The Effects of Water Column Dissolved Oxygen Concentrations on Lake Methane Emissions—Results from a Whole-Lake Oxygenation Experiment

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Abstract Lakes contribute 9%–19% of global methane (CH₄) emissions to the atmosphere. Dissolved molecular oxygen (DO) in lakes can inhibit the production of CH₄ and promote CH₄ oxidation. DO is therefore often considered an important regulator of CH₄ emissions from lakes. Presence or absence of DO in the water above the sediments can affect CH₄ production and emissions by (a) influencing if methane production can be fueled by the most reactive organic matter in the top sediment layer or rely on deeper and less degradable organic matter, and (b) enabling CH₄ accumulation in deep waters and potentially large emissions upon water column turnover. However, the relative importance of these two DO effects on CH₄ fluxes is still unclear. We assessed CH₄ fluxes from two connected lake basins in northern boreal Sweden where one was experimentally oxygenated. Results showed no clear difference in summer CH₄ emissions attributable to water column DO concentrations. Large amounts of CH₄ accumulated in the anoxic hypolimnion of the reference basin but little oxygen addition resulted in negligible CH₄ accumulation in the water column. In the Reference basin, CH₄ oxidation and was emitted at turnover periods, constituting 0%–44% of the yearly CH₄ emissions.

Plain Language Summary Lakes represent 9%–19% of the total sources of the greenhouse gas methane (CH₄), and the concentration of dissolved oxygen is considered important for regulating lake CH₄ cycling. In this study we measured CH₄ emissions from two connected lake basins, one where we increased concentrations of dissolved oxygen in the water column (Experimental basin), and one that was left in a natural state, resulting in deep water oxygen depletion (Reference basin). In the Experimental basin, the dissolved oxygen addition resulted in negligible CH₄ accumulation in the water column. In the Reference basin, CH₄ accumulated in anoxic water layers. However, no clear difference in CH₄ emissions among the two basins could be detected during the summer. The basins only partially mixed in fall and spring and depending on the degree and intensity of water column mixing, we estimated that 0%–24% of CH₄ stored in the water column was released upon fall and spring turnover, while the rest was converted to carbon dioxide by methane-oxidizing bacteria. Accordingly, water column anoxia may not be important for CH₄ emissions from all boreal lakes but can represent a main share of the yearly CH₄ emissions in some lakes.

1. Introduction

Methane (CH₄) is one of the most important greenhouse gases in terms of global warming potential and its concentration in the atmosphere has increased nearly three-fold since pre-industrial times (Ciais et al., 2014; Saunois et al., 2016). Recent works indicate that lakes represent one of the largest sources of CH₄ to the atmosphere, contributing approximately 9%–19% of the total methane sources together with freshwater wetlands (~20%), and anthropogenic sources (~51%) (Bastviken et al., 2011; Johnson et al., 2022; Rosentrete et al., 2021; Saunois et al., 2019). While much previous research has focused on estimating magnitudes of lake CH₄ fluxes, the understanding of how lake fluxes are regulated is at an early stage, and while several potential environmental flux drivers have been identified, their relative importance remains unclear.
The majority of CH₄ produced in lakes results from the decomposition of organic matter in the absence of molecular oxygen (O₂) and other alternative inorganic electron acceptors such as nitrate (NO₃⁻), ferric iron (Fe₃⁺), and sulfate (SO₄²⁻). The final degradation step under such conditions is methanogenesis by methanogenic Archaea (Rudd & Hamilton, 1978; Zeikus & Winfrey, 1976). This process occurs within lake sediments and is considered to contribute most of the lake CH₄, although groundwater input may also add some CH₄ (Dabrowski et al., 2020; Einarsdottir et al., 2017; Lecher et al., 2017; Olid et al., 2022; Schenk et al., 2021), and there is an ongoing debate regarding the extent of oxic CH₄ production in oxygenated surface lake water (Günthel et al., 2019; Peeters et al., 2019). Some of the CH₄ produced in lakes is emitted to the atmosphere through ebullition, that is, rapid and episodic release of bubbles forming in the sediments where CH₄ production creates an oversaturation in CH₄ (Aben et al., 2017; Bastviken et al., 2004; Wik et al., 2013). Remaining CH₄ is dissolved and has primarily two fates, one being transportation from the sediments through the water column by eddy diffusion, and later release to the atmosphere by emission across the diffusive boundary layer at the water-atmosphere interface, referred to as diffusive flux (Bastviken et al., 2004; Denfeld et al., 2018; Liss, 1974; Powell & Jassby, 1974). A second fate of dissolved CH₄ is microbial oxidation, by which CH₄ is converted to CO₂ when it reaches oxygenated waters or locations where other suitable electron acceptors are present (Bastviken, 2022; Jones & Grey, 2011).

CH₄ production is hampered by the presence of dissolved molecular oxygen (DO) (Segers, 1998), and thereby occurs at different depths in the sediments depending on the DO levels in the overlying water. If the overlying water contains DO, the oxycline, that is, the O₂ gradient from oxygenated to anoxic conditions, is located a few millimeters below the sediment surface (Hoppila et al., 2015), where O₂ consumption by degradation processes exceeds O₂ input from the overlying oxygenated water. If the water above the sediment is anoxic, the entire sediment column including the top layer is anoxic. Hence, whether methanogenesis takes place in the uppermost part of the sediments, where the most recent and easily degradable sediment organic material is located, depends on the presence of DO in the water above the sediments. If DO is present in near-sediment water and in the top sediment layer, methanogenesis might be restricted to deeper sediment layers with older and less reactive organic substrates. Therefore, thermal stratification of lakes resulting in seasonal isolation and associated anoxia in deep waters could potentially influence the methanogenesis rates in the sediments. It has been shown, from in vitro incubation experiments where DO levels were altered in the water column above the sediments, that CH₄ released from the sediments increased in conditions where the overlying water column was anoxic (Liikanen et al., 2002, 2003). In addition, the possibility of increased methanogenesis in the top sediment layer following water column anoxia could also increase rates of ebullition (Wilkinson et al., 2015).

Another more frequently addressed impact of water column anoxia on CH₄ in lakes is that large amounts of CH₄ can accumulate in anoxic hypolimnion (Bastviken et al., 2004). This stored CH₄ can rapidly get emitted upon lake turnover when CH₄-rich hypolimnion water reaches the water surface and can exchange gas with the atmosphere (Denfeld et al., 2018; Hounshell et al., 2021; Michmerhuizen et al., 1996; Riera et al., 1999). Estimates of regional or global lake CH₄ emissions therefore often consider emissions of this stored CH₄ to be a potentially large share of the yearly lake CH₄ emissions (Denfeld et al., 2018), that could be enhanced by declines in DO in lakes due to climate change and land-use (Jane et al., 2021, 2023).

