Mokaya et al., 2004) and Mara River Basin, Kenya (Kilonzo et al., 2014; Nyairo et al., 2015) were slightly lower than in our SHA catchments. The mean NO<sub>3</sub>-N concentration in the TTP catchments was in the range of values found in stream water of a catchment dominated by commercial tea plantations in Nandi, Kenya (Maghanga et al., 2012). NO<sub>3</sub>-N concentrations in the natural forest were high compared to values observed in tropical montane forests elsewhere, whereas dissolved organic nitrogen (DON) concentrations were similar (Table 5).

Dissolved organic N has been neglected in water quality research for a long time, the focus being on inorganic N forms such as ammonium and particularly NO<sub>3</sub>-N, which usually dominate N exports from temperate areas in the Northern Hemisphere (Breuer et al., 2015; Perakis and Hedin, 2002; van Breemen, 2002). Similar to our results, many studies show higher contributions of DON to TDN in natural catchments compared to managed catchments, e.g. 16.7% in natural forest compared to 7.6% in smallholder catchments in the Mara Basin, Kenya (Masese et al., 2017) and 20.4% in tropical rainforest versus 2.1–13.4% in maize cultivated catchments in western Kenya (Recha et al., 2013).

Our study found that elevation and tree cover explained 78.2% and 59.8% of the variance in TDN and NO<sub>3</sub>-N concentrations in stream



**Fig. 3.** Percentage of variation in dissolved organic carbon (DOC), total dissolved nitrogen (TDN), nitrate (NO<sub>3</sub>-N) and dissolved organic nitrogen (DON) explained by the different variables included in the multiple regression models, based on partial  $R^2$ . ST = stream temperature, SD = specific discharge, PR = precipitation, EL = elevation, CA = catchment area, DD = drainage density, TWI = Topographical Wetness Index and TC = tree cover.

<sup>\*\*\*\*</sup> *p* < 0.001.

water, respectively. Elevation probably indicates an effect of land use, since the land use types in the studied catchments were highly stratified by elevation. The inclusion of tree cover is also a strong indicator that land use plays a major role in determining stream water TDN and NO<sub>3</sub>-N concentrations, since the three land uses studied here have distinctively different mean tree cover (NF = 97.6  $\pm$  1.4%, SHA = 4.5  $\pm$  2.4% and TTP = 28.5  $\pm$  9.7%, *p* < 0.001). Furthermore, areas under high tree cover receive less or no fertilizer compared to crops and tea plantations. Commercial tea fields receive 4–10 times more N ha<sup>-1</sup> than smallholder farms where tea is grown, and the natural forest does not receive any fertilizer inputs. This is likely to result in differences in N inputs to surface water and thus higher TDN and NO<sub>3</sub>-N concentrations.

The land use effect observed in this study agrees with findings of a study in southwest China, where catchments dominated by rubber plantations depicted higher TDN and NO<sub>3</sub>-N concentrations compared to rainforest catchments (Li et al., 2016). Furthermore, Biggs et al. (2004) found up to 4 times higher TDN concentrations in deforested catchments in the Brazilian Amazon, with the effect being strongest in catchments with >66–75% deforestation. Conversion of montane forest to coffee plantations increased NO<sub>3</sub>-N concentrations from 1.4 to 3.7 mg N l<sup>-1</sup> (Martínez et al., 2009). An exception to this is conversion of forest to pasture, which often leads to a reduction in NO<sub>3</sub>-N concentrations in stream water (e.g. Martínez et al., 2009; Neill et al., 2001).

Despite a significant difference (p < 0.005) in DON contribution to TDN in stream water between land use types, with contributions up to 72% in the NF catchments, DON concentrations were similar in all three land use types. This agrees with findings by Gücker et al. (2016b) in a transition zone between the Brazilian Cerrado savanna and the Atlantic rain forest in Brazil, Neill et al. (2001) in the Brazilian Amazon and Recha et al. (2013) in Kenya. Nevertheless, the stepwise linear regression model included percent tree cover as significant variable, although it only explains 3.6% of the variation in DON concentrations. Tree cover could affect DON concentrations through differences in quantity, quality and composition of organic material in the litter layer and soil compared to tea and crop cover, which would influence the availability of DON for export in stream water.

We found a positive relationship between NO<sub>3</sub>-N concentrations and specific discharge, which is most likely related to land use, as was suggested in Section 4.1 for DOC concentrations. However, specific discharge negatively affected DON concentrations. Due to the lack of difference in DON concentrations between the three land uses, it is unlikely that this reflects a land use effect. Furthermore, 46.7% of the variance in DON concentrations was explained by precipitation in the six weeks preceding the sampling campaigns, suggesting an influence of precedent wetness conditions in the catchments on DON concentrations in the stream. The negative effect of both specific discharge and precipitation indicates that dryer conditions stimulate DON export. Zhang et al. (2016) found that DON concentrations in soil and stream water are strongly related across different climates. This implies that DON concentrations in the soil are also higher under dry conditions, which could be a consequence of reduced mineralization of organic matter.

Stream water temperature is known to have a positive effect on organic matter decomposition, ammonification and nitrification, i.e. the source process of NO<sub>3</sub>-N (Warwick, 1986), which could explain the positive result and correlation between NO<sub>3</sub>-N concentration and stream water temperature. Diurnal variations in parameters such as solar radiation and stream temperature can also cause diurnal variation in stream solute concentrations, through influence on in-stream processing of these solutes. This occurs especially in shallow, less-shaded streams (Nimick et al., 2011). Diurnal variation will therefore be more pronounced during baseflow. Since all TTP sites were sampled in the afternoon, this could have resulted in a significantly higher mean stream water temperature in these catchments compared to other sites and thus also higher NO<sub>3</sub>-N concentrations through organic matter decomposition. However, it is more common to observe lower NO<sub>3</sub>-N concentrations in the afternoon, due to enhanced uptake for in-stream photosynthetic activity (Rusjan and Mikoš, 2010). The coincidence of afternoon sampling of TTP catchments with significantly higher stream water temperatures and higher NO<sub>3</sub>-N concentrations, could also explain the positive relationship with stream temperature. Nevertheless, NO<sub>3</sub>-N concentrations and stream water temperature also show a significant positive relationship for the TTP catchments alone (r = 0.678, p < 0.05). Shading of the streams by riparian forests is unlikely to have affected stream temperatures in this study, because mean stream water temperature in the SHA catchments, with the most degraded riparian forests, was not significantly different from the mean temperatures found in the NF and TTP catchments (p > 0.05). Furthermore, stream water temperatures in well-shaded NF catchments and less-shaded SHA catchments were similar for sites sampled at the same time of the day.

