

Greenhouse gas emission and storage in a small shallow lake

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Abstract Small lakes are likely to show considerable temporal variability in greenhouse gas emissions given their transient stratification and short residence time. To determine the extent that CO₂ and CH₄ emission and storage depends on surface meteorology, we studied a shallow lake during 2 years with contrasting rainfall and thermal stratification. Gas fluxes were estimated with wind-based and surface renewal models and compared to direct measurements obtained with floating chambers. The assessment of greenhouse gases storage revealed that the lake gained CO₂ in association with rainfall in both the rainier (2011) and drier summer (2012). In 2011, stratification was less extensive and disrupted frequently. The lake was a source of CO₂ and CH₄, and ebullition exceeded

diffusive fluxes of CH₄. In 2012, stratification was more persistent, the lake was a sink for CO₂ during dry periods, CO₂ and CH₄ accumulated in the hypolimnion later in the summer when rainfall increased, diffusive fluxes of CH₄ were similar to those in 2011 mid-summer and over four times higher during overturn. Ebullition was lower in the drier summer. Fluxes measured with chambers were closer to estimations from the surface renewal model and about two times values estimated with wind-based models.

Keywords Small lake · Weather variability · Thermal stratification · Greenhouse gases · Storage · Diffusive flux · Ebullition · Gas transfer modeling

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Introduction

Small and shallow lakes and impoundments are abundant in the landscape (Downing et al., 2006; Downing, 2010) and emit substantial quantities of atmospheric greenhouse gases (GHG) (Casper et al., 2000; Repo et al., 2007). They are active reactors where carbon derived from the catchment, atmosphere, and ground waters can be stored, utilized, chemically altered, or released as CO₂ and CH₄ (Kling et al., 1992; Cole et al., 2007). The rate and direction of CO₂ transport from lakes depends on the ratio of primary production to ecosystem respiration which in turn are driven by inputs of inorganic nutrients and allochthonous and autochthonous organic material

(Kortelainen et al., 2006). The rate of CH₄ transport to the atmosphere depends on the rates of methanogenesis (Zeikus & Winfrey, 1976) and methanotrophy (Rudd & Hamilton, 1975; Whiticar et al., 1986). Methane can diffuse from the lake surface or be released via gas bubbles formed in the sediments (Bastviken et al., 2011; Wik et al., 2013). The amount of gas released to the atmosphere in these two modes of transport depends on water depth and temperature (Hofmann et al., 2010), on the composition, temperature, and chemical characteristics of the sediments (Martinez & Anderson, 2013; Wik et al., 2014), and on turbulent mixing as it causes fluxes within the water column and across the air–water interface.

Estimations of GHG flux from inland waters are increasing in accuracy due to improvements in modeling of the gas transfer coefficient k , more extensive data on dissolved gas concentrations (Raymond et al., 2013), and more detailed description of seasonal dynamics in GHG storage (Fernández et al., 2014). Further improvement requires understanding how weather and its effects on stratification and turbulence control the production, emission, and storage of GHG in lakes of different morphometries. For example, GHG emissions from a dimictic lake were shown to increase during cold fronts when water from below the mixed layer was entrained (Aberg et al., 2010), and during fall as summer stratification breaks down (Vesala et al., 2006). The study by Ojala et al. (2011) illustrates between year variability in a dimictic lake due to intrusions from rainfall. Few studies have been undertaken in shallow polymictic lakes in which diel stratification and mixing would be expected to lead to similar GHG storage and fluxes in summer and fall.

In shallow polymictic lakes, water temperature and oxygen concentrations may change rapidly with changing weather (Wilhelm & Adrian, 2008). Hence, the seasonal and inter-annual variability in GHG storage and fluxes, both diffusive and ebullitive, may be markedly different depending on weather conditions (Natchimuthu et al., 2014). These conditions affect GHG through their effect on sediment re-suspension (Bussmann, 2005; Hofmann et al., 2010) and on inflows of ground and stream waters, which can be considerable given the short residence time of such small lakes. They also affect the water column thermal structure and the intensity of turbulent mixing controlling gas diffusion at the air–water interface (Jahne

et al., 1987; MacIntyre, 1993). Diffusive gas fluxes at the lake surface can be assessed using wind-based models (e.g. Cole & Caraco, 1998), surface renewal models (MacIntyre et al., 2010; Tedford et al., 2014), or measured directly using floating chambers (Soja et al., 2014). Depending on the heterogeneity in surface water GHG concentrations and on factors controlling turbulent mixing, the choice of calculation method can introduce biases. The amount of energy incorporated into the water column due to wind stress or heating/cooling of the water column and sediments has also been shown to affect ebullitive fluxes (Wik et al., 2014).

In this study, we describe the inter-annual differences in stratification and surface meteorology between a cool rainy summer and a dry hot summer for a small 2 m deep lake. We hypothesized that when exposed to contrasting weather conditions, the lake will alternatively be polymictic or stably stratified during the summer, with subsequent effect on GHG emission and storage. We compare GHG diffusive fluxes calculated with wind-based and surface renewal models, and evaluate these against floating chamber measurements. We tested if stable stratification as opposed to conditions with more frequent mixing events results in a delayed release of diffused GHG until autumnal overturn and globally higher CH₄ emissions. We also hypothesized that the amount and composition of the gas released via ebullition will depend on water column stratification and hypolimnetic temperature.

Methods

Study site

Lake Jacques is a small (0.18 km²), shallow lake (maximum depth = 1.9 m, mean depth = 0.75 m) located 30 km north of Quebec City (QC, Canada), and supplied with water from two creeks in the eastern part of the lake, as well as from a ground water spring in its southern part. The lake can be classified as meso-eutrophic in terms of total phosphorus (mean summer value of 21 µg l⁻¹), total nitrogen (0.7 mg l⁻¹), and Chl *a* concentrations (17 µg l⁻¹). Approximately, 50% percent of the lake surface area is covered with the macrophyte *Brasenia schreberi* in summer. The upper 10 cm of the sediments has high organic carbon

content (loss on ignition = $38 \pm 5\%$, $n = 10$). The water retention time averages 14–20 days in summer (R. Tremblay, *pers. comm.*). The concentration of dissolved organic carbon ranged between 2.2 and 3.0 mg l^{-1} during the study and an algal bloom formed on the surface in 2012.

