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# Biogeochemistry of a large and deep tropical lake (Lake Kivu, East Africa): insights from a stable isotope study covering an annual cycle

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## Abstract

During this study, we investigated the seasonal variability of the concentration and the stable isotope composition of several inorganic and organic matter reservoirs in the large, oligotrophic and deep tropical Lake Kivu (East Africa). Data were acquired during one year at a fornightly temporal resolution. The $\delta^{13}$C signature of the dissolved inorganic carbon (DIC) increased linearly with time during the rainy season, then suddenly decreased during the dry season due to vertical mixing with $\delta^{13}$C-depleted DIC waters. This pattern reflects the net autotrophic status of the mixed layer of Lake Kivu, contrary to the common observation that oligotrophic aquatic ecosystems tend to be net heterotrophic. The $\delta^{13}$C signature of the particulate organic carbon pool (POC) revealed the presence of a consistently abundant methanotrophic biomass in the oxycline throughout the year. We also noticed a seasonal shift during the dry season toward higher values in the $\delta^{15}$N of particulate nitrogen (PN) in the mixed layer and $\delta^{15}$N-PN was significantly related to the contribution of cyanobacteria to the phytoplankton assemblage, suggesting that rainy season conditions could be more favourable to atmospheric nitrogen-fixing cyanobacteria. Finally, zooplankton were slightly enriched in $\delta^{13}$C compared to the autochtonous POC pool, and the $\delta^{15}$N signature of zooplankton followed well the seasonal variability in $\delta^{15}$N-PN, being consistently $3.0 \pm 1.1$ ‰ heavier than the PN pool. Together, $\delta^{13}$C and $\delta^{15}$N analysis suggests that zooplankton directly incorporate algal-derived organic matter in their biomass, and they would rely almost exclusively on this source of organic matter throughout the year in general agreement with the very low allochthonous organic matter inputs from rivers in Lake Kivu.

## 1 Introduction

Stable carbon (C) and nitrogen (N) isotope analyses of diverse inorganic and organic components have been successfully used to assess the origin of organic matter and better understand its cycling in aquatic systems (Lehmann et al., 2004). For instance,





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an extensive sampling of diverse C and N pools during an annual cycle in the Loch Ness showed important seasonal variation of the $^{13}C/^{12}C$ and $^{15}N/^{14}N$ ratios in the crustacean zooplankton biomass, reflecting a diet switch from allochthonous to autochthonous organic matter sources (Grey et al., 2001). In small humic, boreal lakes with permanently anoxic waters, stable C isotope analyses allowed also to establish that methanotrophic bacteria could be an important food source for crustacean zooplankton, and hence methane-derived C contributed to fuel a large fraction of the lake food web (Kankaala et al., 2006). Analyses of the stable C isotope composition of carbonates and organic matter in sedimentary records of stratified lakes can also provide reliable information about past land use of the catchment (Castañeda et al., 2009), or be used to infer changes in lake productivity and climate (Schelske and Hodell, 1991). However, a detailed understanding of the stable isotope dynamics in the water column is a prerequisite for a good interpretation of isotope data from sedimentary archives (Lehmann et al., 2004).

A new paradigm progressively emerged during the last decade, proposing that freshwaters ecosystems are predominantly net heterotrophic, as respiration of organic matter exceeds autochthonous photosynthetic production (Del Giorgio et al., 1997; Cole, 1999; Duarte and Prairie, 2005). This concept seems to hold especially true for oligotrophic, unproductive ecosystems (Del Giorgio et al., 1997), where the C cycle would be dominated by substantial inputs of allochthonous organic matter of terrestrial origin, which support the production of heterotrophic organisms. Net heterotrophy has been recognised as one of the main cause for the net emission of carbon dioxide ($CO_2$) emissions from freshwater ecosystems to the atmosphere (Prairie et al., 2002). The global net $CO_2$ emissions from lakes would approximate 0.64 $Pg\,C\,yr^{-1}$ (Aufdenkampe et al., 2011). However, the current understanding of the role of inland waters on $CO_2$ and emissions could be biased because most observations were obtained in temperate and boreal systems, and mostly in medium to small-sized lakes, during open-water (ice-free) periods, but tropical and temperate lakes differed in some fundamental characteristics. Among them, the constantly high temperature and irradiance have strong





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effects on water column stratification and biological processes (Sarmento, 2012). For instance, primary production in tropical lakes has been recognised to be twice higher than in temperate lakes, on a given nutrient base (Lewis, 1996). Also, the contribution of dissolved primary production in oligotrophic tropical lake has been found to substantially more important than in their temperate counterparts (Morana et al., 2014).

East Africa harbours the densest aggregation of large tropical lakes (Bootsma and Hecky, 2003). Some of them are among the largest (Lakes Victoria, Tanganyika, Malawi), or deepest lakes in the world (Lakes Tanganyika, Malawi, Kivu) and consequently remain stratified all year round. Due to the size and the morphometric traits of the East African large lakes, pelagic processes are predominant in these systems, with the microbial food web playing a particularly essential role in organic matter transfer between primary producers and higher levels of the food web, as well as in nutrient cycling (Descy and Sarmento, 2008). Most of them are also characterized by highly productive fisheries that provide an affordable food source to local populations (Descy and Sarmento, 2008). However, while these lakes are potentially important components of biogeochemical cycles at the regional scale (Borges et al., 2011), and their significance for local populations from an economic perspective (Kaningini, 1995), the East African large lakes are relatively little studied, most probably because of their remote location combined to frequent political unrest.

In this study, we present a comprehensive data set covering a full annual cycle, including hydrochemical data and measurements of the concentration of dissolved methane ($CH_4$) and the concentrations and stable isotope compositions of dissolved inorganic carbon (DIC), dissolved and particulate organic carbon (DOC and POC), particulate nitrogen (PN), and zooplankton. Data were acquired during one full year at a fortnightly/monthly temporal resolution. We aimed to assess the net metabolic status of Lake Kivu, the seasonal and depth variability of sources of organic matter within the water column, and the relative contribution of autochthonous or allochthonous organic matter to the zooplankton. To our best knowledge, this is the first detailed study to as-





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sess the seasonal dynamics of different organic matter reservoirs by means of their stable isotope composition in any of the large East African lakes.

## 2 Material and methods

Lake Kivu (East Africa) is a large (2370 $km^2$) and deep (maximum depth of 485 m) meromictic lake located at the border between the Democratic Republic of the Congo and Rwanda. Its vertical structure consists of an oxic and nutrient-poor mixed layer down to a maximum of 70 m, and a permanently anoxic monimolimnion rich in dissolved gases ($CH_4$, and $CO_2$) and inorganic nutrients. Seasonal variation of the vertical position of the oxic-anoxic transition is driven by contrasting air humidity and incoming long-wave radiation between rainy (October–May) and dry (June–September) season (Thiery et al., 2014). The euphotic zone, defined at the depth at which light is 1 % of surface irradiance, is relatively shallow (annual average: 18 m, Darchambeau et al., 2014).

Sampling was carried out in the Southern Basin (02°20′ S, 28°58′ E) of Lake Kivu between January 2012 and May 2013 at a monthly or fortnightly time interval. Vertical oxygen ($O_2$), temperature and conductivity profiles were obtained with a Hydrolab DS5 multiprobe. The conductivity cell was calibrated with a 1000 µS $cm^{-1}$ (25 °C) Merck standard and the $O_2$ membrane probe was calibrated with humidity saturated ambient air. Water was collected with a 7 L Niskin bottle (Hydro–Bios) at a depth interval of 5 m from the lake surface to the bottom of the mixolimnion, at 70 m. Additionally, zooplankton was sampled with a 75 cm diameter, 55 µm mesh plankton net hauled along the whole mixolimnion (0–70 m).

