CH$_4$ oxidation in a boreal lake during the development of hypolimnetic hypoxia

Taija Saarela$^1$ · Antti J. Rissanen$^2$ · Anne Ojala$^{3,4,5}$ · Jukka Pumpanen$^1$ · Sanni L. Aalto$^1$ · Marja Tiirola$^6$ · Timo Vesala$^7$ · Helena Jäntti$^1$

Received: 25 February 2019 / Accepted: 17 December 2019 / Published online: 28 December 2019

© The Author(s) 2019

Abstract

Freshwater ecosystems represent a significant natural source of methane (CH$_4$). CH$_4$ produced through anaerobic decomposition of organic matter (OM) in lake sediment and water column can be either oxidized to carbon dioxide (CO$_2$) by methanotrophic microbes or emitted to the atmosphere. While the role of CH$_4$ oxidation as a CH$_4$ sink is widely accepted, neither the magnitude nor the drivers behind CH$_4$ oxidation are well constrained. In this study, we aimed to gain more specific insight into CH$_4$ oxidation in the water column of a seasonally stratified, typical boreal lake, particularly under hypoxic conditions. We used $^{13}$CH$_4$ incubations to determine the active CH$_4$ oxidation sites and the potential CH$_4$ oxidation rates in the water column, and we measured environmental variables that could explain CH$_4$ oxidation in the water column. During hypolimnetic hypoxia, 91% of available CH$_4$ was oxidized in the active CH$_4$ oxidation zone, where the potential CH$_4$ oxidation rates gradually increased from the oxycline to the hypolimnion. Our results showed that in warm springs, which become more frequent, early thermal stratification with cold well-oxygenated hypolimnion delays the period of hypolimnetic hypoxia and limits CH$_4$ production. Thus, the delayed development of hypolimnetic hypoxia may partially counteract the expected increase in the lacustrine CH$_4$ emissions caused by the increasing organic carbon load from forested catchments.

Keywords Boreal lake · Greenhouse gases · Hypoxia · Methane · Oxidation · Stable isotopes · Stratification

Introduction

Freshwater ecosystems cover 3.7% of the Earth’s non-glaciated land area (Verpoorter et al. 2014), and they are one of the largest natural sources of the global greenhouse gas (GHG) methane (CH$_4$) (Bastviken et al. 2011). Approximately half of the lake surface area is located at northern latitudes (Wik et al. 2016), where small lakes in particular tend to have high CH$_4$ emissions per unit area (Juutinen et al. 2009). Processes producing GHGs in lakes are connected to their proximate terrestrial environments, because lakes receive terrestrially fixed carbon (C) and emit part of it back to the atmosphere as CH$_4$ and carbon dioxide (CO$_2$).
production-oxidation processes, it is important to understand (et al. 2010; Borrel et al. 2011; West et al. 2016). Besides the OM (Zeikus and Winfrey 1976; Juutinen et al. 2009; Duc atmosphere, because often a significant fraction of CH4 is (ANME) in sediments (Schubert et al. 2011) and in stratified conditions for CH4 oxidation (Kankaala et al. 2007). How ever, recent studies have also found anaerobic oxidation (Rudd, Hamilton and Campbell 1974; Fallon et al. 1980). However, several studies have also reported methanogenesis in oxic freshwaters (Schulz et al. 2001; Bogard et al. 2014). Once formed in lake sediment or water column, CH4 can be either oxidized to CO2 by methane-oxidizing microbes, assimilated to biomass, or released to the atmosphere (Kuiv- ila et al. 1988; Bastviken et al. 2002; Kankaala et al. 2006; Wik et al. 2016). The production and oxidation of CH4 are controlled by different environmental factors, such as temperature and the availability of oxygen (O2), nutrients and OM (Zeikus and Winfrey 1976; Juutinen et al. 2009; Duc et al. 2010; Borrel et al. 2011; West et al. 2016). Besides the production-oxidation processes, it is important to understand CH4 transport from the sediment to the atmosphere by diffusion and/or ebullition (Bastviken et al. 2008), which may be linked to energy input after ice-out (Wik et al. 2014), changes in the air pressure (Bastviken et al. 2004) and basin morphometry (Rasilo et al. 2015). During the summer stratification, formation of an anoxic hypolimnion typically results in high CH4 concentrations near the bottom due to favorable conditions for methanogenesis, and less favorable conditions for CH4 oxidation (Kankaala et al. 2007). However, this does not necessarily increase CH4 emissions to the atmosphere, because often a significant fraction of CH4 is oxidized in the overlying oxic water column before it enters the surface water (Bastviken et al. 2002; Kankaala et al. 2006; West et al. 2016).

Highest CH4 oxidation rates are detected near the oxycline (Rudd et al. 1974; Fallon et al. 1980; Kankaala et al. 2006; Bastviken et al. 2008), which can occur within the water column or at the sediment–water interface. In the oxycline, O2 is available as EA and CH4 as C and energy source (Rudd, Hamilton and Campbell 1974; Fallon et al. 1980). However, recent studies have also found anaerobic oxidation of methane (AOM) by anaerobic methane-oxidizing archaea (ANME) in sediments (Schubert et al. 2011) and in stratified water columns of freshwater lakes (Eller et al. 2005). While SO4^{2−}-dependent AOM is an efficient CH4 sink in marine environments (Knittel and Boetius 2009), several EAs, such as NO3−, nitrite (NO2−), SO4^{2−}, Fe^{3+} and manganese (Mn^{4+}), have been demonstrated to be important drivers of AOM in freshwaters (Sivan et al. 2011; Deutzmann et al. 2014; Nordi and Thamdrup 2014; Timmers et al. 2017). Nevertheless, the relevance of AOM in reducing CH4 emissions from freshwater lakes is still unclear and needs further research; e.g. Ris sanen et al. (2017) did not detect AOM coupled to any of the inorganic alternative EAs in the sediments of two shallow boreal lakes in Finland, while significant AOM was observed in 13 out of 14 study lake sediments in the temperate, arctic and tropical zone (Martinez-Cruz et al. 2018).

