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RESEARCH ARTICLE

Nitrous oxide and methane seasonal variability in the epilimnion of a large tropical meromictic lake (Lake Kivu, East-Africa)

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Abstract We report a data-set of monthly vertical profiles obtained from January 2012 to October 2013, from the surface to 70 m depth of nitrous oxide (N_2O) and dissolved methane (CH_4) in Lake Kivu, a large and deep meromictic tropical lake (East Africa). Vertical variations of N_2O were modest, with ranges of 6–9 and 0–16 nmol L^{-1} in surface and bottom waters, respectively, and occasionally peaks of N_2O (up to 58 nmol L^{-1}) were observed at the oxic-anoxic interface. On the contrary, steep vertical gradients of CH_4 were observed with values changing several orders of magnitude from surface (19–103 nmol L^{-1}) to 70 m ($\sim$113,000–520,000 nmol L^{-1}). Seasonal variations of CH_4 were caused by annual cycles of mixing and stratification, during the dry and rainy seasons, respectively. This mixing allowed the establishment of a thick oxic layer (maximum 65 m deep), leading to decreased CH_4 concentrations (minimum of 8 nmol L^{-1}), presumably due to bacterial CH_4 oxidation. During the stratification period, the oxic mixed layer was thinner (minimum 25 m deep), and an increase of CH_4 concentrations in surface waters was observed (maximum of 103 nmol L^{-1}), probably due to a lower integrated CH_4 oxidation on the water column. Lake Kivu seasonally alternated between a source and a sink for atmospheric N_2O, but on an annual scale was a small source of N_2O to the atmosphere (on average 0.43 µmol m^{-2} day^{-1}), while it was a small source of CH_4 to the atmosphere throughout the year (on average 86 µmol m^{-2} day^{-1}). Vertical and seasonal variations of N_2O are discussed in terms of nitrification and denitrification, although from the present data-set it is not possible to unambiguously identify the main drivers of N_2O production.

Keywords Nitrous oxide · Methane · Tropical lake · Lake Kivu

Introduction

Methane (CH_4) and nitrous oxide (N_2O) are two important greenhouse gases whose global warming potential are respectively 34 and 298 times higher on a 100-year time frame than carbon dioxide (CO_2) (IPCC 2013). Additionally, N_2O depletes stratospheric ozone. The concentrations of CH_4 and N_2O in the atmosphere have significantly increased during the 20th century due to human activities, agriculture in particular.

N_2O in aquatic systems is mainly produced by nitrification and denitrification with optimal temperature estimated to be in the 25–30 °C range (Saad and Conrad 1993). Hence, an increase of these processes can be expected with increasing temperatures, but N_2O emissions are also strongly linked to nitrogen and oxygen availability. In this sense, the highest N_2O emissions from inland waters are reported from systems enriched by fertilizer use in catchment areas or wastewaters (Zhang et al. 2010; Baulch et al. 2011). Indeed, African rivers have been recently shown to be lower N_2O emitters compared to their temperate counterparts, presumably due to the different

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agricultural practices (i.e., traditional versus fertilizer-intensive) (Borges et al. 2015a).

CH_4 in aquatic systems is mostly produced in the anoxic layers of sediments and is transported to the surface by diffusion, mixing, and ebullition. Aerobic and anaerobic CH_4 oxidation can take place during the transport, and the fraction that is not oxidized is emitted to the atmosphere. Natural wetlands are known to be the major natural source of CH_4 for the atmosphere (175–217 Tg CH_4 $year^{-1}$), as well as inland waters (lakes and rivers), since the latter were estimated to emit between 40 Tg CH_4 $year^{-1}$ (Kirschke et al. 2013) and 103 Tg CH_4 $year^{-1}$ (Bastviken et al. 2011). Furthermore, higher emissions of CH_4 are expected in tropical inland waters than in temperate and boreal counterparts, in accordance with recent reports (Sawakuchi et al. 2014; Borges et al. 2015a), due to the strong dependence of CH_4 production on temperature (Marotta et al. 2014; Yvon-Durocher et al. 2014). Within the tropical aquatic environments, the Amazon wetlands are the best studied in terms of CH_4 dynamics and fluxes (Bartlett et al. 1990; Devol et al. 1990; Engle and Melack 2000; Melack et al. 2004; Bastviken et al. 2010; Borges et al. 2015b). These wetlands consist of flooded forest, floating macrophytes and permanent or temporary floodplain lakes that emit large amounts of CH_4 to the atmosphere. Comparatively, tropical upland lakes are much less studied for CH_4 and N_2O dynamics. In addition, data are particularly scarce in large lakes (Holgerson and Raymond 2016). Furthermore, seasonal variations of CH_4 and N_2O fluxes have seldom been described in lakes, and mostly in boreal systems (e.g. Kankaala et al. 2013; Miettinen et al. 2015). Eddy-covariance allows the direct measurement of CH_4 and N_2O fluxes to the atmosphere in lakes (e.g. Podgrajsek et al. 2014; Xiao et al. 2014), although fluxes are usually computed from dissolved concentrations in surface waters using estimates of the gas transfer velocity (e.g. Schubert et al. 2010; Kankaala et al. 2013; Miettinen et al. 2015).