Samples for $CH_4$ concentrations were collected in 50 mL glass serum bottles from the Niskin bottle with a tube, left to overflow, poisoned with 100 µL of saturated $HgCl_2$ and sealed with butyl stoppers and aluminium caps. Concentrations of $CH_4$ were measured by headspace technique using gas chromatography (Weiss, 1981) with flame ionization detection (SRI 8610C), after creating a 20 mL headspace with $N_2$ in the glass serum bottles, and then analyzed as described by Borges et al. (2011).





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Samples for stable C isotopic composition of dissolved inorganic carbon ($\delta^{13}$C-DIC) were collected by filling with water directly from the Niskin bottle 12 mL headspace vials (Labco Exetainer) without bubbles. Samples were preserved with the addition of 20 µL of a saturated $HgCl_2$ solution. Prior to the analysis of $\delta^{13}$C-DIC, a 2 mL helium headspace was created and 100 µL of phosphoric acid ($H_3PO_4$, 99 %) was added in the vial in order to convert all inorganic C species to $CO_2$. After overnight equilibration, 200 µL of gas was injected with a gastight syringe into a EA-IRMS (Thermo FlashHT with Thermo DeltaV Advantage). The obtained data were corrected for isotopic equilibration between dissolved and gaseous $CO_2$ as described in Gillikin and Bouillon (2007). Calibration of $\delta^{13}$C-DIC measurement was performed with the international certified standards IAEA-CO1 and LSVEC. Measurements of total alkalinity (TA) were carried out by open-cell titration with HCl 0.1 mol $L^{-1}$ according to Gran (1952) on 50 mL water samples, and data were quality checked with certified reference material obtained from Andrew Dickinson (Scripps Institution of Oceanography, University of California, San Diego, USA). Typical reproducibility of TA measurements was better than ±3 µmol $L^{-1}$. DIC concentration was computed from pH and TA measurements using the carbonic acid dissociation constants of Millero et al. (2006).

Samples for DOC concentration and stable C isotopic composition ($\delta^{13}$C-DOC) were filtered through pre-flushed 0.2 µm syringe filters, kept in 40 mL borosilicate vials with Teflon-coated screw caps and preserved with 100 µL of $H_3PO_4$ (50 %). Sample analysis was carried out with a IO Analytical Aurora 1030W where complete oxidation of the sample is ensured by the combination of sodium persulfate addition, heating, and UV radiation. Quantification and calibration of DOC and $\delta^{13}$C-DOC was performed with IAEA-C6 and an internal sucrose standard ($\delta^{13}C = -26.99 \pm 0.04$ ‰) calibrated against international reference materials.

Samples for POC and particulate nitrogen (PN) concentration and stable carbon and nitrogen isotope composition ($\delta^{13}$C-POC; $\delta^{15}$N-PN) were obtained by filtering a known volume of water on pre-combusted (overnight at 450 °C) 25 mm glass fiber filters (Advantec GF-75; 0.3 µm), kept frozen until subsequent processing. The filters were later





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decarbonated with HCl fumes for 4 h, dried and packed in silver cups prior to analysis on a EA-IRMS (Thermo FlashHT with Thermo DeltaV Advantage). Calibration of $\delta^{13}$C-POC, $\delta^{15}$N-PN, POC and PN measurements was performed with acetanilide ($\delta^{13}$C = −27.65 ± 0.05; $\delta^{15}$N = 1.34 ± 0.04) and leucine ($\delta^{13}$C = −13.47 ± 0.07; $\delta^{15}$N = 0.92 ± 0.06) as standards. All standards were internally calibrated against the international standard IAEA-C6 and IAEA-N1. Reproducibility of $\delta^{13}$C-POC and $\delta^{15}$N-PN measurement was typically better than ±0.2 ‰ and relative standard deviation for POC and PN measurement were always below 5 %. Samples for $\delta^{13}$C and $\delta^{15}$N of zooplankton were collected on precombusted 25 mm glass fiber filters (Advantec GF-75; 0.3 µm), and dried. Subsequent preparation of the samples and analysis on the EA-IRMS were performed similarly as described for the $\delta^{13}$C-POC and $\delta^{15}$N-PN samples.

Pigment concentrations were determined by high performance liquid chromatography (HPLC). 2–4 L of waters were filtered through Macherey–Nägel GF-5 filter (average retention of 0.7 µm). Pigment extraction was carried out in 10 mL of 90 % HPLC grade acetone. After two sonication steps of 15 min separated by an overnight period at 4 °C, the pigments extracts were stored in 2 mL amber vials at −25 °C. HPLC analysis was performed following the gradient elution method described in Wright et al. (1991), with Waters system comprising photodiode array and fluorescence detectors. Calibration was made using commercial external standards (DHI Lab Products, Denmark). Reproducibility for pigment concentration measurement was better than 7 %. Pigment concentrations were processed with the CHEMTAX software (CSIRO Marine Laboratories) using input ratio matrices adapted for freshwater phytoplankton (Descy et al., 2000). Data processing followed a procedure similar to that of Sarmento et al. (2006) in Lake Kivu, that allows to estimate chlorophyll *a* (Chl *a*) biomass of cyanobacteria, taking into account variation of pigment ratios with season and depth.





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## 3 Results

Analysis of the vertical and seasonal variability of temperature and dissolved $O_2$ concentrations during 18 months allow to divide the annual cycle into two distinct limnological periods. Rainy season conditions resulted in a thermal stratification within the mixolimnion (October–June) while the dry season was characterized by deeper vertical mixing of the water column down to the upper part of the permanent chemocline at 65 m (July–September) (Fig. 1a). The vertical position of the oxycline varied seasonally: the oxic-anoxic transition reached its deepest point (65 m) during the dry season, then became gradually shallower after the re-establishment of the thermal stratification within the mixolimnion at the start of the following rainy season to finally stabilize at approximately 35 m, corresponding to the bottom of the mixed layer during the rainy season (Fig. 1b). The temporal variability of the vertical distribution of $CH_4$ corresponded well with the seasonal variation of the oxycline. The $CH_4$ concentrations were very high in the monimolimnion throughout the year (average at 70 m: 356 ± 69 µmol $L^{-1}$, $n = 24$) but sharply decreased at the oxic-anoxic transition, and were 4 orders of magnitude lower in surface waters (annual average at 10 m: 0.062 ± 0.016 µmol $L^{-1}$, $n = 24$) (Fig. 1c).

DIC concentrations in the mixed layer were very high (annual average at 10 m: 11.942 ± 0.223 µmol $L^{-1}$, $n = 24$) and did not show any consistent seasonal pattern (not illustrated). The $\delta^{13}$C-DIC values were vertically homogeneous in the mixed layer but gradually decreased in the oxycline to reach minimal values at 70 m (Fig. 2a). $\delta^{13}$C-DIC values in the mixed layer increased linearly with time during the rainy season ($r^2 = 0.79$, $n = 12$), then suddenly decreased at the start of the dry season due to the vertical mixing with $^{13}$C-depleted DIC from deeper waters (Fig. 2b). The DOC concentration (142 ± 20 µmol C $L^{-1}$, $n = 304$) and $\delta^{13}$C-DOC signature (−23.2 ± 0.4 ‰, $n = 304$) did not show any consistent variations with depth or time in the mixolimnion during all the sampling period. A vertical profile performed down to the lake floor revealed that the $\delta^{13}$C-DOC did not vary significantly neither in the monimolimnion (vertical profile





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average: −23.0 ‰ ±0.2, $n = 18$, Fig. 3), however an important increase in DOC concentrations was observed starting at 260 m (Fig. 3), to reach a maximum near the lake floor (350 m, 301 µmol $L^{-1}$).