Before the end of the century, the annual CH4 emissions from boreal lakes are projected to increase by 20–54% due to warming climate and longer ice-free seasons (Wik et al. 2016). Improved estimates of lacustrine CH4 dynamics are still required to forecast the future contributions of boreal lakes to the global CH4 budgets in a changing climate. Therefore, we applied stable isotope methods with 13C-labeled CH4, as well as measurements of natural abundance of 13C-CH4 and 13C-DIC (dissolved inorganic C), to reveal the controlling factors for CH4 production and oxidation in the water column of a typical seasonally O2−-stratified boreal lake. Lake Kuivajärvi is a representative example of the numerous small brown-water lakes, that is located in a boreal landscape with managed coniferous forests and peatland and has high DOC concentrations (Miettinen et al. 2015). Previous work in Lake Kuivajärvi has focused on the lacustrine GHG fluxes, while the drivers behind these processes remain unknown. The objectives of this study were (1) to estimate CH4 production and oxidation during the development of summer stratification, and hypolimnetic hypoxia, and (2) to determine the environmental and biological factors that may explain CH4 oxidation in the water column. We hypothesized that the CH4 oxidation takes place in the hypolimnion, when O2 is below the detection limit of traditional O2 measurement techniques (hypoxia).

Materials and methods

Site description and measurements

Lake Kuivajärvi is a typical humic mesotrophic lake located in the boreal zone in central Finland (61° 50′ N, 24° 17′ E) close to the SMEAR II measuring station (Station for Measuring Ecosystem-Atmosphere Relations; Hari and Kulmala 2005). The lake, which has a northern and southern basin, has a surface area of 0.62 km2, length of 2.6 km and maximum depth of 13 m (Miettinen et al. 2015). The study area has mean annual temperature of
3.5 °C and precipitation of 711 mm (Pirinen et al. 2012). Each year the lake is frozen for approximately 5 months, and it is dimictic with complete turnover occurring immediately after ice-out and in the autumn (Heiskanen et al. 2015). The size of the catchment area is approximately 9.4 km² and it consists of managed forests as well as peat- and agricultural land. For more information and e.g. bathymetric map of Lake Kuivajärvi, see Heiskanen et al. (2015). For total annual GHG fluxes as well as the timing of emissions from Lake Kuivajärvi, see Miettinen et al. (2015).

Water sampling was carried out four times between May and September in 2016 at the deepest point (13 m) of the southern basin of the lake. Sediment sampling was carried out in August. The sampling dates and measured variables (Table 1) were chosen to follow the development of the thermal stratification and the hypolimnetic hypoxia until the autumn turnover. The sampling was done on the measuring platform in the middle of the lake (Heiskanen et al. 2015). Data for weather conditions were obtained from the measuring station of Finnish Meteorological Institute (FMI) close to the SMEAR II station (Fig. S1; available at https://en.ilmatieteenlaitos.fi/open-data).

**O₂ concentration, water temperature and pH measurements**

Vertical profiles of dissolved O₂ concentration (mg l⁻¹), O₂ saturation (%) and water temperature (°C) were measured manually with a field meter YSI ProODO Optical Dissolved Oxygen Instrument (Yellow Springs Instruments, Yellow Springs, OH, USA; accuracy ± 0.2 °C, ± 0.1 mg O₂ l⁻¹ or ± 1% of reading). The measurements were done at 0.5 m intervals, starting from the surface water and continuing close to the bottom (12 m) without disturbing the sediment. The pH was measured in situ from samples taken with Limnos water sampler (length 30 cm, volume 2.0 dm³) at 1 m intervals using WTW ProfiLine pH 3110 (Xylem Inc., Weilheim, Germany).

**Nutrient and DOC analyses**

Samples for nutrient and DOC analyses were collected at 1 m intervals from the surface water close to the bottom (11.5–11.75 m) by using Limnos water sampler. The samples were filtered through a plankton net (mesh size 25 μm) and a filter unit (pore size 0.22 μm, Millipore®, Sterivex, Darmstadt, Germany). The samples for nutrient analyses were stored frozen (−18 °C) until the further analysis with Ion Chromatograph (Dionex DX-120; Thermo Co., Bremen, Germany) for the SO₄²⁻ concentrations, and colorimetric analysis for the NO₂⁻ + NO₃⁻ (NOₓ⁻; Miranda et al. 2001) and NH₄⁺ concentrations (Fawcett and Scott 1960). The samples for DOC analyses were stored at +4 °C until analysis with a standard method (SFS-EN 1484), using Shimadzu TOC-VCPH (Shimadzu Corp., Kyoto, Japan). The concentrations of total iron (Tot Fe)/ferrous iron (Fe²⁺) (the depths of 0–11.5 m) and sulphide (S²⁻) (the depths of 8–11.5 m) were determined with LCK320 and LCK653 cuvette test reagents, respectively, using Hach Lange DR2800 spectrophotometer (Hach Co., Loveland, CO, USA).

**The concentrations of CH₄ and CO₂ and stable isotopic analyses**

The samples for the concentrations of CH₄ and CO₂ and stable isotopic analyses of CH₄ were collected at 1 m intervals from the surface water close to the bottom (11.5–11.75 m) by using Limnos water sampler and processed as described in Miettinen et al. (2015). The CH₄ and CO₂ concentrations were measured using Agilent 7890B Gas Chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with Gilson liquid handler GX271 autosampler (Gilson Inc., Middleton, WI, USA). The concentrations of CH₄ and CO₂ were calculated based on a one-point calibration with standard gas (AGA, Lidingö, Sweden), using Henry’s Law and the appropriate temperature relationships (Stumm and Morgan 1981). The δ¹³C-CH₄ stable isotopes were analysed with Isoprime100 IRMS (Elementar UK Ltd., Cheadle, UK) coupled to an Isoprime TraceGas pre-concentration unit and calibrated using a standard gas mixture with known isotopic value for CH₄ (− 46.7 ‰).

