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 (OM) reservoirs in the large, oligotrophic and deep tropical Lake Kivu (East Africa). Data were acquired during one year at a fornightly temporal resolution. The δ^{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 ^{13}C-depleted DIC waters. The δ^{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 δ^{15}N of particulate nitrogen (PN) in the mixed layer and δ^{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 ^{13}C compared to the autochtonous POC pool, and the δ^{15}N signature of zooplankton followed well the seasonal variability in δ^{15}N-PN, being consistently 3.0 ± 1.1 ‰ heavier than the PN pool. Together, δ^{13}C and δ^{15}N analysis suggests that zooplankton directly incorporate algal-derived OM in their biomass, and they would rely almost exclusively on this source of OM throughout the year in general agreement with the very low allochthonous OM 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 (OM) and better understand its cycling in aquatic systems (Lehmann et al. 2004). For instance, 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 OM 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 OM 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 & 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 OM exceeds autochthonous photosynthetic production (Del Giorgio et al. 1997, Cole 1999, Duarte & 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 OM 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) from freshwater ecosystems to the atmosphere (Prairie et al. 2002), although there is growing evidence of the contribution from external hydrological CO_2 inputs from the catchment (Stets et al. 2009; Finlay et al. 2010; Borges et al. 2014; Marcé et al. 2015). However, the current understanding of the role of inland waters on CO_2 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 effects on water column stratification and biological processes (Sarmento 2012). For instance, primary production in tropical lakes has been recognised to be two times higher than in temperate lakes, on a given nutrient base

(Lewis 1996). Also, the contribution of dissolved primary production in oligotrophic tropical lakes 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 & 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 OM transfer between primary producers and higher levels of the food web, as well as in nutrient cycling (Descy & Sarmento 2008). Most of them are also characterized by highly productive fisheries that provide an affordable food source to local populations (Descy & 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 poorly-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 OM within the water column, and the relative contribution of autochthonous or allochthonous OM to the zooplankton. To our best knowledge, this is the first detailed study to assess the seasonal dynamics of different OM reservoirs by means of their stable isotope composition in any of the large East African lakes. The detailed analysis of the stable isotope composition of diverse organic and inorganic components carried out during this study allowed to trace the OM dynamics in Lake Kivu during a seasonal cycle, and might be useful to improve the interpretation of sedimentary archives of this large and deep tropical lake.

2. Material and methods

Lake Kivu (East Africa) is a large (2370 km²) 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 depth 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 (0-70m).

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).

Samples for stable C isotopic composition of dissolved inorganic carbon (δ^{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 δ^{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 δ^{13}C-DIC measurement was performed with the international certified standards IAEA-CO1 and LSVEC. The reproducibility of δ^{13}C-DIC measurement was typically better than ± 0.2 ‰. 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 (δ^{13}C-DOC) were filtered through pre-flushed 0.2μm syringe filters, kept in 40ml 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 coupled to an IRMS (Thermo delta V Advantage).Quantification and calibration of DOC and δ^{13}C-DOC was performed with IAEA-C6 and an internal sucrose standard (δ^{13}C = -26.99 ± 0.04 ‰) calibrated against international reference materials.

Samples for POC and particulate nitrogen (PN) concentration and stable carbon and nitrogen isotope composition (δ^{13}C-POC; δ^{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 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 δ^{13}C-POC, δ^{15}N-PN, POC and PN measurements was performed with acetanilide (δ^{13}C = - 27.65 ± 0.05 ; δ^{15}N = 1.34 ± 0.04) and leucine (δ^{13}C = - 13.47 ± 0.07 ; δ^{15}N = 0.92 ± 0.06) as standards. All standards were internally calibrated against the international standard IAEA-C6 and IAEA-N1. Reproducibility of δ^{13}C-POC and δ^{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 δ^{13}C and δ^{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 δ^{13}C-POC and δ^{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.

