Influence of water column stratification and mixing patterns on the fate of methane produced in deep sediments of a small eutrophic lake

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Abstract

Methane (CH\textsubscript{4}), a potent greenhouse gas, is produced and emitted from lakes at globally significant rates. The drivers controlling the proportion of produced CH\textsubscript{4} that will reach the atmosphere, however, are still not well understood. We sampled a small eutrophic lake (Soppensee, Switzerland) in 2016–2017 for CH\textsubscript{4} concentrations profiles and emissions, combined with water column hydrodynamics to investigate the fate of CH\textsubscript{4} produced in hypolimnetic sediments. Using a mass balance approach for the periods between April and October of both years, net CH\textsubscript{4} production rates in hypolimnetic sediments ranged between 11.4 and 17.7 mmol m\textsuperscript{-2} d\textsuperscript{-1}, of which 66–88\% was stored in the hypolimnion, 13–27\% was diffused to the epilimnion, and 6–7\% left the sediments via ebullition. Combining these results with a process-based model we show that water column turbulent diffusivity (K\textsubscript{z}) had a major influence on the fate of produced CH\textsubscript{4} in the sediments, where higher K\textsubscript{z} values potentially lead to greater proportion being oxidized and lower K\textsubscript{z} lead to a greater proportion being stored. During fall when the water column mix, we found that a greater proportion of stored CH\textsubscript{4} is emitted if the lake mix rapidly, whereas a greater proportion will be oxidized if the water column mix more gradually. This work highlights the central role of lake hydrodynamics in regulating CH\textsubscript{4} dynamics and further suggests the potential for CH\textsubscript{4} production and emissions to be sensitive to climate-driven alterations in lake mixing regimes and stratification.

Lakes are releasing CH\textsubscript{4} to the atmosphere at globally important rates, even though they cover a relatively small area (Bastviken et al. 2011; Kirschke et al. 2013). Although CH\textsubscript{4} can be directly produced in the surface water of lakes (Bogard et al. 2014; Donis et al. 2017), the majority derives from the anoxic sediments as a result of anaerobic degradation of deposited organic carbon (Bastviken et al. 2004b; Grasset et al. 2018). To reach the atmosphere, sediment-produced CH\textsubscript{4} must be transported through the water column, where it can be consumed by methanotrophs (Rudd and Hamilton 1978; Utsumi et al. 1998; Kankaala et al. 2006; Bastviken et al. 2008). Sediment-produced CH\textsubscript{4} is transported in the water column by turbulent diffusion (Adams 2005), bubble-mediated transport (McGinnis et al. 2006), plant-mediated transport (Juutinen 2003; Carmichael et al. 2014), or migrating zooplankton (McGinnis et al. 2017; Carey et al. 2018). Although considerable efforts have been invested in quantifying the surface aquatic CH\textsubscript{4} fluxes and the relative contribution of the different emissions pathways (Bastviken et al. 2004a; Rinta et al. 2017), the in-lake mechanisms regulating rates of CH\textsubscript{4} production, transport, and oxidation in stratified systems are still poorly understood. Here, we investigate the role of water column hydrodynamics in promoting or restricting the different pathways.

Lake stratification and mixing processes influence the fate of CH\textsubscript{4} produced in the sediments. Although mixing processes in lakes are complex, one cornerstone mechanism for vertical transport of all solutes in stratified waters is the turbulent vertical diffusivity (K\textsubscript{v}), which is mainly driven by kinetic energy input (e.g., wind and convection) and water column stability (Imboden and Wüst 1995; Read et al. 2012). Turbulent vertical diffusivity partly regulates the magnitude of vertical fluxes across the thermocline (Kreling et al. 2014). Strong water column stratification therefore limits vertical gas exchange between the hypolimnion and epilimnion resulting in increasing bottom water CH\textsubscript{4} storage (Juutinen et al. 2009; Kankaala et al. 2013; Rinta et al. 2017). High oxidation rates are often observed near the thermocline of stratified lakes, where both CH\textsubscript{4} and O\textsubscript{2} concentrations overlap (Sundh et al. 2005;
Oswald et al. 2016), although microaerobic CH₄ oxidation can also occur just below the chemocline in anoxic waters (Blees et al. 2014). Furthermore, high Kᵥ values were associated with high rates of CH₄ oxidation in Lake Mendota (Fallon et al. 1980), whereas low Kᵥ values were associated with low oxidation rates in Lake 227 (Rudd and Hamilton 1978). Taken together, these studies highlight the role of Kᵥ on CH₄ oxidation and storage in stratified lakes.

The transport through the water column via rising bubbles (i.e., ebullition) account for about half of the total CH₄ emission in lakes (Bastviken et al. 2004a). Ebullition allows a fraction of methane to bypass the oxidation barrier and therefore efficiently conveys sediment-produced CH₄ to the atmosphere (McGinnis et al. 2006). When net gas production (mainly CH₄ but also CO₂, N₂O, and N₂) rates occur faster than the diffusive flux out of the sediments, the dissolved CH₄ in porewater can reach oversaturation (i.e., total gas pressure exceeds absolute pressure at depth) and CH₄ ebullition will occur (Schmid et al. 2017). Ebullition is more frequent in shallow sediments (Bastviken et al. 2004a) due to the role of hydrostatic pressure in regulating bubble formation. In deeper sediments, the critical CH₄ concentration at which bubbles form is higher due to increased solubility with lower temperatures and higher pressures. For these reasons, only systems with intense sediment CH₄ production are able to form bubbles from deep sediments (West et al. 2016) or in meromictic lakes where bubble formation can benefit from the important total gas pressure accumulated in the trapped bottom waters (Horn et al. 2017).

In fall when deeper vertical mixing occurs, CH₄-rich bottom waters are rapidly mixed with surface oxygenated waters. This results in enhanced CH₄ oxidation rates (Rudd and Hamilton 1978; Kankaala et al. 2006) but also to higher diffusive fluxes to the atmosphere. Atmospheric CH₄ emission during lake turnover usually corresponds only to about 15% to 45% of the CH₄ stored in the hypolimnion (Rudd and Hamilton 1978; Kankaala et al. 2006; Schubert et al. 2012; Encinas Fernández et al. 2014). However, the vertical mixing process in fall is not always complete, where accumulated CH₄ during summer can remain trapped in the bottom waters over winter. The accumulation of solutes in the deep layers during summer increases the bottom water stability and can prevent the lake from complete mixing (i.e., biogenic meromixis; Boehr et al. 2017; Schultz et al. 2017). The ultimate fate of this longer term CH₄ storage induced by incomplete vertical mixing, and its potential impact on lake CH₄ dynamics has rarely been reported (see Itoh et al. 2015).

