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## Reference

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## LETTER

## Methane emission offsets carbon dioxide uptake in a small productive lake

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### Scientific Significance Statement

Carbon budgets of natural and impacted ecosystems, including lakes, are critical to quantify their role in regulating Earth's climate. Excessive nutrient loading to lakes both increases their algal production resulting in atmospheric CO<sub>2</sub> uptake and increases CH<sub>4</sub> production due to anaerobic decomposition of organic matter. The net balance between CO<sub>2</sub> uptake and CH<sub>4</sub> emissions from lakes, however, has not been extensively addressed. Our work reveals that a substantial proportion of the organic carbon supplied by the net ecosystem production is used for methanogenesis and emitted back to the atmosphere as CH<sub>4</sub>. From a climate change perspective, exchanging CO<sub>2</sub> uptake with CH<sub>4</sub> release is an “unfair trade” for the atmosphere, as CH<sub>4</sub> has a much greater global warming potential than CO<sub>2</sub>.

### Abstract

Here, we investigate the importance of net CH<sub>4</sub> production and emissions in the carbon (C) budget of a small productive lake by monitoring CH<sub>4</sub>, CO<sub>2</sub>, and O<sub>2</sub> for two consecutive years. During the study period, the lake was mostly a net emitter of both CH<sub>4</sub> and CO<sub>2</sub>, while showing positive net ecosystem production. The analyses suggest that during the whole study period, 32% ± 26% of C produced by net ecosystem production was ultimately converted to CH<sub>4</sub> and emitted to the atmosphere. When converted to global warming potential, CH<sub>4</sub> emission (in CO<sub>2</sub> equivalents) was about 3–10 times higher than CO<sub>2</sub> removal from in-lake net ecosystem production over 100-yr and 20-yr time frames, respectively. Although more work in similar systems is needed to generalize these findings, our results provide evidence of the important greenhouse gas imbalance in human-impacted aquatic systems.

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**Data Availability Statement:** Data and metadata are available in the Dryad data repository at <https://doi.org/10.5061/dryad.3bk3j9kf4>. Weather data are available through the MeteoSwiss online platform IDAweb: <https://gate.meteoswiss.ch/idaweb/login.do>.

Additional Supporting Information may be found in the online version of this article.

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Constraining uncertainties of the various carbon (C) sources and sinks of natural and human-impacted systems is critical to understand their impact on the Earth's climate (Le Quéré et al. 2018; Nisbet et al. 2019). By emitting and storing C, freshwater systems have a significant role in the global C cycle (Battin et al. 2009), which can be altered by anthropogenic forcing (Tranvik et al. 2009; Regnier et al. 2013). For example, productive systems affected by nutrient loading can remove CO<sub>2</sub> from the atmosphere and store this organic C in their sediments (Anderson et al. 2014; Pacheco et al. 2014). At the same time, productive lakes and reservoirs have been shown to release CH<sub>4</sub> globally (DelSontro et al. 2018). As CO<sub>2</sub> and CH<sub>4</sub> are two important greenhouse gases (GHGs) with different atmospheric warming potentials, a deeper understanding of their coupled cycle in productive freshwater ecosystems is paramount to better evaluate their potential role for the Earth's climate system.

Freshwater CH<sub>4</sub> emissions are usually less substantial than CO<sub>2</sub> fluxes (Bastviken et al. 2011); however, CH<sub>4</sub> has a warming potential 28 and 84 times greater than CO<sub>2</sub> over 100-yr and 20-yr time frames, respectively (Myhre et al. 2013). Although CH<sub>4</sub> production can be relatively important in surface waters (Günthel et al. 2019), most production occurs in anoxic environments, such as isolated bottom waters and sediments, and is mostly fueled by excess organic matter from primary production (Kelly and Chynoweth 1981; West et al. 2012). Other factors like temperature (Yvon-Durocher et al. 2014), hydrodynamics (Vachon et al. 2019a), and the availability of other oxidants (e.g., nitrate, sulfate, and ferric iron) also affect CH<sub>4</sub> dynamics in freshwater systems. The link between productivity and CH<sub>4</sub> emissions has been shown empirically in various freshwater systems (Whiting and Chanton 1993; DelSontro et al. 2016); however, the net balance between CO<sub>2</sub> uptake by positive net ecosystem production and CH<sub>4</sub> emissions has not been extensively addressed and may have critical implications on the net GHG atmospheric exchange balance.

Here, we evaluate the contribution of CH<sub>4</sub> production to the whole-lake C cycle in a small productive lake (Soppensee, Switzerland). Due to the high primary productivity and extended bottom anoxia found in this lake (Vachon et al. 2019a), we hypothesized that fresh organic matter production in the summer leads to substantial CH<sub>4</sub> production, which may significantly offset net CO<sub>2</sub> uptake by ecosystem production. We test this by applying a mass balance approach using high-frequency measurements, including vertical profiles of O<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> concentrations and surface fluxes for two consecutive years, to derive whole ecosystem net gas production rates and to determine the fraction of organic carbon input that is ultimately converted to CH<sub>4</sub>.