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 35m, 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 : 11.9 ± 0.2 mmol L^{-1}, n = 24) and did not show any consistent seasonal pattern (not shown). The δ^{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). δ^{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). Taking into account the analytical precision of δ^{13}C-DIC measurement (better than ± 0.2 ‰), this small but linear ^{13}C enrichment with time was significant. The DOC concentration (142 ± 20 μmol C L^{-1}, n = 304) and δ^{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 δ^{13}C-DOC did not vary significantly in the monimolimnion (vertical profile 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 C L^{-1}).

The concentration of POC was substantially higher in the mixed layer than below in the mixoliminion throughout the year. However during the dry season, POC concentrations in the oxycline (~50-65m) 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, δ^{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). δ^{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). δ^{15}N-zooplankton mirrored the seasonal variability of δ^{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 δ^{15}N-zooplankton and δ^{15}N-PN was on average 3.0 ± 1.1 ‰ (n = 19) and did not follow any clear seasonal pattern. The δ^{13}C signature of the zooplankton was on average -22.9 ± 0.8 ‰ (n = 19) and did not vary between seasons (not shown).

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 ; $p < 0.01$, mean$_{jan-jun}$ = 23.4 ± 5.5%, mean$_{jul-sep}$ = 9.4 ± 1.3%) and the following (*t*-test ; $p < 0.05$, mean$_{oct-may}$ = 14.6 ± 3.8%, mean$_{jul-sep}$ = 9.4 ± 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 OM. Primary producers preferentially incorporate the lighter isotope (^{12}C) into the biomass with the consequence that the heavier isotope (^{13}C) accumulates into the DIC pool, whereas mineralization releases ^{13}C-depleted CO_2 from the OM being respired, into the DIC pool. Therefore, increasing primary production leads to higher δ^{13}C-DIC but increasing respiration should tend to decrease δ^{13}C-DIC (Bade et al. 2004). For instance, several studies conducted in temperate lakes have reported a significant increase in δ^{13}C-DIC during summer, resulting from primary production (Herczeg 1987, Hollander & McKenzie 1991). In Lake Kivu, the δ^{13}C-DIC increased linearly with time during the stratified rainy season, deviating gradually from the δ^{13}C-DIC value expected if the DIC pool was at equilibrium with the atmospheric CO_2 (~ 0.49 ‰). It appears unlikely that this linear isotopic enrichment of the DIC pool would be due to physical processes : the δ^{13}C-DIC signature of the DIC input from the inflowing rivers (Borges et al. 2014) and deep waters (Fig. 3a) was indeed lower than the measured δ^{13}C-DIC in the mixed layer. Therefore, biological processes (i.e. photosynthetic CO_2 uptake) would be responsible of the isotopic enrichment of the DIC pool observed during the stratified rainy season. Nevertheless, a small decrease in δ^{13}C-DIC was recorded at the beginning of the dry season (early in July 2012), but was concomitant with the characteristic deepening of the mixed layer observed during the dry season. As the depth profile of δ^{13}C-DIC revealed that the DIC pool was isotopically lighter in the bottom of the mixolimnion, the measurement of lower δ^{13}C-DIC values during the dry season could have resulted from the seasonal vertical mixing of surface waters with bottom waters containing relatively ^{13}C-depleted DIC.

Overall, the data suggest that the input of DIC originating from the monimolimnion during the dry season provided the dominant imprint on δ^{13}C-DIC in the mixolimnion, but the seasonal variability of δ^{13}C-DIC observed in the mixed layer hold information on biological processes. The gradual increase with time of the δ^{13}C-DIC in the mixed layer supports the conclusions of other studies carried out in Lake Kivu (Morana et al. 2014, Borges et al. 2014) which showed, based on a detailed DIC and DI^{13}C mass balance approach and several microbial processes measurements, that photosynthetic CO_2 fixation should exceed the respiration of OM. Indeed, in Lake Kivu, riverine inputs of allochthonous OM from the catchment (0.7 – 3.3 mmol m^{-2} d^{-1}, Borges et al. 2014) are minimal compared to primary production (49 mmol m^{-2} d^{-1} ; Darchambeau et al. 2014) and the export of organic carbon to the monimolimnion (9.4 mmol m^{-2} d^{-1}) reported by Pasche et al. (2010). The outflow of organic carbon through the Ruzizi River is also relatively low and was computed to be 0.6 mmol m^{-2} d^{-1} (this study) based on the long term discharge average of Ruzizi (83.2 m^3 s^{-1}, Borges et al. 2014), the average POC and DOC in surface waters (0.052 and 0.142 mmol L^{-1}, this study). It implies that the outputs of OM (9.4 + 0.7 = 10.1 mmol m^{-2} d^{-1}) are higher than the inputs of OM from the catchment (0.7-3.3 mmol m^{-2} d^{-1}) suggesting a net autotrophic status of Lake Kivu.