Here, we investigate the interaction among CH₄ transport pathways, fate, and specific physical environmental characteristics such as water column stability and length of stratification period. We hypothesize that (1) higher water column stability during summer stratification results in reduced upward turbulent CH₄ flux and higher CH₄ storage (Fig. 1) and that (2) increasingly isolated hypolimnion due to longer stratification periods or incomplete turnover promotes higher CH₄ concentrations, CH₄ production, and CH₄ ebullition from deep sediments (Fig. 1). To test these hypotheses, we measured hypolimnetic CH₄ dynamics and deep sediments ebullition from a small eutrophic lake (Soppensee, Switzerland) over approximately two full years. Using mass balance approaches, we estimate net CH₄ production in the hypolimnion and its fate during the stratified and mixing period. We then use a simple process-based model to further investigate the potential role of water column stratification strength for CH₄ fate. We concluded that water column physical structure and hydrodynamics affect the fate of CH₄ produced in the deep sediments by reallocating the oxidation and emissions pathways. Moreover, we show that an incomplete mixing in winter 2016/2017 had critical implications for the following summer CH₄ dynamics and during the following year complete turnover event.

**Methods**

**Study site and sampling frequency**

The study was conducted in the small eutrophic lake Soppensee (47°09′N, 8°08′E) situated in the Canton of Lucerne, Switzerland (lake area: 23 ha, maximum depth: 26 m, mean depth: 12.2 m). Average total phosphorus integrated over the whole water column was about 70 μg P L⁻¹ in 2016–2017. The lake was sampled on a ~ monthly basis (more frequently in summer but less in winter) from April 2016 to January 2018 (discussed below). In addition to manual sampling, moored instruments were deployed for continuous measurements of temperature and oxygen. Inverted funnels (3) were deployed for gas ebullitive fluxes from deep sediments. During summer, sediment cores were taken to estimate the porewater CH₄ concentration and potential CH₄ production (August–September 2016 and July–September in 2017). A bathymetric map of Soppensee with the location of the moored instruments and gas funnels is shown in Supporting Information Fig. S1.

**Water temperature and dissolved oxygen**

In the deepest point of the lake (~ 26 m; Supporting Information Fig. S1), a string of temperature loggers (Vemco Minilog-IlT; temperature accuracy ± 0.1°C, resolution 0.01°C) was moored from 26 April 2016 to January 2018, measuring water temperature every minute at several depths (2, 5, 8, 10.8, 13.5, 16, 18.5, 23, and 26 m). In 2017, seven additional loggers were added to the mooring (1, 4, 6.5, 12.1, 14.7, 19.8, and 21 m). A dissolved O₂ probe (miniDOT, Precision Measurements Engineering) was installed at 1 m depth and logged temperature, dissolved O₂ concentration (mg O₂ L⁻¹), and saturation (%) every minute.

In addition to continuous measurements, manual CTD (conductivity, temperature, depth and dissolved oxygen) profiles were performed every 3-weeks to 1-month intervals using a multiparameter sonde (Yellow Spring Instrument EXO2, after May 2017 a Seabird pumped CTD profiler, SBE19). Water column stability was calculated as $N^2 = \frac{g \rho_z}{\rho} (s^{-2})$, where $g$ is the gravitational acceleration (m s⁻²), $z$ is the depth (m), and $\rho$ is the water density (kg m⁻³). Water density was calculated using
temperature ($T$) and specific conductivity at 20°C ($\kappa_{20}$) from the CTD profiles (Imboden and Wüest 1995, eqs. 29 and 35). The O2 profiles from May to October were used to determine the anoxic–oxic interface (AOI) for the mass balance purpose (here determined to be at 8 m), which corresponds to the depth at which dissolved O2 is below 1 mg L$^{-1}$.

Vertical turbulent diffusivities ($K_z$) below 5 m were estimated for each sampling date during the stratified periods using the heat budget method (Jassby and Powell 1975). The continuous temperature measurements were used to calculate the temporal rates of temperature change. This method assumes that turbulent transport of heat at depth $z$ is a function of the rate of change of heat content below that depth. Rates of heat transfer were calculated as the slope of temperature change over time measured between 7 d before and after each sampling date. These temperature slopes were vertically linearly interpolated at each meter depth and CTD profiles were used to calculate the vertical temperature gradient with depth (Wüest et al. 2000). We assumed that solar radiation had minimal direct effect on the temperature change below 5 m as the lake was turbid, with the averaged measured Secchi depth of about 2 m. As a result, a $K_z$ profile from 5 m to bottom was resolved for each sampling date, which corresponds to the integrated $K_z$ over about 14 d (7 d before and after the sampling date).

**Methane concentration and stable isotope ($\delta^{13}$C-CH$_4$)**

Dissolved CH$_4$ and stable C isotope values ($\delta^{13}$C-CH$_4$) in the water column were measured using a 1-liter bottle headspace method as described in Donis et al. (2017). Briefly, lake water was sampled at defined depth using a 5-liter Niskin water sampler. The vertical sampling resolution was variable between the sampling dates, but samples were taken usually every 1–3 m down to 10 m and then every 5 m down to the bottom. Water from the Niskin bottle was gently poured into a 1-liter glass bottle, letting overflow to replace 1-liter bottle volume several times. A volume of 400 mL of water was carefully removed and replaced with ambient air without creating turbulence. The bottle was capped and shaken vigorously for at least 2 min. The headspace was transferred into a gas-tight atmospheric sampling bag (Supel™ Inert Multi-Layer Foil) for further gas analysis on a Cavity Ring-Down Spectrometer (Picarro G2201-i). In case of high CH$_4$ concentration (e.g., samples below 10 m in Soppensee), an additional dilution was applied before the analysis by subsampling the bag and diluting into a 50 mL glass gas-tight syringe (Carbagas: 80% N$_2$, 20% O$_2$ ± 1%). In these cases, the gas was subsampled two or three times and the average was taken. The average coefficient of variation (C.V.) for all these diluted replicates was 5% ($n = 67$). Lake water dissolved CH$_4$ concentration and $\delta^{13}$C-CH$_4$ was back calculated by applying a mass balance in the bottle, with information about air CH$_4$ concentration, water temperature, and atmospheric pressure. A second sample was occasionally taken for a given depth to test for replicability of the method. The average C.V. for all the replicates was 9.7% ($n = 8$).

**CH$_4$ ebullitive fluxes**

We measured ebullition fluxes from sediments below 8 m using bubble traps made of inverted funnels with bubble collectors (DelSontro et al. 2010). In May 2016, two bubble traps (opening of 0.79 m$^2$) were deployed about 4 m below the
surface water over sediments of 10 and 21 m depths. Another
bubble trap (also 0.79 m²) was installed in June 2017 over 15 m
deep sediments to provide a better spatial coverage, also
moored at about 4 m below surface (see Supporting Informa-
tion Fig. S1 for Suppensee map with bubble traps locations).
Bubble traps were moored with an inverted-V configuration to
avoid disturbing the sediments below them. At each sampling
date, the traps were gently brought to the surface and the gas
volume was sampled using a 60-mL plastic syringe with a nee-
dle through the gas collector septum. Total gas volume was
converted to moles of gas according to the Ideal Gas Law using in
situ temperature and atmospheric pressure at the day of sampling.
Total gas flux (mmol m⁻² d⁻¹) received by the funnel (sitting at
4 m depth) was calculated accounting for funnel area, gas volume
sampled, and deployment duration. When bubbles rise from the
sediments to the funnel, the different gases in the bubble
exchange with the water column. To convert to total gas (and
CH₄) fluxes at the sediment water interface (SWI), a correction
for gas exchange of the rising bubbles was made using a single bubble
simulation model (McGinnis et al. 2006). The bubble model sim-
ulations estimated that about 30% of CH₄ in the rising bubble
was dissolved back in the hypolimnion (below 8 m). Further
information for these steps is provided in the Supporting Infor-
mation Section S1.

