

Diffusive methane emissions to the atmosphere from Lake Kivu (Eastern Africa)

A. V. Borges,¹ G. Abril,^{2,3} B. Delille,¹ J.-P. Descy,⁴ and F. Darchambeau^{1,4}

Received 1 February 2011; revised 24 May 2011; accepted 7 June 2011; published 9 September 2011.

[1] We report a data set of methane (CH₄) concentrations in the surface waters of Lake Kivu obtained during four cruises (March 2007, September 2007, June 2008, and April 2009) covering the two main seasons, rainy (October to May) and dry (June to September). Spatial gradients of CH₄ concentrations were modest in the surface waters of the main basin. In Kabuno Bay (a small subbasin), CH₄ concentrations in surface waters were significantly higher than in the main basin. Seasonal variations of CH₄ in the main basin were strongly driven by deepening of the mixolimnion and mixing of surface waters with deeper waters rich in CH₄. On an annual basis, both Kabuno Bay and the main basin of Lake Kivu were over-saturated in CH₄ with respect to atmospheric equilibrium (7330% and 2510%, respectively), and emitted CH₄ to the atmosphere (39 mmol m⁻² yr⁻¹ and 13 mmol m⁻² yr⁻¹, respectively). The source of CH₄ to atmosphere was two orders of magnitude lower than the CH₄ upward flux. The source of CH₄ to the atmosphere from Lake Kivu corresponded to ~60% of the terrestrial sink of atmospheric CH₄ over the lake's catchment. A global cross-system comparison of CH₄ in surface waters of lakes shows that both Kabuno Bay and the main basin are at the lower end of values in lakes globally, despite the huge amounts of CH₄ in the deeper layers of the lake. This is related to the strongly meromictic nature of the lake that promotes an intense removal of CH₄ by bacterial oxidation.

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

1. Introduction

[2] Freshwater environments are important components of the global carbon (C) cycle, as they transport organic and inorganic C from the terrestrial biosphere to the oceans. This transport of C is not passive, and freshwater ecosystems produce, degrade, store organic C and exchange C with the atmosphere [Cole and Caraco, 2001; Cole et al., 2007; Battin et al., 2008; Tranvik et al., 2009]. Degradation of organic C in freshwater environments is partly mediated by anaerobic processes, including methanogenesis, which leads to the emission of methane (CH₄) to the atmosphere. The global emission of CH₄ to the atmosphere from freshwater ecosystems has been recently reevaluated by Bastviken et al. [2011] to 103 Tg CH₄ yr⁻¹ which is significant when compared to other natural (168 Tg CH₄ yr⁻¹) and anthropogenic (428 Tg CH₄ yr⁻¹) CH₄ emissions [Chen and Prinn, 2006].

The CH₄ emission from freshwater ecosystems is broken down into 72 Tg CH₄ yr⁻¹ from lakes, 20 Tg CH₄ yr⁻¹ from reservoirs, 1 Tg CH₄ yr⁻¹ from rivers, and 10 Tg CH₄ yr⁻¹ plant mediated (all aquatic systems). About 49% of the CH₄ emission to the atmosphere from freshwater ecosystems occurs in the tropics, although tropical lakes are under-sampled. In the Bastviken et al. [2011] compilation, only 9 out of 36 publications, and only 7 out of 106 data entries deal with tropical lakes.

[3] We report the seasonal and spatial variability of CH₄ in the epilimnion of Lake Kivu [2.50°S 1.59°S 29.37°E 28.83°E] one of the East African great lakes (2370 km² surface area, 550 km³ volume). Lake Kivu is a deep (maximum depth of 485 m) meromictic lake, with an oxic mixolimnion down to 70 m, and a deep monolimnion rich in dissolved gases and nutrients [Degens et al., 1973; Schmid et al., 2005]. Lake Kivu is permanently stratified and deep layers receive heat, salts, and CO₂ from deep geothermal springs [Schmid et al., 2005]. Seasonality of the physical and chemical vertical structure and biological activity 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 a deepening of the mixolimnion [Sarmiento et al., 2006]. This seasonal mixing favors the input of dissolved nutrients and the development of diatoms, while, during the rest of the

¹Unité d'Océanographie Chimique, Université de Liège, Liège, Belgium.

²Laboratoire Environnements et Paléoenvironnements Océaniques, UMR CNRS 5805, Université de Bordeaux 1, Talence, France.

³Institut de Recherche pour le Développement, Laboratório de Potamologia Amazônica, Universidade Federal do Amazonas, Manaus, Brazil.

⁴Laboratoire d'écologie des Eaux Douces, URBE, University of Namur, Namur, Belgium.