However, 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). Net heterotrophy implies that heterotrophic prokaryotes rely on a substantial amount of allochthonous OM, however in Lake Kivu, riverine inputs of allochthonous OM from the catchment (0.7 – 3.3 mmol m^{-2} d^{-1}, Borges et al. 2014) are minimal. Indeed, the magnitude of allochthonous OM inputs relative to phytoplankton production depends strongly on the catchment to surface area ratio (Urban et al 2005), that is particularly low (2.2) in Lake Kivu. Therefore, Lake Kivu is relatively poor in organic C, with DOC concentrations of ~0.15 mmol L^{-1} in contrast to smaller boreal humic lakes which show DOC concentrations of on average ~1 mmol L^{-1} (Sobek et al. 2007), and with values up to ~4.5 mmol L^{-1} (Weyhenmeyer & Karlsson 2009). Humic substances are usually low quality substrates for bacterial growth (Castillo et al. 2003), but limit primary production by absorbing incoming light. Hence, heterotrophic production in the photic zone of humic lakes usually exceeds phytoplankton production and DOC concentrations, despite the low substrate quality of humic substance, have been found to be a good predictor of the metabolic status of lakes in the boreal region, with a prevalence of net heterotrophy in organic-rich lakes (Jansson et al. 2000). However, low allochthonous OM inputs and low DOC concentration do not necessary cause a system to be net autotrophic. For instance, Lake Superior has a lower catchment to surface area ratio (1.6), is subsidized by a similar amount of allochthonous OM (~ 3 mmol m^{-2} d^{-1}) and the DOC concentration is even lower than in Lake Kivu (~ 0.1 mmol L^{-1}), but it has been found to be net heterotrophic despite the limited allochthonous OM inputs (Urban et al. 2005). Lake Superior, as the majority of the lakes of the world, is holomictic, meaning that the mixing of its water column can seasonally reach the lake floor, and a substantial amount of sediments, including OM, could then be resuspended during these mixing events and hence re-exposed to microbial mineralization in well-oxygenated waters (Meyers and Eadie 1993, Cotner 2000, Urban et al. 2005). The resuspension of bottom sediments could be important in the ecological functioning of these systems. In constrast, Lake Kivu, as other East African large lakes such as Lake Tanganyika and Malawi, are particularly deep meromictic lakes, so that their water column is characterized by an almost complete decoupling between the surface and deep waters, avoiding any resuspended bottom sediment to reach the surface waters in this system. In consequence, the coupling between the phytoplankton production of DOC and its heterotrophic consumption by prokaryotes in the clear, nutrient-depleted waters of Lake Kivu was found to be high throughout the year (Morana et al. 2014).