Methane ebullition fluxes were extrapolated to the whole
hypolimnetic area (i.e., sediment area below 8 m) by allocat-
ing the three funnel-derived results to three different bathy-
metric zones. We multiplied the rates from the 10-m funnel
with the sediment area between 8 and 14 m, rates from the
15-m funnel with the area between 15 and 21 m, and the 21-m
funnel rates with the area between 21 and 26 m. The sum of
ebulition from these areas was then divided by the sediment
area below 8 m to get the integrated CH₄ ebullition below 8 m
(mmol m⁻² d⁻¹). As we did not install a funnel at 15 m in 2016,
ebulition rates from 15 m depth in 2016 were extrapolated
using a linear relationship linking ebullition rates at 10 and
15 m using the 2017 data (n = 10, r² = 0.30).

**Diffusive CH₄ fluxes at AOI**

Diffusive flux at the AOI (F_{diff, AOI}; mmol m⁻² d⁻¹) was estimated
following Fick’s First Law:

\[ F_{diff, AOI} = K_z \frac{\partial CH₄}{\partial z} \]  

(1)

The CH₄ concentration gradient (\( \frac{\partial CH₄}{\partial z} \)) crossing the AOI
was determined from CH₄ measurements between 7 and 10 m. K_{z, AOI} was determined from derived K_z values from the heat
budget method and log-averaged between 7 and 10 m to
match the associated CH₄ gradient thickness.

**Diffusive CH₄ flux measurements at the air–water interface**

Surface diffusive CH₄ fluxes with the atmosphere were mea-
sured using a floating chamber connected in a closed loop to a
portable greenhouse gas analyzer (Los Gatos Research) as de-
scribed in McGinnis et al. (2015). At each sampling occasion, a
series of three to six chamber deployments were performed from
the boat at the center of the lake during the day (between
9:00 and 16:00 h). Each deployment lasted about 6 min, and
diffusive flux was calculated as the slope of the linear CH₄ increase
(McGinnis et al. 2015).

**Hypolimnetic CH₄ mass balance**

We used a CH₄ mass balance approach during the stable stratified period (May to October) of both studied years. The
daily change in CH₄ storage below 8 m (\( \frac{dC_{CH₄}}{dt} \) V_{hypo}; mmol d⁻¹) is described as:

\[ \frac{dC_{CH₄}}{dt} V_{hypo} = a F_{ebu, SWI, AOI} + F_{diff, SWI, AOI} - F_{diff, AOI, AOI} \]  

(2)

where \( F_{ebu, SWI} \) (mmol m⁻² d⁻¹) is the ebullition of CH₄ leaving
the sediments, \( a \) is the dissolution factor of CH₄ from bubbles
into the hypolimnetic water (0.3; determined from the bubble
simulation), \( F_{diff,SWI} \) (mmol m⁻² d⁻¹) is the diffusion of CH₄
across the SWI, \( F_{diff, AOI} \) (mmol m⁻² d⁻¹) is the diffusion from
hypolimnion to the epilimnion across the AOI, \( A_{sed} \) (m²) is
the sediment area, and \( A_{AOI} \) (m²) is the area at the AOI (8 m).
As the hypolimnion was anoxic during the integration period, we
assumed that CH₄ oxidation was insignificant compared to the
other fluxes (Schmid et al. 2017). However, we acknowledge that
anaerobic CH₄ oxidation (Reed et al. 2017) and microaerobic CH₄
oxidation (Blees et al. 2014) might however have occurred
(see Discussion section for implication on the results). Change in
CH₄ storage below 8 m was calculated as the linear increase of
the volume-weighted average CH₄ concentration of the sampling
dates between May and October each year (n = 7 in 2016 and
n = 6 in 2017). For each sampling date, the volume-weighted
average CH₄ concentration was estimated from the vertical linear
interpolation of measured CH₄ concentrations combined with
volume of each depth strata below 8 m. \( F_{ebu, SWI} \) was estimated as
the temporally averaged ebullition below 8 m over the integrated
period of the mass balance each year (as the cumulative ebullition
divided by the number of days). \( F_{diff, AOI} \) is the average diffusive flux
at the AOI of the same sampling date included in the mass balance
period. By rearranging Eq. 2, we can derive the temporally inte-
grated and spatially integrated diffusion at the SWI (\( F_{diff, SWI} \)) as:

\[ F_{diff, SWI} = \left[ \frac{\Delta C_{CH₄}}{\Delta t} V_{hypo} - a F_{ebu, SWI, AOI} + F_{diff, AOI, AOI} \right] / A_{sed} \]  

(3)

Similarly, by assuming the rate of net CH₄ production
in the sediment is equal to the CH₄ transported out via methane
flux and ebullition, then the temporally integrated and spatially
integrated net CH₄ production (\( P_{sed} \)) can be defined as:

\[ P_{sed} = F_{ebu, SWI} + F_{diff, SWI} \]  

(4)
As the mass balance equations consist in sources (additions) and sinks (subtractions), we assessed the general uncertainties of $P_{sed}$ and $F_{diff,SWI}$ by applying the rule of error propagation as:

$$\sigma Q = \sqrt{(\sigma A)^2 + (\sigma B)^2 + (\sigma C)^2 + ...} \quad (5)$$

where $\sigma Q$ is the uncertainty around a quantity $Q$ (here $P_{sed}$ and $F_{diff,SWI}$) and $\sigma A$, $\sigma B$, and $\sigma C$ are the uncertainties of each component of the mass balance equation ($F_{ebu, SWI}$, $F_{diff, AOI}$) in Eq. 3 and $F_{ebu, SWI}$, $F_{diff, SWI}$ for Eq. 4. Here, we use the term uncertainty as a general assessment of error due to methodology and/or intermittency of the processes. Uncertainty in $\Delta CH_4$ was determined as the standard error of the linear slope (LINEST function in Microsoft Excel), and uncertainty in $P_{sed}$ and $F_{diff, AOI}$ was determined as the standard deviation of the estimated fluxes at each sampling date during the integrated mass balance period. For $F_{ebu,SWI}$ the uncertainty can be due to the methods (e.g., bubble model correction and interpolation of the missing ebullition measurement at 15 m in 2016) and to the spatial variability of ebullition. Previous study by Wik et al. (2016) suggested that for two to three sampling locations (like in our case), the risk of overestimating or underestimating ebullition fluxes is between 25% and 50%, with more risk of underestimating. As we believe that the uncertainty is mainly due to spatial variability, we applied a conservative 50% uncertainty around the average $F_{ebu,SWI}$ used in the mass balance. As $F_{ebu,SWI}$ contribution to the mass balance was relatively small compared to the other components, the ebullition uncertainty did not significantly influence the final production and diffusion estimates (see Discussion section for further details).

