Science of the Total Environment 636 (2018) 411–419

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Eutrophication exacerbates the impact of climate warming on lake methane emission

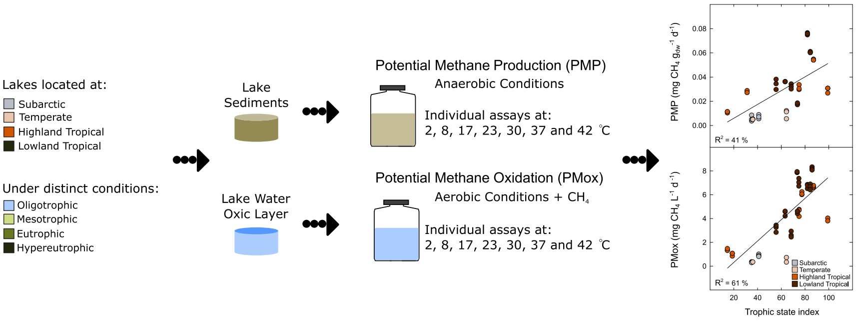
Armando Sepulveda-Jauregui [a,b,1,2], Jorge Hoyos-Santillan [c,1], Karla Martinez-Cruz [b,d,2], Katey M. Walter Anthony [a], Peter Casper [b], Yadira Belmonte-Izquierdo [d], Frédéric Thalasso [d,*]

[a] Water and Environmental Research Center, University of Alaska Fairbanks, Fairbanks, AK 99775, United States
[b] Department of Experimental Limnology, Leibniz Institute of Freshwater Ecology and Inland Fisheries, 16775 Stechlin, Germany
[c] Division of Agricultural and Environmental Sciences, University of Nottingham, Nottingham, East Midlands LE12 5RD, United Kingdom
[d] Biotechnology and Bioengineering Department, Cinvestav, Mexico City 07360, Mexico

HIGHLIGHTS

- Net methane emission from lakes depends on methanogenesis and methanotrophy
- Methanogenesis is more sensitive to temperature increments than methanotrophy
- Rates of methanogenesis and methanotrophy are positively influenced by eutrophication
- A temperature buildup of 2 °C would lead to an increase in CH4 emissions by 47–183%

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 February 2018
Received in revised form 19 April 2018
Accepted 20 April 2018
Available online 27 April 2018

Editor: Jay Gan

Keywords:
Climate warming
Greenhouse gases
Lakes
Carbon cycle
Trophic status
Latitudinal gradient

ABSTRACT

Net methane (CH_4) emission from lakes depends on two antagonistic processes: CH_4 production (methanogenesis) and CH_4 oxidation (methanotrophy). It is unclear how climate warming will affect the balance between these processes, particularly among lakes of different trophic status. Here we show that methanogenesis is more sensitive to temperature than methanotrophy, and that eutrophication magnifies this temperature sensitivity. Using laboratory incubations of water and sediment from ten tropical, temperate and subarctic lakes with contrasting trophic states, ranging from oligotrophic to hypereutrophic, we explored the temperature sensitivity of methanogenesis and methanotrophy. We found that both processes presented a higher temperature sensitivity in tropical lakes, followed by temperate, and subarctic lakes; but more importantly, we found that eutrophication triggered a higher temperature sensitivity. A model fed by our empirical data revealed that increasing lake water temperature by 2 °C leads to a net increase in CH_4 emissions by 101–183% in hypereutrophic lakes and 47–56% in oligotrophic lakes. We conclude that climate warming will tilt the CH_4 balance towards higher lake emission and that this impact will be exacerbated by the eutrophication of the lakes.

---

[*] Corresponding author.
E-mail addresses: armando.sepulveda@umag.cl, (A. Sepulveda-Jauregui), jhoyosantillan@hotmail.com, (J. Hoyos-Santillan), karla.martinez@umag.cl, (K. Martinez-Cruz), kmwalteranthony@alaska.edu, (K.M. Walter Anthony), pc@igb-berlin.de, (P. Casper), thalasso@cinvestav.mx. (F. Thalasso).

[1] Note: A.S.J. and J.H·S contributed equally to this work.

[2] Present address: Department of Sciences and Natural Resources, University of Magallanes, Punta Arenas, 113-D University of Magallanes, Chile.

https://doi.org/10.1016/j.scitotenv.2018.04.283

1. Introduction

Among the natural sources of CH_4 to the atmosphere, lakes represent a major source of uncertainty to the overall budget (Dean et al., 2018; Holgerson and Raymond, 2016; Saunois et al., 2016; Wik et al., 2016), with annual emissions ranging from 37 to 112 Tg CH_4 to the atmosphere (Saunois et al., 2016). Most lakes are found in northern latitudes, and are relatively small (Verpoorter et al., 2014). However, lakes located in tropical latitudes are highly dynamic, and despite their minor contribution to the overall lake area (~27%), they represent an important source of CH_4 to the atmosphere, contributing ~49% of the global lake and reservoir CH_4 emissions (Holgerson and Raymond, 2016; Bastviken et al., 2011).