Meteorological and physicochemical characteristics

In 2011, hourly data on air temperature, relative humidity, wind speed, wind direction, dew point, and precipitation were obtained from the meteorological station of Environment Canada located 7 km from the lake (anemometer threshold 1 m s^{-1}). In 2012, a meteorological station WeatherHawk 511 (anemometer threshold 0.6 m s^{-1}) mounted 25 m from the lake shore and 7 m above the water level, recorded air temperature, relative humidity, wind speed and wind direction every 30 min. Between 21 July and 6 August 2012, the on-site anemometer had to undergo maintenance and wind speed data were replaced by those from the Environment Canada station. To correct the wind speed data from the Environment Canada meteorological station, we performed a linear regression analysis when both sensors were operational in 2012. We used the resulting equation, $u_1 = 0.442 + 0.791u_2$ ($R^2 = 0.65$, $P < 0.001$), to correct wind speeds (u) from 2011 and those from 21 July and 6 August in 2012. Downwelling hourly solar irradiance data (short wave and long wave) for both years were obtained from high spatial resolution (0.125°) surface meteorological forcing model from NASA (Giovanni Interactive Tool for Data Visualization and Analysis). Upwelling short wave and long wave were computed as in MacIntyre et al. (2014). Diffuse attenuation coefficient for downward visible light (LICOR spherical quantum sensor LI-193) was calculated as the slope of the linear regression of $\ln(E_z/E_0)$ versus depth, where E_z is the irradiance at depth z and E_0 is the surface irradiance, and used in surface renewal model computing. The value was on average equal to 2.4 m^{-1} .

In 2011, surface temperature, conductivity, dissolved oxygen (DO), and pH were assessed fortnightly with a 600R multiparametric probe (Yellow Springs Instrument). The oxygen probe was calibrated at the beginning of each sampling day in water-saturated air. Surface water samples (100–500 ml) were filtered on

GF/F glass fiber filters ($0.7 \mu\text{m}$ nominal mesh size; Advantec MFS Inc.) for the determination of chlorophyll-*a* concentration (Chl *a*) using a UV–Vis spectrophotometer at 750 and 665 nm (Wintermans & De Mots, 1965). In 2012, all measurements were performed weekly from May until the end of August, and then fortnightly until the ice cover was formed. The lake properties were always assessed between 10:00 a.m. and 2:00 p.m. Time series of water temperature were obtained with a thermistor chain installed from June to September 2011 and from May to October 2012. In 2011, seven temperature loggers (Onset Tidbit v2; accuracy 0.2°C , resolution 0.2°C , response time 5 min) were deployed at 0, 0.2, 0.4, 0.7, 1.0, 1.5, and 2.0 m, and acquired data every 15 min (sampling site 1.9 m deep at time of deployment, Fig. 1). In 2012, the loggers were deployed at the same site (depth of 1.7 m at time of deployment) at 0, 0.2, 0.35, 0.5, 0.75, 1.2, and 1.5 m, and acquired data every 8 min. Isotherms were calculated using linear interpolation. The surface energy budget and computation of dissipation rate of turbulent kinetic energy used in gas transfer coefficient calculations were computed following MacIntyre et al. (1995, 2002) and Tedford et al. (2014).

Indirect estimations of k with wind-based and surface renewal models

The wind speed normalized at 10 m (u_{10}), according to the logarithmic wind profile relationship including atmosphere stability effects (Smith, 1988), was used to calculate the gas transfer coefficients (k_{600}) standardized to a Schmidt number (Sc) of 600 following Wanninkhof (1992). Using the equations of Cole & Caraco (1998; hereafter *CC*), we calculated

$$k_{600} = 2.07 + 0.215u_{10}^{1.7} \quad (1)$$

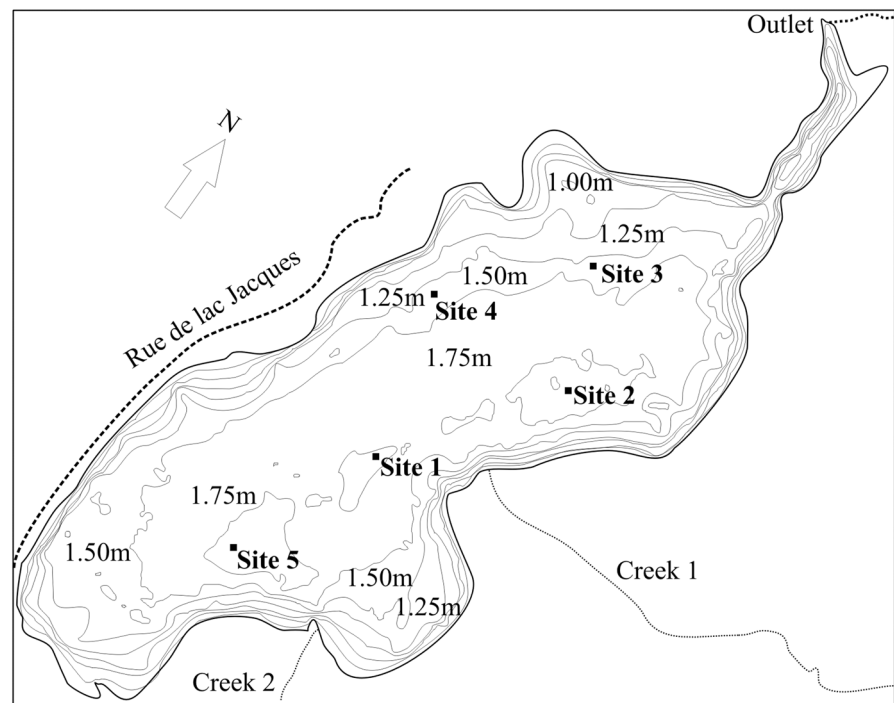
and the equation of Crusius & Wanninkhof (2003; hereafter *CW*)

$$k_{600} = 0.168 + 0.228u_{10}^{2.2} \quad (2)$$

The equation in Cole & Caraco (1998) applies for wind speeds up to 9 m s^{-1} whereas that of Crusius & Wanninkhof (2003) to winds up to 6 m s^{-1} .

We also computed the gas transfer coefficient with the surface renewal model (MacIntyre et al., 1995; Zappa et al., 2007, hereafter *SC*):

Fig. 1 The morphometry and bathymetry of Lake Jacques. The thermistor chain was positioned at *site* 1 and ebullition funnels at *sites* 1–4 (2011) and 1–5 (2012)



$$k_{600} = a_1(\varepsilon/\nu)^{1/4} Sc^{-1/2}, \quad (3)$$

where a_1 is an experimental constant (assumed as 0.5 in this study), ε is the kinetic energy dissipation rate, and the kinematic viscosity. The kinetic energy dissipation rate, describing turbulence in the surface mixing layer where mixing is directly energized by wind shear and convection (Imberger, 1998), was calculated during heating as $\varepsilon = 0.6 u_{*w}^3/kz$ and during cooling as $\varepsilon = 0.56 u_{*w}^3/kz + 0.77\beta$, where u_{*w} is the water friction velocity computed from wind shear stress, k is the von Karman constant, z is the depth equal to 15 cm, and β is the surface buoyancy flux (Tedford et al., 2014). For details on computing u_{*w} and β , see MacIntyre et al. (2002, 2014). The first equation implies wind as the dominant factor responsible for turbulence at the lake surface, while the second one includes cooling as an additional factor that generates turbulence.