Along the above lines of deduction, depletion of DO in lake hypolimnion could increase CH₄ emissions not only upon water column turnover but also directly during lake stratification periods. Such a link between CH₄ accumulation in anoxic deep water and ebullition was suggested by Vachon et al. (2019) based on temporal correspondence between ebullition and water column CH₄ accumulation.

Overall, the current understanding points toward DO having a potentially large effect on yearly CH₄ emissions. However, results from a small number of studies indicate that the extent to which water column-stored CH₄ is emitted is highly variable, ranging from 2%–46%, and it was suggested that this variability depends on how quickly the water column is mixed upon lake turnover (Encinas Fernandez et al., 2014; Mayr et al., 2020; Vachon et al., 2019; Zimmermann et al., 2021). While previous studies primarily focused on the emission of stored CH₄ at turnover periods, the influence of DO on CH₄ emissions during periods of stratification seems hitherto untested in situ. Therefore, we hypothesized that (a) the hypolimnetic oxygenation would lead to a rapid decline in water column stored CH₄, and (b) that the oxygenation would reduce CH₄ emissions not only following water column turnover but also during lake stratification periods in line with previous suggestions (e.g., in Vachon et al. (2019)).

The hypotheses were addressed by a whole-lake experiment. Such ecosystem-level studies take the full complexity of the system into consideration, including in situ scale hydrodynamics, ebullition, and legacy effects...
regarding spatiotemporal patterns in concentrations and process rates. Such conditions are challenging to mimic in small-scale incubations or mesocosms. The present study was conducted in a small boreal lake with two lake basins, one left in a natural state, and one where we manipulated DO levels aiming to evaluate how CH₄ emissions are influenced by lake water column DO levels, with consideration to both stratification and lake turnover periods.

2. Material and Methods

2.1. Study Site and Hypolimnion Oxygenation Experiment

The studied lake, Ljusvattentjärn, is a boreal lake located in northern Sweden (64°05′33.5″N, 18°55′50.7″E), and is divided into two similar basins (Figure S1 in Supporting Information S1). The southern basin—the experimental basin (EXP)—has an area of 0.64 ha, a maximum depth of 9.5 m, and a water residence time (WRT) of 28 days. The northern basin—the reference basin (REF)—has an area of 1.12 ha, a maximum depth of 9.6 m, and a WRT of 69 days. The basins were similar with regard to water chemistry (Table S1 in Supporting Information S1). This type of lake is common in terms of lake surface area, mean depth, and maximum depth both globally (Cael et al., 2017; Cael & Seekell, 2016, 2022; Verpoorter et al., 2014) and in the boreal parts of Sweden (Seekell et al., 2018), and represent boreal biome glacial lakes (Meybeck, 1995; Seekell et al., 2021).

Monthly temperature and DO depth profiles were measured at the deepest point of both basins during the open water seasons of 2018 (May–September) to identify the mixing and stratification patterns of the basins prior to the hypolimnetic oxygenation. The hypolimnion of EXP was oxygenated between 19 June and 26 August 2019, by a full-lift aeration system with two tubes, one inner tube (0.6 m diameter) injecting oxygen gas into the bottom water resulting in aeration and rising of oxygenated water to the surface layers, and an outer tube (1.2 m diameter) letting the cold aerated water sink back to the hypolimnion and spread horizontally (Burris & Little, 1998) (Figure S2 in Supporting Information S1). This type of system is designed to increase oxygen concentration without changing temperature, stratification patterns, and movement of nutrients in the water column (Fast et al., 1975; McQueen & Lean, 1986). Hence, an attempt was made to minimize potential confounding factors of other approaches, such as bubble-plume diffusers (Fast et al., 1975). The full–lift aeration system was placed on a raft at the deepest part of EXP (64.092016°N, 18.931312°E; see Figure S1 in Supporting Information S1). From April to November 2019, monthly measurement campaigns were carried out to assess the CH₄ fluxes to the atmosphere, and the water column CH₄ storage and oxidation. In total there were eight sampling campaigns (SC) of which two were made before spring ice melt (April to the beginning of May), five were made during the open water season (early June to early October), and one was made when ice had just formed on the lake in fall (late October).

2.2. Data Collection

2.2.1. CH₄ Flux and Surface Water Concentrations

In each basin, 12 lightweight plastic floating chambers were distributed along three transects from shore toward the center of the basins in different depth zones (0–1.5, 1.5–2.5, 2.5–4.5, and >4.5 m), to account for known influences of depth or distance to shore on CH₄ fluxes (Bastviken et al., 2004; Natchimuthu et al., 2016; Peixoto et al., 2015; Schilder et al., 2016; West et al., 2016). Each covered an area of 0.075 m², had a volume of 8.6 L, and was laterally attached with a one m line to an anchored float in accordance with the design previously shown to yield reliable gas flux measurements in lakes (Cole et al., 2010; Erkkilä et al., 2018; Gålfalk et al., 2013). Between 5 June and 2 October 2019, monthly measurements, totaling 5 SC were carried out for one week each with repeated 24–48-hr deployments to account for diel variability and increase the potential to capture ebullition events (Wik et al., 2016). After each period of gas accumulation, 180 mL of the floating chambers headspace gas was withdrawn manually using three 60 mL syringes (Becton–Dickinson) with luer-lock manifolds and transferred into 22 mL glass vials (Agilent; fitting the Agilent GC autosampler; see below) capped with a butyl rubber stopper and aluminum crimp seal. The vial was first flushed with 150 mL of the floating chamber gas sample. The last 30 mL of gas was used as sample creating some overpressure in the glass vial that was released just prior to analysis (Natchimuthu et al., 2016). Surface water samples to assess dissolved CH₄ concentration (CH₄aq) were collected at each floating chamber approximately 5 cm below the surface directly before and after floating chambers deployment periods, and 5 mL was transferred to 22 mL glass vials prefilled with...
2.3. Fates of Accumulated Dissolved CH\textsubscript{4} During Lake Turnover

Depth profiles of CH\textsubscript{4}\textsubscript{aq} samples were collected close to the deepest location of each lake basin, at depths of 8.6 m and 8.9 m for EXP and REF, respectively. A total of 231 samples in both lake basins were collected during the eight SC. Water was sampled at 0.25–0.5 m intervals with a syringe connected to a polyurethane tube (inner diameter 3 mm, outer diameter 5 mm; 14 m long). Before collecting each sample, a volume of water equivalent to twice the volume of the tube was withdrawn for rinsing the tube and syringe. Thereafter, 5 mL of water was gently pulled into a 10 mL syringe and injected into capped glass vials as described above for the surface water CH\textsubscript{4}\textsubscript{aq} samples. The water inlet part of the tube was attached to a submersible probe (HACH LDO with a HQ40d control unit), used to measure temperature and DO at half meter intervals down to the sediments.

