

**This is a self-archived version of an original article. This version may differ from the original in pagination and typographic details.**

**Author(s):** Saarela, Taija; Rissanen, Antti J.; Ojala, Anne; Pumpanen, Jukka; Aalto, Sanni L.; Tirola, Marja; Vesala, Timo; Jäntti, Helena

**Title:** CH<sub>4</sub> oxidation in a boreal lake during the development of hypolimnetic hypoxia

**Year:** 2020

**Version:** Published version

**Copyright:** © The Author(s) 2019

**Rights:** CC BY 4.0

**Rights url:** <https://creativecommons.org/licenses/by/4.0/>

**Please cite the original version:**

Saarela, T., Rissanen, A. J., Ojala, A., Pumpanen, J., Aalto, S. L., Tirola, M., Vesala, T., & Jäntti, H. (2020). CH<sub>4</sub> oxidation in a boreal lake during the development of hypolimnetic hypoxia. *Aquatic Sciences*, 82, Article 19. <https://doi.org/10.1007/s00027-019-0690-8>



# CH<sub>4</sub> oxidation in a boreal lake during the development of hypolimnetic hypoxia

Taija Saarela<sup>1</sup> · Antti J. Rissanen<sup>2</sup> · Anne Ojala<sup>3,4,5</sup> · Jukka Pumpanen<sup>1</sup> · Sanni L. Aalto<sup>1</sup> · Marja Tiirola<sup>6</sup> · Timo Vesala<sup>7</sup> · Helena Jäntti<sup>1</sup>

Received: 25 February 2019 / Accepted: 17 December 2019  
© The Author(s) 2019

## Abstract

Freshwater ecosystems represent a significant natural source of methane (CH<sub>4</sub>). CH<sub>4</sub> produced through anaerobic decomposition of organic matter (OM) in lake sediment and water column can be either oxidized to carbon dioxide (CO<sub>2</sub>) by methanotrophic microbes or emitted to the atmosphere. While the role of CH<sub>4</sub> oxidation as a CH<sub>4</sub> sink is widely accepted, neither the magnitude nor the drivers behind CH<sub>4</sub> oxidation are well constrained. In this study, we aimed to gain more specific insight into CH<sub>4</sub> oxidation in the water column of a seasonally stratified, typical boreal lake, particularly under hypoxic conditions. We used <sup>13</sup>CH<sub>4</sub> incubations to determine the active CH<sub>4</sub> oxidation sites and the potential CH<sub>4</sub> oxidation rates in the water column, and we measured environmental variables that could explain CH<sub>4</sub> oxidation in the water column. During hypolimnetic hypoxia, 91% of available CH<sub>4</sub> was oxidized in the active CH<sub>4</sub> oxidation zone, where the potential CH<sub>4</sub> 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<sub>4</sub> production. Thus, the delayed development of hypolimnetic hypoxia may partially counteract the expected increase in the lacustrine CH<sub>4</sub> 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<sub>4</sub>) (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<sub>4</sub> 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<sub>4</sub> and carbon dioxide (CO<sub>2</sub>)

**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s00027-019-0690-8>) contains supplementary material, which is available to authorized users.

✉ Taija Saarela  
taija.saarela@uef.fi

- <sup>1</sup> Department of Environmental and Biological Sciences, University of Eastern Finland, Yliopistonranta 1 E, 70210 Kuopio, Finland
- <sup>2</sup> Faculty of Engineering and Natural Sciences, Tampere University, Korkeakoulunkatu 6, 33720 Tampere, Finland
- <sup>3</sup> Ecosystems and Environment Research Programme, Faculty of Biological and Environmental Sciences, University of Helsinki, Viikinkaari 1, 00014 Helsinki, Finland
- <sup>4</sup> Institute of Atmospheric and Earth System Research (INAR)/Forest Sciences, Faculty of Agriculture and Forestry,

University of Helsinki, Viikinkaari 1, 00014 Helsinki, Finland

- <sup>5</sup> Helsinki Institute of Sustainability Science (HELSUS), Faculty of Biological and Environmental Sciences, University of Helsinki, Viikinkaari 1, 00014 Helsinki, Finland
- <sup>6</sup> Department of Biological and Environmental Sciences, University of Jyväskylä, Surfontie 9 C, 40014 Jyväskylä, Finland
- <sup>7</sup> Institute of Atmospheric and Earth System Research (INAR)/Physics, Faculty of Sciences, University of Helsinki, Gustaf Hällströmin katu 2, 00560 Helsinki, Finland

(Algesten et al. 2003). These processes are especially pronounced in boreal lakes with high loads of dissolved organic matter (DOM) from forested, peat-dominated catchment areas (Kortelainen 1993). Recent studies have shown an increasing trend in the lake and stream water dissolved organic C (DOC) concentrations throughout the boreal zone (Sarkkola et al. 2009; Couture et al. 2012; Pumpanen et al. 2014). This increase is mainly driven by changes in hydro-meteorology, i.e. precipitation and air temperature (Sarkkola et al. 2009; Pumpanen et al. 2014); thus, the significance of terrestrial organic C load to aquatic ecosystems might further increase under a changing climate.

