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Implications of temperature and sediment characteristics on methane formation and oxidation in lake sediments

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Abstract Methane emissions from aquatic environments depend on methane formation (MF) and methane oxidation (MO) rates. One important question is to what extent increased temperatures will affect the balance between MF and MO. We measured potential MF and MO rates simultaneously at 4, 10, 20 and 30°C in sediment from eight different lakes representing typical boreal and northern temperate lake types. Potential MF rates ranged between 0.002 and 3.99 μmol CH_4 $g_{d.w.}{}^{-1}$ day^{-1}, potential MO rates ranged from 0.01 to 0.39 CH_4 $g_{d.w.}{}^{-1}$ day^{-1}. The potential MF rates were sensitive to temperature and increased 10 to 100 fold over the temperature interval studied. MF also differed between lakes and was correlated to sediment water content, percent of organic material and C:N ratio. Potential MO did not depend on temperature or sediment characteristics but was instead well explained by MF rates at the in situ temperature. It implies that elevated temperatures will enhance MF rates which may cause increased methane release from sediments until MO increases as well, as a response to higher methane levels.

Keywords Global warming · Greenhouse gas · Methane formation · Methane oxidation · Littoral sediment · Lake

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Introduction

Methane (CH_4) is a strong greenhouse gas that is produced among the final products of anaerobic carbon mineralization. Its greenhouse warming potential is about 23 times greater than that of CO_2 on a molecular basis over a 100 year perspective (Forster et al. 2007). Lake sediment is one of the most important natural CH_4 sources (Bastviken et al. 2004; Crill et al. 1991; Walter et al. 2006). It has been demonstrated that littoral sediments are particularly important since CH_4 produced in littoral sediments is much more likely to reach the atmosphere than CH_4 produced in deeper profundal sediments (Bastviken et al. 2008; Murase et al. 2005). Hence, many of the remaining questions concerning the contribution of sediment CH_4 production to the global CH_4 budget and subsequent climate feedbacks by and on CH_4 emissions are the result of our limited understanding of shallow littoral sediment CH_4 dynamics. CH_4 emission from lake sediment is ultimately regulated by microbial production and oxidation (Bartlett and

Harriss 1993; King 1992; Reeburgh 2007). Methanogenesis is a final step in the anaerobic degradation of organic carbon in which CH_4 is produced by methanogenic microorganisms (Kiene 1991). The overall methane formation (MF) depends not only on the methanogenesis but also on the preceding degradation steps, e.g. organic matter hydrolysis and fermentation that produce substrates for methanogenesis. In the presence of suitable electron acceptors (e.g. O_2), CH_4 is oxidized as an energy source for methane oxidizing bacteria (MOB) (King 1992). Both MF and methane oxidation (MO) are potentially regulated through microbial activity by several environmental factors including temperature, organic substrate quality and supply, nutrient availability and oxygen concentration (Megonigal et al. 2005). Considering direct influence of temperature, past research have correlated temperature to both potential MF and MO in wetland soils but MF seems to be more sensitive to temperature than MO (Segers 1998). Hence, increased temperatures are likely to result in increased MF while it is unclear if this leads to increased methane emissions. Can MO counterbalance an enhanced MF rate and thereby limit emission changes? The hypotheses behind the present study are that (1) CH_4 formation is related to both temperature and sediment characteristics and (2) that CH_4 oxidation is less temperature sensitive and more directly controlled by CH_4 concentration. If correct, increasing temperatures would result in enhanced MF as a direct effect but also in elevated MO as a consequence of increasing CH_4 concentrations in situ. In turn, this would indicate a more complex climate regulation of CH_4 emissions and illustrate the need of future studies addressing other aspects besides temperature sensitivity of participating processes.

There are numerous studies of either MF or MO including temperature responses in individual systems, while cross-system comparison using the same methodology to evaluate potential temperature effects on the CH_4 dynamics including both MF and MO of littoral lake sediment seem rare. Therefore, in the context of understanding potential feedbacks of global warming on shallow littoral sediment CH_4 dynamics, we measured potential MF and MO rates and their temperature response in sediments collected at the same time from eight different lakes. The lakes and their sediments varied widely in terms of organic matter and nutrient content and are representative of both boreal and northern temperate environments, where a large proportion of the world water bodies are situated (Downing et al. 2006).

Method and analysis

Study site and sediment sampling

Experiments were carried out with sediments from the littoral zone of eight lakes in central Sweden, including Ljustjärn, Lilla Sången, Oppsveten, Svarttjärn in the region of Dalarna and Funbosjön, Lötsjön, Limmaren, Valloxen in the region of Uppland. These lakes were chosen according to the differences in nutrients and quantity and quality of organic matter as shown in Table 1. The lakes in Dalarna, surrounded by coniferous forest, podsol soils and granitic bedrock, represent boreal lakes with low productivity, low nutrient concentrations and low ionic strength. These four lakes were selected to cover a gradient regarding content of organic matter as indicated by water color (absorbance at 430 nm) and dissolved organic matter in Table 1. They span a gradient from extremely clear water (essentially groundwater; Ljustjärn) to very dark brown humic water (Svarttjärn). The surface sediment of all these four lakes was highly influenced by flocculated humic material as reflected by a high C:N ratio (Table 2) with almost no mineral content in the most humic lakes (Svarttjärn and Oppsveten). The other four lakes in Uppland (Lötsjön, Limmaren, Valloxen, and Funbosjön) represent mesotrophic or eutrophic lakes with catchments dominated by agriculture and soils rich in clay. They were moderately to highly productive and the sediments had a lower C:N ratio reflecting greater importance of autochthonous organic matter (from algal production within the lake). The four Uppland lakes were selected to cover a range in productivity found in the agricultural northern temperate landscapes. All lakes were situated at nearby latitudes and surface water temperatures typically range from 0 (under ice) to 30°C (occasionally during extreme summer heat waves).