Microbial methanogenesis in lakes mainly occurs in anoxic zones, with CH_4 being produced mostly in anoxic sediments, whereas methanotrophy in lakes primarily takes place in oxic zones, consuming CH_4 in the presence of oxygen (O_2). Methanogenesis in lakes is strongly dependent on the availability of labile substrates and is consequently affected by autochthonous (*e.g.* decaying aquatic biomass such as phytoplankton) and allochthonous (*e.g.* runoff from adjacent ecosystems) carbon inputs (Conrad, 1999; Grasset et al., 2018; Peura et al., 2014; Schulz et al., 1997; West et al., 2016). Methanotrophy depends on the availability of CH_4 and O_2, and thus primarily occurs in the oxic zones within the water column (Bastviken et al., 2008; Kankaala et al., 2007; Martinez-Cruz et al., 2015). Oxygenated water can be found throughout the entire water column in well mixed or shallow lakes or can be restricted to the epilimnion in some stratified lakes; but it is estimated that a large fraction of the CH_4 migrating through the water column in lakes is suitable for oxidation by methanotrophs (Bastviken et al., 2002; Bastviken et al., 2008; Kankaala et al., 2007). In addition, the availability of dissolved O_2 in lakes varies according to season, trophic state, stratification, and geomorphology; being the depth of particular relevance (Jenny et al., 2016; Lewis, 1996; Nürnberg, 1996), making methanotrophy spatio-temporally variable.

Since methanogenesis and methanotrophy are strongly dependent on temperature (Duc et al., 2010; Dunfield et al., 1993; Lofton et al., 2014; Zeikus and Winfrey, 1976), temperature changes throughout the year can influence the seasonal patterns of CH_4 net emission from lakes (Aben et al., 2017; Davidson et al., 2018; Marotta et al., 2014; Yvon-Durocher et al., 2014; Yvon-Durocher et al., 2017). Methanogenesis increases exponentially with temperature until reaching an optimal value and then declines rapidly due to inactivation and cellular decay (Schulz et al., 1997; Svensson, 1984). Moreover, methanogenesis is carried out by two coexisting biochemical pathways; *i.e.*, autotrophy and heterotrophy, which have different thermal dependencies and distinct temperature optima (Conrad, 1999; Schulz et al., 1997; Svensson, 1984). The thermal dependency of methanotrophy may be less complex. Lofton et al. (2014) reported a linear response of methanotrophy to temperature increase under substrate-saturated conditions, and Duc et al. (2010) and Dunfield et al. (1993) have observed that substrate availability (*i.e.*, CH_4 and O_2) positively affects methanotrophy rates in a stronger way than temperature. The response of methanogenesis and methanotrophy to temperature comprises a complicated matrix of factors, and its understanding is fundamental to predict how net CH_4 emission from aquatic ecosystems will respond to climate warming (Aben et al., 2017; Audet et al., 2017; Davidson et al., 2018; Marotta et al., 2014; Negandhi et al., 2016; Yvon-Durocher et al., 2014; Yvon-Durocher et al., 2017).

In this context, eutrophication, which has become a major problem affecting biodiversity and biogeochemical cycles in aquatic ecosystems (Moss et al., 2011; Schilder et al., 2017; Schindler, 2012), may play an important role in CH_4 cycling, because it modifies O_2 and substrate availability in lakes, regulating methanogenesis and methanotrophy. Furthermore, climate warming exacerbates some symptoms of eutrophication, such as deoxygenation of the water column and increased phytoplankton biomass (Moss et al., 2011). Currently, eutrophication in lakes, associated to climate warming and anthropogenic activities, has increased, with ecosystems showing scarce or null resilience (Jenny et al., 2016). Therefore, it is plausible that severe eutrophication could alter the magnitude and net balance of CH_4 production and oxidation in lakes (Aben et al., 2017; Adrian et al., 2016; Davidson et al., 2018).

Until now, it has been difficult to determine whether climate warming in conjunction with eutrophication will tilt the CH_4 balance in lakes towards higher or lower CH_4 emissions to the atmosphere. To address this question, we conducted anaerobic potential methanogenic (PMP) and aerobic potential methanotrophic (PMox) assays, using sediments and water samples, respectively. Samples were collected from ten lakes located in tropical, temperate and subarctic latitudes. These lakes varied in their trophic state, ranging from oligotrophic to hypereutrophic. The samples were incubated at temperatures ranging from 2 to 42 °C, and from these assays, the temperature dependence of both methanogenic and methanotrophic processes was determined and used to model the impact of a potential climate warming scenario on net CH_4 emission from lakes.