## Materials and methods

### Study site and background limnological information

The study was conducted in the small eutrophic lake Soppensee (47.09°N, 8.08°E) situated in the Canton Lucerne,

Switzerland (lake area: 23 ha, maximum depth: 26 m, mean depth: 12.2 m) during the years 2016 and 2017 (meteorological conditions shown in Supporting Information Fig. S1 were provided by the Swiss Federal Office of Meteorology and Climatology). The lake basin is characterized by steep sides and a relatively flat bottom and the drainage basin (1.6 km<sup>2</sup>) is mainly occupied by agricultural land (Lotter 1989). The water residence time is about 3.1 yr (Gruber et al. 2000). In 2016–2017, total phosphorus measured spectrophotometrically after potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) digestion, was on average ( $\pm$  1 standard deviation [SD])  $28 \pm 16 \mu\text{g P L}^{-1}$  in the surface water and  $71 \pm 15 \mu\text{g P L}^{-1}$  when integrated over the whole water column. Dissolved organic carbon was more equally distributed in the water column, with an average ( $\pm$  1SD) of  $5.2 \pm 0.5 \text{ mg C L}^{-1}$  (Canton of Lucerne pers. comm.). The lake was strongly thermally stratified from May to October each year, after which the water column mixed partially in winter 2016/2017 (with ice cover) and completely in winter 2017/2018. Vertical profiles of water temperature and conductivity, as well as a more detailed physical description of the water column, are provided in Vachon et al. (2019a).

### Dissolved O<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> measurements

Dissolved O<sub>2</sub> and CO<sub>2</sub> sensors were deployed at about 1.5 m depth on a mooring situated at the deepest point of the lake. The dissolved O<sub>2</sub> probe (optode, miniDOT, Precision Measurements Engineering, range = 0–150% saturation, accuracy =  $\pm 10 \mu\text{mol L}^{-1}$ ) logged temperature, dissolved O<sub>2</sub> concentration (mg O<sub>2</sub> L<sup>-1</sup>), and saturation (%) every minute. CO<sub>2</sub> partial pressure (*p*CO<sub>2</sub>,  $\mu\text{atm}$ ) was measured every hour by a GasPro probe (detection limit between 10 and 20  $\mu\text{atm}$ ) (Graziani et al. 2014). Both probes were fitted with a copper mesh to prevent biomass growth. The measurement of *p*CO<sub>2</sub> is based on equilibration of the surrounding water with a small-volume headspace containing a miniature nondispersive infrared (NDIR) detector (model IRC-A1; Alphasense) via diffusion through a gas permeable membrane (Teflon AF 2400; Biogeneral). Continuous *p*CO<sub>2</sub> measurements were not available from April 2016 to July 2016 and from September to November 2016. During those periods, daily *p*CO<sub>2</sub> values were linearly interpolated.

In addition to high-frequency measurements from the loggers, profiles of dissolved gases were performed approximately on a monthly basis at the deepest point of the lake. Dissolved O<sub>2</sub> profiles were measured using a multiparameter sonde (Yellow Spring Instrument EXO2, after May 2017 a Seabird CTD profiler, SBE19) and a 1 m resolution was used for the mass balance calculation. Dissolved CH<sub>4</sub> and CO<sub>2</sub> in the water column were measured using the headspace method (Tang et al. 2018; Vachon et al. 2019a). Dissolved inorganic carbon (DIC) concentrations were derived from CO<sub>2</sub> and alkalinity (Alk) using water temperature and the carbonate system dissociation constants (Stumm and Morgan 1995). More details are provided in Supporting Information Section S1. All dissolved

gases measurements data are available in the Dryad data repository (Vachon et al. 2020).