The concentration of POC was substantially higher in the mixed layer than below in the mixoliminion all over the year. However during the dry season, POC concentrations in the oxycline (∼ 50–65 m) were found to be as high as in surface water (Fig. 4a). POC concentration integrated over the mixolimnion (0–70 m) averaged 2157 ± 4 mmol $m^{-2}$ ($n = 19$) and did not vary between the rainy and dry seasons. The isotopic signature of the POC pool stayed almost constant throughout the year in the mixed layer (at 10 m: −23.8 ± 0.8 ‰, $n = 19$), but at the top of the oxic-anoxic transition, $\delta^{13}$C-POC values systematically decreased sharply (at the oxic-anoxic transition: −33.9 ± 4.3 ‰, $n = 19$) (Fig. 4b). The vertical position of this abrupt excursion toward more negative values followed closely the oxycline, and was therefore located deeper in the water column during the dry season.

The concentrations of the PN pool in the water column followed the same pattern than POC (Fig. 4c). The PN pool was larger in the mixed layer than below in the water column during most of year. However, higher PN concentrations were measured in the oxycline during the dry season (Fig. 4c). The molar C : N ratio in the mixolimnion varied depending on season, being significantly higher ($t$ test; $p < 0.05$) during the rainy season (11.2 ± 2.4, $n = 15$) than during the dry season (8.1 ± 0.9, $n = 4$). $\delta^{15}$N-PN values in the mixed layer oscillated between 0 and 1 ‰ during the rainy season but shifted toward significantly higher values during the dry season (3–4 ‰) (Fig. 5a). $\delta^{15}$N-zooplankton mirrored the seasonal variability of $\delta^{15}$N-PN in the mixed layer with a small time-shift, ranging between 3–5 ‰ during the rainy season, then increasing at the start of dry season to reach a maximum of 7.5 ‰ (Fig. 5a). The difference between $\delta^{15}$N-zooplankton and $\delta^{15}$N-PN was on average 3.0 ± 1.1 ‰ ($n = 19$) and did not follow any clear seasonal pattern. The $\delta^{13}$C signature of the zooplankton was on average −22.9 ± 0.8 ‰ ($n = 19$) and did not vary between seasons (not shown).





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Chlorophyll *a* concentrations exhibited little variation during the rainy season (average 74 ± 15 mg Chl $a\,m^{-2}$, $n = 16$) but increased significantly during the dry season to reach a maximal value (190 mg Chl $a\,m^{-2}$) in September 2012 (Fig. 5b). This increase corresponded with a change in phytoplankton community composition. The relative contribution of cyanobacteria to the phytoplankton assemblage, as assessed from the concentration of marker pigments, was smaller during the dry season than in the preceding (*t* test; $p < 0.01$, $\text{mean}_{\text{January–June}} = 23.4 \pm 5.5\,\%$, $\text{mean}_{\text{July–September}} = 9.4 \pm 1.3\,\%$) and the following (*t* test; $p < 0.05$, $\text{mean}_{\text{October–May}} = 14.6 \pm 3.8\,\%$, $\text{mean}_{\text{July–September}} = 9.4 \pm 1.3\,\%$) rainy seasons (Fig. 5b).

## 4 Discussion

Stable isotope analysis of DIC is a useful tool for understanding the fate of C in aquatic ecosystems and could provide information on the lake metabolism, defined as the balance between gross primary production and community respiration of organic matter. Primary producers preferentially incorporate the lighter isotopes ($^{12}C$) into the biomass with the consequence that the heavier isotopes ($^{13}C$) accumulate into the DIC pool, whereas mineralization releases $^{13}C$-depleted $CO_2$ from the organic matter being respired, into the DIC pool. Therefore, increasing primary production leads to higher $\delta^{13}C$-DIC but increasing respiration should tends to decrease $\delta^{13}C$-DIC (Bade et al., 2004). For instance, several studies conducted in temperate lakes have reported a significant increase in $\delta^{13}C$-DIC during summer, resulting from increased primary production (Herczeg, 1987; Hollander and McKenzie, 1991). In Lake Kivu, a linear increase of $\delta^{13}C$-DIC with time was observed during the stratified rainy season. It appears unlikely that this linear isotopic enrichment of the DIC pool in the mixed layer would be due to physical processes: the $\delta^{13}C$-DIC signature of the DIC input from the inflowing rivers (Borges et al., 2014) and deep waters (Fig. 3a) was lower than the $\delta^{13}C$-DIC in the mixed layer. Therefore, the increase in $\delta^{13}C$ during the rainy season would reflect a net DIC biogenic uptake of a biological origin. However, a small de-





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crease in $\delta^{13}$C-DIC was recorded early in July 2012, but was concomitant with the deepening of the mixed layer observed during the dry season. As the depth profile of $\delta^{13}$C-DIC revealed that the DIC pool was isotopically lighter in the bottom of the mixolimnion, the measurement of lower $\delta^{13}$C-DIC values during the dry season could resulted from the seasonal vertical mixing of surface waters with bottom waters containing relatively $^{13}$C-depleted DIC. Overall, the seasonal variability of $\delta^{13}$C-DIC in the mixed layer would suggests that photosynthetic $CO_2$ fixation exceed the respiration of organic matter, implying that the surface waters of Lake Kivu are net autotrophic, and hence that the microbial food web would be supported by autochthonous organic C sources. This observation is supported by the recent study of Borges et al. (2014) who reported, based on a DIC mass balance approach, that the mixed layer of Lake Kivu was net autotrophic while acting as a source of $CO_2$ to atmosphere driven by geogenic $CO_2$ inputs. These results are in contradiction with the commonly held view that oligotrophic lacustrine and marine systems tend to be net heterotrophic (Del Giorgio et al., 1997; Cole, 1999). However, paradigms established with data from comparatively small temperate or humic boreal lakes may not directly apply to large tropical lakes (Bootsma and Hecky, 2003). First, due to the warmer temperature in the tropics phytoplankton production is comparatively higher in the East African large lakes compared with the Laurentian Great lakes, despite similar phytoplankton abundance (Bootsma and Hecky, 2003). Second, the fact that organic matter respiration in Lake Kivu would not exceed autochtonous primary production may partly be related to some of the morphometrical traits of the lake. The ratio between the lake surface area (2370 km$^2$) and its catchment area (5100 km$^2$) is particularly small, among the lowest globally (Spigel and Coulter, 1996), and therefore riverine inputs of dissolved and particulate organic matter from its catchment area (0.7–3.3 mmol m$^{-2}$ d$^{-1}$, Borges et al., 2014) are minimal compared to the phytoplankton particulate primary production (49 mmol m$^{-2}$ d$^{-1}$; Darchambeau et al., 2014), being approximately 50 times lower. Further, Lake Kivu is relatively organic poor with DOC concentrations of $\sim$ 0.2 mmol L$^{-1}$ in contrast with boreal





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humic lakes with DOC concentrations on average of ~ 1 mmol $L^{-1}$ (Sobek et al., 2007) with values up to ~ 4.5 mmol $L^{-1}$ (Weyhenmeyer and Karlsson, 2009).