In freshwater lakes, dissolved oxygen (DO) depletion due to the decomposition of organic matter (OM) creates suitable redox conditions for methanogenesis, in which  $\text{CH}_4$  is the final product of anaerobic OM decomposition in the absence of alternative electron acceptors (EAs), e.g. nitrate ( $\text{NO}_3^-$ ), sulphate ( $\text{SO}_4^{2-}$ ) and iron ( $\text{Fe}^{3+}$ ) (Capone and Kiene 1988). 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,  $\text{CH}_4$  can be either oxidized to  $\text{CO}_2$  by methane-oxidizing microbes, assimilated to biomass, or released to the atmosphere (Kuivila et al. 1988; Bastviken et al. 2002; Kankaala et al. 2006; Wik et al. 2016). The production and oxidation of  $\text{CH}_4$  are controlled by different environmental factors, such as temperature and the availability of oxygen ( $\text{O}_2$ ), 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  $\text{CH}_4$  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  $\text{CH}_4$  concentrations near the bottom due to favorable conditions for methanogenesis, and less favorable conditions for  $\text{CH}_4$  oxidation (Kankaala et al. 2007). However, this does not necessarily increase  $\text{CH}_4$  emissions to the atmosphere, because often a significant fraction of  $\text{CH}_4$  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  $\text{CH}_4$  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,  $\text{O}_2$  is available as EA and  $\text{CH}_4$  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  $\text{SO}_4^{2-}$ -dependent AOM is an efficient  $\text{CH}_4$  sink in marine environments (Knittel and Boetius 2009), several EAs, such as  $\text{NO}_3^-$ , nitrite ( $\text{NO}_2^-$ ),  $\text{SO}_4^{2-}$ ,  $\text{Fe}^{3+}$  and manganese ( $\text{Mn}^{4+}$ ), have been demonstrated to be important drivers of AOM in freshwaters (Sivan et al. 2011; Deutzmann et al. 2014; Norđi and Thamdrup 2014; Timmers et al. 2017). Nevertheless, the relevance of AOM in reducing  $\text{CH}_4$  emissions from freshwater lakes is still unclear and needs further research; e.g. Rissanen 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  $\text{CH}_4$  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  $\text{CH}_4$  dynamics are still required to forecast the future contributions of boreal lakes to the global  $\text{CH}_4$  budgets in a changing climate. Therefore, we applied stable isotope methods with  $^{13}\text{C}$ -labeled  $\text{CH}_4$ , as well as measurements of natural abundance of  $^{13}\text{C}$ - $\text{CH}_4$  and  $^{13}\text{C}$ -DIC (dissolved inorganic C), to reveal the controlling factors for  $\text{CH}_4$  production and oxidation in the water column of a typical seasonally  $\text{O}_2$ -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  $\text{CH}_4$  production and oxidation during the development of summer stratification, and hypolimnetic hypoxia, and (2) to determine the environmental and biological factors that may explain  $\text{CH}_4$  oxidation in the water column. We hypothesized that the  $\text{CH}_4$  oxidation takes place in the hypolimnion, when  $\text{O}_2$  is below the detection limit of traditional  $\text{O}_2$  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 km<sup>2</sup>, 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 km<sup>2</sup> 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>).

### O<sub>2</sub> concentration, water temperature and pH measurements

Vertical profiles of dissolved O<sub>2</sub> concentration (mg l<sup>-1</sup>), O<sub>2</sub> 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 O<sub>2</sub> l<sup>-1</sup> 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 dm<sup>3</sup>) 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 SO<sub>4</sub><sup>2-</sup> concentrations, and colorimetric analysis for the NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup> (NO<sub>x</sub><sup>-</sup>; Miranda et al. 2001) and NH<sub>4</sub><sup>+</sup> 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-V<sub>CPH</sub> (Shimadzu Corp., Kyoto, Japan). The concentrations of total iron (Tot Fe)/ferrous iron (Fe<sup>2+</sup>) (the depths of 0–11.5 m) and sulphide (S<sub>2</sub><sup>-</sup>) (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 CH<sub>4</sub> and CO<sub>2</sub> and stable isotopic analyses

The samples for the concentrations of CH<sub>4</sub> and CO<sub>2</sub> and stable isotopic analyses of CH<sub>4</sub> 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 CH<sub>4</sub> and CO<sub>2</sub> 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 CH<sub>4</sub> and CO<sub>2</sub> 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 δ<sup>13</sup>C-CH<sub>4</sub> 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 CH<sub>4</sub> (− 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 O <sub>2</sub> , CH <sub>4</sub> and CO <sub>2</sub>
18 July	Temperature, pH, the concentrations of O <sub>2</sub> , CH <sub>4</sub> , CO <sub>2</sub> , NO <sub>x</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> and SO <sub>4</sub> <sup>2-</sup> , δ <sup>13</sup> C-CH <sub>4</sub> , δ <sup>13</sup> C-DIC
15 August	Temperature, pH, the concentrations of O <sub>2</sub> , CH <sub>4</sub> , CO <sub>2</sub> , NO <sub>x</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> , SO <sub>4</sub> <sup>2-</sup> and DOC, δ <sup>13</sup> C-CH <sub>4</sub> , δ <sup>13</sup> C-DIC, <sup>13</sup> C-CH <sub>4</sub> oxidation experiment
5 September	Temperature, pH, the concentrations of O <sub>2</sub> , CH <sub>4</sub> , CO <sub>2</sub> , NO <sub>x</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> , Fe, SO <sub>4</sub> <sup>2-</sup> , S <sub>2</sub> <sup>-</sup> and DOC, δ <sup>13</sup> C-CH <sub>4</sub> , δ <sup>13</sup> C-DIC, <sup>13</sup> C-CH <sub>4</sub> oxidation experiment

Water samples for the natural abundance of  $\delta^{13}\text{C}$ -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  $\mu\text{l}$  of  $\text{H}_3\text{PO}_4$  (85%) to ensure the transformation of bicarbonate ions to  $\text{CO}_2$ . 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  $\delta^{13}\text{C}$ -DIC measurements were calibrated according to Coplen et al. (2006). The isotope results are reported in  $\delta$  units (‰) relative to the international Vienna Pee Dee Belemnite (VPDB) standard.

### $^{13}\text{CH}_4$ incubation experiment

The samples for  $^{13}\text{CH}_4$  oxidation measurement were collected from the water column from depths chosen on the basis of vertical profiles of  $\text{O}_2$ . In August, the samples were collected at 6 m (2.48  $\text{mg l}^{-1} \text{O}_2$ ), 11.5 m (1.35  $\text{mg l}^{-1} \text{O}_2$ ) and the sediment surface (0.59  $\text{mg l}^{-1} \text{O}_2$ ), and in September at 8 m (1.72  $\text{mg l}^{-1} \text{O}_2$ ), 10 m (0.59  $\text{mg l}^{-1} \text{O}_2$ ) and 11.5 m (0.44  $\text{mg l}^{-1} \text{O}_2$ ). 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  $\text{O}_2$  introduced during the sampling, 0.1 ml of  $^{13}\text{CH}_4$  trace gas mixture was injected to each sample and the vials were shaken vigorously, resulting in the estimated final concentration of 25  $\mu\text{mol l}^{-1} \text{CH}_4$  in each vial.  $^{13}\text{CH}_4$  trace gas mixture contained 140 ml of  $\text{N}_2$  and 10 ml of 99%  $^{13}\text{C}$ - $\text{CH}_4$  in a  $\text{N}_2$ -flushed,  $\text{O}_2$ -free glass bottle with NaOH powder to remove any contaminating  $\text{CO}_2$ . The disappearance of the  $^{13}\text{CH}_4$  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  $\mu\text{l}$  of  $\text{H}_3\text{PO}_4$  (85%) in the bottom. The samples were analyzed for  $^{13}\text{C}$ -DIC with Isoprime100 IRMS. The excess  $^{13}\text{C}$ -DIC was calculated from the difference between the

background  $^{13}\text{C}$ -DIC and the measured  $^{13}\text{C}$ -DIC for each time point. The excess  $^{13}\text{C}$ -DIC concentrations of each sampling depth were then plotted against time, and the slope of the line was used to describe the potential  $\text{CH}_4$  oxidation rate ( $\text{nmol l}^{-1} \text{day}^{-1}$ ). Considering that the incubations were amended with  $^{13}\text{C}$ - $\text{CH}_4$  above ambient levels (0.02–0.9  $\mu\text{mol l}^{-1}$  in Lake Kuivajärvi), and that the proportion of  $\text{CH}_4$ -C bound to the microbial biomass was not measured, these values represent a potential or conservative rate.