**Hypolimnetic CH₄ dynamics model**

The observed dynamics among CH₄ storage, net production, diffusion fluxes at the SWI and AOI, and CH₄ ebullition at SWI were reproduced with a simple process-based model (Supporting Information Fig. S2). The model main equation was directly derived from the mass balance (Eq. 2) to predict hypolimnetic CH₄ ([CH₄]$_{hypo}$) concentration and was solved numerically with the Euler method with a daily time step ($\Delta t$):

$$[CH₄]_{hypo,t} = [CH₄]_{hypo,t-1} + \left( F_{diff,SWI} \frac{A}{V} - F_{diff,AOI} \frac{A}{V} + aF_{ebu,SWI} \frac{A}{V} \right) \Delta t \quad (6)$$

where $F_{diff,SWI}$ is the diffusion flux at the sediment–water interface, $F_{diff,AOI}$ is the flux across the AOI and was a function of $K_{diff} \times [CH₄]_{hypo}$, and the ebullition $F_{ebu,SWI} = P_{sed} - F_{diff,SWI}$. However, for ebullition to occur, $P_{sed}$ has to be greater than the maximum $F_{diff,SWI}$ determined as $K_{diff} \times ([CH₄]_{pw,crit} - [CH₄]_{hypo})$. If $P_{sed}$ is smaller than the maximum $F_{diff,SWI}$, no ebullition occurs and $P_{sed} = F_{diff,SWI}$ (Supporting Information Fig. S2).

$[CH₄]_{pw,crit}$ is the critical CHᵴ concentration in the porewater of sediment over which bubbles can form (i.e., local pressure $>$ atmospheric + hydrostatic pressures assuming N₂ as the only other gas contributing to total gas pressure). If we assume that N₂ partial pressure ($p$N₂) in the porewater is equivalent to atmospheric $p$N₂, i.e., 79%, then the CH₄ partial pressure ($p$CH₄) required to form bubbles in the porewater is estimated as $p$CH₄ = $loc$$_{pressure} - 0.79 \times atm$_{pressure}$. Local pressure ($loc$$_{pressure}$) was determined as atm$_{pressure}$ + $\frac{zg}{101325}$, where atm$_{pressure}$ is in atm, $\rho$ is the density of water ($\sim 1000$ kg m$^{-3}$), $z$ is the depth of the sediments (m), and $g$ is the gravitational acceleration ($9.81$ m s$^{-2}$). This critical pCH₄ was converted to $[CH₄]_{crit}$ using Henry’s Law (Sander 1999) and averaged $4870 \mu$mol L$^{-1}$ for Soppensee hypolimnetic sediments (mean depth of $15.5$ m at water temperature of $5.6^\circ$ C and local atmospheric pressure of $0.94$ atm). Note also that $[CH₄]_{crit}$ is assumed to be constant over time, however, processes like porewater stripping of other dissolved gases (i.e., N₂) may slightly influence this value (Chanton et al. 1989; Langenegger et al. 2019). $K_{diff}$ is the gas transfer velocity (m d$^{-1}$) at the SWI and $K_{diff,eff}$ is the effective turbulent diffusivity over 1 m at the AOI (m$^2$ d$^{-1}$). To test the model behavior, we parameterize $K_{diff}$ to fit the average observed diffusive flux at SWI determined by the mass balance $F_{diff,SWI}$ and $K_{diff,eff}$ to fit the average observed $F_{diff,AOI}$ (see Supporting Information Section S2 for further details on model and Table S1 for model calibration parameters).

**Estimating CH₄ emissions during lake turnover**

The proportion of CH₄ emission during the lake turnover was estimated as the average CH₄ flux at the air–water interface ($F_{CH₄,AWI}$) divided by the whole water-column CH₄ mass loss. Whole water-column CH₄ mass loss was estimated from the linear decrease in whole water-column CH₄ mass (mmol m$^{-2}$) measured during the lake turnover period, i.e., from 17 November 2016 to 10 March 2017 for the first year and from 02 November 2017 to 23 January 2018 for the second year. The whole water-column CH₄ mass was estimated on each sampling occasion from the vertical linear interpolation of measured CH₄ concentration, multiplied by the volume of each meter strata and divided by the lake surface area.

Surface CH₄ diffusive emissions during the turnover periods was estimated using Fick’s First Law of diffusion as:

$$F_{CH₄,AWI} = k_{CH₄} \left( [CH₄]_{sw} - [CH₄]_{eq} \right) \quad (7)$$

where $k_{CH₄}$ is the daily gas transfer velocity (m d$^{-1}$), $[CH₄]_{sw}$ is the daily surface water CH₄ concentration interpolated linearly from the monthly sampling, and $[CH₄]_{eq}$ is the CH₄ concentration in equilibrium with the atmosphere. Gas transfer velocity ($k_{600}$) was estimated from standardized gas transfer velocity ($k_{600}$) derived from a wind-based model developed during positive buoyancy flux (MacIntyre et al. 2010) using daily averaged wind speed measured from a meteorological tower situated about 12 km north of the lake (Egolzwil station,
Federal Office of Meteorology and Climatology MeteoSwiss). A portable weather station (Kestrel 3000) was deployed occasionally in the center of the lake (two deployments of about 2–3 h) on October 2016 and August 2017. When comparing both wind speed measurements corrected to 10 m height (Crusius and Wanninkhof 2003), systematically lower $U_{10}$ was recorded on the lake than at the Egolzwil station due to the wind shelter effect by the surrounding trees and hills, whereas the inland meteorological tower is situated in an open field. An empirical correction was therefore used to infer the Egolzwil measured $U_{10}$ for the lake situation (Supporting Information Fig. S3; $U_{10\text{Ego}} = 0.515 \times U_{10\text{tower}}$, $r^2 = 0.95$, $n = 55$). The relationship covered a range of recorded $U_{10}$ between 0.2 and 7.4 m s$^{-1}$. Then, $k_{600}$ was converted to $k_{\text{CH}_4}$ (Jähne et al. 1987) using CH$_4$ Schmidt number estimated from surface water temperature (Wanninkhof 1992) and using $n$ exponent of $-2/3$ for smooth surfaces. [CH$_4$]$_{eq}$ is the water concentration in equilibrium with the atmosphere (assuming constant atmospheric pCH$_4$ of 2 μatm and using Henry’s Law).