---

Table 1  Sampling schedule and the measured variables during each sampling of this study in 2016

| Sampling date | Measured variables |
|---------------|--------------------|
| 25 May        | Temperature, pH, the concentrations of O₂, CH₄ and CO₂ |
| 18 July       | Temperature, pH, the concentrations of O₂, CH₄, CO₂, NO₃⁻, NH₄⁺ and SO₄²⁻, δ¹³C-CH₄, δ¹³C-DIC |
| 15 August     | Temperature, pH, the concentrations of O₂, CH₄, CO₂, NO₃⁻, NH₄⁺, SO₄²⁻ and DOC, δ¹³C-CH₄, δ¹³C-DIC, δ¹³C-CH₄ oxidation experiment |
| 5 September   | Temperature, pH, the concentrations of O₂, CH₄, CO₂, NO₃⁻, NH₄⁺, Fe, SO₄²⁻, S²⁻ and DOC, δ¹³C-CH₄, δ¹³C-DIC, δ¹³C-CH₄ oxidation experiment |
Water samples for the natural abundance of δ\(^{13}\)C-DIC were collected at 1 m intervals from the surface water close to the bottom (11.5–11.75 m) and 3 ml of sample was injected into pre-evacuated 12 ml Labco Exetainers® (over-pressure released before injection). Exetainers® contained 300 μl of H\(_2\)PO\(_4\) (85%) to ensure the transformation of bicarbonate ions to CO\(_2\). The samples were then stored upside down at +4 °C until the analysis. The samples from July were analysed with Delta Plus XP GC-IRMS (Thermo Co., Bremen, Germany), and the samples from August and September were analysed with Isoprime100 IRMS. The δ\(^{13}\)C-DIC measurements were calibrated according to Coplen et al. (2006). The isotope results are reported in δ units (‰) relative to the international Vienna Pee Dee Belemnite (VPDB) standard.

\(^{13}\)CH\(_4\) incubation experiment

The samples for \(^{13}\)CH\(_4\) oxidation measurement were collected from the water column from depths chosen on the basis of vertical profiles of O\(_2\). In August, the samples were collected at 6 m (2.48 mg l\(^{-1}\) O\(_2\)), 11.5 m (1.35 mg l\(^{-1}\) O\(_2\)) and the sediment surface (0.59 mg l\(^{-1}\) O\(_2\)), and in September at 8 m (1.72 mg l\(^{-1}\) O\(_2\)), 10 m (0.59 mg l\(^{-1}\) O\(_2\)) and 11.5 m (0.44 mg l\(^{-1}\) O\(_2\)). The sample water was transferred from Limnos sampler to 12 ml Exetainers® without a headspace and allowed to overflow. In August, the sediment samples were collected from the sediment surface (top 1 cm) by using Limnos sediment sampler with a slicing system and mixed with water collected right above the sediment surface at 1:4 ratio (2.4 ml of sediment and 9.6 ml of water). After 12 h pre-incubation in the dark at +4 °C to remove any traces of O\(_2\) introduced during the sampling, 0.1 ml of \(^{13}\)CH\(_4\) trace gas mixture was injected to each sample and the vials were shaken vigorously, resulting in the estimated final concentration of 25 µmol l\(^{-1}\) CH\(_4\) in each vial. \(^{13}\)CH\(_4\) trace gas mixture contained 140 ml of N\(_2\) and 10 ml of 99% \(^{13}\)C-CH\(_4\) in a N\(_2\)-flushed, O\(_2\)-free glass bottle with NaOH powder to remove any contaminating CO\(_2\). The disappearance of the \(^{13}\)CH\(_4\) bubble with sample water was observed visually for each vial. In August, there were four replicates and two non-labeled background samples for each sampling depth and time point. In September, each sampling depth had two replicates for 0 h time point, six replicates for 8, 16 and 24 h time points, and one non-labeled background sample for each time point. The incubations at +4 °C were terminated at 8-h intervals (0, 8, 16 and 24 h) by injecting 3 ml of incubated sample into evacuated 12 ml Exetainers® (over-pressure released before injection) that had 300 μl of H\(_2\)PO\(_4\) (85%) in the bottom. The samples were analyzed for \(^{13}\)C-DIC with Isoprime100 IRMS. The excess \(^{13}\)C-DIC was calculated from the difference between the background \(^{13}\)C-DIC and the measured \(^{13}\)C-DIC for each time point. The excess \(^{13}\)C-DIC concentrations of each sampling depth were then plotted against time, and the slope of the line was used to describe the potential CH\(_4\) oxidation rate (nmol l\(^{-1}\) day\(^{-1}\)). Considering that the incubations were amended with \(^{13}\)C-CH\(_4\) above ambient levels (0.02–0.9 µmol l\(^{-1}\) in Lake Kuivajärvi), and that the proportion of CH\(_4\)-C bound to the microbial biomass was not measured, these values represent a potential or conservative rate.

Statistical analysis

Two-tailed Spearman correlations were calculated between the gas concentrations/stable isotope values and variables such as depth, O\(_2\), temperature, pH, NO\(_x\)\(^{-}\), NH\(_4\)\(^{+}\), Fe\(^{3+}\), SO\(_4^{2-}\), and DOC. Spearman’s rank correlation coefficient was chosen based on the Kolmogorov–Smirnov and Shapiro–Wilk normality test results (non-parametric data). Furthermore, simple linear regression analysis was used to study the relationship between the excess \(^{13}\)C-DIC production and incubation time in the \(^{13}\)CH\(_4\) oxidation experiments. Statistical analyses were performed with IBM SPSS Statistics 23.

Results

Thermal stratification associated development of hypolimnetic hypoxia

The depths of the warmer epilimnion and cooler hypolimnion were defined by assuming the metalimnion (thermocline) at the depth with a temperature change of more than 1 °C per meter. Water temperature in the epilimnion was highest in July (Fig. 1b) and lowest in September (Fig. 1d), while the hypolimnetic temperature was stable at about +6–7 °C throughout the study period. A thermocline varied in depth with changing seasons. In May, the thermal stratification was strongest, and temperature steeply decreased between 3 and 4 m (Fig. 1a), while in July there was no steep thermocline (Fig. 1b). In August, the temperature decreased after 5 m depth (Fig. 1c) and in September, there was a steep decrease of temperature at 8 m depth (Fig. 1d).

The whole water column was oxygenated in July (Fig. 1b), and the hypolimnetic hypoxia developed late in summer 2016. The oxycline ascended from the sediment to the water column during the development of summer stratification. Hypoxic conditions (< 2 mg l\(^{-1}\)) were detected below 6 m depth in August (Fig. 1c), and below 8 m depth in the beginning of September (Fig. 1d).
Depth profiles of water-quality variables

In every sampling occasion, the NO$_x^-$ concentrations peaked in the hypolimnion (max. 3.5 μmol l$^{-1}$), while the concentrations were mainly < 1 μmol l$^{-1}$ at the depths of 0–8 m in August and September (Fig. 2b, c), and below the detection limit in July (Fig. 2a). The NH$_4^+$ concentrations remained mainly at < 2.5 μmol l$^{-1}$, but in September, the hypolimnetic concentrations peaked to 5 μmol l$^{-1}$ (Fig. 2c). In September, Total Fe concentrations slightly increased towards the hypolimnion (max. 27 μmol l$^{-1}$; Fig. 2c). The SO$_4^{2-}$ concentrations stayed mainly between 30–45 μmol l$^{-1}$ throughout the water column, except in July when the hypolimnetic concentrations of SO$_4^{2-}$ peaked to 94 μmol l$^{-1}$ (Fig. 2a). In September, S$_2^-$ was not detected in the water column. DOC concentrations remained at < 1.1 mmol l$^{-1}$, being highest in the epilimnion (Fig. 2b, c).

