Chapter 4
Variability of Carbon Dioxide and Methane in the Epilimnion of Lake Kivu

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Abstract We report a dataset of the partial pressure of CO_2 (pCO_2) and methane concentrations (CH_4) in the surface waters of Lake Kivu obtained during four cruises covering the two main seasons (rainy and dry). Spatial gradients of surface pCO_2 and CH_4 concentrations were modest in the main basin. In Kabuno Bay, pCO_2 and CH_4 concentrations in surface waters were higher, owing to the stronger influence of subaquatic springs from depth. Seasonal variations of pCO_2 and CH_4 in the main basin of Lake Kivu were strongly driven by deepening of the epilimnion and the resulting entrainment of water characterized by higher pCO_2 and CH_4 concentrations. Physical and chemical vertical patterns in Kabuno Bay were seasonally stable, owing to a stronger stratification and smaller surface area inducing fetch limitation

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of wind driven turbulence. A global and regional cross-system comparison of pCO_2 and CH_4 concentrations in surface waters of lakes highlights the peculiarity of Kabuno Bay in terms of pCO_2 values in surface waters. In terms of surface CH_4 concentrations, both Kabuno Bay and the main basin of Lake Kivu are at the lower end of values in lakes globally, despite the huge amounts of CH_4 and CO_2 in the deeper layers of the lake.

4.1   Introduction

Freshwater environments are important components of the global carbon (C) cycle, as they fix carbon dioxide (CO_2) into organic matter and transport organic and inorganic C from the terrestrial biosphere to the oceans. This transport of C is not passive and freshwater ecosystems transform, store and exchange C with the atmosphere (Cole et al. 2007; Battin et al. 2008; Marotta et al. 2009; Tranvik et al. 2009). Freshwater ecosystems are considered to be frequently net heterotrophic, whereby the consumption of organic C is higher than the autochthonous production of organic C, and excess organic C consumption is maintained by inputs of allochthonous organic C (Cole and Caraco 2001). Net heterotrophy in freshwater ecosystems promotes the emission of CO_2 to the atmosphere, with the global emission from continental waters estimated at ~0.75 Pg C year^{-1} (Cole et al. 2007; 0.11 Pg C year^{-1} from lakes, 0.28 Pg C year^{-1} from reservoirs, 0.23 Pg C year^{-1} from rivers, 0.12 Pg C year^{-1} from estuaries, and 0.01 Pg C year^{-1} from ground waters). Such an emission of CO_2 from continental waters is comparable to the sink of C by terrestrial vegetation and soils of ~1.3 Pg C year^{-1} (Cole et al. 2007) and the sink of CO_2 in open oceans of ~1.4 Pg C year^{-1} (Takahashi et al. 2009). Part of the degradation of organic C that occurs in freshwater ecosystems is mediated by anaerobic processes, among which methanogenesis, which leads to the emission of methane (CH_4) to the atmosphere. The global emission of CH_4 to the atmosphere from freshwater ecosystems has been recently re-evaluated by Bastviken et al. (2011) to 103 Tg CH_4 year^{-1} (72 Tg CH_4 year^{-1} from lakes) which is significant when compared

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to other natural (168 Tg CH_4 year^{-1}) and anthropogenic (428 Tg CH_4 year^{-1}) CH_4 emissions (Chen and Prinn 2006).

Our present understanding of the role of lakes on C emissions could be biased because most observations were obtained in temperate and boreal systems, and in general in medium to small sized lakes, while much less observations are available from large tropical lakes. Tropical freshwater environments are indeed under-sampled compared to temperate and boreal systems in terms of C dynamics in general, and specifically in terms of CO_2 and CH_4 dynamics. Yet, about 50% of freshwater and an equivalent fraction of organic C is delivered by rivers to the oceans at these latitudes (Ludwig et al. 1996). Tropical lakes represent about 16% of the total surface of lakes (Lehner and Döll 2004), and Lakes Victoria, Tanganyika and Malawi belong to the seven largest lakes by area in the world.

We report the seasonal and spatial variability of CO_2 and CH_4 in the epilimnion of Lake Kivu, the smallest of the East African Rift lakes (2,370 km^2). It is a deep (maximum depth of 485 m), meromictic and oligotrophic lake (Chap. 5), characterized by a relatively simple pelagic foodweb (Chap. 8), with physical processes (vertical mixing and transport processes) that are different from most other lakes in the world (Chap. 2). Subaquatic springs provide heat, dissolved salts and CO_2 to the bottom waters of the lake (Chap. 2). A prominent feature of Lake Kivu is the huge amounts of CO_2 and CH_4 (300 and 60 km^3, respectively, at 0°C and 1 atm, Schmid et al. 2005) that are dissolved in its deep waters. While CO_2 is mainly of magmatic origin, CH_4 originates for two thirds from anoxic bacterial reduction of CO_2 and for one third from anaerobic degradation of settling organic material (Schoell et al. 1988).

Seasonality of the physical and chemical vertical structure (Chap. 2) and biological activity (Chaps. 5, 6, 7) in surface waters of Lake Kivu is driven by the oscillation between the dry season (June–September) and the rainy season (October–May), the former characterized by dryer winds and a deepening of the surface mixed layer.

4.2 Material and Methods

In order to capture the seasonal variation of the studied quantities, four cruises were carried out in Lake Kivu on 15/03–29/03/2007 (mid rainy season), 28/08–10/09/2007 (late dry season), 21/06–03/07/2008 (early dry season) and 21/04–05/05/2009 (late rainy season). Sampling was carried out at 15 stations distributed over the whole lake (Fig. 4.1).