Dissolved GHG measurements and flux estimations

Aqueous concentrations of CO_2 and CH_4 were determined fortnightly from June to mid-September in 2011, and weekly from May to the end of August in

2012, then fortnightly until the ice cover was formed. Gas sampling was performed by equilibrating 2 l of lake water with 20 ml of ambient air, shaking for 3 min, and then injecting the headspace gases into a 5.9 ml Exetainer (Labco Scientific) previously flushed with helium and vacuumed (Hesslein et al., 1991). The procedure was always repeated three times and yielded CV on average less than 10%. Gas samples were taken within 5 min after collecting the lake water, and were kept in the dark at 4°C until analyzed by gas chromatography (Varian 3800 with a COMBI PAL head space injection system). In addition, vertical profiles of CO_2 and CH_4 (resolution 0.25 m) were taken monthly or fortnightly from June to September in 2011 and from May to October in 2012 following the procedure described above. To assess gas storage, the total mass of CO_2 and CH_4 above (or below) saturation was calculated by multiplying the average concentration over a depth interval by the water volume within that depth interval, and summing over the depth of the lake (Rudd & Hamilton, 1978).

Diffusive CO_2 and CH_4 flux ($Flux_d$) was calculated using the gas transfer coefficients for a given gas k (cm h^{-1}) estimated with either *CC*, *CW*, or *SC* models as:

$$Flux_d = k(C_{sur} - C_{eq}), \quad (4)$$

where C_{sur} is the gas concentration in surface water (mmol l^{-1}) and C_{eq} is the gas concentration in the water at equilibrium with the atmosphere. Global values of atmospheric partial pressures (IPCC, 2007) were used to determine C_{eq} . The gas transfer coefficient was calculated as:

$$k = k_{600}(Sc/600)^c, \quad (5)$$

where c equals -0.5 for rough surfaces (Csanady, 1990).

Synchronized with the determination of aqueous CO_2 and CH_4 concentrations, a floating chamber (circular, 23.4 l, hereafter *FC*), made of 10 mm thick PVC plastic with floaters distributed evenly on the sidewall, extending 4 cm into the water, was coupled with an infra-red gas analyser (EGM-4, PP-Systems), and deployed 2 m from the boat on the surface of the lake to directly assess CO_2 flux ($Flux_c$) according to

$$Flux_c = SM_w V_{ch}(V_m A)^{-1}, \quad (6)$$

where S is the slope of the linear regression of gas concentration in the chamber versus time (measurements taken for a maximum of 20 min depending on flux rate), M_w the gas molecular weight, V_{ch} the volume of the chamber, V_m the gas molar volume at ambient temperature, and A the area of the chamber. Atmospheric and surface water dissolved CO_2 together with direct measurements of CO_2 flux were used to estimate the floating chamber gas transfer coefficients using the equation:

$$k = Flux_c / (C_{sur} - C_{eq}) \quad (7)$$

k was standardized to k_{600} using Eq. 5. Gas transfer coefficients obtained from the *FC* were used to calculate the chamber CH_4 flux following Eq. 4.

Ebullition measurements

The rate of gas ebullition was measured with four (2011) or five (2012) submersible inverted funnels installed monthly from June to September 2011 ($n = 14$ measurements, only two funnels worked in August), and 2012 ($n = 20$ measurements). The funnels consisted of a soft PVC cone-shaped body mounted on a metal frame, with a plastic syringe and luer-lock valve installed on top, and maintained with

floaters at approximately 20 cm below the water surface. At each sampling date, the funnels were submerged in the lake at one of the four or five pelagic sites (Fig. 1) and moored with three weights deployed at least 2 m away from the funnel to avoid the collection of bubbles escaping at installation and to keep the funnel upright in the same position for 4–24 h depending on the flux rate. The collected bubbles were sampled in triplicate vials, and the samples diluted 100 times with helium before they were analyzed by gas chromatography as described above. The ebullitive flux was calculated as:

$$Flux_e = C V_g V_m^{-1} A^{-1}, \quad (8)$$

where C is the concentration of a given gas in the syringe, V_g is the total volume of the gas in the syringe, V_m is the gas molar volume at ambient temperature obtained from meteorological station, and A is the area of the funnel.

Finally, the total global warming potential over a 100 year period (GWP) was calculated as the sum of diffusive and ebullitive GHG fluxes with CH_4 having 34 times higher GWP than CO_2 (nominal 1; Myhre et al., 2013).

Results

Meteorological conditions and mixing of the lake

Air temperatures varied on seasonal and diel time scales. Maxima in summer were near 30°C ; shifts between warm and cold fronts caused $5^\circ\text{--}10^\circ\text{C}$ changes in air temperatures, similar to variations over the course of a day (Fig. 2). Three to four day long cold fronts prevailed in 2011 starting from the end of June. In early July 2011, they were associated with rainfall and wind speeds reaching 5 m s^{-1} . Warm fronts later in July caused the lake surface to warm to 26°C , brought heavy rains and winds up to 8 m s^{-1} during the daytime. Winds often declined at night below the anemometer's threshold (1 m s^{-1}). Cold fronts with air temperature falling to 15°C and rainfall dominated the weather of early August 2011, but the winds at this period did not exceed 5 m s^{-1} . Early in September, cold fronts were associated with heavy rains, but the highest winds, 6 m s^{-1} , were recorded later in the month during a warm front. The rate of