The uppermost 5 cm of the sediment were retrieved from sediment cores collected at 1–2 m water depth on 23 and 24 June 2007. At sampling time, the surface sediment temperature ranged from 19 to 21°C among the lakes. Sediment material from

Table 1 Summer surface water chemistry of the lakes where sediment was collected

Lake	Position	Area (ha)	A_{430} (cm^{-1})	DOC (mg l^{-1})	TP (μg l^{-1})	TN (μg l^{-1})	Max depth (m)
Ljustjärn	59°55′21.31″N 15°27′13.19″E	12	0.004	4.4	8	179	10
Lilla Sången	59°54′10.43″N 15°23′36.99″E	23.8	0.020	7.4	12	275	17
Oppsveten	60°00′53.9″N 15°28′38.34″E	65.3	0.078	19.2	12	623	11
Svarttjärn	59°53′25.12″N 15°15′26.68″E	0.7	0.105	18.8	14	502	6
Lötsjön	59°52′0.82″N 17°56′51.42″E	63	0.007	10.7	30	905	11
Limmaren	59°43′43.23″N 18°45′2.17″E	590	0.040	9.0	54	1026	8
Valloxen	59°44′29.62″N 17°49′41.06″E	290	0.031	22.0	61	656	6
Funbosjön	59°51′39.26″N 17°51′81.08″E	207	0.162	18.5	110	1016	5

A_{430}, TP and TN denote absorbance at 430 nm, total phosphorous and total nitrogen concentrations, respectively. The lakes were ordered by TP concentrations

Table 2 Sediment characteristics of the lake sediments used

Lake	Water content (%)	Bulk density (g/cm^3)	Organic carbon (%)	C:N ratio
Ljustjärn	95.0	0.93	34.0	23.4
Lilla Sången	91.4	1.51	7.6	12.0
Oppsveten	92.8	0.79	30.4	23.6
Svarttjärn	93.8	0.82	21.7	18.4
Lötsjön	93.4	1.15	14.9	9.4
Limmaren	44.5	2.61	1.1	8.6
Valloxen	78.8	2.05	6.0	9.1
Funbosjön	85.5	1.60	9.9	9.7

Lakes are ordered according to Table 1 to facilitate comparison

at least five cores per lake was retrieved and transferred to a plastic container. The sediment was stored at 4°C in the dark overnight before the experiments were started. Portions of the sediments were transferred to 118 ml serum bottles for incubation experiments as described below. The remaining sediment was used to determine water content and for elemental analyses of carbon and nitrogen.

Experimental setup

Potential rates of MF and MO were determined separately by incubating sediment slurries and monitoring headspace CH_4 concentration over time. Incubations were carried out in the dark at 4 temperature levels: 4, 10, 20 and 30°C. For both MF and MO, there were three replicate slurry bottles per temperature level for each sediment. The original core material was mixed by gentle stirring to decrease the within sediment spatial variability. Very gentle stirring was used to minimize the disruption of microbial consortia that can be important for MF (Dannenberg et al. 1997; Metje and Frenzel 2005). Hence, the slurry used for measurements was a composite sample and the three replicates represented experimental replicates. A specified volume slurry was transferred into the serum bottle using a 10 ml plastic syringe whose tip was cut away to widen the syringe opening.

In the MF incubation, 30-ml of slurry was transferred into each serum bottle. The bottles were

sealed with 10 mm thick butyl rubber stoppers (Apodan, Denmark) with aluminum crimp caps. O_2 was removed from the headspace by evacuation and flushing with CH_4 free N_2. This cycle was repeated three times. The bottle headspace pressure was equilibrated with atmospheric pressure by releasing excess N_2 via a needle inserted through the stopper. CH_4 formation incubations were conducted in an initially CH_4 free N_2 headspace. The first CH_4 sampling and analysis was done 2 days after the start of the incubation to allow depletion possible remaining traces of O_2. Potential MF rate was calculated using the change of CH_4 concentration during the 4 days following the first measurements (linear regression using daily measurements yielded five data points per bottle). Due to our interest in overall net temperature effects, the experiments address the MF in a broad sense, including influence of prior degradation steps providing substrates for the methanogenesis. In line with this, we did not try to isolate and decouple methanogenesis from other sediment processes which is often done by the addition of specific substrates for methanogenesis (Segers 1998).

In the MO incubation, 10-ml slurry in the serum bottle was purged by zero-air (CH_4 free air, less than 0.1 ppm CH_4) and immediately thereafter crimp sealed with 10 mm thick butyl rubber stoppers (Apodan, Denmark). One ml of 3.5% CH_4 was added to the headspace creating an initial headspace CH_4 concentration of approximately 330 ppmv. The initial concentration in each bottle was confirmed by immediate measurements. Potential MO rates were calculated from the loss of CH_4 in the MO vessels during the first 2 days (three data points). Simple linear regression was used to determine MO rates instead of exponential relationships typically used over longer time intervals (see also "Discussion"). All dynamic results were normalized to dry weight of sediment for cross-system comparisons within this study. For cross-checking with other studies, the units can be converted by using the data in Table 2.

CH_4 sampling and analysis

CH_4 concentrations were analyzed daily using gas chromatography with flame ionization detection (GC-FID). At each sampling, 2 ml of make up gas (CH_4 free nitrogen for MF or CH_4 free air for MO incubations) was first added to the bottle by syringe and mixed with the headspace gas. Two milliliter headspace gas were then withdrawn and analyzed by GC-FID. The injection of make up gas ensured maintenance of the headspace pressure. Correction for dilution of the headspace gas by the injection of make up gas was calculated and verified by tests using blank bottles with no sediment. The GC-FID (Shimadzu 8A) was equipped with a 500 µl injection loop and a 2 m × 3.2 mm stainless steel column packed with HayeSep Q 80/100. The column oven temperature was 40°C and the carrier gas was N_2 setting at 80 kPa inlet pressure (about 10 ml min^{-1}). Certified 99.9 ± 2 ppm, 1000 ± 20 ppm and 1.95 ± 0.02% CH_4 standards (Air Liquide) were used for calibration.

Sediment characteristics

Sediment water content was determined by the difference in slurry weights before and after being dried. A portion of the sediment was freeze dried and then homogenized by grinding in a mortar. For organic CN elemental analysis, a portion of freeze dried sediment was weighed into silver cups and carbonates were removed by adding 2 M hydrochloric acid to sediment sub-samples. These sediments were then dried at 60°C and combusted with a Carlo Erba/NC 2500 analyzer.