Vertical profiles of temperature, conductivity, oxygen and pH were obtained with a Yellow Springs Instrument (YSI) 6600 V2 probe. Calibration of sensors was carried out prior to the cruises and regularly checked during the cruises. The conductivity cell was calibrated with a 1,000 µS cm^{-1} (25°C) YSI standard. The pH electrode was calibrated with pH 4.00 (25°C) and pH 7.00 (25°C) National Institute of Standards and Technology (YSI) buffers. The oxygen membrane probe was calibrated with humidity saturated ambient air. Salinity was computed from specific conductivity according to Chap. 2.
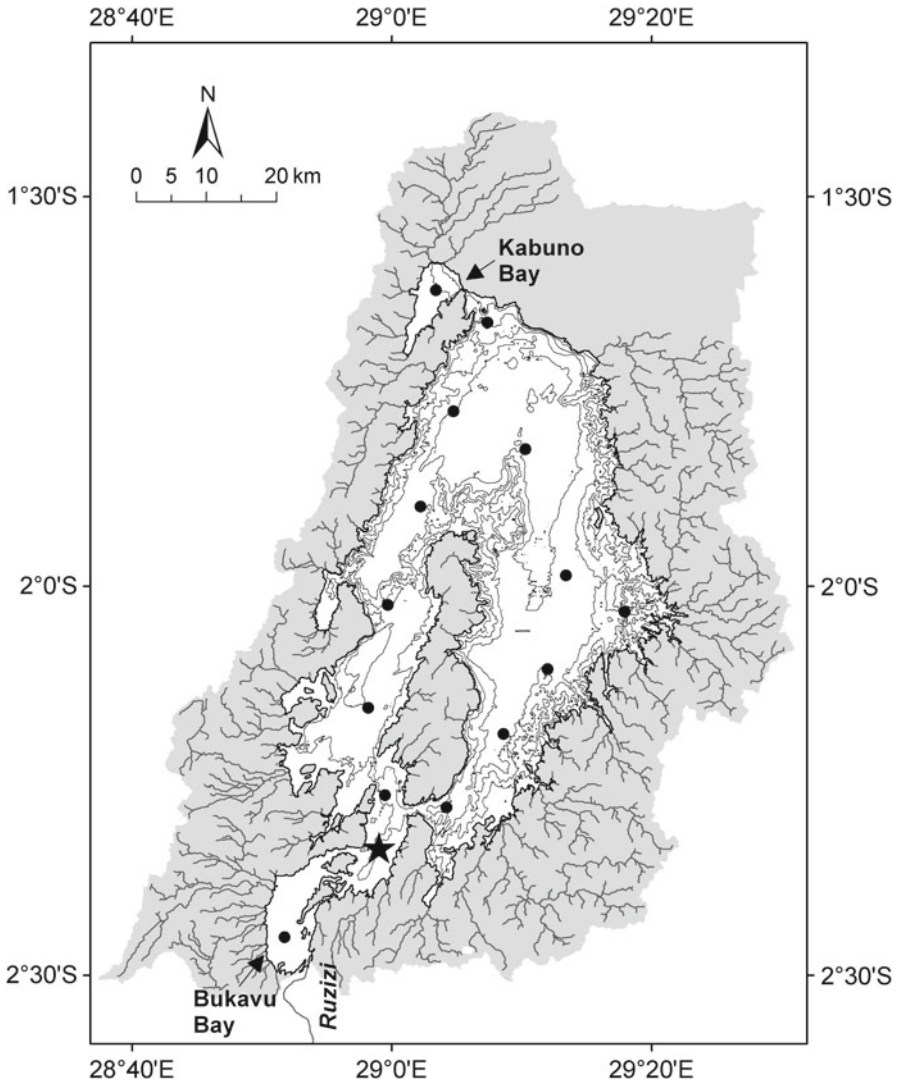
Fig. 4.1 Map of Lake Kivu, showing bathymetry (isobaths at 100 m intervals), catchment area (shaded in grey), tributaries (courtesy of Martin Schmid), and sampling stations. The station identified with a star corresponds to the site of 24 h measurement cycle carried out in March 2007

Sampling for the partial pressure of CO_2 (pCO_2) was carried out at 10 m, with the exception of a 24 h cycle in March 2007 for which data at 1 and 5 m are also presented. Measurements of pCO_2 were carried out with a non-dispersive infrared (NDIR) analyzer coupled to an equilibrator (Frankignoulle et al. 2001) through which water was pumped with a peristaltic pump (Masterflex E/S portable

sampler). The sampling depth was determined with a DIMED S.A. Electronic Engineering PDCR 1730 pressure transducer. *In situ* temperature and temperature at the outlet of the equilibrator were determined with Li-Cor 1000-15 probes. The NDIR analyzer (Li-Cor, Li-820) was calibrated with pure nitrogen, and four gas standards with a CO_2 molar fraction of 363, 819, 3,997 and 8,170 ppm (Air Liquide Belgium).

Water for the determination of pH, CH_4 concentrations, $\delta^{13}C$ of dissolved inorganic carbon (DIC), total alkalinity (TA) and total organic carbon (TOC) concentrations was sampled with a 5 L Niskin bottle (Hydro-Bios). Samples were collected every 10 m from 10 to 60–80 m depending on the cruise and station, except for CH_4 which was only sampled at 10 m. Additional samples for pH, $\delta^{13}C_{DIC}$ and TA were collected at 5 m in Kabuno Bay. Water for CH_4 analysis was collected in glass serum bottles from the Niskin bottle with tubing, left to overflow, poisoned with 100 μL of saturated $HgCl_2$ and sealed with butyl stoppers and aluminium caps. Water samples for the analysis of $\delta^{13}C_{DIC}$ were taken from the same Niskin bottle by gently overfilling 12 mL glass headspace vials, poisoning with 20 μL of a saturated $HgCl_2$ solution, and gas-tight capped. A water volume of 50 mL was filtered through a 0.2 μm pore size polysulfone filter and was stored at ambient temperature in polyethylene bottles for the determination of TA. Unfiltered water samples (20 mL) were preserved with NaN_3 (0.05% final concentration) for the determination of TOC.

Measurements of pH in water sampled from the Niskin bottle were carried out with a Metrohm (6.0253.100) combined electrode calibrated with US National Bureau of Standards buffers of pH 4.002 (25°C) and pH 6.881 (25°C) prepared according to Frankignoulle and Borges (2001). Measurements of TA were carried out by open-cell titration with HCl 0.1 M according to Gran (1952) on 50 mL water samples, and data were quality checked with Certified Reference Material acquired from Andrew Dickson (Scripps Institution of Oceanography, University of California, San Diego). DIC was computed from pH and TA measurements using the carbonic acid dissociation constants of Millero et al. (2006). For the analysis of $\delta^{13}C_{DIC}$, a He headspace was created in 12 mL glass vials, and ~300 μL of H_3PO_4 was added to convert all inorganic carbon species to CO_2. After overnight equilibration, part of the headspace was injected into the He stream of an elemental analyser – isotope ratio mass spectrometer (ThermoFinnigan Flash1112 and ThermoFinnigan Delta + XL, or Thermo FlashEA/HT coupled to Thermo Delta V) for $\delta^{13}C$ measurements. The obtained $\delta^{13}C$ data were corrected for the isotopic equilibration between gaseous and dissolved CO_2 using an algorithm similar to that presented by Miyajima et al. (1995), and calibrated with LSVEC and NBS-19 certified standards or internal standards calibrated with the former. TOC was determined using a Dohrman Apollo 2000 TOC analyzer. As in surface waters of Lake Kivu particulate organic carbon contributes to ~20% of TOC (not shown), we refer to dissolved organic carbon (DOC) for the purpose of the cross-lake pCO_2 comparison (hereafter). Concentrations of CH_4 were determined by gas chromatography (GC) with flame ionization detection (GC-FID, Hewlett Packard HP 5890A), after creating a 12 mL headspace with N_2 in 40 mL glass serum bottles, as described by Abril and Iversen (2002). After creating the N_2 headspace, samples were vigorously shaken during 1 min, were

placed in a thermostated bath overnight (~16 h) after which samples were again vigorously shaken during 1 min before starting the GC analysis. Certified CH_4:N_2 mixtures (Air Liquide France) of 10 and 500 ppm CH_4 were used as standards. For the March 2009 cruise, CH_4 measurements were carried out with the same procedures but using 30 mL headspace with N_2 in 70 mL serum bottles, and a SRI 8610C GC-FID calibrated with CH_4:CO_2:N_2 mixtures (Air Liquide Belgium) of 1 and 10 ppm CH_4. The concentrations were computed using the CH_4 solubility coefficient given by Yamamoto et al. (1976).

