**Land Use, Not Stream Order, Controls N$_2$O 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$_2$O) 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$_2$O 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$_2$O concentration and flux than stream size. Agricultural stream sites had the highest fluxes (26.38 ± 5.37 N$_2$O-N μg·m$^{-2}$·hr$^{-1}$) compared to both forest and livestock sites (5.66 ± 1.38 N$_2$O-N μg·m$^{-2}$·hr$^{-1}$ and 6.95 ± 2.96 N$_2$O-N μg·m$^{-2}$·hr$^{-1}$, respectively). N$_2$O 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$_2$O 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$_2$O production in agricultural and forest streams, whereas complete denitrification led to the consumption of N$_2$O 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$_2$O and for process-based studies.

**Plain Language Summary** Humans affect the emission of nitrous oxide (N$_2$O), 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$_2$O 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$_2$O emission from the headwaters of the Mara River, Kenya. We found that N$_2$O 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$_2$O 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$_2$O concentration is of global concern, as N$_2$O 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$_2$O 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;
Maavara et al., 2018). While older IPCC and modeled estimates suggested that rivers and estuaries contribute up to 20–35% of global anthropogenic N2O emissions (Kroeze & Seitzinger, 1998; Mosier et al., 1998), some studies later suggested that streams and rivers contribute considerably more to global N2O 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 N2O 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 N2O 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 N2O production rates are still not well understood, and the large range of reported estimates (e.g., from above studies, ~11 to 905 N2O-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 N2O (Beaulieu et al., 2011; Harrison & Matson, 2003). Nitrification is a chemoautotrophic process in which dissolved carbon dioxide (CO2(aq)) is fixed by ammonium oxidizing bacteria, which ultimately convert NH4 to NO3, releasing N2O in the process (Harrison & Matson, 2003). However, heterotrophic nitrification of organic N producing N2O 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 NH4 availability (Ward, 2013) and indirectly through competition for NH4 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 NH4 (Strauss & Lamberti, 2000). For denitriﬁcation, N2O is produced as an intermediary by heterotrophic bacteria that reduce NO3 to N2 in anaerobic conditions. Thus, organic C availability (DOC), NO3, and oxygen (O2) 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 N2O in stream ecosystems is still not well understood (Beaulieu et al., 2011).

Stream order is also a possible control of N2O flux rates in riverine ecosystems (Marzadri et al., 2017; Turner et al., 2015), with most studies predicting that N2O 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 N2O fluxes declined with an increase in stream order in U.S. Corn Belt streams, and Marzadri et al. (2014, 2017) also found that N2O fluxes reduced along the river continuum and proposed a model to incorporate this into observation for scaling N2O fluxes across a river basin; however, this study considers denitrification to be the main source of N2O 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 N2O 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 N2O emissions might not always be true.

Catchment land use also influences N2O 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 N2O gas is increasing by 0.2–0.3% yearly (Nevison, 1998), and this can possibly translate to N2O 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, N2O concentrations were highest in agricultural streams. Schade et al. (2016) also found higher N2O 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 N₂O 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 N₂O flux. However, uncertainties remain in the magnitude of N₂O flux from river systems in the region, despite their potential as a substantial contributor to the global N₂O 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 N₂O emissions from streams in agricultural intensified lands in the region is increasing.

Our study seeks to quantify N₂O 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 N₂O concentration and flux. We hypothesized that these relationships could be used to assess whether denitrification or nitrification was responsible for N₂O production in each land use and that the environmental C:N ratio (DOC:DIN) controlled N₂O 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-leaved 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, N₂O 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
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 % O2 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 (NH4-N) within 1–2 days of collection using AKVOs field kit (tintometers MD 610 spectrophotometer at 610 nm) and for nitrate (NO3-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 CPM 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 a 12-ml extainers (Labco vials) and stored for analysis at the Yale Analytical and Stable Isotope Center on a Shimadzu GC2014 with an FID for CO2 measurements and an ECD calibrated for N2O measurements. Standard gas concentrations were 0.25, 0.509, 0.951, 2.5, and 4.983 ppm for N2O measurements. Equilibration was achieved by shaking the syringe for 2 min in the stream, which maintained constant temperature at ambient conditions. Samples for atmospheric N2O 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.

