



Emission and oxidation of methane in a meromictic, eutrophic and temperate lake (Dendre, Belgium)



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HIGHLIGHTS

- The studied lake was meromictic and characterized by high methane, nutrients and sulfate concentrations in the water column.
- High aerobic and anaerobic methane oxidation rates were observed in the water column, and were dependent on the season.
- Anaerobic methane oxidation was linked to sulfate reduction, and potentially to nitrate reduction.
- Despite high methane oxidation rates, methane fluxes to the atmosphere were high.

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ABSTRACT

We sampled the water column of the Dendre stone pit lake (Belgium) in spring, summer, autumn and winter. Depth profiles of several physico-chemical variables, nutrients, dissolved gases (CO₂, CH₄, N₂O), sulfate, sulfide, iron and manganese concentrations and δ¹³C-CH₄ were determined. We performed incubation experiments to quantify CH₄ oxidation rates, with a focus on anaerobic CH₄ oxidation (AOM), without and with an inhibitor of sulfate reduction (molybdate). The evolution of nitrate and sulfate concentrations during the incubations was monitored. The water column was anoxic below 20 m throughout the year, and was thermally stratified in summer and autumn. High partial pressure of CO₂ and CH₄ and high concentrations of ammonium and phosphate were observed in anoxic waters. Important nitrous oxide and nitrate concentration maxima were also observed (up to 440 nmol L⁻¹ and 80 μmol L⁻¹, respectively). Vertical profiles of δ¹³C-CH₄ unambiguously showed the occurrence of AOM. Important AOM rates (up to 14 μmol L⁻¹ d⁻¹) were observed and often co-occurred with nitrate consumption peaks, suggesting the occurrence of AOM coupled with nitrate reduction. AOM coupled with sulfate reduction also occurred, since AOM rates tended to be lower when molybdate was added. CH₄ oxidation was mostly aerobic (~80% of total oxidation) in spring and winter, and almost exclusively anaerobic in summer and autumn. Despite important CH₄ oxidation rates, the estimated CH₄ fluxes from the water surface to the atmosphere were high (mean of 732 μmol m⁻² d⁻¹ in spring, summer and autumn, and up to 12,482 μmol m⁻² d⁻¹ in winter).

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1. Introduction

Methane (CH₄) is known to be an important natural and anthropogenic greenhouse gas. CH₄ concentrations in the atmosphere have increased dramatically during the 20th century to reach 1850 ppb in 2015, mainly due to human activities

(agriculture, waste disposal and energy extraction and production) (IPCC, 2013; Kirschke et al., 2013; NOAA, 2015). In natural environments, CH₄ is anaerobically produced by methanogenic archaea. The total CH₄ emission to the atmosphere has been estimated to 540 Tg CH₄ yr⁻¹, with a significant contribution from inland waters (Bastviken et al., 2011; Borges et al., 2015; Holgerson and Raymond, 2016). The actual amount of CH₄ produced is higher, as a significant fraction of CH₄ produced is biologically oxidized before reaching the atmosphere (Bastviken et al., 2002). CH₄ oxidation limits the flux of CH₄ to the atmosphere, and in inland waters can fuel a

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microbial based food-web (Jones and Grey, 2011).

CH₄ oxidation can be performed under both aerobic and anaerobic conditions. It is now commonly assumed that anaerobic CH₄ oxidation (AOM) can occur with different final electron acceptors: sulfate (SO₄²⁻), nitrate (NO₃⁻), nitrite (NO₂⁻), iron (Fe) and/or manganese (Mn) (Borrel et al., 2011). In seawater, NO₃⁻ concentrations are low (usually < 5 μmol L⁻¹), while SO₄²⁻ concentrations are much higher (~30 mmol L⁻¹). Also, Fe and Mn concentrations (on the order of pmol L⁻¹) in seawater are negligible compared to SO₄²⁻ concentrations. So, even if denitrification, Fe- and Mn-reduction are thermodynamically more favorable than SO₄²⁻ reduction, the latter remains the main anaerobic pathway for the degradation of organic matter in the oceans, including the degradation of CH₄. While AOM is thus generally coupled to SO₄²⁻ reduction (SDMO) in marine waters and sediments (e.g. Iversen and Jørgensen, 1985; Boetius et al., 2000; Jørgensen et al., 2001), other electron acceptors of AOM have been much less frequently studied in freshwater systems. Due to low the SO₄²⁻ concentrations usually observed in freshwaters environments, AOM is often considered to be negligible compared to aerobic CH₄ oxidation (Rudd et al., 1974). However, AOM in freshwaters can also be coupled to NO₂⁻ and NO₃⁻ reduction (NDMO), which is thermodynamically much more favorable than SDMO (free Gibbs energy of -928, -765 and -17 kJ mol⁻¹ CH₄, with NO₂⁻, NO₃⁻ and SO₄²⁻ reduction, respectively; Raghoebarsing et al., 2006; Borrel et al., 2011). NDMO has been observed in experimental environments with enrichment of bacteria of interest (e.g. Ettwig et al., 2010; Hu et al., 2011; Haroon et al., 2013), or in sediments cultures with electron acceptors added (e.g. Deutzmann and Schink, 2011; á Norði and Thamdrup, 2014). Despite numerous laboratory observations, the significance of NDMO in natural environments is still largely unknown. Although AOM coupled with Fe- and Mn-reduction (FDMO and MDMO, respectively) has been proposed to occur in various freshwater environments (e.g. ferruginous lakes Matano and Kinneret; Crowe et al., 2011; Sivan et al., 2011; á Norði et al., 2013), to our knowledge no direct rate measurements have been reported in the literature.