Diffusive air–water CO_2 and CH_4 fluxes (F) were computed according to:

$$F = k\Delta[C]$$

where k is the gas transfer velocity and $\Delta[C]$ is the air–water gradient of CO_2 or CH_4, using an atmospheric pCO_2 value ranging from ~372 to ~376 ppm (depending on the cruise) and an atmospheric CH_4 partial pressure of 1.8 ppm.

k was computed from wind speed using the parameterization of Cole and Caraco (1998) and the Schmidt number of CO_2 or CH_4 in fresh water according to the algorithms given by Wanninkhof (1992). Wind speed data were acquired with a Davis Instruments meteorological station in Bukavu (2.51°S 28.86°E). F was computed with daily wind speed averages for a time period of one month centred on the date of the middle of each field cruise. Such an approach allows to account for the day-to-day variability of wind speed, and to provide F values that are seasonally representative.

4.3   Results and Discussion

4.3.1   *Spatial Variability of pCO₂ and CH₄*

In the surface waters (10 m depth) of the main basin of Lake Kivu (excluding Kabuno Bay but including Bukavu Bay), pCO_2 values were systematically above atmospheric equilibrium (~372 to ~376 ppm depending on the cruise), and varied within narrow ranges of 537–603 ppm in March 2007, 702–775 ppm in September 2007, 597–640 ppm in June 2008, and 581–711 ppm in April 2009 (Fig. 4.2). The coefficient of variation of pCO_2 in surface waters of the main basin ranged for each cruise between 3% and 6%, below the range reported by Kelly et al. (2001) in five large boreal lakes (range 5–40%).

The most prominent feature of the spatial variation was the much higher pCO_2 values in Kabuno Bay ranging between 13,158 and 14,793 ppm (between 18 and 26 times higher than in the main basin). Compared to the main basin, surface and deep waters of Kabuno Bay were characterized by higher salinity, DIC and TA values (Figs. 4.3 and 4.4) and by lower pH and $\delta^{13}C_{DIC}$ values (Figs. 4.3 and 4.4). Comparison of DIC and TA profiles (Fig. 4.4) shows that the relative contribution of CO_2 to DIC is more important in Kabuno Bay than in the main lake, since TA is
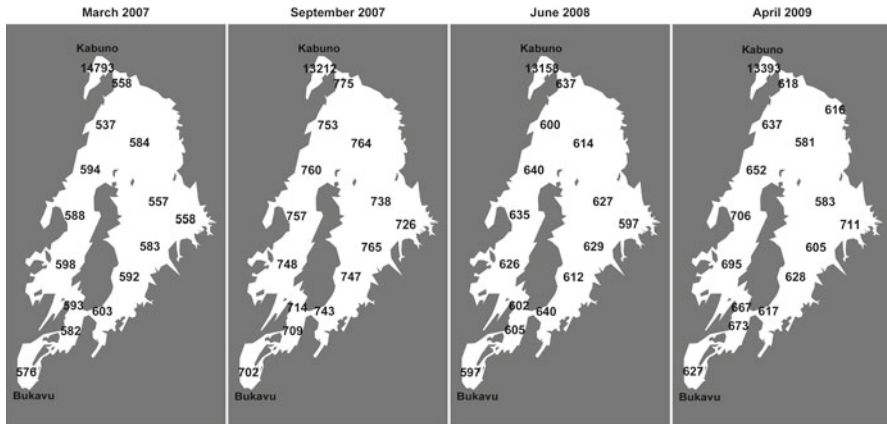
Fig. 4.2 Spatial distribution of the partial pressure of CO_2 (pCO_2, ppm) in the surface waters of Lake Kivu (10 m depth) in March 2007, September 2007, June 2008 and April 2009

mainly as HCO_3^-, and if the CO_2 contribution to DIC is low, then DIC and TA should be numerically close. At 60 m depth, CO_2 contributes ~30% to DIC in Kabuno Bay, and ~1% in the main basin. Kabuno Bay was also characterized by a very stable chemocline (salinity, pH) and oxycline at ~11 m irrespective of the sampling period (Fig. 4.3). In the main basin of Lake Kivu, the oxycline varied seasonally between ~35 m in March and September 2007 and ~60 m in June 2008 (Fig. 4.3). Overall, these vertical patterns indicate that there is a much larger contribution of subaquatic springs to the whole water column including surface waters in Kabuno Bay than in the main basin of Lake Kivu. This is related to the different geomorphology, since Kabuno Bay is shallower than the main basin (maximum depth of 110 m vs. 485 m) and exchanges little water with the main basin (narrow connection ~10 m deep). Also, Kabuno Bay is smaller (~48 km^2) than the main basin (~2,322 km^2). Hence, there is a stronger fetch limitation of wind induced turbulence that also contributes to the stability of the water column vertical structure in Kabuno Bay whatever the season.