### Statistical analysis

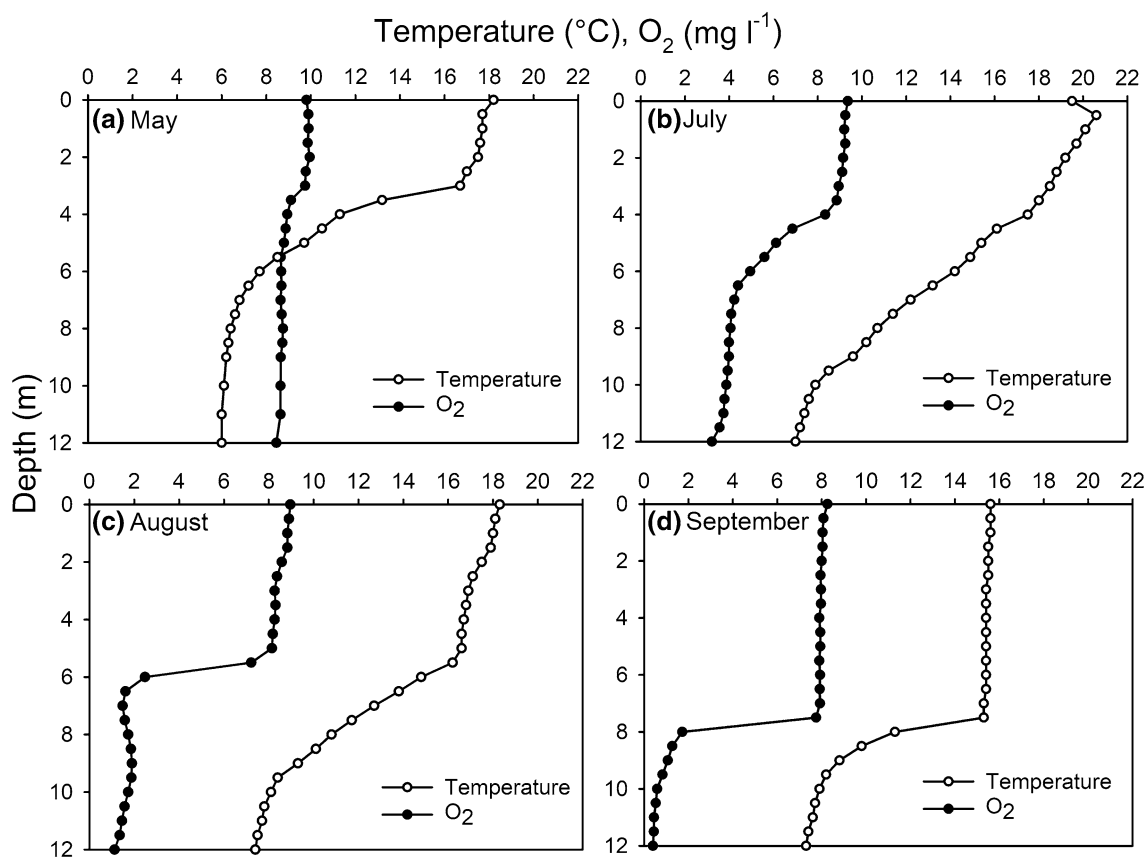
Two-tailed Spearman correlations were calculated between the gas concentrations/stable isotope values and variables such as depth,  $\text{O}_2$ , temperature, pH,  $\text{NO}_x^-$ ,  $\text{NH}_4^+$ ,  $\text{Fe}^{3+}$ ,  $\text{SO}_4^{2-}$ , and DOC. Spearman's rank correlation coefficient was chosen 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  $^{13}\text{C}$ -DIC production and incubation time in the  $^{13}\text{CH}_4$  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 ( $< 2 \text{ mg l}^{-1}$ ) were detected below 6 m depth in August (Fig. 1c), and below 8 m depth in the beginning of September (Fig. 1d).



**Fig. 1** Depth profiles of water temperature (°C) and O<sub>2</sub> concentration (mg l<sup>-1</sup>) in **a** May, **b** July, **c** August and **d** September

### Depth profiles of water-quality variables

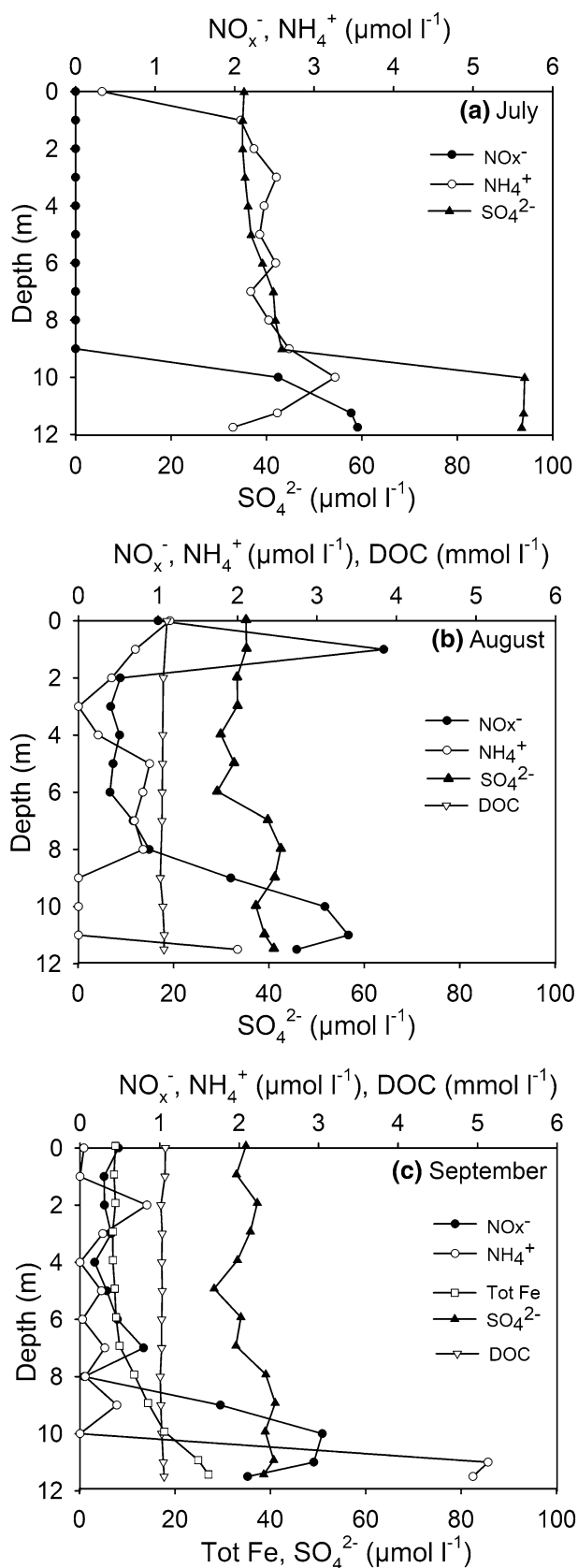
In every sampling occasion, the NO<sub>x</sub><sup>-</sup> concentrations peaked in the hypolimnion (max. 3.5 μmol l<sup>-1</sup>), while the concentrations were mainly < 1 μmol l<sup>-1</sup> at the depths of 0–8 m in August and September (Fig. 2b, c), and below the detection limit in July (Fig. 2a). The NH<sub>4</sub><sup>+</sup> concentrations remained mainly at < 2.5 μmol l<sup>-1</sup>, but in September, the hypolimnetic concentrations peaked to 5 μmol l<sup>-1</sup> (Fig. 2c). In September, Total Fe concentrations slightly increased towards the hypolimnion (max. 27 μmol l<sup>-1</sup>; Fig. 2c). The SO<sub>4</sub><sup>2-</sup> concentrations stayed mainly between 30–45 μmol l<sup>-1</sup> throughout the water column, except in July when the hypolimnetic concentrations of SO<sub>4</sub><sup>2-</sup> peaked to 94 μmol l<sup>-1</sup> (Fig. 2a). In September, S<sub>2</sub><sup>-</sup> was not detected in the water column. DOC concentrations remained at < 1.1 mmol l<sup>-1</sup>, being highest in the epilimnion (Fig. 2b, c).