In this study, we investigated biogeochemistry of the water column of Dendre stone pit lake (Belgium), a relatively deep (maximum depth 30 m) but small (0.032 km²) water body in a former limestone quarry, with a focus on quantifying AOM rates and related electron acceptors. This lake was chosen to be an ideal system for studying AOM dynamics because it is known to be meromictic (waters anoxic below 20 m depth throughout the year) and rich in both organic matter (eutrophic) and sulfide (HS⁻) in the anoxic layers. The lake is fed by springs at 7 and 18 m depth, providing potentially NO₃⁻ rich groundwater due to generalized fertilizer contamination that is common in Belgium (SPW-DGO3, 2015). We thus hypothesized that high organic matter supply and bottom layer anoxia sustain high methanogenesis rates, and that CH₄ production is removed by SDMO and/or NDMO based on occurrence of high HS⁻ concentrations, and potentially high NO₃⁻ concentrations.

2. Material and methods

2.1. Physico-chemical parameters and sampling

Sampling in the Dendre stone pit lake (50.6157°N, 3.7949°E) was carried out in spring (May 2014), summer (August 2014), winter (February 2015) and autumn (October 2015). Depth profiles of dissolved oxygen (O₂) concentrations, temperature, pH and specific conductivity were obtained with Yellow Springs Instrument 6600 V2 and Hydrolab DS5 multiparameter probes. The conductivity, pH and oxygen probes were calibrated the day before

each sampling using the protocols and standards recommended by the manufacturer.

2.2. CH₄ oxidation measurements and water column chemical analyses

At each depth of interest, duplicate samples for N₂O and CH₄ concentration analyses were collected in 60 mL glass serum bottles from a Niskin bottle through a silicon tube connected to the outlet, left to overflow, poisoned with 200 μL of a saturated HgCl₂ solution and immediately sealed with butyl stoppers and aluminium caps. Ten other bottles per depth were incubated in the dark and constant temperature (close to in-situ temperature): five of them received 250 μL of a solution of molybdate (1 mol L⁻¹, hence a final concentration of 4 mmol L⁻¹), an inhibitor of sulfur-reducing bacteria and five received no treatment. The biological activity of two incubated bottles (one from each treatment) was stopped at 12, 24, 48, 72 and 96 h by the addition of a saturated 200 μL HgCl₂ solution. CH₄ and N₂O concentrations were determined via the headspace equilibration technique (20 mL N₂ headspace in 60 mL serum bottles) and measured by gas chromatography (GC) with electron capture detection (ECD) for N₂O and with flame ionization detection (FID) for CH₄ (Weiss, 1981). The SRI 8610C GC-ECD-FID was calibrated with certified CH₄:CO₂:N₂O:N₂ mixtures (Air Liquide, Belgium) of 1, 10, 30 and 509 ppm CH₄ and of 0.2, 2.0 and 6.0 ppm N₂O. Concentrations were computed using the solubility coefficients of Yamamoto et al. (1976) and Weiss and Price (1980), for CH₄ and N₂O, respectively. The precision of measurements was ±3.9% and ±3.2% for CH₄ and N₂O, respectively. CH₄ oxidation rates were calculated based on the decrease of CH₄ concentrations in the incubations.

In autumn, triplicate samples for the determination of the partial pressure of CO₂ (pCO₂) were collected in 60 ml plastic syringes directly from the Niskin. The pCO₂ was measured with an infra-red gas analyzer (Licor Li-840) after headspace equilibration in the syringe (Abril et al., 2015; Borges et al., 2015). The Li-840 was calibrated with N₂ and certified CO₂:N₂ mixtures (Air Liquide, Belgium) of 388, 813, 3788 and 8300 ppm CO₂. The precision of measurements was ±4.1%.

Water extracted for creating the headspace in the serum bottles was used to quantify SO₄²⁻, NH₄⁺, NO₂⁻, NO₃⁻, Mn and Fe concentrations. SO₄²⁻, NO₂⁻ and NH₄⁺ concentrations were quantified colorimetrically using a 5-cm optical path and a Genesys 10vis spectrophotometer (Thermo Spectronic). SO₄²⁻ concentrations were determined by the nephelometric method according to Rodier et al. (1996), after being precipitated in barium sulfate in an acid environment. NH₄⁺ concentrations were determined using the dichloroisocyanurate-salicylate-nitroprussiate colorimetric method (Westwood, 1981), and NO₂⁻ concentrations were determined by the sulfanilamide coloration method (APHA, 1998). NO₃⁻ concentrations were determined after vanadium reduction to NO₂⁻ and quantified with a Multiskan Ascent Thermo Scientific multiplates reader (APHA, 1998; Miranda et al., 2001). The detection limits for these methods were 52, 0.3, 0.15 and 0.03 μmol L⁻¹, for SO₄²⁻, NH₄⁺, NO₃⁻ and NO₂⁻, respectively.

The samples for total Fe and Mn determination were digested and mineralized in nitric acid, using specific Teflon bombs in a microwave digestion labstation (Ethos D, Milestone Inc.). They were finally diluted into milli-Q water to a volume of 50 ml. The total Fe and Mn concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS) using dynamic reaction cell (DRC) technology (ICP-MS SCIEX ELAN DRC II, PerkinElmer inc.). Analytical accuracy was verified by a certified reference material (BCR 715, Industrial Effluent Wastewater).

Additional samples to determine vertical profiles of NO₃⁻, NH₄⁺,

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