N2O fluxes were calculated using the gas transfer velocity (k) calculated from the k600 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 N2O, where k600 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 N2O N μg·m⁻2·hr⁻¹, k is gas transfer velocity in meters per hour, N2Oobs is the observed concentration of N2O in micrograms per cubic meter, and N2Oatm is the theoretical concentration of N2O in micrograms per cubic meter if the water were in equilibrium with the atmosphere:

\[ k_{600} = V S^{0.76} \times 951.5 \]  
\[ F = k(N_{2O_{OBS}} - N_{2O_{ATM}}) \]  

2.5. Statistical Analysis

Physicochemical water variables, N2O 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 N2O concentration and water chemistry variables that had the potential to affect N2O 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 N2O production. Analyses were done on N2O concentration because stream velocity and slope also strongly affect flux (see above). Water chemistry variables included in the multiple linear regression model were CO2-C(aq), DOC, NO3-N, NH4-N, and DO, and these were interpreted as direct drivers controlling nitrification and denitrification rates that produce N2O 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
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 N2O 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$_2$O Concentrations and Fluxes

N$_2$O-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$_2$O fluxes from streams were mostly net positive to the atmosphere with a few negative fluxes (range −11 to 323 N$_2$O-N μg·m$^{-2}$·hr$^{-1}$; 16 ± 2.67 N$_2$O-N μg·m$^{-2}$·hr$^{-1}$). The negative fluxes, indicating a net movement of N$_2$O 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$_2$O Flux

No significant differences among stream orders were found for N$_2$O concentration, N$_2$O 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).
Agricultural sites had the highest mean N₂O 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 N₂O concentrations

Velocity and slope did not significantly predict N₂O concentrations in our sampled stream sites ($p > 0.05$). However, the strongest relationships were found for water quality variables more directly related to N₂O production. N₂O concentrations in forest streams were positively correlated to CO₂-C$_{(aq)}$ and NH₄-N concentrations but negatively correlated to DOC concentrations (Figure 4 and Table 4). A similar pattern was found in agricultural streams, where CO₂-C$_{(aq)}$ was also positively correlated to N₂O concentrations and DOC showed a negative relationship with N₂O concentrations (Figure 5 and Table 4). Contrary to forest and agricultural sites, N₂O concentrations in livestock sites were negatively correlated to CO₂-C$_{(aq)}$ and marginally positively correlated to DOC (Figure 6 and Table 4). N₂O concentrations were also negatively correlated with

### Table 3

| 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 d |
| 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 b |
| 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) | 17.76 ± 0.33 a | 16.30 ± 0.33 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 | 232.68 ± 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 |
| NO₃-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 |
| NH₄-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 |
| TN (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 |
| NO₂-N (mg/L) | 0.36 ± 0.15 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 |
| N₂O-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 ($p < 0.05$).
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$_2$O-N concentration and the environmental C:N ratio (DOC:DIN), with a threshold occurring at a ratio of 4–6, in which N$_2$O-N concentration is low (~<0.6 μg/L for most of the sampling points; Figure 7).

**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.
4. Discussion

4.1. Variation in N\textsubscript{2}O Flux

N\textsubscript{2}O flux quantified in this study (−11 to 323 N\textsubscript{2}O-N μg·m\textsuperscript{−2}·hr\textsuperscript{−1}, mean 16 N\textsubscript{2}O-N μg·m\textsuperscript{−2}·hr\textsuperscript{−1}) suggests that the Mara river upper catchment is mostly a net source of N\textsubscript{2}O 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\textsubscript{2}O-N μg·m\textsuperscript{−2}·hr\textsuperscript{−1} while Borges et al. (2015) recorded mean fluxes of 2 to 32 N\textsubscript{2}O-N μg·m\textsuperscript{−2}·hr\textsuperscript{−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\textsubscript{2}O 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\textsubscript{2}O 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 μg·m\textsuperscript{−2}·hr\textsuperscript{−1} for agriculturally dominated Swedish streams, while Beaulieu et al. (2008) reported a relatively comparable mean flux of 32.5 μg·m\textsuperscript{−2}·hr\textsuperscript{−1} for 12 streams in Michigan, USA.