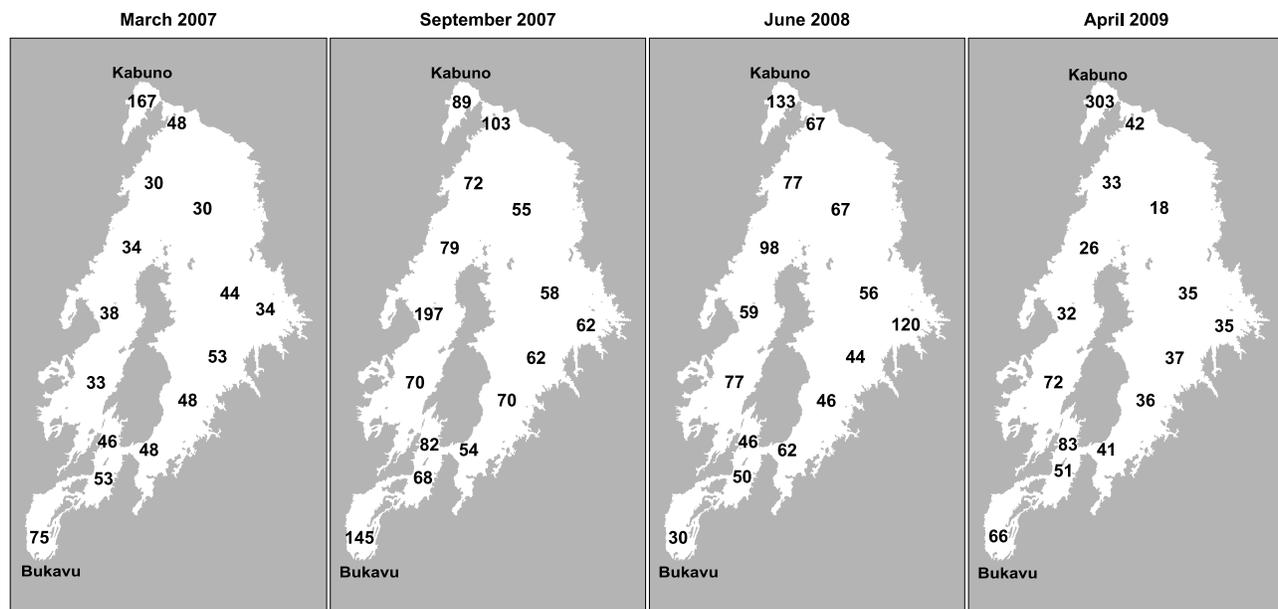


Figure 1. Distribution of the CH₄ concentration (nM) in surface waters of Lake Kivu (10 m depth in the main basin and 5 m depth in Kabuno Bay) in March 2007, September 2007, June 2008, and April 2009.

year, the phytoplankton assemblage is dominated by cyanobacteria, chrysophytes and cryptophytes.

[4] Huge amounts of carbon dioxide (CO₂) and CH₄ (300 km³ and 60 km³, respectively, at 0°C and 1 atm) [Schmid *et al.*, 2005] are dissolved in the deep layers of Lake Kivu. While CO₂ is mainly geogenic, two thirds of the CH₄ originates from anoxic bacterial reduction of CO₂ and one third from anaerobic degradation of settling organic material [Schoell *et al.*, 1988; Pasche *et al.*, 2011]. Large scale industrial extraction of CH₄ from the deep layers of Lake Kivu is planned [Nayar, 2009] which could affect the ecology and biogeochemical cycling of C of the lake and change for instance the emission of greenhouse gases such as CH₄ and CO₂. To monitor, understand and quantify the consequences of the industrial extraction of CH₄ it is required to establish the baseline of ecological and biogeochemical settings.

2. Material and Methods

[5] In order to capture the seasonal and spatial variations of CH₄ in surface waters, four cruises were carried out in Lake Kivu on 15–29 March 2007 (middle of the rainy season), 28 August to 10 September 2007 (late dry season), 21 June to 3 July 2008 (early dry season), and 21 April to 5 May 2009 (late rainy season). Sampling was carried out at 15 stations distributed in a relatively regular grid covering the whole lake (Figure 1).

[6] 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. Conductivity cell was calibrated with a 1000 μS cm⁻¹ (25°C) YSI standard, pH electrode was calibrated with pH 4.00 (25°C) and pH 7.00 (25°C) National Institute of Standards

and Technology (YSI) buffers, oxygen membrane probe was calibrated with humidity saturated ambient air. Water was sampled with a 5 L Niskin bottle (Hydro-Bios) at 5 m in Kabuno Bay (48 km²) and at 10 m in the rest of the lake (hereafter referred to as main basin, 2322 km²). During the April 2009 cruise, samples were also collected at all stations at 0.5 m, and vertical profiles were made down to 80 m depth at two stations. Water was collected in glass serum bottles from the Niskin bottle with tubing, left to overflow, poisoned with 100 μl of saturated HgCl₂ and sealed with butyl stoppers and aluminum caps.

[7] Concentrations of CH₄ were determined by gas chromatography (GC) with flame ionization detection (GC-FID, Hewlett Packard HP 5890A), after creating a 12 ml headspace with N₂ in 40 ml glass serum bottles, as described by Abril and Iversen [2002]. Certified CH₄:N₂ mixture (Air Liquide France) of 10.0 ± 0.2 ppm CH₄ was used as standard. For the April 2009 cruise, CH₄ measurements were carried out with the same procedures but using 30 ml headspace with N₂ in 70 ml serum bottles, and a SRI 8610C GC-FID calibrated with CH₄:CO₂:N₂O:N₂ mixtures (Air Liquide Belgium) of 1.05 ± 0.02, 10.2 ± 0.2 and 509 ± 10 ppm CH₄. Precision estimated from multiple injections of gas standards was on average ±4% for the 10.0 ppm standard with the HP 5890A GC-FID. Precision was better than ±3% for the 1.05 ppm standard and better than ±0.5% for both the 10.2 ppm and 509 ppm standards with the SRI 8610C GC-FID. The concentrations were computed using the CH₄ solubility coefficient given by Yamamoto *et al.* [1976].