### Gas fluxes with the atmosphere

Surface diffusive fluxes of CH<sub>4</sub> ( $F_{\text{CH}_4}$ ) and CO<sub>2</sub> ( $F_{\text{CO}_2}$ ) at the air–water interface were measured using a floating chamber connected in a closed-loop to a portable greenhouse gas analyzer (Los Gatos Research, California, U.S.A.) as described in McGinnis et al. (2015). During each sampling campaign, a series of 3–9 chamber deployments were performed during the day (between 09:00 h and 16:00 h) from an anchored boat at the center of the lake ( $n = 136$ ). From these diffusive flux measurements, 74 and 84 measurements were performed in combination with surface-water measurements of dissolved CO<sub>2</sub> and CH<sub>4</sub> concentrations, respectively. These combined flux and dissolved concentration measurements were used to calculate the gas transfer velocity ( $k$ ) to develop specific wind- $k$  models (see Section S2 and Fig. S2 in Supporting Information). These models (one derived from CO<sub>2</sub> and the other from CH<sub>4</sub>) were used to estimate daily surface diffusive fluxes ( $F_X$ , where  $X$  is either O<sub>2</sub>, CO<sub>2</sub>, or CH<sub>4</sub>; mmol m<sup>-2</sup> d<sup>-1</sup>) using Fick’s First Law of diffusion as  $F_X = k_X([X]_{\text{sw}} - [X]_{\text{eq}})$ .  $k_X$  is the gas transfer velocity (m d<sup>-1</sup>) derived from the specific wind-based model ( $k$  derived from CH<sub>4</sub> was used for O<sub>2</sub> and CH<sub>4</sub> fluxes, and  $k$  derived from CO<sub>2</sub> was used for CO<sub>2</sub> fluxes),  $[X]_{\text{sw}}$  is the surface-water O<sub>2</sub>, CO<sub>2</sub>, or CH<sub>4</sub> concentration and  $[X]_{\text{eq}}$  is the O<sub>2</sub>, CO<sub>2</sub>, or CH<sub>4</sub> concentration in equilibrium with the atmosphere calculated using Henry’s Law with water temperature. Model-derived  $k_{600}$  (standardized for CO<sub>2</sub> at 20°C) were converted to gas specific  $k_X$  using gas Schmidt numbers estimated from surface-water temperature and using an  $n$  exponent of  $-2/3$  for smooth surfaces and  $-1/2$  for rough surfaces (Jähne et al. 1987).

We measured ebullition fluxes using five bubble traps made of inverted funnels with collectors deployed at various depths (Vachon et al. 2019a). Total gas flux (mmol m<sup>-2</sup> d<sup>-1</sup>) received by each funnel was calculated by accounting for funnel area, gas volume sampled, and deployment duration (usually 20–30 d). Total gas flux was multiplied by the fraction of CH<sub>4</sub> found in the bubbles collected locally from the sediment. The proportion of CH<sub>4</sub> fraction in the sediment bubbles was measured at various depths (Langenegger et al. 2019) and the proportion left at the surface was estimated using a discrete bubble model (McGinnis et al. 2006). Methane ebullition fluxes were extrapolated to the whole lake area by allocating the five funnel-derived results to five different bathymetric zones (more detailed information is provided in Supporting Information Section S3).

### Net gas production calculation

We used O<sub>2</sub>, CO<sub>2</sub>, DIC, and CH<sub>4</sub> profiles and continuous surface fluxes to estimate the rates of net gas (or DIC) production using the following mass balance approach:  $\text{net}X_{\text{prod}} = \frac{\Delta X_{\text{mass}}}{\Delta t} + \text{surface} \times \text{flux}$ , where  $X$  is O<sub>2</sub>, CO<sub>2</sub> (and DIC),

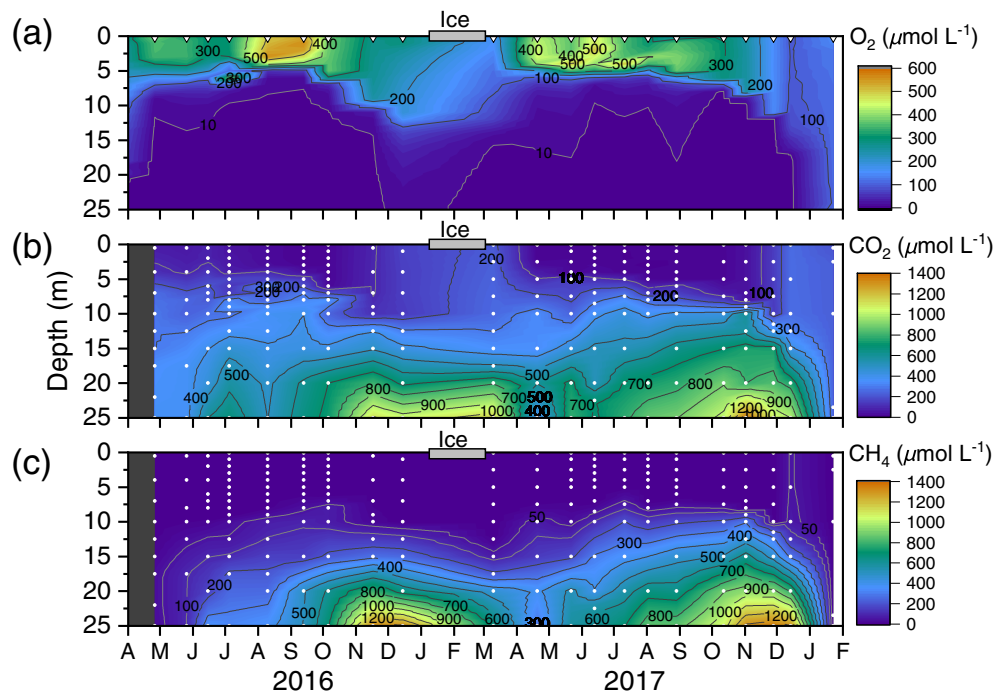
or CH<sub>4</sub>. The argument  $\frac{\Delta X_{\text{mass}}}{\Delta t}$  corresponds to the change in the whole water column  $X$  mass (mmol m<sup>-2</sup>) between the two sampling days. Whole water column masses of dissolved O<sub>2</sub>, CO<sub>2</sub>, DIC, and CH<sub>4</sub> (mmol m<sup>-2</sup>) for each sampling date were calculated by summing the gas masses (mmol) of each 1 m strata (concentration multiplied by the volume of the strata) and then dividing by the lake surface area (m<sup>2</sup>). For this, CO<sub>2</sub>, DIC, and CH<sub>4</sub> concentrations had to be linearly interpolated between sampled depths (whereas O<sub>2</sub> was measured at each meter). The daily surface fluxes for each gas were summed for each period (mmol m<sup>-2</sup>). In winter 2016–2017, all gas fluxes with the atmosphere were set to 0 during the ice-covered period. For the DIC mass balance, integrated surface CO<sub>2</sub> flux from daily estimates was used. For netCH<sub>4</sub><sub>prod</sub>, the surface CH<sub>4</sub> flux is the integration of daily diffusive flux and ebullition rates. Integrated rates of net gas production were estimated for each period ( $\Delta t \sim 20$ –30 d) between two sampling dates (total of 20 periods). Daily rates of net gas production (mmol m<sup>-2</sup> d<sup>-1</sup>) were calculated by dividing by the number of days in each period. All fluxes and net gas production rates uncertainties were evaluated from  $k_{600}$  and gas measurement uncertainties using a Monte Carlo resampling procedure (Supporting Information Section S4).