Besides morphometrical features, the net autotrophic status of Lake Kivu might also be related to general latitudinal and climatic patterns. 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 & Hecky 2003). Alin and Johnson (2007) reviewed phytoplankton primary production and CO_2 emission to the atmosphere fluxes in large lakes of world (>500 km^2). At the global scale, they found a statistically significant increase of the areal phytoplankton production in large lakes with the mean annual water temperature and the insolation ; and in consequence, a significant decrease of phytoplankton production with latitude. Also, they report a significant decrease of the CO_2 emission to the atmosphere with the mean annual water temperature and therefore an increase of the CO_2 emission with the latitude. According to their estimations, less than 20% of the phytoplankton primary production would be sufficient to balance the carbon loss through CO_2 evasion and OM burial in sediments in large lakes located between the equator and the latitude 30°, but the CO_2 emission and OM accumulation in sediments would exceed the phytoplankton primary production in systems located at latitude higher than 40° (Alin and Johnson 2007). Overall, in morphometrically comparable systems, this global analysis suggests a trend from autotrophic to increasingly heterotrophic conditions with increasing latitude and decreasing mean annual water temperature and insolation (Alin and Johnson 2007). Therefore, our study supports the view that paradigms established with data gathered in comparatively small temperate and boreal lakes may not directly apply to larger, tropical lakes (Bootsma & Hecky 2003). It also highlights the need to consider the unique limnological characteristics of a vast region of the world that harbours 16% of the total surface of lakes (Lehner & Döll 2004), and would account for 50% of the global inputs of OM from continental waters to the oceans (Ludwig et al. 1996).

The δ^{13}C data indicate a difference in the origins of the POC and DOC pools in the mixed layer. Indeed, the δ^{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 δ^{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 the standing stock 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 δ^{13}C signature of the DOC in the monimolimnion (80 m – 370 m, -23.0 ± 0.2 ‰, n = 24) did not differ from the δ^{13}C-DOC in the mixolimnion (0 m – 70 m, -23.2 ± 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 0-20m layer, i.e. roughly the euphotic zone. However, during the dry season, POC concentrations were 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 of the resuspension of bottom 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 δ^{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 Sea, has sometimes been interpreted as a result of to the heterotrophic mineralization of the sedimenting OM (Coban-Yildiz et al. 2006), but it seems unlikely that, in Lake Kivu, heterotrophic processes could have caused an abrupt excursion of δ^{13}C-POC to values as low as -41.6 ‰ (65 m, 22/08/12). Such large isotopic depletion of the POC pool in the water column has been reported by Blees et al. (2014), who measured δ^{13}C-POC as low as -49‰ in Lake Lugano, and it was related to high methanotrophic activity. In Lake Kivu, CH_4 concentrations were found to decrease sharply with decreasing depth 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 δ^{13}C signature of approximately -60 ‰ (Pasche et al. 2011, Morana et al. 2014). Therefore, the vertical patterns in CH_4 concentrations and δ^{13}C-POC values observed during this study suggest 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 δ^{13}C-CH_4 at each sampling point, it is possible to estimate the theoretical δ^{13}C signature of methanotrophic organisms at each depth. Note that the δ^{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 δ^{13}C-CH_4 was found along vertical profiles performed in February and September 2012 in Lake Kivu ($\delta^{13}\text{C-CH}_4 = -7.911 \log(\text{CH}_4) - 13.027$; $r^2 = 0.87$, n = 34 ; Morana et al. submitted). Hence the δ^{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 δ^{13}C signature of methanotrophs and the average δ^{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 % (n = 13) and 6.4 ± 1.6 % (n = 5) of the depth-integrated POC pool in the mixolimnion was 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 δ^{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, 22/08/12). We hypothesize that microbial CH_4 oxidation could play an important role in the ecological functioning of Lake Kivu. Along with heterotrophic mineralization of the sinking OM, 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 uptake of dissolved inorganic phosphorus (DIP), 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 suffer from a severe P limitation throughout the year as pointed out by the relatively high sestonic C:P ratio (256 ± 75 ; Sarmento et al. 2009 ; Darchambeau et al 2014).