In this study, we report a 2-year time series of monthly measurements of CH_4, N_2O and nitrate (NO_3^-) concentrations in a large tropical lake (Lake Kivu, East Africa). Lake Kivu is a deep (maximum 485 m) meromictic lake characterized by anoxic deep waters rich in dissolved CH_4 and nutrients (Degens et al. 1973; Schmid et al. 2005; Tassi et al. 2009). Surface waters are oligotrophic and are characterized by relatively low primary production ranging between 143 and 278 g C m^{-2} $year^{-1}$ (Darchambeau et al. 2014, Morana et al. 2014), and have been shown to be net autotrophic (Morana et al. 2014), yet they emit carbon dioxide (CO_2) to the atmosphere due to geogenic CO_2 inputs from deep waters (Borges et al. 2014). A first study of CH_4 dynamics in Lake Kivu showed very low CH_4 concentrations in surface waters (Borges et al. 2011), presumably due to intense CH_4 oxidation as CH_4 is transported upwards (Borges et al. 2011; Pasche et al. 2011; Morana et al. 2015a). The first study of CH_4 in surface waters (Borges et al. 2011) was based on a coarse seasonal coverage (only four cruises), focused on surface waters and did not describe the vertical variability of CH_4 in the top 100 m. While most previous studies have focused on carbon cycling in Lake Kivu, nitrogen cycling has received much less attention. The aim of this study is to describe seasonal variations of CH_4 and N_2O in the epilimnion of a tropical lake and attempt to unravel the underlying processes. Moreover, as a large scale industrial extraction of CH_4 from the deep layers of Lake Kivu is planned (Nayar 2009), it is important to establish the baseline of ecological and biogeochemical settings to monitor, understand and quantify the consequences of this industrial extraction of CH_4. Information on the temporal variability of the vertical structure in the top 100 m is required to achieve a comprehensive description of base-line conditions of CH_4 in Lake Kivu prior to industrial extraction.

The present study focuses on one station in the Southern Basin of the lake (Ishungu station), and thus provides temporally resolved data compared to previous reports of CH_4 concentrations focusing on spatial variations in surface waters by Borges et al. (2011). The present paper also complements the work of Morana et al. (2015b) based on the same two-year sampling at Ishungu, which mainly focused on the biogeochemistry of organic matter.

Materials and methods

Study site

Lake Kivu is located at the border between Rwanda and Democratic Republic of the Congo (DRC) [2.50°S 1.59°S 29.37°E 28.83°E]. Sampling was carried out every month from late January 2012 to October 2013, at one station in the Southern Basin of the Lake (Ishungu station; −2.3374°N, 28.9775°E; Fig. 1).

Physico-chemical parameters and sampling

Vertical profiles of temperature, conductivity and oxygen (O_2) were obtained with a Hydrolab DS4 multiparameter probe. Water was collected with a vertical 7L Niskin bottle (Hydro-Bios) every 5 m from the surface to 70 m.

Water column chemical analyses

Samples for N_2O and CH_4 concentrations were collected in 50 mL glass serum bottles from the Niskin bottle through a silicon tube connected to the outlet, left to overflow, poisoned with 100 µL of saturated $HgCl_2$ and immediately