[8] During the April 2009 cruise, on all stations, CH₄ data were acquired at two depths, near surface (~0.5 m) and below (10 m in the main basin and 5 m in Kabuno Bay), and were not significantly different (paired *t* test, *p* = 0.125, *n* = 15). Hence, CH₄ concentrations at 10 m in the main basin and at 5 m in Kabuno Bay were used for the 4 cruises to

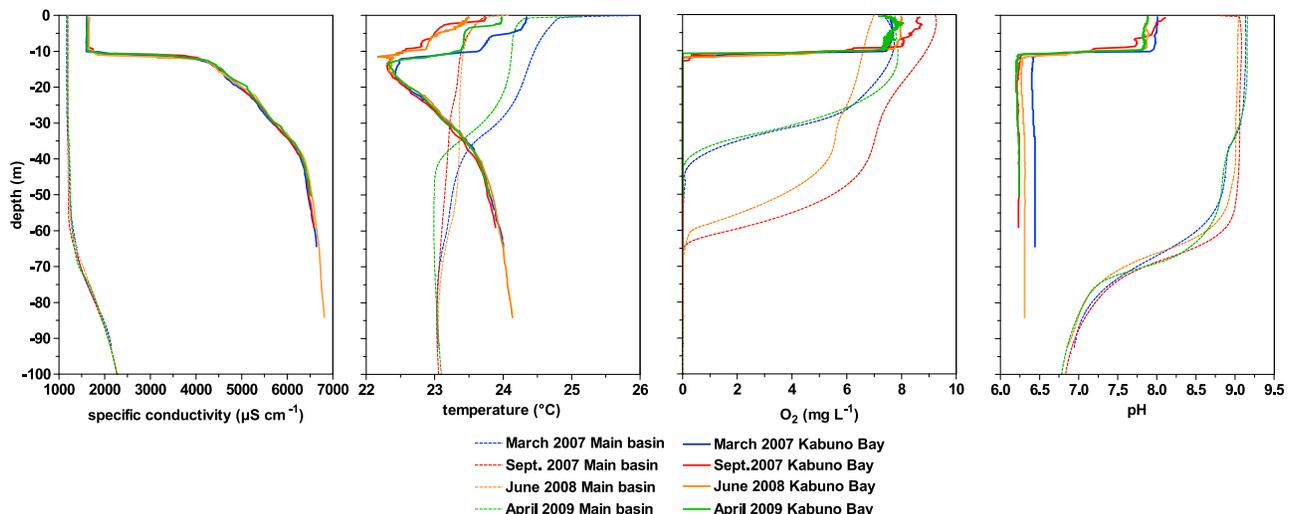


Figure 2. Vertical profiles of specific conductivity (25°C, $\mu\text{S cm}^{-1}$), temperature ($^{\circ}\text{C}$), dissolved O₂ (mg L^{-1}), and pH in the main basin of Lake Kivu (average of all stations) and Kabuno Bay in March 2007, September 2007, June 2008, and April 2009.

compute the diffusive air-water CH₄ flux (F_{CH_4}), according to

$$F_{\text{CH}_4} = k \Delta[\text{CH}_4]$$

where k is the gas transfer velocity of CH₄ and $\Delta[\text{CH}_4]$ is the air-water gradient of CH₄ computed from CH₄ concentration in the water and a constant atmospheric CH₄ concentration of 1.8 ppm (corresponding to the global average mixing ratio).

[9] The value k was computed from wind speed using the parameterization of *Cole and Caraco* [1998] and the Schmidt number of CH₄ in freshwater according to the algorithm given by *Wanninkhof* [1992]. Wind speed data were acquired with a Davis Instruments meteorological station in Bukavu (2.51°S 28.86°E). During the April 2009 cruise, wind speed was measured at 11 stations on the lake with a THIES anemometer, and data were not significantly different from those acquired at Bukavu (paired t test, $p = 0.593$, $n = 11$). F_{CH_4} was computed with daily wind speed averages for a time period of one month centered 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_{CH_4} values that are seasonally representative.

3. Results and Discussion

[10] In the main basin of Lake Kivu, the seasonal variation of temperature in surface waters was modest, ranging between 23.35 ± 0.18 (standard deviation) $^{\circ}\text{C}$ in September 2007 and $24.43 \pm 0.18^{\circ}\text{C}$ in March 2007. The oxycline varied seasonally between ~ 35 m in March 2007 and April 2009 and ~ 60 m in September 2007 and June 2008, while the chemocline (conductivity, pH) was relatively stable and started at 60 m (Figure 2). In Kabuno Bay, the amplitude of the seasonal variations of temperature in surface waters was similar ($\sim 1.1^{\circ}\text{C}$) but values were systematically lower than in the main basin between 0.3°C and 0.7°C depending on the cruise. Kabuno Bay was characterized by a very stable

chemocline (conductivity, pH) and oxycline at ~ 10.5 m, irrespective of the sampling period. At 60 m, conductivity and water temperature were markedly higher in Kabuno Bay than in the main basin. These vertical patterns and their lack of seasonality indicate that Kabuno Bay is distinct from the main basin. There seems to be a much larger contribution of internal geothermal inputs to the whole water column including surface waters in Kabuno Bay than in the main basin of Lake Kivu (not necessarily in terms of absolute inputs but possibly in terms of the ratio of inputs to volume). This is related to the different geomorphology, since Kabuno Bay is shallower than the main basin (maximum depth of 110 m versus 485 m) and exchanges little water with the main basin (narrow connection ~ 10 m deep).