The δ^{15}N signature of the autochthonous OM 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 δ^{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 δ^{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 & Cifuentes 1991). Several studies carried out in marine (Pacific Ocean and Gulf of Mexico) and lacustrine (Lake Lugano) systems have shown that δ^{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 δ^{15}N-PN and the abundance of N_2-fixing cyanobacteria has already been reported for others systems, such as coastal lagoon (Lesutiene 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 autochthonous OM 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 & Kling, 1987; Reynolds, 2006; 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 significantly, 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 between consumers and diet is usually considered to be less than 1 ‰ (Sirevag 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 *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 autochthonous POC pool, $\delta^{13}C$ and $\delta^{15}N$ analysis suggests that zooplankton directly incorporate phytoplankton-derived OM in their biomass (Masilya 2011), and they would rely almost exclusively on this source of OM throughout the year. This is in general agreement with the very low allochthonous OM inputs from rivers in Lake Kivu (Borges et al. 2014).

In conclusion, 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 supports the view that the mixed layer of Lake Kivu is net autotrophic, as demonstrated by Borges et al. (2014) based on DIC and $DI^{13}C$ mass balance considerations. The $\delta^{13}C$-POC showed an important variation with depth due to 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 indicate 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 phytoplankton-derived biomass as a organic C source.

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Figures

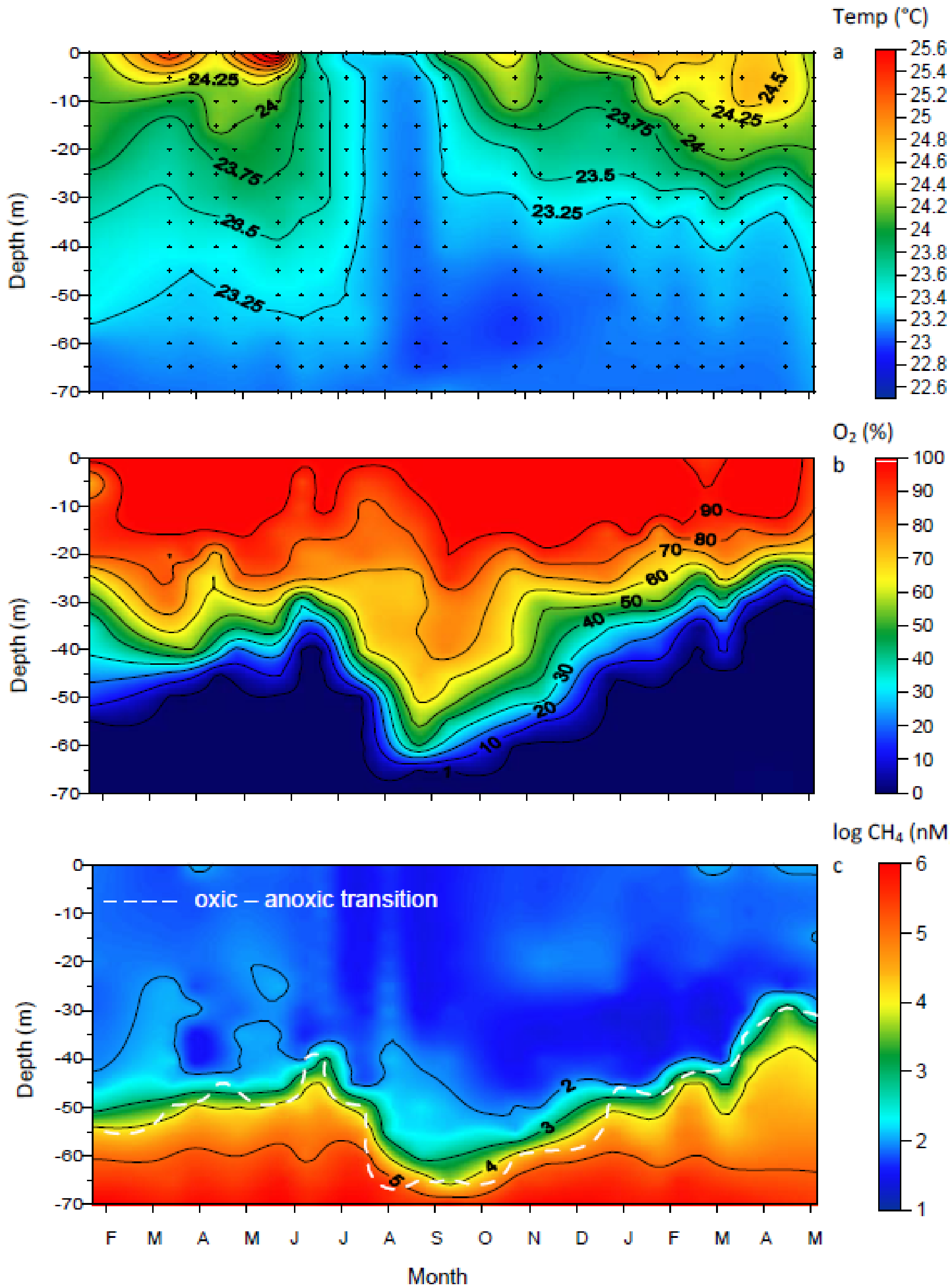

Figure 1. Temporal variability of (a) temperature (°C), (b) oxygen saturation (%), and (c) the log-transformed CH_4 concentration (nmol L^{-1}) in the mixolimnion of Lake Kivu, between February 2012 and May 2013. Small crosses in the figure (a) represent each sampling points.

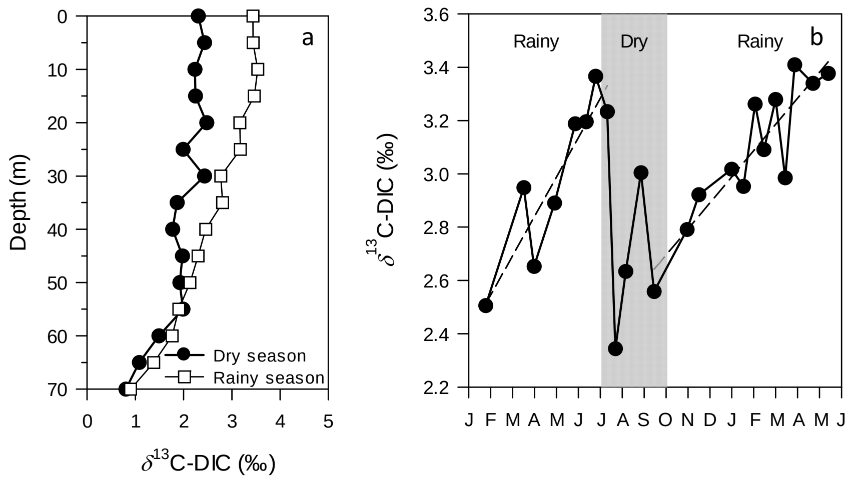

Figure 2. Depth profile of the δ^{13}C of the dissolved inorganic carbon (DIC) pool in the mixolimnion during the dry (18/07/12) and the rainy (20/03/13) season and (b) temporal variation of the δ^{13}C-DIC in the mixed layer of Lake Kivu between January 2012 and June 2013.

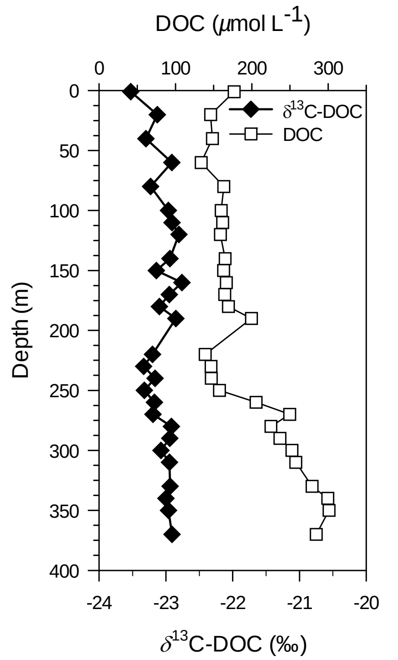

Figure 3. Vertical profile from the lake surface to the lake floor of the dissolved organic carbon (DOC) concentration (μmol L^{-1}) and the δ^{13}C signature of the DOC pool, in September 2012.