### 4.3. Interactions between the C and N cycles

Despite the distinctly different drivers for DOC and dissolved N fractions observed in this study, the C and N cycle are not completely independent. Several studies in temperate regions observed a significant positive relationship between DOC and DON (Chapman et al., 2001; Hood et al., 2003; Kaushal and Lewis, 2003; Willett et al., 2004), but our data showed no correlation between the two variables (r = 0.06, p > 0.05). This could be a result of the low use of N fertilizer and the tendency of soil N mining in our study area (Zhou et al., 2014) or different relationships between the two fractions in catchments with different dominant land use. Nevertheless, both dissolved organic C and N concentrations were more influenced by natural than anthropogenic drivers.

Other interactions between the C and N cycles are related to the N inputs and its effect on primary productivity. Nosrati et al. (2012) mention increased organic matter production, utilization of organic fertilizers and increased in-stream productivity due to increased nutrient input as potential causes for such increases in stream water DOC concentrations. It is unlikely that increased nutrient inputs to the stream affected in-stream DOC production and thus DOC concentrations in our study area, because the TTP catchments with the highest nutrient inputs showed lowest DOC concentrations in stream water. On the other hand, there is also evidence that increased soil N-inputs decrease DOC release rates in the soil due to increased microbial metabolism (Gundersen et al., 1998), although results of lab and field studies are not consistent (Kalbitz et al., 2000). This potentially results in reduced stream water DOC concentrations catchments with high fertilizer inputs, which could be a reason for the lower DOC concentrations observed in the TTP catchments. If this mechanism applies here, it implies that DOC concentrations are indirectly affected by land use as well.

#### 4.4. Implications for downstream regions

The Sondu river basin studied in this paper eventually discharges into Lake Victoria, which is largely N limited. Since 22%-32.7% of all N inputs to the lake are from riverine origin, large-scale changes in land use could lead to a significant increase in N inputs (Scheren et al., 2000; Zhou et al., 2014). However, despite the significantly higher TDN and NO<sub>3</sub>-N concentrations found in non-forest catchments, the effect of land use in the headwaters on the concentration of these solutes downstream is most likely reduced through mixing of water from other catchments. A simple estimation of solute concentrations at the outlet of the Sondu basin, using means of specific solute loads and specific discharge weighted by relative catchment area covered by the three land use types (23% for forest, 68% for smallholder agriculture and 9% for commercial tea and tree plantations, based on the 2013 land use map) reveals that estimated TDN and NO3-N concentrations during baseflow (0.90 and 0.74 mg N  $l^{-1}$ , respectively) are similar to those of the SHA catchments. Although this is a coarse estimate, it suggests that areas

Studies reporting concentrations for dissolved organic carbon (DOC), total dissolved nitrogen (TDN), nitrate (NO<sub>3</sub>-N) and dissolved organic nitrogen (DON) in Kenyan headwater streams, tropical montane forest streams and selected tropical lowland forest streams (and paired catchments with different land use) worldwide. Values represent reported mean (±SD when available) concentrations. When means for several catchments with the same land use were reported, the range of means for that particular land use is given instead.

Source	Location	Study period	Coordinates	Land use	Elevation	Area	п	DOC	TDN	NO <sub>3</sub> -N	DON
					m	km <sup>2</sup>		mg C l <sup>-1</sup>	mg N $l^{-1}$	mg N $l^{-1}$	mg N $l^{-1}$
Current study	Sondu Basin, South-West Mau, Kenya	Feb 2015,	0° 32′ S, 35° 22′ E	Montane forest	2177-2269	9.5-46.0	30	$1.53 \pm 0.43^{a}$	$0.55 \pm 0.15^{a}$	$0.30\pm0.08^{a}$	$0.26\pm0.16^{a}$
·		Feb/Mar 2016	0° 25′ S, 35° 29′ E	Agriculture	2445-2651	7.7-103.7	32	$2.09 \pm 0.65^{a}$	$0.82\pm0.13^{a}$	$0.57\pm0.17^{a}$	$0.24\pm0.14^{a}$
			0° 30′ S, 35° 14′ E	Tea and tree plantation	1949-1992	4.3-33.2	15	$1.00\pm0.25^{a}$	$1.80\pm0.50^a$	$1.62\pm0.60^{a}$	$0.20\pm0.15^a$
Headwater catchments	s in Kenya										
(Bouillon et al.,	Aberdare Mountains, Tana River	Feb 2008	n.a.	Montane forest	2010-3020	n.a.	4	0.67-2.48 <sup>a</sup>	n.a.	0.02-0.19 <sup>a</sup>	n.a.
2009)	Basin, Kenya										
	Mount Kenya, Tana River Basin, Kenya		n.a.	Agriculture	1350-1590	n.a.	5	0.29–1.21 <sup>a</sup>	n.a.	0.08–0.80 <sup>a</sup>	n.a.
(Kilonzo et al., 2014)	Upper Mara Basin, Mau Forest, Kenya	Feb-Apr 2011	1° 2′ 15.2″ S, 35° 14′ 31.7″	Montane forest and	1800-3000	n.a.	16	n.a.	n.a.	0.21-2.7	n.a.
			E	agriculture							
(Maghanga et al., 2012)	Nandi Hills, western Kenya	2004-2006	n.a.	Tea plantation	1600-2000	n.a.	90	n.a.	n.a.	0.8–2.3	n.a.
(Masese et al., 2014)	Mara River Basin, Mau Forest, Kenya	Jan-Feb 2011	n.a.	Agriculture	1900-2300	n.a.	7	$3.6 \pm 0.9^{a}$	$1.1 \pm 0.3^{a}$	$1.2\pm0.3^{a}$	n.a.
		•		Ū.			7	$8.1 \pm 0.92^{b}$	$1.3\pm0.4^{b}$	$1.2\pm0.3^{b}$	n.a
				Montane forest	1900-2300	n.a.	10	$2.7 \pm 0.4^{a}$	$0.3\pm0.2^{a}$	$0.3\pm0.1^{a}$	n.a.
							10	$3.5 \pm 0.6^{b}$	$1.0\pm0.4^{ m b}$	$0.3\pm0.1^{b}$	n.a.
				Mixed	1900-2300	n.a.	7	$3.9 \pm 0.3^{a}$	$1.2 \pm 0.3^{a}$	$1.2 \pm 0.4^{a}$	n.a.
							7	$4.2 \pm 1.23^{b}$	$2.8 \pm 0.5^{b}$	$1.2 \pm 0.4^{b}$	n.a.
(Masese et al., 2017)	Mara River Basin, Mau Forest, Kenya	Dec 2011–Jan	n.a.	Montane forest	1900-2300	2.02-59.85	19	$1.7~\pm~0.4$	$1.2\pm0.5$	$1.0\pm0.4$	$0.2\pm0.1$
		2012		Mixed	1900-2300	2.02-59.85	14	$1.1\pm0.4$	$1.7 \pm 1.2$	$1.5\pm1.1$	$0.2\pm0.2$
				Agriculture	1900-2300	2.02-59.85	17	$1.4\pm0.7$	$6.6\pm2.6$	$6.1\pm6.1$	$0.5\pm0.2$
(Mokaya et al., 2004)	Njoro River, Mau Forest, Kenya	May-Aug 2000	0° 22′ 32″ S, 35° 56′ 18″ E	Agriculture	2255	n.a.	6	n.a.	n.a.	$0.36\pm0.06$	n.a.
(Nyairo et al., 2015)	Nyangores River, Mara River Basin,	n.a.	0° 40′–1° 02′ S, 35°	Agriculture and	1665-2105	n.a.	n.a.	n.a.	n.a.	0.101–0.26 <sup>a</sup>	n.a.
	Mau Forest, Kenya		14′-35° 28′ E	settlement			n.a.	n.a.	n.a.	0.147–0.274 <sup>b</sup>	n.a.
	Amala River, Mara River Basin, Mau Forest, Kenya		0° 45′–1° 02′ S, 35° 14′–35° 38′ E	Agriculture and settlement	1665–2096	n.a.	n.a.	n.a.	n.a.	0.080-0.21 <sup>a</sup>	n.a.
	•						n.a.	n.a.	n.a.	0.221-0.443 <sup>b</sup>	n.a.
(Recha et al., 2013)	Kapchorwa, Nandi County, Kenya	2006	0° 10′ 0″ N, 35° 0′ 0″ E	Rainforest	1800	0.128	12	1.31	0.49	0.4	0.1
				Maize 5 years	1800	0.144	12	1.48	0.67	0.58	0.09
				Maize 10 years	1800	0.091	12	1.47	4.83	4.71	0.1
				Maize 50 years	1800	0.100	12	1.52	4.64	4.52	0.12
(Tamooh et al., 2012)	Aberdare Mountains, Tana River Basin, Kenya	Nov 2009, Jun-Jul 2010	0° 21′–0° 31′ S, 36° 40′–36° 53′ F	Montane forest	1991-3003	n.a.	7	1.1-3.5	n.a.	n.a	n.a.
	Mount Kenya, Tana River Basin, Kenya		0° 09′–0° 23′ S, 37° 18′–37° 26′ E	Montane forest	1461-2964	n.a.	5	0.6-4.1	n.a.	n.a	n.a.
Tropical montane fores	sts and selected studies in tropical lowland	forests									
(Boy et al., 2008)	San Francisco catchment, Andes,	Apr 1998–Apr	4° 00′ S, 79° 05′ W	Montane forest	1900-2200	0.08-0.13	302	n.a.	n.a.	0.02-0.10 <sup>a</sup>	0.10-0.17
	Ecuador	2003					487	n.a.	n.a.	0.03-0.22 <sup>b</sup>	0.09-0.42
(Bücker et al., 2011)	San Francisco catchment, Andes,	Apr 2007–May	3° 58′ 30″ S, 79° 4′ 25″ W	Montane forest	1800-3140	1.3-4.5	n.a.	n.a.	n.a.	0.54-0.69	n.a.
	Ecuador	2008		Mixed	1800-3140	0.7-76	n.a.	n.a.	n.a.	0.55-0.62	n.a.