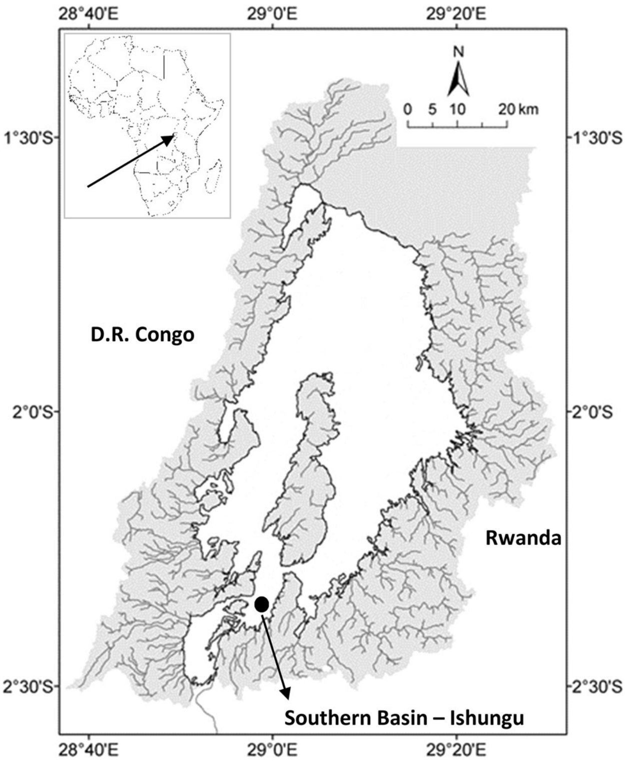


Fig. 1 Map of Lake Kivu, showing sampling site in the Southern Basin

sealed with butyl stoppers and aluminium caps. CH_4 and N_2O concentrations were determined via the headspace equilibration technique (20 mL N_2 headspace in 50 mL serum bottles) and measured by gas chromatography (GC) (Weiss 1981) with electron capture detection (ECD) for N_2O and with flame ionization detection (FID) for CH_4. The SRI 8610C GC-ECD-FID was calibrated with certified CH_4:CO_2:N_2O:N_2 mixtures (Air Liquide, Belgium) of 1, 10, 30 and 509 ppm CH_4 and of 0.2, 2.0 and 6.0 ppm N_2O. Concentrations were computed using the solubility coefficients of Yamamoto et al. (1976) and Weiss and Price (1980), for CH_4 and N_2O, respectively. The precision of measurements was ±3.9 and ±3.2 % for CH_4 and N_2O, respectively.

When preparing the headspaces, excess water was collected to quantify NO_3^- and NH_4^+ concentrations by spectrophotometry. NO_3^- were determined after vanadium reduction to nitrite (NO_2^-) and quantified under this form with a Multiskan Ascent Thermo Scientific multi-plates reader (APHA 1998; Miranda et al. 2001). NH_4^+ were quantified according to the dichloroisocyanurate-salicylate-nitroprussiate colorimetric method (Westwood 1981), using a 5-cm light path on a spectrophotometer Thermo Spectronic Genesys 10vis. The detection limits for these methods were 0.15 and 0.3 µmol L^{-1} for NO_3^- and NH_4^+, respectively.

CH_4 and N_2O flux calculations

CH_4 and N_2O fluxes with respect to the atmosphere were calculated based on temperature, CH_4 and N_2O concentrations, and the gas transfer velocity computed from wind speed according to the Cole and Caraco (1998) relationship. By convention, a positive flux value corresponds to a gas transfer from the water to the atmosphere, and, conversely, a negative flux corresponds to a gas transfer from the atmosphere to the water. Wind speeds were obtained from the National Centers for Environmental Prediction (NCEP) gridded daily product (grid point −0.952°N, 30.000°E). These values were adjusted to fit field measurements from a meteorological station of the Institut Supérieur Pédagogique (ISP) of Bukavu. The ISP wind values were adjusted by the addition of 2 m s^{-1} to account for differences in wind speed between lake and inland where the station is located as suggested by Thiery et al. (2014).