Despite the net autotrophic status of the mixed layer of Lake Kivu, the $\delta^{13}C$ data indicate a difference in the origins of the POC and DOC pools in the mixed layer. Indeed, the $\delta^{13}C$-DOC showed very little variation and appeared to be vertically and temporally uncoupled from the POC pool in the mixed layer (Fig. 6). A recent study (Morana et al., 2014) demonstrated that phytoplankton extracellular release of DOC is relatively high in Lake Kivu, and the fresh and labile autochthonous DOC produced by cell lysis, grazing or phytoplankton excretion, that would reflect the $\delta^{13}C$ signature of POC, is quickly mineralized by heterotrophic bacteria. Therefore, it appears that the freshly produced autochtonous DOC would contribute less than 1 % of the total DOC pool (Morana et al., 2014), and as standing stocks of phytoplankton-derived DOC seems very small, it can be hypothesized that the bulk DOC pool is mainly composed of older, more refractory compounds that would reach the mixed layer through vertical advective and diffusive fluxes. Indeed, the $\delta^{13}C$ signature of the DOC in the monimolimnion (80–370 m, $-23.0 \pm 0.2$ ‰, $n = 24$) did not differ from the $\delta^{13}C$-DOC in the mixolimnion (0–70 m, $-23.2 \pm 0.2$ ‰, $n = 5$), suggesting that they share the same origin (Fig. 4).

The concentration of the POC pool varied largely with depth, being the highest in the 0–20 m layer, i.e. roughly the euphotic zone. However, during the dry season, POC concentrations was almost as high in the oxycline than in surface waters. High POC concentrations in deep waters have frequently been observed in lakes, usually as a result from the resuspension of benthic sediments near the lake floor or to the accumulation of sedimenting material in density gradients (Hawley and Lee, 1999). However, in the deep Lake Kivu, this maximum POC zone is located approximately 300 m above the lake floor and is characterized by a strong depletion in $^{13}C$ of the POC pool. While DIC would be the major C source of the POC pool in the mixed layer, the important decrease of $\delta^{13}C$-POC values observed in the oxycline suggests that another $^{13}C$-depleted C source was actively incorporated into the biomass at the bottom of the mixolimnion. Slight depletion in $^{13}C$ of the POC pool in oxyclines, such as in the Black





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Sea, has sometimes been interpreted as a result of to the heterotrophic mineralization of the sedimenting organic matter (Çoban-Yıldız et al., 2006), but it seems unlikely that, in Lake Kivu, heterotrophic processes could have caused an abrupt excursion of $\delta^{13}$C-POC to values as low as −41.6 ‰ (65 m, 22 August 2012). Such large isotopic depletion of the POC pool in the water column have been reported by Blees et al. (2014), who measured $\delta^{13}$C-POC as low as −49 ‰ in Lake Lugano, and they were related to high methanotrophic activity. In Lake Kivu, $CH_4$ concentrations were found to decrease sharply at the oxic-anoxic transition (Borges et al., 2011), and the dissolved $CH_4$ that reached the oxycline via turbulent diffusivity and vertical advection (Schmid et al., 2005) is known to be isotopically light, with a $\delta^{13}$C signature of approximately −60 ‰ (Pasche et al., 2011; Morana et al., 2014). Therefore, the vertical patterns in $CH_4$ concentrations and $\delta^{13}$C-POC values observed during this study suggests that a substantial part of $CH_4$ was consumed and incorporated into the microbial biomass in the oxycline. Indeed, experiments carried out in Lake Kivu in February 2012 and September 2012 showed that microbial $CH_4$ oxidation was significant in the oxycline, and phospholipid fatty acids analysis revealed high abundance of methanotrophic bacteria of type I at the same depths (Morana et al., 2014). With estimates of the isotope fractionation factor during microbial $CH_4$ oxidation (1.016, Morana et al., 2014), and of the $\delta^{13}$C-$CH_4$ at each sampling point, it is possible to estimate the theoretical $\delta^{13}$C signature of methanotrophic organisms at each depth. Note that the $\delta^{13}$C-$CH_4$ was not directly measured during this study but a very strong linear correlation between the log-transformed $CH_4$ concentrations and $\delta^{13}$C-$CH_4$ was found along vertical profiles performed in February and September 2012 in Lake Kivu ($\delta^{13}$C-$CH_4$ = −7.911 log($CH_4$) − 13.027; $r^2$ = 0.87, $n$ = 34; Morana et al., 2014). Hence the $\delta^{13}$C-$CH_4$ at each sampling point between January 2012 and May 2013 can be approximated from the measured $CH_4$ concentrations, using this empirical relationship. Then, a simple isotope mixing model with the calculated $\delta^{13}$C signature of methanotrophs and the average $\delta^{13}$C-POC in the mixed layer as end-members allowed to determine the contribution of $CH_4$-derived C to POC at each sampling depth. It appears that 4.4 ± 1.9 %





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($n$ = 13) and 6.4 ± 1.6 % ($n$ = 5) of the depth-integrated POC pool in the mixolimnion derived from $CH_4$ incorporation into the biomass during the rainy and dry season, respectively, and these percentages did not significantly differ between seasons (two-tailed $t$ test, $p$ = 0.055). Nevertheless, the low $\delta^{13}C$ signatures measured locally in the oxycline indicate that the contribution of $CH_4$-derived C could be episodically as high as 50 % (65 m, 22 August 2012). Overall, this illustrates that, whatever the season, $CH_4$-derived organic C accounted for a significant part of the POC pool, and highlight the ecological importance of microbial $CH_4$ oxidation processes in the water column of Lake Kivu. Along with heterotrophic mineralization of the sinking organic matter, and presumably other chemoautotrophic processes occurring in the oxycline such as nitrification (Llirós et al., 2010), $CH_4$ oxidation would have contributed substantially to $O_2$ consumption in the water column and was partly responsible for the seasonal uplift of the oxycline observed after the re-establishment of the thermal stratification during the rainy season. Furthermore, the methanotrophs in the oxycline would actively participate to the dissolved inorganic phosphorus (DIP) uptake, and hence would contribute to exert an indirect control on phytoplankton by constantly limiting the vertical DIP flux to the illuminated surface waters (Haberyan and Hecky, 1987). Indeed, phytoplankton in Lake Kivu suffers of a severe P limitation throughout the year as pointed out by the relatively high sestonic C : P ratio (256.3 ± 75.1 ; Sarmento et al., 2009; Darchambeau et al., 2014).

The $\delta^{15}N$ signature of the autochthonous organic matter in the mixed layer of Lake Kivu oscillated around 0 ‰ during the rainy season in Lake Kivu but was significantly higher during the dry season (3–4 ‰). Also, the $\delta^{15}N$-PN in the mixed layer correlated negatively with the proportion of cyanobacteria in waters (Fig. 7, Pearson's $r$: −0.65, $p$ = 0.004, $n$ = 17). This pattern may highlight the seasonal importance of $N_2$-fixing cyanobacteria in Lake Kivu during the rainy season. Indeed, the $\delta^{15}N$ signature of atmospheric $N_2$ is close to 0 ‰ and isotope fractionation during cyanobacterial $N_2$-fixation is known to be small (Fogel and Cifuentes, 1993). Several studies carried out in marine (Pacific Ocean and Gulf of Mexico) and lacustrine (Lake Lugano) systems