Depth profiles of CH$_4$ and CO$_2$

The epilimnetic CH$_4$ concentrations were stable at approximately 0.1 μmol l$^{-1}$ during the whole study period, while the concentrations in the metalimnion and hypolimnion changed seasonally. In early summer, the CH$_4$ concentrations were highest in the upper water column; the water column maxima occurred at 3 m depth in May (0.115 ± 0.002 μmol l$^{-1}$; Fig. 3a) and at 6 m depth in July and August (0.151 ± 0.013 μmol l$^{-1}$ and 0.132 ± 0.002 μmol l$^{-1}$; Fig. 3b, c). Below the peak, the CH$_4$ concentrations started to decrease towards the bottom, until they slightly increased again at 11 m depth. In contrast, the CH$_4$ concentrations in September were relatively low in the epilimnion and metalimnion but peaked in the hypoxic hypolimnion (0.91 ± 0.07 μmol l$^{-1}$; Fig. 3d). The CH$_4$ concentration correlated positively with water temperature, pH and the NH$_4^+$ concentration, and negatively with the water column depth and the concentrations of NO$_x^-$ and SO$_4^{2-}$ (Table 2).

There was a negative correlation between the CH$_4$ and CO$_2$ concentrations (Table 2), their depth profiles being reflections of each other’s, particularly in May (Fig. 3a), but also during other sampling months. The epilimnetic CO$_2$ concentrations remained stable from May to September, while the CO$_2$ concentrations in the hypolimnion clearly increased from spring (0.179 ± 0.004 mmol l$^{-1}$; Fig. 3a) to autumn (0.370 ± 0.008 mmol l$^{-1}$; Fig. 3d). In May and July, the CO$_2$ concentrations started to increase below 3 m depth (Fig. 3a, b), whereas in August and September, the CO$_2$ concentrations increased simultaneously with the decreasing O$_2$.
concentrations (Fig. 3c, d). Throughout the sampling period, the CO₂ concentration correlated negatively with water temperature, pH and the O₂ concentration. There was also a positive correlation for CO₂ with the water column depth, NO₃⁻ and SO₄²⁻. In addition, the CO₂ and Fe³⁺ concentrations correlated positively in September (Table 2).

**Depth profiles of δ¹³C-CH₄ and δ¹³C-DIC**

There was a substantial temporal variation in the depth profiles of δ¹³C-CH₄. In the hypolimnion, δ¹³C-CH₄ decreased from − 36.8 ± 0.2 ‰ in July (Fig. 4a) to − 71.5 ± 1.8 ‰ in September (Fig. 4c). In August and September, the maximum δ¹³C-CH₄ values were detected close to the oxycline at 9 m depth (− 51.8 ± 1.2 ‰ and − 37.6 ± 2.0 ‰, respectively). There was a significant negative correlation for the δ¹³C-CH₄ with water temperature, pH, DOC concentration and CH₄ concentration, while the δ¹³C-CH₄ correlated positively with the SO₄²⁻ concentration (Table 2).

Similarly to the profiles of CO₂ and CH₄, the depth profiles of δ¹³C-CH₄ and δ¹³C-DIC were reflections of each other, and the δ¹³C-DIC values generally decreased from summer to autumn. The δ¹³C-DIC ranged from − 6.8 ± 0.7 to − 17.5 ± 0.9 ‰ in the epilimnion, and from − 21.5 ± 0.4 to − 29.3 ± 0.1 ‰ in the hypolimnion. In August and September, a notable decrease of δ¹³C-DIC occurred at the depths of 6–7 m (Fig. 4b, c), simultaneously with sudden O₂ depletion, while in July the decrease of δ¹³C-DIC towards the bottom was more stable (Fig. 4a). The δ¹³C-DIC values correlated positively with water temperature, the O₂ concentration and pH, whereas the δ¹³C-DIC correlated negatively with water column depth and the concentrations of NO₃⁻, Fe³⁺, SO₄²⁻ and CO₂ (Table 2).

**The extent and potential rates of CH₄ oxidation**

In August, the estimated fraction of CH₄ oxidized in the water column was 34% (calculated from the difference between δ¹³C-CH₄ at the bottom and the maximum value of δ¹³C-CH₄ at 9 m, as described in Kankaala et al. 2007). In September, the corresponding proportion was 91%.

Potential CH₄ oxidation was detected in September. Potential CH₄ oxidation rates increased with depth from 10.8 ± 3.4 nmol l⁻¹ day⁻¹ at 8 m (p < 0.006**) to 34.8 ± 12.3 nmol l⁻¹ day⁻¹ at 11.5 m (p < 0.012*; Fig. 5). In contrast, the results from August did not show clear evidence of CH₄ oxidation, since the tracer addition did not cause significant linear increase with time in samples from 6 m depth (p > 0.134) and sediment surface (p > 0.113). At 11.5 m depth, the values (Atom%) of labeled samples

---

Fig. 2 Concentrations of NO₃⁻, NH₄⁺ and SO₄²⁻ in a July, b August and c September, concentrations of DOC in b August and c September, and concentrations of Tot Fe in c September. Note different scales on X-axis

© Springer
increased linearly with time (p > 0.349), but the large variation between replicates complicated interpretation of results and thus, CH4 oxidation during August cannot be confirmed (Fig. S2).
Discussion

The vertical distribution of CH₄ in the water column

The epilimnetic concentrations of CH₄ were similar to those previously recorded in Lake Kuivajärvi (Miettinen et al. 2015) and in Finnish lakes in general (e.g. 207 lakes studied by Juutinen et al. 2009). The hypolimnetic CH₄ concentrations, however, were relatively low, even in September, when the hypolimnetic hypoxia created favorable conditions for methanogenesis (Capone and Kiene 1988). The low concentrations of CH₄ were probably caused by the well-oxygenated water column in early summer.