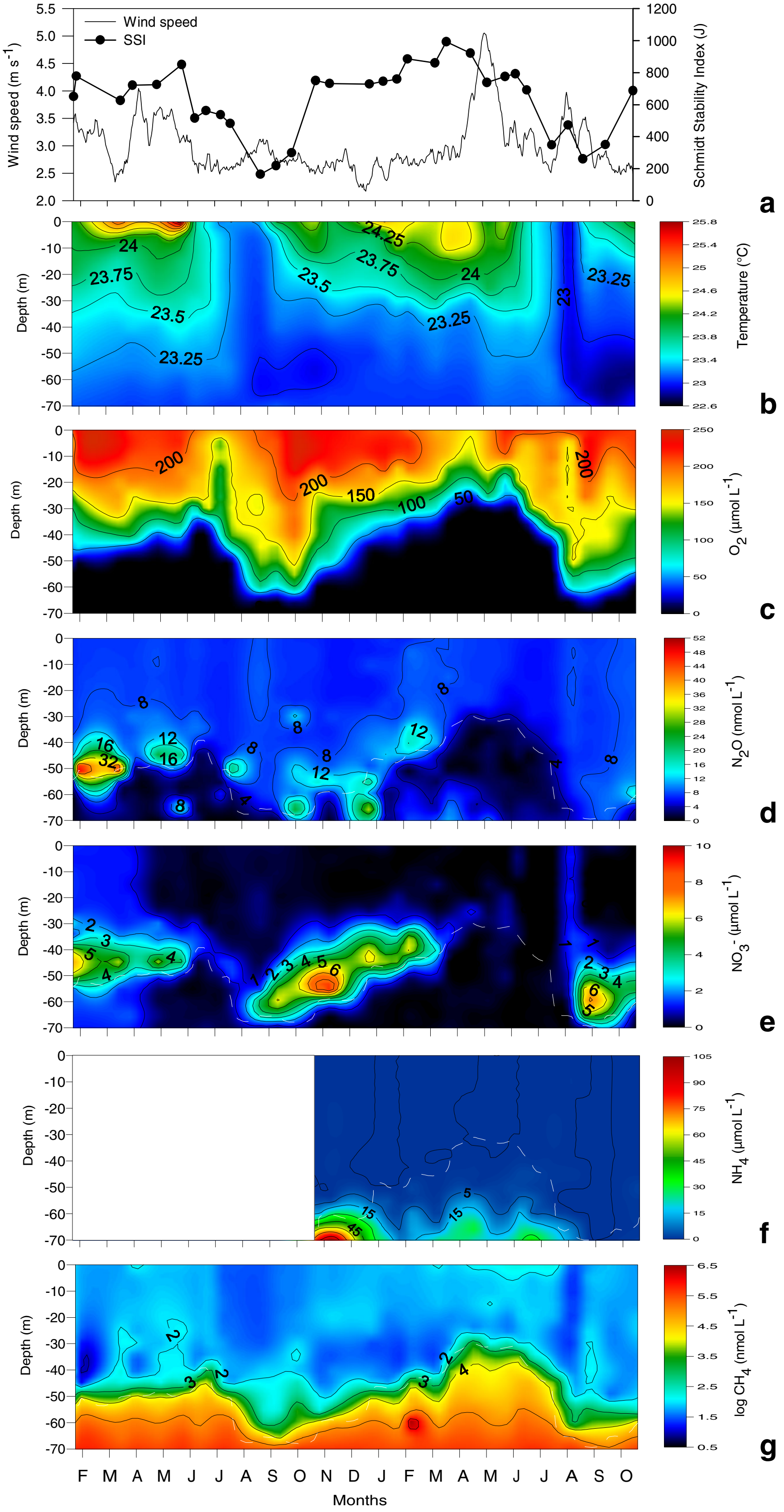
Schmidt Stability Index calculations

Schmidt Stability Index (SSI) defines the thermal stability of the water column over a certain depth and expresses the amount of energy needed for its full mixing over that depth (Schmidt 1928). SSI from the surface to 65 m was calculated from density vertical gradients according to Schmidt (1928), and density was computed from temperature and salinity derived from conductivity according to Schmid and Wüest (2012).

Results

For both years, SSI (Fig. 2a) and temperature variability (Fig. 2b) showed one mixing period, from July to October (dry season), with a maximum mixing in September, while the water column was stratified the rest of the year (rainy season). Mixing periods did not co-occur with higher wind speeds (Fig. 2a), which were observed a few weeks before the mixing. The location of the oxycline (Fig. 2c) followed the seasonal cycling of mixing and stratification, and ranged from 35 to 70 m depth during the rainy and dry seasons, respectively. Deep waters (from 70 m) remained anoxic throughout the year, while surface waters (at 5 m) were well oxygenated (oxygen concentrations range 122–243 µmol L^{-1}). N_2O profiles showed on various occasions higher concentration peaks (maximum peak of 52 nmol L^{-1}) in the oxycline, while concentrations remained relatively low in surface waters (from 6.6 to 9.3 nmol L^{-1}, at 5 m) and at 70 m (from 0.1 to 16.4 nmol L^{-1}) (Fig. 2d). The maximum peaks of N_2O were usually observed below the maximum peaks of NO_3^-

