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Key Points:
- Land use, not stream size, was the strongest predictor of nitrous oxide (N_2O) flux and concentration from the Mara River headwaters
- Agricultural land use showed the highest N_2O flux, while livestock watering holes in the showed the lowest, similar to forest sites
- Nitrification appears to be an important source of N_2O in agricultural and forest sites, while denitrification dominates in livestock sites

Supporting Information:
- Supporting Information S1
- Table S1
- Table S2
- Table S3

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Land Use, Not Stream Order, Controls N_2O Concentration and Flux in the Upper Mara River Basin, Kenya

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Abstract Anthropogenic activities have led to increases in nitrous oxide (N_2O) emissions from river systems, but there are large uncertainties in estimates due to lack of data in tropical rivers and rapid increase in human activity. We assessed the effects of land use and river size on N_2O flux and concentration in 46 stream sites in the Mara River, Kenya, during the transition from the wet (short rains) to dry season, November 2017 to January 2018. Flux estimates were similar to other studies in tropical and temperate systems, but in contrast to other studies, land use was more related to N_2O concentration and flux than stream size. Agricultural stream sites had the highest fluxes (26.38 ± 5.37 N_2O-N $\mu g \cdot m^{-2} \cdot hr^{-1}$) compared to both forest and livestock sites (5.66 ± 1.38 N_2O-N $\mu g \cdot m^{-2} \cdot hr^{-1}$ and 6.95 ± 2.96 N_2O-N $\mu g \cdot m^{-2} \cdot hr^{-1}$, respectively). N_2O concentrations in forest and agriculture streams were positively correlated to stream carbon dioxide (CO_2-$C_{(aq)}$) but showed a negative correlation with dissolved organic carbon, and the dissolved organic carbon:dissolved inorganic nitrogen ratio. N_2O concentration in the livestock sites had a negative relationship with CO_2-$C_{(aq)}$ and a higher number of negative fluxes. We concluded that in-stream chemoautotrophic nitrification was likely the main biogeochemical process driving N_2O production in agricultural and forest streams, whereas complete denitrification led to the consumption of N_2O in the livestock stream sites. These results point to the need to better understand the relative importance of nitrification and denitrification in different habitats in producing N_2O and for process-based studies.

Plain Language Summary Humans affect the emission of nitrous oxide (N_2O), a potent greenhouse gas, from river systems through land use change and increased nitrogen use in catchments. We know little about this in sub-Saharan Africa, where human activity is increasing rapidly. Previous studies have found that N_2O may be related to the size of the river, with smaller rivers having higher emissions than large ones, due to their close connection to the catchment. This study addressed whether land use (i.e., native forest, crop production, and livestock watering holes) affect N_2O emission from the headwaters of the Mara River, Kenya. We found that N_2O emissions were not related to the stream size but were more strongly affected by land use, with the highest emissions occurring in the agricultural areas. We also examined which processes in the river were responsible for the emissions by relating water quality parameters to N_2O concentration. We found that different processes were most likely responsible in different land uses, with nitrification dominating in forested and agricultural areas, and denitrification dominating in livestock watering sites. These results illustrate the unique features of tropical rivers in montane ecosystems undergoing land use change. Further research should investigate processes and seasonal dynamics.

1. Introduction

Increasing atmospheric N_2O concentration is of global concern, as N_2O has 265 times greater impact on climate warming than CO_2 on a molecular basis (Intergovernmental Panel on Climate Change [IPCC], 2016) and has been increasing in the atmosphere at a rate of ~0.73 ppb/year over the last three decades (IPCC, 2014). Estimated global riverine N_2O flux contributions are, however, highly uncertain with estimates ranging from 32.2 to 2,100 Gg N/year (Beaulieu et al., 2011; Hu et al., 2016; Kroeze & Seitzinger, 1998;

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Maavara et al., 2018). While older IPCC and modeled estimates suggested that rivers and estuaries contribute up to 20–35% of global anthropogenic N_2O emissions (Kroeze & Seitzinger, 1998; Mosier et al., 1998), some studies later suggested that streams and rivers contribute considerably more to global N_2O flux than was previously accounted for in the IPCC estimates (Beaulieu et al., 2011; Turner et al., 2015; Venkiteswaran et al., 2014). Most recently, however, models showed much lower estimates by an order of magnitude (Hu et al., 2016; Maavara et al., 2018). All these studies have little data from tropical regions and highlight the need for empirical studies to help constrain riverine N_2O fluxes.

Within river systems, headwater streams are disproportionately responsible for greenhouse gas emissions, due in part to high connectivity to landscapes and the relatively high surface area to volume ratio, which increases the influence of benthic processes (Hotchkiss et al., 2015; Marzadri et al., 2017; Raymond et al., 2013). Recent efforts, mainly from North America and Europe, have been made to quantify N_2O fluxes from rivers and headwater streams (e.g., Baulch et al., 2011; Beaulieu et al., 2008; Hama-Aziz et al., 2017; Schade et al., 2016; Turner et al., 2015, Venkiteswaran et al., 2014). However, patterns and processes controlling N_2O production rates are still not well understood, and the large range of reported estimates (e.g., from above studies, −11 to 905 N_2O-N·μg·m^{-2}·hr^{-1}) result in remaining uncertainties, particularly with respect to biogeochemical controls and effects of land use.

In lotic ecosystems, nitrification and denitrification are the main biogeochemical processes producing N_2O (Beaulieu et al., 2011; Harrison & Matson, 2003). Nitrification is a chemoautotrophic process in which dissolved carbon dioxide ($CO_{2\ (aq)}$) is fixed by ammonium oxidizing bacteria, which ultimately convert NH_4 to NO_3, releasing N_2O in the process (Harrison & Matson, 2003). However, heterotrophic nitrification of organic N producing N_2O has been reported in soils with high C:N ratios (Zhang et al., 2015), although no published study has reported it in lotic ecosystems. Nitrification rates can be controlled by NH_4 availability (Ward, 2013) and indirectly through competition for NH_4 with heterotrophic bacteria when organic C availability is high (Strauss et al., 2002; Strauss & Lamberti, 2000). Previous work has demonstrated that the "environmental C:N" ratio, or dissolved organic carbon:dissolved inorganic nitrogen (DOC:DIN), results in lower nitrification rates because nitrifiers cannot compete with heterotrophs for NH_4 (Strauss & Lamberti, 2000). For denitrification, N_2O is produced as an intermediary by heterotrophic bacteria that reduce NO_3 to N_2 in anaerobic conditions. Thus, organic C availability (DOC), NO_3, and oxygen (O_2) are possible controlling factors (e.g., Inwood et al., 2007; Knowles, 1982). The IPCC estimates in stream nitrification rates to be twice that of denitrification (Mosier et al., 1998), but the relative importance of these processes in the production of N_2O in stream ecosystems is still not well understood (Beaulieu et al., 2011).

Stream order is also a possible control of N_2O flux rates in riverine ecosystems (Marzadri et al., 2017; Turner et al., 2015), with most studies predicting that N_2O emissions decrease with increasing stream order as a result of decreasing impact of the hyporheic zone on water column processes. Turner et al. (2015) found that the magnitude of N_2O fluxes declined with an increase in stream order in U.S. Corn Belt streams, and Marzadri et al. (2014, 2017) also found that N_2O fluxes reduced along the river continuum and proposed a model to incorporate this into observation for scaling N_2O fluxes across a river basin; however, this study considers denitrification to be the main source of N_2O production and only indirectly considers nitrification. In contrast, Teodoru et al. (2015) and Borges et al. (2015) found contradictory results across more than 12 sub-Saharan African river basins, in which N_2O flux showed the opposite pattern, with higher fluxes in larger rivers (Borges et al., 2019, 2015) or idiosyncratic patterns associated with hotspots for either sources or sinks, including wetlands, floodplains, and reservoirs (Teodoru et al., 2015). Thus, other factors may be important in controlling the spatial variation of the emissions along the river continuum, and the correlation between river size and N_2O emissions might not always be true.