From May to August, the highest concentrations of CH₄ occurred in the upper water layers and the lowest concentrations in the hypolimnion. Even though the CH₄ concentrations are expected to decrease in the well-oxygenated water column due to the methanotrophic activity (Kankaala et al. 2006; Bastviken et al. 2008), the lateral transport of CH₄ from the littoral zone or surrounding peatlands (Murase et al. 2003; Ojala et al. 2011; López Bellido et al. 2013; Miettinen et al. 2015), as well as a rapid vertical release of CH₄ from the sediment to the surface layers by ebullition (McGinnis et al. 2006), could cause such profiles. Also, internal lake oscillations might have contributed in vertical transfer of CH₄ to the upper layers (Heiskanen et al. 2014; Stepanenko et al. 2016). Since there were no extreme rain events during the sampling periods to enable efficient lateral transport, an internal source for CH₄ in the oxic water column seems more likely.

Although the CH₄ concentrations did not correlate with the O₂ conditions, simultaneous changes in the depth profiles of CH₄ and nutrients (i.e. NO₃⁻, NH₄⁺ and SO₄²⁻; Table 2) suggest that the availability of O₂ was a major factor regulating both CH₄ and nutrient concentrations in the water column. In the summer, well-oxygenated water column created favorable conditions for aerobic nitrification and oxidation of S²⁻ to SO₄²⁻, while these conditions were less favorable for...
methanogenesis. Conversely, hypolimnetic hypoxia in September probably stimulated methanogens and ammonium-producing microbes simultaneously with denitrifying and sulphate-reducing bacteria. The measured δ13C-CH4 values agreed with previous studies in boreal lakes (e.g. Bastviken et al. 2002, 2008; Kankaala et al. 2007). The δ13C-CH4 decreased with increases in CH4 concentration. Also, increases in temperature and DOC were associated with decreasing δ13C-CH4 values, as they are the key controlling factors for methanogenesis (Table 2; Bastviken et al. 2004, 2008; Duc et al. 2010). In August and September, CH4 production at the lake bottom was visible from the δ13C-CH4 profiles. The hypolimnetic decrease of δ13C-CH4 was substantial, particularly with maximum CH4 concentrations in September, which is consistent with biogenic CH4 being strongly 13C-depleted due to fractionation (Whiticar 1999). In July, 13C-enriched values of CH4 (~37 %e) at the lake bottom indicate that most of CH4 was formed and consumed within the sediment (Whiticar 1999).

Throughout the study period, the increases in CO2 with depth, simultaneously with decreasing δ13C-DIC and O2 concentration, indicate consumption of O2 and production of CO2 through in situ decomposition of OM in the hypolimnion (Miettinen et al. 2015). Furthermore, the decomposition of OM releases nutrients, such as NO3− (McManus, Heinen and Baehr 2003), thus explaining the positive relationship between CO2 and NO3−.

In this study, we did not directly estimate the lake-atmosphere C gas exchange in Lake Kuivajärvi. However, the measured surface water CH4 and CO2 concentrations together with a 2-year (2011–2012) data set on atmospheric fluxes of C gases (Miettinen et al. 2015) confirm that Lake Kuivajärvi acts as a source of CH4 and CO2 to the atmosphere (the 2-year mean for CH4 approx. 0.06 mol m⁻² y⁻¹ and for CO2 25.5 mol m⁻² y⁻¹).

Water column CH4 oxidation and future perspectives in a changing climate

The transition of the active CH4 oxidation zone was clearly indicated by the δ13C-CH4 profiles. In July, CH4 remained 13C-enriched at the bottom, suggesting that CH4 was already oxidized in the sediment, because CH4 oxidation leaves a residual CH4 enriched in 13C (Whiticar 1999). During August and September, the most 13C-enriched values of CH4 were detected close to the oxycline, indicating the transition of CH4 oxidation from the sediment to the water column.

The estimated proportion of CH4 oxidized within the water column was 34% in August and 91% in September. The high efficiency of CH4 oxidation agrees well with previous studies, where the proportions of CH4 oxidized within the water column during summer stratification have ranged from 50 to 80% (Kankaala et al. 2006; Bastviken et al. 2008). Even though lakes generally represent an important natural source of atmospheric CH4, these results show that methanotrophic activity substantially reduces CH4 emissions from this typical, seasonally stratified lake.

In September, the potential CH4 oxidation rates gradually increased from the oxycline (8 m) to the hypoxic hypolimnion (11.5 m). Simultaneously, δ13C-CH4 strongly decreased, while δ13C-DIC remained stable. Although the highest CH4 oxidation rates are typically observed at the oxycline in the presence of O2 (Kankaala et al. 2006; Oswald et al. 2015), the maximum rates in the hypolimnion could be explained by the higher ambient concentration of CH4 (0.9 µmol l⁻¹) at 11.5 m depth sustaining a larger population of methanotrophs (Sundh et al. 2005; Bastviken et al. 2008). However, the CH4 pool turnover time in September, calculated by dividing the CH4 concentration with the potential CH4 oxidation rate (e.g. Lin et al. 2005), was most rapid near the oxycline at the depths of 8–10 m (<8 days), and slowest at 11.5 m (26 days).

When comparing the potential CH4 oxidation rates in Lake Kuivajärvi to other stratified systems (Milucka et al. 2015; Oswald et al. 2015, 2016), and assuming that the potential CH4 oxidation rate is proportional to the concentration of the added 13CH4 tracer, the maximum CH4 oxidation rates in Lake Kuivajärvi were approximately 5–8 times lower than in those lakes. Again, the higher ambient concentrations of CH4 (10–100-fold) in those systems most likely sustained a larger population of methanotrophs, thus leading to higher CH4 oxidation rates.

As noted in previous anoxic incubation studies (Blees et al. 2014; Norði and Thamdrup 2014; Rissanen et al. 2017), possibility of minor O2 contamination from the tracer injection cannot be excluded even with originally anoxic freshwater samples. Also, there might have been some residual O2 available for CH4 oxidation close to the detection limit of O2 sensor. Indeed, the maximum CH4 oxidation rates in the hypolimnion imply that episodic appearance of O2 (e.g. downwelling of oxygenated water) in otherwise hypoxic layers potentially fueled methanotrophy below the oxycline, thus stimulating microaerobic CH4 oxidation (Kalyuzhnaya et al. 2013; Blees et al. 2014; Kits et al. 2015). Recently, aerobic gamma-proteobacterial methanotrophs have been reported to almost exclusively dominate the methanotrophic community in both oxic and anoxic layers of boreal and temperate lakes (Milucka et al. 2015; Oswald et al. 2016; Rissanen et al. 2018). Further research identifying the microbial communities involved in these processes is required to confirm whether the metabolism of methane-oxidizing microbes in Lake Kuivajärvi was aerobic or anaerobic.