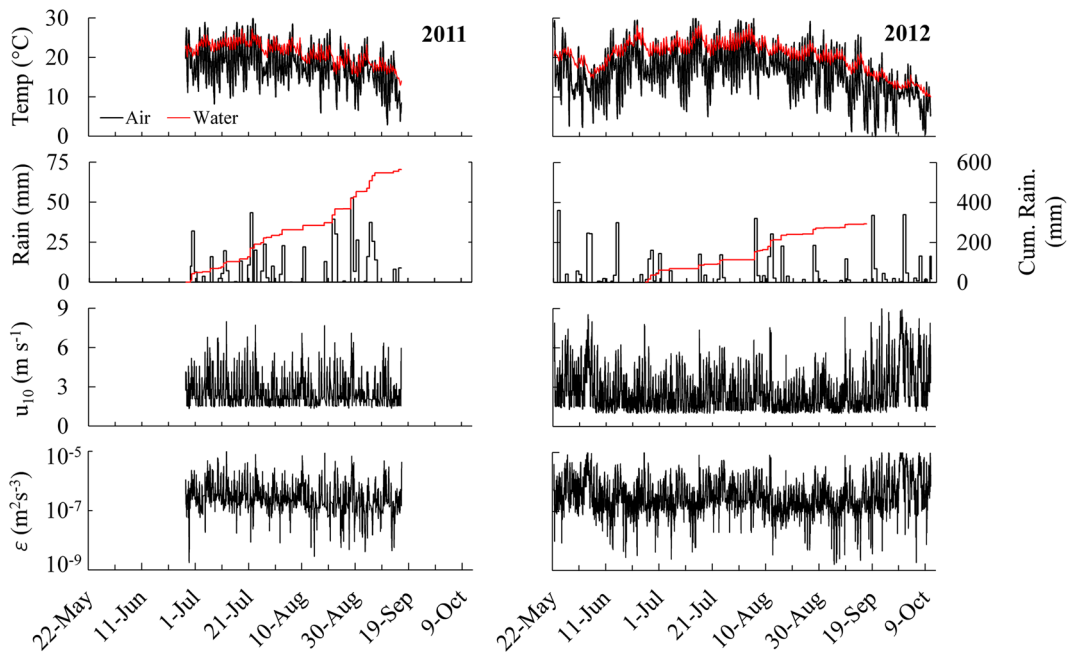


Fig. 2 Meteorological conditions including air and surface water temperatures, daily and cumulative rainfall, wind speed at 10 m (u_{10} when winds were above 1 m s^{-1}), as well as kinetic energy dissipation rate (ϵ) following Tedford et al. (2014)

dissipation of turbulent kinetic energy computed at 15 cm depth following Tedford et al. (2014) indicated that ϵ ranged between 10^{-8} and $10^{-6} \text{ m}^2 \text{ s}^{-3}$, that is, the upper water column was moderately turbulent (MacIntyre et al., 2009).

In 2012, warm fronts prevailed, starting from May when air temperatures reached 28°C and afternoon winds remained above 6 m s^{-1} . As in 2011, winds were low at night. In early June cooler air masses were associated with rain and daytime winds above 6 m s^{-1} . At this time, the lake was cooling also during the day and buoyancy contributed to the turbulence at the surface. The weather in July and August 2012 was dominated by warm fronts with little rain particularly in July. On average, 2011 was cooler and windier than 2012 and had almost two times higher rainfall (Table 1).

Thermal stratification, pronounced in both years despite the lake's shallow depth, was greater in 2012 than 2011 (Fig. 3). For example, the temperature difference from top to bottom was 8°C in mid-July 2011 and 13°C in mid-July 2012. The strong near surface heating is a result of the relatively high diffuse attenuation coefficient in this lake, 2.4 m^{-1} . In both summers, shallow diurnal thermoclines formed in the

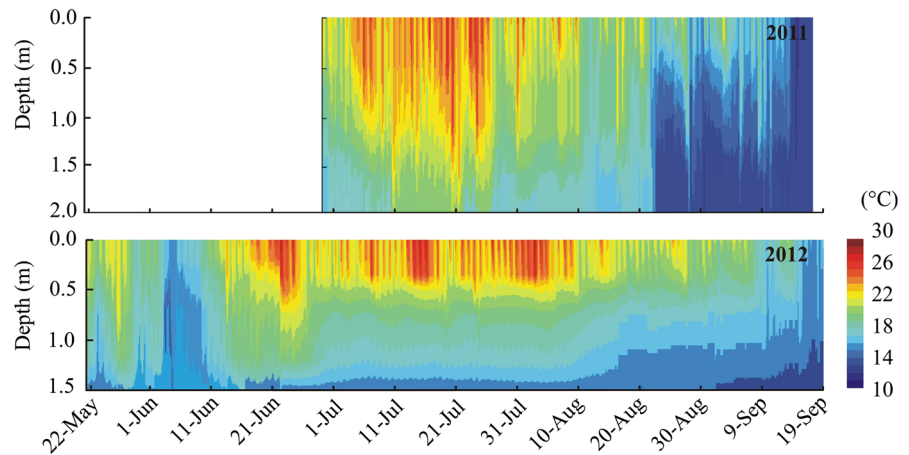
Table 1 Meteorological conditions, including air temperature (air T), cumulative precipitation (cum. rain), daily precipitation (daily rain), wind speed (wind), downwelling short wave (SW) and long wave (LW) irradiation, relative humidity (RH), and the dissipation rate of turbulent kinetic energy (ϵ) as a mixing index at Lake Jacques in summer 2011 and 2012

Meteorology	2011	2012
Air T ($^\circ\text{C}$)	17.5	18.2
Cum. rain (mm)	563	292
Daily rain (mm day^{-1})	8.4	4.3
Wind (m s^{-1})	2.9	2.4
SW (W m^{-2})	213	222
LW (W m^{-2})	349	365
RH (%)	75.6	73.5
$\epsilon \times 10^8$ ($\text{m}^2 \text{ s}^{-3}$)	62.4	49.6

The comparison of wind speeds and dissipation rates in the actively mixing layer was done for winds exceeding 1 m s^{-1}

upper 20–60 cm. In 2011, the afternoon winds caused episodes of apparent mixed layer deepening. These patterns result from winds tilting the thermocline; on relaxation, the warm water was found at shallower depths and cooler water upwelled. Similar events occurred in 2012, but the penetration of warm water

Fig. 3 Thermal structure of the lake during rainy, cooler summer 2011 and dry, hotter summer 2012



was restricted to shallower depths. Intervals with warm temperatures in the upper meter were interspersed with ones with cooler due to the passage of cold fronts during which near surface temperatures dropped by $\sim 10^{\circ}\text{C}$. In consequence, the temperature differences within the water column were reduced to 2°C in 2011 and 7°C in 2012 (Fig. 3).

During cold fronts, temperatures often decreased in the lower water column. The large decreases in temperature in the lower water column in 2011 co-occurred with rain events and may be the signature of cold inflows of stream water. The transport could also be associated with differential cooling between pelagic and littoral zones. For example, at the pelagic site, temperatures cooled from 20 to 22°C in July in the thermocline between 40 and 80 cm but not at one meter depth. As inflows from rain were low at that time, the mid-water column cooling, with temperatures similar to the inshore site, is indicative of offshore flows from differential cooling. Even in 2012, cold fronts tended to be associated with rainfall, so cool water intrusions may have been due to the combination of increased stream/ground water inflows and/or differential cooling.