(Da Costa et al., 2017)	Northeast Brazil	21 weeks in 2012–2013	14° 27′ 27.7 S, 39° 04′ 17.6″ W	Sub-montane forest	n.a.	0.36	16	2.6 <sup>a</sup> 3.1	n.a. n.a.	n.a. n.a.	n.a. n.a.
,			16° 46′ 16.2″ S, 40° 01′	Cacao plantation	n.a.	0.73	17	4.06 <sup>a</sup>	n.a.	n.a.	n.a.
			21.2″ W	-				13.1	n.a.	n.a.	n.a.
(Da Silva et al., 2007)	Paulicéia, Santa Rita do Passa Quatro,	Jun 2005-May	21° 38′ 85″ S, 47° 38′ 09″ W	Savannah	660-730	11.5	12	$1.47 \pm 1.52$	n.a.	$0.04\pm0.013$	n.a.
	Brazil	2006	21° 39′ 47″ S, 47° 37′ 56″ W	Savannah and Eucalyptus	660–730	17.5	12	$1.71\pm2.02$	n.a.	$0.11\pm0.010$	n.a.
	Água Santa. Santa Rita do Passa		21° 40′ 11″ S. 47° 36′ 87″ W	Sugar cane	660-730	2.87	12	2.23 + 1.61	n.a.	0.55 + 0.16	n.a.
	Ouatro. Brazil		22° 69′ 55″ S. 47° 01′ 87″ W	Sugar cane	660-730	12.0	12	3.44 + 1.30	n.a.	$0.45 \pm 0.085$	n.a.
	Cara Prata, Santa Rita do Passa Quatro, Brazil		21° 36′ 51″ S, 47° 34′ 43″ W	Eucalyptus	660–730	4.23	12	1.38 ± 1.42	n.a.	$0.47~\pm~0.11$	n.a.
(Goller et al., 2006)	San Francisco catchment, Andes, Ecuador	May 1999–Apr 2002	4° 00′ S, 79° 05′ W	Montane forest	1900-2200	0.08-0.13	156	4.6-5.6	0.34-0.39	0.08-0.16	0.1-0.21
(Gücker et al.,	20 sites on Rio das Mortas, Brazil	Mar, May, Sep,	n.a.	Atlantic forest	n.a.	0.08-11.9	20	0.9-4.3	n.a.	n.a.	0.065-0.23
2016a)		Dec 2012		Pasture	n.a.	0.08-11.9	20	0.6-0.9	n.a.	n.a.	0.073-0.11
				Urban	n.a.	0.08-11.9	20	9.9-14.6	n.a.	n.a.	0.32-1.70
				Agriculture	n.a.	0.08-11.9	20	0.7-2.0	n.a.	n.a.	0.063-0.35
(Martínez et al.,	La Antigua, Mexico	Jul 2005–May	19° 05′–19° 34′ N, 96°	Montane forest	480-4200	n.a.	22	n.a.	n.a.	$1.4\pm0.94$	n.a.
2009)		2006	06'-97° 16' W	Coffee plantation	480-4200	n.a.	33	n.a.	n.a.	$3.7 \pm 2.8$	n.a.
				Grassland	480-4200	n.a.	33	n.a.	n.a.	$0.3\pm0.19$	n.a.
(McDowell and Asbury, 1994)	Rio Icacos, Luquillo Experimental Forest, Puerto Rico	Jun 1983–May 1986	18° 15′ N, 65° 50′ W	Rainforest	n.a.	0.162-3.26	352-477	1.36-2.13	n.a.	0.062-0.066	0.11-0.15
(Neill et al., 2001)	Fazenda Nova Vida, Rondônia, Brazil	1994-1998	10° 30′ S, 62° 30′ W	Evergreen forest	200-500	n.a.	24-30	n.a.	n.a.	0.13-0.15 <sup>a</sup>	0.02-0.26 <sup>a</sup>
							36-40	n.a.	n.a.	0.03–0.10 <sup>b</sup>	0.16-0.18 <sup>b</sup>
				Pasture	200-500	n.a.	25-32	n.a.	n.a.	0.011-0.02 <sup>a</sup>	$0.42 - 0.50^{a}$
							36-44	n.a.	n.a.	0.011-0.020 <sup>b</sup>	0.18–0.23 <sup>b</sup>
(Saunders et al.,	Yanachaga-Chemillen National Park,	Mar 2002-Mar	10° 32′ 45.9″ S, 75° 31′	Montane forest	2414	n.a.	20	$3.13 \pm 1.55^{a}$	n.a.	$0.011 \pm 0.034^{a}$	$0.12 \pm 0.084^{a}$
2006)	Peru	2003	28.4″ W				27	n.a.	n.a.	$0.024 \pm 0.020^{b}$	n.a.
(Wilcke et al., 2001)	San Francisco catchment, Andes, Ecuador	Mar 1998–Apr 1999	4° 00′ S, 79° 05′ W	Montane forest	1900-2200	0.08-0.13	174	n.a.	n.a.	0.047-0.081	n.a.
(Wilcke et al., 2013)	San Francisco catchment, Andes, Ecuador	Apr 1998–Dec 2010	4° 00′ S, 79° 05′ W	Montane forest	1850-2200	0.091	108	n.a.	n.a.	0.08	0.12
(Yamashita et al., 2014)	Baru experimental catchment, Sabah, Borneo	Apr 2008–Dec 2011	5° 01′ N, 117° 48.75′ E	Rainforest	171–255	0.441	90	3.1	n.a.	0.12	0.11