In the future, as the aquatic systems in the boreal zone are exposed to increasing terrestrial organic C load due to climate-induced changes in precipitation and air temperature
(Lepistö et al. 2008; Sarkkola et al. 2009; Couture et al. 2012; Puurunen et al. 2014; Kiuru et al. 2018), the accelerated decomposition of OM might emphasize the role of alternative inorganic EAs in CH$_4$ oxidation. The development of summer stratification, on the other hand, suggests that the annual CH$_4$ emissions will remain largely regulated by aerobic CH$_4$ consumption due to the well-oxygenated water column throughout the summer.

**Potential effects of warming climate on the onset of thermal stratification and hypolimnetic hypoxia**

As a consequence of warm spring, Lake Kuivajärvi began to thermally stratify soon after ice-out and rapidly formed a warm epilimnetic layer, while the bottom waters remained cold and oxygenated. Long-term trends of thermal conditions have previously shown an extension of the summer stratification period in dimictic lakes of the boreal and temperate region (Gerten and Adrian 2002; Rößner et al. 2012; Magee and Wu 2017). Browning of boreal lakes together with warming climate causes earlier thermal stratification due to dark humic waters absorbing solar radiation (Heiskanen et al. 2015). Since the mean air temperatures during spring months from March to May have clearly increased in Finland (Mikkonen et al. 2015) and will continue to increase in the future (Ruosteenoja et al. 2016), this kind of early thermal stratification is becoming more common in boreal brown-water lakes (Heiskanen et al. 2015; Davidson et al. 2018; Kiuru et al. 2018; Mammarella et al. 2018). Since the hypolimnetic hypoxia did not begin until early autumn, it most likely lasted only few weeks before the autumn turnover. Previously, the duration of hypolimnetic hypoxia in Lake Kuivajärvi has varied from 3 weeks to more than 2 months (Miettinen et al. 2015), after which the autumn turnover has taken place in the beginning of October (e.g. Heiskanen et al. 2015). The results of this experiment represent the future O$_2$ conditions in boreal lakes, showing that earlier thermal stratification with cold hypolimnion delays the period of hypolimnetic hypoxia and thus limits CH$_4$ production.

**Conclusions**

The zone of CH$_4$ oxidation ascended from the sediment to the water column in the late phases of summer stratification, and our results showed that the CH$_4$ oxidation potential was highest in the hypoxic hypolimnion. During hypolimnetic hypoxia, 91% of available CH$_4$ was oxidized in the active CH$_4$ oxidation zone, while 9% was potentially released to the atmosphere. Even though lakes represent an important natural source of atmospheric CH$_4$ due to their large areal extent, our results demonstrate that earlier thermal stratification with cold, well-oxygenated hypolimnion will delay the period of hypolimnetic hypoxia, thus limiting CH$_4$ production. Moreover, changes in the stratification dynamics of boreal lakes are expected due to the higher atmospheric temperatures and brownification. Therefore, the expected increase in the lacustrine CH$_4$ emissions as a consequence of increasing organic C load from forested catchments may be partially counteracted by the later development of hypoxia.

**Acknowledgements** Open access funding provided by University of Eastern Finland (UEF) including Kuopio University Hospital. This study was supported by Olvi-säätiö (Grant No. 201720037) and Maa-ja Vesitekniikan tuki ry (Grant No. 34348) for TS, Academy of Finland (project No. 286642 for AJK, project No. 275127 for HI, and project No. 310302 for SLA), and European Research Council (ERC) CoG project No. 615146 for MT. The authors acknowledge the Academy of Finland Centre of Excellence (project No. 272041, 118780 and 307331) and ARCTICFIRE-project (project No. 286685) funded by Academy of Finland for JP, Academy Professor projects (No. 1284701 and 1282842), ICOS-Finland (project No. 281255) and CarLAC-project (project No. 281196) funded by Academy of Finland for TV. In addition, the authors acknowledge University of Eastern Finland Water Research Programme funded by Olvi-säätiö, Jenny and Antti Wihuri Foundation and Saastamoinen Foundation for HJ.

**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

**References**

Algesten G, Sobek S, Bergström AK, Ågren A, Tranvik LJ, Jansson M (2003) Role of lakes for organic carbon cycling in the boreal zone, Glob Change Biol 10:141–147. https://doi.org/10.1046/j.1365-2486.2003.00721.x

Bastviken D, Ejlertsson J, Tranvik L (2002) Measurement of methane oxidation in lakes: a comparison of methods. Environ Sci Technol 36:3354–3361. https://doi.org/10.1021/es010311p

Bastviken D, Cole J, Pace M, Tranvik L (2004) Methane emissions from lakes: dependence of lake characteristics, two regional assessments, and a global estimate. Global Biogeochem Cycl. https://doi.org/10.1029/2004GB002238

Bastviken D, Cole JJ, Pace ML, Van de Bogert MC (2008) Fates of methane from different lake habitats: connecting whole-lake budgets and CH$_4$ emissions. J Geophys Res Biogeosci. https://doi.org/10.1029/2007JG000608

Bastviken D, Tranvik LJ, Downing JA, Crill PM, Enrich-Prast A (2011) Freshwater methane emissions offset the continental carbon sink. Science 331:50. https://doi.org/10.1126/science.1196808

Bellido JL, Tulonen T, Kankaala P, Ojala A (2013) Concentrations of CO$_2$ and CH$_4$ in water columns of two stratified boreal lakes...
during a year of atypical summer precipitation. Biogeochemistry 113:613–627. https://doi.org/10.1007/s10533-012-9792-2

Blees J, Niemann H, Wenk CB, Zopfi J, Schubert CJ, Kfir MK et al (2014) Micro-aerobic bacterial methane oxidation in the chemoclinal and anoxic water column of deep south-Alpine Lake Lugano (Switzerland). Limnol Oceanogr 59:311–324. https://doi.org/10.4319/lo.2014.59.2.0311

Bogard MJ, Del Giorgio PA, Boutet L, Chaves MCG, Prairie YT, Mermante A et al (2014) Oxic water column methanogenesis as a major component of aquatic CH4 fluxes. Nat Commun 5:5530. https://doi.org/10.1038/ncomms6350