## Results

### Gas dynamics and atmospheric exchange

Dissolved gases measured in the center of Soppensee were highly dynamic among seasons and showed strong vertical variation due to thermal stratification (Fig. 1). The water column was mostly anoxic under 10 m depth (O<sub>2</sub> < 10 μmol L<sup>-1</sup>) from May to October of both years, while surface-water O<sub>2</sub> concentrations varied from oversaturation in summer to undersaturation in fall and winter (Supporting Information Fig. S3). Dissolved CO<sub>2</sub> and CH<sub>4</sub> accumulated in the bottom waters to reach concentrations of about 1.2 mmol L<sup>-1</sup> and 1.3 mmol L<sup>-1</sup>, respectively (Fig. 1). In the surface waters, CO<sub>2</sub> was oversaturated with respect to atmospheric concentration, except in September and October 2016 and summer 2017 (Supporting Information Fig. S3a). Surface-water CH<sub>4</sub> was consistently oversaturated during the summer months with measured concentrations ranging from 0.5 μmol L<sup>-1</sup> to 1.5 μmol L<sup>-1</sup> and from 0.8 μmol L<sup>-1</sup> to 1.2 μmol L<sup>-1</sup> in 2016 and 2017, respectively (Supporting Information Fig. S3b). During fall turnover, surface-water dissolved CO<sub>2</sub> and CH<sub>4</sub> concentrations drastically increased up to about 250 μmol L<sup>-1</sup> and 50 μmol L<sup>-1</sup>, respectively.

Daily modeled air–water diffusive CO<sub>2</sub> and O<sub>2</sub> fluxes both showed fluctuation between efflux (positive values) and influx (negative values), while CH<sub>4</sub> was being consistently emitted (except during the ice-covered period; Fig. 2). Average of modeled CO<sub>2</sub> and O<sub>2</sub> fluxes during the stratified season (May–October) was higher in 2016 (average ± 1 SD; 35.7 ± 31.9 mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> and 64.0 ± 72.9 mmol O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>) compared to 2017 (average ± 1 SD;



**Fig 1.** Contour plots based on vertical profiles of dissolved (a) oxygen ( $O_2$ ), (b) carbon dioxide ( $CO_2$ ), and (c) methane ( $CH_4$ ) concentrations ( $\mu\text{mol L}^{-1}$ ) measured at the deepest point of the lake. Inverted triangles in (a) show the sampling dates for all profiles and white dots in (b, c) show the depths sampling resolution for  $CO_2$  and  $CH_4$ . Dissolved oxygen concentration was measured at a higher resolution.

$3.9 \pm 10.4 \text{ mmol } CO_2 \text{ m}^{-2} \text{ d}^{-1}$  and  $44.1 \pm 62.0 \text{ mmol } O_2 \text{ m}^{-2} \text{ d}^{-1}$ ). Modeled diffusive  $CH_4$  fluxes were stable during the stratified seasons (May–October), averaging ( $\pm 1 \text{ SD}$ )  $0.7 \pm 0.4 \text{ mmol m}^{-2} \text{ d}^{-1}$  and  $0.7 \pm 0.2 \text{ mmol m}^{-2} \text{ d}^{-1}$  for 2016 and 2017, respectively. During fall turnover (November–December),  $CO_2$  and  $CH_4$  fluxes increased drastically, while  $O_2$  fluxes decreased (Fig. 2). This pattern was more pronounced in the second year. Ebullitive  $CH_4$  fluxes were low in winter (both years winter average of  $0.1 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) and higher in late summer and fall (both summer and fall averages of  $0.6 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) (Fig. 2b and Supporting Information Fig. S4). Average ( $\pm 1 \text{ SD}$ )  $CH_4$  ebullition between May and October was  $0.6 \pm 0.3 \text{ mmol m}^{-2} \text{ d}^{-1}$  and  $1.0 \pm 0.4 \text{ mmol m}^{-2} \text{ d}^{-1}$  for 2016 and 2017, respectively.  $CH_4$  ebullition accounted for 45% and 57% of total summer  $CH_4$  emissions (2016 and 2017, respectively), and about 25% on an annual basis. A summary of annually integrated gas fluxes at the air–water interface for 2016, 2017, and the whole study period are presented in Table 1.