n.a. = Data not provided. <sup>a</sup> Concentrations measured during baseflow. <sup>b</sup> Concentrations measured during stormflow.

with higher N-export are buffered by the low N-export from forested areas, as long as a substantial forest area remains. Biggs et al. (2004) observed, for example, that TDN concentrations increased in catchments with >66–75% deforestation. Reduced baseflow and precipitation as consequence of large-scale deforestation (Lawrence and Vandecar, 2015) could also reduce this buffering effect. Further deforestation of the South-West Mau would therefore increase TDN and NO<sub>3</sub>-N concentrations during baseflow.

The results of this study cover baseflow conditions only, which occur two to three months per year. During high flow, solute concentrations can increase through mobilization of solutes stored in the topsoil (Creed and Band, 1998) and overland flow, or decrease through dilution. In case of increased mobilization, the difference in TDN and NO<sub>3</sub>-N concentrations between the land use types can be amplified during storm flow, because of higher N-availability through fertilizer inputs. Conversely, dilution by increased discharge in combination with mixing with water from forested catchment could further reduce the land use effect on the scale of the Sondu basin. However, the lack of reliable knowledge on the behaviour of nitrate and discharge within the Sondu basin, does not allow extrapolation of our results to periods of stormflow.

# 4.5. Conclusions

This study found a significant effect of land use on TDN and NO<sub>3</sub>-N, which agrees with results of many other studies, emphasizing the importance of good land management to reduce N inputs and risks to surface water eutrophication.

Although we found lower DOC concentrations in the tea catchments and a small but significant effect of tree cover on DON, it appears that DOC and DON fractions were more controlled by natural factors than by land use. Both fractions showed an influence of hydrological regime through precipitation and specific discharge, whereas catchment area, topographical wetness index and drainage density were also important drivers for DOC concentrations. Although both models explain the majority of variation in DOC and DON concentrations in stream water, the inclusion of soil properties, such as soil organic matter content and C and N stocks, could increase model performance for both fractions, since many studies identified these as relevant predictors. However, this information was not available for our study area at the time. In addition, sampling throughout different seasons could further increase our understanding of the role of land use versus physical catchment characteristics and weather variables in determining water quality, because a potential effect of variations in dominant flow paths might be observed.

Some previous studies in East Africa looked at anthropogenic effects on water quality. This study is the first that looks into the role of land use and other catchment characteristics on concentrations of dissolved carbon and nitrogen. These results can help to unravel the complex relationships between these drivers and to identify areas of research that will increase our understanding of the processes behind nutrient cycling in these tropical environments.

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.scitotenv.2017.06.100.

These data include the Google map of the most important areas described in this article.