Part of the observed horizontal gradients of pCO_2 in the main basin of Lake Kivu could be related to diel variations, since measurements were carried out irrespective of the time of the day (mostly from dawn to dusk, but sometimes at night). We investigated the diel cycle of pCO_2 during a 24 h cycle on 23/03–24/03/2007 (Fig. 4.5). The amplitudes of the daily variations of pCO_2 at the three depths were similar (~30 ppm), but pCO_2 during day-time was up to ~30 ppm higher at 1 m than at 5 m and 10 m depth. This was related to shallow stratification during day-time, with temperatures at 1 m depth up to 1.05°C and 1.15°C higher than at 5 and 10 m depth, respectively. At the end of the night the top 10 m water column became isothermal, due to heat loss to the atmosphere and convection of surface waters. In order to remove the effect of temperature change on the CO_2 solubility coefficient,
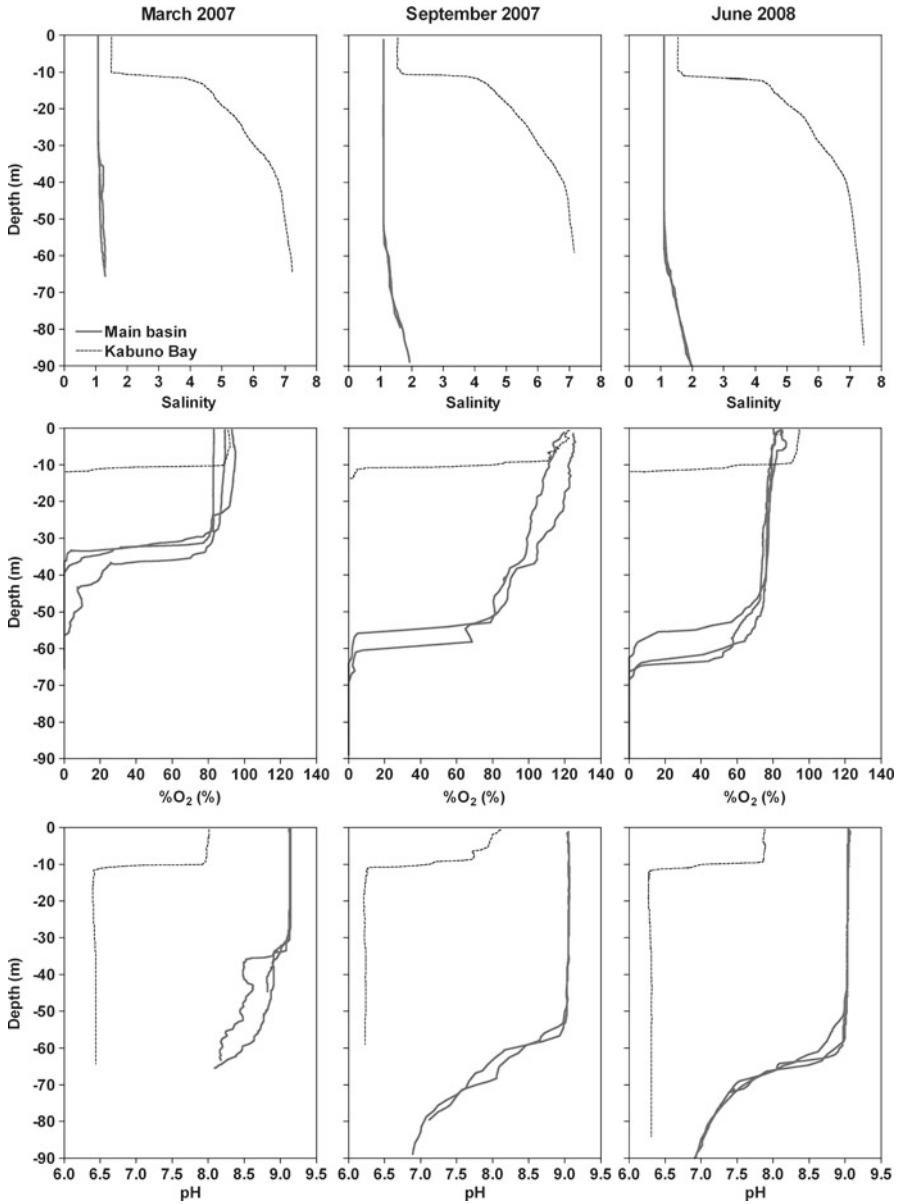
Fig. 4.3 Vertical profiles of salinity, oxygen saturation level (%O$_2$, %) and pH in Kabuno Bay and in the three northernmost stations of the main basin of Lake Kivu, in March 2007, September 2007 and June 2008 (vertical profiles were not acquired in April 2009)
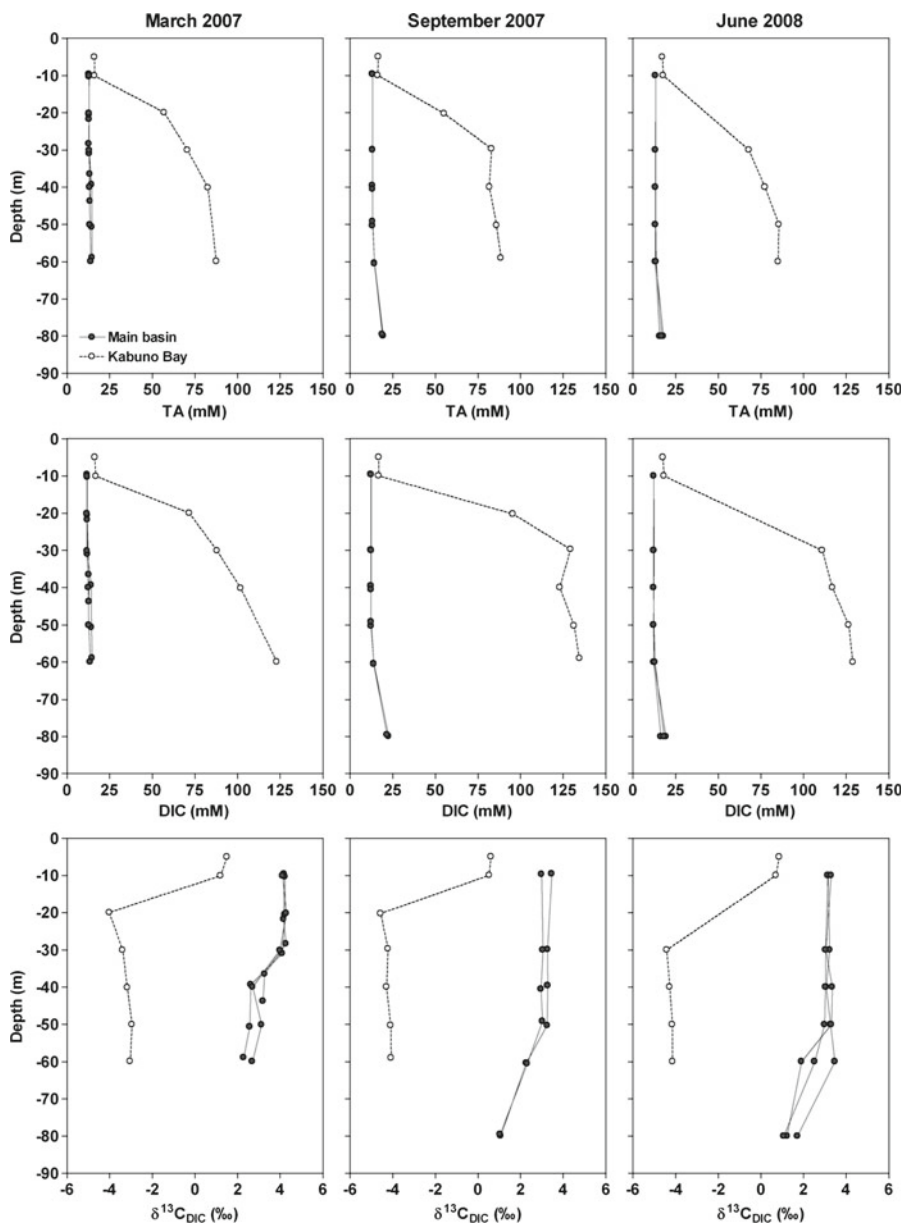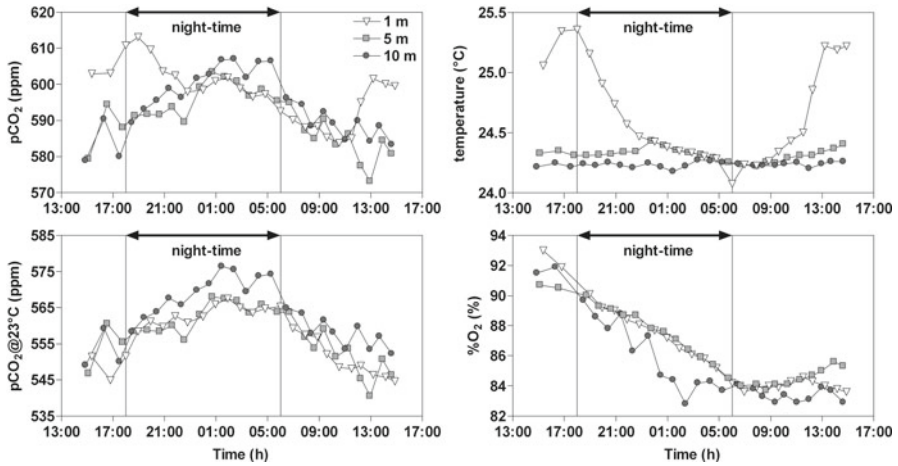
Fig. 4.4 Vertical profiles of total alkalinity (TA, mM), dissolved inorganic carbon (DIC, mM) and $\delta^{13}C_{DIC}$ (‰) in Kabuno Bay and in the three northernmost stations of the main basin of Lake Kivu, in March 2007, September 2007 and June 2008 (vertical profiles were not acquired in April 2009)