Statistics

Possible relationships between MF and MO and temperature among sediments from different lakes were tested statistically in several ways including correlations between pairs of variables and by two-way ANOVA with MF or MO as dependent variables, temperature as factor and sediment water content, organic carbon content and C:N ratio as covariates. In the ANOVA with MO as the dependent variable, MF at 20°C, representative of MF at the in situ temperature, was added as a covariate. Many of the variables were not normally distributed. Log-transformation was not sufficient to reach normality for some variables and therefore the tests were made with ranked values for all variables.

Temperature sensitivity calculations

Temperature sensitivity is expressed in two ways in this study; as Q_{10} values and the apparent Arrhenius

equation activation energy (E'_a). Q_{10} values were calculated according to

$$Q_{10} = \left(\frac{R_2}{R_1}\right)^{\left(\frac{10}{T_2 - T_1}\right)} \quad (1)$$

where R_2 and R_1 are process rates at the different temperatures T_2 and T_1. E_a was obtained from the slope of Arrhenius equation expressed as

$$\ln(k) = \frac{-E'_a}{R}\frac{1}{T} + \ln(A) \quad (2)$$

where the natural logarithm of the process rate (k) is plotted against $1/T$ where T is the temperature (K). R is the universal gas constant (8.314472 J K^{-1} mol^{-1}). A is Arrhenius constant which is experimentally determined.

Results

Sediment and lake characteristics

Sediment water content, organic carbon content and C:N elemental ratio are shown in Table 2. These variables were also highly correlated (Fig. 1). High organic carbon content was positively correlated with water content and C:N ratios. These correlations demonstrate that the eight lake sediments were different in terms of physical and chemical properties providing a range of characteristics representative of sediments in boreal and northern temperate lakes in the region.

Methane formation (MF)

CH_4 concentrations increased linearly in all sediments except some of the incubation bottles for Ljustjärn, Lilla Sångenand Svarttjärn sediment at low temperatures (Table 3). Potential rates ranged between 0.002 and 3.99 µmol CH_4 $g_{d.w.}{}^{-1}$ day^{-1}. MF was highly sensitive to temperature with higher rates at higher temperatures in all sediments (Tables 4, 5; Fig. 2). The temperature response was exponential in most cases with the most drastic increase between 20 and 30°C (Fig. 2). Thereby most of the lake sediments that had low potential MF at 20°C produced much more CH_4 when the temperature increased to 30°C. This MF trend was detected in sediment from Svarttjärn, Oppsveten and Ljustjärn (Tables 3, 5).

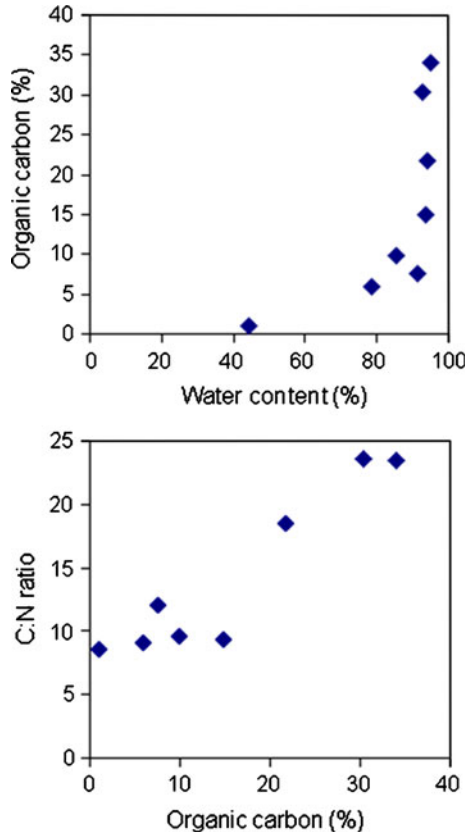

Fig. 1 Relationships between water content, organic carbon content and C:N ratio in the sediment from the different lakes. The lakes with the highest organic carbon content and the highest C:N ratio also had the highest water content

MF also differed between the sediments and was correlated with the C:N ratio (Table 4). The two-way ANOVA analysis showed that MF rates were significantly affected by temperature as well as all included sediment characteristics that were tested (water content, organic carbon content and C:N ratio; $p < 0.005$ for all factors and covariates; see "Methods" section for statistics details). None of sediment characteristics were truly independent of any other variables (Fig. 1), making it difficult to relate the results to any single variable. Rather, the ANOVA shows that MF rates differed both among temperatures and among sediment types.

The effect of the sediment characteristics indicated highest MF rates in sediments with lower water and organic carbon content and C:N ratios <10 (Fig. 3). Using this information, the MF rates can be classified

Table 3 Potential methane formation rates at different incubation temperatures

Lake	MF rate (μmol CH_4 $g_{d.w.}^{-1}$ day^{-1})			
	4°C	10°C	20°C	30°C
Ljustjärn	0.006 (0.46–0.90)	0.006 (0.58–0.95)	0.028 (0.43–0.96)	0.318 (0.84–0.92)
Lilla Sången	0.002 (0.23–0.84)	0.002 (0.35–0.66)	0.012 (0.45–0.94)	0.037 (0.12–0.92)
Oppsveten	0.019 (0.87–0.97)	0.018 (0.67–0.79)	0.031 (0.60–1.00)	0.481 (0.87–0.90)
Svarttjärn	0.010 (0.78–0.90)	0.009 (0.64–0.75)	0.041 (0.69–0.96)	1.004 (0.92–0.96)
Lötsjön	0.069 (0.92–0.97)	0.170 (0.99–1.00)	1.369 (0.99–1.00)	3.990 (0.99–1.00)
Limmaren	0.041 (0.99–1.00)	0.067 (0.99–0.99)	0.198 (1.00–1.00)	0.388 (1.00–1.00)
Valloxen	0.012 (0.91–0.95)	0.024 (0.98–0.99)	0.151 (0.99–1.00)	0.425 (0.99–1.00)
Funbosjön	0.085 (0.82–1.00)	0.186 (0.98–0.99)	0.920 (1.00–1.00)	2.038 (1.00–1.00)