### Depth profiles of CH<sub>4</sub> and CO<sub>2</sub>

The epilimnetic CH<sub>4</sub> concentrations were stable at approximately 0.1 μmol l<sup>-1</sup> during the whole study period, while the concentrations in the metalimnion and hypolimnion changed seasonally. In early summer, the CH<sub>4</sub>

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<sup>-1</sup>; Fig. 3a) and at 6 m depth in July and August (0.151 ± 0.013 μmol l<sup>-1</sup> and 0.132 ± 0.002 μmol l<sup>-1</sup>; Fig. 3b, c). Below the peak, the CH<sub>4</sub> concentrations started to decrease towards the bottom, until they slightly increased again at 11 m depth. In contrast, the CH<sub>4</sub> concentrations in September were relatively low in the epilimnion and metalimnion but peaked in the hypoxic hypolimnion (0.91 ± 0.07 μmol l<sup>-1</sup>; Fig. 3d). The CH<sub>4</sub> concentration correlated positively with water temperature, pH and the NH<sub>4</sub><sup>+</sup> concentration, and negatively with the water column depth and the concentrations of NO<sub>x</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> (Table 2).

There was a negative correlation between the CH<sub>4</sub> and CO<sub>2</sub> 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<sub>2</sub> concentrations remained stable from May to September, while the CO<sub>2</sub> concentrations in the hypolimnion clearly increased from spring (0.179 ± 0.004 mmol l<sup>-1</sup>; Fig. 3a) to autumn (0.370 ± 0.008 mmol l<sup>-1</sup>; Fig. 3d). In May and July, the CO<sub>2</sub> concentrations started to increase below 3 m depth (Fig. 3a, b), whereas in August and September, the CO<sub>2</sub> concentrations increased simultaneously with the decreasing O<sub>2</sub>



**Fig. 2** Concentrations of  $\text{NO}_x^-$ ,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  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

concentrations (Fig. 3c, d). Throughout the sampling period, the  $\text{CO}_2$  concentration correlated negatively with water temperature, pH and the  $\text{O}_2$  concentration. There was also a positive correlation for  $\text{CO}_2$  with the water column depth,  $\text{NO}_x^-$  and  $\text{SO}_4^{2-}$ . In addition, the  $\text{CO}_2$  and  $\text{Fe}^{3+}$  concentrations correlated positively in September (Table 2).

### Depth profiles of $\delta^{13}\text{C}\text{-CH}_4$ and $\delta^{13}\text{C}\text{-DIC}$

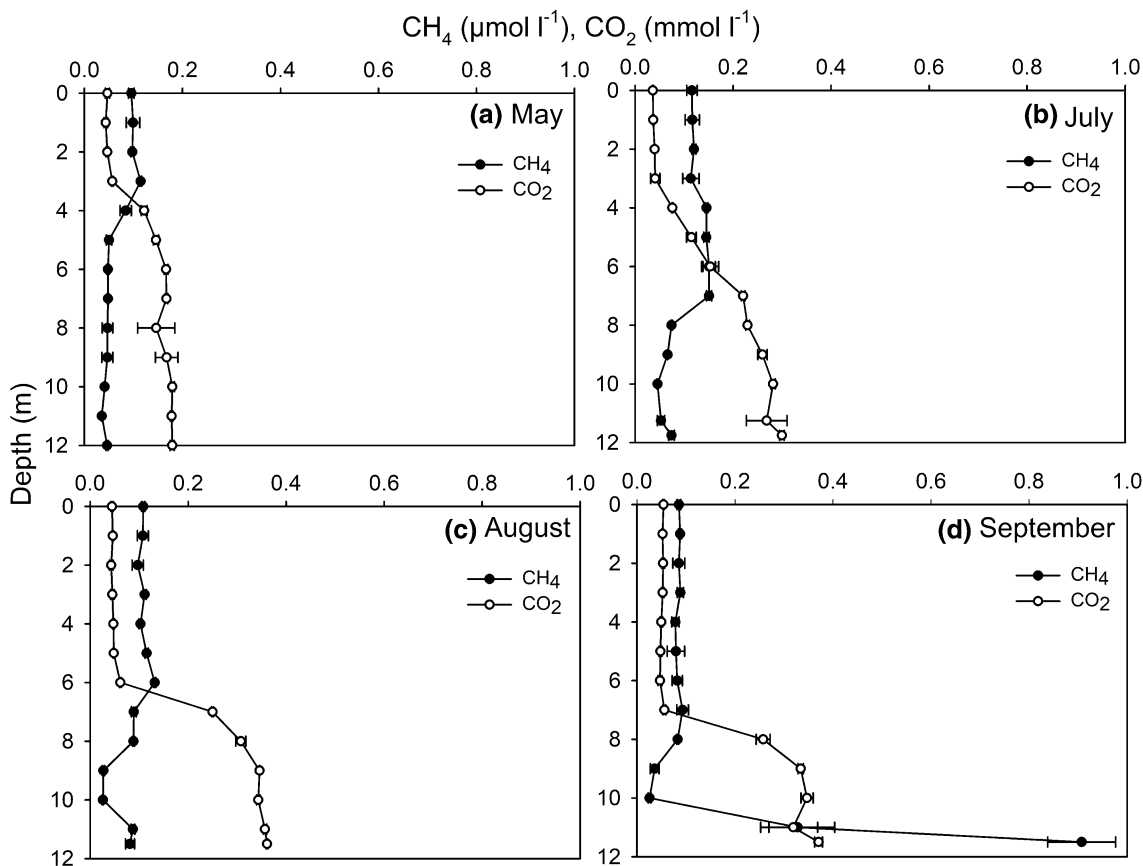
There was a substantial temporal variation in the depth profiles of  $\delta^{13}\text{C}\text{-CH}_4$ . In the hypolimnion,  $\delta^{13}\text{C}\text{-CH}_4$  decreased from  $-36.8 \pm 0.2\text{‰}$  in July (Fig. 4a) to  $-71.5 \pm 1.8\text{‰}$  in September (Fig. 4c). In August and September, the maximum  $\delta^{13}\text{C}\text{-CH}_4$  values were detected close to the oxycline at 9 m depth ( $-51.8 \pm 1.2\text{‰}$  and  $-37.6 \pm 2.0\text{‰}$ , respectively). There was a significant negative correlation for the  $\delta^{13}\text{C}\text{-CH}_4$  with water temperature, pH, DOC concentration and  $\text{CH}_4$  concentration, while the  $\delta^{13}\text{C}\text{-CH}_4$  correlated positively with the  $\text{SO}_4^{2-}$  concentration (Table 2).