2. Materials and methods

2.1. Study sites and sampling

Incubations were conducted using sediment and water samples from 10 lakes located across different latitudes (Table 1). Two were located at high-latitude (Alaska), two at temperate latitude (Germany) and six at tropical latitude (Mexico). Among the six lakes located in Mexico, three were in highlands (altitudes between 2255 and 2840 m *asl*) and three in lowlands (0–20 m *asl*). The ecosystems were selected according to four main criteria: (i) lake characteristics that are typical from the region, (ii) availability of limnological and biogeochemical information, (iii) accessibility to the ecosystem, and (iv) priority was given to the selection of ecosystems with distinct nutrient regimes. For this purpose, the trophic state index (TSI) and physicochemical parameters, determined in previous studies, were considered for the selection of the study sites (Table 1). The physicochemical parameters discussed in this study included: Secchi disk depth (m), determined with a 0.2 m Secchi disk; ammonium-NH_4^+ (mg L^{-1}), nitrate-NO_3^- (mg L^{-1}), and soluble reactive phosphorous-SRP (mg L^{-1}), determined according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2005); chlorophyll *a* (mg L^{-1}), determined in Mexico and Germany according to standard methods, while a calibrated multiparametric probe Hydrolab Data Sonde (Hach, Loveland, Colorado, USA) was used for the chlorophyll *a* analyses of the water samples from Alaskan lakes. Whereas total organic carbon-TOC (mg L^{-1}) and total nitrogen-TN (mg L^{-1}) were measured using carbon elemental analyzers (TOC Shimadzu-Vcsn + TN1 module, in Mexico and Germany; Aurora TOC 1030 W, O·I Analytical, in Alaska).

Surficial sediment samples (for incubation tests) were collected in the central region of each lake using a mud sampler (Ekman dredge for Alaskan and Mexican lakes, and a gravity core for German lakes), with the objective of obtaining samples of the most active anaerobic sediment layer (Marotta et al., 2014). Simultaneously, water samples were collected from the oxycline using a water sampler (2.2 L horizontal Van Dorn Bottle for Alaskan and Mexican lakes and a 2 L Limnos water sampler for German lakes). When the oxycline was absent, samples were taken from the epilimnion at 1 m depth (*e.g.*, Otto and Llano lakes samples), since it has been observed that methanotrophy rates are similar throughout the water column (Martinez-Cruz et al., 2015; Utsumi et al., 1998). Sediment and water samples were stored for about a day at 2 °C, until incubation tests where initiated. The estimation of aerobic and anaerobic methanotrophy occurring on surficial sediments was out of the scope of the present study.

Table 1
Location and characteristics of study sites.

Name	Latitude (°N)	Longitude (°W)	Biome	TSI Classification	TSI[a]	Area (km^2)	MD[b] (m)	References
Goldstream[c]	64.916	147.908	Subarctic yedoma-type thermokarst lake	Mesotrophic	41	0.01	3.3	Sepulveda-Jauregui et al. (2015)
Otto	63.842	149.037	Subarctic non-yedoma-type lake	Oligotrophic	35	0.52	3.1	Sepulveda-Jauregui et al. (2015)
Dagow	53.150	13.051	Temperate lake	Eutrophic	64	0.24	9.5	Casper (1992); Casper et al. (2005)
Stechlin	53.152	13.026	Temperate lake	Oligotrophic	34	4.24	68	Casper (1992); Casper et al. (2005)
Guadalupe	19.627	99.269	Tropical man-made highland lake	Hypereutrophic	85	4.50	17	Sepulveda-Jauregui et al. (2013)
Llano	19.658	99.507	Tropical man-made highland lake	Oligotrophic	22	0.06	14.2	Sepulveda-Jauregui et al. (2013)
Tezozomoc	19.499	99.211	Tropical man-made highland lake	Hypereutrophic	99	0.02	1.2	Martinez-Cruz et al. (2017)
San Julian	19.254	96.262	Tropical lowland lake	Eutrophic	66	0.83	1.5	This study
Olmeca	19.149	96.15	Tropical man-made lowland lake	Hypereutrophic	90	0.62	1.5	Gonzalez-Valencia et al. (2014)
Encanto	19.168	96.156	Tropical man-made lowland lake	Hypereutrophic	80	0.02	1.7	This study

[a] TSI = Trophic state index based on reported data.
[b] MD = Maximum known depth.
[c] Colloquial lake name.