The fact that N\textsubscript{2}O was not related to stream order is also consistent with other studies in Africa. Borges et al. (2015) found that N\textsubscript{2}O flux was generally larger in rivers with widths >100 m wide compared to streams with widths <100 m. Teodoro et al. (2015) also found that N\textsubscript{2}O 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\textsubscript{2}O emissions.
4.2. Controls of N₂O Concentration in Different Land Uses

N₂O concentration showed different relationships with water chemistry variables in forested, agricultural, and livestock streams, suggesting different biogeochemical controls on N₂O production. Dissolved CO₂-C was the strongest predictor of N₂O 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 CO₂ through H⁺ production.

The process of nitrification in forested sites is also supported by the fact that N₂O production was positively related to NH₄-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 N₂O and NH₄-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, NO₃-N 6.1 ± 6.1 mg/L, NH₄-N 0.04 ± 0.03 mg/L; Masese et al., 2017), although lower

![Component + residual plots from the multiple linear regression model (Table 5) of N₂O concentration in response to CO₂-C(aq), dissolved organic carbon (DOC), NO₃-N, NH₄-N, and dissolved oxygen (DO) concentrations for forested sites (n = 14), with significant relationships (p < 0.05) represented by the dashed line.](image-url)
values (TDN 1.80 ± 1.50 mg/L, NO₃⁻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 N₂O and NO₃⁻N concentrations in the agricultural sites, they had higher N₂O concentration and flux as well as significantly higher NO₃⁻N concentration compared to the other land uses (Figure 2). Elevated NO₃⁻N concentration further supports the idea that nitrification dominated, presumably due to higher inputs of ammonium due to fertilizer application.

### Table 4
Regression Table of a Multiple Linear Regression Model Predicting N₂O Concentration From CO₂-C\(_{aq}\), NH₄-N, NO₃-N, DOC, and DO Concentration in Forest, Agricultural, and Livestock Sites

| Predictor variables | N₂O concentration (µg/L) | Forest | Agricultural | Livestock |
|---------------------|---------------------------|--------|--------------|-----------|
|                     | 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 |
| CO₂-C\(_{aq}\) (mg/L) | 0.10 | 0.02 | 9.71E−06 | 0.27 | 0.03 | 1.49E−15 | −0.42 | 0.09 | 0.00037 |
| NO₃⁻N (mg/L)        | 1.71 | 0.42 | 0.00015 | 0.31 | 0.07 | 0.31 |
| NH₄-N (mg/L)        | 1.71 | 0.42 | 0.00015 | 0.31 | 0.07 | 0.31 |
| DO (mg/L)           | −0.03 | 0.02 | 0.042 | −0.05 | 0.02 | 0.04 |
| DO (mg/L)           | 1.00 | 0.00015 | 0.31 | 0.07 | 0.31 |
| r²                  | 0.59 | 0.77 | 0.45 |
| Model p value       | 1.01E−07 | <2.2E−16 | 0.006 |

B = model coefficients of intercept and slope

### Agriculture

| Predictor variables | N₂O 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)    | −0.32 | 0.05 | ns | 0.06 | 0.02 | ** | ns |
| pH                  | −0.32 | 0.05 | ns | 0.06 | 0.02 | ** | ns |
| r²                  | 0.5 | 0.3 | *** | 0.79 | 0.16 | *** | ns |
| Model significance  | ns | ns | ns |