[11] In surface waters of the main basin of Lake Kivu, CH₄ concentrations 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 (Figure 1). The coefficient of variation of CH₄ in surface waters of the main basin ranged between 26% in March 2007 and 46% in September 2007. We cannot provide a straightforward explanation for these small spatial variations of CH₄ concentrations. For a given cruise, CH₄ concentrations did not correlate with mixed layer depth nor water temperature. For the whole data set, CH₄ concentrations in surface waters of Kabuno Bay were significantly higher than in the main basin (repeated measures ANOVA, $f_{4,10} = 61.85$, $p < 0.0001$). The CH₄ 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 CH₄ 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 contribution of deepwater springs in Kabuno Bay than in the main basin increases the upward flux of solutes and might explain the higher CH₄ concentrations we observed in Kabuno Bay than in the main basin. Also, the

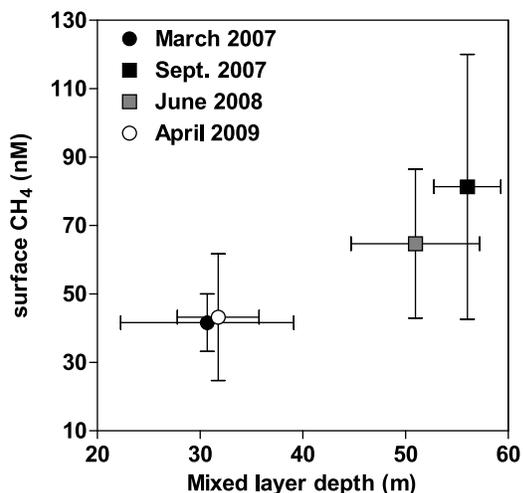


Figure 3. Mean values in the main basin of Lake Kivu of CH₄ concentration in surface waters (10 m, nM) versus mixed layer depth in March 2007, September 2007, June 2008, and April 2009. Error bars correspond to standard deviation on the mean.

shallower oxycline in Kabuno Bay (Figure 2) than in the main basin could promote less removal of CH₄ by aerobic bacterial oxidation in the oxic layer.

[12] Seasonal variations of CH₄ in the main basin of Lake Kivu were significant (one-way ANOVA, log-transformed data, $f_{3,52} = 10.55$, $p < 0.0001$). Average CH₄ concentrations for each cruise were positively correlated (Pearson $r^2 = 0.96$, $p = 0.0214$) to mixed layer depth (Figure 3). This suggests that the deepening of the mixed layer and mixing of deeper waters rich in CH₄ with surface waters was a major driver of seasonal variability of CH₄ concentrations in surface waters of the main basin of Lake Kivu. Vertical profiles obtained in April 2009 in the main basin, show that CH₄ concentrations at 60 m are ~2100 to ~2600 times higher than in surface waters (Figure 4).

[13] Deepening of the mixed layer is induced by enhanced turbulence in surface waters which will also increase k and the loss of CH₄ to the atmosphere. However, CH₄ is a sparingly soluble gas and the exchange of CH₄ across the air-water interface is a slow process. For the conditions in September 2007, the reduction by 50% of the initial surface average CH₄ concentration (81 nM) by loss to the atmosphere would require about 67 days and the reduction by 95% would require 354 days (with a constant wind speed of 1.2 m s⁻¹ and a mixed layer of 56 m). As the loss of CH₄ to