Catchment land use also influences N_2O flux from headwater streams (Audet et al., 2017; Beaulieu et al., 2009; Borges et al., 2018; Schade et al., 2016). In agricultural land use types, it is estimated that the global release of N_2O gas is increasing by 0.2–0.3% yearly (Nevison, 1998), and this can possibly translate to N_2O fluxes from rivers as they also receive excess N inputs from fertilizers (Carpenter et al., 1998). In a study conducted by Beaulieu et al. (2009) on 12 headwater streams in Kalamazoo basin in Michigan, USA, N_2O concentrations were highest in agricultural streams. Schade et al. (2016) also found higher N_2O fluxes in a stream that drained an organic dairy farm in New Hampshire, USA, while Borges et al. (2018) found similar results for streams draining agricultural and pasture lands in the Meuse River. These studies further highlighting the influence of land use on N_2O fluxes and the potential for hotspots related to either agricultural or animal influence, presumably because of N and organic matter inputs.

In African tropical riverine systems, very few studies have been conducted to either quantify emissions or explain the major factors controlling them (Borges et al., 2015; Marwick et al., 2014; Teodoru et al., 2015; Upstill-Goddard et al., 2017). It is estimated that the African tropical river network, including the Congo River Basin, contributes approximately 12% to the global surface river network (Raymond et al., 2013), making it a potentially important contributor to global N_2O flux. However, uncertainties remain in the magnitude of N_2O flux from river systems in the region, despite their potential as a substantial contributor to the global N_2O flux (Borges et al., 2015; Upstill-Goddard et al., 2017). With agricultural intensification in Africa increasing to meet the rising food demand from its growing population (Tilman et al., 2011), the risk of increased N_2O emissions from streams in agricultural intensified lands in the region is increasing.

Our study seeks to quantify N_2O flux and concentration from headwater streams of an African tropical riverine system while determining the influence of stream order, land use, and in situ water quality variables on controlling N_2O concentration and flux. We hypothesized that these relationships could be used to assess whether denitrification or nitrification was responsible for N_2O production in each land use and that the environmental C:N ratio (DOC:DIN) controlled N_2O production in them. We focused on the upper Mara basin, Kenya, which is a typical catchment in many sub-Saharan African countries that contains fragments of native vegetation, especially in the headwaters, but is increasingly experiencing land use change due to pressure from both urban development and small holder and commercial agriculture (Mati et al., 2008).

2. Materials and Methods

2.1. Study Area

The study was conducted in the Nyangores and Amala tributaries of the Mara River (Figure 1), originating in western part of the Mau escarpment (elevation 1,745–2,147 m above sea level). The Mara River is an important transboundary river crossing from Kenya into Tanzania through two National Parks (Masai Mara and Serengeti) and forming the Mara wetland at its mouth in Lake Victoria. The headwater streams generally originate in the protected Mau Forest Complex, which is characterized by high rainfall (1,000–1,750 mm/year) and dense vegetation comprising tropical broad-leafed trees (supporting information Figure S1). About 32% of forest cover was cleared between 1973 and 2000 (Mati et al., 2008), and as the streams move downstream, they encounter cleared land that is developed for commercial tea production at the forest edge, and further downstream, a mix of small holder tea and subsistence agriculture, which includes food crops such as maize, beans and potatoes, and low-density livestock rearing, usually in zero-grazing practice (Figure S1). Farming in the region is not mechanized, but residents use nitrogen-based fertilizers (calcium ammonium nitrate) according to communication with local farmers. Further downstream, particularly in the Amala basin, crop-cover reduces and becomes rangeland dominated by grasses and shrubs. Residents practice animal husbandry more intensively for their livelihoods, and livestock density is much higher (~15 heads of cattle per household) than in the upper part of the catchment (~3 heads of cattle per household). Livestock watering holes in streams are characterized by deep pools, eroded banks, and slower flow (Figure S1). In addition to the spatial variability in rainfall patterns, there is temporal variation, with two rainy seasons occurring March–June (long rains) and September–December (short rains). Temperatures are mostly in the range of 18 °C in the highlands and 25 °C in the lowlands depending on the month of the year (Masese et al., 2017).

2.2. Sampling Strategy

A total of 46 stream sites was selected based on their dominating reach scale land use type and stream size category. The sites were then sampled at weekly to biweekly intervals from 1 November 2017 to 15 January 2018 using a synoptic survey approach in which nutrients (ammonium and nitrate), DOC, N_2O concentration, and hydrologic and geomorphological characteristics were measured (Table S1). Streams were classified into stream order according to the Strahler system and also into three land use categories (forest [$n = 14$], agriculture [$n = 19$], and livestock [$n = 7$]). Here, we considered "agriculture" to be cropland systems, and "livestock" to be where watering was taking place in the stream systems, which was more frequent in the drier, rangeland study area. Agriculture and forestland use classification was based on an analysis of the land use in the subcatchment drainage area, which was delineated using digital elevation model with a

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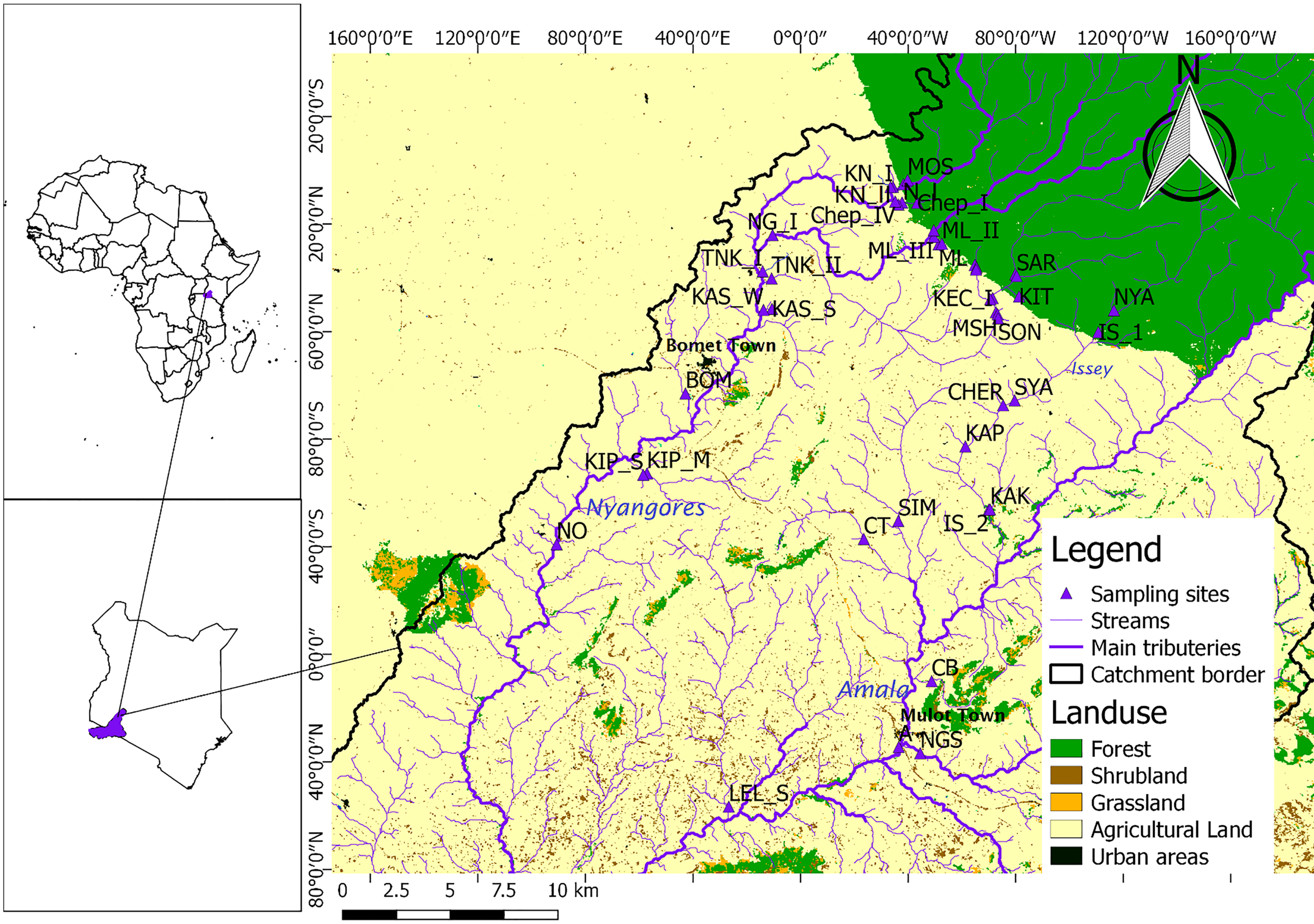

Figure 1. Map showing location and dominant land use of the Mara River basin and sampling points in the upper basin tributaries, Kenya.