Similarly to the profiles of  $\text{CO}_2$  and  $\text{CH}_4$ , the depth profiles of  $\delta^{13}\text{C}\text{-CH}_4$  and  $\delta^{13}\text{C}\text{-DIC}$  were reflections of each other, and the  $\delta^{13}\text{C}\text{-DIC}$  values generally decreased from summer to autumn. The  $\delta^{13}\text{C}\text{-DIC}$  ranged from  $-6.8 \pm 0.7\text{‰}$  to  $-17.5 \pm 0.9\text{‰}$  in the epilimnion, and from  $-21.5 \pm 0.4\text{‰}$  to  $-29.3 \pm 0.1\text{‰}$  in the hypolimnion. In August and September, a notable decrease of  $\delta^{13}\text{C}\text{-DIC}$  occurred at the depths of 6–7 m (Fig. 4b, c), simultaneously with sudden  $\text{O}_2$  depletion, while in July the decrease of  $\delta^{13}\text{C}\text{-DIC}$  towards the bottom was more stable (Fig. 4a). The  $\delta^{13}\text{C}\text{-DIC}$  values correlated positively with water temperature, the  $\text{O}_2$  concentration and pH, whereas the  $\delta^{13}\text{C}\text{-DIC}$  correlated negatively with water column depth and the concentrations of  $\text{NO}_x^-$ ,  $\text{Fe}^{3+}$ ,  $\text{SO}_4^{2-}$  and  $\text{CO}_2$  (Table 2).

### The extent and potential rates of $\text{CH}_4$ oxidation

In August, the estimated fraction of  $\text{CH}_4$  oxidized in the water column was 34% (calculated from the difference between  $\delta^{13}\text{C}\text{-CH}_4$  at the bottom and the maximum value of  $\delta^{13}\text{C}\text{-CH}_4$  at 9 m, as described in Kankaala et al. 2007). In September, the corresponding proportion was 91%.

Potential  $\text{CH}_4$  oxidation was detected in September. Potential  $\text{CH}_4$  oxidation rates increased with depth from  $10.8 \pm 3.4 \text{ nmol l}^{-1} \text{ day}^{-1}$  at 8 m ( $p < 0.006^{**}$ ) to  $34.8 \pm 12.3 \text{ nmol l}^{-1} \text{ day}^{-1}$  at 11.5 m ( $p < 0.012^*$ ; Fig. 5). In contrast, the results from August did not show clear evidence of  $\text{CH}_4$  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. 3** Depth profiles of CH<sub>4</sub> and CO<sub>2</sub> in **a** May, **b** July, **c** August and **d** September. Concentrations are presented as averages ± standard deviations (n=2 or 3)

**Table 2** Spearman’s rank correlations between the average gas concentrations (n=52) and stable isotopic values (n=39) of CH<sub>4</sub> and CO<sub>2</sub>, water column depth, temperature, the O<sub>2</sub> concentration, pH (n=52), and the concentrations of DOC (n=23), NO<sub>x</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup> (n=39) and Fe<sup>3+</sup> (n=13)

	CH <sub>4</sub> –concentration	CO <sub>2</sub> concentration	δ <sup>13</sup> C-CH <sub>4</sub>	δ <sup>13</sup> C-DIC
Depth	- 0.490**	0.884**	n.s	- 0.872**
Temperature	0.638**	- 0.839**	- 0.332*	0.927**
O <sub>2</sub>	n.s	- 0.776**	n.s	0.975**
pH	0.625**	- 0.773**	- 0.347*	0.813**
DOC	n.s	n.s	- 0.444*	n.s
NO <sub>x</sub> <sup>-</sup>	- 0.403*	0.519**	n.s	- 0.494**
NH <sub>4</sub> <sup>+</sup>	0.396*	n.s	n.s	n.s
SO <sub>4</sub> <sup>2-</sup>	- 0.330*	0.705**	0.351*	- 0.652**
Fe <sup>3+</sup>	n.s	0.863**	n.s	- 0.802**
CH <sub>4</sub>		- 0.462**	- 0.726**	n.s
CO <sub>2</sub>	- 0.462**		n.s	- 0.946**