Methane formation rates (MF rate) represent the slope of how amounts of methane changed over time and R^2 values are given between brackets (see text for details)

Table 4 Correlations between ranked values of methane formation rates (MF; μmol CH_4 $g_{d.w.}^{-1}$ day^{-1}), methane oxidation rates (MO; μmol CH_4 $g_{d.w.}^{-1}$ day^{-1}), methane formation rates at 20°C (MF20), sediment water content (WA; %), sediment organic carbon content (OC; % dry weight), and sediment C:N ratio (CN)

	Temp	MF	MF20	WA	OC	CN
MF						
R^2	**0.683**			−0.195	−0.142	**−0.346**
p-value	**<0.001**			0.057	0.167	**0.001**
MO						
R^2	−0.039	**0.326**	**0.493**	0.188	**0.262**	0.020
p-value	0.708	**0.001**	**<0.001**	0.068	**0.010**	0.851

Bold numbers indicate statistical significance (Pearsson correlation). The correlations were calculated with ranked values. MF20 was chosen as a variable since 20°C is representative of the summer in situ temperature of littoral sediments in the sampled lakes

Table 5 Temperature sensitivity for methane formation rates expressed as Q_{10} values for the studied temperature intervals and the activation energy (E'_a) as given by Arrhenius equation (Eqs. 1 and 2 in the text)

Lake	Q_{10} values			E'_a (kJ mol^{-1})
	4–10°C	10–20°C	20–30°C	
Ljustjärn	1.0	4.4	11.5	109.5
Lilla Sången	1.4	4.9	3.1	86.4
Oppsveten	0.9	1.7	15.7	83.8
Svarttjärn	0.9	4.4	24.5	124.8
Lötsjön	4.5	8.1	2.9	113.5
Limmaren	2.3	3.0	2.0	62.3
Valloxen	3.2	6.3	2.8	100.7
Funbosjön	1.9	5.0	2.2	87.2

into two groups yielding sediments with high potential MF and low potential MF. The high potential MF sediments from Limmaren, Funbosjön, Lötsjön and Valloxen were characterized by approximately doubled CH_4 headspace concentration over 6 days (Table 3). The low potential MF group includes Lilla Sången, Ljustjärn, Oppsveten and Svarttjärn in which CH_4 concentration did not change much at the lower temperatures.

C:N ratios are usually associated with the organic material sources (Wetzel 2001). The low MF potential sediments were dominated by organic material from terrestrial sources (C:N ratio ~20), primarily refractory flocculated humic substances (Meyers 1994). The high potential MF sediments were dominated by organic matter from lake primary production which was considered to be more labile. In sediments with C:N ratios <10 methane formation rates increased on an average 1.4 orders of magnitude from 4 to 30°C. Methane formation rates in sediments with C:N ratios >10 increased on an average 1.6 orders of magnitude and the difference in MF rates between the sediment types decreased with increasing temperature (Fig. 3).

Methane oxidation (MO)

MO was detected in all treatments and the methane concentration change in the vials was linear during

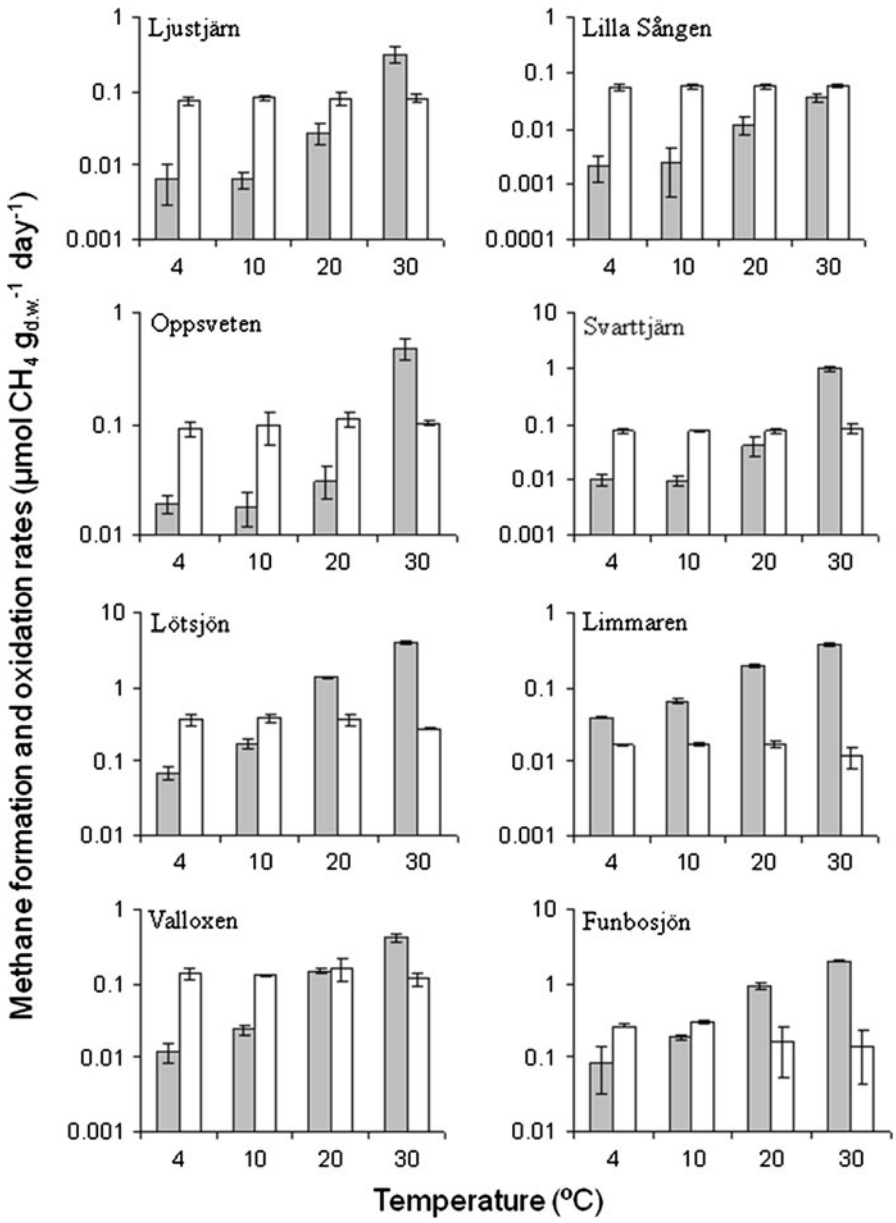

Fig. 2 Potential methane formation (*grey bars*) and methane oxidation (*white bars*) rates at different temperatures in the studied sediments. The graphs were ordered by total phosphorous concentration in the water to some extent reflecting lake productivity (see Table 1). *Error bars* denote ±1SD ($n = 3$). Note that the *y* axis is logarithmic and that scales differ between the lakes