90 by 90 resolution obtained from the Shuttle Topography Radar Mission satellite. Sites with >70% of a land cover type were classified accordingly (e.g., >70% forest land use were considered as forested sites), while sites with <60% either forested or agricultural land use were considered mixed sites. Though there is a land use gradient within the catchment according to elevation, we tried to find sites that represented an orthogonal relationship between land use and stream order (i.e., first-order streams were represented in all land use types).

2.3. Stream Geomorphological Variables

Slope and discharge were measured at all wadeable streams, and width and velocity were measured at higher-order rivers that we were not able to cross. The slope of the reach at each sampling location was measured once using a clinometer, while discharge was measured for every sampling time following the velocity-area method as described by Gore (2007). In the method, streams larger than 0.84 m were divided into 12 equal parts, where depth and velocity measurements were taken across each stream, and for smaller streams, measurements were taken every 7 cm. Velocity was determined using a Seba Mini current Meter Model M1. During the first synoptic survey, we were not able to determine Q in the fifth- and sixth-order streams, because they were not wadeable. On these dates, stream width was determined using a range finder, and velocity was estimated following the floating method (Gore, 2007) using floating leaves. Canopy cover was estimated within transects of 100 m along the study sites reach using visual characterization.

2.4. Water Chemistry and Gasses

Specific conductivity, water temperature, pH and dissolved oxygen (DO), and % O_2 saturation were determined in situ using a WTW LF 330i conductivity meter, WTW 340 pH meter, and WTW Oxi 3310 oxygen meter, respectively. Water samples were collected in duplicate and filtered on site using GF/F filters (Whatman International Ltd.), which had been ashed at 500 °C for 4 hr. Nutrient samples were collected in acid-washed 20-ml polypropylene bottles, and DOC and total dissolved nitrogen (TDN) samples were collected in preleached 30-ml high density polyethylene bottles, acidified to pH < 2, and stored at 4 °C for later analysis at the IHE-Delft laboratory in the Netherlands (DOC blanks from the high density polyethylene bottles are below detection limit). Dissolved inorganic nitrogen samples were stored at 4 °C and analyzed for ammonium (NH_4-N) within 1–2 days of collection using AKVOs field kit (tintometers MD 610 spectrophotometer at 610 nm) and for nitrate (NO_3-N) using wet chemistry (Brucine method (Bain et al., 2009) at 410 nm) on a spectrophotometer at the Eldoret University chemistry laboratory. DOC and TDN samples were analyzed using Shimadzu TOC-V CPN with a total nitrogen analyzer unit (TNM-1).

Gas samples were collected in duplicate using the headspace equilibration technique (Raymond et al., 1997) where 80 ml of water was equilibrated with a 20-ml atmospheric headspace in a 100-ml syringe, and 15 ml of the equilibrated headspace was transferred to pre-evacuated 12-ml exetainers (Labco vials) and stored for analysis at the Yale Analytical and Stable Isotope Center on a Shimadzu GC2014 with an FID for CO_2 measurements and an ECD calibrated for N_2O measurements. Standard gas concentrations were 0.25, 0.509, 0.951, 2.5, and 4.983 ppm for N_2O measurements. Equilibration was achieved by shaking the syringe for 2 min in the stream, which maintained constant temperature at ambient conditions. Samples for atmospheric N_2O concentration throughout the sampling day were also taken to correct for the atmospheric headspace. Barometric pressure and air temperature were also measured at each site.

N_2O fluxes were calculated using the gas transfer velocity (k) calculated from the k_{600} estimated based on equation (4) from Raymond et al. (2012) study (equation (1)). Equation (4) was used because it is most appropriate for small streams and based on turbulent dissipation theory (Raymond et al., 2012). The equation uses the Schmidt number of N_2O, where k_{600} is the gas transfer velocity in meters per day, V is the velocity in meters per second, and S is the dimensionless slope. Flux was calculated according to equation (2) modified from Baulch et al. (2011), where F is flux in N_2O-N $\mu g \cdot m^{-2} \cdot hr^{-1}$, k is gas transfer velocity in meters per hour, N_2Oobs is the observed concentration of N_2O in micrograms per cubic meter, and N_2Oatm is the theoretical concentration of N_2O in micrograms per cubic meter if the water were in equilibrium with the atmosphere:

$$k_{600} = VS^{0.76} \times 951.5 \tag{1}$$

$$F = k(N_2O_{OBS} - N_2O_{ATM}) \tag{2}$$

2.5. Statistical Analysis

Physicochemical water variables, N_2O concentration, and flux between the different land uses and stream orders were compared using mixed linear regression models, which included random effects of sites. To correct for dependence of repeated time measurements for the synoptic campaigns, autocorrelation among sampling times was calculated and corrected for in the models. Different mixed model structures were compared, and the best model was selected for the overall analysis based on the one which gave the lowest AIC value (Zuur et al., 2007).

Relationships between N_2O concentration and water chemistry variables that had the potential to affect N_2O production through biogeochemical processes (nitrification and denitrification) were analyzed using a multiple linear regression model within each land use type in order to determine which process may be responsible for N_2O production. Analyses were done on N_2O concentration because stream velocity and slope also strongly affect flux (see above). Water chemistry variables included in the multiple linear regression model were CO_2-$C_{(aq)}$, DOC, NO_3-N, NH_4-N, and DO, and these were interpreted as direct drivers controlling nitrification and denitrification rates that produce N_2O in aquatic ecosystems based on previous studies (Beaulieu et al., 2011; Harrison & Matson, 2003; Strauss & Lamberti, 2000). Colinearity for the independent variables was checked, and models were carefully assessed if the independent variables showed relationships greater than 50% (i.e., models tested including variables alone and in combination). Correlation of

Table 1
N_2O Concentration and Flux Mean and Ranges for the Different Land Uses

		N_2O concentration (N_2O-N μg L^{-1})		N_2O flux (N_2O-N μg m^{-2} h^{-1})	
Land use	(*n*)	Range	M ± SE	Range	M ± SE
Forest	14	0.18–0.79	0.34 ± 0.02	(−)7.97–56.59	5.66 ± 1.38
Mixed	7	0.18–0.55	0.34 ± 0.02	(−)4.61−32.62	10.55 ± 2.53
Agricultural	18	0.18–2.59	0.69 ± 0.06	0–323.71	27.04 ± 5.56
Livestock	7	0.03–0.88	0.35 ± 0.04	(−)11.96–67.12	6.94 ± 2.95

Note. The minimum flux in agricultural streams was zero for nonflowing streams with the lowest flux of 0.80 N_2O-N μg·m^{-2}·hr^{-1} measured for the flowing streams. Sign (−) in the table represent negative fluxes.

the independent variables is shown in the supporting information Table S2. Velocity and slope were also used in a separate multiple regression model to see whether these variables had any significant effect on concentration. Partial regression plots (component + residual plots) were used to show the individual effects of each independent variable on N_2O concentration, according to the procedure shown by Moya-Laraño & Corcobado, 2008. Diagnostic tests were performed to test the assumptions (homogeneity and normal distribution) made for each analytical test used. Data were log transformed whenever necessary to get better model fits. R statistical software Version 3.3.3 was used for all analysis.

3. Results

3.1. Stream Characteristics

Stream width ranged from 0.07 to 23.88 m, with an overall mean of 2.42 m across all the sampled stream sites. Depth ranged from 0.01 to 0.49 m with a mean of 0.09. The mean discharge value was 0.77 m^3/s, with a peak measurement of 16.28 m^3/s in the upper Nyangores main stream at the start of the sampling period (after short rains in October). First-order streams were small with a mean width of 0.46 m and an average discharge of 0.05 m^3/s. Slope ranged between 0.44% to 6.55% (supporting information Table S1).

Canopy cover in the riparian zone was >70% for all forested sites, while livestock sites had little or no canopy cover, and mixed and agricultural sites had moderate canopy cover (supporting information S1). Agricultural sites were mostly within tea plantations, but subsistence farming of maize, potatoes, and other crops was also practiced in smaller patches, and riparian zones comprising planted eucalyptus or native trees were common. Turbid water and eroded banks with reduced riparian zone vegetation were characteristic for most of the livestock sites.