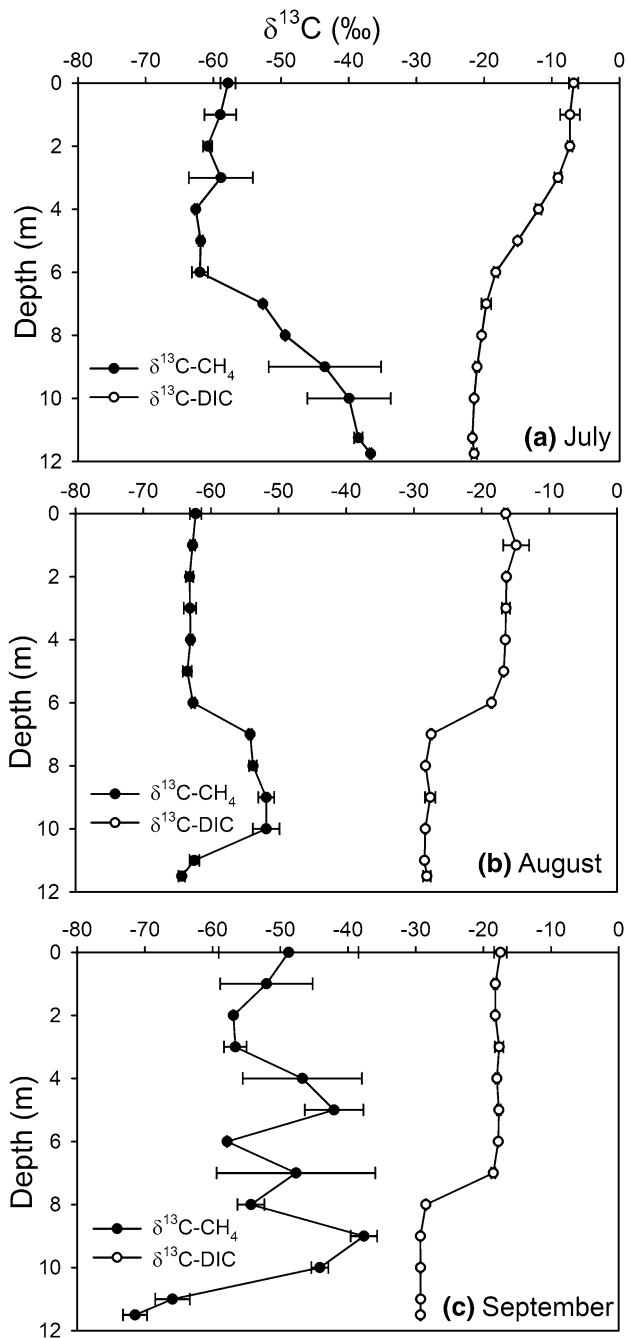
\*Correlation is significant at the p < 0.05 level (2-tailed)

\*\*Correlation is significant at the p < 0.01 level (2-tailed)

increased linearly with time (p > 0.349), but the large

variation between replicates complicated interpretation of results and thus, CH<sub>4</sub> oxidation during August cannot be confirmed (Fig. S2).



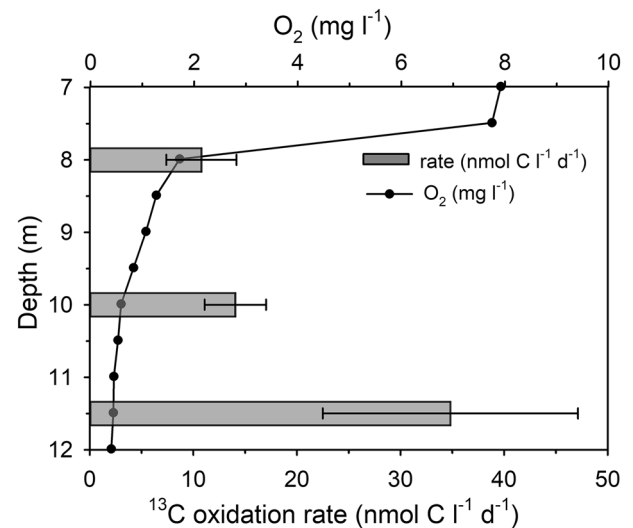


**Fig. 4** Depth profiles of  $\delta^{13}\text{C-CH}_4$  and  $\delta^{13}\text{C-DIC}$  (‰) in **a** July, **b** August and **c** September. Values are presented as averages  $\pm$  standard deviations ( $n=2$  or  $3$ )

## Discussion

### The vertical distribution of $\text{CH}_4$ in the water column

The epilimnetic concentrations of  $\text{CH}_4$  were similar to those previously recorded in Lake Kuivajärvi (Miettinen et al. 2015) and in Finnish lakes in general (e.g. 207 lakes studied



**Fig. 5** The  $\text{O}_2$  concentration ( $\text{mg l}^{-1}$ ) and the potential  $\text{CH}_4$  oxidation rates ( $\text{nmol C l}^{-1} \text{d}^{-1}$ )  $\pm$  standard errors determined with  $^{13}\text{C-CH}_4$ -tracer in September ( $n=18$  at the depths of 8 and 11.5 m, and  $n=17$  at 10 m depth)

by Juutinen et al. 2009). The hypolimnetic  $\text{CH}_4$  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  $\text{CH}_4$  were probably caused by the well-oxygenated water column in early summer.

From May to August, the highest concentrations of  $\text{CH}_4$  occurred in the upper water layers and the lowest concentrations in the hypolimnion. Even though the  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  in the oxic water column seems more likely.

Although the  $\text{CH}_4$  concentrations did not correlate with the  $\text{O}_2$  conditions, simultaneous changes in the depth profiles of  $\text{CH}_4$  and nutrients (i.e.  $\text{NO}_x^-$ ,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$ ; Table 2) suggest that the availability of  $\text{O}_2$  was a major factor regulating both  $\text{CH}_4$  and nutrient concentrations in the water column. In the summer, well-oxygenated water column created favorable conditions for aerobic nitrification and oxidation of  $\text{S}_2^-$  to  $\text{SO}_4^{2-}$ , 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  $\delta^{13}\text{C}\text{-CH}_4$  values agreed with previous studies in boreal lakes (e.g. Bastviken et al. 2002, 2008; Kankaala et al. 2007). The  $\delta^{13}\text{C}\text{-CH}_4$  decreased with increases in CH<sub>4</sub> concentration. Also, increases in temperature and DOC were associated with decreasing  $\delta^{13}\text{C}\text{-CH}_4$  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, CH<sub>4</sub> production at the lake bottom was visible from the  $\delta^{13}\text{C}\text{-CH}_4$  profiles. The hypolimnetic decrease of  $\delta^{13}\text{C}\text{-CH}_4$  was substantial, particularly with maximum CH<sub>4</sub> concentrations in September, which is consistent with biogenic CH<sub>4</sub> being strongly <sup>13</sup>C-depleted due to fractionation (Whiticar 1999). In July, <sup>13</sup>C-enriched values of CH<sub>4</sub> (− 37 ‰) at the lake bottom indicate that most of CH<sub>4</sub> was formed and consumed within the sediment (Whiticar 1999).