Results

Stratification and mixing patterns

In both 2016 and 2017, the lake water column was strongly thermally stratified from May to October (Fig. 2a), with the thermocline situated between 5 and 7 m depth. Water temperature in summer normally reached about 24–26 °C in the surface layer and remained at around 4–5 °C in the bottom water throughout the year. During the summer, specific conductivity ($\kappa_{20\text{C}}$ μS cm$^{-1}$) decreased in the surface waters, reaching values around 250 μS cm$^{-1}$, and increased in the hypolimnion with values reaching ~ 400 μS cm$^{-1}$ (Fig. 2b). During the first winter (Dec 2016–March 2017), ice formed for approximately 50 d (from beginning of January until end of February 2017). The buildup of solutes as indicated from the specific conductivity in the hypolimnion increased the bottom water density. Combined with the development of the ice cover, the higher density of the hypolimnetic water prevented complete turn-over during the first winter. During winter of the second year (January 2018), the water column was mixed completely and more rapidly (Fig. 2a,b).

We used monthly profiles of temperature and specific conductivity to calculate the water column stability ($N^2$). Continuous measurements of water column temperature from the moored temperature loggers and profiles were used to estimate the basin-scale vertical turbulent diffusivity profiles ($K_z$). Average $N^2$ between 6 and 10 m (log-average) increased from low values in early spring (from about $10^{-4}$ s$^{-2}$) to up to maximum values in August and September of both years (around $10^{-3}$ s$^{-2}$; Supporting Information Fig. S4a). In October, $N^2$ between 6 and 10 m decreased sharply to low values around November (down to around $10^{-4}$ s$^{-2}$). From April to October, $K_z$ values between 6 and 10 m (log-average) were comparable between 2016 (4.2 $\times$ $10^{-7}$– 2.1 $\times$ $10^{-6}$ m$^2$ s$^{-1}$) and 2017 (3.5 $\times$ $10^{-7}$–3.8 $\times$ $10^{-6}$ m$^2$ s$^{-1}$), with minimum diffusivities occurring in October and late August for 2016 and 2017, respectively (Supporting Information Fig. S4b). Average $K_z$ values just below (11–15 m) were slightly lower in 2016 (8.5 $\times$ $10^{-7}$–4.9 $\times$ $10^{-6}$ m$^2$ s$^{-1}$) compared to 2017 (1.3 $\times$ $10^{-5}$–1.0 $\times$ $10^{-5}$ m$^2$ s$^{-1}$; Supporting Information Figs. S4b, S5). Taking both years together, average $N^2$ and $K_z$ values (between 6 and 10 m) showed a strong negative relationship (Supporting Information Fig. S6).

Dissolved oxygen dynamics

The stratified water column during summer of both years led to an extended period of hypolimnetic anoxia (here defined as dissolved O$_2$ < 1 mg L$^{-1}$) between May to October (Fig. 2c). The transition between anoxic and oxic waters (defined as the AOI) varied slightly between 6 and 9 m during the summer stratification and also corresponded to the upper limit of the hypolimnion for both years (here assumed to 8 m). Although temporal resolution of sampling in winter was coarse, we did not measure O$_2$ above 1 mg L$^{-1}$ below 19 m during winter 2016–2017, while in January 2018, bottom O$_2$ concentrations were above 1 mg L$^{-1}$ down to 25 m after turn-over (Fig. 2c). In the surface waters, O$_2$ saturation was highly variable, with periods of O$_2$ oversaturation (> 100%) down to 5 m depth (Fig. 2c,d). The highest O$_2$ saturation values were measured between August and September 2016, with values reaching over 200% saturation (Fig. 2c,d). In 2017, extensive oversaturation values (up to about 175%) were observed between early May and mid-July (Fig. 2d). Between November and March, surface O$_2$ saturation was usually below 100% and decreased drastically to 0% for ~ 10 d in January 2018 during the complete lake overturn (Fig. 2d).

Lake CH$_4$ concentration, storage, and vertical fluxes

Figure 3 shows the vertical profiles of dissolved CH$_4$ concentrations and their C stable isotopes ($\delta^{13}$C-CH$_4$). Dissolved CH$_4$ concentration reached the highest values near the bottom (25 m), starting from 30 μmol L$^{-1}$ (April 2016), and due to incomplete turn-over, starting at ~ 300 μmol L$^{-1}$ in April 2017. Maximum concentrations of ~1300 μmol L$^{-1}$ were observed in November during both 2016 and 2017 (Figs. 3–4a). Dissolved CH$_4$ was significantly lower and relatively constant at the lake surface, ranging between 0.5 and 1.5 μmol L$^{-1}$ between April and October of both years and increasing during fall convective mixing to values up to ~7 μmol L$^{-1}$ in November 2016 and up to 54.5 μmol L$^{-1}$ in December 2017. During the well-stratified seasons, CH$_4$ concentrations were the lowest near the thermocline just above the AOI (between 5 and 8 m depth; Fig. 3a,c) with values around 0.3–0.5 μmol L$^{-1}$; however, winter surface CH$_4$ concentrations were even lower around 0.01 μmol L$^{-1}$ (Fig. 3b,d). During the well-stratified periods, values of $\delta^{13}$C-CH$_4$ were around ~66‰ below 10 m, associated with the highest CH$_4$ concentrations, while ranging between ~56‰ and ~35‰ in the surface waters (Fig. 3a,c). $\delta^{13}$C-CH$_4$ values were the highest (around ~20‰) around the thermocline (5–7 m) just
above the AOI and are associated with the lowest CH4 concentrations (Fig. 3a,c). During fall mixing and winter, $\delta^{13}$C-CH4 values were higher at the surface (between $-40^{\%}$ and $-30^{\%}$), whereas the bottom waters $\delta^{13}$C-CH4 values were low at around $-65^{\%}$ (Fig. 3b,d).

Volume-weighted average CH4 concentrations below 8 m increased linearly with a higher rate observed in 2017 (1.6 $\mu$mol L$^{-1}$ d$^{-1}$) than in 2016 (1.2 $\mu$mol L$^{-1}$ d$^{-1}$; Fig. 4b). Due to the incomplete mixing event, the entire water column CH4 storage was about 10 times higher in April 2017 (697 mmol m$^{-2}$) than during the same time of the previous year (72 mmol m$^{-2}$).

Water column storage also reached the highest values in November 2017 (2402 mmol m$^{-2}$) compared to the same period in 2016 (1320 mmol m$^{-2}$). During the well-stratified period (May to October) surface diffusive CH4 fluxes to the atmosphere measured with floating chambers were on average 1.4 $\pm$ 1.0 mmol m$^{-2}$ d$^{-1}$ ($\pm$ 1 SD; $n = 69$) and 1.8 $\pm$ 0.9 mmol m$^{-2}$ d$^{-1}$ ($\pm$ 1 SD; $n = 39$) for 2016 and 2017, respectively. In November and December 2016, we measured surface diffusive CH4 fluxes of 3.1 $\pm$ 0.3 mmol m$^{-2}$ d$^{-1}$ ($\pm$ 1 SD; $n = 3$) and 0.6 $\pm$ 0.2 mmol m$^{-2}$ d$^{-1}$ ($\pm$ 1 SD; $n = 7$), respectively. In November and December 2017, surface diffusive CH4 fluxes were on average 2.1 $\pm$ 0.9 mmol m$^{-2}$ d$^{-1}$ ($\pm$ 1 SD; $n = 13$) and 141.3 $\pm$ 18.4 mmol m$^{-2}$ d$^{-1}$ ($\pm$ 1 SD; $n = 6$), respectively.