3.2. N_2O Concentrations and Fluxes

N_2O-N concentrations ranged from 0.03 to 2.60 μg/L with an overall mean ± standard error of 0.51 ± 0.03 μg/L. The estimated gas transfer velocity (k) calculated from velocity and slope measurements ranged from 0.06 to 5.50 m/day with a mean value of 1.42 ± 0.10 m/day. N_2O fluxes from streams were mostly net positive to the atmosphere with a few negative fluxes (range −11 to 323 N_2O-N μg·m^{-2}·hr^{-1}; 16 ± 2.67 N_2O-N μg·m^{-2}·hr^{-1}). The negative fluxes, indicating a net movement of N_2O into the water from the atmosphere, were found in three out of the seven livestock sites. However, the fifth-order stream that was classified as a forest stream upstream and a mixed stream downstream also recorded negative fluxes (Table 1). Generally, agricultural and forest streams had positive fluxes (Table 1).

3.3. Effect of Stream Order on Physical-Chemical Variables and N_2O Flux

No significant differences among stream orders were found for N_2O concentration, N_2O flux, and most physical-chemical variables after taking into account variation that was due to repeated measurements and random effects (Table 2). That said, pH, DOC, and CO_2-$C_{(aq)}$ exhibited exceptions (Table 2). From the Tukey post hoc analysis of least square means, the pH of first-order streams was significantly lower than that of third- and sixth-order streams while DOC concentration was also lower in first-order streams compared to third-order streams. However, first-order streams had significantly higher CO_2-$C_{(aq)}$ concentration compared to sixth-order streams (Table 3).

Table 2
Analysis of Variance Table From Linear-Mixed Models Highlighting Significant Differences Among the Different Land Uses and Stream Orders

	Land use		Order	
Variables	Chisq	p value	Chisq	p value
Temperature	81.55	<2.2E−16	4.39	0.36
pH	8.26	0.04	28.74	0.00
DO	96.72	<2E−16	7.84	0.10
Conductivity (μs/cm)	239.77	<2E−16	10.48	0.03
NH_4 (mg/L)	8.46	0.04	3.46	0.48
NO_3 (mg/L)	57.87	0.00	4.64	0.33
DOC (mg/L)	265.74	<2.2E−16	41.28	0.00
CO_2-C $_{(aq)}$ (mg/L)	4.07	0.25	15.41	0.00
N_2O concentration (μg/L)	80.04	<2E−16	6.29	0.18
N_2O flux(N_2O-N μg·m^{-2}·hr^{-1})	20.40	0.00	1.08	0.90

3.4. Effect of Catchment Land Use on Water Chemistry Variables and N_2O Concentration and Fluxes

In contrast to stream order, land use differences affected most of the physical-chemical variables, nutrients, and DOC, as well as N_2O flux and concentration. Forest sites had significantly lower temperatures compared to livestock and agricultural sites, and pH also varied significantly among the four land uses (Figure 2). Livestock stream sites had significantly lower mean DO concentrations compared to forest sites; however, they were similar to agricultural sites (Figure 2). Livestock sites also had the highest NH_4-N than the other land uses. However, agricultural streams had significantly higher TDN and NO_3-N compared to forest and livestock sites (Figure 2). For DOC, livestock sites had a significantly higher mean value when compared to agricultural and forest sites, but stream CO_2-$C_{(aq)}$ showed no significant differences with land uses (Figure 2). Flux and concentration also showed variation with land use. Agricultural sites had the highest mean N_2O flux and concentration compared to forest and livestock sites (Figure 3).

3.5. Effect of Physical-Chemical Water Variables and the Environmental C:N ratio on N_2O concentrations

Velocity and slope did not significantly predict N_2O concentrations in our sampled stream sites ($p > 0.05$). However, the strongest relationships were found for water quality variables more directly related to N_2O production. N_2O concentrations in forest streams were positively correlated to CO_2-$C_{(aq)}$ and NH_4-N concentrations but negatively correlated to DOC concentrations (Figure 4 and Table 4). A similar pattern was found in agricultural streams, where CO_2-$C_{(aq)}$ was also positively correlated to N_2O concentrations and DOC showed a negative relationship with N_2O concentrations (Figure 5 and Table 4). Contrary to forest and agricultural sites, N_2O concentrations in livestock sites were negatively correlated to CO_2-$C_{(aq)}$ and marginally positively correlated to DOC (Figure 6 and Table 4). N_2O concentrations were also negatively correlated with

Table 3
Mean ± Standard Error of Stream Hydrogeological Variables, Water Quality Variables, and N_2O Concentration and Flux by Stream Order Classifications

	Order				
Variable	First	Second	Third	Fifth	Sixth
Hydrogeological variables					
Slope	1.21 ± 0.13 ab	0.64 ± 0.06^{bc}	0.66 ± 0.06^{a}	0.65 ± 0.07^{b}	0.65 ± 0.10^{b}
Width	0.46 ± 0.03^{a}	1.17 ± 0.16^{a}	2.49 ± 0.32^{a}	12.00 ± 2.79^{b}	27.33 ± 2.02^{c}
Depth	0.04 ± 0.01^{a}	0.10 ± 0.02^{b}	0.16 ± 0.03^{ab}	0.34 ± 0.06^{c}	0.49 ± 0.08^{d}
Velocity	0.17 ± 0.02^{a}	0.20 ± 0.02^{b}	0.50 ± 0.07^{d}	1.03 ± 0.09^{cd}	0.45 ± 0.17^{abc}
Discharge	4.53 ± 0.71^{a}	27.04 ± 7.63^{a}	615.44 ± 182.40^{a}	4633.50 ± 1319.19^{a}	4859.50 ± 1628.39^{a}
Water-quality variables					
Temperature (° C)	17.78 ± 0.33^{a}	16.30 ± 0.38^{a}	18.56 ± 0.33^{a}	17.56 ± 0.87^{a}	19.67 ± 0.77^{a}
pH	7.10 ± 0.03^{a}	7.34 ± 0.08^{ab}	7.55 ± 0.04^{b}	7.42 ± 0.07^{ab}	7.71 ± 0.06^{b}
DO (mg/L)	6.04 ± 0.13^{a}	6.40 ± 0.26^{a}	5.67 ± 0.26^{a}	6.81 ± 0.36^{a}	6.81 ± 0.15^{a}
Alkalinity (mg/L)	34.64 ± 2.70^{a}	40.58 ± 7.46^{a}	71.27 ± 12.78^{a}	76.72 ± 32.39^{a}	223.68 ± 90.73^{a}
Conductivity	115.38 ± 7.94^{a}	131.68 ± 23.08^{a}	192.71 ± 34.52^{a}	139.83 ± 55.66^{a}	80.50 ± 55.66^{a}
NO_3-N (mg/L)	1.77 ± 0.14^{a}	1.37 ± 0.22^{a}	1.13 ± 0.15^{a}	0.65 ± 0.08^{a}	0.71 ± 0.19^{a}
NH_4-N (mg/L)	0.09 ± 0.01^{a}	0.06 ± 0.01^{a}	0.19 ± 0.06^{a}	0.03 ± 0.01^{a}	0.02 ± 0.01^{a}
TDN (mg/L)	2.55 ± 0.17^{a}	2.35 ± 0.33^{a}	1.56 ± 0.22^{a}	0.81 ± 0.13^{a}	0.99 ± 0.08^{a}
CO_2-C $_{(aq)}$ (mg/L)	1.36 ± 0.14^{a}	0.76 ± 0.08^{ab}	0.80 ± 0.09^{ab}	0.48 ± 0.13^{ab}	0.28 ± 0.08^{b}
DOC (mg/L)	2.67 ± 0.21^{a}	3.63 ± 0.55^{ab}	4.43 ± 0.37^{b}	3.44 ± 0.89^{ab}	3.44 ± 0.89^{ab}
N_2O-N					
Concentration (μg/L)	0.60 ± 0.05^{a}	0.42 ± 0.07^{a}	0.43 ± 0.05^{a}	0.26 ± 0.02^{a}	0.26 ± 0.02^{a}
Flux (μg·m^{-2}·hr^{-1})	19.73 ± 4.26^{a}	6.15 ± 1.37^{a}	15.98 ± 4.74^{a}	6.49 ± 3.15^{a}	6.69 ± 3.08^{a}

Note. Different letters indicate significant differences in the means according to Tukey post hoc comparisons ($p < 0.05$).