#### References

- Baldyga, T.J., Miller, S.N., Driese, K.L., Gichaba, C.M., 2008. Assessing land cover change in Kenya's Mau Forest region using remotely sensed data. Afr. J. Ecol. 46:46–54. http:// dx.doi.org/10.1111/j.1365-2028.2007.00806.x.
- Beven, K.J., Kirkby, M.J., 1979. A physically based, variable contributing area model of basin hydrology. Hydrol. Sci. Bull. 24, 43–69.
- Bewernick, T., 2016. Mapping Forest Degradation in the Mau Forest Complex using NDFI Time Series (MSc Thesis). Wageningen University, Wageningen, the Netherlands.
- Biggs, T.W., Dunne, T., Martinelli, L.A., 2004. Natural controls and human impacts on stream nutrient concentrations in a deforested region of the Brazilian Amazon basin. Biogeochemistry 68, 227–257.
- Billett, M.F., Cresser, M.S., 1996. Evaluation of the use of soil ion exchange properties for predicting streamwater chemistry in upland catchments. J. Hydrol. 186:375–394. http://dx.doi.org/10.1016/S0022-1694(96)03041-7.
- Billett, M.F., Deacon, C.M., Palmer, S.M., Dawson, J.J.C., Hope, D., 2006. Connecting organic carbon in stream water and soils in a peatland catchment. J. Geophys. Res. 111, G02010. http://dx.doi.org/10.1029/2005/G000065.
- Binge, F.W., 1962. Geology of the Kericho Area (No. 50). Ministry of Commerce, Industry and Communications, Geological Survey of Kenya.
- Bouillon, S., Abril, G., Borges, A.V., Dehairs, F., Govers, G., Hughes, H.J., Merckx, R., Meysman, F.J.R., Nyunja, J., Osburn, C., Middelburg, J.J., 2009. Distribution, origin and cycling of carbon in the Tana River (Kenya): a dry season basin-scale survey from headwaters to the delta. Biogeosciences 6:2475–2493. http://dx.doi.org/10. 5194/bg-6-2475-2009.
- Boy, J., Valarezo, C., Wilcke, W., 2008. Water flow paths in soil control element exports in an Andean tropical montane forest. Eur. J. Soil Sci. 59:1209–1227. http://dx.doi.org/ 10.1111/j.1365-2389.2008.01063.x.
- van Breemen, N., 2002. Nitrogen cycle: natural organic tendency. Nature 415:381–382. http://dx.doi.org/10.1038/415381a.
- Breuer, L., Hiery, N., Kraft, P., Bach, M., Aubert, A.H., Frede, H.-G., 2015. HydroCrowd: a citizen science snapshot to assess the spatial control of nitrogen solutes in surface waters. Sci Rep 5:16503. http://dx.doi.org/10.1038/srep16503.
- Bruijnzeel, L.A., 2001. Hydrology of tropical montane cloud forests: a reassessment. Land Use Water Resour. Res 1, 1.1–1.18.
- Bücker, A., Crespo, P., Frede, H.-G., Breuer, L., 2011. Solute behaviour and export rates in neotropical montane catchments under different land-uses. J. Trop. Ecol. 27: 305–317. http://dx.doi.org/10.1017/S0266467410000787.
- Burns, D.A., Plummer, L.N., McDonnell, J.J., Busenberg, E., Casile, G.C., Kendall, C., Hooper, R.P., Freer, J.E., Peters, N.E., Beven, K., Schlosser, P., 2003. The geochemical evolution of riparian ground water in a forested Piedmont catchment. Ground Water 41: 913–925. http://dx.doi.org/10.1111/j.1745-6584.2003.tb02434.x.
- Bustillo, V., Victoria, R.L., de Moura, J.M.S., de Victoria, D.C., Toledo, A.M.A., Collicchio, E., 2011. Factors driving the biogeochemical budget of the Amazon River and its statistical modelling. Compt. Rendus Geosci. 343:261–277. http://dx.doi.org/10.1016/j. crte.2011.01.003.
- Caine, N., Thurman, E.M., 1990. Temporal and spatial variations in the solute content of an alpine stream, Colorado Front Range. Geomorphology 4:55–72. http://dx.doi.org/10. 1016/0169-555X(90)90026-M.
- Calder, I.R., 2002. Forest and hydrological services reconciling public and science perceptions. Land Use Water Resour. Res. 2, 2.1–2.12.
- Chacha, J.S., 2015. Building local capacity and creating awareness in conserving the Mau Forest and water resources. In: Picard, L.A., Buss, T.F., Seybolt, T.B., Lelei, M.C. (Eds.), Sustainable Development and Human Security in Africa. Governance as the Missing Link. CRC Press, Taylor and Francis Group, Boca Raton FL, USA, pp. 121–131.
- Chapman, P.J., Edwards, A.C., Cresser, M.S., 2001. The nitrogen composition of streams in upland Scotland: some regional and seasonal differences. Sci. Total Environ. 265: 65–83. http://dx.doi.org/10.1016/S0048-9697(00)00650-1.
- Chaves, J., Neill, C., Germer, S., Neto, S.G., Krusche, A., Elsenbeer, H., 2008. Land management impacts on runoff sources in small Amazon watersheds. Hydrol. Process. 22: 1766–1775. http://dx.doi.org/10.1002/hyp.6803.
- Chuman, T., Hruška, J., Oulehle, F., Gürtlerová, P., Majer, V., 2013. Does stream water chemistry reflect watershed characteristics? Environ. Monit. Assess. 185: 5683–5701. http://dx.doi.org/10.1007/s10661-012-2976-3.
- Conrad, O., Bechtel, B., Bock, M., Dietrich, H., Fischer, E., Gerlitz, L., Wehberg, J., Wichmann, V., Boehner, J., 2015. System for automated geoscientific analyses (SAGA) v. 2.4.1. Geosci. Model Dev. 8, 1991–2007.
- Covaleda, S., Gallardo, J.F., García-Oliva, F., Kirchmann, H., Prat, C., Bravo, M., Etchevers, J.D., 2011. Land-use effects on the distribution of soil organic carbon within particle-size fractions of volcanic soils in the Transmexican Volcanic Belt (Mexico). Soil Use Manag. 27:186–194. http://dx.doi.org/10.1111/j.1475-2743.2011.00341.x.
- Creed, I.F., Band, L.E., 1998. Export of nitrogen from catchments within a temperate forest: evidence for a unifying mechanism regulated by variable source area dynamics. Water Resour. Res. 34:3105–3120. http://dx.doi.org/10.1029/98WR01924.
- Da Costa, E.N.D., De Souza, J.C., Pereira, M.A., De Souza, M.F.L., De Souza, W.F.L., Da Silva, D.M.L., 2017. Influence of hydrological pathways on dissolved organic carbon fluxes in tropical streams. Ecol. Evol. 7:228–239. http://dx.doi.org/10.1002/ece3.2543.
- Da Silva, D.M.L., Ometto, J.P.H.B., de Lobo, G.A., de Lima, W.P., Scaranello, M.A., Mazzi, E., da Rocha, H.R., 2007. Can land use changes alter carbon, nitrogen and major ion transport in subtropical Brazilian streams? Sci. Agric. 64:317–324. http://dx.doi.org/ 10.1590/S0103-90162007000400002.

Edwards, K.A., Blackie, J.R., 1979. The Kericho research project. East Afr. Agric. For. J. 43, 44–50.