**Ebullitive CH4 fluxes**

Ebullition flux measured with bubble traps varied significantly both temporally (interannual and intraannual) and spatially between the different locations (Supporting Information Fig. S7a,b). Total gas fluxes were converted to CH4 bubble gas leaving the sediment (hereafter referred to as ebullition). Ebullition at 10 m depth usually showed the highest rates, often two times higher than ebullition at 21 m depth (Supporting Information Fig. S7b). The lowest ebullition rates were measured at the 15-m funnel site (Supporting Information Fig. S7a,b). Spatially averaged CH4 ebullition rates were estimated for sediments below 8 m and are shown on Fig. 4c (see Supporting Information Fig. 2.)
In 2016, ebullition began in early June and gradually increased to up to about 2.0 mmol m$^{-2}$ d$^{-1}$ toward the end of the year. In winter 2016–2017, ebullition slowed down to ~ 0.5 mmol m$^{-2}$ d$^{-1}$. Between June and November 2017, ebullition below 8 m varied between 1.4 and 2.7 mmol CH$_4$ m$^{-2}$ d$^{-1}$ (Fig. 4c). In December 2017, ebullition decreased to about 1 mmol m$^{-2}$ d$^{-1}$ and completely stopped after turnover with no ebullition observed at any funnel from 23 January to 10 April 2018.

**CH$_4$ mass balance and system analysis during the stratified periods**

We performed a mass balance to derive spatially integrated and temporally integrated rates of net CH$_4$ production in sediments and CH$_4$ diffusion at the SWI during the stratified season. The mass balance revealed that net CH$_4$ production in the hypolimnetic sediments (below 8 m) in 2017 was ~ 1.6 times higher than the net production in 2016 (Table 1). Over the integrated period of the mass balance, ebullition flux in 2017 was almost two times higher than in 2016, and the proportion of production that left via ebullition was similar (8% and 11%), although slightly higher in 2017 (Table 1). The sediment diffusive flux at the SWI accounts for ~ 90% of the CH$_4$ leaving the sediment (Table 1), and the majority of the CH$_4$ produced in the sediments was stored in the hypolimnion (81% in 2016 and 66% in 2017), including the 30% redissolution of bubble CH$_4$.

To evaluate the role of thermal stratification and changing CH$_4$ production on hypolimnetic CH$_4$ dynamics, we developed a CH$_4$ model based on the hypolimnetic mass balance equation (Eq. 6; Supporting Information Fig. S2). The model predicts the hypolimnetic CH$_4$ concentration at a daily time step based on three parameters: effective diffusivity at the thermocline ($K_{z,eff}$), gas transfer velocity across SWI ($k_{sed}$), and CH$_4$ production rate in sediments. First, we performed a model calibration by fitting parameter $K_{z,eff}$ to observed $F_{dil,AOI}$ and parameter $k_{sed}$ to measured $F_{dil,SWI}$ in Soppensee in both 2016 and 2017 (Supporting Information Table S1 and Section S2). From this calibration, the model was able to accurately reproduce the hypolimnetic CH$_4$ concentrations measurements (Supporting Information Fig. S8a,b). Then by modulating the CH$_4$ production...
within the observed range in Soppensee, the model was able to reproduce the ranges of the observed CH$_4$ ebullition rates (Supporting Information Fig. S8c,d). The model was then used to simulate a changing thermocline $K_z$ under three different CH$_4$ production rates (Fig. 5). This modeling exercise revealed that storage rate (here represented as averaged hypolimnetic CH$_4$ concentration) is strongly affected by the reduced diffusive flux across the AOI associated with a decreasing $K_z$ value. That is, as $K_z$ becomes smaller, the proportion of CH$_4$ production going into storage increases, whereas the proportion going out to the upper layers decreases. The CH$_4$ ebullitive flux is primarily driven by CH$_4$ production rates, however, ebullitive rates are secondarily affected by the accumulation of methane in the hypolimnion (Langenegger et al. 2019) and therefore by $K_z$.

### Methane budget during mixing

We used a whole water-column mass balance to estimate the proportion of the stored CH$_4$ that was emitted during the fall/winter periods. During the first-year turnover including the ice-covered period (November 2016 to March 2017), averaged CH$_4$ surface diffusive fluxes were 0.7 mmol m$^{-2}$ d$^{-1}$ (Supporting Information Fig. S9a). During the second-year turnover (without ice, from November 2017 to January 2018) averaged CH$_4$ fluxes were 18 times higher at 12.7 mmol m$^{-2}$ d$^{-1}$ (Supporting Information Fig. S9b). In 2016, we observed the whole water-column CH$_4$ storage decrease linearly at a rate of 7.2 mmol m$^{-2}$ d$^{-1}$ between 17 November 2016 and 10 March 2017. In 2017, whole water-column CH$_4$ storage also decreased linearly at a rate of 28.9 mmol of CH$_4$ m$^{-2}$ d$^{-1}$ between 02 November 2017 and 23 January 2018. As a result, about 10% and 44% of whole water-column storage net loss rate was due to atmospheric diffusive emission in 2016 and 2017, respectively.

### Discussion

**Assessing sediment CH$_4$ rates from mass balances**

By using a mass balance approach, we were able to estimate CH$_4$ diffusive fluxes and net production rates from hypolimnetic sediments during the summer stratified seasons of two
consecutive years. The mass balance results for both years were compared with sediment flux measurements and potential CH₄ production rates determined from sediment cores used in a companion study (Langenegger et al. 2019; Table 2). Potential CH₄ production rates were determined from laboratory incubation of sediments collected from cores taken in July 2016, while diffusive sediment CH₄ fluxes were determined in situ from several cores retrieved in 2016 and 2017 (see Supporting Information S3 for further details). Both core measurements and mass balance approaches resulted in similar ranges in CH₄ diffusion at the SWI and production rates (Table 2) even though their spatial and temporal integrations are different. Core-derived rates were variable among samples indicating some within-lake spatial variability. This spatial variability can be due, for example, to depth and sampled location, which both influence the environmental conditions (e.g., light, oxygen level, and temperature) and the local organic matter quantity and quality. As the mass balance approach integrates this spatial variability, a full method comparison requires the core-derived estimates to be extrapolated spatially over the full depth range (from 8 to 26 m).