Stratification, quantified as buoyancy frequency, $N^2 = g \rho^{-1} d\rho/dz$, where g is the acceleration constant due to gravity, ρ is the water density, and $d\rho/dz$ is the vertical density gradient, showed layering with features typical of seasonally stratified lakes. The upper water column stratified in the day and mixed at night, and comprised the epilimnion. For the first half of summer 2011, the metalimnion, with more persistent

stratification, began at 0.8 or 1 m and extended nearly to the bottom with N having maximal values of 60 cycles per hour ($60 \text{ cph} = 0.1 \text{ rad s}^{-1}$). To provide context, oceanographers consider water to be strongly stratified when $N > 20 \text{ cph}$. For most of summer 2012, the metalimnion began between 0.3 and 0.6 m and extended to 0.6–0.8 m with maximal values of N near 100 cph. Below the metalimnion, buoyancy frequencies were higher than in 2011. Importantly, in 2011, the stratification across the metalimnion intermittently weakened throughout its depth, with values dropping to 30 or 40 cph. In contrast, this weakening did not occur in 2012. The weakening is indicative of periods with increased mixing, which reduce the stratification and enable transport of dissolved gases across the metalimnion.

In both years, increased rainfall after mid-August weakened the stratification in the lower water column, with N dropping below 30 cph in 2011 and below 50 cph in 2012. During this latter period in 2011, there were intervals when buoyancy frequencies became nearly uniform throughout the water column. In 2012, buoyancy frequencies only became near uniform with values below 20 cph in concert with the large rainfall event on 16 September (Fig. 2). Thus, rainfall contributed to weakening of vertical stratification. We infer that the persistent rainfall in summer 2011 enabled frequent exchanges between the upper and lower water column. The persistently high metalimnetic values of N in 2012 (50 cph), until the rainfall events later in the summer, imply reduced vertical fluxes between the metalimnion and epilimnion.

Variability in GHG vertical distribution and departure from saturation

The differences in stratification and rainfall between years led to differences in vertical distribution of dissolved gases. The oxycline tended to be located between 0.5 and 1.5 m in both years, with anoxia prevalent below 1.5 m in 2012 (Fig. 4). Concentrations of dissolved gases differed between sampling periods in both years, with large increases prevalent either near the bottom or in mid-water intrusions (Fig. 4). In 2011, increases of CO_2 were associated with the higher frequency of rainstorms. For example, the large increase of CO_2 in the hypolimnetic waters on 6 August followed heavy rains on 5 August. Dissolved CH_4 did not accumulate in the lower water column during summer 2011. The higher temperature and oxygen levels in the lower water column in 2011 relative to 2012 provide evidence for larger vertical exchanges in 2011. Were CH_4 produced in 2011, it would have been oxidized quickly. In 2012, high concentrations of CO_2 and CH_4 did not occur in bottom waters during July but increased in August, and de-gassing occurred when stratification was eroded in September. Increases in gas concentrations in August 2012 co-occurred with increased rainfall,

decreases in near-bottom temperatures, and cooling indicated by heat budgets (averaged over 2 days). Concentrations of CH_4 also increased inshore (data not shown). Thus, rainfall events appear to have caused loading of either organic matter or CO_2 in both years, with stronger stratification, anoxia and weaker mixing in 2012 enabling the persistence of CH_4 in the hypolimnion.

Surface CO_2 concentrations were significantly higher in 2011 than in 2012 (mean of 16.3 and 8.6 μM respectively, $P < 0.05$). On average, surface CH_4 concentrations were higher in 2012 than in 2011 (0.89 and 2.1 μM respectively, $P < 0.05$), but this latter difference was mainly due to the large increase of dissolved CH_4 in the water column during fall overturn. The variability in GHG saturation levels was higher in 2012 (CV = 145 and 210% for CO_2 and CH_4 respectively) than in 2011 (CV = 58 and 45%).

Comparison of gas transfer coefficients calculated with wind-based and surface renewal models

The comparison of gas transfer coefficients was done for data with wind speeds above 1 m s^{-1} (anemometer thresholds) and below 6 m s^{-1} (upper wind speed limit for the CW model), thus allowing similar conditions for

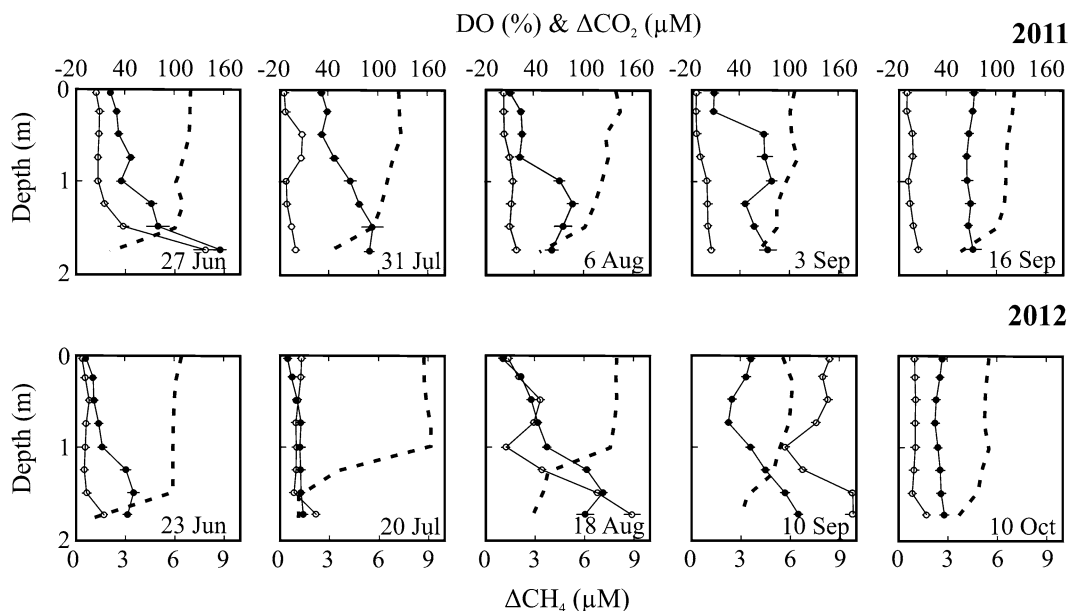


Fig. 4 Profiles of dissolved oxygen saturation (dotted line, upper axis) as well as the departure from saturation of CO_2 (closed circles, upper axis) and CH_4 (open circles, lower axis) in Lake Jacques during 2011 and 2012