Throughout the study period, the increases in CO<sub>2</sub> with depth, simultaneously with decreasing  $\delta^{13}\text{C}\text{-DIC}$  and O<sub>2</sub> concentration, indicate consumption of O<sub>2</sub> and production of CO<sub>2</sub> through in situ decomposition of OM in the hypolimnion (Miettinen et al. 2015). Furthermore, the decomposition of OM releases nutrients, such as NO<sub>3</sub><sup>−</sup> (McManus, Heinen and Baehr 2003), thus explaining the positive relationship between CO<sub>2</sub> and NO<sub>x</sub><sup>−</sup>.

In this study, we did not directly estimate the lake-atmosphere C gas exchange in Lake Kuivajärvi. However, the measured surface water CH<sub>4</sub> and CO<sub>2</sub> 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 CH<sub>4</sub> and CO<sub>2</sub> to the atmosphere (the 2-year mean for CH<sub>4</sub> approx. 0.06 mol m<sup>−2</sup> y<sup>−1</sup> and for CO<sub>2</sub> 25.5 mol m<sup>−2</sup> y<sup>−1</sup>).

### Water column CH<sub>4</sub> oxidation and future perspectives in a changing climate

The transition of the active CH<sub>4</sub> oxidation zone was clearly indicated by the  $\delta^{13}\text{C}\text{-CH}_4$  profiles. In July, CH<sub>4</sub> remained <sup>13</sup>C-enriched at the bottom, suggesting that CH<sub>4</sub> was already oxidized in the sediment, because CH<sub>4</sub> oxidation leaves a residual CH<sub>4</sub> enriched in <sup>13</sup>C (Whiticar 1999). During August and September, the most <sup>13</sup>C-enriched values of CH<sub>4</sub> were detected close to the oxycline, indicating the transition of CH<sub>4</sub> oxidation from the sediment to the water column.

The estimated proportion of CH<sub>4</sub> oxidized within the water column was 34% in August and 91% in September. The high efficiency of CH<sub>4</sub> oxidation agrees well with previous studies, where the proportions of CH<sub>4</sub> 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 CH<sub>4</sub>, these results show that methanotrophic activity substantially reduces CH<sub>4</sub> emissions from this typical, seasonally stratified lake.

In September, the potential CH<sub>4</sub> oxidation rates gradually increased from the oxycline (8 m) to the hypoxic hypolimnion (11.5 m). Simultaneously,  $\delta^{13}\text{C}\text{-CH}_4$  strongly decreased, while  $\delta^{13}\text{C}\text{-DIC}$  remained stable. Although the highest CH<sub>4</sub> oxidation rates are typically observed at the oxycline in the presence of O<sub>2</sub> (Kankaala et al. 2006; Oswald et al. 2015), the maximum rates in the hypolimnion could be explained by the higher ambient concentration of CH<sub>4</sub> (0.9 μmol l<sup>−1</sup>) at 11.5 m depth sustaining a larger population of methanotrophs (Sundh et al. 2005; Bastviken et al. 2008). However, the CH<sub>4</sub> pool turnover time in September, calculated by dividing the CH<sub>4</sub> concentration with the potential CH<sub>4</sub> 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 CH<sub>4</sub> oxidation rates in Lake Kuivajärvi to other stratified systems (Milucka et al. 2015; Oswald et al. 2015, 2016), and assuming that the potential CH<sub>4</sub> oxidation rate is proportional to the concentration of the added <sup>13</sup>CH<sub>4</sub> tracer, the maximum CH<sub>4</sub> oxidation rates in Lake Kuivajärvi were approximately 5–8 times lower than in those lakes. Again, the higher ambient concentrations of CH<sub>4</sub> (10–100-fold) in those systems most likely sustained a larger population of methanotrophs, thus leading to higher CH<sub>4</sub> oxidation rates.

As noted in previous anoxic incubation studies (Blees et al. 2014; Noröi and Thamdrup 2014; Rissanen et al. 2017), possibility of minor O<sub>2</sub> contamination from the tracer injection cannot be excluded even with originally anoxic freshwater samples. Also, there might have been some residual O<sub>2</sub> available for CH<sub>4</sub> oxidation close to the detection limit of O<sub>2</sub> sensor. Indeed, the maximum CH<sub>4</sub> oxidation rates in the hypolimnion imply that episodic appearance of O<sub>2</sub> (e.g. downwelling of oxygenated water) in otherwise hypoxic layers potentially fueled methanotrophy below the oxycline, thus stimulating microaerobic CH<sub>4</sub> 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; Pumpanen et al. 2014; Kiuru et al. 2018), the accelerated decomposition of OM might emphasize the role of alternative inorganic EAs in CH<sub>4</sub> oxidation. The development of summer stratification, on the other hand, suggests that the annual CH<sub>4</sub> emissions will remain largely regulated by aerobic CH<sub>4</sub> 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; Rösner 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<sub>2</sub> conditions in boreal lakes, showing that earlier thermal stratification with cold hypolimnion delays the period of hypolimnetic hypoxia and thus limits CH<sub>4</sub> production.