the first two days of the incubation (R^2 range 0.83–1.00). MO rates ranged from 0.01 to 0.39 µmol CH_4 $g_{d.w.}{}^{-1}$ day^{-1} (Table 6). MO was not affected by temperature but it was correlated with MF and the sediment organic matter content (Fig. 2; correlation analyses, Table 4; Fig. 4). The two-way ANOVA (temperature as factor; MF at 20°C, sediment water, organic matter content and C:N ratio as covariates) showed significant connections with MF at 20°C only ($p < 0.005$; $\alpha < 0.05$; see Fig. 4). The potential MO was similar to or exceeded potential MF in all sediments at low temperatures. However, because MO was not as strongly affected by temperature, MF rates were typically higher than MO at higher temperatures (Fig. 2).

Discussion

Across a wide variety of littoral lake sediments, this study found that potential MF and MO range from 0.001 to 4.06 µmol CH_4 m^{-3} s^{-1} and from 0.04 to

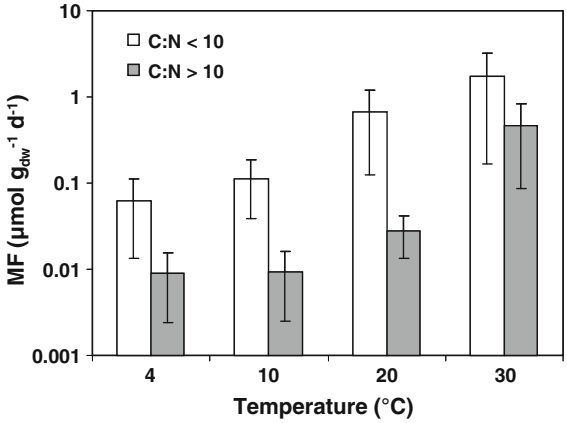

Fig. 3 Methane formation rates (MF; µmol $g_{d.w.}^{-1}$ day^{-1}) in sediments with a C:N ration <10 and >10, respectively, versus temperature. *Bars* show averages and *error bars* denote ±1SD ($n = 12$)

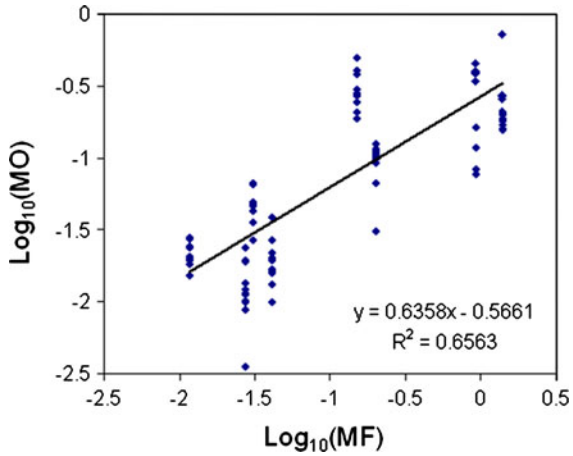

Fig. 4 Logarithms of measured methane oxidation rates (MO) at all temperatures versus average methane formation rates at 20°C (MF20). Original unit for both MO and MF was µmol CH_4 $g_{d.w.}^{-1}$ day^{-1}. All replicates for MO are shown while the average MF value was used for each sediment because MF and MO values were not strictly paired (see text for details)

0.87 µmol CH_4 m^{-3} s^{-1}, respectively (the unit was converted from µmol CH_4 $g_{d.w.}^{-1}$ day^{-1} to µmol CH_4 m^{-3} s^{-1} by dividing the rate in Table 3 or 6 with "bulk density" which is available in Table 2). The review paper by Segers (1998) summarized the typical wetland potential MF and MO and reported rate ranges from 0.01 to 10 µmol CH_4 m^{-3} s^{-1} and from 0.1 to 100 µmol CH_4 m^{-3} s^{-1}, respectively. Our results are within the lower part of the previously published range. Possible reasons are (1) that some previous potential rate experiments included addition of specific substrates favoring methanogenesis (e.g. acetate or H_2/CO_2) (Chin and Conrad 1995; Sugimoto and Wada 1993) or (2) that previously studied wetland sediments often came from environments with a high abundance of macrophytes and often high nutrient conditions as well (King 1994; Krumholz et al. 1995). This probably resulted in high microbial activity compared to the lakes of this study where no substrates were added and all lake sediments used were collected at locations without nearby macrophytes. In the lakes with high C:N ratio the sediments consisted primarily of flocculated humic matter or peat which are poor substrates for microbial activity. The four lakes with a low C:N ratio had dense belts of *Phragmites australis* along some parts of the shore and zones with high abundance of *Potamogeton* spp., but in relation to previous wetland studies this corresponds to a low macrophyte abundance. In the