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have shown that $\delta^{15}$N-PN varied between −2 and +1 ‰ when $N_2$-fixing cyanobacteria were dominating the phytoplankton assemblage (Wada, 1976; Macko et al., 1984; Lehmann et al., 2004). Moreover, a good relationship between the $\delta^{15}$N-PN and the abundance of $N_2$-fixing cyanobacteria has already been reported for others systems, such as coastal lagoon (Lesutienė et al., 2014). In Lake Victoria, biological $N_2$ fixation has been identified has the largest input of N, exceeding atmospheric deposition and river inputs, and $N_2$ fixation has been found to increase with light availability (Mugidde et al., 2003). This suggests that during the rainy season, when thermal stratification of the mixolimnion leads to reduced nitrogen supply combined with exposure to high light levels, $N_2$-fixing cyanobacteria would have a competitive advantage which may explain their seasonally higher contribution to the autochtonous organic matter pool (Sarmento et al., 2006). Indeed, the significantly higher molar C : N ratio during the rainy season than the dry season indicates that N-limitation in the mixed layer was stronger during the rainy season (this study, Sarmento et al., 2009). By contrast, the deepening of the mixed layer during the dry season leads to increased nutrients input and reduced light availability that favours alternative phytoplankton strategies (Hecky and Kling, 1987; Sarmento et al., 2006; Darchambeau et al., 2014), and consequently the proportion $N_2$-fixing cyanobacteria decreases. A similar seasonal pattern of $N_2$ fixation was reported in Lake Victoria by Mugidde et al. (2003). In contrast with the rather constant $\delta^{13}$C signature of zooplankton (−22.9 ± 0.8 ‰), the $\delta^{15}$N analysis revealed that the $\delta^{15}$N of zooplankton varied importantly, following well the seasonal change in $\delta^{15}$N-PN in the mixed layer. The difference between $\delta^{15}$N-zooplankton and $\delta^{15}$N-PN ($\Delta^{15}N_{Zoo\text{-}PN}$) was on average 3.2 ± 1.0 ‰ throughout the year while it was on average enriched in $^{13}$C ($\Delta^{13}C_{Zoo\text{-}POC}$) by 0.9 ± 0.8 ‰. In nature, comparison of the $\delta^{15}$N signature of consumers and their diet indicates that the $\delta^{15}$N value increases consistently with the trophic level, because of the preferential excretion of the isotopically lighter $^{14}$N (Montoya et al., 2002). However the C isotope fractionation consumers and diet is usually considered to be less than 1 ‰ (Sirevåg et al., 1977) The constant $\Delta^{15}N_{Zoo\text{-}PN}$ value found in Lake Kivu is within the range of trophic level enrichment between algae and





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*Daphnia magna* (~ 2 to 5 ‰) estimated in laboratory experiment (Adams and Sterner, 2000), and very close to the cross-system trophic enrichment value (3.4 ± 1.0 ‰) proposed by Post (2002). Together with the slight enrichment in $^{13}C$ compared with the autochtonous POC pool, $\delta^{13}C$ and $\delta^{15}N$ analysis suggests that zooplankton directly incorporate algal-derived organic matter in their biomass (Masilya, 2011), and they would rely almost exclusively on this source of organic matter throughout the year. This is in general agreement with the very low allochthonous organic matter inputs from rivers in Lake Kivu (Borges et al., 2014).

In summary, stable isotope data revealed large seasonal variability in the $\delta^{15}N$ signature of the PN pool, most likely related to changes in the phytoplankton assemblage and to $N_2$-fixation. In contradiction with the common observation that oligotrophic aquatic ecosystems tend to be net heterotrophic, the seasonality of $\delta^{13}C$-DIC suggests that the mixed layer of Lake Kivu is net autotrophic, supporting the conclusions of Borges et al. (2014), based on DIC mass balance considerations. The $\delta^{13}C$-POC showed an important variation with depth due the abundance of methanotrophic bacteria in the oxycline that fixed the lighter $CH_4$-derived C into their biomass. The $\delta^{13}C$-POC and $\delta^{13}C$-DOC appeared to be uncoupled vertically and temporally, which could indicates that most of the DOC pool was composed of relatively refractory compounds. Finally, the $\delta^{13}C$ of zooplankton mirrored the $\delta^{13}C$ signature of the autochthonous POC pool, and its $\delta^{15}N$ signature followed the seasonal variability of the $\delta^{15}N$-PN pool in good agreement with the expected consumer-diet isotope fractionation. This suggests that zooplankton would rely throughout the year on algal-derived biomass as a organic C source. Finally, the detailed analysis of the stable isotope composition of diverse organic and inorganic components carried out during this study allowed to trace the organic matter dynamics in Lake Kivu during one seasonal cycle, and might be useful to improve the interpretation of sedimentary archives of this large and deep tropical lake.

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## References

Adams, T. S. and Sterner, R. W.: The effect of dietary nitrogen content on trophic level $^{15}N$ enrichment, Limnol. Oceanogr., 45, 601–607, 2000.

Aufdenkampe, A. K., Mayorga, E., Raymond, P. A., Melack, J. M., Doney, S. C., Alin, S. R., Aalto, R. E., and Yoo, K.: Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere, Front. Ecol. Environ., 9, 53–60, 2011.

Bade, D. L., Carpenter, S. R., Cole, J. J., Hanson, P. C., and Hesslein, R. H.: Controls of $\delta^{13}C$-DIC in lakes: geochemistry, lake metabolism, and morphometry, Limnol. Oceanogr., 49, 1160–1172, 2004.

Blees, J., Niemann, H., Wenk, C. B., Zopfi, J., Schubert, C. J., Kirf, M. K., Veronesi, M. L., Hitz, C., and Lehmann, M. F.: Micro-aerobic bacterial methane oxidation in the chemocline and anoxic water column of deep south-Alpine Lake Lugano (Switzerland), Limnol. Oceanogr., 59, 311–324, 2014.

Bootsma, H. A. and Hecky, R. E.: A comparative introduction to the biology and limnology of the African Great Lakes, J. Great Lakes Res., 29, 3–18, 2003.

Borges, A. V., Abril, G., Delille, B., Descy, J. P., and Darchambeau, F.: Diffusive methane emissions to the atmosphere from Lake Kivu (Eastern Africa), J. Geophys. Res., 116, G03032, doi:10.1029/2011JG001673, 2011.

Borges, A. V., Morana, C., Bouillon, S., Servais, P., Descy, J.-P., and Darchambeau, F.: Carbon cycling of Lake Kivu (East Africa): net autotrophy in the epilimnion and emis-