Fig. 2 Seasonal profiles of (**a**) wind speed (m s^{-1}) and Schmidt Stability Index (SSI; J), and seasonal and vertical depth profiles of **b** temperature (°C), **c** O_2 (µmol L^{-1}), **d** N_2O (nmol L^{-1}), **e** NO_3^- (µmol L^{-1}), **f** NH_4^+ (µmol L^{-1}) and **g** log CH_4 (nmol L^{-1}) from late January 2012 to October 2013, and **g** NH_4^+ (µmol L^{-1}) from late October 2012 to October 2013. *White dotted line* is the oxic-anoxic transition zone



concentrations (Fig. 2e), and sometimes with a time delay. Three NO_3^- accumulation zones (nitraclines) were observed: from late January to June 2012, from late August to late December 2012, and from late August to September 2013. Maximum NO_3^- concentrations associated to these nitraclines ranged between 7 and 10 µmol L^{-1}. NH_4^+ concentrations tended to be higher in anoxic waters, with concentrations up to 110 µmol L^{-1} at 70 m depth (Fig. 2f). In oxic surface waters (at 5 m), CH_4 concentrations (Fig. 2g) remained low throughout the year and ranged between 19 and 103 nmol L^{-1}. At 70 m, CH_4 concentrations were higher and ranged from ~113,000 to 520,000 nmol L^{-1}.

N_2O concentrations at 5 m depth showed no correlation to SSI (Fig. 3a). The seasonal variations of NO_3^- concentrations and SSI were linked (Fig. 3b): when vertical mixing occurred (low SSI; August and September 2012 and 2013), NO_3^- concentrations began to increase to reach their maximum 1–2 months later. Contrary to N_2O, CH_4 concentrations in surface waters followed the pattern of the SSI (Fig. 3c) and were significantly correlated ($R^2 = 0.23$, $p < 0.01$, $n = 29$); minima of CH_4 concentrations co-occurred with SSI minima.

N_2O fluxes (Fig. 3d) showed large fluctuations during the studied period. Negative fluxes were observed in January 2012, July–August 2012, November 2012–January 2013 and June–August 2013 (ranging between −2.2 and −0.001 µmol m^{-2} day^{-1}). The rest of the year, N_2O fluxes were positive, with a maximum flux of 3.5 µmol m^{-2} day^{-1} in February 2013. The average N_2O flux for both years of sampling was 0.4 µmol m^{-2} day^{-1}. The highest CH_4 flux to the atmosphere was in June 2013 (222 µmol m^{-2} day^{-1}) and the lowest was in August 2013 (24 µmol m^{-2} day^{-1}) (Fig. 3e). The average CH_4 flux for the 2 years of sampling was 85 µmol m^{-2} d^{-1}. The seasonal differences in CH_4 fluxes were very low (rainy season mean flux of 96 µmol m^{-2} day^{-1} and dry season mean flux of 64 µmol m^{-2} d^{-1}).