To estimate the total lake basin storage of CH\textsubscript{4}, representing the maximum possible emission upon water column turnover events, the mean CH\textsubscript{4}\textsubscript{aq} in each depth layer (C \textsubscript{aq}; mol m\textsuperscript{−3}) was multiplied by the total volume of the corresponding depth layer (V\textsubscript{d}; m\textsuperscript{3}). Detailed information explaining how CH\textsubscript{4}\textsubscript{aq} and basin CH\textsubscript{4} storage were calculated can be found in Text S2 of Supporting Information S1.

The fraction of CH\textsubscript{4} oxidized in the water column was estimated using mass balance models of carbon stable isotopes. Such models are based on the discrimination of stable carbon isotopes due to the preferential assimilation of \textsuperscript{12}C relative to \textsuperscript{13}C during microbial consumption of CH\textsubscript{4} (Bastviken et al., 2002; Coleman et al., 1981; Thottathil et al., 2018; Whiticar, 1999). Water samples for stable carbon isotopic composition of CH\textsubscript{4} (\textsuperscript{\delta}13C–CH\textsubscript{4}) dissolved in the water were collected at the same time and location as CH\textsubscript{4}\textsubscript{aq} samples, but at approximately 1.5 m depth-intervals, including right above the hypolimnion and in the anoxic hypolimnion as well as 50 cm above the sediment. 2.5 L of water from each depth was collected using a Ruttner water sampler and the entire volume was used to overflow and fill a 1.2 L bottle by placing the outlet tubing from the sampler at the bottom of the bottle. The bottle was carefully closed with a rubber stopper while avoiding trapping any air inside. The rubber stopper was modified with two tubes going through it, one reaching the bottom of the bottle and the other ending near the upper part of the bottle. The outside ends of the two tubes were closed with luer-lock valves allowing subsequent transfer of 60 mL of high-purity synthetic air via the short tube and simultaneous removal of the same volume of water via the long tube, using 60 mL plastic syringes (Becton–Dickinson). After 2 min of vigorous shaking, the equilibrated headspace gas was withdrawn (simultaneously injecting water via the long tube while pulling out the headspace gas into a syringe via the short tube) and transferred to pre-evacuated glass vials closed with butyl rubber stoppers and sealed with an aluminum crimp cap. Gas samples were analyzed for \textsuperscript{\delta}13C–CH\textsubscript{4} using a cavity ring-down spectrometer (CRDS; Picarro Inc., model G2201–I with an SSIM module) calibrated with certified isotopic standards (−66.5 ± 0.2‰ and −23.9 ± 0.2‰; Isometric Instruments, Canada) at different CH\textsubscript{4} concentrations to account for a concentration dependence at CH\textsubscript{4} concentrations below 10 ppm.

2.3. Fates of Accumulated Dissolved CH\textsubscript{4} During Lake Turnover

In the year of the study, and despite the end of the temperature stratification, no complete fall turnover took place and CH\textsubscript{4} remained stored in the hypolimnion of REF until the following year. Therefore, no direct data on the fates of stored CH\textsubscript{4} could be obtained as planned. Nevertheless, we tried to use our data to estimate what would have been the fates of the stored CH\textsubscript{4} by developing a mass balance model for a turnover period if it had happened during a time represented by our data. The aim was to assess the relative importance of oxidation versus emission of stored CH\textsubscript{4} upon lake turnover under different scenarios.
The model was made to consider the stored CH₄ present when the lake turnover started and to represent the turnover event (i.e., the gradual lowering of the thermocline, explained as the thermocline lowering rate (TLR) (Text S3 in Supporting Information S1) until it reached the lake bottom and the stored CH₄ had disappeared by either emission to the atmosphere or by CH₄ oxidation (MOX). The continuous background input of CH₄ to the water column, occurring regardless of the continuous mixing, was not considered because our focus was on the fraction of the stored CH₄ that is emitted versus oxidized, with an underlying assumption that continuously added CH₄ during the turnover event would largely follow the same relative fates as the CH₄ present upon start of the turnover event.

During mixing, the lowering of the thermocline exposes the CH₄ in the upper hypolimnion to O₂, allowing extensive MOX to happen. We estimated MOX constraining the mass-balance model with the δ¹³C–CH₄ data using two different fractionation models. The closed-system Rayleigh model is often used to estimate the fraction of CH₄ being oxidized from the stable isotopic shift in a closed system during an incubation experiment where the only loss is due to MOX (Liptay et al., 1998). Hence, considering the mixed surface layer in a timestep model, the fraction of MOX in the mixed layer over time can be estimated, timestep by timestep, using the Rayleigh model:

\[ \ln(1 - f_{MOX\text{closed}}) = \frac{[\ln(\delta_{source} + 1000) - \ln(\delta_{surface} + 1000)]}{(\alpha - 1)} \]

where \( f_{MOX\text{closed}} \) is the total fraction of CH₄ oxidized (%), \( \delta_{source} \) is the endmember δ¹³C–CH₄ value for anoxic water 50 cm above the sediment at the deepest point of each basin, \( \delta_{surface} \) is the δ¹³C–CH₄ value observed above the thermocline, and \( \alpha \) is the isotopic fractionation factor. We used an \( \alpha \)-value of 1.020, based on measurements obtained in several Swedish boreal lakes (Bastviken et al., 2002). Second, an open steady-state model for ¹³CH₄ isotopic fractionation previously used by Happell et al. (1994) (Equation 2) was also applied to evaluate the sensitivity of our model to the closed system assumption:

\[ f_{MOX\text{open}} = \frac{(\delta_{surface} - \delta_{source})}{(\alpha - 1) \times 1000} \]

After oxygenation of the hypolimnion in EXP, the CH₄aq and the δ¹³C–CH₄ in the anoxic water close to the sediment, used as endmember, drastically changed, indicating oxidation as the result of aeration. Hence, we assumed the endmember δ¹³C–CH₄ from REF to be representative also for EXP in the calculations.

The overall approach was to run a mass balance model at different TLR, MOX, and CH₄ emission rate scenarios 1,000 combinations and deriving the variability of the total fluxes from these estimates. The open water period turnover event (i.e., the gradual lowering of the thermocline, explained as the thermocline lowering rate (TLR)) until it reached the lake bottom and the stored CH₄ had disappeared by either emission to the atmosphere or by CH₄ oxidation (MOX). The continuous background input of CH₄ to the water column, occurring regardless of the continuous mixing, was not considered because our focus was on the fraction of the stored CH₄ that is emitted versus oxidized, with an underlying assumption that continuously added CH₄ during the turnover event would largely follow the same relative fates as the CH₄ present upon start of the turnover event.