Table 6 Methane oxidation rates (MO rate) at different incubation temperatures

Lake	MO rate (µmol CH_4 $g_{d.w.}^{-1}$ day^{-1})			
	4°C	10°C	20°C	30°C
Ljustjärn	0.08 (0.95–0.98)	0.08 (0.99–0.99)	0.08 (0.99–0.99)	0.08 (0.98–1.00)
Lilla Sången	0.06 (0.98–1.00)	0.06 (0.97–1.00)	0.06 (0.95–0.97)	0.06 (0.98–0.99)
Oppsveten	0.09 (0.98–1.00)	0.10 (0.99–1.00)	0.11 (0.97–0.98)	0.10 (0.98–1.00)
Svarttjärn	0.07 (0.98–1.00)	0.08 (0.85–1.00)	0.08 (0.98–0.99)	0.09 (0.98–1.00)
Lötsjön	0.37 (0.96–0.99)	0.63 (0.86–0.98)	0.37 (0.87–0.91)	0.28 (0.87–0.89)
Limmaren	0.02 (1.00–1.00)	0.02 (0.92–1.00)	0.02 (0.96–0.97)	0.01 (0.96–1.00)
Valloxen	0.14 (0.97–0.98)	0.13 (0.96–0.97)	0.17 (0.88–0.94)	0.12 (0.85–0.90)
Funbosjön	0.27 (0.93–0.95)	0.31 (0.92–0.95)	0.16 (0.89–0.98)	0.14 (0.83–0.98)

R^2 values are given within parentheses (see text for details)

other lakes, single plants of *Nuphar lutea* and *Potamogeton natans* occurred but their abundances were negligible on an area basis.

At in situ temperature (e.g. 20°C), different lake sediments had different potential MF rates (Fig. 2). There could be several reasons for these differences. The sediments with low MF potential consisted of peat or flocculated humic matter with a high C:N ratio. Hence these sediments were characterized by refractory organic substrates and low nutrient concentrations which should result in slow overall anoxic degradation (Bastviken et al. 2003; Hulthe et al. 1998) leading to low MF rates. Low microbial activity in these littoral sediments (expected to be well oxygenated due to resuspension by wave turbulence) may also have reduced MF rates as the result of the availability of alternative electron acceptors (such as dissolved NO_3^-, Fe^{3+}, Mn^{4+} and SO_4^{2-}) which are all known to inhibit methanogenesis (Huttunen et al. 2006; Zehnder and Stumm 1988). The alternative electron acceptors were likely consumed after O_2 was removed in the MF bottles which could explain the low MF rates at low temperatures. However, high temperature (≥30°C) enhancement of general microbial activity probably resulted in an increased supply of organic degradation products for methanogenesis and more rapid depletion of the alternative electron acceptors resulting in substantially higher MF rates (Liikanen et al. 2002). Similarly, given high concentrations of labile organic matter, faster degradation rates should lead to more substrate for methanogenesis and a more rapid depletion of alternative electron acceptors. This could explain the results at the in situ temperature level, the high potential MF group is composed of low C:N ratio sediments (Limmaren, Funbosjön, Lötsjön and Valloxen) and the low potential MF sediment is characterized by high C:N ratio (Lilla Sången, Ljustjärn, Oppsveten and Svarttjärn).

We did not know to what extent methane oxidizing bacteria were present and active in the sediments before conducting the experiment. This affected our choice of CH_4 concentration in the MO bottles. If presence or activity of MOB was very low in situ, it would be difficult to detect any MO if a high starting CH_4 concentration was used. We also expected low amounts of CH_4 in sediments having a high C:N ratio. Therefore, we used a low initial CH_4 concentration in the MO experiment. Based on Henry's law calculations and given initial headspace concentration of 330 ppmv, the concentration of dissolved CH_4 in the slurry was 0.42–0.75 μM depending on temperature (Wiesenburg and Guinasso 1979). The drawback with using low initial CH_4 levels is that the CH_4 may be rapidly depleted and rates underestimated. We therefore based our calculations on the headspace concentration change in 2 days after the start of the incubations. The decline of CH_4 in every vial was linear and there were no indications of CH_4 depletion during this time. In addition, up to 50 fold different MO rates among treatments were detected (Table 6) indicating that the experimental setup detected MO over a wide range.

MO rates differed between lakes and the ANOVA as well as correlation tests (Table 4; Fig. 4) indicate that MO rates were primarily related to MF rates rather than sediment characteristics. This relation supports the conclusion that MO is primarily substrate regulated and depends on CH_4 and O_2 levels. Hence, under stable conditions and given availability of O_2, MO may be regulated by MF rates and the subsequent supply of CH_4 into the oxygenated zone in the sediment where MO occurs.

Temperature is a major factor influencing rates of all biogeochemical processes. In our study, potential MF rates increased from 10 to 100 times while potential MO rates only changed by a factor of 1 to 2 over a temperature range of 4–30°C (Tables 3, 6). MF was clearly much more sensitive to temperature than MO in all sediments (Fig. 2). Dunfield et al. (1993), studying peat soils, also found MF to be more temperature dependent (activation energies 123–271 kJ mol^{-1}, Q_{10} values 5.3–16) than MO (activation energies 20–80 kJ mol^{-1}, Q_{10} values 1.4–2.1) in peat samples. In a review of wetland soil incubations by Segers (1998) based on 1046 MF and 328 MO measurements similar results were noted. Q_{10} values ranged from 1.5 to 28 for MF and 1.4–2.3 for MO. Possible reasons for the low temperature sensitivity of MO include a low temperature sensitivity of the involved enzymes and the decreasing solubility of CH_4 and O_2 with increasing temperature (Benson and Krause 1984; Brazeau and Lipscomb 2000; Wiesenburg and Guinasso 1979). The latter could counteract possible temperature stimulation of enzyme activity by decreasing the substrate availability. In contrast, all possible substrates for MF except H_2 is highly soluble in water and MF rates may also depend on

previous steps in the anaerobic degradation chain which are known to be highly temperature dependent (Kelly and Chynoweth 1981; Kotsyurbenko et al. 1993; Metje and Frenzel 2005).

We use Q_{10} and E'_a values (Table 5) as empirical descriptors for temperature sensitivity of MF. Q_{10} values describe the change in rate when temperature increases 10°C. Q_{10} varies with temperature and therefore we calculated different values for different temperature intervals. Another important aspect is awareness of exactly what processes are described by the Q_{10} value. Long-term studies favoring methanogens by the addition of substrates such as H_2/CO_2 or acetate (Nozhevnikova et al. 2007) may yield Q_{10} values specific for methanogenesis. However, in this study, MF rates depend not only on methanogenesis but also on indirectly related processes, such as (1) other organic matter degradation reactions providing MF substrates or (2) processes of depleting alternative electron acceptors inhibiting MF. Hence, our empirical temperature dependency descriptors incorporate many linked processes and not a single specific reaction.