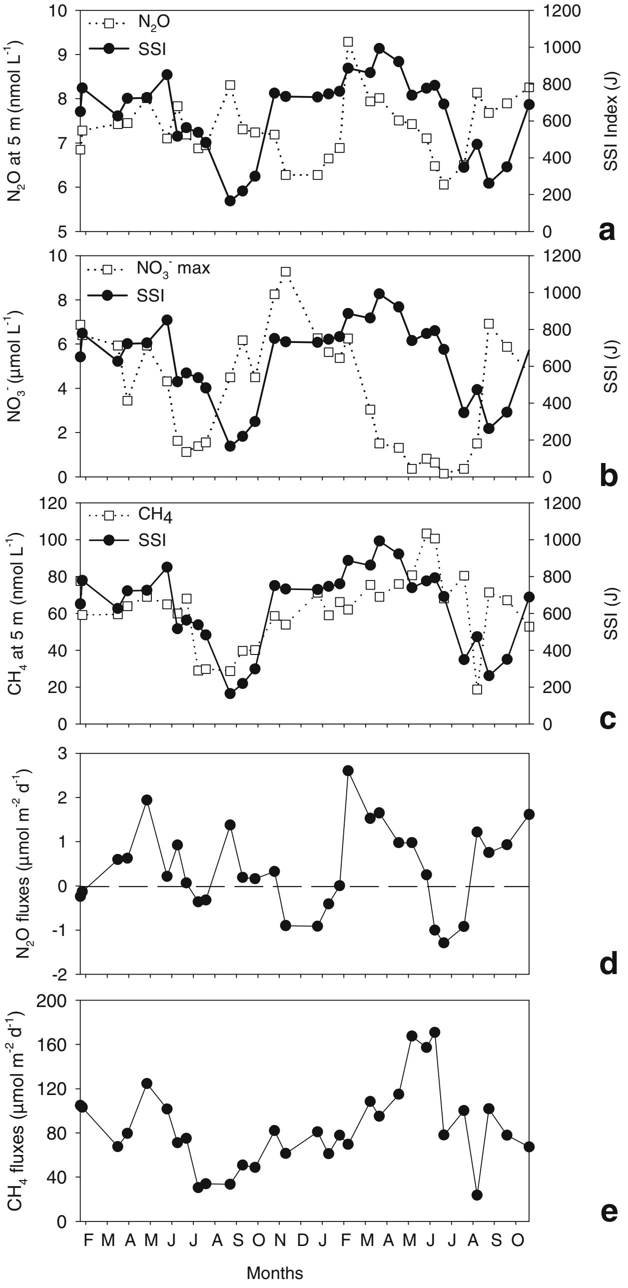


Fig. 3 **a–c** Comparison between Schmidt Stability Index (SSI; J; *black circles*) and N_2O concentrations (nmol L^{-1}; *white squares*) at 5 m depth, maximum NO_3^- concentrations (µmol L^{-1}; *white squares*) and CH_4 concentrations (nmol L^{-1}; *white squares*) at 5 m depth, respectively; **d**, **e** atmospheric N_2O and CH_4 fluxes (µmol m^{-2} d^{-1}), respectively, from late January 2012 to October 2013

Discussion

The alternation between stratification of the water column in rainy season and mixing events in dry season is a typical behavior for Lake Kivu (Schmid and Wüest 2012). Mixing periods did not co-occur with higher wind speeds, which were observed a few weeks before the mixing. This strongly suggests that wind stress is not the main factor for the mixing of the water column in Lake Kivu contrary to what is reported for the nearby Lake Tanganyika (Thiery et al. 2014). Indeed, increased heat fluxes due to evaporation related to changes in solar radiation and air humidity is the main driver of mixing during the dry season in Lake Kivu (Thiery et al. 2014).

N_2O fluxes fluctuated widely during the two-year sampling, and we observed both positive and negative fluxes, indicating that Lake Kivu acted as a sink and a source for atmospheric N_2O. N_2O fluxes are driven by nitrification/denitrification processes in the water column. Nitrification is considered as an important source of N_2O, while denitrification, by consuming N_2O to produce N_2, is often considered as a sink. However, in the oxic-anoxic transition zone, when O_2 level is low (below 6 µmol L^{-1}), the last step of denitrification, i.e. N_2O reduction to N_2, can be inhibited while the NO_3^- reduction to N_2O step can still occur leading to a net N_2O production (Seitzinger et al. 2006). A few factors allow us to suggest the occurrence of these two processes in the water column of Lake Kivu. N_2O profiles, showed on some occasions concentrations peaks in the oxycline, a common feature for meromictic lakes (Mengis et al. 1997). Nitrification was evidenced by the presence of NO_3^- accumulation zones (nitraclines) during the rainy season, which in turn can sustain denitrification in the anoxic water column. Nitraclines are the result of vertical mixing of superficial waters occurring during the dry season. During this vertical mixing event, oxygen penetrated deep in the water column, down to the bottom of the mixolimnion, where reduced species such as NH_4^+ are abundant. NH_4^+ thus became available for phytoplankton and nitrifying bacteria and archaea growth. Accordingly, nitrification led to the establishment of a nitracline that appeared with some delay after the initial mixing event that brought NH_4^+ in contact with oxic waters. The fact that maximums of NO_3^- concentrations were observed 1–2 months after the mixing event (reflected by SSI) can be explained by the time required for the nitrifier community to develop and for NO_3^- to accumulate in the water column.

In late January 2012, high N_2O values were observed in oxic waters (e.g., 47.5 m) corresponding to maximum NO_3^- values. The presence of higher abundances of a NO_2^--oxidizing bacteria (*Nitrospira*) (İnceoğlu et al. 2015a) at those depths strongly suggests the occurrence of nitrification. Nitrification rates in Lake Kivu have never been directly quantified, but the study of Llirós et al. (2010) showed the presence of a nitrifying archaeal community in the oxycline, suggesting a potentially important role of archaeal nitrification. In late January 2012, a diversified archaeal community was also observed (İnceoğlu et al. 2015a). The *Marine Group I* (*Thaumarcheota*), which are ammonia oxidizing archaea (AOA), was well represented in the superficial oxic waters, where they represented the whole archaeal community at some depths. AOA are thought to be dominant over ammonia oxidizing bacteria (AOB) in most environments (Stieglmeier et al. 2014), and they seem to be predominant in oligotrophic environments (Stahl and De La Torre 2012), such as the oxic waters of Lake Kivu (Llirós et al. 2010, İnceoğlu et al. 2015a). However, some N_2O peaks were clearly located in anoxic waters, as in late January 2012 which suggest the involvement of other processes in N_2O production, such as denitrification. Pyrosequencing data obtained by İnceoğlu et al. (2015a) showed the presence of *Betaproteobacteria*, which were highly abundant at the oxic-anoxic interface. This class includes in particular two well-known denitrifiers, *Denitratisoma* sp. and *Thiobacillus* sp., which can potentially be responsible for denitrification in Lake Kivu, and some bacterial nitrifiers, such as *Nitrosomonas* sp. As nitrification, denitrification has never been quantified in Lake Kivu, but conditions for the occurrence of this process are present in rainy season, since non-negligible NO_3^- concentrations are often observed at the oxic-anoxic interface.