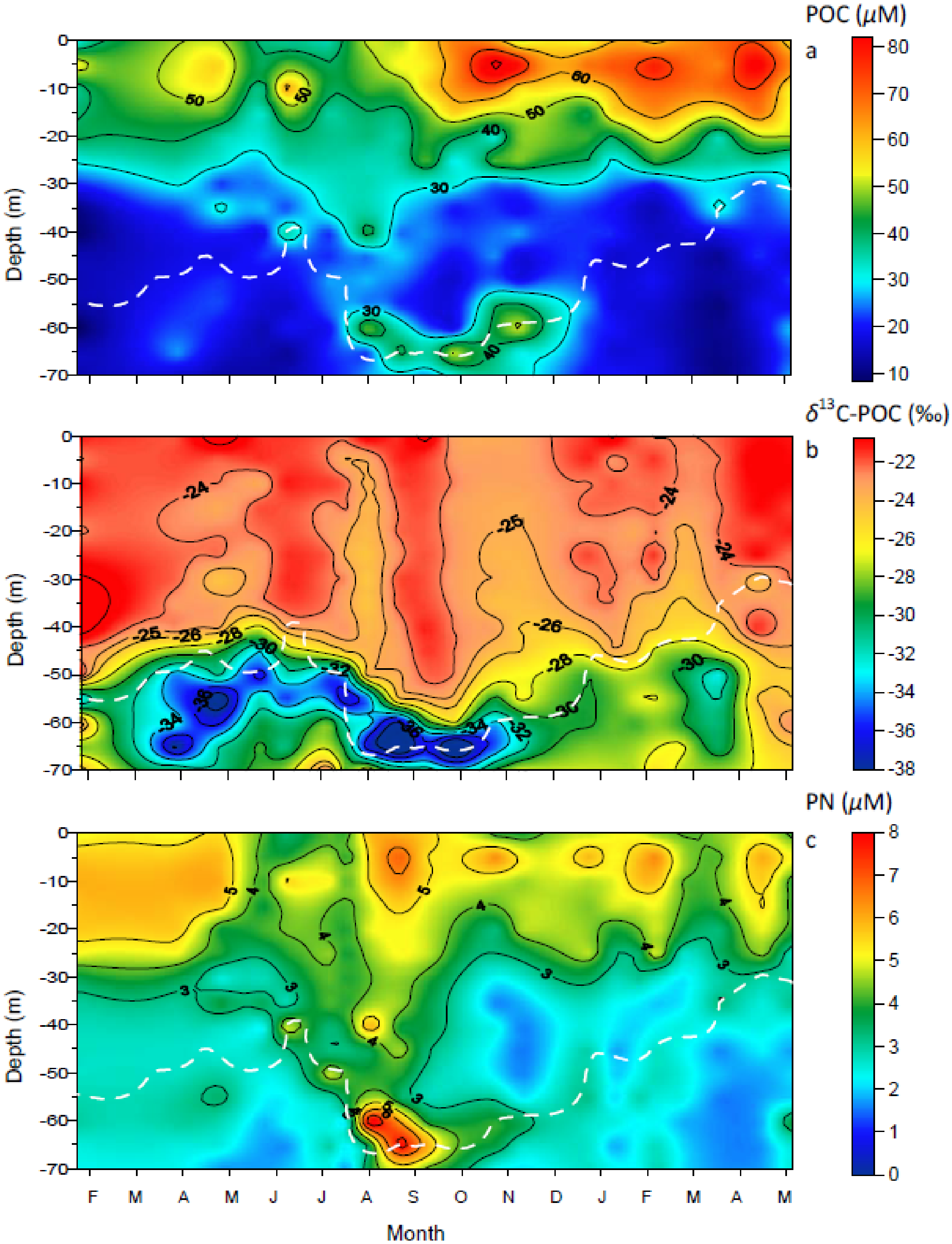

Figure 4. Temporal variability of (a) the particulate organic carbon (POC) concentration (μmol L^{-1}), (b) the δ^{13}C signature of the POC pool, and (c) the particulate nitrogen (PN) concentration (μmol L^{-1}) in the mixolimnion of Lake Kivu, between February 2012 and May 2013.