Borrel G, Jézéquel D, Biderre-Petit C, Morel-Desrosiers N, Morel JP, Peyret P et al (2011) Production and consumption of methane in freshwater lake ecosystems. Res Microbiol 162:832–847. https://doi.org/10.1016/j.resmic.2011.06.004

Capone DG, Kiene RP (1988) Comparison of microbial dynamics in marine and freshwater sediments: contrasts in anaerobic carbon catabolism. Limnol Oceanogr 33:725–749. https://doi.org/10.4319/lo.1988.33.4part2.0725

Coplen TB, Brand WA, Gehele M, Gröning M, Meijer HA, Toman B et al (2006) New guidelines for δ13C measurements. Anal Chem 78:2439–2441. https://doi.org/10.1021/ac050272c

Couture S, Houle D, Gagnon C (2012) Increases of dissolved organic carbon in temperate and boreal lakes in Quebec, Canada. Environ Sci Pollut Res 19:361–371. https://doi.org/10.1007/s11356-011-0565-6

Davidson TA, Audet J, Jeppesen E, Landkildehus F, Lauridsen TL, Couture S, Houle D, Gagnon C (2012) Increases of dissolved organic carbon in temperate and boreal lakes in Quebec, Canada. Environ Sci Pollut Res 19:361–371. https://doi.org/10.1007/s11356-011-0565-6

Fallon RD, Harrits S, Hanson RS, Brock TD (1980) The role of methanogenesis in internal carbon cycling in Lake Mendota during summer stratification. Limnol Oceanogr 25:357–360. https://doi.org/10.4319/lo.1980.25.2.0357

Fawcett JK, Scott J (1960) A rapid and precise method for the determination of urea. J Clin Pathol 13:156–159. https://doi.org/10.1136/jcp.13.2.156

Finnish Meteorological Institute (2016) The Finnish Meteorological Institute’s open data. https://en.ilmatieteenlaitos.fi/open-data

Gerten D, Adrian R (2002) Effects of climate warming, North Atlantic Oscillation, and El Niño-Southern Oscillation on thermal conditions and plankton dynamics in Northern Hemispheric lakes. Sci World J 2:586–606. https://doi.org/10.1100/tsw.2002.141

Hari P, Kulmala M (2005) Station for measuring ecosystem-atmosphere relations (SMEAR II). Boreal Environ Res 10:315–322

Heiskanen JJ, Mammarella I, Haapanala S, Pumpanen J, Vesala T, MacIntyre S et al (2014) Effects of cooling and internal wave motions on gas transfer coefficients in a boreal lake. Tellus Ser B Chem Phys Meteorol 66:22827. https://doi.org/10.3402/tellusb.v66.22827

Heiskanen JJ, Mammarella I, Ojala A, Stepaknevo V, Ertkiliä KM, Miettinen H et al (2015) Effects of water clarity on lake stratification and lake-atmosphere heat exchange. J Geophys Res Atm 120:7412–7428. https://doi.org/10.1002/2014JD022938

Juutinen S, Rantakari M, Kortelainen P, Huttunen JT, Larmola T, Alm J et al (2009) Methane dynamics in different boreal lake types. Biogeosciences 6:209–223. https://doi.org/10.5194/bg-6-209-2009

Kalyuzhnaya MG, Yang S, Rozova ON, Smalley NE, Clubb J, Lamb A et al (2013) Highly efficient methane biocatalysis revealed in a methanotrophic bacterium. Nat Commun. https://doi.org/10.1038/ncomms3785

Kankaala P, Huotari J, Pelomaa E, Saloranta T, Ojala A (2006) Methanotrophic activity in relation to methane efflux and total heterotrophic bacterial production in a stratified, humic, boreal lake. Limnol Oceanogr 51:1195–1204. https://doi.org/10.4319/lo.2006.51.2.1195

Kankaala P, Taipale S, Nykänen H, Jones RI (2007) Oxidation, efflux, and isotopic fractionation of methane during autumnal turnover in a polyhumic, boreal lake. J Geophys Res Biogeo. https://doi.org/10.1029/2006JD006036

Kits KD, Klotz MG, Stein LY (2015) Methane oxidation coupled to nitrate reduction under hypoxia by the “Gammaproteobacterium Methylomonas denitrificans”, sp. nov. type strain FJG1. Environ Microbiol 17:3219–3232. https://doi.org/10.1111/1462-2920.12772

Kiuru P, Ojala A, Mammarella I, Heiskanen J, Käärämäinen M, Vesala T et al (2019) Effects of climate change on CO2 concentration and efflux in a humic boreal lake: a modeling study. J Geophys Res Biogeo 123:2212–2223. https://doi.org/10.1029/2018J G004585

Knittel K, Boetius A (2009) Anaerobic oxidation of methane: progress with an unknown process. Annu Rev Microbiol 63:311–334. https://doi.org/10.1146/annurev.micro.61.080706.093130

Kortelainen P (1993) Content of total organic carbon in Finnish lakes and its relationship to catchment characteristics. Can J Fish Aquat Sci 50:1477–1483. https://doi.org/10.1139/f93-168

Kuivila KM, Murray JW, Devol AH, Lidstrom ME, Reimers CE (1988) Methane cycling in the sediments of Lake Washington. Limnol Oceanogr 33:571–581. https://doi.org/10.4319/lo.1988.33.4.0571

Lepistö A, Kortelainen P, Matsson T (2008) Increased organic C and N leaching in a northern boreal river basin in Finland. Global Biogeochem Cycles 22:GB3029. https://doi.org/10.1029/2007GC001715

Lin JL, Joyce SB, Scholten JC, Schäfer H, McDonald IR, Murrell JC (2005) Analysis of methane monoxygenase genes in Mono Lake suggests that increased methane oxidation activity may correlate with a change in methanotroph community structure. Appl Environ Microbiol 71:6458–6462. https://doi.org/10.1128/AEM.71.12.6458-6462.2005

M agee MR, Wu CH (2017) Response of water temperatures and stratification to changing climate in three lakes with different morphometry. Hydrol Earth Syst Sci 21:6253–6274. https://doi.org/10.5194/hess-21-6253-2017

Mammarella I, Gavrylenko G, Zdorovenova G, Ojala A, Erkkiä KM, Zdorovenov R et al (2018) Effects of similar weather patterns on the thermal stratification, mixing regimes and hypolimnetic oxygen depletion in two boreal lakes with different water transparency. Boreal Environ Res 23:237–247