BGD
11, 17227–17254, 2014



sion of $CO_2$ to the atmosphere sustained by geogenic inputs, PloS One, 9, e109500, doi:10.1371/journal.pone.0109500, 2014.
Castañeda, I. S., Werne, J. P., Johnson, T. C., and Filley, T. R.: Late Quaternary vegetation history of southeast Africa: the molecular isotopic record from Lake Malawi, Palaeogeogr. Palaeocl., 275, 100–112, 2009.
Çoban-Yıldız, Y., Altabet, M. A., Yılmaz, A., and Tğru, S.: Carbon and nitrogen isotopic ratios of suspended particulate organic matter (SPOM) in the Black Sea water column, Deep-Sea Res. Pt. II, 53, 1875–1892, 2006.
Cole, J. J.: Aquatic microbiology for ecosystem scientists: new and recycled paradigms in ecological microbiology, Ecosystems, 2, 215–225, 1999.
Darchambeau, F., Sarmento, H., and Descy, J.-P.: Primary production in a tropical large lake: the role of phytoplankton composition, Sci. Total Environ., 473, 178–188, 2014.
Del Giorgio, P. A., Cole, J. J., and Cimbleris, A.: Respiration rates in bacteria exceed phytoplankton production in unproductive aquatic systems, Nature, 385, 148–151, 1997.
Descy, J. P. and Sarmento, H.: Microorganisms of the East African Great Lakes and their response to environmental changes, Freshwater Reviews, 1, 59–73, 2008.
Descy, J. P., Higgins, H. W., Mackey, D. J., Hurley, J. P., and Frost, T. M.: Pigment ratios and phytoplankton assessment in northern Wisconsin lakes, J. Phycol., 36, 274–286, 2000.
Duarte, C. M. and Prairie, Y. T.: Prevalence of heterotrophy and atmospheric $CO_2$ emissions from aquatic ecosystems, Ecosystems, 8, 862–870, 2005.
Fogel, M. L. and Cifuentes, L. A.: Isotope fractionation during primary production, in: Organic Geochemistry, edited by: Engel, M. H. and Macko S. A., Plenum Press, New York, 73–98, 1993.
Gillikin, D. P. and Bouillon, S.: Determination of $\delta^{18}O$ of water and $\delta^{13}C$ of dissolved inorganic carbon using a simple modification of an elemental analyserisotope ratio mass spectrometer: an evaluation, Rapid Commun. Mass Sp., 21, 1475–1478, 2007.
Gran, G.: Determination of the equivalence point in potentiometric titrations. Part II, Analysis, 77, 661–671, 1952.
Grey, J., Jones, R. I., and Sleep, D.: Seasonal changes in the importance of the source of organic matter to the diet of zooplankton in Loch Ness, as indicated by stable isotope analysis, Limnol. Oceanogr., 46, 505–513, 2001.
Haberyan, K. A. and Hecky, R. E.: The late Pleistocene and Holocene stratigraphy and paleolimnology of Lakes Kivu and Tanganyika, Palaeogeogr. Palaeocl., 61, 169–197, 1987.





BGD
11, 17227–17254, 2014



Hawley, N. and Lee, C. H.: Sediment resuspension and transport in Lake Michigan during the unstratified period, Sedimentology, 46, 791–805, 1999.
Hecky, R. E. and Kling, H. J.: Phytoplankton ecology of the great lakes in the rift valleys of Central Africa, Arch. Hydrobiol. – Beiheft Ergebnisse der Limnologie, 25, 197–228, 1987.
Herczeg, A. L.: A stable carbon isotope study of dissolved inorganic carbon cycling in a softwater lake, Biogeochemistry, 4, 231–263, 1987.
Hollander, D. J. and McKenzie, J. A.: $CO_2$ control on carbon-isotope fractionation during aqueous photosynthesis: a paleo-$pCO_2$ barometer, Geology, 19, 929–932, 1991.
Kaningini, M.: Etude de la croissance, de la reproduction et de l'exploitation de *Limnothrissa miodon* au lac Kivu, bassin de Bukavu (Zaïre), Ph.D. thesis, Facultés Universitaires Notre Dame de la Paix, Namur, Belgium, 1995.
Kankaala, P., Taipale, S., Grey, J., Sonninen, E., Arvola, L., and Jones, R. I.: Experimental $\delta^{13}C$ evidence for a contribution of methane to pelagic food webs in lakes, Limnol. Oceanogr., 51, 2821–2827, 2006.
Lehmann, M. F., Bernasconi, S. M., McKenzie, J. A., Barbieri, A., Simona, M., and Veronesi, M.: Seasonal variation of the $\delta^{13}C$ and $\delta^{15}N$ of particulate and dissolved carbon and nitrogen in Lake Lugano: constraints on biogeochemical cycling in a eutrophic lake, Limnol. Oceanogr., 49, 415–429, 2004.
Lesutienė, J., Bukaveckas, P. A., Gasūnaitė, Z. R., Pilkaitytė, R., and Razinkovas-Baziukas, A.: Tracing the isotopic signal of a cyanobacteria bloom through the food web of a Baltic Sea coastal lagoon, Estuar. Coast. Shelf S., 138, 47–56, 2014.
Lewis, W. M. J.: Tropical lakes: how latitude makes a difference. in: Perspectives Tropical Limnology, edited by: Schiemer, F. and Boland, K. T., SPB Academic Publishing, Amsterdam, 43–64, 1996.
Llirós, M., Gich, F., Plasencia, A., Auguet, J. C., Darchambeau, F., Casamayor, E. O., Descy, J.-P., and Borrego, C.: Vertical distribution of ammonia-oxidizing crenarchaeota and methanogens in the epipelagic waters of Lake Kivu (Rwanda-Democratic Republic of the Congo), Appl. Environ. Microb., 76, 6853–6863, 2010.
Macko, S. A., Fogel, M. L., Hare, P. E., and Hoering, T. C.: Isotopic fractionation of nitrogen and carbon in the synthesis of amino acids by microorganisms, Chemical Geology: Isotope Geoscience Section, 65, 79–92, 1987.





BGD
11, 17227–17254, 2014



Masilya, P.: Ecologie alimentaire compare de Limnothrissa miodon et de Lamprichthys tanganicanus au lac Kivu (Afrique de l'Est), Ph.D. thesis, Facultés Universitaires Notre Dame de la Paix, Namur, Belgium, 2011.

Millero, F. J., Graham, T. B., Huang, F., Bustos-Serrano, H., and Pierrot, D.: Dissociation constants of carbonic acid in sea water as a function of salinity and temperature, Mar. Chem., 100, 80–94, 2006.

Montoya, J. P., Carpenter, E. J., and Capone, D. G.: Nitrogen fixation and nitrogen isotope abundances in zooplankton of the oligotrophic North Atlantic, Limnol. Oceanogr., 47, 1617–1628, 2002.

Morana, C., Sarmento, H., Descy, J.-P., Gasol, J. M., Borges, A. V., Bouillon, S., and Darchambeau, F.: Production of dissolved organic matter by phytoplankton and its uptake by heterotrophic prokaryotes in large tropical lakes, Limnol. Oceanogr., 59, 1364–1375, 2014.

Mugidde, R., Hecky, R. E., Hendzel, L. L., and Taylor, W. D.: Pelagic nitrogen fixation in Lake Victoria (East Africa), J. Great Lakes Res., 29, 76–88, 2003.

Pasche, N., Schmid, M., Vazquez, F., Schubert, C. J., Wüest, A., Kessler, J. D., Pack, M. A., Reeburgh, W. S., and Bürgmann, H.: Methane sources and sinks in Lake Kivu, J. Geophys. Res., 116, G03006, doi:10.1029/2011JG001690, 2011.

Post, D. M.: Using stable isotopes to estimate trophic position: models, methods, and assumptions, Ecology, 83, 703–718, 2002.

Prairie, Y. T., Bird, D. F., and Cole, J. J.: The summer metabolic balance in the epilimnion of southeastern Quebec lakes, Limnol. Oceanogr., 47, 316–321, 2002.

Sarmento, H.: New paradigms in tropical limnology: the importance of the microbial food web, Hydrobiologia, 686, 1–14, 2012.

Sarmento, H., Isumbisho, M., and Descy, J.-P.: Phytoplankton ecology of Lake Kivu (eastern Africa), J. Plankton Res., 28, 815–829, 2006.

Sarmento, H., Isumbisho, M., Stenuite, S., Darchambeau, F., Leporcq, B., and Descy, J.-P.: Phytoplankton ecology of Lake Kivu (eastern Africa): biomass, production and elemental ratios, Proc. Int. Assoc. Theor., 30, 709–713, 2009.

Schelske, C. L. and Hodell, D. A.: Recent changes in productivity and climate of Lake Ontario detected by isotopic analysis of sediments, Limnol. Oceanogr., 36, 961–975, 1991.