#### Net gas production rates and annual C balance

Rates of net gas production were highly variable in time (Supporting Information Fig. S5), and covaried among each other (Fig. 3). Whole water column rates of  $netO_{2\text{prod}}$  were positive during summer months and early autumn when the water column was stratified, and negative during fall and winter months (Fig. 3 and Supporting Information Fig. S5). Rates of  $netCO_{2\text{prod}}$  (and  $netDIC_{\text{prod}}$ ) were almost always positive, except occasionally during the summer, and were negatively

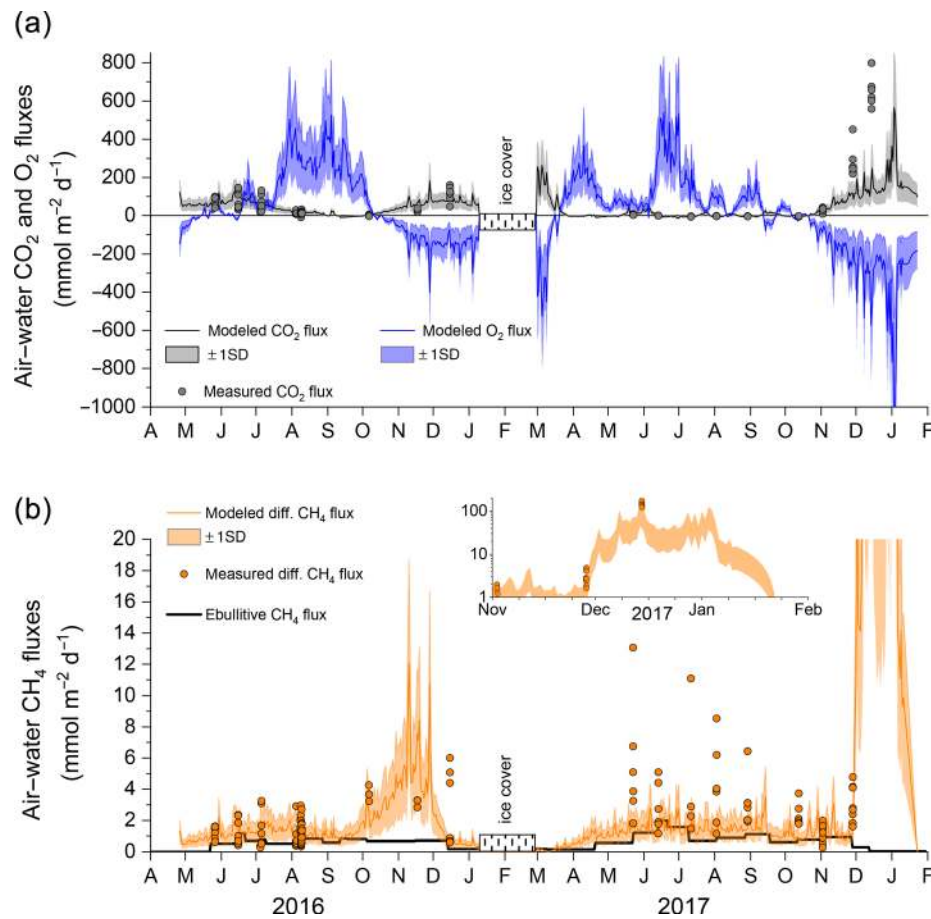
correlated to  $netO_{2\text{prod}}$  (Fig. 3a). Over the course of the study period,  $netCH_{4\text{prod}}$  rates were always positive except during late fall and winter where negative  $netCH_{4\text{prod}}$  shows net  $CH_4$  consumption (Supporting Information Fig. S5). Positive rates of  $netO_{2\text{prod}}$  and  $netCH_{4\text{prod}}$  co-occurred during summer stratified periods, while during negative  $netO_{2\text{prod}}$  the  $netCH_{4\text{prod}}$  rates were highly variable (Fig. 3b). Annually integrated rates of net gas production are summarized in Table 1.