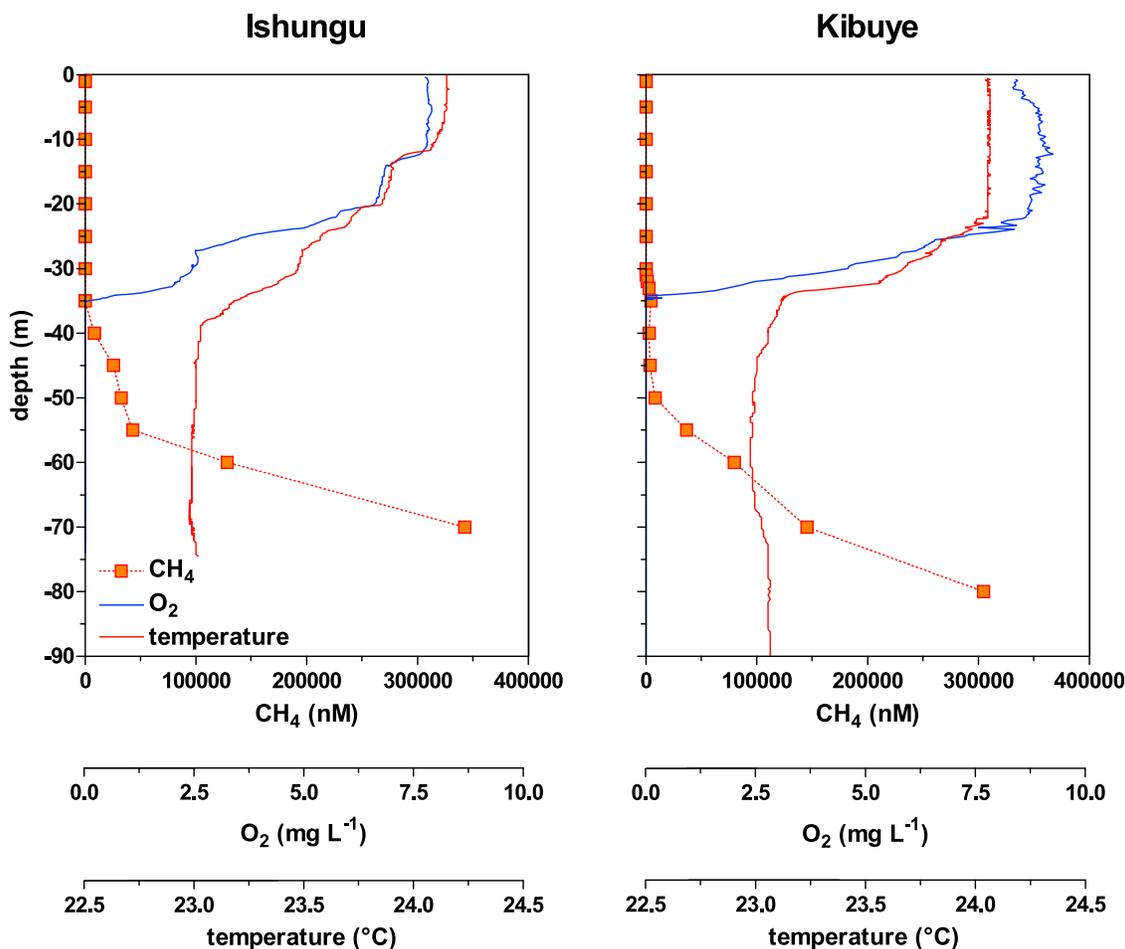


Figure 4. Vertical profiles of CH₄ (nM), temperature (°C), and dissolved O₂ (mg L⁻¹) in April 2009 at two stations in the main basin of Lake Kivu (Ishungu (2.34°S, 28.98°E) and Kibuye (2.05°S, 29.29°E)).

Table 1. Average of Wind Speed, CH₄ Saturation and FCH₄ in the Main Basin of Lake Kivu and Kabuno Bay During Four Cruises and Overall Average^a

	Wind Speed (m s ⁻¹)	CH ₄ Saturation (%)	FCH ₄ (μmol m ⁻² d ⁻¹)
<i>March 2007</i>			
Kabuno Bay	1.3 ± 0.4	7143	103 ± 7
Main basin	1.3 ± 0.4	1897 ± 494	26 ± 7
<i>September 2007</i>			
Kabuno Bay	1.2 ± 0.4	3736	53 ± 4
Main basin	1.2 ± 0.4	3552 ± 1642	50 ± 24
<i>June 2008</i>			
Kabuno Bay	1.6 ± 0.2	5593	85 ± 4
Main basin	1.6 ± 0.2	2722 ± 957	41 ± 15
<i>April 2009</i>			
Kabuno Bay	1.3 ± 0.2	12840	185 ± 8
Main basin	1.3 ± 0.2	1887 ± 772	26 ± 11
<i>Average</i>			
Kabuno Bay	1.4 ± 0.4	7328 ± 3930	106 ± 57
Main basin	1.4 ± 0.4	2514 ± 795	36 ± 12

^aAverage is plus or minus the standard deviation. Lake Kivu main basin at ~2322 km²; Kabuno Bay at ~48 km².

the atmosphere is a slow process and does not balance at short time scales the input of CH₄ by vertical mixing, the net effect of enhanced turbulence in Lake Kivu is an increase of CH₄ in the mixed layer.

[14] In Kabuno Bay, seasonal variations were opposed to those observed in the main lake with values lower during the dry season (September 2007, June 2008) than during the wet season (March 2007, April 2009). We cannot provide a straightforward explanation for the seasonal variations of CH₄ in surface waters of Kabuno Bay, that are probably related to variations of input terms (the upward flux of CH₄) and/or loss terms (performance and abundance of methanotrophic bacteria or emission of CH₄ to the atmosphere).

[15] Average wind speed values were significantly different among the four cruises (one-way ANOVA, $f_{3,81} = 5.93$, $p = 0.00104$), and average value in June 2008 was significantly higher than during the other cruises (post hoc Tukey's honestly significant difference test, $p < 0.05$). Yet, seasonal variations of wind speed were rather modest (coefficient of variation of 13%), hence, seasonal FCH₄ variations closely tracked those of CH₄ concentrations with FCH₄ values ranging between 26 and 50 μmol m⁻² d⁻¹ in the main basin, and between 53 and 185 μmol m⁻² d⁻¹ in Kabuno Bay (Table 1).

[16] Vertical mixing in surface of Lake Kivu follows a regular bimodal seasonal cycle according to the two main seasons (wet and dry). Mixed layer is shallowest in April (late wet season) and deepest in August–September (late dry season) [Sarmiento *et al.*, 2006]. Hence, our four cruises bracket reasonably well the seasonality of physical structure of surface waters in Lake Kivu. Since vertical mixing seems to be the main driver of CH₄ seasonal variations in surface waters of Lake Kivu (Figure 3), this allows evaluating robustly annual CH₄ emission rates. The annually integrated CH₄ emission to the atmosphere was 13 mmol m⁻² yr⁻¹ (30.5 10⁶ mol yr⁻¹) for the main basin of Lake Kivu and 39 mmol m⁻² yr⁻¹ (1.9 10⁶ mol yr⁻¹) for Kabuno Bay (Table 1).

The total emission of CH₄ to the atmosphere (32.4 10⁶ mol yr⁻¹) was extremely small compared to the total inventory of CH₄ predominantly in deeper layers of 2.7 10¹² mol (based on values reported by Schmid *et al.* [2005]). The emission of CH₄ to the atmosphere (14 mmol m⁻² yr⁻¹) was also very small compared to the upward flux of CH₄ of 2917 mmol m⁻² yr⁻¹ [Pasche *et al.*, 2011], consistent with a comparable CH₄ oxidation rate of 2628 mmol m⁻² yr⁻¹ [Jannasch, 1975].