Schmid, M., Halbwachs, M., Wehrli, B., and Wüest, A.: Weak mixing in Lake Kivu: new insights indicate increasing risk of uncontrolled gas eruption, Geochem. Geophy. Geosy., 6, 2005.





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11, 17227–17254, 2014



Sirevåg, R., Buchanan, B. B., Berry, J. A., and Troughton, J. H.: Mechanisms of $CO_2$ fixation in bacterial photosynthesis studied by the carbon isotope fractionation technique, Arch. Microbiol., 112, 35–38, 1977.

Sobek, S., Tranvik, L. J., Prairie, Y. T., Kortelainen, P., and Cole, J. J.: Patterns and regulation of dissolved organic carbon: an analysis of 7500 widely distributed lakes, Limnol. Oceanogr., 52, 1208–1219, 2007.

Spigel, R. H. and Coulter, G. W.: Comparison of hydrology and physical limnology of the East African Great Lakes: Tanganyika, Malawi, Victoria, Kivu, and Turkana (with reference to some North American Great Lakes), in: The Limnology, Climatology and Paleoclimatology of the East Afican Lakes, edited by: Johnson, T. C. and Odada, E. O., Gordon and Breach Publishers, The Netherlands, 103–139, 1996.

Thiery, W., Martynov, A., Darchambeau, F., Descy, J.-P., Plisnier, P.-D., Sushama, L., and van Lipzig, N. P. M.: Understanding the performance of the FLake model over two African Great Lakes, Geosci. Model Dev., 7, 317–337, doi:10.5194/gmd-7-317-2014, 2014.

Wada, E. and Hattori, A.: Natural abundance of $^{15}N$ in particulate organic matter in the North Pacific Ocean, Geochim. Cosmochim. Ac., 40, 249–251, 1976.

Weiss, R. F.: Determinations of carbon dioxide and methane by dual catalyst flame ionization chromatography and nitrous oxide by electron capture chromatography, J. Chromatogr. Sci., 19, 611–616, 1981.

Weyhenmeyer, G. A. and Karlsson, J.: Nonlinear response of dissolved organic carbon concentrations in boreal lakes to increasing temperatures, Limnol. Oceanogr., 54, 2513–2519, 2009.

Wright, S. W., Jeffrey, S. W., Mantoura, R. F. C., Llewellyn, C. A., Bjornland, T., Repeta, D., and Welschmeyer, N.: Improved HPLC method for the analysis of chlorophylls and carotenoids from marine phytoplankton, Mar. Ecol.-Prog. Ser., 77, 183–196, 1991.





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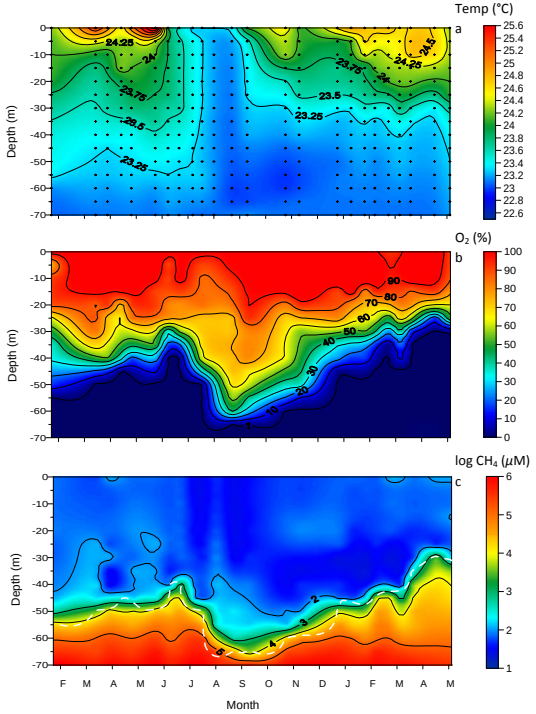


**Figure 1.** Temporal variability of **(a)** temperature (°C), **(b)** oxygen saturation (%), and **(c)** the log-transformed $CH_4$ concentration (µmol $L^{-1}$) in the mixolimnion of Lake Kivu, between February 2012 and May 2013. Small crosses in the figure **(a)** represent each sampling points. The white dashed line is the transition between the oxic waters and oxygen-depleted waters (dissolved $O_2$ saturation < 1 %).





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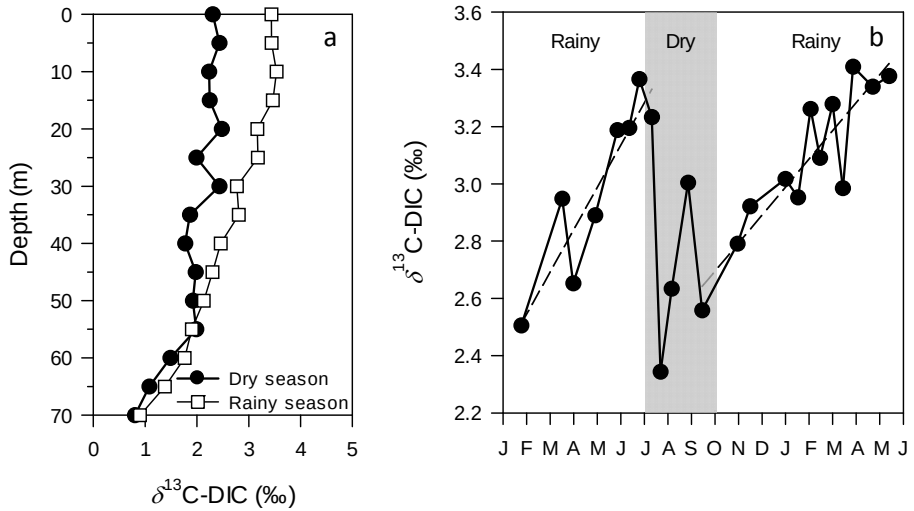


**Figure 2.** Depth profile of the $\delta^{13}$C of the dissolved inorganic carbon (DIC) pool in the mixolimnion during the dry (18 July 2012) and the rainy (20 March 2013) season and **(b)** temporal variation of the $\delta^{13}$C-DIC in the mixed layer of Lake Kivu between January 2012 and June 2013.





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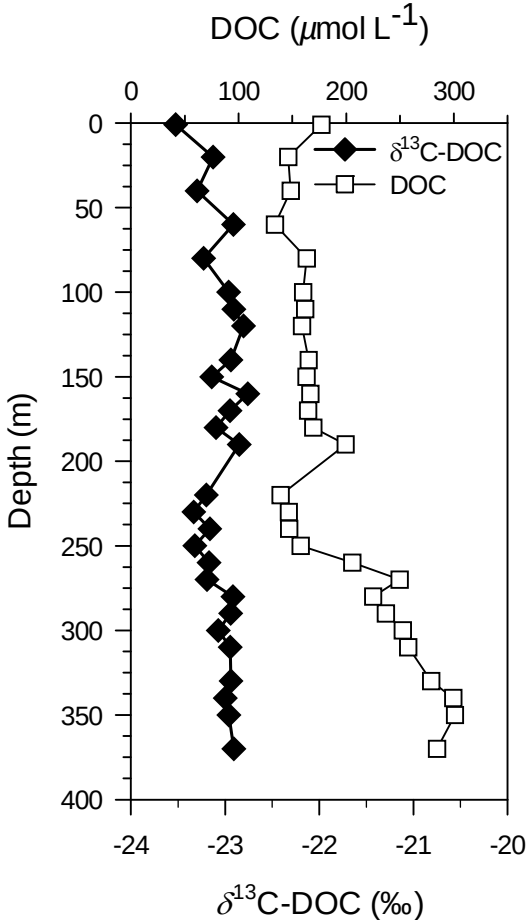


**Figure 3.** Vertical profile from the lake surface to the lake floor of the dissolved organic carbon (DOC) concentration (μmol $L^{-1}$) and the $\delta^{13}C$ signature of the DOC pool, in September 2012.