During the  $\sim 22$  month study period (April 2016–January 2018), Soppensee was a net C emitter to the atmosphere, with  $CO_2$  emissions about 10 times higher than  $CH_4$  emissions (Fig. 4; Table 1). The lake showed positive net ecosystem production on an annual basis (i.e., positive  $netO_{2\text{prod}}$ ; biomass and organic matter production). We estimated that about  $32\% \pm 26\%$  of the C produced by net ecosystem production (assuming a 1:1 molar conversion from  $O_2$  to C) was converted into net  $CH_4$  production (as methanogenesis minus  $CH_4$  oxidation) which sustained the annual  $CH_4$  emissions (Fig. 4). This  $netCH_{4\text{prod}} : netO_{2\text{prod}}$  ratio varied between years, from  $9\% \pm 5\%$  in 2016 to  $38\% \pm 30\%$  in 2017.

#### Discussion

Here, we estimated net gas production rates as a whole ecosystem process that accounts for local production and removal, in addition to potential external inputs and outputs. The different processes in which the various gases are





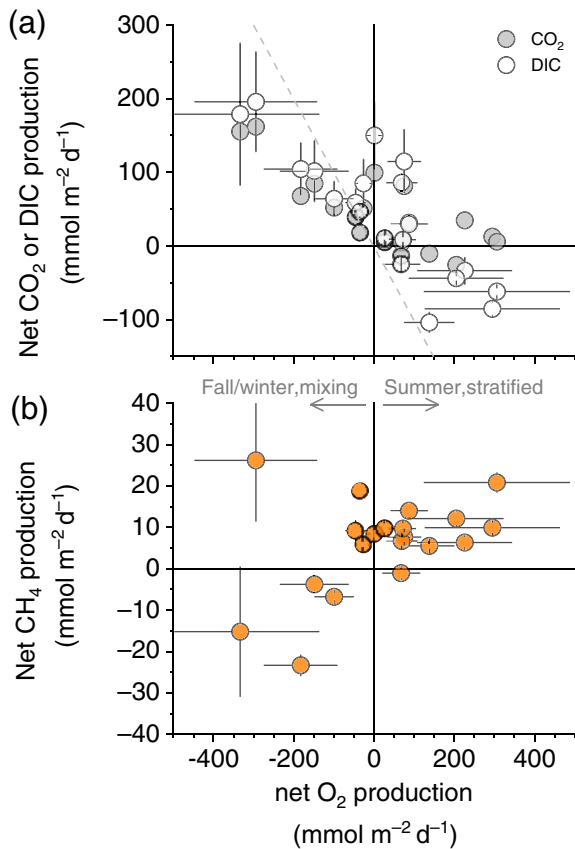
**Fig 2.** Modeled and measured gas fluxes at the air–water interface during the studied period (2016–2017). **(a)** Diffusive O<sub>2</sub> and CO<sub>2</sub> fluxes with the atmosphere (measured with chambers CO<sub>2</sub> fluxes are the gray circles). **(b)** CH<sub>4</sub> diffusive and ebullitive fluxes (measured diffusive CH<sub>4</sub> fluxes with chambers are the orange circles). Inset in **(b)** shows the November 2017 to January 2018 period on a log scale for better visualization. Lighter colored areas in both panels represent the SD around the mean.

**Table 1** Annual air–water gas fluxes and net ecosystem gas production rates ( $\pm 1$ SD) in mol m<sup>-2</sup> yr<sup>-1</sup> integrated for 2016 (from April 2016 to April 2017), 2017 (from December 2016 to December 2017), and the whole study period (from April 2016 to January 2018). Proportions of ebullition to total CH<sub>4</sub> flux are shown in parentheses.

|                 | 2016           |                    | 2017           |                    | Whole period   |                    |
|-----------------|----------------|--------------------|----------------|--------------------|----------------|--------------------|
|                 | Air–water flux | Net gas production | Air–water flux | Net gas production | Air–water flux | Net gas production |
| O <sub>2</sub>  | 14.7±8.4       | 15.0±8.4           | 5.8±3.3        | 4.4±3.3            | 5.0±2.9        | 4.7±2.9            |
| CO <sub>2</sub> | 14.7±7.9       | 15.5±7.9           | 8.8±4.9        | 9.9±4.9            | 15.0±8.1       | 15.2±8.1           |
| DIC             | —              | 9.4±7.7            | —              | 9.9±4.9            | —              | 14.4±8.1           |
| CH <sub>4</sub> | 0.7±0.3(25%)   | 1.3±0.3            | 1.0±0.5(24%)   | 1.7±0.5            | 1.6±0.8(13%)   | 1.5±0.8            |

involved allowed us to explore the various facets of the lake C cycle. We used netO<sub>2</sub>prod as an estimate of whole-lake net ecosystem production (i.e., net organic matter production) which was comparable to the commonly used O<sub>2</sub> diel based method (Supporting Information Section S5). Rates of