Deep isoclines of CH_4 concentrations followed the bottom of the oxycline, strongly suggesting the occurrence of CH_4 oxidation in the water column of Lake Kivu, as recently evidenced by mass balance (Borges et al. 2011; Pasche et al. 2011) or stable isotopic signature and processes measurement studies (Morana et al. 2015a, b). İnceoğlu et al. (2015a) observed the presence of an important community of aerobic and anaerobic methanotrophs (mainly *Methylomonas*-related operational taxonomic units and anaerobic methanotrophic archaea (ANME), respectively) in the Southern Basin (Ishungu Basin) of Lake Kivu, giving support to the occurrence of intense CH_4 oxidation in the water column. They also observed archaeal methanogens which suggested that methanogenesis could occur in the water column, whereas previous research on CH_4 dynamics assumed that sediments were the only source of CH_4 in Lake Kivu (Pasche et al. 2011). In aquatic environments, CH_4 is mainly produced in sediments but some studies also reported CH_4 production in anoxic waters (e.g. Winfrey and Zeikus 1979; Iversen et al. 1987; Borrel et al. 2011; Crowe et al. 2011).

During our study, CH_4 concentrations at 5 m were significantly correlated with SSI and were higher during the rainy season (high SSI) than during the dry season (low SSI). During the rainy season, the oxic layer became thinner and anoxic waters rich in CH_4 were closest to the surface, limiting CH_4 losses by aerobic oxidation. On the contrary, during the dry season the oxic layer deepened and integrated aerobic CH_4 oxidation on the oxic water column might be higher leading to lower CH_4 concentrations in surface waters. In general, the seasonal amplitude of CH_4 concentrations in surface waters was low (84 nmol L^{-1}) compared to higher latitude lakes (range 100–65,000 nmol L^{-1}; Supplemental Table 1). This might be explained by the large CH_4 accumulation during winter below the frozen lake surface and by more frequent lake overturn which mixes deep and surface waters, a typical process in holomictic lakes unlike Lake Kivu which is permanently stratified. Seasonal changes in oxic and anoxic conditions also contribute to seasonal amplitudes, as anoxia can develop through the water column below frozen lake surface leading to very high CH_4 concentrations. Seasonal variations of oxic layer thickness was highlighted in the present case of Lake Kivu as the driver of seasonal variations.

The importance of CH_4 oxidation in the water column of Lake Kivu may explain low CH_4 fluxes observed. Only diffusive CH_4 fluxes are reported here, since ebullitive fluxes are supposed to be negligible due to the deepness of Lake Kivu and absence of extensive shallow zones (Borges et al. 2011), that according to Natchimuthu et al. (2015) contribute to strong spatial heterogeneity in CH_4 emissions from small shallow lakes. It should be noted that the parameterization used in the present work (Cole and Caraco 1998) might underestimate the computations of gas transfer velocities due to the large size (Read et al. 2012; Schilder et al. 2013) and diurnal temperature variations (Polsenaere et al. 2013; Podgrajsek et al. 2014) in Lake Kivu which have been reported to be large (Borges et al. 2012). Anyway, the Southern Basin of Lake Kivu was a source of CH_4 for the atmosphere throughout the year, but was a very small source of CH_4 for the atmosphere compared to other lakes globally, by an order of magnitude. The overall CH_4 emission for lakes is 3281 µmol m^{-2} day^{-1} globally, and 7779 µmol m^{-2} day^{-1} for tropical systems according to Bastviken et al. (2011), whereas the value for Lake Kivu was 85 µmol m^{-2} day^{-1}. Besides CH_4 oxidation, the low CH_4 emission can also be linked to the morphometric characteristics of Lake Kivu: large, deep and meromictic. Indeed, despite the fact that deep waters of Lake Kivu are extremely rich in CH_4 (60 km^3 of CH_4 are dissolved in deep waters; Schmid et al. 2005), the stratification of the water column (especially the main chemocline located at 250 m; Pasche et al. 2009) prevents the upward rise of this CH_4 towards surface waters. CH_4 from the upper part of the monimolimnion can only rise to surface waters by slow diffusion throughout the year, and by seasonal mixing of the epilimnion, which erodes the upper part of the monimolimnion (Borges et al. 2011; Pasche et al. 2011). Thus, due to this water column structure and an important bacterial CH_4 oxidation, surface waters of Lake Kivu have extremely low CH_4 concentrations when compared with bottom waters, which limits the CH_4 emissions to the atmosphere. Accordingly, the seasonal variations of CH_4 fluxes were estimated to be very low (rainy season mean flux of 96 µmol m^{-2} day^{-1} and dry season mean flux of 64 µmol m^{-2} day^{-1}).