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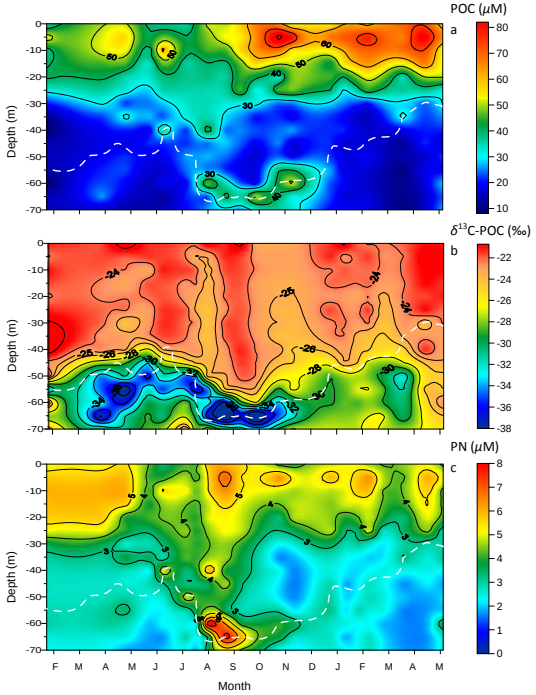


**Figure 4.** Temporal variability of **(a)** the particulate organic carbon (POC) concentration (μmol $L^{-1}$), **(b)** the $\delta^{13}C$ signature of the POC pool, and **(c)** the particulate nitrogen (PN) concentration (μmol $L^{-1}$) in the mixolimnion of Lake Kivu, between February 2012 and May 2013. The white dashed line is the transition between the oxic waters and oxygen-depleted waters (dissolved $O_2$ saturation < 1 %).





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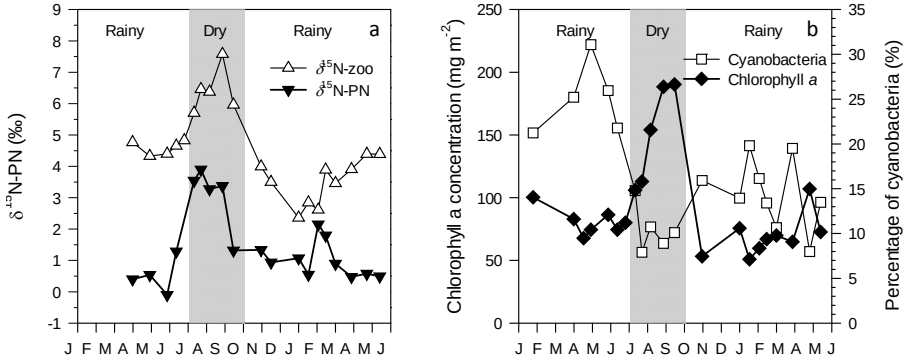


**Figure 5.** Temporal variability of **(a)** the $\delta^{15}$N signature of the particulate nitrogen (PN) pool and zooplankton in the mixed layer, and **(b)** the chlorophyll *a* concentration (mg m$^{-2}$) and the relative contribution of cyanobacteria to the phytoplankton assemblage (%) in the mixolimnion, assessed from pigments analyses, between February 2012 and May 2013.





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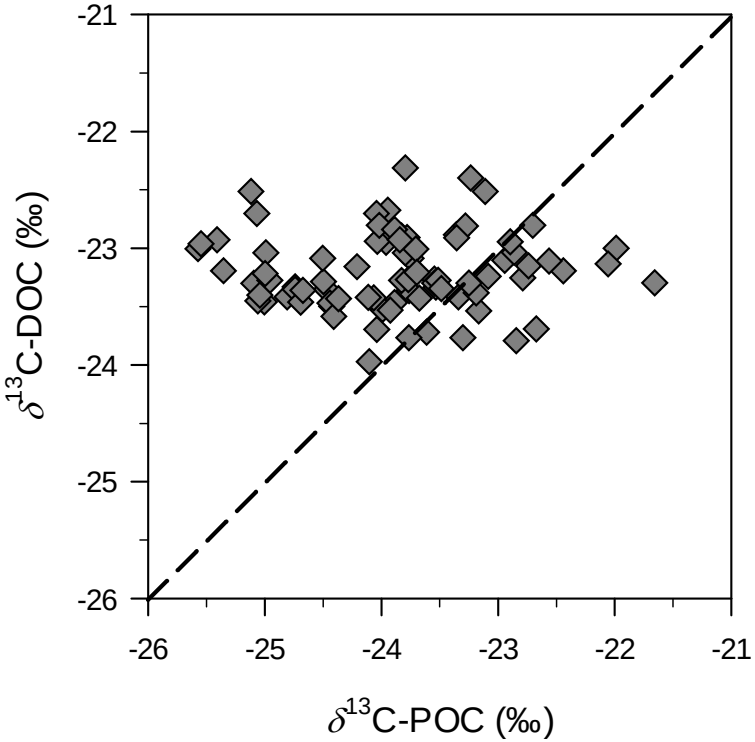


**Figure 6.** Relationship between the $\delta^{13}C$ signature of the particulate and dissolved organic carbon pool (POC and DOC, respectively) in the mixed layer.





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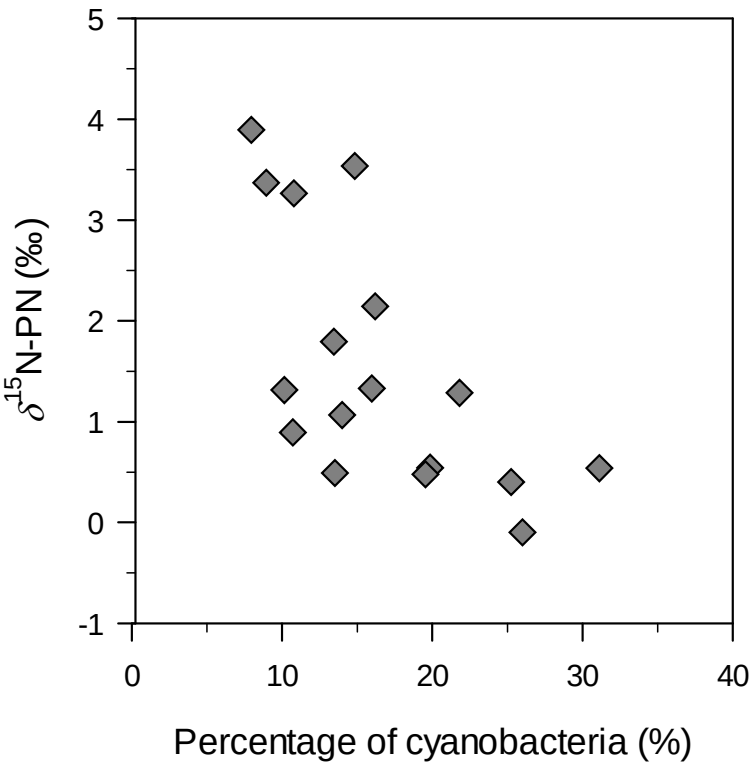


**Figure 7.** Relationship between the relative contribution of cyanobacteria to the phytoplankton assemblage (%) and the $\delta^{15}$N signature of the particulate nitrogen pool in the mixed layer.





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