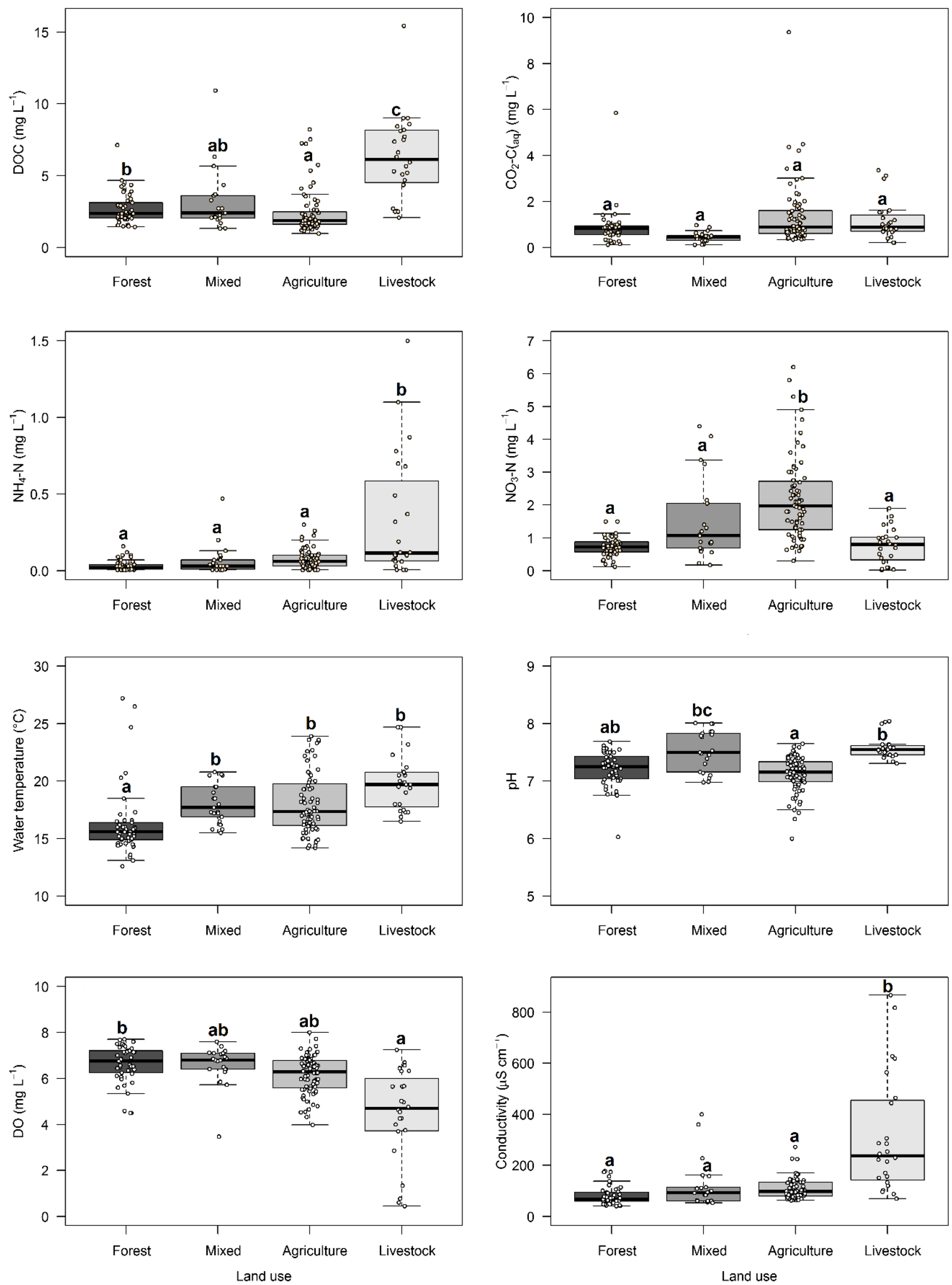

Figure 2. Box and dot plots of temperature, pH, dissolved oxygen, conductivity, dissolved organic carbon, aqueous CO_2, NH_4-N, and NO_3-N for streams in different land uses. Differences among groups are indicated by letters from Tukey post hoc comparisons ($p < 0.05$) above the standard error bars as determined by best fit models taking into account correlation among sampling times and including random effects on site.

DO in agricultural and livestock sites but not in forest sites (Table 4). For forest and agricultural sites that showed a similar pattern with DOC, there was an overall negative relationship between N_2O-N concentration and the environmental C:N ratio (DOC:DIN), with a threshold occurring at a ratio of 4–6, in which N_2O-N concentration is low (~<0.6 μg/L for most of the sampling points; Figure 7).

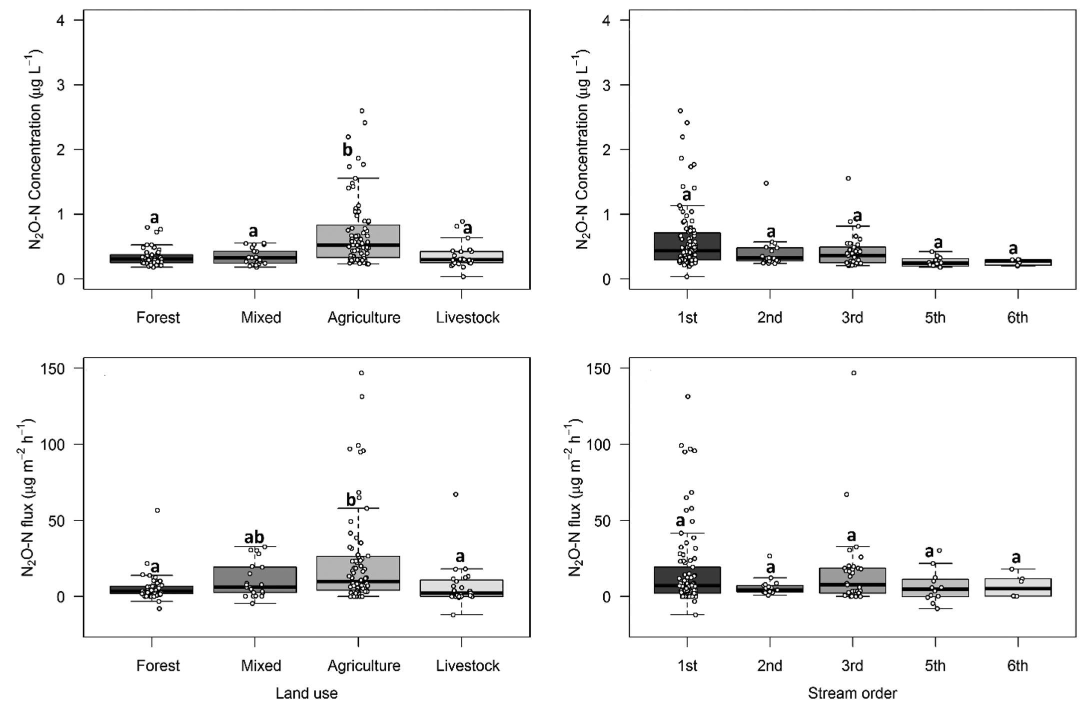

Figure 3. Box and dot plots of N_2O flux and concentration by stream order and land use. Differences among groups are indicated by letters from Tukey post hoc comparisons ($p < 0.05$) above the standard error bars as determined by best fit models taking into account correlation among sampling times and including random effects on site.

4. Discussion

4.1. Variation in N_2O Flux

N_2O flux quantified in this study (−11 to 323 N_2O-N $\mu g \cdot m^{-2} \cdot hr^{-1}$, mean 16 N_2O-N $\mu g \cdot m^{-2} \cdot hr^{-1}$) suggests that the Mara river upper catchment is mostly a net source of N_2O to the atmosphere, which is in line with studies done in other African tropical riverine systems (Table 6). Upstill-Goddard et al. (2017) in their study of rivers in the western Congo basin recorded fluxes ranging from − 22 to 106 N_2O-N $\mu g \cdot m^{-2} \cdot hr^{-1}$ while Borges et al. (2015) recorded mean fluxes of 2 to 32 N_2O-N $\mu g \cdot m^{-2} \cdot hr^{-1}$ for 12 sub-Saharan rivers. The mean flux reported in this study is in range, but intermediate between two other rivers in Kenya—higher than the Tana River but lower than that reported for the Athi-Galana-Sabaki Rivers (Table 5).