This study focused on one station in the Southern Basin of Lake Kivu. However, due to the large size of Lake Kivu, some spatial heterogeneity can be observed. Numerous studies underline the importance of spatial variations of CH_4 emissions (e.g. Bastviken et al. 2004; Hofmann 2013; Schilder et al. 2013; Natchimuthu et al. 2015). During our study, 5 profiles were collected in the Northern Basin of the lake, which has a larger surface and is more exposed to wind. Available data (Supplemental Fig. 1) suggest that the station of Ishungu, in the Southern Basin, is not representative of the whole lake, since large differences in stratifications can be observed. Indeed, the Northern Basin showed deeper mixings and more pronounced gradients, which clearly influence vertical profiles of CH_4 and N_2O. The differences between the depths of the oxyclines impacted CH_4 concentrations in deep waters, and N_2O profiles were also quite different. Stratification clearly influences bacterial and archaeal communities; for example, İnceoğlu et al. (2015a) estimated that the relative abundances of *Betaproteobacteria* were 28 % and 46 % for the Northern and Southern Basins, respectively. Moreover, due to the large size of the lake, we cannot expect that wind velocities in the Northern Basin are the same as those in the Southern Basin.

However, CH_4 concentrations in surface waters (at 5 m) were quite similar in both stations ($R^2 = 0.625$), and means of N_2O concentrations in surface waters were 7 and 8 nmol L^{-1} in the Northern and Southern Basins, respectively. This suggests that CH_4 and N_2O fluxes in the Northern Basin are probably of the same order of magnitude as in the Southern Basin. Also, based on O_2 and temperature vertical profiles data obtained from March 2007 to April 2009 at nine stations in the lake (Borges et al. 2011), we can assume that the station of Ishungu is well representative of the Southern Basin, and even of the Western Basin and of the south part of the Eastern Basin (Supplemental Fig. 2 and Supplemental Table 2).

This study is, to our knowledge, the first one to report detailed data and long time-series of CH_4 and N_2O in a large tropical lake. Our data confirms that Lake Kivu has a very low CH_4 emission to the atmosphere despite having extremely large quantities of CH_4 in the bottom waters. Yet, CH_4 in surface waters showed seasonal variations that relate mixing events and deepening of the mixolimnion. The emissions of N_2O to the atmosphere were also modest although vertical profiles of N_2O show dynamic patterns with marked sources and sinks of N_2O in the water column. We were not able to determine from vertical profiles of N_2O concentrations if nitrification or denitrification or a combination of both was the process leading to N_2O accumulation in the water column that occurred at the oxic-anoxic interface. This suggests that process orientated studies quantifying denitrification and nitrification are required to further unravel C and N dynamics in this large meromictic tropical lake, as well as additional data on bacterial diversity and activity that are limited to two samplings (İnceoğlu et al. 2015a, b). The present data-set is the first to give a detailed description of the seasonal variations of the vertical distribution of CH_4 and N_2O in upper Lake Kivu (<100 m). Any deviation from the reported patterns will be indicative of changes in CH_4 and N_2O cycling and potential emission to the atmosphere related to the CH_4 extraction (Nayar 2009). Once the CH_4 is extracted in surface plants, the water is re-injected above the extraction point (to avoid diluting the resource). This re-injection could lead to the enrichment in NH_4^+ and changes in *N* cycling which could enhance N_2O emissions to the atmosphere. The water re-injection might lead to changes in water column stratification that as we have shown allows an effective removal of upward diffusing CH_4 by bacterial CH_4 oxidation. A decrease in this water column CH_4 sink would lead to enhanced CH_4 emissions to the atmosphere.

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