[17] Air-soil CH₄ fluxes were scaled to the lake's catchment using the total catchment area of 5097 km² with a 72% coverage by cropland and pasture, and a 28% coverage by shrubland and evergreen forest [Muvundja *et al.*, 2009]. We used for the air-soil CH₄ fluxes a value of -1 μmol m⁻² d⁻¹ for cropland based on measurements in Burkina Faso [Brümmer *et al.*, 2009] and a value of -95 μmol m⁻² d⁻¹ for forests derived from the average from several sites (excluding flooded forests) across East, Central and West Africa [Delmas *et al.*, 1992; Tathy *et al.*, 1992; Macdonald *et al.*, 1998, 1999; Werner *et al.*, 2007]. Potential terrestrial sources of CH₄ related to biomass burning, termites and cattle could not be quantified due to lack of appropriate information. The sink of atmospheric CH₄ on the catchment of Lake Kivu can be evaluated on first approximation at -51 10⁶ mol yr⁻¹. Hence, the emission of CH₄ from the lake's surface to the atmosphere (32 10⁶ mol yr⁻¹) corresponds to 63% of the terrestrial sink of CH₄ on the lake's catchment area.

[18] When compared to other lakes globally as reported by Bastviken *et al.* [2004], the main basin of Lake Kivu ranks 47th and Kabuno Bay ranks 30th in terms of CH₄ concentration in surface waters (out of 49 lakes). Cross-system comparison of CH₄ in surface waters of lakes was carried out as function of lake surface area (Figure 5). Both Kabuno Bay and the main basin of Lake Kivu fall on the negative relationship between CH₄ and lake surface area. There is probably no unique explanation of the negative relationship between CH₄ concentrations and lake surface area, but rather a combination of several factors. In smaller

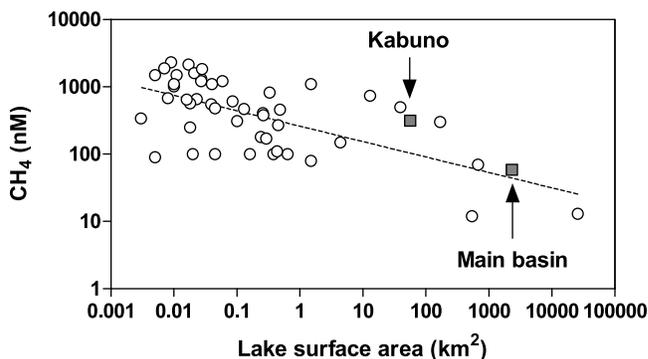


Figure 5. CH₄ concentration (nM) versus lake surface area (km²) in the main basin of Lake Kivu and Kabuno Bay and from the compilation by Bastviken *et al.* [2004]. Relationship between CH₄ concentration and lake surface area (log(CH₄) = 2.42 - 0.229 log(lake surface area); $r^2 = 0.40$; $p < 0.0001$; $n = 47$) was not originally reported by Bastviken *et al.* [2004] but is based on the same data set. Note the higher number of observations of CH₄ in lakes smaller than 10 km².

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). Hence, in smaller systems, higher levels of benthic degradation of organic C should occur in relation to higher availability of allochthonous organic carbon and of autochthonous organic carbon (the former sustained by higher allochthonous nutrient inputs) [Schindler, 1971; Rasmussen *et al.*, 1989; Fee *et al.*, 1992, 1994; Curtis and Schindler, 1997; Cole *et al.*, 2006; Weidel *et al.*, 2008]. This will promote a higher flux of CH₄ from sediments to the water column in smaller systems. As a first approximation, we can also assume that the smaller systems are shallower than larger ones. In shallow systems, there will be a lower removal of CH₄ 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 *k* [Wanninkhof, 1992; Fee *et al.*, 1996] leading to a higher loss of CH₄ by emission to the atmosphere (for an identical air-water gradient of CH₄). The lower fetch limitation of wind induced turbulence in larger systems will also promote deeper oxygenated mixed layers, promoting CH₄ loss by bacterial aerobic CH₄ oxidation.

4. Conclusions

[19] Surface waters of Lake Kivu were oversaturated with respect to CH₄ atmospheric equilibrium, with saturation levels ranging seasonally between 1887% and 3552% in the main basin, and between 3736% and 12840% in Kabuno Bay (Table 1). Yet, the CH₄ concentrations in surface waters of Lake Kivu are surprisingly low compared to lakes globally (Figure 5), considering the huge amounts of CH₄ contained in the deep layer of the lake, i.e., concentrations up to 10⁶ 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 CH₄ by bacterial oxidation [Jannasch, 1975] leading to low CH₄ concentrations in surface waters. Indeed, the average CH₄ oxidation rate (2628 mmol m⁻² yr⁻¹) reported by Jannasch [1975] in the main basin of Lake Kivu is 200 times higher than the average CH₄ emission to the atmosphere in the main basin (Table 1). The annually integrated CH₄ emissions to the atmosphere from the main basin of Lake Kivu (13 mmol m⁻² yr⁻¹; 30.5 10⁶ mol yr⁻¹) and Kabuno Bay (39 mmol m⁻² yr⁻¹; 1.9 10⁶ mol yr⁻¹, Table 1) are minimal estimates since we did not quantify plant mediated and ebullition CH₄ fluxes. Plant mediated CH₄ fluxes and shallow sediment CH₄ ebullition fluxes are expected to be marginal in Lake Kivu, since the littoral zone is very narrow owing to the steep shores [Degens *et al.*, 1973]. Ebullition CH₄ fluxes remain to be determined in the deeper areas of the lake, however, since Lake Kivu is very deep, it can be expected that if CH₄ bubbles occur, they dissolve before reaching surface waters [e.g., McGinnis *et al.*, 2006].