Stream order did not influence N_2O flux in our study area as shown in other studies on riverine systems (Marzadri et al., 2017; Turner et al., 2015), with the spatial variation of N_2O flux in our study area significantly linked to differences in catchment land use (Figure 3). The higher fluxes recorded in our agricultural stream sites are in line with previous studies on streams located in agriculturally dominated landscapes (Audet et al., 2017; Beaulieu et al., 2008). Audet et al. (2017) reported a higher mean flux of 108 $\mu g \cdot m^{-2} \cdot hr^{-1}$ for agriculturally dominated Swedish streams, while Beaulieu et al. (2008) reported a relatively comparable mean flux of 32.5 $\mu g \cdot m^{-2} \cdot hr^{-1}$ for 12 streams in Michigan, USA.

The fact that N_2O was not related to stream order is also consistent with other studies in Africa. Borges et al. (2015) found that N_2O flux was generally larger in rivers with widths >100 m wide compared to streams with widths <100 m. Teodoru et al. (2015) also found that N_2O flux did not show a consistent longitudinal trend along the Zambezi River and was more related to the presence of and connection to wetlands and reservoirs that is lower in wetlands and higher in reservoirs compared to the river. These results show that previous models based on whole-basin scaling functions related only to geomorphology or stream order (e.g. Marzadri et al., 2017; Turner et al., 2015) are not fully adequate to predict basin-scale N_2O emissions.

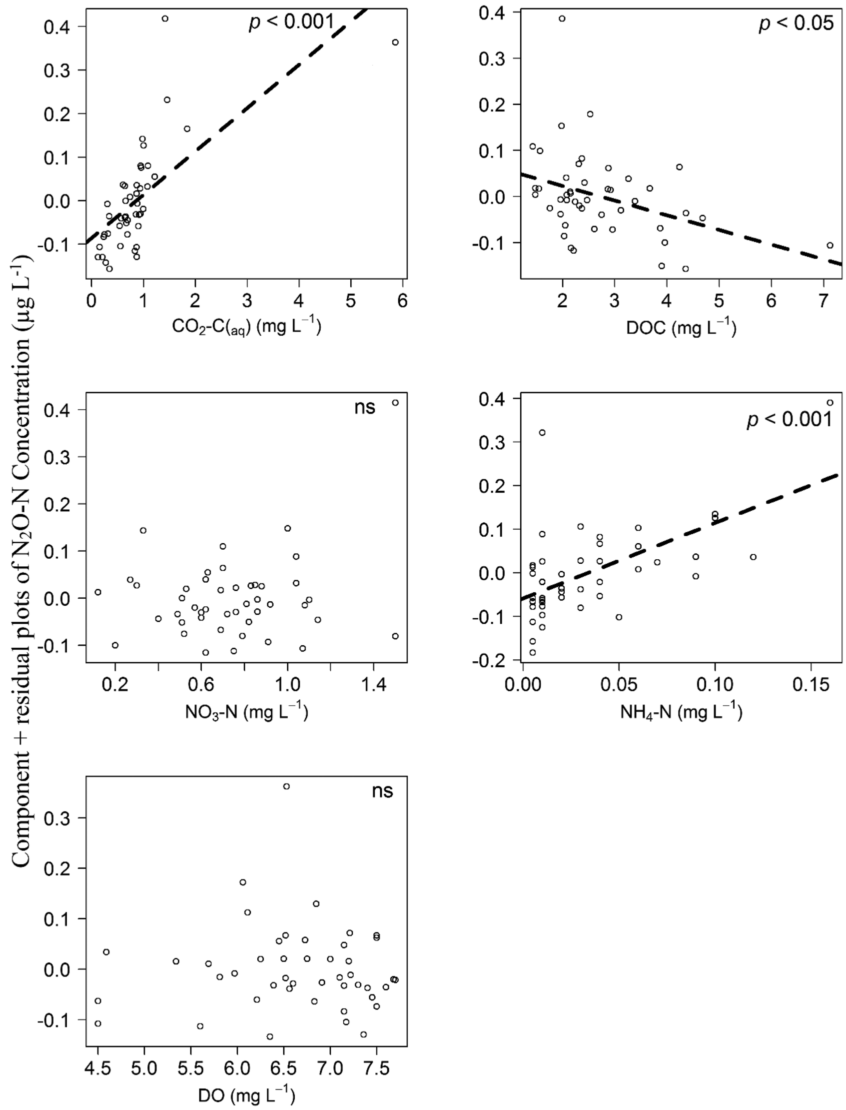

Figure 4. Component + residual plots from the multiple linear regression model (Table 5) of N_2O concentration in response to CO_2-$C_{(aq)}$, dissolved organic carbon (DOC), NO_3-N, NH_4-N, and dissolved oxygen (DO) concentrations for *forested sites* (n = 14), with significant relationships ($p < 0.05$) represented by the dashed line.

4.2. Controls of N_2O Concentration in Different Land Uses

N_2O concentration showed different relationships with water chemistry variables in forested, agricultural, and livestock streams, suggesting different biogeochemical controls on N_2O production. Dissolved CO_2-C was the strongest predictor of N_2O production for the forest and agricultural stream sites, explaining 58% and 77% of its variation, respectively. This relationship may be a cocorrelation, resulting from nitrification generating CO_2 through H^+ production.

The process of nitrification in forested sites is also supported by the fact that N_2O production was positively related to NH_4-N concentration, which was also found in other studies (Harrison & Matson, 2003; Strauss et al., 2002). In agricultural sites, nitrification was likely not N limited due to the lack of correlation between N_2O and NH_4-N, and this is consistent with the higher dissolved inorganic N concentrations in agricultural systems compared to forest streams, likely due to the use of the N-based fertilizer (in this case, calcium ammonium nitrate), which enters streams as runoff or leachate. Higher dissolved N values were also reported from other studies in agricultural systems, including some from the same tributaries (e.g., TDN 6.6 ± 2.60 mg/L, NO_3-N 6.1 ± 6.1 mg/L, NH_4-N 0.04 ± 0.03 mg/L; Masese et al., 2017), although lower

Table 4
Regression Table of a Multiple Linear Regression Model Predicting N_2O Concentration From CO_2-$C_{(aq)}$, NH_4-N, NO_3-N, DOC, and DO Concentration in Forest, Agricultural, and Livestock Sites

	N_2O concentration (μg/L)								
	Forest			Agricultural			Livestock		
Predictor variables	*B*	std.err	*p value*	*B*	std.err	*p value*	*B*	std.err	p-value
(Intercept)	0.23	0.16	0.15	1.49	0.35	7.55E−05	1.52	0.26	5.39E-05
CO_2-C $_{(aq)}$ (mg/L)	0.10	0.02	9.71E−06	0.27	0.03	1.49E−15	−0.42	0.09	0.00037
NO_3-N (mg/L)			0.21			0.97			0.15
NH_4-N (mg/L)	1.71	0.42	0.00015			0.31			0.40
DO (mg/L)			1.00	−0.18	0.05	0.00042	−0.22	0.05	0.00039
DOC (mg/L)	−0.03	0.02	0.042	−0.05	0.02	0.04			0.41
r^2		0.59			0.77			0.45	
Model *p* value		1.01E−07			<2.2E−16			0.006	
B = model coefficients of intercept and slope									
Degrees of freedom		39			69			18	
Number of sites		14			18			7	

	Agriculture								
Predictor variables	N_2O concentration (μg/L)								
	Forest			Agricultural			Livestock		
	B	*std.err*	*sig*	*B*	*std.err*	*sig*	*B*	*std.err*	*sig*
(Intercept)	2.76	0.36	***	5.27	1.26	***			ns
Temperature (°C)			ns	0.06	0.02	**			ns
pH	−0.32	0.05	***	−0.79	0.16	***			ns
r^2	0.5			0.3			ns		
Model significance	***			***			ns		
	Significance levels								
B = model coefficients of intercept and slope	*	$p < 0.05$							
	**	$p < 0.01$							
	***	$p < 0.001$							
	ns	$p > 0.05$							
Degrees of freedom		39			69			24	
Number of sites		14			18			9	

	N_2O concentration (μg/L)								
	Forest			Agricultural			Livestock		
Predictor variables	*B*	*std.err*	*p value*	*B*	*std.err*	*p value*	*B*	*std.err*	*p−value*
(Intercept)	0.36	0.033	1.02E−13	0.66	0.11	1.74E−07	0.33	0.085	0.00076
Slope	0.03	0.013	0.040			0.75			
Velocity	−0.14	0.05	0.01			0.74			
r^2		0.23							
Model *p* value		0.00145			0.902			0.198	
B = model coefficients of intercept and slope									
Degrees of freedom		39			69			18	
Number of sites		14			18			7	

Note. DO = dissolved oxygen; DOC = dissolved organic carbon.

values (TDN 1.80 ± 1.50 mg/L, NO_3-N 1.62 ± 0.60 mg/L) have been reported in similar streams in the Sondu River located in the South west part of the Mau Forest Complex (Jacobs et al., 2017). These differences could be in part due to the sampling season as the latter sampling was conducted in the dry season (February–March), while both Mara studies were conducted after the short rains (November–January).