2.4. Time Integrated Lake CH₄ Emissions

Total open water CH₄ emissions were estimated as follows: (a) The mean flux per m² in each depth zone and measurement period (3 floating chambers per depth zone and measurement period) was multiplied by the area of the depth zone, yielding a mean depth zone flux for each of the 13 measurement periods. (b) Exponential relationships between mean total depth zone flux and water temperature during the open water measurement period (\( R^2 \) ranging from 0.29 to 0.79; see Figure S3 in Supporting Information S1) were used to extrapolate emissions in time between the measurement periods to generate mean depth zone flux estimates for each 24-hr–period during ice-free conditions. Information on water temperature used in the extrapolation was extracted from surface water temperature logger data (measurement period mean of continuous measurements from one RBR solo temperature logger (RBR solo) per transect, located 6 cm below the water surface directly underneath a 40 × 40 cm flat Styrofoam floats, which provided shade to the loggers). (c) Total Lake CH₄ emissions for each 24-hr period was estimated by summing each daily depth zone flux, accounting for the area of each depth zone. (d) Total open water period flux for each basin was estimated by summing all the 24-hr flux estimates. (e) To estimate flux variability on a yearly basis, a Monte Carlo analysis was carried out by selecting 2/3 of all flux measurements in 1,000 combinations and deriving the variability of the total fluxes from these estimates. The open water period CH₄ fluxes derived from floating chambers were then compared with the total accumulation of CH₄ in the water column per m² during the measurement period, and the estimated share of the accumulated water column CH₄ that was emitted upon turnover based on the mass-balance model described above.
To enable discussions about the ice-covered period we combined our under-ice data with assumptions that (a) during winter, anoxic water layers would accumulate CH$_4$ at similar rates as during summer after a lag phase of 60 days after complete water column turnover (Jansen et al., 2019), (b) a baseline ebullition persisted under ice at rates corresponding to the temperature relationships at 5°C and resulted in CH$_4$ bubbles in or under the ice that was released upon ice melt (Wik et al., 2014), (c) no diffusive flux happened during the ice-covered period, and (d) fates of the CH$_4$ accumulated in the water column under ice could be estimated by the mass balance model described in Section 2.3 (active MOX during ice-out was also supported by our $\delta^{13}$C–CH$_4$ data). Note that results generated regarding the ice-covered period and ice-out emissions have limited data support from the studied systems and attempt to make reasonable estimates for an annual cycle with spring and fall turnover, given the data available locally and in the literature.

2.5. Statistics

Differences in total CH$_4$ emissions between EXP and REF basins were estimated using a general linear model (GLM; Two-way ANOVA), accounting for depth zone and measurement period as independent factors and using log-transformed data to account for the common log-normal distribution resulting from rare but high flux ebullition events. Differences in total flux between specific measurement periods within basins were evaluated using the non-parametric two-tailed Mann-Whitney U test. P-values below 0.05 were considered significant. Statistical tests were performed in IBM SPSS 28 (IBM Corp, 2021).

3. Results

3.1. Water Column Profiles of Temperature, DO, CH$_4$ Concentration, and $\delta^{13}$C–CH$_4$

Water temperature profiles showed a similar pattern of stratification in both basins with a clear start and end of the stratification period in both 2018 and 2019 (Figures 1a and 1b). A minor increase in temperature (0.5–1°C) was observed in the bottom water temperature of the EXP basin in 2019 after the oxygenation period. Our DO measurements show that a complete turnover of the water column did not happen either after the ice out (REF and EXP) nor after the end of the thermal stratification (REF) (Figure 1). DO levels at water depths below 6–7 m were below the detection limit of the sensor used (0.05 mg L$^{-1}$) over the whole period (2018–2019) in the REF basin and before the oxygenation in EXP. Between June and the end of August 2019, during the oxygenation treatment in EXP, DO in the hypolimnion was above 3 mg O$_2$ L$^{-1}$ with minor influence on the thermal stratification, compared to conditions observed in the previous year.

The CH$_4$ concentrations (CH$_4$aq) were consistently higher below 6 m depth (Figure 2). In both basins, there was a decrease in deep water CH$_4$aq at ice-off between May and June (Figures 2a and 2b). In REF, there was a slight CH$_4$ accumulation under the ice, while the CH$_4$aq in EXP was lower under the ice (Figures 2c and 2d). In EXP, this deep CH$_4$aq decrease coincided with a slight CH$_4$aq increase at 1–6 m, indicating a partial turnover temporarily transporting deep CH$_4$ to surface waters before the stratification was established (Figure 2d). Because the proportion of shallow (<6 m depth) compared to deeper CH$_4$ rich water (>6 m depth)is smaller in EXP than in REF, deep water upwelling can impact the concentration more in EXP.

The $\delta^{13}$C–CH$_4$ values measured in the lake and used to account for the MOX component were in the range of −79.6 to −77.9‰ for CH$_4$ samples from anoxic bottom waters. CH$_4$ samples taken just above the oxycline during spring partial turnover in REF and EXP yielded −49.7 to −26.5‰. During the fall sampling in REF the most negative $\delta^{13}$C–CH$_4$ was in late September (−37.6‰). During full stratification in July and August, $\delta^{13}$C–CH$_4$ above the oxycline was −17.0 to −13.6‰.

3.2. Methane Storage, Oxidation, and Sediment Release

Large amounts of CH$_4$ were stored below 6 m depth in both basins at the beginning of 2019 (Figure 3). Note that the storage was normalized per m$^2$ of lake basin (mmol CH$_4$ m$^{-2}$) leading to higher values in EXP having a smaller area not underlain with CH$_4$-rich bottom water. Hence the difference between basins before the oxygenation has links to the bathymetry differences. The overall change in water column CH$_4$ storage right after ice-out (May–June) was modest (Figure 3) and the ice-out mixing primarily redistributed CH$_4$aq within the water column in both REF and EXP (Figure 2). The start of the oxygenation experiment in mid-June effectively reduced the amount
of CH$_4$ stored in EXP and prevented the accumulation of CH$_4$ in the hypolimnion as it became oxic. The CH$_4$ storage in EXP ranged between 0.7 and 1.7 mmol m$^{-2}$ during the rest of the measurement period (until 23 October), which is nearly two orders of magnitude lower than the maximum storage observed in May (94 mmol m$^{-2}$; Figure 3).