[20] **Acknowledgments.** We are grateful to Boniface Kaningini and Pascal Mwapu Isumbisho (Institut Supérieur Pédagogique, Bukavu, République Démocratique du Congo) and Laetitia Nyinawamwiza (National University of Rwanda, Butare, Rwanda) and their respective teams for logistic support during the cruises; to M.-V. Commarieu, C. Morana, G. Lepoint,

and M. K. Živadinović for help in field sampling; to D. Poirier for analytical assistance; and to the Editor (D. Baldocchi), the Associate Editor (P. Raymond), and one anonymous reviewer for constructive comments on a previous version of the manuscript. This work was funded by the Fonds National de la Recherche Scientifique (FNRS) under the CAKI (Cycle du carbone et des nutriments au Lac Kivu, contract 2.4.598.07) and MICKI (Microbial diversity and processes in Lake Kivu, contract 2.4.515.11) projects and contributes to the European Research Council starting grant project AFRIVAL (African river basins: Catchment-scale carbon fluxes and transformations, 240002) and to the Belgian Federal Science Policy Office EAGLES (East African Great Lake Ecosystem Sensitivity to changes, SD/AR/02A) project. A.V.B. and B.D. are research associates at the F.R.S-FNRS.

References

- Abril, G., and N. Iversen (2002), Methane dynamics in a shallow, non-tidal, estuary (Randers Fjord, Denmark), *Mar. Ecol. Prog. Ser.*, **230**, 171–181, doi:10.3354/meps230171.
- Bastviken, D., J. Cole, M. Pace, and L. Tranvik (2004), Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate, *Global Biogeochem. Cycles*, **18**, GB4009, doi:10.1029/2004GB002238.
- Bastviken, D., L. J. Tranvik, J. A. Downing, P. M. Crill, and A. Enrich-Prast (2011), Freshwater methane emissions offset the continental carbon sink, *Science*, **331**, 50, doi:10.1126/science.1196808.
- Battin, T. J., L. A. Kaplan, S. Findlay, C. S. Hopkinson, E. Marti, A. I. Packman, J. D. Newbold, and F. Sabater (2008), Biophysical controls on organic carbon fluxes in fluvial networks, *Nat. Geosci.*, **1**, 95–100, doi:10.1038/ngeo101.
- Brümmer, C., H. Papen, R. Wassmann, and N. Brüggemann (2009), Fluxes of CH₄ and CO₂ from soil and termite mounds in south Sudanian savanna of Burkina Faso (West Africa), *Global Biogeochem. Cycles*, **23**, GB1001, doi:10.1029/2008GB003237.
- Chen, Y.-H., and R. G. Prinn (2006), Estimation of atmospheric methane emission between 1996–2001 using a 3-D global chemical transport model, *J. Geophys. Res.*, **111**, D10307, doi:10.1029/2005JD006058.
- Cole, J. J., and N. F. Caraco (1998), Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF₆, *Limnol. Oceanogr.*, **43**, 647–656, doi:10.4319/lo.1998.43.4.0647.
- Cole, J. J., and N. F. Caraco (2001), Carbon in catchments: Connecting terrestrial carbon losses with aquatic metabolism, *Mar. Freshwater Res.*, **52**, 101–110, doi:10.1071/MF00084.
- Cole, J., S. Carpenter, M. Pace, M. Van de Bogert, J. Kitchell, and J. Hodgson (2006), Differential support of lake food webs by three types of terrestrial organic carbon, *Ecol. Lett.*, **9**, 558–568, doi:10.1111/j.1461-0248.2006.00898.x.
- Cole, J. J., *et al.* (2007), Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget, *Ecosystems*, **10**, 172–185, doi:10.1007/s10021-006-9013-8.
- Curtis, P. J., and D. W. Schindler (1997), Hydrologic control of dissolved organic matter in low-order Precambrian Shield lakes, *Biogeochemistry*, **36**, 125–138, doi:10.1023/A:1005787913638.
- Degens, E. T., R. P. von Herzen, H.-K. Wong, W. G. Deuser, and H. W. Jannasch (1973), Lake Kivu: Structure, chemistry and biology of an East African rift lake, *Geol. Rundsch.*, **62**, 245–277, doi:10.1007/BF01826830.
- Delmas, R. A., J. Servant, J. P. Tathy, B. Cros, and M. Labat (1992), Sources and sinks of methane and carbon dioxide exchanges in mountain forest in Equatorial Africa, *J. Geophys. Res.*, **97**(D6), 6169–6179, doi:10.1029/90JD02575.
- Fee, E. J., J. A. Shearer, E. R. Debruyne, and E. U. Schindler (1992), Effects of lake size on phytoplankton photosynthesis, *Can. J. Fish. Aquat. Sci.*, **49**, 2445–2459, doi:10.1139/f92-270.
- Fee, E. J., R. E. Hecky, G. W. Regehr, L. L. Hendzel, and P. Wilkinson (1994), Effects of lake size on nutrient availability in the mixed layer during summer stratification, *Can. J. Fish. Aquat. Sci.*, **51**, 2756–2768, doi:10.1139/f94-276.
- Fee, E. J., R. E. Hecky, S. E. M. Kasian, and D. R. Cruikshank (1996), Effects of lake size, water clarity, and climatic variability on mixing depths in Canadian Shield lakes, *Limnol. Oceanogr.*, **41**, 912–920, doi:10.4319/lo.1996.41.5.0912.
- Jannasch, H. W. (1975), Methane oxidation in Lake Kivu (central Africa), *Limnol. Oceanogr.*, **20**, 860–864, doi:10.4319/lo.1975.20.5.0860.
- Macdonald, J. A., P. Eggleton, D. E. Bignell, F. Forzi, and D. Fowler (1998), Methane emission by termites and oxidation by soils, across a forest disturbance gradient in the Mbalmayo Forest Reserve, Cameroon, *Global Change Biol.*, **4**, 409–418, doi:10.1046/j.1365-2486.1998.00163.x.
- Macdonald, J. A., D. Jeeva, P. Eggleton, R. Davies, D. E. Bignell, D. Fowler, J. Lawton, and M. Maryati (1999), The effect of termite biomass and