Although there was not a significant relationship between N_2O and NO_3-N concentrations in the agricultural sites, they had higher N_2O concentration and flux as well as significantly higher NO_3-N concentration compared to the other land uses (Figure 2). Elevated NO_3-N concentration further supports the idea that nitrification dominated, presumably due to higher inputs of ammonium due to fertilizer application.

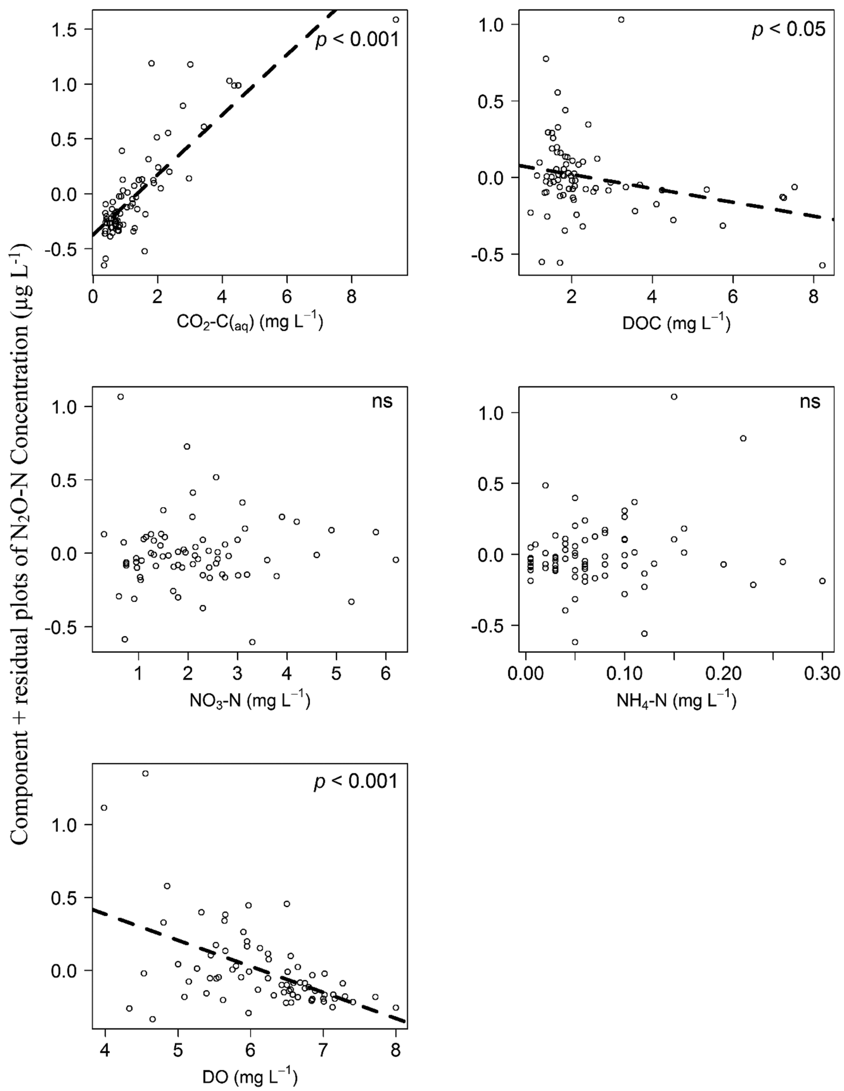

Figure 5. Component + residual plots from the multiple linear regression model for *agricultural* sites (n = 18; Table 5) of N_2O concentration in response to CO_2-$C_{(aq)}$, dissolved organic carbon (DOC), NO_3-N, NH_4-N, and dissolved oxygen (DO) concentrations (n = 18). Broken lines in the graphs represent significant relationships given by the overall model ($p < 0.05$).

Previous studies have also linked the positive correlation of N_2O to NO_3-N to a nitrification-dominated N_2O production process, further supporting this argument (Hama-Aziz et al., 2017; Ueda et al., 1993). The agricultural sites, however, also show a negative relationship with DO, which is also consistent with what would be expected either nitrification or denitrification (Codispoti & Christensen, 1985). It is feasible that both processes are contributing to N_2O production through a coupled nitrification-denitrification process (Audet et al., 2017; Hama-Aziz et al., 2017; Harrison & Matson, 2003); however, if denitrification were the dominant process, we also might expect to see at least a positive relationship of N_2O with DOC concentration and not a negative one (Beaulieu et al., 2011; Schade et al., 2016).

With high DOC concentration, there is evidence for an indirect control on nitrification through competition for inorganic nitrogen from heterotrophic bacteria (Ward, 2013). It is possible that this indirect control was detected in the forest and agricultural sites in this study. Indirect control has been shown particularly for high environmental C:N ratios (considered to be DOC:DIN) for stream sediments from the upper Midwestern United States (Strauss et al., 2002; Strauss & Lamberti, 2000). Strauss et al. (2002) reported a DOC:DIN threshold ratio of 20, above which nitrification was inhibited. A lower threshold ratio of 9.6–

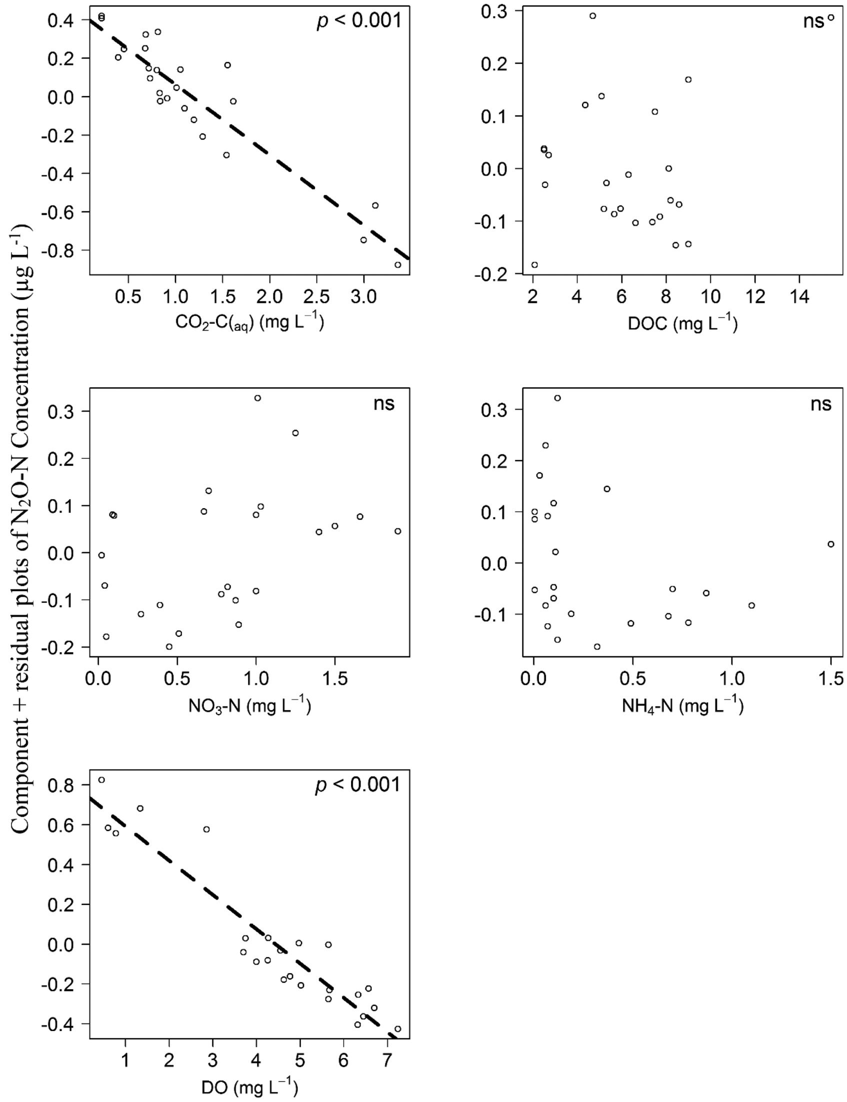

Figure 6. Component + residual plots from the multiple linear regression model (Table 5) of N_2O concentration in response to CO_2-$C_{(aq)}$, dissolved organic carbon (DOC), NO_3-N, NH_4-N, and dissolved oxygen (DO) concentrations for *livestock* sites (n = 7), with significant predictor variables represented by broken lines.