### Conclusions

The zone of CH<sub>4</sub> oxidation ascended from the sediment to the water column in the late phases of summer stratification, and our results showed that the CH<sub>4</sub> oxidation potential was highest in the hypoxic hypolimnion. During hypolimnetic hypoxia, 91% of available CH<sub>4</sub> was oxidized in the active CH<sub>4</sub> oxidation zone, while 9% was potentially released to the atmosphere. Even though lakes represent an important natural source of atmospheric CH<sub>4</sub> 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<sub>4</sub> 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<sub>4</sub> 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 Vesitekniiikan tuki ry (Grant No. 34348) for TS, Academy of Finland (project No. 286642 for AJR, project No. 275127 for HJ, 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/10.1111/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<sub>4</sub> 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<sub>2</sub> and CH<sub>4</sub> 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, Kirf MK et al (2014) Micro-aerobic bacterial methane oxidation in the chemocline 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, Merante A et al (2014) Oxidic water column methanogenesis as a major component of aquatic CH<sub>4</sub> fluxes. *Nat Commun* 5:5350. <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, Gehre M, Gröning M, Meijer HA, Toman B et al (2006) New guidelines for  $\delta^{13}\text{C}$  measurements. *Anal Chem* 78:2439–2441. <https://doi.org/10.1021/ac052027c>
- 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, Søndergaard M et al (2018) Synergy between nutrients and warming enhances methane ebullition from experimental lakes. *Nat Clim Change* 8:156–160. <https://doi.org/10.1038/s41558-017-0063-z>
- Deutzmann JS, Stief P, Brandes J, Schink B (2014) Anaerobic methane oxidation coupled to denitrification is the dominant methane sink in a deep lake. *Proc Natl Acad Sci* 111:18273–18278. <https://doi.org/10.1073/pnas.1411617111>
- Dinsmore KJ, Wallin MB, Johnson MS, Billett MF, Bishop K, Pumpanen J, Ojala A (2013) Contrasting CO<sub>2</sub> concentration discharge dynamics in headwater streams: a multi-catchment comparison. *J Geophys Res Biogeosci* 118:445–461. <https://doi.org/10.1002/jgrg.20047>
- Duc NT, Crill P, Bastviken D (2010) Implications of temperature and sediment characteristics on methane formation and oxidation in lake sediments. *Biogeochemistry* 100:185–196. <https://doi.org/10.1007/s10533-010-9415-8>
- Eller G, Känel L, Krüger M (2005) Cooccurrence of aerobic and anaerobic methane oxidation in the water column of Lake Plußsee. *Appl Environ Microb* 71:8925–8928. <https://doi.org/10.1128/AEM.71.12.8925-8928.2005>
- Fallon RD, Harrits S, Hanson RS, Brock TD (1980) The role of methane 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, Stepanenko V, Erkkilä KM, Miettinen H et al (2015) Effects of water clarity on lake stratification and lake-atmosphere heat exchange. *J Geophys Res Atmos* 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. *Biogeochemistry* 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, Peltomaa 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/10.1029/2006JG000336>
- 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, Kämäräinen M, Vesala T et al (2018) Effects of climate change on CO<sub>2</sub> concentration and efflux in a humic boreal lake: a modeling study. *J Geophys Res Biogeosci* 123:2212–2233. <https://doi.org/10.1029/2018JG004585>
- 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, Mattson T (2008) Increased organic C and N leaching in a northern boreal river basin in Finland. *Global Biogeochem Cycles* 22:GB3029. <https://doi.org/10.1029/2007G B003175>
- Lin JL, Joye SB, Scholten JC, Schäfer H, McDonald IR, Murrell JC (2005) Analysis of methane monooxygenase genes in Mono Lake suggests that increased methane oxidation activity may correlate with a change in methanotroph community structure. *Appl Environ Microb* 71:6458–6462. <https://doi.org/10.1128/AEM.71.10.6458-6462.2005>
- Magee 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, Zdorovennova G, Ojala A, Erkkilä KM, Zdorovennov 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, Smemo KA, Thalasso F (2018) Ubiquitous and significant anaerobic oxidation of methane in freshwater lake sediments. *Water Res* 144:332–340. <https://doi.org/10.1016/j.watres.2018.07.053>
- McGinnis 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, Pumpanen J, 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 CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O 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, Lahtinen M et al (2015) Trends in the average temperature in Finland, 1847–2013. *Stoch Environ Res Risk Assess* 29:1521–1529. <https://doi.org/10.1007/s00477-014-0992-2>
- Milucka J, Kirf M, Lu L, Krupke A, Lam P, Littmann S et al (2015) Methane oxidation coupled to oxygenic photosynthesis in anoxic waters. *ISME J* 9:1991–2002. <https://doi.org/10.1038/ismej.2015.12>
- 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>
- Murase J, Sakai Y, Sugimoto A, Okubo K, Sakamoto M (2003) Sources of dissolved methane in Lake Biwa. *Limnology* 4:91–99. <https://doi.org/10.1007/s10201-003-0095-0>
- Norði K, 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.0132574>
- 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/lno.10312>
- Pirinen P, Simola H, Aalto J, Kaukoranta JP, Karlsson P, Ruuhela R (2012) Climatological Statistics of Finland 1981–2010. Reports 2012: 1, Finnish Meteorological Institute, Helsinki
- Pumpanen J, Linden A, Miettinen H, Kolari P, Ilvesniemi H, Mammarella I et al (2014) Precipitation and net ecosystem exchange are the most important drivers of DOC flux in upland boreal catchments. *J Geophys Res Biogeosci* 119:1861–1878. <https://doi.org/10.1002/2014JG002705>
- Rasilo T, Prairie YT, del Giorgio PA (2015) Large-scale patterns in summer diffusive CH<sub>4</sub> fluxes across boreal lakes, and contribution to diffusive C emissions. *Glob Change Biol* 21:1124–1139. <https://doi.org/10.1111/gcb.12741>
- Rissanen AJ, Karvinen A, Nykänen H, Peura S, Tiirola M, Mäki A et al (2017) Effects of alternative electron acceptors on the activity and community structure of methane-producing and consuming microbes in the sediments of two shallow boreal lakes. *FEMS Microbiol Ecol*. <https://doi.org/10.1093/femsec/fix078>
- Rissanen AJ, Saarenheimo J, Tiirola M, Peura S, Aalto SL, Karvinen A et al (2018) Gammaproteobacterial methanotrophs dominate methanotrophy in aerobic and anaerobic layers of boreal lake waters. *Aquat Microb Ecol* 81:257–276. <https://doi.org/10.3354/ame01874>
- Rösner RR, Müller-Navarra DC, Zorita E (2012) Trend analysis of weekly temperatures and oxygen concentrations during summer stratification in Lake Plußsee: a long-term study. *Limnol Oceanogr* 57:1479–1491. <https://doi.org/10.4319/lo.2012.57.5.1479>
- Rudd JW, Hamilton RD, Campbell NE (1974) Measurement of microbial oxidation of methane in lake water. *Limnol Oceanogr* 19:519–524. <https://doi.org/10.4319/lo.1974.19.3.0519>
- Ruosteenoja K, Jylhä K, Kämäräinen M (2016) Climate projections for Finland under the RCP forcing scenarios. *Geophysica* 51:17–50
- Sarkkola S, Koivusalo H, Laurén A, Kortelainen P, Mattson T, Palviainen M et al (2009) Trends in hydrometeorological conditions and stream water organic carbon in boreal forested catchments. *Sci Total Environ* 408:92–101. <https://doi.org/10.1016/j.scitotenv.2009.09.008>
- Schubert CJ, Vazquez F, Lösekann-Behrens T, Knittel K, Tonolla 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/archiv-hydrobiol/151/2001/157>
- Sivan O, Adler M, Pearson A, Gelman F, Bar-Or 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, Vesala 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, Koehorst JJ, Plugge 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, Creamer KP, Jones SE (2016) Productivity and depth regulate lake contributions to atmospheric methane. *Limnol Oceanogr*. <https://doi.org/10.1002/lno.10247>
- Whiticar MJ (1999) Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chem Geol* 161:291–314. [https://doi.org/10.1016/S0009-2541\(99\)00092-3](https://doi.org/10.1016/S0009-2541(99)00092-3)
- Wik 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>
- Wik 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.