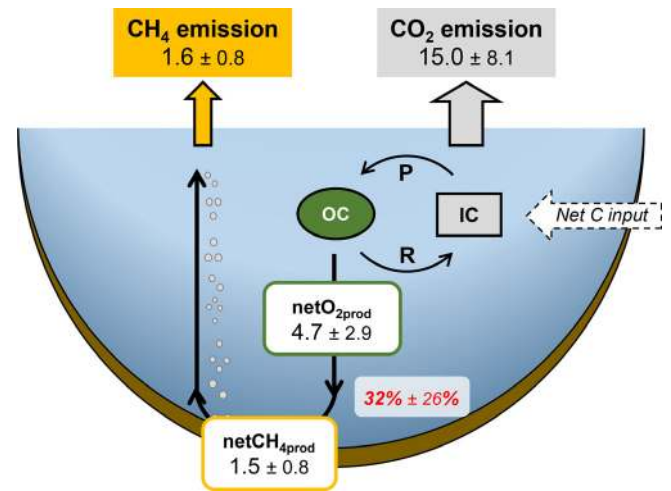
netCO<sub>2</sub>prod (and netDIC<sub>prod</sub>) can be complementary to netO<sub>2</sub>prod, although they also account for anaerobic DIC production and potential C inputs from the catchment. Rates of netCH<sub>4</sub>prod correspond to the net balance between methanogenesis and CH<sub>4</sub> oxidation, while external CH<sub>4</sub>



**Fig 3.** Whole water column net O<sub>2</sub>, CO<sub>2</sub>, DIC, and CH<sub>4</sub> production rates derived from mass balance calculations for each specific period. **(a)** Net O<sub>2</sub> production relationship with net ecosystem CO<sub>2</sub> (and DIC) production. The dashed gray line is the 1: -1 line. **(b)** Net O<sub>2</sub> production relationship with net CH<sub>4</sub> production. Error bars represent 1SD.

inputs did not seem significant (Supporting Information Section S6). Reliable rates of net gas production depend mainly on robust estimates of surface fluxes and gas profile measurements. Achieving these estimates required a few assumptions regarding their spatial and temporal coverage, with implications for net gas production rates (Supporting Information Section S7).

Over the studied period, the lake showed a positive net ecosystem production rate and net CO<sub>2</sub> emissions (Fig. 4, Table 1). Positive net ecosystem production implies net CO<sub>2</sub> removal in the water column; however, there are only a few periods where the lake showed net CO<sub>2</sub> removal in summer (i.e., negative netCO<sub>2</sub><sub>prod</sub> or netDIC<sub>prod</sub>; Fig. 3a). If the lake metabolism was entirely driven by aerobic processes and independent from external C inputs, the relationship between netO<sub>2</sub><sub>prod</sub> and netCO<sub>2</sub><sub>prod</sub> should be close to the 1: -1 line (Vachon et al. 2019b). However, both rates did not follow this reference line. At higher netO<sub>2</sub><sub>prod</sub> rates on the right side of Fig. 3a, the corresponding netCO<sub>2</sub><sub>prod</sub> rates were relatively higher (above the 1: -1 line). During these periods, an offset



**Fig 4.** Summary of the annually integrated net ecosystem O<sub>2</sub> (netO<sub>2</sub><sub>prod</sub>) and CH<sub>4</sub> productions (netCH<sub>4</sub><sub>prod</sub>) and CO<sub>2</sub> and total CH<sub>4</sub> emissions (diffusive and ebullitive) to the atmosphere integrated over the 22 month study period. netCH<sub>4</sub><sub>prod</sub> is the net balance between gross production and the removal via oxidation in both the sediments and the whole water column. Respiration (R) and production (P) represent cycling between organic carbon (OC) produced using inorganic carbon (IC) occurring in the whole water column and the sediments. To support CO<sub>2</sub> emission and netO<sub>2</sub><sub>prod</sub>, an external C source is needed (dashed arrow). All flux units are in mol m<sup>-2</sup> yr<sup>-1</sup>. Over the whole study period, 32% of the organic C produced by netO<sub>2</sub><sub>prod</sub> was transformed to CH<sub>4</sub> to be emitted via diffusion and ebullition through netCH<sub>4</sub><sub>prod</sub> (assuming that for 1 mol of O<sub>2</sub> produced, 1 mol of CO<sub>2</sub> is used, and 1 mol of organic C is produced).

in netCO<sub>2</sub><sub>prod</sub> compared to netO<sub>2</sub><sub>prod</sub> can be observed (i.e., y-axis intercept) at about 100 mmol m<sup>-2</sup> d<sup>-1</sup> (Fig. 3a). Because of the extent of bottom water anoxia during summer, part of the netCO<sub>2</sub><sub>prod</sub> offset could have resulted from anaerobic organic matter degradation, which produces CO<sub>2</sub> without consuming O<sub>2</sub> (e.g., denitrification, sulfate reduction, and methanogenesis). This offset could also correspond to external loading of DIC from, for example, groundwater or surface runoff. Either way, external C inputs from surface runoff or groundwater must be provided, in agreement with results from a previous study in Soppensee (Gruber et al. 2000) and several northern lakes (Bogard and del Giorgio 2016). We estimated that 19.7 mol m<sup>-2</sup> yr<sup>-1</sup> of additional C would be needed to sustain both CO<sub>2</sub> emissions and netO<sub>2</sub><sub>prod</sub>. Considering the water residence time, this external input would require the C concentration of the inflowing water to be about 5 mmol L<sup>-1</sup>, which is reasonable since the average DIC concentration in the water column is about 4 mmol L<sup>-1</sup>.