It is useful to note how MF Q_{10} values varied at different temperature intervals (Table 5). The change was small at low temperatures (Q_{10} values <4.5 at 4–10°C), while the change was dramatic at high temperatures (Q_{10} values up to 24.5 at 20–30°C). In addition, there was a difference in the MF temperature response in different sediment types. MF of sediments with a C:N ratio >10 (e.g. dominated by humic matter or peat) were much more sensitive to temperature between 20 and 30°C than sediments with C:N ratios <10 (Table 5; Fig. 3). This pattern could be explained by the slow depletion of alternate electron acceptors in humic rich sediments at low temperatures inhibiting MF. At higher temperatures, this depletion is much faster, resulting in much higher MF.

At low temperatures, most of the lakes were characterized by potential MO rates that were similar or higher than the measured MF rates (Fig. 2). However, MF rates typically exceeded MO rates at higher temperatures due to the stronger temperature response of MF relative to that of MO. This raises the question of whether rising temperatures could result in higher CH_4 emissions. Considering temperature as a single variable acting on MF or MO alone, it is tempting to suggest that CH_4 emissions would increase (Fig. 2). This may happen if the climate gets both warmer and more variable. For example, short periods of warm weather in the boreal zone may temporarily increase epilimnion temperatures and thereby also the temperature of the littoral sediment which is in contact with the epilimnion, resulting in increased CH_4 release from sediments. Such periods are not uncommon and during August 2008 the lakes in Dalarna, which typically have a mean late summer epilimnion temperature close to 20°C, experienced 2 weeks with littoral temperatures of 27–29°C. However, the result that MO depends on MF also means that MO could catch up with an increasing MF given sufficient time for the methane oxidizing microbial community to grow in response to elevated CH_4 concentrations (Fig. 4). This would only be true for flux pathways in which CH_4 has to diffuse through an oxygenated zone with MO prior to emission (e.g. diffusive flux). CH_4 emitted via such pathways have been shown to be partly oxidized (Bastviken et al. 2002; Ström et al. 2005). However, emissions would still increase in certain flux pathways that are dominated by advective processes or transport mechanisms allowing the CH_4 to effectively bypass zones with MO, such as ebullition (Bastviken et al. 2004; Walter et al. 2006). Plant mediated transport represents an important flux pathway in which the role of MO is less clear. CH_4 probably have to pass an oxygenated zone with MO surrounding the plant roots before entering the plant tissue, but the thickness of this zone and the transfer rate may differ between plants and sediments. There are indications that CH_4 emitted through plants have been subjected to oxidation (Ström et al. 2005).

Our result that potential MO rates were correlated to potential MF rates across different sediment types which are representative of sediments in the temperate and boreal climate zones (Fig. 4) is consistent with observation that MO kinetics depend on CH_4 concentration (Bender and Conrad 1995; King 1997; Knief and Dunfield 2005). A comparison of half saturation constants for MO (K_{m,CH_4}) from different studies showed that K_{m,CH_4} from highly producing CH_4 samples was greater than K_{m,CH_4} from MF samples with low production rates (Segers 1998). Another study also pointed out that potential MO from sediment samples was about 100 times higher than that from a CH_4 consuming forest soil that demonstrated very low potential MF rates (Bender and Conrad 1994). Another study by (Moore and Dalva 1997) comparing potential MF and MO in peat

soils also found a weak but significant positive log–log relationship (R^2 of 0.165 which is lower than our R^2 of 0.66 in Fig. 4). The ability of sedimentary methanotrophic community to adapt to increased CH_4 concentrations has also been noted. Potential MO rates could increase to 176 fold the initial rate within a few days after an increase in CH_4 500 times higher than in situ levels (Bender and Conrad 1994, 1995). Under continuous elevated CH_4, MO rates also rise with time (Knief and Dunfield 2005).

Altogether our results and evidence from literature indicate that MO will adapt to rising CH_4 concentrations. Therefore, we cannot simply assume that all types of lake CH_4 emissions will increase following warming. Instead MO may respond rapidly enough to counteract large increases in the emissions from sediments by diffusion across oxic–anoxic interfaces at the sediment surface or surrounding plant roots in a warmer climate. The present study focus on process rates in laboratory incubations and although yielding the hypothesis that MO can catch up with MF which seems valid across many different sediment types, this has to be further explored before predictions about in situ situations can be made. To learn more about climate effects on methane emissions from lakes, it seems necessary to study the sensitivity of MO to the changes in MF as well as the effects of transient periods of elevated temperatures on MF and MO rates.

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References

Bartlett KB, Harriss RC (1993) Review and assessment of methane emissions from wetlands. Chemosphere 26:261–320

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

Bastviken D, Olsson M, Tranvik L (2003) Simultaneous measurements of organic carbon mineralization and bacterial production in oxic and anoxic lake sediments. Microb Ecol 46:73–82

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 Cycles 18:GB4009. doi:4010.1029/2004GB002238

Bastviken D, Cole JJ, Pace ML, MC Van de Bogert (2008) Fates of methane from different lake habitats: connecting whole-lake budgets and CH_4 emissions. J Geophys Res 113:G02024. doi:02010.01029/02007JG000608

Bender M, Conrad R (1994) Methane oxidation activity in various soils and freshwater sediments: occurrence, characteristics, vertical profiles, and distribution on grain size fractions. J Geophys Res 99. doi:10.1029/1094JD00266

Bender M, Conrad R (1995) Effect of CH_4 concentrations and soil conditions on the induction of CH_4 oxidation activity. Soil Biol Biochem 27:1517–1527

Benson BB, Krause D Jr (1984) The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere. Limnol Oceanogr 29:620–632

Brazeau BJ, Lipscomb JD (2000) Kinetics and activation thermodynamics of methane monooxygenase compound Q formation and reaction with substrates. Biochemistry 39:13503–13515

Chin K-J, Conrad R (1995) Intermediary metabolism in methanogenic paddy soil and the influence of temperature. FEMS Microbiol Ecol 18:85–102