The accuracy of the CH₄ diffusion at the SWI and net production rates derived from mass balance depends on the different flux component uncertainties, which in our case is ebullition. Methane ebullition in lakes is highly variable in space and time and is thus probably the most uncertain flux. Achieving unbiased CH₄ ebullition estimates over a whole lake requires an extensive number of measurements at multiple locations (Wik et al. 2016). In our case, the extrapolation of two to three bubble traps estimates over the whole hypolimnetic area can be precarious, even if the lake is relatively small. Our different bubble traps show different ebullition rates among sites, the highest rates recorded by the 10-m funnel and the 15-m funnel the lowest. The temporal evolution of ebullition fluxes was (however) consistent among the different traps (Supporting Information Fig. S7), suggesting that most of the uncertainty is related to the spatial variability. It has been suggested that for two to three sampling locations, the risk of misestimating ebullition fluxes is between 25% and 50%, with a higher risk of underestimating (Wik et al. 2016). To evaluate the impact of underestimation on the mass balance rates, we performed a sensitivity analysis. Increasing ebullition by 50% resulted in a CH₄ production increase of 4% and 5% for 2016 and 2017, respectively. Increasing ebullition by 100% resulted in increasing CH₄ production by 8% and 11% for 2016 and 2017, respectively. Although ebullition is an important pathway for surface CH₄ emissions (Bastviken et al. 2004a), the ebullition fluxes at SWI of deep sediments have a relatively small impact on the estimates of CH₄ production from mass balance calculations. The current uncertainties around mass-balance-derived CH₄ production rates (11% and 15% for 2016 and 2017, respectively; Table 1) are mainly due to storage accumulation rates and diffusive flux at the AOI.

Additional uncertainties regarding estimates of CH₄ production and diffusion at the SWI may occur due to the unaccounted potential CH₄ oxidation occurring below 8 m. Here, we assumed no CH₄ oxidation due to the mostly anoxic conditions found below 8 m in Soppensee. However, CH₄ oxidation could still occur by microaerobic CH₄ oxidizing bacteria just below the AOI (Blees et al. 2014), by anaerobic CH₄ oxidizing bacteria at the surface of sediments (Schubert et al. 2011).
or in the anoxic bottom waters (Eller et al. 2005). We suspect that microaerobic CH$_4$ oxidation may have occurred just below the AOI as we observed relatively higher values of $\delta^{13}$C-CH$_4$ just below 8 m (Fig. 3a,b). As CH$_4$ oxidation seemed to have occurred only between 8 and 10 m and mostly early in the season, we can assume a limited effect on the CH$_4$ budget. However, it is important to interpret the reported production rates and diffusion at the SWI here as net (i.e., gross rate minus potential oxidation), even though the reported rates derived by the mass balance compared well with the measurements (Table 2).

**Summer stratification strength and fate of sediment-produced CH$_4$**

Net hypolimnetic sediments CH$_4$ production and diffusive fluxes in Soppensee were comparable to fluxes estimated from a similar approach in two temperate oligotrophic lakes (Peter and Paul Lakes; Bastviken et al. 2008). Despite similar rates, the fate of the sediment-derived CH$_4$ was different. In Peter and Paul Lakes, the majority of the CH$_4$ produced in the deep layers was oxidized (67–80%), whereas in Soppensee, the majority was stored in the hypolimnion (66–81%; Table 1). We suggest that the low $K_z$ values found in Soppensee may have prevented upward CH$_4$ diffusion at the AOI toward the oxygenated waters where it is oxidized, in line with our hypothesis that strong summer stratification should result in greater CH$_4$ storage and less oxidation at the thermocline (Fig. 1). $K_z$ values between 6 and 10 m in Soppensee were comparable between both years, yet we observed different rates (and proportion) of storage and diffusive fluxes at the AOI (Table 1). In summer 2016, a greater proportion of the produced CH$_4$ was stored, while in 2017, CH$_4$ transport across the thermocline became relatively more important (Table 1). Although the average vertical diffusivities ($K_z$) at 6–10 m were comparable in both years (Supporting Information Figs. S4, S5), the CH$_4$ gradient approaching the AOI was much steeper in 2017 due to the upward migration of the methane front (Fig. 3). This was probably the result of the higher net CH$_4$ production in 2017 and higher starting concentrations, combined with the higher turbulent diffusivities $K_z$ below the AOI (between 11 and 15 m; Supporting Information Fig. S5). Higher $K_z$ below the AOI may have caused a more efficient vertical redistribution of CH$_4$ in the hypolimnion (Fig. 3c) and thus increased the gradient at the AOI and the CH$_4$ fluxes across the AOI. The potential reasons for the increase of the $K_z$ in the layer from 11 to 15 m are to be further investigated and might be related to difference in energy inputs (i.e., wind forcing); however, these results highlight the importance of $K_z$ at and below the AOI for the vertical CH$_4$ diffusion.

As measured $K_z$ at AOI were similar in both years, we could not explicitly test the effect of $K_z$ on CH$_4$ storage and vertical diffusion at the AOI, therefore we applied a system analytical approach (Fig. 5; Supporting Information Fig. S2). As expected, increasing $K_{z_{\text{eff}}}$ resulted in more CH$_4$ diffusion across the AOI and less storage in the hypolimnion. When CH$_4$ is diffused up to the oxic waters, it can be assumed that most of it will be oxidized. This assumption is based on the persistence of a CH$_4$ minimum between 6 and 8 m during the summer stratified period associated with higher $\delta^{13}$C-CH$_4$ values (Fig. 3a,c). Alternatively, when stratification is strong and $K_z$ values are low, more CH$_4$ will be protected from oxidation and thus be stored due to the reduced flux at the AOI (Fig. 5).

When CH$_4$ leaves via ebullition (instead of diffusion across the SWI), less CH$_4$ is stored in the hypolimnion and diffused across the AOI and more can directly reach the atmosphere (Schmid et al. 2017). In Soppensee, the proportion of CH$_4$ production leaving via ebullition was higher in 2017 than in 2016 (Table 1) and is likely partly caused by the CH$_4$ concentration accumulation in the bottom waters (Boehrer et al. 2017; Horn et al. 2017). Accumulated CH$_4$ in the water column effectively reduces the CH$_4$ gradient between porewater and overlaying water, thus diminishing the diffusive flux at the SWI (Langenegger et al. 2019). Assuming that $F_{\text{ebu}} = P_{\text{sed}} - F_{\text{diff,SWI}}$, reducing diffusive fluxes should have the effect of reallocating the produced CH$_4$ into ebullition. The model also confirmed that increasing storage by decreasing $K_{z_{\text{eff}}}$ slightly increases the proportion of CH$_4$ leaving by ebullition (Fig. 5c), an effect that is independent of sediment CH$_4$ production (i.e., similar decrease Fig. 5b,c). Looking at absolute rates of ebullition however, the effect of $K_{z_{\text{eff}}}$ is more apparent. For example, decreasing $K_{z_{\text{eff}}}$ from $10^{-6}$ to $10^{-7}$ m$^2$ s$^{-1}$ will double the average ebullition rate (from about 0.5 to 1 mmol CH$_4$ m$^{-2}$ d$^{-1}$) at CH$_4$ production ranges of 14–15 mmol m$^{-2}$ d$^{-1}$. However, the same $K_{z_{\text{eff}}}$ reduction over a CH$_4$ production range of 17–18 mmol m$^{-2}$ d$^{-1}$ would cause ebullition rates to increase by about 10% (from about 3.5 to 3.9 mmol CH$_4$ m$^{-2}$ d$^{-1}$).