The $\delta^{13}$C–CH$_4$ values during the partial spring turnover (representing a situation with rapid CH$_4$ upwelling) along with both the closed and open steady-state system assumptions, resulted in 73 to >99% of the CH$_4$ being oxidized before reaching right above the oxycline, serving as input to our lake mass balance model. The open steady-state system assumption, presumably being most representative of a turnover event, exclusively yielded >99% of CH$_4$ being oxidized. Hence, using the open steady-state system assumption alone, without allowing the possibility of a more delayed CH$_4$ transport (e.g., a mix between fully open steady-state and closed system conditions), would lead to the conclusion that none of the stored CH$_4$ would be emitted. However, to not risk underestimating the potential for emission of stored CH$_4$ in the mass balance model that we present (method Section 2.3 and Text S3 in Supporting Information S1), we also considered the closed system assumption, and set the fraction oxidized for the open steady-state system to 99% (which is conservative given $\delta^{13}$C–CH$_4$ data).

### 3.3. CH$_4$ Emissions to the Atmosphere

In both basins, higher fluxes were observed from the floating chambers located in the shallowest depth zone (<1.5 m) compared to the floating chambers in the other depth zones (>1.5 m) (GLM; REF: $p$-value <0.05 and
The CH$_4$ flux from the shallow depth zone was on average 2.7 times higher than at other depth zones (0.46 compared to 0.17 mmol m$^{-2}$ d$^{-1}$) (Figure 4). In early June 2019 (SC1), before the experiment started, average CH$_4$ fluxes in the EXP basin were higher than the average CH$_4$ fluxes measured in the REF basin (0.29 mmol m$^{-2}$ d$^{-1}$ and 0.20 mmol m$^{-2}$ d$^{-1}$, respectively; Mann Whitney $p$-value <0.001). This difference was likely attributed to the partial spring turnover event occurring in May–June 2019, resulting in an upwelling of CH$_4$ from the deeper parts of EXP to the surface, temporarily fueling higher CH$_4$ fluxes until mid-June when thermal stratification was established (Figure 2d). In each of the two basins, CH$_4$ fluxes were lower in late September and beginning of October (SC5) compared to the previous SC (GLM, $p$-value <0.001 for both basins). There were no statistically significant differences in open-water CH$_4$ flux between the two basins after the establishment of stratification when supply of bottom water CH$_4$ to the surface became blocked, neither when all depth zones were included (Mann-Whitney U, $p$-value = 0.46) nor when only the floating chambers from the deepest depth zone, where underlying bottom water DO was altered by the oxygenation experiment, was considered; (Mann-Whitney U, $p$-value = 0.69) (Figure 4). Accordingly, the DO experiment had no visible effect on CH$_4$ fluxes during the stratification period and the fluxes in all depth zones were similar between the two basins regardless of the presence of DO in the hypolimnion (Figure 5).

Figure 2. Dissolved CH$_4$ concentration (CH$_4$aq; μmol L$^{-1}$) between 3 April and 23 October 2019 in the reference (REF) basin (a and c) and the experimental (EXP) basin (b and d). Note that the color scales are linear in a and b and Log$_{10}$ in c and d to illustrate weaker gradients ($N = 117$ for REF, $N = 114$ for EXP). Black dots represent the dates and depths where CH$_4$aq was measured. The ice-covered period, extending from November 2018 to early May 2019 is indicated with a white rectangle. Note that the color gradients are based on standard linear interpolation (scipy.interpolate.interp2d, Virtanen et al., 2020) between the depths and measurement times. This is only an approximation—that is, it is likely that deep water CH$_4$ depletion in the EXP basin upon the oxygenation (between two measurement times) was more rapid than indicated in panel (d).

Figure 3. CH$_4$ storage normalized per m$^2$ lake area for the reference (orange) and experimental (blue) basins in 2019. The white dashed line indicates the start of the oxygenation experiment (19 June), and the black dashed line indicates the end of the oxygenation experiment (26 August). Values have been calculated by linearly interpolating measurements at 0.5 m depth resolution. It is likely that CH$_4$ storage decreased more rapidly after the oxygenation start than the figure indicates because of linear interpolation between measurement times.
3.4. Fates of Water Column Stored Methane

The empirically determined 24–hr mean gas transfer velocities \( k \) values; Text S1 in Supporting Information S1) during the whole sampling period ranged between 0.1 and 1.2 m d\(^{-1} \) (mean: 0.23 and 0.27 m d\(^{-1} \) in EXP and REF, respectively). In the model, we allowed \( k \) to range between 0.07 and 3.5 m d\(^{-1} \), exceeding the measured range to include the possibility of more extreme conditions. The model results were insensitive to the rate of downward mixing, that is, TLR (a range of 0.1–30 days for complete water column overturn was tested)—the reason being that regardless of the rate of thermocline deepening, the mass transport of CH\(_4\) to the atmosphere is limited by \( k \) and the concentration gradient and it would take many days to emit the stored CH\(_4\) using the highest measured \( k \) value even if all stored CH\(_4\) was instantaneously distributed into the whole lake volume. This gives time for CH\(_4\) depletion by MOX even if downward water column mixing is rapid (Figure 6b). Hence, the fate of the water column CH\(_4\), that is, MOX or emission, depended primarily on the balance between the specific CH\(_4\) oxidation rate \( S_{\text{ox}} \) (fraction oxidized per day; Text S3 in Supporting Information S1) and \( k \) (Figure 6).

In REF, we estimated that 11% of the stored CH\(_4\) was lost (primarily to MOX) during the partial spring turnover from April to June (Figure 3 and Table 1), corresponding to a loss of 13.4 mmol m\(^{-2} \). In EXP, the loss of stored CH\(_4\) during the ice-out mixing was equivalent to 20% of the total amount of CH\(_4\) stored in the water column in May (Figure 3 and Table 1), corresponding to a loss of 18.9 mmol m\(^{-2} \). From July and onwards, CH\(_4\) stored in the REF hypolimnion increased steadily, corresponding to a sediment CH\(_4\) release rate of 0.45 mmol m\(^{-2} \) d\(^{-1} \) (Table 1), yielding an almost linear increase in water column CH\(_4\) storage (Figure 3). This indicated that lake turnover did not occur before 23 October in the REF basin, and it is likely that no turnover of the entire water column

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**Figure 4.** Temporal variability of the Log\(_{10}\) CH\(_4\) fluxes (mmol m\(^{-2} \) d\(^{-1} \)) in the reference (REF) (a) and experimental (EXP) (b) basins. Depths are represented by box colors. The light-gray line marks the start of oxygenation and the black line marks the end. The sampling campaigns (SC) 1 to 5 (x-axis) were carried out during the open-water season between 5 June and 2 October 2019. Number of flux measurements in each SC was: SC1 = 24 (3 per depth zone and basin; 1 day); SC2 to SC5 = 72 (12 per depth zone and basin, 6 days per campaign). Box plots show quartile margins and the median is the black line. Whiskers show the 5th and 95th percentile range and outliers are shown as circles and stars.