Fig. 4.5 Time series of the partial pressure of CO_2 (pCO_2, ppm), temperature (°C), pCO_2 normalized to a temperature of 23°C (pCO_2@23°C, ppm) and oxygen saturation level (%O_2, %) at 1, 5 and 10 m depth at the station indicated by a star in Fig. 4.1 from 23/03/2007 (13:00) to 24/03/2007 (14:00)

pCO_2 values were normalized to a temperature of 23°C (pCO_2@23°C). At 1, 5 and 10 m depth, pCO_2@23°C values increased during night-time and decreased during day-time, as expected from the dominance of community respiration during night-time and occurrence of primary production during day-time. This was consistent with the %O_2 variations that roughly mirrored those of pCO_2. The daily variations of pCO_2@23°C at all depths were very consistent, and pCO_2@23°C values were lower at 1 m than at 10 m, as expected from higher biological activity in relation to lower light attenuation in surface waters, and possibly also the loss of CO_2 to the atmosphere. Daily variability of pCO_2 in March 2007 was similar to the spatial horizontal gradients in surface waters in the main basin of Lake Kivu observed during that cruise.

CH_4 concentrations in the surface waters of the main basin were systematically above atmospheric equilibrium (~2 nM), and varied within relatively narrow ranges of 30–75 nM in March 2007, 54–197 nM in September 2007, 30–120 nM in June 2008, and 18–83 nM in April 2009 (Fig. 4.6). In September 2007, CH_4 concentrations in Kabuno Bay were within the range of values in the main basin, but they were ~6 times higher in April 2009, and ~8 times higher in both March 2007 and June 2008. CH_4 concentrations in surface waters of lakes result from the balance of inputs from depth or laterally from the littoral zone, and of loss terms (bacterial oxidation and evasion to the atmosphere) (Bastviken et al. 2004). Tietze et al. (1980) showed that CH_4 concentrations in deep waters of Kabuno Bay are similar to the ones for similar depths in the main basin of Lake Kivu. The likely higher relative contribution of deepwater springs in Kabuno Bay than in the main basin increases the upward flux of solutes and might explain the higher CH_4 concentrations observed
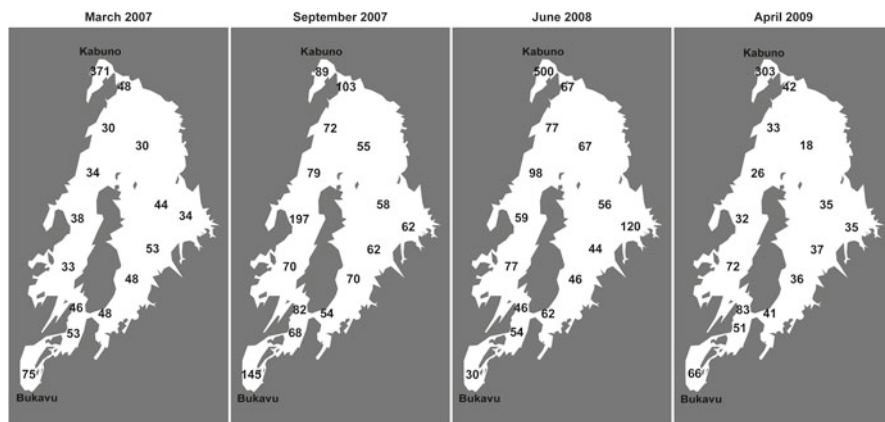
Fig. 4.6 Spatial distribution of the CH_4 concentration (nM) in the surface waters of Lake Kivu (10 m depth) in March 2007, September 2007, June 2008 and April 2009 (Borges et al. 2011)

in Kabuno Bay than in the main basin. The shallower oxycline in Kabuno Bay could also promote less removal of CH_4 by aerobic bacterial oxidation.

4.3.2   Seasonal Variations of pCO_2 and CH_4 and Diffusive Air–Water Fluxes

The average pCO_2 in surface waters of each of the four cruises in the main basin of Lake Kivu was positively related to the mixed layer depth and CH_4 concentrations, and negatively related to $\delta^{13}C_{DIC}$ (Fig. 4.7). This suggests than the deepening of the mixed layer and entrainment of deeper waters to the surface mixed layer is a major driver of seasonal variability of pCO_2 and CH_4 concentrations in surface waters of the main basin of Lake Kivu. Indeed, deeper waters are richer in pCO_2 and DIC (Fig. 4.4; Tietze et al. 1980; Schmid et al. 2005) and CH_4 (Tietze et al. 1980; Schmid et al. 2005) than surface waters, and the DIC in deeper waters is more ^{13}C-depleted than that in surface waters (Fig. 4.4; Tassi et al. 2009).