Table 2 The gas transfer coefficient k_{600} and its variability (CV) for two wind-based models (*CW* and *CC*) and a surface renewal model (*SC*) at Lake Jacques during the rainy, cooler (2011) and dry, hotter summer (2012)

Model	2011		2012	
	k_{600} (cm h ⁻¹)	CV (%)	k_{600} (cm h ⁻¹)	CV (%)
<i>CW</i>	2.94	80	2.22	100
<i>CC</i>	3.47	27	3.15	28
<i>SC</i>	5.22	30	5.28	29

all models used in calculations. Overall, k was higher when estimated with the surface renewal (*SC*) model than when estimated with wind-based models and k was higher with *CC* than *CW* (Table 2). The contribution from buoyancy flux was negligible. The application of different models to estimate k_{600} revealed significant differences between years in average values (Mann–Whitney test, $P < 0.05$), significant differences between models ($0.001 < P < 0.05$) in the same year, and significant differences in the magnitude of k_{600} variability (coefficient of variation, CV) calculated with wind-based (*CW*) and surface renewal models ($P < 0.05$). The higher values using the surface renewal model result because k_{600} increases more rapidly with wind speed than in the Cole & Caraco (1998) formulation, similar to results shown in MacIntyre et al. (2010) under heating. The larger variance with *CW* results because it is a power law formulation with steep curvature relative to *CC*, and the lower average values result because the curve goes through zero at low winds and provides lower estimates of k at low winds than *CC* (Banerjee & MacIntyre, 2004). Because of this bias, we do not include *CW* in the comparisons with the floating chamber to follow.

Comparison of GHG fluxes estimated with floating chambers and models

The relative magnitude of fluxes measured with the floating chambers was similar to modeled values (Table 3). The winds were above the anemometer threshold when chamber measurements were conducted. With respect to CO₂, chamber fluxes were more similar to fluxes estimated using the surface renewal model (*SC*) than with *CC* wind-based model (Fig. 5A, B). The correspondence was still good between measured fluxes and *SC* estimates during autumnal overturn.

With respect to CH₄, results of both models differed at most by 30% from these calculated with the floating chamber in 2011 (Fig. 5C). During 2012, *FC* fluxes were again similar to both models early in the season, they were lower than both models in mid-summer, and similar to *CC*-modeled fluxes during autumnal overturn (Fig. 5D).

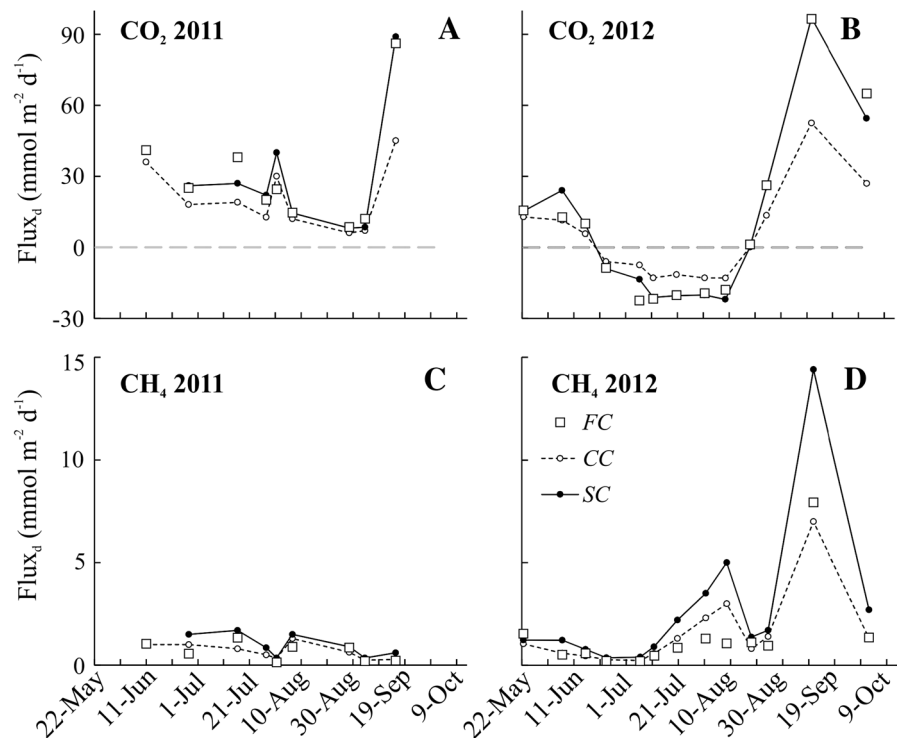
Temporal variability in GHG diffusive fluxes and storage

On average, higher CO₂ diffusive fluxes occurred in 2011 than in 2012 (June–September; $P < 0.01$, ANOVA with Tukey test; Table 4; Fig. 5). In summer 2011, the lake was continuously a net source of CO₂ to the atmosphere. Similarly, it was a source in early and late summer 2012, but a sink in mid-summer. In contrast, diffusive CH₄ fluxes were higher on average in 2012 than in 2011 ($P < 0.01$). The highest CO₂ fluxes occurred in September when stratification was eroded, with estimates averaging 89 and 97 mmol m⁻² day⁻¹ for *SC* model and 86.5 and 96.5 mmol m⁻² day⁻¹ for *FC*, in 2011 and 2012, respectively. The CH₄ emissions also increased at the autumnal overturn, but only in 2012, with diffusive fluxes reaching 14 mmol m⁻² day⁻¹ for *SC* model and 7.95 mmol m⁻² day⁻¹ for *FC* measurements (Fig. 5).