**Potential consequences of incomplete winter mixing on summer CH$_4$ dynamics**

In 2017, net CH$_4$ production in the hypolimnion increased by nearly 60% compared to 2016. Although several factors may influence across-system differences in lake sediments CH$_4$ production (West et al. 2012, 2015), our results suggest the potential implications of incomplete mixing of the water column during the previous winter. In March 2016, dissolved O$_2$ penetrated deeper in the water column compared to March 2017, when anoxia persisted in the hypolimnetic waters (Supporting Information Fig. S10). We suggest that this persistence of anoxia in 2017 probably allowed better conditions for methanogenesis, as opposed to 2016, when anoxia gradually developed later in the season. As the stratification season progresses, the more energetically favorable electron acceptors (e.g., NO$_3^-$, Mn [IV], SO$_4^{2–}$) are no longer available for microbial anaerobic organic matter degradation, thus CH$_4$ production will likely dominate the overall biogeochemical transformations. For example, in March 2016, NO$_3^-$ and SO$_4^{2–}$ mean concentrations below 10 m were 325 $\mu$g L$^{-1}$ and 6.6 mg L$^{-1}$, respectively, while in November 2016, both solutes were below detection limit below
Fate of CH₄ storage during fall vertical mixing

As an important amount of CH₄ is stored in the hypolimnion in stratified lakes, the fate of this CH₄ when the lake does turnover in fall/winter is critical for annual CH₄ emission budgets. Our results show the marked difference in CH₄ dynamics during the turnover period of both years, where the net CH₄ loss rate (CH₄ storage decrease rate; Fig. 4b) in 2017 was significantly greater than in 2016. This suggests that both CH₄ oxidation and evasion to the atmosphere were more important during fall 2017 compared to fall 2016, where a portion of the stored CH₄ remained in the bottom waters over winter. By estimating the diffusive CH₄ fluxes to the atmosphere during these periods, we found that a higher proportion was emitted the second year (44%) compared to the first year (10%). However, these estimates rely on the CH₄ emissions estimates, which in our case were constrained by the low temporal resolution of the sampling. We compared the flux derived from the wind-speed model with floating chambers measurements. Although they are comparable most of the time, the floating chamber CH₄ flux estimates showed much higher values in December 2017 compared to the modeled flux used in this calculation (Supporting Information Fig. S9b). Thus, using the generally lower wind-model-derived estimate, we consider our estimates to be conservative. Determining with precision the proportion emitted vs. oxidized however requires high temporal resolution CH₄ flux or oxidation rate measurements (Schubert et al. 2012; Encinas Fernández et al. 2014).

The estimate of the proportion of stored CH₄ that is emitted during fall was completely different between years (10% and 44%). In 2016–2017, the winter was colder, and the lake was quickly ice-covered in early January to end of February 2017. Consequently, the mixing was incomplete (down to 19 m instead of the maximum depth of 26 m) and lasted about 120 d until the upper mixed layer reached about 19 m. Conversely, the winter of 2017–2018 was warmer with strong wind events (Supporting Information Fig. S9) and no ice formation, resulting in complete turnover (down to the bottom) in 82 d. The turnover was so rapid in fact that the lake became completely anoxic, even in the surface waters, for about 10 d (Fig. 2d). We suggest that the potentially higher proportion of CH₄ emitted in 2017–2018 was due to a combination of the lower O₂ content in the water column, the complete anoxia episode (thus negligible CH₄ oxidation), and the more efficient vertical mixing. We compared the results from Soppensee to published values and found a linear relationship between the speed of mixing (lake maximum depth divided by mixing duration) and the proportion of CH₄ emitted during that period (Fig. 6). Although nonsignificant, this relationship suggests that a rapid and constant mixing will favor higher CH₄ emissions. If the lake mixes slowly, with occasional restratification and/or ice formation, a
higher proportion of the stored CH$_4$ will be oxidized (Kankaala et al. 2007). The lakes departure from the regression line (red and blue arrows) suggest that some lakes are more or less efficient to oxidize CH$_4$ (e.g., due to biological or chemical reasons) and some lakes are more or less efficient to exchange gas (e.g., due to morpho-physical reasons; Vachon and Prairie 2013).

High CH$_4$ oxidation rates suggest that the lake O$_2$ can be highly stressed during fall/winter turnover, as 1 mol of CH$_4$ consume 2 mol of O$_2$ during oxidation. Using this stoichiometric conversion, in early November 2016, the CH$_4$ content in the whole lake would have been enough to consume 1.2 times the whole-lake O$_2$ content (assuming instantaneous mixing and no supply of O$_2$). In November 2017, the CH$_4$ content alone could have consumed 2.4 times the O$_2$ content. The combination of incomplete mixing in winter 2016–2017 and higher CH$_4$ production during the following summer led to extreme CH$_4$ storage in 2017. This high CH$_4$ content (in addition to the accumulation of other reduced solutes, e.g., NH$_4$, H$_2$S, Mn(II), and Fe(II)) put an enormous stress on the lake O$_2$ content (Müller et al. 2012), and as the lake completely mixed during winter 2017–2018, the O$_2$ atmospheric inputs were not enough to avoid complete anoxia (Fig. 2d). By affecting O$_2$ episodes of incomplete followed by complete mixing can have crucial consequences on the whole-lake ecology in addition to the lake CH$_4$ dynamics.

Conclusions

Here, we showed that, independent of biological CH$_4$ production and oxidation processes, the physical environment of lakes greatly regulates the fate of CH$_4$ produced in the deeper sediments and oxidation processes, the physical environment of lakes greatly regulates the fate of CH$_4$ produced in the deeper sediments. Environmental-driven physical changes to the lake seasonal hydrodynamics—e.g., induced by climate change, eutrophication, or browning—will certainly impact lakes CH$_4$ dynamics, emissions and the overall carbon flow in the system. For example, warmer summers will potentially lead to longer stratified seasons and stronger density gradients (Winslow et al. 2014; Butcher et al. 2015). Similarly, browning or decreased water transparency due to biomass growth (eutrophication) could also result in stronger density gradients (Foley et al. 2012). Our results suggest that these environmental changes affecting lake physics could potentially increase the role of CH$_4$ production, CH$_4$ storage, and ebullition from lakes during the summer months and concurrently reduce CH$_4$ oxidation at the thermocline. Such a scenario of strong summer stratification (resulting in higher $K_z$; Fig. 5) combined with rapid water mixing in fall/winter (Fig. 6) could potentially increase the proportion of stored CH$_4$ in the lake bottom waters to be emitted to the atmosphere instead of being oxidized. The exact response of lake CH$_4$ dynamics to changes in lake hydrodynamics is however very challenging to predict, as these potential environmental and climate changes also affect biological processes, with possibilities for complex interactions and positive feedbacks. Disentangling the respective roles of physics and biology in regulating CH$_4$ in lakes however greatly improves our current understanding and provides better tools to assess the system-specific sensitivity of such environmental and climate changes.

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Conflict of Interest
None declared.

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