Seasonal variations of wind speed were rather modest (coefficient of variation of 13%), ranging between 1.2 ± 0.4 m s^{-1} in September 2007 and 1.6 ± 0.2 m s^{-1} in June 2008. Hence, seasonal variations of diffusive air–water fluxes of CH_4 and CO_2 closely tracked those of CH_4 concentrations and pCO_2. Emissions of CH_4 from surface waters in the main basin ranged between 26 µmol m^{-2} day^{-1} in March 2007 and April 2009 and 50 µmol m^{-2} day^{-1} in September 2007. Emissions of CH_4 from surface waters in Kabuno Bay ranged between 53 µmol m^{-2} day^{-1} in September 2007 and 185 µmol m^{-2} day^{-1} in April 2009. Emissions of CO_2 from surface waters in the main basin ranged between 4 mmol m^{-2} day^{-1} in March 2007 and 8 mmol m^{-2} day^{-1} in September 2007. Emissions of CO_2 from surface waters
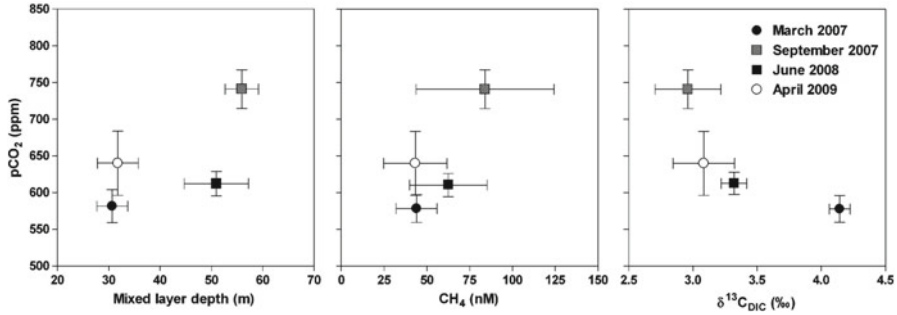
Fig. 4.7 Mean values of the partial pressure of CO_2 (pCO_2, ppm) in the surface waters (10 m) versus mixed layer depth (m), versus CH_4 concentration in surface waters (10 m, nM) and versus $\delta^{13}C_{DIC}$ (‰) in surface waters (10 m) in the main basin of Lake Kivu in March 2007, September 2007, June 2008 and April 2009. Error bars correspond to standard deviations on the mean

in Kabuno Bay ranged between 270 mmol m^{-2} day^{-1} in September 2007 and 307 mmol m^{-2} day^{-1} in March 2007.

4.3.3   Global and Regional Comparison with Other Lakes

When compared to other lakes globally (Bastviken et al. 2004; Sobek et al. 2005), the main basin of Lake Kivu ranks 3,629th in terms of pCO_2 in surface waters (out of 4,904 lakes) and 47th in terms of CH_4 concentration in surface waters (out of 49 lakes) (Fig. 4.8). Kabuno Bay ranks 7th in terms of pCO_2 and 30th in terms of CH_4 concentrations in surface waters.

The comparison of pCO_2 and DOC has been frequently used in limnology for cross-system analysis of pCO_2 data (del Giorgio et al. 1999; Riera et al. 1999; Kelly et al. 2001; Sobek et al. 2003, 2005; Roehm et al. 2009; Teodoru et al. 2009). There is in general a positive relationship between pCO_2 and DOC that can be indicative of terrestrial organic matter inputs (as traced by DOC) sustaining net heterotrophy in freshwater ecosystems (as indicated by pCO_2). Alternatively and not incompatibly, this positive relationship can also be indicative of lateral inputs of both DOC and CO_2 from soils by ground-waters and surface run-off. Values in the main basin of Lake Kivu compare surprisingly well to the relationship of pCO_2 and DOC established from a global compilation of lakes across all climatic zones (Fig. 4.9), yet at the lower end of values in agreement with the oligotrophic nature of Lake Kivu. Values in Kabuno Bay stand clearly above the relationship of pCO_2 and DOC in lakes globally, testifying the role of large contribution of CO_2 from subaquatic springs.

$\delta^{13}C_{DIC}$ signatures for surface waters in Lake Kivu range between +2.6‰ and +3.5‰ for the main basin and between +0.3‰ and +1.5‰ for Kabuno Bay, which is in the higher range of that reported earlier for lakes (Fig. 4.10). $\delta^{13}C_{DIC}$ signatures
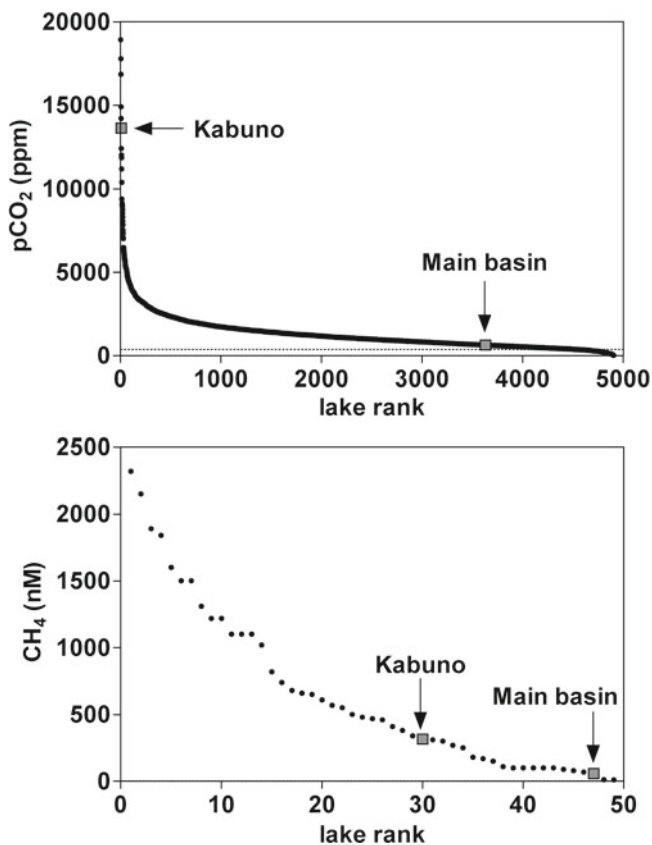
Fig. 4.8 Comparison by rank of the partial pressure of CO_2 (pCO_2, ppm) and of CH_4 concentration (nM) in surface waters of the main basin of Lake Kivu and Kabuno Bay (average of the four cruises at 10 m) with global compilations in lakes by Sobek et al. (2005) and Bastviken et al. (2004), respectively