The assessment of GHG storage revealed that, despite an efflux at the surface, the lake was gaining CO₂ early in 2011 (June–July) in association with heavy rainfalls (Figs. 2, 6). By the end of August, rainfall increased again, and so did the CO₂ concentrations in the lake. This rise continued until mid-September when CO₂ exceeded 16×10^3 mol. The CH₄ tended to follow a pattern opposite to CO₂ as it decreased early in the summer during the rainy period, increased when rainfall was relatively low, and decreased again later in the season. In 2012, the lake lost CO₂ between June and July when rainfall was low and Chl *a* increased from 13 to 37 μg l⁻¹. The lake gained CO₂ beginning in August with large increases in mid-August and in September when rainfall increased and temperatures in the lower water column decreased (Figs. 2, 3). The stable stratification resulted in the development of anoxia in the hypolimnion in the summer, and accumulation of CO₂ and CH₄ reaching 12.6×10^3 and 19.7×10^2 mol, respectively, despite the efflux of both gases at the surface (Fig. 5). While a considerable amount of GHG was

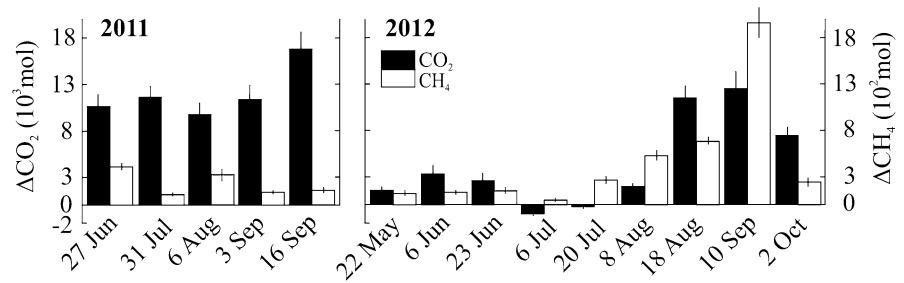
Table 3 Average GHG diffusive fluxes (CO_2/CH_4) in 2011 (June–September) and 2012 (May–October) measured with floating chambers (FC) or calculated using a wind-based model(CC) and a surface renewal model (SC), as well as the correlation coefficients (R) between modeled and measured CO_2 fluxes considering FC as the reference ($P < 0.01$)

$Flux_d$ (CO_2/CH_4)	FC ($\text{mmol m}^{-2} \text{day}^{-1}$)	CC ($\text{mmol m}^{-2} \text{day}^{-1}$)	SC ($\text{mmol m}^{-2} \text{day}^{-1}$)	$R_{FC:CC}$	$R_{FC:SC}$
2011	29.1/0.6	18.7/0.65	29.4/1.02	0.84	0.96
2012	9.0/1.35	4.5/1.52	9.2/2.80	0.90	0.98

Fig. 5 The CO_2 and CH_4 diffusive fluxes ($Flux_d$) in 2011 and 2012 estimated with wind-based (CC , dashed line) and surface renewal model (SC , solid line) or measured directly (CO_2) and estimated with floating chambers (FC , open squares)**Table 4** Monthly average diffusive fluxes ($Flux_d$) using surface renewal model (SC), ebullition fluxes ($Flux_e$), partial pressure of CH_4 and CO_2 in the collected bubbles ($P_e\text{CH}_4$ and $P_e\text{CO}_2$ in %), and the global warming potential (GWP) of GHG emitted by Lake Jacques in summer 2011 and 2012 (given as CO_2 -equivalent)

	$\text{CO}_2 Flux_d$ ($\text{mmol m}^{-2} \text{day}^{-1}$)	$\text{CH}_4 Flux_d$ ($\text{mmol m}^{-2} \text{day}^{-1}$)	$\text{CH}_4 Flux_e$ ($\text{mmol m}^{-2} \text{day}^{-1}$)	$P_e\text{CH}_4$ (%)	$P_e\text{CO}_2$ (%)	GWP ($\text{mmol m}^{-2} \text{day}^{-1}$)
2011						
June	26.5	1.4	3.4	21.4	4.1	192
July	29.7	1.0	5.3	30.5	0.8	242
August	11.3	1.2	5.1	31.2	1.8	225
September	48.8	0.5	2.4	42.3	0.6	146
2012						
June	8.3	0.7	1.1	14.4	5.0	72
July	-18.7	1.7	0.5	39.1	2.3	57
August	1.2	2.6	0.3	42.5	0.7	102
September	75.5	8.5	0.5	51.3	0.02	376

Fig. 6 The storage (mass relative to saturation \pm SD) of CO₂ (closed bars, scale on right axis) and CH₄ (open bars, scale on left axis) in Lake Jacques in 2011 and 2012



lost during the overturn period in 2012, the mass of each gas above saturation was still significant in October.

GHG ebullition

Methane ebullition was higher during the rainier summer 2011 ($4.1 \text{ mmol m}^{-2} \text{ day}^{-1}$; $n = 14$) than 2012 ($0.6 \text{ mmol m}^{-2} \text{ day}^{-1}$, $n = 20$; $P < 0.01$, Table 4). It was also higher during rainier months of 2012. Overall in 2011, ebullition contributed 66% of the total lake CH₄ flux in June, and more than 80% in July, August and September (comparing with SC diffusive flux). In 2012, the contribution of ebullition decreased from 58% in June, to 24% in July, 16% in August, and 5% in September. The collected gas bubbles contained, on average, more CH₄ in 2012 than in 2011 ($P < 0.01$; $n = 34$, partial pressures are provided in Table 4). The bubbles contained small amounts of CO₂, thus ebullition contributed only from 0.02 to 4% of the total CO₂ flux, respectively, for both years. Interestingly in 2012, when diffusive CO₂ flux was negative, CO₂ ebullition flux ranged from $0.28 \text{ mmol m}^{-2} \text{ day}^{-1}$ in July to $0.015 \text{ mmol m}^{-2} \text{ day}^{-1}$ in August. The total GWP of the lake was 32% higher in 2011 ($201 \text{ mmol CO}_2 \text{ equivalent m}^{-2} \text{ day}^{-1}$) than in 2012 ($152 \text{ mmol CO}_2 \text{ equivalent m}^{-2} \text{ day}^{-1}$; Table 4).

Discussion

Despite its small size, Lake Jacques had a persistent layered structure over the summer, similar to deeper lakes, and stratification was strong. For example, buoyancy frequencies in the metalimnion were higher and more persistently higher than those reported during diel stratification in tropical lakes with high insolation (MacIntyre et al., 2002), higher than those

observed in the pycnocline in a much larger meromictic lake (MacIntyre et al., 1999), and similar to values computed using data from a turbid subarctic thaw pond (Laurion et al., 2010). The stratification was weakened during the passage of cold fronts, with such events occurring more frequently and causing a greater weakening of the stratification in 2011 than in 2012. The variability in stratification moderated exchanges between the upper and lower water column, the extent of oxygenation of the lower water column, and the speciation of GHG.

The between-year differences in weather led to variability in storage and emissions of GHG. Frequent cold fronts associated with rain in 2011 resulted in accumulation of CO₂, but not CH₄, in the lower water column of the lake and higher effluxes of CO₂ at the surface than in the warmer dryer year. The strong thermal stratification in 2012 resulted in persistent anoxia starting early in the summer. However, increases of both CO₂ and CH₄ in the lake occurred later in summer 2012 in association with rainfall. As a result of the stratification, emissions were delayed until a large rainfall event weakened the stratification in mid-September. The approach taken here, which included time series data and gas storage assessment, similar to that in Aberg et al. (2010), enabled us to illustrate that increased CO₂ within the lake was associated with rainfall and how the between-year differences in meteorology moderated stratification, which in turn moderated concentrations and proportions of CO₂ and CH₄, and their evasion to the atmosphere.