Martinez-Cruz K, Sepulveda-Jauregui A, Casper P, Anthony KW, McEwan DF, Greinert J, Artemov Y, Beaubien SE, Wüest AN (2006) Fate of rising methane bubbles in stratified waters: how much...
methane reaches the atmosphere? J Geophys Res Oceans. https://doi.org/10.1029/2005JC003183
McManus J, Heinen EA, Baehr MM (2003) Hypolimnetic oxidation rates in Lake Superior: role of dissolved organic material on the lake’s carbon budget. Limnol Oceanogr 4:1624–1632. https://doi.org/10.4319/lo.2003.48.4.1624
Miettinen H, Pumpenjan H, Heiskanen JJ, Aaltonen H, Mammarella I, Ojala A et al (2015) Towards a more comprehensive understanding of lacustrine greenhouse gas dynamics—two-year measurements of concentrations and fluxes of CO2, CH4 and N2O in a typical boreal lake surrounded by managed forests. Boreal Environ Res 20:75–89
Mikkonen S, Laine M, Mäkelä HM, Gregow H, Tuomenvirta H, Rasilo T, Prairie YT, del Giorgio PA (2015) Large-scale patterns in methane emissions in boreal ecosystems in Finland under the RCP forcing scenarios. Geophysica 51:17–50
Milucka J, Kirf M, Littmann S et al (2015) Aerobic gammaproteobacterial methanotrophs mitigate methane emissions from seasonally stratified lakes. PLoS ONE. https://doi.org/10.1371/journal.pone.0132574
Miranda KM, Espey MG, Wink DA (2001) A rapid, simple spectrophotometric method for simultaneous detection of nitrate and nitrite. Nitric Oxide 5:62–71. https://doi.org/10.1006/niox.2000.0319
Muraš G, Yagimoto A, Okubo K, Sakamoto M (2003) Sources of dissolved methane in Lake Biwa. Limnology 4:91–99. https://doi.org/10.1111/j.1574-6941.2003.00095-0
Norbi T, Thamdrup B (2014) Nitrate-dependent anaerobic methane oxidation in a freshwater sediment. Geochim Cosmochim Acta 132:141–150. https://doi.org/10.1016/j.gca.2014.01.032
Ojala A, Bellido JL, Tulonen T, Kankaala P, Huotari J (2011) Carbon gas fluxes from a brown-water and a clear-water lake in the boreal zone during a summer with extreme rain events. Limnol Oceanogr 56:61–76. https://doi.org/10.4319/lo.2011.56.1.0061
Oswald K, Milucka J, Brand A, Littmann S, Wehrli B, Kuypers MM et al (2015) Light-dependent aerobic methane oxidation reduces methane emissions from seasonally stratified lakes. PLoS ONE. https://doi.org/10.1371/journal.pone.0135274
Oswald K, Milucka J, Brand A, Hach P, Littmann S, Wehrli B et al (2016) Aerobic gammaproteobacterial methanotrophs mitigate methane emissions from oxic and anoxic lake waters. Limnol Oceanogr 61:101–118. https://doi.org/10.1002/limn.10312
Pirinen P, Simola I, Aalto J, Kaukoranta JP, Karlsson P, Ruheila R (2012) Climatological Statistics of Finland 1981–2010. Reports of the Finnish Meteorological Institute, Helsinki
Pumpenjan H, Heiskanen JJ, Aaltonen H, Mammarella I, Ojala A, Miettinen H, Lykosov V, M, Boetius A (2011) Evidence for anaerobic oxidation of methane in sediments of a freshwater system (Lago di Cadagno). FEMS Microbiol Ecol 76:26–38. https://doi.org/10.1111/j.1574-6941.2010.01036.x
Schulz M, Faber E, Hollerbach A, Schröder HG, Güde H (2001) The methane cycle in the epilimnion of Lake Constance. Fundam Appl Limnol 151:157–176. https://doi.org/10.1127/arch-hydrobiol/151/2001/157
Sivan O, Adler M, Pearson A, Gelman F, Bar-Ori I, John SG et al (2011) Geochemical evidence for iron-mediated anaerobic oxidation of methane. Limnol Oceanogr 56:1536–1544. https://doi.org/10.4319/lo.2011.56.4.1536
Stepanenko V, Mammarella I, Ojala A, Miettinen H, Lykosov V, Vesa T (2016) LAKE 2.0: a model for temperature, methane, carbon dioxide and oxygen dynamics in lakes. Geosci Model Dev 9:1977–2006. https://doi.org/10.5194/gmd-9-1977-2016
Stumm W, Morgan JJ (1981) Aquatic chemistry: an introduction emphasizing chemical equilibria in natural waters. Wiley, New York
Sundh I, Bastviken D, Tranvik LJ (2005) Abundance, activity, and community structure of pelagic methane-oxidizing bacteria in temperate lakes. Appl Environ Microb 71:6746–6752. https://doi.org/10.1128/AEM.71.11.6746-6752.2005
Timmers PH, Welte CU, Kochoerst JJ, Plagge CM, Jetten MS, Stams AJ (2017) Reverse methanogenesis and respiration in methanotrophic archaea. Archaea. https://doi.org/10.1155/2017/1654237
Verpoorter C, Kutser T, Seekell DA, Tranvik LJ (2014) A global inventory of lakes based on high resolution satellite imagery. Geophys Res Lett 41:6396–6402. https://doi.org/10.1002/2014GL060641
West WE, Crazzolara KP, Jones SE (2016) Productivity and depth regulate lake contributions to atmospheric methane. Limnol Oceanogr. https://doi.org/10.1002/lno.10347
Whiticar MJ (1999) Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. Chem Geol 161:181–187. https://doi.org/10.1016/S0009-2541(99)00092-3
Wick M, Thornton BF, Bastviken D, MacIntyre S, Varner RK, Crill PM (2014) Energy input is primary controller of methane bubbling in subarctic lakes. Geophys Res Lett 41:555–560. https://doi.org/10.1002/2013GL058510
Wick M, Varner RK, Anthony KW, MacIntyre S, Bastviken D (2016) Climate-sensitive northern lakes and ponds are critical components of methane release. Nat Geosci 9:99. https://doi.org/10.1038/ngeo2578
Zeikus JG, Winfrey MR (1976) Temperature limitation of methanogenesis in aquatic sediments. Appl Environ Microb 31:99–107

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.