in lakes are to a large extent determined by the geochemistry of the watershed, but are further influenced by biological processes including respiration (which adds ^{13}C-depleted CO_2), photosynthesis (which preferentially removes $^{12}CO_2$, and subsequently leads to higher $\delta^{13}C_{DIC}$), and methane oxidation (which adds highly ^{13}C-depleted CO_2). In Lake Kivu, the majority of DIC is thought to be of magmatic origin (Schoell et al. 1988), with typically rather ^{13}C-enriched signatures between $^-7‰$ and $-4‰$ (Tietze et al. 1980). $\delta^{13}C_{DIC}$ in surface waters of Lake Kivu are slightly higher and DIC concentrations are consistently higher in Lake Kivu than in Lakes Tanganyika and Malawi (Table 4.1), where the contribution of subaquatic springs is thought to be significantly lower (Table 4.2). Given the very high DIC concentrations in Lake Kivu, the magmatic inputs likely provide the dominant imprint on $\delta^{13}C_{DIC}$ signatures, although seasonal and depth variations (Figs. 4.4 and 4.7) clearly hold information on the mixing regime and biological processes which
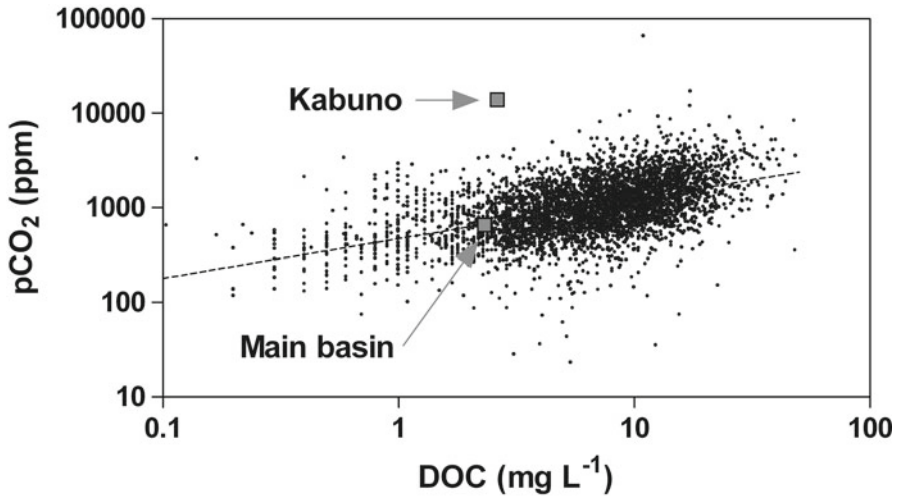
Fig. 4.9 Relationship between partial pressure of CO_2 (pCO_2, ppm) and dissolved organic carbon (DOC, mg L^{-1}) in lakes reported by Sobek et al. (2005; $\log(pCO_2) = 2.67 + 0.414 \log(DOC)$; $r^2 = 0.26$) and values in the main basin of Lake Kivu and Kabuno Bay (average of the four cruises at 10 m)

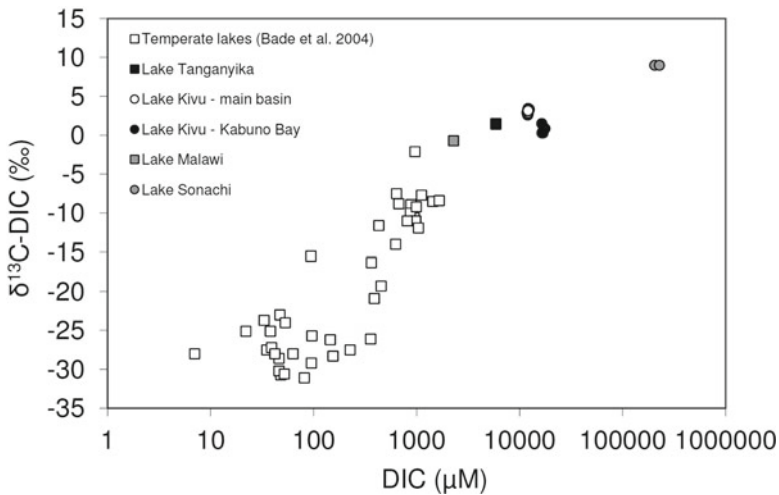**Fig. 4.10** Comparison of dissolved inorganic carbon (DIC, µM) concentrations and $\delta^{13}C_{DIC}$ (‰) across a range of lakes: Lake Kivu (surface waters from main basin and Kabuno Bay, this study), Lake Tanganyika (Craig 1974), Lake Malawi (Hecky and Hesslein 1995), Lake Sonachi (Kenya, own unpublished data), and from a survey in a range of temperate lakes (Bade et al. 2004)

need to be examined in more detail. Interestingly, data from Lake Sonachi, a small crater lake adjacent to Lake Naivasha, Kenya (see e.g. Verschuren 1999) show even more extreme DIC concentrations (200–230 mM) and $\delta^{13}C_{DIC}$ signatures of +9‰ (Fig. 4.10) which is among the highest recorded so far in any lake system. The latter

Table 4.1 Comparison of salinity, total alkalinity (TA, mM), dissolved inorganic carbon (DIC, mM) and the partial pressure of CO_2 (pCO_2, ppm) from surface waters of Lake Malawi (Hecky and Hesslein 1995; Branchu et al. 2010), Lake Tanganyika (Craig 1974), the main basin of Lake Kivu and Kabuno Bay (this study)

	Salinity	TA (mM)	DIC (mM)	pCO$_2$ (ppm)
Lake Malawi	0.2	2.33	2.3	N/A
Lake Tanganyika	0.7	6.54	5.9	280
Main basin of Lake Kivu	1.2	13.00	12.0	640
Kabuno Bay	1.6	16.90	17.3	13,640

pCO$_2$ data in Lake Tanganyika were computed from original DIC and TA data reported by Craig (1974) using the carbonic acid dissociation constants of Millero et al. (2006), and adjusted to 2008 by accounting for the increase of atmospheric CO_2

Table 4.2 Morphometry and hydrology of Lakes Kivu (Chap. 2), Tanganyika and Malawi (Branchu 2001)

	Lake Kivu	Lake Tanganyika	Lake Malawi
Surface (km^2)	2,370	32,600	28,800
Volume (km^3)	580	18,880	8,400
Precipitation (km^3 year^{-1})	3.3	32.6	44.1
Evaporation (km^3 year^{-1})	3.6	55.3	59.6
Surface inflows (km^3 year^{-1})	2.0	29.0	28.8
Outflow (km^3 year^{-1})	3.0	6.3	12.1
Flow from subaquatic springs (km^3 year^{-1})	1.3	?	1.3
Flushing time (years)[a]	193	2,997	697
Residence time (years)[b]	88	306	113

[a]Volume/outflow

[b]Volume/(precipitation+inflow)

values would be consistent with high primary production and predominantly mantle-derived CO_2 inputs in this enclosed system.