Our comparison of CO₂ fluxes measured with chambers versus surface renewal and wind-based models was good, with comparisons within 30% between the chamber and surface renewal approach (Fig. 5). The comparisons with CH₄ were also good, with the largest discrepancy reaching a factor of two.

These comparisons differ from those in Schubert et al. (2012) who report greater than four-fold differences between floating chamber and modeled fluxes of CH₄. In our experiments, the flux measurements and water samples for the model calculations were obtained at the same location. In contrast, Schubert et al. (2012) studied a larger lake and deployed multiple chambers to obtain appropriate coverage. As indicated in the analysis in Heiskanen et al. (2014), the combination of internal wave motions and convective cooling can induce spatial variability in greenhouse gas concentrations. This variability should be taken into account for robust comparisons of measured and modeled results and for model development. The good agreement we demonstrate by working at one location indicates floating chambers and model approaches can obtain similar results and points to the utility of the approach for developing accurate models of the gas transfer coefficient.

Accuracy in predicting GHG emissions also requires understanding controls on temporal variability. Temporal variability in GHG fluxes depends on the size of water bodies (small > large, Roulet et al., 1997) and on sampling frequency (Weyhenmeyer, 1999). Besides our results showing that emissions varies between years in association with difference in ambient meteorology, they also show that they depend on the method used for estimating k . Models, such as the power law formulation of Crucius & Wanninkhoff (2003), which force k to low values at low wind speeds, generate more variable GHG fluxes (max. CV = 100%). The surface renewal model approach gives less variable estimates. As it also includes the various processes mediating turbulence (Zappa et al., 2007; MacIntyre et al., 2010), it offers an approach for inclusion of a range of hydrodynamic controls on the gas transfer coefficient. In support of that model, we obtained better congruence with CO₂ fluxes from floating chamber and the surface renewal model than with the two wind-based models used in our comparison. Since the differences in gas transfer coefficient parameterizations can cause biases in predicting the contribution of lakes to the global carbon cycle (Rypdal & Winiwarter, 2001), model results should be evaluated against direct measurements particularly in changeable weather conditions.

During the rainy summer 2011, Lake Jacques was continuously a source of CO₂ to the atmosphere indicating the prevalence of respiration and net

heterotrophy. The increased CO₂ concentrations lower in the water column tended to co-occur with rainfall, thus it may have resulted from direct inputs of CO₂ or labile organic carbon from the drainage basin which fueled bacterial respiration in the lake. The higher winds in that year caused more frequent water column mixing, enabling evasion and possibly more frequent re-suspension of organic matter from the sediments, which also may have stimulated bacterial respiration. In 2012, surface waters were undersaturated in CO₂ from the end of June until early August, concomitant with supersaturation in dissolved oxygen. This depression indicates a drawdown of CO₂ by photosynthesis combined with reduced vertical fluxes due to stable stratification separating the lower and upper water column. In 2012, if CH₄ flux was not taken into account, the lake would have been a net sink for atmospheric carbon. However, when CH₄ was included in the carbon budget, the lake became a source of carbon to the atmosphere except in July (GWP in Table 4).

Weather conditions also affected the ratios of CO₂ to CH₄ diffusing from the lake and the amount of CH₄ emitted via ebullition. High amounts of oxygen introduced to the water column during stormy weather led to lower concentrations of dissolved CH₄, likely resulting from enhanced methanotrophy and suppressed methanogenesis (Huttunen et al., 2006; Juutinen et al., 2009). When oxygen concentration was low, CH₄ accumulated in the lower water column. We did not determine whether CH₄ was derived from microbial processing of the CO₂ associated with rainfall events or directly from the sediments as in other studies (Rudd & Hamilton, 1978; Huttunen et al., 2003). Nevertheless, since the CH₄ only began to accumulate after rainfall, even though the lower water column was anoxic for most of 2012, it suggest that methanogenesis was stimulated by the microbial processing of the organic matter (Huttunen et al., 2003) or CO₂ (Wand et al., 2006) introduced with runoff. Moreover, stormy weather resulted in significantly higher CH₄ release from the lake via ebullition, possibly linked to warmer sediment temperatures (Wik et al., 2014) due to weaker stratification enabling a larger downward flux of heat. The higher frequency of frontal activity would have led to rapid changes in atmospheric pressure that also induces ebullition (Fechner-Levy & Hemond, 1996; Tokida et al., 2007). In Lake Jacques, ebullition was a

more important CH₄ emission pathway than diffusion, as demonstrated in several recent studies (e.g., Delsontro et al., 2010; Schubert et al., 2012; Shakhova et al., 2014), but only during stormy weather. Interestingly, during the dry, hot summer, the volume of gas evading from the sediments was considerably lower, but it contained a higher proportion of CH₄. This inter-annual variability may have resulted from the difference in the size of bubbles, with smaller ones rising more often from the sediments during the more frequent mixing events in 2011. Relatively smaller bubbles would have lost relatively more of their initial CH₄ (Ostrovsky et al., 2008).

Weather patterns and oxygen availability may have also mediated the cycling of CH₄ by microbial processes. Significantly, more dissolved CH₄ was found in lake water after summer rainfall events when the lake was more strongly stratified. The stratification could have allowed a more efficient exploitation of this carbon source by methanotrophic bacteria and a greater input of CH₄-derived carbon to higher trophic levels (Bastviken et al., 2003; Sanseverino et al., 2012). In contrast, during stormy weather, most of the CH₄ was released from the sediments as gas bubbles avoiding oxidation in the water column and incorporation to the lake food web. Hence, CH₄ may be a larger carbon source for bacteria during hot and dry weather or in wind-sheltered lakes than during stormy weather or in wind-exposed lakes (Kankaala et al., 2013).

In summary, depending on weather conditions, small and shallow temperate lake can be polymictic or remain stably stratified for periods longer than a month. Our correlative data indicated that rainfall and associated runoff introduced carbon directly into the lake with inflows generally near the bottom. The duration and extent of stratification moderated both the vertical distribution and processing of CO₂ and CH₄, and their flux at the air–water interface. The frequency of frontal events and the magnitude of wind and rain associated with these fronts caused year-to-year variability in GHG emissions and storage. Climate induced modification of the frequency of weather events such as rainstorms and concomitant changes in thermal stratification thus can lead to different pathways of GHG cycling in shallow lakes.

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