**Figure 5.** Mean CH\(_4\) flux (mmol m\(^{-2} \) d\(^{-1} \)) observed in each of the 12 flux chambers distributed at different depth zones in the Reference (REF) (a) and Experimental (EXP) (b) basins. The mean was calculated from measurements done between 3 July to 2 October 2019. In total 144 full 24-hr flux chamber measurements were done in each basin, and the oxygenation experiment occurred between 19 June and 8 August 2019. The blue line corresponds to the mean near-sediment DO concentrations (right y-axis; mg L\(^{-1} \)) extrapolated from measurements of monthly depth profiles for DO assuming horizontal mixing. Error bars represent ±1 standard deviation.
occurred in the REF basin in the fall of 2019. Overall, given the empirically determined local ranges of $k$ and $S_{\text{mox}}$ rates, the model indicates that likely less than 24% of the stored CH$_4$ would be emitted upon lake turnover assuming closed system conditions and less than 18% would be emitted under the open steady-state assumption. This is equivalent to a potential fall turnover emission of 0–12 mmol m$^{-2}$ (Table 1).

The total potential yearly CH$_4$ emission from the REF basin, combining all data and a presumptive dimictic whole-year scenario, was estimated to 33.2–59.2 mmol m$^{-2}$, with the main uncertainty being the fate of the CH$_4$ stored in anoxic water, representing 0%–44% of the yearly emissions (Table 1). We assumed winter CH$_4$ accumulation at rates similar to those of summer accumulation after a 60–day lag phase following full fall turnover and oxygenation (Jansen et al., 2019) (possibly an overestimation because winter supply of easily accessible organic matter fueling CH$_4$ production is likely lower than during summer). Under such a scenario, 60.9 mmol CH$_4$ m$^{-2}$ accumulated in the water column under ice, and 0–14 mmol m$^{-2}$, 0%–24% of the storage, was emitted during a presumed complete spring overturn event (Table 1). Ice-out emission (i.e., from CH$_4$ accumulated in or under the ice, partly in bubbles), was estimated to be 5.9 mmol m$^{-2}$.

Table 1

<table>
<thead>
<tr>
<th>CH$_4$ Budget component</th>
<th>Time period</th>
<th>EXP</th>
<th>REF</th>
<th>Estimated uncertainty (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured emissions, open water period</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before oxygenation</td>
<td>8 May–18 June</td>
<td>7.0</td>
<td>5.5</td>
<td>66–111</td>
</tr>
<tr>
<td>After oxygenation</td>
<td>19 June–23 October</td>
<td>27.8</td>
<td>21.8</td>
<td>64–110</td>
</tr>
<tr>
<td>Total emission May 8–Oct 23</td>
<td></td>
<td>34.8</td>
<td>27.3</td>
<td>79–91</td>
</tr>
<tr>
<td>Storage, open water period</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring change</td>
<td>3 April–6 June</td>
<td>−18.9</td>
<td>−13.4</td>
<td>5</td>
</tr>
<tr>
<td>Summer change</td>
<td>6 June–23 October</td>
<td>−74.0</td>
<td>52.1</td>
<td>5</td>
</tr>
<tr>
<td>Rate of summer change (mmol m$^{-2}$ d$^{-1}$)</td>
<td>N/A</td>
<td>0.45</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Potential emission of stored CH$_4$ upon fall turnover</td>
<td>N/A</td>
<td>0–12.0</td>
<td>See range$^b$</td>
<td></td>
</tr>
<tr>
<td>Potential accumulation under ice$^c$</td>
<td>23 October–8 May</td>
<td>N/A if oxic</td>
<td>60.9</td>
<td>12</td>
</tr>
<tr>
<td>Potential emission of stored CH$_4$ upon spring turnover</td>
<td>8 May–6 June</td>
<td>N/A</td>
<td>0–14.0</td>
<td>See range$^b$</td>
</tr>
<tr>
<td>Potential ice out emissions$^d$</td>
<td></td>
<td>5.8</td>
<td>5.9</td>
<td>66–111</td>
</tr>
<tr>
<td>Total yearly emission</td>
<td>Whole year$^e$</td>
<td>40.6</td>
<td>33.2–59.2</td>
<td>See range$^b$</td>
</tr>
<tr>
<td>Emission linked to anoxia in hypolimnion</td>
<td>Whole year$^e$</td>
<td>N/A</td>
<td>0–26.0</td>
<td>See range$^b$</td>
</tr>
<tr>
<td>% of yearly emissions linked to anoxia in hypolimnion</td>
<td>Whole year$^e$</td>
<td>N/A</td>
<td>0–44</td>
<td>See range$^b$</td>
</tr>
</tbody>
</table>

Note. Because basin area differs, all fluxes were normalized to the total basin area, which implies that the unit is mmol m$^{-2}$ unless otherwise noted. The word “Potential” denotes budget parts for which direct measurements were missing and estimates were derived by modeling from combinations of own data, literature information, and assumptions. See Methods Section 2.3 and 2.4 for details on how the numbers were derived if not explained in the table notes. Note that maximum numbers related to anoxia may be overestimated and that the partial spring turnover generated no additional emissions in REF but did so in EXP.

$^a$Uncertainty estimates: Estimated from Monte Carlo simulations with own data or from relevant literature (e.g., Bastviken et al., 2008). Ranges are reported when uncertainty differed markedly among basins. $^b$Range denotes min–max values. $^c$Assuming a lag time of 60 days after complete fall turnover (Jansen et al., 2019), ice cover on the lake from 23 October to 8 May (195 days), and similar accumulation rate as the estimated summer hypolimnetic CH$_4$ accumulation rate (0.45 mmol m$^{-2}$ d$^{-1}$). $^d$Assuming ice-out emission of an accumulated winter flux stored in or just under the ice corresponding to observed emissions at 5°C (sediment temperature adding a 1°C contribution from metabolic heat to the maximum density water of 4°C; EXP 178 mmol d$^{-1}$ basin$^{-1}$; REF 325 mmol d$^{-1}$ basin$^{-1}$), and 195 days with ice cover on the lake. It is assumed that this flux is not reduced by MOX as indicated by Denfeld et al. (2016) and Sawakuchi et al. (2021). $^e$A presumptive scenario year with dimictic lake behavior, assuming no transfer of water column stored CH$_4$ between years.
4. Discussion

The accumulation of CH₄ in anoxic water layers in REF during summer (0.45 mmol m⁻² d⁻¹) was approximately 10-fold lower than past similar estimates from eutrophic and mesotrophic lakes (Bastviken et al., 2008), which is not surprising in a humic lake with more persistent organic matter and lower nutrient levels. The clear and significant drop in CH₄ stored in the hypolimnion (>6 m depth) after oxygenation in EXP is consistent with what has been reported earlier regarding the effects of hypolimnetic aeration on dissolved CH₄, both from in vitro enclosures (McQueen & Lean, 1983), and from in situ experiments (Hounshell et al., 2021). Previous studies, suggesting that DO is a major controller of CH₄ storage in the water column, inhibiting CH₄ storage when present (Bastviken et al., 2008; Encinas Fernandez et al., 2014; Hounshell et al., 2021; Vachon et al., 2019) are thereby supported by our experimental observations, which confirmed Hypothesis 1.