- Ekirapa, E.A., Shitakha, F.M., 1996. Semi Detailed Soil Survey of the African Highland Produce Company Farm (No. S29 1996). Kenya Agricultural Research Institute, Nairobi, Kenya.
- Figueiredo, R.O., Markewitz, D., Davidson, E.A., Schuler, A.E., Dos, S., Watrin, O., de Souza Silva, P., 2010. Land-use effects on the chemical attributes of low-order streams in the eastern Amazon. J. Geophys. Res. 115, G04004. http://dx.doi.org/10.1029/ 2009JG001200.
- Glendell, M., Brazier, R.E., 2014. Accelerated export of sediment and carbon from a landscape under intensive agriculture. Sci. Total Environ. 476–477:643–656. http://dx.doi. org/10.1016/j.scitotenv.2014.01.057.
- Goller, R., Wilcke, W., Fleischbein, K., Valarezo, C., Zech, W., 2006. Dissolved nitrogen, phosphorus, and sulfur forms in the ecosystem fluxes of a montane forest in Ecuador. Biogeochemistry 77:57–89. http://dx.doi.org/10.1007/s10533-005-1061-1.
- Government of Kenya, 2009. Rehabilitation of the Mau Forest Ecosystem (A project concept prepared by the Interim Coordinating Secretariat, Office of the Prime Minister, on behalf of the Government of Kenya).
- Graeber, D., Gelbrecht, J., Kronvang, B., Gücker, B., Pusch, M.T., Zwirnmann, E., 2012a. Technical note: comparison between a direct and the standard, indirect method for dissolved organic nitrogen determination in freshwater environments with high dissolved inorganic nitrogen concentrations. Biogeosciences 9:4873–4884. http://dx.doi. org/10.5194/bg-9-4873-2012.
- Graeber, D., Gelbrecht, J., Pusch, M.T., Anlanger, C., von Schiller, D., 2012b. Agriculture has changed the amount and composition of dissolved organic matter in Central European headwater streams. Sci. Total Environ. 438:435–446. http://dx.doi.org/10.1016/j. scitotenv.2012.08.087.
- Grayson, R.B., Gippel, C.J., Finlayson, B.L., Hart, B.T., 1997. Catchment-wide impacts on water quality: the use of "snapshot" sampling during stable flow. J. Hydrol. 199, 121–134.
- Gücker, B., Silva, R.C.S., Graeber, D., Monteiro, J.A.F., Boëchat, I.G., 2016a. Urbanization and agriculture increase exports and differentially alter elemental stoichiometry of dissolved organic matter (DOM) from tropical catchments. Sci. Total Environ. 550: 785–792. http://dx.doi.org/10.1016/j.scitotenv.2016.01.158.
- Gücker, B., Silva, R.C.S., Graeber, D., Monteiro, J.A.F., Brookshire, E.N.J., Chaves, R.C., Boëchat, I.G., 2016b. Dissolved nutrient exports from natural and human-impacted Neotropical catchments. Glob. Ecol. Biogeogr. 25:378–390. http://dx.doi.org/10. 1111/geb.12417.
- Gundersen, P., Emmett, B.A., Kjønaas, O.J., Koopmans, C.J., Tietema, A., 1998. Impact of nitrogen deposition on nitrogen cycling in forests: a synthesis of NITREX data. For. Ecol. Manag. 101:37–55 (The Whole Ecosystem Experiments of the NITREX and EXMAN Projects). http://dx.doi.org/10.1016/S0378-1127(97)00124-2.
- Hagedorn, F., Schleppi, P., Waldner, P., Flühler, H., 2000. Export of dissolved organic carbon and nitrogen from Gleysol dominated catchments - the significance of water flow paths. Biogeochemistry 50, 137–161.
- Hood, E.W., Williams, M.W., Caine, N., 2003. Landscape controls on organic and inorganic nitrogen leaching across an alpine/subalpine ecotone, Green Lakes Valley, Colorado Front Range. Ecosystems 6:0031–0045. http://dx.doi.org/10.1007/s10021-002-0175-8.
- Hope, D., Billett, M.F., Cresser, M.S., 1994. A review of the export of carbon in river water: fluxes and processes. Environ. Pollut. 84:301–324. http://dx.doi.org/10.1016/0269-7491(94)90142-2.
- Jennings, D.J., 1971. Geology of the Molo area (No. 86). Ministry of Natural Resources, Geological Survey of Kenya.
- Kalbitz, K., Solinger, S., Park, J.-H., Michalzik, B., Matzner, E., 2000. Controls on the dynamics of dissolved organic matter in soils: a review. Soil Sci. 165, 277–304.
- Kaushal, S.S., Lewis, W.M., 2003. Patterns in the chemical fractionation of organic nitrogen in Rocky Mountain streams. Ecosystems 6:483–492. http://dx.doi.org/10.1007/ s10021-003-0175-3.
- Kilonzo, F., Masese, F.O., Van Griensven, A., Bauwens, W., Obando, J., Lens, P.N.L., 2014. Spatial-temporal variability in water quality and macro-invertebrate assemblages in the Upper Mara River basin, Kenya. Phys. Chem. Earth Part A, B, C 67–69: 93–104. http://dx.doi.org/10.1016/j.pce.2013.10.006.
- Kinyanjui, M.J., 2010. NDVI-based vegetation monitoring in Mau Forest Complex, Kenya. Afr. J. Ecol. 49, 165–174.
- Krhoda, G.O., 1988. The impact of resource utilization on the hydrology of the Mau Hills Forest in Kenya. Mt. Res. Dev. 8, 193–200.
- Lawrence, D., Vandecar, K., 2015. Effects of tropical deforestation on climate and agriculture. Nat. Clim. Chang. 5:27–36. http://dx.doi.org/10.1038/nclimate2430.
- Li, H., Ma, Y., Liu, W., 2016. Land use and topography as predictors of nitrogen levels in tropical catchments in Xishuangbanna, SW China. Environ. Earth Sci. 75:539. http:// dx.doi.org/10.1007/s12665-015-5241-6.
- Maghanga, J.K., Kituyi, J.L., Kisinyo, P.O., Ng'etich, W.K., 2012. Impact of nitrogen fertilizer applications on surface water nitrate levels within a Kenyan tea plantation. J. Chem. 2013, e196516. http://dx.doi.org/10.1155/2013/196516.
- Maloney, K.O., Weller, D.E., 2011. Anthropogenic disturbance and streams: land use and land-use change affect stream ecosystems via multiple pathways. Freshw. Biol. 56: 611–626. http://dx.doi.org/10.1111/j.1365-2427.2010.02522.x.
- Martínez, M.L., Pérez-Maqueo, O., Vázquez, G., Castillo-Campos, G., García-Franco, J., Mehltreter, K., Equihua, M., Landgrave, R., 2009. Effects of land use change on biodiversity and ecosystem services in tropical montane cloud forests of Mexico. For. Ecol. Manag. 258:1856–1863. http://dx.doi.org/10.1016/j.foreco.2009.02.023.
- Masese, F.O., Kitaka, N., Kipkemboi, J., Gettel, G.M., Irvine, K., McClain, M.E., 2014. Litter processing and shredder distribution as indicators of riparian and catchment influences on ecological health of tropical streams. Ecol. Indic. 46:23–37. http://dx.doi. org/10.1016/j.ecolind.2014.05.032.