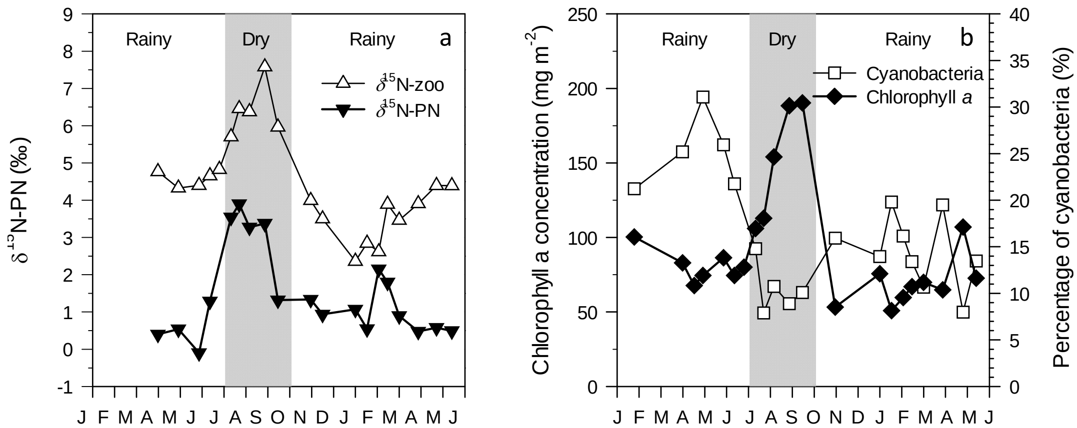

Figure 5. Temporal variability of (a) the δ^{15}N signature of the particulate nitrogen (PN) pool and zooplankton in the mixed layer, and (b) the chlorophyll a concentration (mg m^{-2}) and the relative contribution of cyanobacteria to the phytoplankton assemblage (% of biomass) in the mixolimnion, assessed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

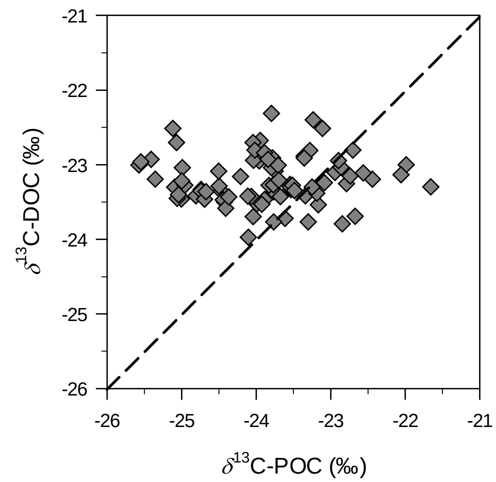

Figure 6. Relationship between the δ^{13}C signature of the particulate and dissolved organic carbon pool (POC and DOC, respectively) in the mixed layer.

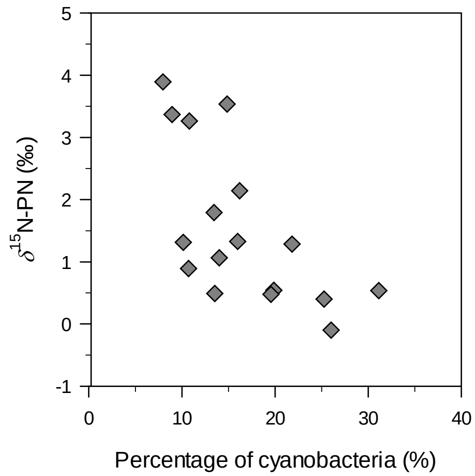

Figure 7. Relationship between the relative contribution of cyanobacteria to the phytoplankton assemblage (% of biomass) and the δ^{15}N signature of the particulate nitrogen pool in the mixed layer.