Hypothesis 2 on the other hand was not supported. The water column DO did not have any clear effect on the CH₄ emissions during the summer stratification (Figures 4 and 5). This is logical for diffusive flux because CH₄ transport across the thermocline and/or the active MOX layer in the oxycline is very limited and cannot fuel diffusive emissions from stratified waters (Bastviken et al., 2008; Murase et al., 2005; Rudd & Hamilton, 1978; Thalasso et al., 2020). This is evident in Figure 2d where the surface water concentration is higher than in the oxygenated hypolimnion, showing independence from the oxygenation experiment and that surface water CH₄ may have been sustained by lateral input from littoral sediments. Nor was there any clear support for the idea that anoxic bottom water would increase ebullition by making fresh organic material settling on top of the sediments immediately available for methanogenesis, in spite of unusually extensive field measurements with chambers distributed across the lake in the order of 25% of the time during summer to capture ebullition events. As expected from previous studies in Swedish forest lakes, our observed pattern of higher and more variable CH₄ fluxes in the shallow parts of the lake indicates a higher frequency of ebullition events in littoral areas (Bastviken et al., 2004; Natchimuthu et al., 2016).

The oxygenation experiment successfully added DO to bottom waters with no detectable effects on temperature, DO, or CH₄aq in the epilimnion (Figures 1 and 2). There were always DO present down to at least 4.5 m in both basins from the June sampling before the experiment started until the end of the measurements. In addition, CH₄aq concentration gradients show a clear separation between the transport of dissolved CH₄ from 3 to 8 m and <2 m depth during the same period (Figure 2d). Hence, while oxygenation had large effects in the deep waters (6–8 m), we could not identify any links between experimental effects and CH₄ emissions. Similarly, we could not link the oxygenation to the difference between REF and EXP fluxes prior to the experiment start. This difference was driven by the stronger effect of the partial spring mixing in EXP. The smaller shallow water volume compared to the CH₄-rich volume (>6 m depth) in EXP enhances the surface water concentration change from the temporary upwelling of CH₄-rich water, in turn enhancing emissions until surface water concentrations decline. The resupply of deep CH₄ to the surface waters ceased upon stratification, and because the oxygenation experiment did not influence DO levels above 4.5 m depth (and there were always DO present there anyway), we found no credible mechanisms by which the oxygenation could have caused the initial REF-EXP flux difference or influenced its development. The observed δ¹³C–CH₄ values, used in the mass balance calculations, were within the ranges previously reported in northern lake studies regarding δ¹³C–CH₄ in anoxic waters near the sediments (Schenk et al., 2021; Thalasso et al., 2020), and in the DO-rich epilimnion (Schenk et al., 2021; Thottathil et al., 2019). Accordingly, the results of fMOX were also similar to previous studies, for example, Bastviken et al. (2002). Relatively few studies have combined data on δ¹³C–CH₄ and fMOX with dynamic mass balance models also considering residence times of CH₄ on various sub-environments (note that fMOX is not time specific and cannot be compared for environments where the residence times differ), although this is needed for rigorous estimation of how much stored CH₄ is oxidized versus emitted upon lake turnover events. The identified studies making comparable estimates in Temperate and Boreal zones are compiled in Table 2. Their reported fractions of the stored CH₄ that was emitted ranged from 0% to 46% (Kankaala et al., 2007; Schubert et al., 2012; Utsumi, Nojiri, Nakamura, Takeshi, et al., 1998; Vachon et al., 2019). Hence, the result that only 0%–24% of the stored CH₄ was eventually emitted in the studied lake is consistent with the previously reported range (Table 2).

The lack of direct effects of hypolimnetic DO depletion on summer CH₄ fluxes suggests that the potential release of water column stored CH₄ depends on lake turnover or partial upwelling events.

Previous studies on lakes undergoing seasonal thermal mixing, either once (monomictic), or twice per year (dimictic), have highlighted patterns of CH₄ accumulation during the stable stratification periods, followed by the release of CH₄ during the water column turnover events (e.g. Denfeld et al., 2018; Encinas Fernandez et al., 2014; Bastviken et al., 2002; McQueen & Lean, 1983; Thalasso et al., 2020).
However, several factors may limit turnover related CH4 emissions. First, CH4 accumulation requires that substantial water volumes become anoxic, and this is not always the case for stratified water bodies, although a trend toward reduced DO in lakes has been recently pointed out and linked to climate change (Jane et al., 2021, 2023). Second, complete turnover may be less common than expected. Our data showed that the two basins (EXP and REF) in our studied lake did not mix completely during two consecutive years (Figure 1). Similar observations of incomplete turnover events exist, both during spring (Gorsky et al., 2021; Kankaala et al., 2006; McIntosh Marcek et al., 2021) and fall (Vachon et al., 2019) resulting in different emission patterns. For example, a short and incomplete spring turnover followed by a significant hypolimnetic accumulation of CH4 in the deep anoxic layers during summer stratification resulted in a substantial emission of dissolved CH4 upon fall turnover in a Finnish lake (Kankaala et al., 2006). A different pattern was observed in a small eutrophic Swiss lake where the late fall–early winter deepening of the surface mixed layer reached only ∼73% of the whole water column depth, resulting in a loss of only 10% of the stored hypolimnetic CH4 to the atmosphere (Vachon et al., 2019).

Clearly, the frequency and completeness of water column turnover, and the resulting extent of stored CH4 being emitted, varies widely among lakes. Further, even during time windows with complete thermal homogenization of the water column, there can be cases when the bottom water would not mix if the input of kinetic energy (e.g., from wind) is insufficient. This may happen more frequently in small, wind-sheltered lakes.