Lake conditions favorable to CH<sub>4</sub> production are typically characterized by extended anoxia and fresh organic matter supply (Whiting and Chanton 1993; West et al. 2012). In Soppensee, positive rates of netCH<sub>4</sub><sub>prod</sub> were mainly found during summer and usually co-occurred with periods of

positive netO<sub>2prod</sub> (Fig. 3b). However, for the resulting fresh organic matter produced in the surface of the lake to be used for methanogenesis certainly requires a time lag. This means that the observed co-occurrence of positive netO<sub>2prod</sub> and netCH<sub>4prod</sub> is because both take place during the summer stratified period, where greater light availability favors primary production in the surface and bottom anoxic waters favor methanogenesis. Due to this potential delay, it is thus more likely that some portion of algal-derived organic material produced in summer 2016 (higher netO<sub>2prod</sub> than in 2017) was then used for methanogenesis in 2017 (higher netCH<sub>4prod</sub> than in 2016), highlighting the importance of integrating multiple years to account for this legacy effect (Finlay et al. 2019). Taken over the entire study period, the ratio of netCH<sub>4prod</sub> to netO<sub>2prod</sub> was about 32%; however, if we use netO<sub>2prod</sub> from 2016 and netCH<sub>4prod</sub> from 2017, this ratio becomes 11% ± 7%. Note that this ratio is not sensitive to the *k*<sub>600</sub> used in the calculation since the same *k*<sub>600</sub> is used when calculating netO<sub>2prod</sub> and netCH<sub>4prod</sub> (Supporting Information Section S8). In terms of GHG, our results suggest that net ecosystem production in Soppensee removed 207 g CO<sub>2</sub> m<sup>-2</sup> yr<sup>-1</sup> and netCH<sub>4prod</sub> produced 396–2080 g CO<sub>2</sub>-eq m<sup>-2</sup> yr<sup>-1</sup> (using 28–84 as global warming potential of CH<sub>4</sub> over a 100–20 yr time frame). If we assume that methanogenesis mostly uses autochthonous C (West et al. 2012), this loop from netO<sub>2prod</sub> to netCH<sub>4prod</sub> (Fig. 4) would represent a GHG release to the atmosphere of about 3–10 times more than the GHG removed by primary production. Due to its greater warming potential, CH<sub>4</sub> dynamics thus become a critical component of this productive lake GHG budget.

There are a few specific conditions occurring in Soppensee that may have favored net CH<sub>4</sub> production, and that may not occur in similar productive lakes. It has been shown in Soppensee that the extended anoxic environment (from 10 m to bottom) promoted methanogenesis and the strong stratification reduced oxidation at the thermocline (Vachon et al. 2019a). High O<sub>2</sub> concentrations at the surface and light may in addition inhibit CH<sub>4</sub> oxidation (Shelley et al. 2017; Thottathil et al. 2019). Soppensee also produced CH<sub>4</sub> ebullition at depths deeper than generally expected (> 10 m) (Bastviken et al. 2004; West et al. 2016). However, ebullition at greater depths has also been observed in a meromictic lake (Horn et al. 2017) and is suggested to be caused by the high CH<sub>4</sub> concentration in deeper waters (Langenegger et al. 2019) due to strong thermal stratification (Vachon et al. 2019a). Although these specific conditions may suggest that Soppensee is a special case, the C fluxes observed are comparable with other lakes of similar size and trophic status, with CO<sub>2</sub> and CH<sub>4</sub> fluxes within or below the interquartile range of published open water values (DelSontro et al. 2018) (Supporting Information Fig. S6), suggesting that this GHG imbalance could be common among similar lakes.

## Conclusions

Enhanced production due to nutrient loading to aquatic systems (i.e., eutrophication) is a major threat for freshwaters ecological functioning and services. Here, we suggest that such productive lakes can emit CH<sub>4</sub> as a result of anaerobic processing of organic matter, which in turn significantly reduces the lake carbon sink. The lake “efficiency” of converting primary production into CH<sub>4</sub> emissions involves several factors that can vary greatly among lakes. Since CH<sub>4</sub> has a warming potential up to 80 times more than CO<sub>2</sub> on a 20 yr period, this lacustrine CO<sub>2</sub> to CH<sub>4</sub> transformation has paramount implications for the global GHG budget. The GHG emission “cost” of eutrophication has hardly been considered until now (Beaulieu et al. 2019) and conclusions from Soppensee suggest the need to investigate more deeply the CH<sub>4</sub> cycling mechanisms in human-impacted freshwater systems.

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#### **Conflict of Interest**

None declared.

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