- anthropogenic disturbance on the CH₄ budgets of tropical forests in Cameroon and Borneo, *Global Change Biol.*, *5*, 869–879, doi:10.1046/j.1365-2486.1999.00279.x.
- McGinnis, D. F., J. Greinert, Y. Artemov, S. E. Beaubien, and A. Wüest (2006), Fate of rising methane bubbles in stratified waters: How much methane reaches the atmosphere?, *J. Geophys. Res.*, *111*, C09007, doi:10.1029/2005JC003183.
- Muvundja, F., N. Pasche, F. W. B. Bugenyi, M. Isumbusho, B. Müller, J. N. Namugize, P. Rinta, M. Schmid, R. Stierli, and A. Wüest (2009), Balancing nutrient inputs to Lake Kivu, *J. Great Lakes Res.*, *35*(3), 406–418, doi:10.1016/j.jglr.2009.06.002.
- Nayar, A. (2009), A lakeful of trouble, *Nature*, *460*, 321–323, doi:10.1038/460321a.
- Pasche, N., M. Schmid, F. Vazquez, C. Schubert, A. Wüest, J. D. Kessler, M. A. Pack, W. S. Reebergh, and H. Bürgmann (2011), Methane sources and sinks in Lake Kivu, *J. Geophys. Res.*, *116*, G03006, doi:10.1029/2011JG001690.
- Rasmussen, J. B., L. Godbout, and M. Schallenberg (1989), The humic content of lake water and its relationship to watershed and lake morphology, *Limnol. Oceanogr.*, *34*, 1336–1343, doi:10.4319/lo.1989.34.7.1336.
- Sarmiento, H., M. Isumbusho, and J.-P. Descy (2006), Phytoplankton ecology of Lake Kivu (Eastern Africa), *J. Plankton Res.*, *28*, 815–829, doi:10.1093/plankt/fbl017.
- Schindler, D. W. (1971), A hypothesis to explain differences and similarities among lakes in the Experimental Lakes Area, northwestern Ontario, *J. Fish. Res. Board Can.*, *28*, 295–301, doi:10.1139/f71-039.
- Schmid, M., M. Halbwachs, B. Wehrli, and A. Wüest (2005), Weak mixing in Lake Kivu: New insights indicate increasing risk of uncontrolled gas eruption, *Geochem. Geophys. Geosyst.*, *6*, Q07009, doi:10.1029/2004GC000892.
- Schoell, M., K. Tietze, and S. M. Schoberth (1988), Origin of methane in Lake Kivu (East-Central Africa), *Chem. Geol.*, *71*, 257–265, doi:10.1016/0009-2541(88)90119-2.
- Tathy, J. P., B. Cros, R. A. Delmas, A. Marengo, J. Servant, and M. Labat (1992), Methane emission from flooded forest in Central Africa, *J. Geophys. Res.*, *97*(D6), 6159–6168, doi:10.1029/90JD02555.
- Tietze, K., M. Geyh, H. Müller, L. Schröder, W. Stahl, and H. Wehner (1980), The genesis of the methane in Lake Kivu (Central Africa), *Geol. Rundsch.*, *69*, 452–472, doi:10.1007/BF02104549.
- Tranvik, L. J., et al. (2009), Lakes and reservoirs as regulators of carbon cycling and climate, *Limnol. Oceanogr.*, *54*, 2298–2314, doi:10.4319/lo.2009.54.6_part_2.2298.
- Wanninkhof, R. (1992), Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, *97*, 7373–7382, doi:10.1029/92JC00188.
- Weidel, B., S. Carpenter, J. Cole, J. Hodgson, J. Kitchell, M. Pace, and C. Solomon (2008), Carbon sources supporting fish growth in a north temperate lake, *Aquat. Sci.*, *70*, 446–458, doi:10.1007/s00027-008-8113-2.
- Werner, C., R. Kiese, and K. Butterbach-Bahl (2007), Soil-atmosphere exchange of N₂O, CH₄, and CO₂ and controlling environmental factors for tropical rain forest sites in western Kenya, *J. Geophys. Res.*, *112*, D03308, doi:10.1029/2006JD007388.
- Yamamoto, S., J. B. Alcauskas, and T. E. Crozier (1976), Solubility of methane in distilled water and seawater, *J. Chem. Eng. Data*, *21*, 78–80, doi:10.1021/je60068a029.
- G. Abril, Laboratoire Environnements et Paléoenvironnements Océaniques, UMR CNRS 5805, Université de Bordeaux 1, Avenue des Facultés, F-33405 Talence, France.
- A. V. Borges, F. Darchambeau, and B. Delille, Unité d'Océanographie Chimique, Université de Liège, Bât B5, Liège B-4000, Belgium. (alberto.borges@ulg.ac.be)
- J.-P. Descy, Laboratoire d'Écologie des Eaux Douces, URBE, University of Namur, Rue des Bruxelles 61, Namur B-5000, Belgium.