B = model coefficients of intercept and slope

### Livestock

| Predictor variables | N₂O concentration (µg/L) | Forest | Agricultural | Livestock |
|---------------------|---------------------------|--------|--------------|-----------|
|                     | 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 | 0.05 | 0.75 | 0.74 |
| Velocity            | −0.14 | 0.05 | 0.01 | 0.23 | 0.902 | 0.198 |
| Model p value       | 0.00145 | 0.14 | 0.18 |

B = model coefficients of intercept and slope

### Note

DO = dissolved oxygen; DOC = dissolved organic carbon.
Previous studies have also linked the positive correlation of N2O to NO3-N to a nitrification-dominated N2O 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 N2O 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 N2O 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–
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$_2$O–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$_2$O–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$_2$O, 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$_2$O could be consumed through complete denitrification. While the livestock systems are different due to their modified stream geomorphology as a result of cattle and

Figure 6. Component + residual plots from the multiple linear regression model (Table 5) of N$_2$O 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.
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., N₂O entering the water from the atmosphere) and N₂O 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 NO₃ concentrations lower (along with higher NH₄ concentrations; Table 4). Upstill-Goddard et al. (2017) also hypothesized that complete denitrification was responsible for the negative N₂O fluxes in low DO waters in swamp rivers in the Congo. N₂O consumption through complete denitrification has also been previously reported in Amazon floodplain rivers.

**Table 5**

| Study site                                      | Range          | Mean           | Reference                      | Original reported unit |
|------------------------------------------------|----------------|----------------|-------------------------------|------------------------|
| Upper Mara River, Kenya                        | −11–323 N₂O-N μg·m⁻²·hr⁻¹ | 16 N₂O-N μg·m⁻²·hr⁻¹ | This study                    | μmol·m⁻²·day⁻¹ᵃ       |
| South central Ontario, Canada                  | −3.73–905 N₂O-N μg·m⁻²·hr⁻¹ | 2–32 N₂O-N μg·m⁻²·hr⁻¹ | Baulch et al., 2011           | μmol·m⁻²·day⁻¹ᵃ       |
| 12 sub-Saharan Rivers, Africa                  | −22–106 N₂O-N μg·m⁻²·hr⁻¹ | 7 N₂O-N μg·m⁻²·hr⁻¹ | Borges et al., 2015           | μmol·m⁻²·day⁻¹ᵃ       |
| Western Congo Rivers                           |                | 19 N₂O-N μg·m⁻²·hr⁻¹ | Upstill-Goddard et al., 2017  | μmol·m⁻²·day⁻¹ᵃ       |
| Tana River, Kenya                              |                |                | Borges et al., 2015           | μmol·m⁻²·day⁻¹ᵃ       |
| Athi-Galana-Sabaki River, Kenya                |                |                | Borges et al., 2015           | μmol·m⁻²·day⁻¹ᵃ       |
| Agricultural systems                           |                |                | Upstill-Goddard et al., 2017  | μmol·m⁻²·day⁻¹ᵃ       |
| Agricultural streams in the Mara river, Kenya  |                |                | Beaulieu et al., 2008         | μg·m⁻²·hr⁻¹           |
| Agricultural streams in Sweden                 | 0.015–28.98 N₂O-N μg·m⁻²·hr⁻¹ | 32.5 N₂O-N μg·m⁻²·hr⁻¹ | Audet et al., 2017  | μmol·m⁻²·s⁻¹ᵇ         |
| U.S. corn belt                                  |                |                | Turner et al., 2015           | μmol·m⁻²·s⁻¹ᵇ         |
| Agricultural streams Michigan, USA             |                |                | Strauss et al. (2002)         | μg·m⁻²·hr⁻¹           |

**Figure 7.** Scatter plot of N₂O 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 N₂O, attributing it to consumption through complete denitrification in low ambient NO₃⁻N conditions.

5. Conclusions

Land use was more important than stream order in determining N₂O concentration and flux in the upper Mara River network, and land use seemed to influence the biogeochemical process responsible for N₂O 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 N₂O 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 N₂O emissions models to incorporate land use, geomorphology, and the appropriate biogeochemical processes at basin scales.

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