Crill PM, Harriss RC, Bartlett KB (1991) Methane fluxes from terrestrial wetland environments. In: Rogers JE, Whitman WB (eds) Microbial production and consumption of the greenhouse gases: methane, nitrogen oxides and halomethanes. American Society for Microbiology, Washington, pp 91–109

Dannenberg S, Wudler J, Conrad R (1997) Agitation of anoxic paddy soil slurries affects the performance of the methanogenic microbial community. FEMS Microbiol Ecol 22:257–263

Downing JA, Prairie YT, Cole JJ, Duarte CM, Tranvik LJ, Striegl RG, McDowell WH, Kortelainen P, Caraco NF, Melack JM, Middelburg JJ (2006) The global abundance and size distribution of lakes, ponds, and impoundments. Limnol Oceanogr 51:2388–2397

Dunfield P, Knowles R, Dumont R, Moore TR (1993) Methane production and consumption in temperate and subarctic peat soils: response to temperature and pH. Soil Biol Biochem 25:321–326

Forster P, Ramaswamy V, Artaxo P, Berntsen T, Betts R, Fahey DW, Haywood J, Lean J, Lowe DC, Myhre G, Nganga J, Prinn R, Raga G, Schulz M, Van Dorland R (2007) Changes in atmospheric constituents and in radiative forcing. In: Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL (eds) Climate change 2007: the physical science basis. Contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change. Cambridge University Press, Cambridge

Hulthe G, Hulth S, Hall POJ (1998) Effect of oxygen on degradation rate of refractory and labile organic matter in continental margin sediments. Geochim Cosmochim Acta 62:1319–1328

Huttunen JT, Väisänen TS, Hellsten SK, Martikainen PJ (2006) Methane fluxes at the sediment–water interface in some boreal lakes and reservoirs. Boreal Environ Res 11:27–34

Kelly CA, Chynoweth DP (1981) The contributions of temperature and of the input of organic matter in controlling rates of sediment methanogenesis. Limnol Oceanogr 26:891–897

Kiene RP (1991) Production and consumption of methane in aquatic systems. In: Rogers JE, Whitman WB (eds) Microbial production and consumption of greenhouse gases: methane, nitrogen oxides, and halomethanes. American Society for Microbiology, Washington, pp 111–145

King GM (1992) Ecological aspects of methane consumption, a key determinant of global methane dynamics. Adv Microb Ecol 12:431–468

King GM (1994) Associations of methanotrophs with the roots and rhizomes of aquatic vegetation. Appl Environ Microbiol 60:3220–3227

King GM (1997) Responses of atmospheric methane consumption by soils to global climate change. Glob Chang Biol 3:351–362

Knief C, Dunfield PF (2005) Response and adaptation of different methanotrophic bacteria to low methane mixing ratios. Environ Microbiol 7:1307–1317

Kotsyurbenko OR, Nozhevnikova AN, Zavarzin GA (1993) Methanogenic degradation of organic matter by anaerobic bacteria at low temperature. Chemosphere 27:1745–1761

Krumholz LR, Hollenback JL, Roskes SJ, Ringelberg DB (1995) Methanogenesis and methanotrophy within a Sphagnum peatland. FEMS Microbiol Ecol 18:215–224

Liikanen A, Murtoniemi T, Tanskanen H, Vaisanen T, Martikainen PJ (2002) Effects of temperature and oxygen availability on greenhouse gas and nutrient dynamics in sediment of a eutrophic mid-boreal lake. Biogeochemistry 59:269–286

Megonigal JP, Hines ME, Visscher PT (2005) Anaerobic metabolism: linkages to trace gases and aerobic process. In: Schlesinger WH (ed) Biogeochemistry: treatise on geochemistry. Elsevier-Pergamon, Oxford, pp 317–424

Metje M, Frenzel P (2005) Effect of temperature on anaerobic ethanol oxidation and methanogenesis in acidic peat from a northern wetland. Appl Environ Microbiol 71:8191–8200

Meyers PA (1994) Preservation of elemental and isotopic source identification of sedimentary organic matter. Chem Geol 114:289–302

Moore TR, Dalva M (1997) Methane and carbon dioxide exchange potentials of peat soils in aerobic and anaerobic laboratory incubations. Soil Biol Biochem 29:1157–1164

Murase J, Sakai Y, Kametani A, Sugimoto A (2005) Dynamics of methane in mesotrophic Lake Biwa, Japan. Ecol Res 20: 377–385

Nozhevnikova AN, Nekrasova V, Ammann A, Zehnder AJB, Wehrli B, Holliger C (2007) Influence of temperature and high acetate concentrations on methanogenensis in lake sediment slurries. FEMS Microbiol Ecol 62:336–344

Reeburgh WS, Heinrich DH, Karl KT (2007) Global methane biogeochemistry. In: Keeling RF (ed) Treatise on Geochemistry, vol 4. The Atmosphere. Pergamon, Oxford, pp 1–32

Segers R (1998) Methane production and methane consumption: a review of processes underlying wetland methane fluxes. Biogeochemistry 41:23–51

Ström L, Mastepanov M, Christensen T (2005) Species-specific effects of vascular plants on carbon turnover and methane emissions from wetlands. Biogeochemistry 75: 65–82

Sugimoto A, Wada E (1993) Carbon isotopic composition of bacterial methane in a soil incubation experiment: contributions of acetate and CO_2/H_2. Geochim Cosmochim Acta 57:4015–4027

Walter KM, Zimov SA, Chanton JP, Verbyla D, Chapin FS (2006) Methane bubbling from Siberian thaw lakes as a positive feedback to climate warming. Nature 443:71–75

Wetzel RG (2001) The nitrogen cycle. In: Wetzel RG (ed) Limnology: lake and river ecosystems. Academic Press, London

Wiesenburg DA, Guinasso NL (1979) Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and sea water. J Chem Eng Data 24:356–360

Zehnder AJB, Stumm W (1988) Geochemistry and biogeochemistry of anaerobic habitats. In: Zehnder AJB (ed) Biology of anaerobic microorganisms. Wiley, New York