In Table 4.1, salinity, TA, DIC and pCO_2 values from surface waters of Lake Kivu are compared to limited data-sets from Lakes Malawi and Tanganyika. The higher salinity and TA values in Lake Tanganyika than in Lake Malawi are probably related to the higher residence time, flushing time and ratio of evaporation to precipitation in Lake Tanganyika (Table 4.2). The higher salinity, TA, DIC and pCO_2 values in Lake Kivu than Lake Tanganyika cannot be explained in terms of higher residence time and flushing time. This would suggest that higher values of these quantities in Lake Kivu are due to subaquatic springs that are undocumented in Lake Tanganyika. Subaquatic springs in Lake Kivu are similar in terms of flow to those in Lake Malawi but the volume of Lake Kivu is more than 14 times smaller, leading to a more intense impact on the chemistry of Lake Kivu. Based on available data, Lake Tanganyika behaves as a sink for atmospheric CO_2, while the present data shows that Lake Kivu is a source of CO_2 to the atmosphere throughout the annual cycle. The sink of CO_2 in Lake Tanganyika should be sustained by an export
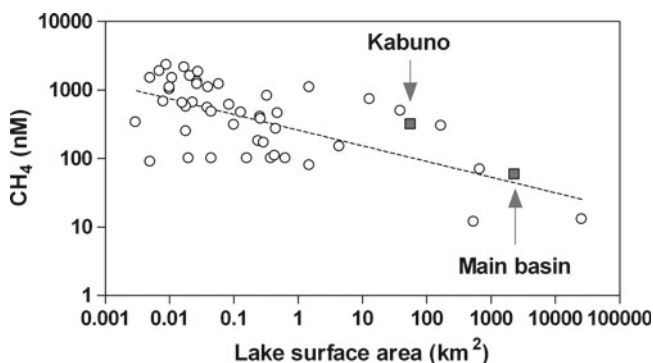
Fig. 4.11 Relationship between CH_4 concentration (nM) and lake surface area (km²) in the main basin of Lake Kivu and Kabuno Bay (average of the four cruises at 10 m) and from the compilation by Bastviken et al. (2004). Relationship between CH_4 concentration and lake surface area ($\log(CH_4) = 2.42 - 0.229 \log$(lake surface area); $r^2 = 0.40$; $p < 0.0001$; $n = 47$) was not originally reported by Bastviken et al. (2004) but is based on the same data-set. Note the higher number of observations of CH_4 in lakes smaller than 10 km² (adapted from Borges et al. 2011)

of organic carbon from surface to depth. There is no reason to believe that Lake Kivu should behave otherwise in the terms of export of organic C to depth. This would imply that the source of CO_2 to atmosphere in Lake Kivu is mainly sustained from inputs to surface waters of DIC from depth (subaquatic springs).

The CH_4 concentrations in surface waters of Lake Kivu were surprisingly low compared to lakes globally, considering the huge amounts of CH_4 contained in the deep layer of the lake, i.e. concentrations up to 10^6 higher than in surface waters (Schmid et al. 2005). Cross-system comparison of CH_4 in surface waters of lakes was carried out as a function of lake surface area (Fig. 4.11). Both Kabuno Bay and the main basin of Lake Kivu fall on the negative relationship between CH_4 and lake surface area. There is probably not a unique explanation of the negative relationship between CH_4 concentrations and lake surface area, but rather a combination of several factors. In smaller systems there is a higher supply of allochthonous inputs (from catchment and littoral zone) of nutrients and organic C relative to volume of lake (i.e., large ratio of catchment area to lake surface area). This will sustain high levels of degradation in sediments of organic C of allochthonous and autochthonous nature (the former sustained by allochthonous nutrient inputs) (Schindler 1971), and promotes a higher flux of CH_4 from sediments to the water column in smaller systems. As a first approximation, we can also assume that smaller systems are shallower than larger ones. In shallow systems there will be a higher probability of sediment re-suspension coupled to a lower removal of CH_4 by bacterial oxidation, due to a shorter distance between sediments and the air-water interface. Finally, in larger systems, there will be a lower fetch limitation of wind induced turbulence and gas transfer velocity (Wanninkhof 1992; Fee et al. 1996) leading to a higher loss of CH_4 by

emission to the atmosphere (for an identical air-water gradient of CH_4). The lower fetch limitation of wind induced turbulence in larger systems will also promote deeper oxygenated mixed layers, promoting CH_4 loss by bacterial aerobic CH_4 oxidation.

4.4 Conclusions

There are several lines of evidence (see Chaps. 5 and 6) that suggest that the epilimnion of Lake Kivu is net autotrophic, whereby gross primary production exceeds community respiration. This is consistent with the fact that the watershed of Lake Kivu is only about twice as large as the lake surface (Chap. 2), and a very narrow littoral zone due to steep shores, whereby the contribution of allochthonous organic C inputs to the overall organic C fluxes in the lake is expected to be minor. We then conclude that the over-saturation of surface waters with respect to atmospheric CO_2 and emission of CO_2 to the atmosphere (on average for the four cruises: 6 and 289 mmol m^{-2} day^{-1}, in the main basin and Kabuno Bay, respectively) are sustained by inputs of CO_2 from depth derived from subaquatic springs and the degradation of organic carbon.

The CH_4 concentrations in surface waters of Lake Kivu were surprisingly low compared to lakes globally, considering the huge amounts of CH_4 contained in the deep layer of the lake, i.e. concentrations up to 10^6 higher than in surface waters (Schmid et al. 2005). This is related to highly stratified conditions of the lake that promote a very strong removal of CH_4 by bacterial oxidation (Jannasch 1975; Pasche et al. 2011) leading to low CH_4 concentrations in surface waters, and a modest emission of CH_4 to the atmosphere (on average for the four cruises: 36 and 106 μmol m^{-2} day^{-1}, in the main basin and Kabuno Bay, respectively).

Kabuno Bay showed distinct pCO_2, CH_4, pH and $\delta^{13}C_{DIC}$ values compared to the main basin of Lake Kivu, which are related to a larger contribution of subaquatic springs inputs as suggested by vertical profiles of all reported variables. A large contribution of CO_2 from subaquatic springs could also explain that Kabuno Bay ranks seventh in terms of pCO_2 in surface waters compared to lakes globally, and that values strongly deviate from the relationship between pCO_2 and DOC in lakes globally.

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