A third factor that limits turnover related emissions is MOX, which can rapidly consume large amounts of dissolved CH4 (Table 2). Vachon et al. (2019) concluded that a greater proportion of the stored CH4 would be emitted if the water column mixes rapidly. In contrast, our study suggests a regulation of the balance between k and MOX, rather than by how quickly the whole water column mixes. We note that the rate of mixing and k can be correlated, but the release of a large share of the stored CH4 to the atmosphere takes many days at normal k levels (and wind speeds). Hence, an event with high wind speeds for some hours that may trigger complete water column turnover will usually not last long enough to “degas” all excess CH4 from the water. After the event with

### Table 2

Compiled Estimates of Emitted CH4 as a Fraction of Total Stored CH4 During Lake Turnover, From Studies That Consider the Potential of Methane Oxidation to Limit Emissions

<table>
<thead>
<tr>
<th>Source</th>
<th>Lake</th>
<th>Ecoclimatic zone</th>
<th>Latitude (°N)</th>
<th>Lake area (km²)</th>
<th>Mean depth (m)</th>
<th>Max depth (m)</th>
<th>Lake type</th>
<th>Season studied</th>
<th>Stored CH4 emitted (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Encinas Fernandez et al. (2014)</td>
<td>Lake Mindelsee</td>
<td>Temperate</td>
<td>47</td>
<td>1.02</td>
<td>8.5</td>
<td>13.5</td>
<td>Mesotrophic</td>
<td>Fall</td>
<td>46</td>
</tr>
<tr>
<td>Encinas Fernandez et al. (2014)</td>
<td>Lake Mindelsee</td>
<td>Temperate</td>
<td>47</td>
<td>1.02</td>
<td>8.5</td>
<td>13.5</td>
<td>Mesotrophic</td>
<td>Spring</td>
<td>NS</td>
</tr>
<tr>
<td>Santoso et al. (2020)</td>
<td>Lake Okaro</td>
<td>Temperate</td>
<td>47</td>
<td>0.5</td>
<td>16</td>
<td>26</td>
<td>Eutrophic</td>
<td>Fall</td>
<td>37</td>
</tr>
<tr>
<td>Schubert et al. (2012)</td>
<td>Lake Rotsee</td>
<td>Temperate</td>
<td>47</td>
<td>0.5</td>
<td>16</td>
<td>26</td>
<td>Eutrophic</td>
<td>Fall</td>
<td>25</td>
</tr>
<tr>
<td>Striegl &amp; Michmerhuizen (1998)</td>
<td>Shingobee lake</td>
<td>Temperate</td>
<td>47</td>
<td>0.56</td>
<td>5.8</td>
<td>10.7</td>
<td>Oligotrophic</td>
<td>Spring to Fall</td>
<td>21</td>
</tr>
<tr>
<td>Striegl and Michmerhuizen (1998)</td>
<td>Williams lake</td>
<td>Temperate</td>
<td>47</td>
<td>0.37</td>
<td>5.5</td>
<td>9.8</td>
<td>Mesotrophic</td>
<td>Spring to Fall</td>
<td>38</td>
</tr>
<tr>
<td>Kankaala et al. (2007)</td>
<td>Mekkojärvi</td>
<td>Boreal</td>
<td>61</td>
<td>0.0035</td>
<td>3.5</td>
<td>Polyhumic</td>
<td>Fall</td>
<td>12–17</td>
<td></td>
</tr>
<tr>
<td>Mayr et al. (2020) and Zimmermann et al. (2021)</td>
<td>Lake Rotsee</td>
<td>Temperate</td>
<td>47</td>
<td>0.5</td>
<td>16</td>
<td>26</td>
<td>Eutrophic</td>
<td>Fall</td>
<td>2–7</td>
</tr>
<tr>
<td>Vachon et al. (2019)</td>
<td>Soppensee</td>
<td>Temperate</td>
<td>47</td>
<td>0.23</td>
<td>12.2</td>
<td>26</td>
<td>Eutrophic</td>
<td>Fall</td>
<td>10–44</td>
</tr>
<tr>
<td>This study REF basin</td>
<td>Ljusvattentjärn</td>
<td>Boreal</td>
<td>64</td>
<td>0.01</td>
<td>5.7</td>
<td>9.7</td>
<td>Humic</td>
<td>Spring or fall</td>
<td>0–24</td>
</tr>
</tbody>
</table>

Note. NS denotes no significant storage of CH4.
high wind speed has ended, the transport of stored CH₄ to the atmosphere will most likely still take long enough time to allow substantial CH₄ depletion by MOX, mitigating much of the potential emission. Overall, this study of one of the most common lake types globally in one of the most lake-rich biomes, shows that (a) CH₄ accumulation in anoxic water can represent a large part of the lake CH₄ budget, but also that (b) only a relatively small share of this CH₄ may be emitted. However, (c) it is challenging to directly measure turnover CH₄ emissions because turnover timing is rarely predictable. Thereby the fluxes associated with water column turnover are highly uncertain and require more attention. It is important to measure emissions, dissolved CH₄, and isotope values (δ¹³C–CH₄), as well as DO and temperatures over seasonal changes for multiple years, taking care to cover both stratification and turnover events. Lake turnover events might also differ markedly among lakes and between years, being either complete, having different effects on the vertical movement of dissolved gases, and resulting in a variety of conditions favoring MOX or CH₄ emissions. Therefore, the classical conceptual categories of lake mixing patterns (Lewis, 1983), leading to expectations of many boreal lakes to be dimictic, seem no longer satisfactory in the developing global limnology paradigm. Consideration of irregular and incomplete lake turnover is needed to avoid inaccurate estimates of the total yearly CH₄ emission from these lakes, and a biased understanding of the relationship between MOX and dissolved CH₄. This in turn has implications for the global lake CH₄ inventories, as uncertainties in lake seasonal emission patterns may lead to large uncertainties in global lake fluxes.

5. Conclusions
The conclusions of this study can be summarized by the following points:

• Not all boreal lakes turnover yearly which means that DO and CH₄ levels, as well as water-column turnover CH₄ fluxes, can be irregular among years.
• The water column DO levels had no clear impact on CH₄ emissions during summer.
• Water column DO was a strong regulator of water column CH₄ storage.
• Turnover-related emissions are substantially reduced by MOX. The fraction of stored CH₄ emitted was 0%–24% in the studied basins.
• Emission of stored CH₄ constituted 0%–44% of the total yearly flux. Hence, the fates of stored CH₄ are important for large-scale lake flux estimates and carry a large underexplored lake CH₄ flux uncertainty.
• High-resolution studies of lake CH₄ fluxes capable of capturing episodic events are important to constrain the uncertainty related to turnover fluxes.

Conflict of Interest
The authors declare no conflicts of interest relevant to this study.

Data Availability Statement
Data from all measurements supporting the findings of this study and used in the figures are presented in the main article or are publicly available through the institutional repository DIVA via https://doi.org/10.48360/ce6v-gb22 (Pajala et al., 2022).

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References From the Supporting Information