11.6 was reported in soils (Verhagen & Laanbroek, 1991). The results from our study are consistent with these studies, also showing a negative relationship between N_2O-N and DOC:DIN ratio (Figure 6) but with a lower threshold occurring at a DOC:DIN of 4–6. Variation in the threshold ratio is likely due to DOC quality and the dominant form of inorganic N in the system, both of which can affect the competitiveness of the heterotrophic bacterial community. These results point to the importance of considering process-rate measurements and complex interactions between nitrifiers and heterotrophic microorganisms in forested versus agricultural landscapes.

Livestock sites showed the opposite relationship between N_2O-N concentration and CO_2-$C_{(aq)}$ than forest and agricultural sites, suggesting different biogeochemical controls (Figure 5). The relationship is consistent with the two other major studies in Africa and their proposed mechanisms. Teodoru et al. (2015) and Borges et al. (2015) also found a negative correlation between CO_2 and N_2O, and both studies attributed this to higher in stream respiration rates associated with wetlands and floodplain systems, which have high organic matter and low dissolved oxygen, where N_2O could be consumed through complete denitrification. While the livestock systems are different due to their modified stream geomorphology as a result of cattle and

Table 5
Comparison of N_2O Flux From This Study With Other Studies From African Tropical Riverine Systems and Agricultural Headwater Streams in North America and Europe

Study site	N_2O flux		Reference	Original reported unit
	Range	Mean		
Upper Mara River, Kenya	−11–323 N_2O-N μg·m^{-2}·hr^{-1}	16 N_2O-N μg·m^{-2}·hr^{-1}	This study	
South central Ontario, Canada	−3.73−905 N_2O-N μg·m^{-2}·hr^{-1}		Baulch et al., 2011	μmol·m^{-2}·day^{-1a}
12 sub-Saharan Rivers, Africa		2−32 N_2O-N μg·m^{-2}·hr^{-1}	Borges et al., 2015	μmol·m^{-2}·day^{-1a}
Western Congo Rivers	−22−106 N_2O-N μg·m^{-2}·h^{-1}		Upstill-Goddard et al., 2017	μmol·m^{-2}·day^{-1a}
Tana River, Kenya		7 N_2O-N μg·m^{-2}·hr^{-1}	Borges et al., 2015	μmol·m^{-2}·day^{-1a}
Athi-Galana-Sabaki River, Kenya		19 N_2O-N μg·m^{-2}·hr^{-1}	Borges et al., 2015	μmol·m^{-2}·day^{-1a}
Agricultural systems				
Agricultural streams in the Mara river, Kenya		27 N_2O-N μg·m^{-2}·hr^{-1}	This study	
Agricultural streams in Sweden		108 N_2O-N μg·m^{-2}·hr^{-1}	Audet et al., 2017	μg·m^{-2}·hr^{-1}
U.S. corn belt	0.015−28.98 N_2O-N μg·m^{-2}·hr^{-1}		Turner et al., 2015	μmol·m^{-2}·s^{-1b}
Agricultural streams Michigan, USA		32.5 N_2O-N μg·m^{-2}·hr^{-1}	Beaulieu et al., 2008	μg·m^{-2}·hr^{-1}

[a]The daily fluxes were converted to hourly flux rates assuming uniform fluxes within a 24-hr period. [b]Fluxes per second were converted to hourly fluxes assuming uniform fluxes within the hour.

other animals that tends to increase water residence time and reduce exchange with the atmosphere, the patterns observed suggest a similar mechanism. Livestock sites had the highest number of negative fluxes (i.e., N_2O entering the water from the atmospheres) and N_2O concentration at livestock sites was negatively related to DO (Figure 5). Furthermore, the other water quality parameters suggest ideal conditions for complete denitrification compared to the agriculture and forested sites: DOC concentration was significantly higher, DO significantly lower, and NO_3 concentrations lower (along with higher NH_4 concentrations; Table 4). Upstill-Goddard et al. (2017) also hypothesized that complete denitrification was responsible for the negative N_2O fluxes in low DO waters in swamp rivers in the Congo. N_2O consumption through complete denitrification has also been previously reported in Amazon floodplain rivers

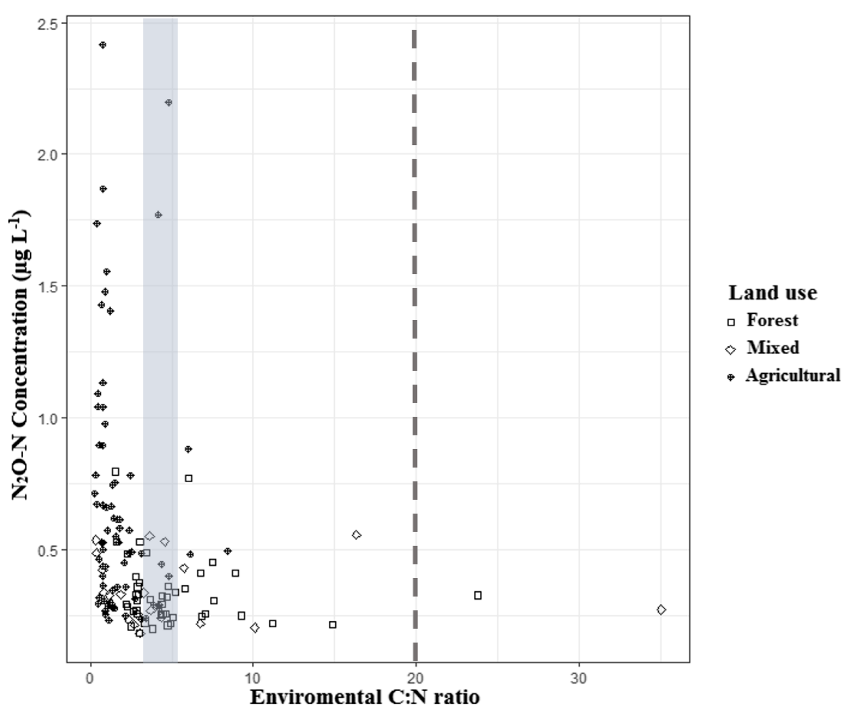

Figure 7. Scatter plot of N_2O concentration in response to the environmental C:N ratio, defined by dissolved organic carbon:dissolved inorganic nitrogen, in the forest, agricultural, and mixed stream sites. The shaded gray box indicates a threshold ratio indicating N limitation of nitrification in this study. The dashed line represents previously reported ratio from Strauss et al. (2002).

characterized by low DO, low nitrate and high DOC (Richey et al., 1988). Baulch et al. (2011) also found similar results in Canadian headwater streams undersaturated with N_2O, attributing it to consumption through complete denitrification in low ambient NO_3-N conditions.

5. Conclusions

Land use was more important than stream order in determining N_2O concentration and flux in the upper Mara River network, and land use seemed to influence the biogeochemical process responsible for N_2O emissions. Nitrification seemed to dominate in forest and agricultural sites, and denitrification seemed to dominate in livestock watering places. The fundamental differences between native forest, agriculture, and livestock sites in this region point to the importance of understanding how these systems will change with respect to N_2O emissions under increasing pressures of land use and climate change. This study has not accounted for seasonality, and higher flow rates may diminish differences between land use types and increase the importance of stream geomorphology associated with stream order. Process rate measurements will confirm the relative importance of nitrification, denitrification, or coupled nitrification-denitrification in these sites. These measurements will allow N_2O emissions models to incorporate land use, geomorphology, and the appropriate biogeochemical processes at basin scales.

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