- Masese, F.O., Salcedo-Borda, J.S., Gettel, G.M., Irvine, K., McClain, M.E., 2017. Influence of catchment land use and seasonality on dissolved organic matter composition and ecosystem metabolism in headwater streams of a Kenyan river. Biogeochemistry 132:1–22. http://dx.doi.org/10.1007/s10533-016-0269-6.
- McDowell, W.H., Asbury, C.E., 1994. Export of carbon, nitrogen, and major ions from three tropical montane watersheds. Limnol. Oceanogr. 39:111–125. http://dx.doi.org/10. 4319/lo.1994.39.1.0111.
- Mitchell, M.J., 2001. Linkages of nitrate losses in watersheds to hydrological processes. Hydrol. Process. 15:3305–3307. http://dx.doi.org/10.1002/hyp.503.
- Mokaya, S.K., Mathooko, J.M., Leichtfried, M., 2004. Influence of anthropogenic activities on water quality of a tropical stream ecosystem. Afr. J. Ecol. 42:281–288. http://dx. doi.org/10.1111/j.1365-2028.2004.00521.x.
- Monteith, D.T., Henrys, P.A., Evans, C.D., Malcolm, I., Shilland, E.M., Pereira, M.G., 2015. Spatial controls on dissolved organic carbon in upland waters inferred from a simple statistical model. Biogeochemistry 123, 363–377.
- Moore, R.D., 2004. Introduction to salt dilution gauging for streamflow measurement: part 1. Streamline Watershed Management Bulletin. Vol. 7, pp. 20–23.
- Neff, K.J., Schwartz, J.S., Moore, S.E., Kulp, M.A., 2013. Influence of basin characteristics on baseflow and stormflow chemistry in the Great Smoky Mountains National Park, USA. Hydrol. Process. 27:2061–2074. http://dx.doi.org/10.1002/hyp.9366.
- Neill, C., Deegan, L.A., Thomas, S.M., Cerri, C.C., 2001. Deforestation for pasture alters nitrogen and phosphorus in small Amazonian streams. Ecol. Appl. 11:1817–1828. http:// dx.doi.org/10.2307/3061098.
- Neill, C., Deegan, L.A., Thomas, S.M., Haupert, C.L., Krusche, A.V., Ballester, V.M., Victoria, R.L., 2006. Deforestation alters the hydraulic and biogeochemical characteristics of small lowland Amazonian streams. Hydrol. Process. 20:2563–2580. http://dx.doi. org/10.1002/hyp.6216.
- Neill, C., Chaves, J.E., Biggs, T., Deegan, L.A., Elsenbeer, H., Figueiredo, R.O., Germer, S., Johnson, M.S., Lehmann, J., Markewitz, D., Piccolo, M.C., 2011. Runoff sources and land cover change in the Amazon: an end-member mixing analysis from small watersheds. Biogeochemistry 105:7–18. http://dx.doi.org/10.1007/s10533-011-9597-8.
- Nimick, D.A., Gammons, C.H., Parker, S.R., 2011. Diel biogeochemical processes and their effect on the aqueous chemistry of streams: a review. Chem. Geol. 283, 3–17.
- Nosrati, K., Govers, G., Smolders, E., 2012. Dissolved organic carbon concentrations and fluxes correlate with land use and catchment characteristics in a semi-arid drainage basin of Iran. Catena 95:177–183. http://dx.doi.org/10.1016/j.catena.2012.02.019.
- Nottingham, A.T., Turner, B.L., Whitaker, J., Ostle, N.J., McNamara, N.P., Bardgett, R.D., Salinas, N., Meir, P., 2015. Soil microbial constraints along a tropical forest elevation gradient: a belowground test of a biogeochemical paradigm. Biogeosciences 12, 6071–6083.
- Nyairo, W.N., Owuor, P.O., Kengara, F.O., 2015. Effect of anthropogenic activities on the water quality of Amala and Nyangores tributaries of River Mara in Kenya. Environ. Monit. Assess. 187:691. http://dx.doi.org/10.1007/s10661-015-4913-8.
- O'Brien, R.M., 2007. A caution regarding rules of thumb for Variance Inflation Factors. Qual. Quant. 41:673–690. http://dx.doi.org/10.1007/s11135-006-9018-6.
- Olang, L.O., Kundu, P.M., 2011. Land degradation of the Mau Forest Complex in Eastern Africa: a review for management and restoration planning. In: Ekundayo, E.O. (Ed.), Environmental Monitoring. InTech, Rijeka, Croatia, pp. 245–262.
- Ometo, J.P.H.B., Martinelli, L.A., Ballester, M.V., Gessner, A., Krusche, A.V., Victoria, R.L., Williams, M., 2000. Effects of land use on water chemistry and macroinvertebrates in two streams of the Piracicaba river basin, south-east Brazil. Freshw. Biol. 44: 327–337. http://dx.doi.org/10.1046/j.1365-2427.2000.00557.x.
- Oni, S.K., Futter, M.N., Molot, L.A., Dillon, P.J., 2014. Adjacent catchments with similar patterns of land use and climate have markedly different dissolved organic carbon concentration and runoff dynamics. Hydrol. Process. 28:1436–1449. http://dx.doi.org/10. 1002/hyp.9681.
- Owuor, S.O., Butterbach-Bahl, K., Guzha, A.C., Rufino, M.C., Pelster, D.E., Díaz-Pinés, E., Breuer, L., 2016. Groundwater recharge rates and surface runoff response to land use and land cover changes in semi-arid environments. Ecol. Process. 5:16. http:// dx.doi.org/10.1186/s13717-016-0060-6.
- Owuor, S.O., Butterbach-Bahl, K., Guzha, A.C., Jacobs, S., Merbold, L., Rufino, M.C., Pelster, D., Díaz-Pinés, E., Breuer, L., 2017. Conversion of natural forest results in a significant degradation of soil hydraulic properties in the highlands of Kenya. Soil Tillage Res. (in review).
- Perakis, S.S., Hedin, L.O., 2002. Nitrogen loss from unpolluted South American forests mainly via dissolved organic compounds. Nature 415:416–419. http://dx.doi.org/10. 1038/415416a.
- R Core Team, 2015. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria.
- Raymond, P.A., Oh, N.-H., 2007. An empirical study of climatic controls on riverine C export from three major U.S. watersheds. Glob. Biogeochem. Cycles 21 (GB2022). http://dx.doi.org/10.1029/2006GB002783.
- Recha, J.W., Lehmann, J., Walter, M.T., Pell, A., Verchot, L., Johnson, M., 2013. Stream water nutrient and organic carbon exports from tropical headwater catchments at a soil degradation gradient. Nutr. Cycl. Agroecosyst. 95:145–158. http://dx.doi.org/10. 1007/s10705-013-9554-0.
- Roa-García, M.C., Weiler, M., 2010. Integrated response and transit time distributions of watersheds by combining hydrograph separation and long-term transit time modeling. Hydrol. Earth Syst. Sci. 14:1537–1549. http://dx.doi.org/10.5194/hess-14-1537-2010.
- Rodhe, A., Seibert, J., 1999. Wetland occurrence in relation to topography: a test of topographic indices as moisture indicators. Agric, For. Meteorol. 98–99:325–340. http:// dx.doi.org/10.1016/S0168-1923(99)00104-5.
- Rothwell, J.J., Dise, N.B., Taylor, K.G., Allott, T.E.H., Scholefield, P., Davies, H., Neal, C., 2010. A spatial and seasonal assessment of river water chemistry across North West England. Sci. Total Environ. 408:841–855. http://dx.doi.org/10.1016/j.scitotenv.2009. 10.041.

- Rusjan, S., Mikoš, M., 2010. Seasonal variability of diurnal in-stream nitrate concentration oscillations under hydrologically stable conditions. Biogeochemistry 97:123–140. http://dx.doi.org/10.1007/s10533-009-9361-5.
- Saunders, T.J., McClain, M.E., Llerena, C.A., 2006. The biogeochemistry of dissolved nitrogen, phosphorus, and organic carbon along terrestrial-aquatic flowpaths of a montane headwater catchment in the Peruvian Amazon. Hydrol. Process. 20: 2549–2562. http://dx.doi.org/10.1002/hyp.6215.
- Scheren, P.A.G.M., Zanting, H.A., Lemmens, A.M.C., 2000. Estimation of water pollution sources in Lake Victoria, East Africa: application and elaboration of the rapid assessment methodology. J. Environ. Manag. 58:235–248. http://dx.doi.org/10.1006/jema. 2000.0322.
- Singh, S., Mishra, A., 2014. Spatiotemporal analysis of the effects of forest covers on stream water quality in Western Ghats of peninsular India. J. Hydrol. 519 (Part A): 214–224. http://dx.doi.org/10.1016/j.jhydrol.2014.07.009.
- Singh, S., Inamdar, S., Mitchell, M., 2015. Changes in dissolved organic matter (DOM) amount and composition along nested headwater stream locations during baseflow and stormflow. Hydrol. Process. 29:1505–1520. http://dx.doi.org/10.1002/hyp.10286.
- Spracklen, D.V., Righelato, R., 2014. Tropical montane forests are a larger than expected global carbon store. Biogeosciences 11:2741–2754. http://dx.doi.org/10.5194/bg-11-2741-2014.
- Stephens, W., Othieno, C.O., Carr, M.K.V., 1992. Climate and weather variability at the Tea Research Foundation of Kenya. Agric. For. Meteorol. 61:219–235. http://dx.doi.org/ 10.1016/0168-1923(92)90051-5.
- Swart, R., 2016. Monitoring 40 Years of Land Use Change in the Mau Forest Complex, Kenya. A Land Use Change Driver Analysis. (BSc Thesis). Wageningen University, Wageningen, the Netherlands.
- Tamooh, F., Van den Meersche, K., Meysman, F., Marwick, T.R., Borges, A.V., Merckx, R., Dehairs, F., Schmidt, S., Nyunja, J., Bouillon, S., 2012. Distribution and origin of suspended matter and organic carbon pools in the Tana River Basin, Kenya. Biogeosciences 9:2905–2920. http://dx.doi.org/10.5194/bg-9-2905-2012.
- UNEP, Kenya Wildlife Service, Kenya Forest Working Group, Ewaso Ngiro South Development Authority, 2008. Mau Complex Under Siege. Values and Threats.
- USGS, 2000. Shuttle Radar Topography Mission (SRTM) 1 Arc-Second Global. Varanka, S., Hjort, J., Luoto, M., 2015. Geomorphological factors predict water quality in boreal rivers. Earth Surf. Process. Landf. 40:1989–1999. http://dx.doi.org/10.1002/esp.3601.
- Warwick, J.J., 1986. Diel variation of in-stream nitrification. Water Res. 20, 1325–1332. Were, K.O., Dick, Ø.B., Singh, B.R., 2013. Remotely sensing the spatial and temporal land
- cover changes in Eastern Mau forest reserve and Lake Nakuru drainage basin, Kenya. Appl. Geogr. 41, 75–86.

- Were, K., Singh, B.R., Dick, O.B., 2016. Spatially distributed modelling and mapping of soil organic carbon and total nitrogen stocks in the Eastern Mau Forest Reserve, Kenya. J. Geogr. Sci. 26, 102–124.
- Wilcke, W., Yasin, S., Valarezo, C., Zech, W., 2001. Change in water quality during the passage through a tropical montane rain forest in Ecuador. Biogeochemistry 55, 45–72.
- Wilcke, W., Leimer, S., Peters, T., Emck, P., Rollenbeck, R., Trachte, K., Valarezo, C., Bendix, J., 2013. The nitrogen cycle of tropical montane forest in Ecuador turns inorganic under environmental change. Glob. Biogeochem. Cycles 27 (2012GB004471). http://dx.doi.org/10.1002/2012GB004471.
- Willett, V.B., Reynolds, B.A., Stevens, P.A., Ormerod, S.J., Jones, D.L., 2004. Dissolved organic nitrogen regulation in freshwaters. J. Environ. Qual. 33, 201–209.
- Williams, M.R., Melack, J.M., 1997. Solute export from forested and partially deforested catchments in the Central Amazon. Biogeochemistry 38, 67–102.
- Williams, M.R., Fisher, T.R., Melack, J.M., 1997. Solute dynamics in soil water and groundwater in a Central Amazon catchment undergoing deforestation. Biogeochemistry 38, 303–335.
- Wilson, H.F., Xenopoulos, M.A., 2008. Ecosystem and seasonal control of stream dissolved organic carbon along a gradient of land use. Ecosystems 11:555–568. http://dx.doi. org/10.1007/s10021-008-9142-3.
- Wohlfart, T., Exbrayat, J.-F., Schelde, K., Christen, B., Dalgaard, T., Frede, H.-G., Breuer, L., 2012. Spatial distribution of soils determines export of nitrogen and dissolved organic carbon from an intensively managed agricultural landscape. Biogeosciences 9: 4513–4525. http://dx.doi.org/10.5194/bg-9-4513-2012.
- Woolley, A.R., 2001. Alkaline Rocks and Carbonatites of the World Part 3: Africa. The Geological Society, Bath, UK.
- Yamashita, N., Sase, H., Kobayashi, R., Leong, K.-P., Hanapi, J.M., Uchiyama, S., Urban, S., Toh, Y.Y., Muhamad, M., Gidiman, J., Chappell, N.A., 2014. Atmospheric deposition versus rock weathering in the control of streamwater chemistry in a tropical rain-forest catchment in Malaysian Borneo. J. Trop. Ecol. 30:481–492. http://dx.doi.org/10. 1017/S0266467414000303.
- Zhang, J., Tian, P., Tang, J., Yuan, L., Ke, Y., Cai, Z., Zhu, B., Müller, C., 2016. The characteristics of soil N transformations regulate the composition of hydrologic N export from terrestrial ecosystem. J. Geophys. Res. Biogeosci. 121 (2016JG003398). http://dx.doi. org/10.1002/2016JG003398.
- Zhou, M., Brandt, P., Pelster, D., Rufino, M.C., Robinson, T., Butterbach-Bahl, K., 2014. Regional nitrogen budget of the Lake Victoria Basin, East Africa: syntheses, uncertainties and perspectives. Environ. Res. Lett. 9:105009. http://dx.doi.org/10.1088/1748-9326/ 9/10/105009.