2.2. Experimental setup

The aim of our study was to improve our understanding of the factors influencing methanogenesis and methanotrophy in lakes, including the underlying processes. With that purpose, both processes were quantified through incubations. However, it is of the utmost importance to note that both the CH_4 production and oxidation rates obtained from these incubations do not reflect *in situ* rates and should only be considered as potential. This is mainly due to the disturbance exerted upon the sediment and water samples during the sampling process and the experimental set up (Hoyos-Santillan et al., 2016a; Moore and Dalva, 1997).

The PMP was estimated using surficial sediments from the top 20 cm layer where higher methanogenic activity is located, whereas PMox was estimated using water samples. Sediment used for PMP assays were diluted (1:1 *v*/v) with CH_4-free anaerobic water that was previously boiled and degassed with Ultra-High Purity N_2 (UHP, 99.999%). From the resulting slurry, 30 mL were transferred to serological bottles (60 mL) under continuous flushing with N_2 UHP. Nitrogen flushing was maintained for an additional five minutes. Subsequently, serological vials were air-tight sealed with rubber stoppers and aluminium crimp caps. Incubations were run in triplicate at 2, 8, 17, 23, 30, 37 and 42 °C for 30 to 45 days. PMox was determined using 30 mL water samples, which were transferred to 60 mL serological bottles under

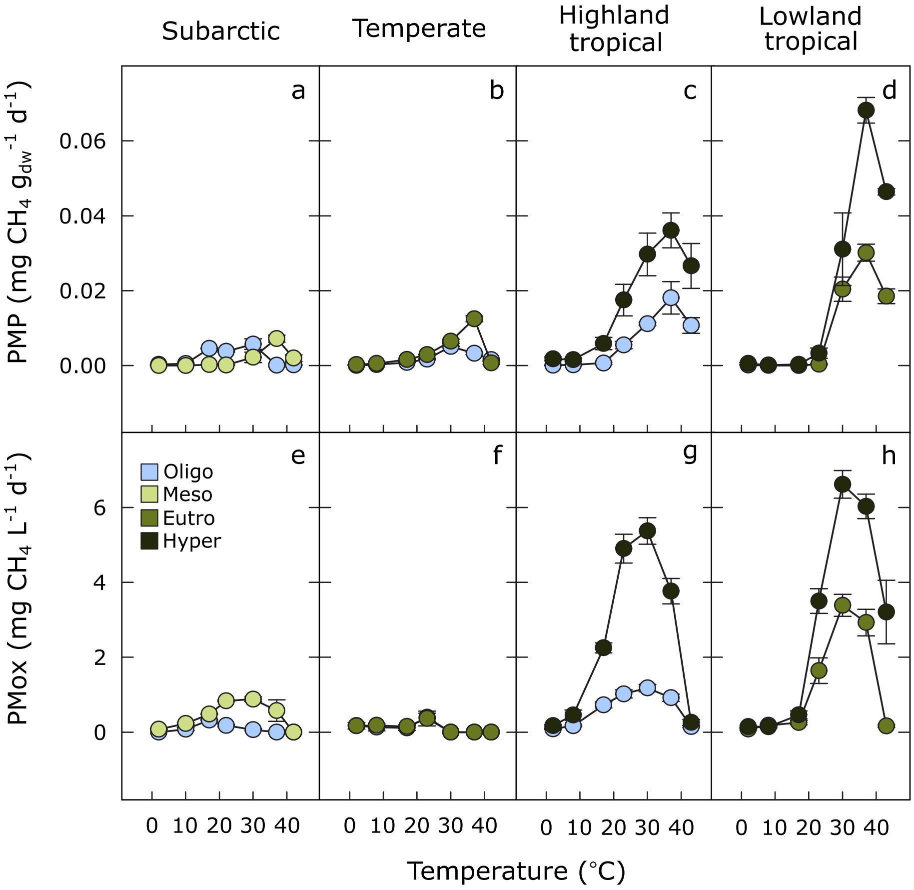


Fig. 1. Temperature sensitivity of the potential CH_4 production-PMP in sediments (a-d) and the potential CH_4 oxidation- PMox in water column (e-h). Colour circles represent the trophic state of the lake; oligotrophic (blue), mesotrophic (light green), eutrophic (medium green) and hypereutrophic (dark green). Errors bars indicate standard error of incubation set of triplicate incubation; two subarctic, two temperate, three highland tropical and three lowland tropical lakes analyzed.

continuous flushing with synthetic air (21% O_2, balance N_2). Flushing was maintained for additional five minutes; afterwards, vials were airtight sealed with butyl-rubber stoppers and aluminium crimp caps. Each PMox incubation vial was spiked with 1 mL of CH_4 (99.0% CH_4), giving a final gas phase CH_4 concentration of 3.33%. PMox incubations were run by triplicate at 2, 8, 17, 23, 30, 37 and 42 °C for 15 days. PMP and PMox rates were calculated from the linear accumulation or consumption of CH_4 in the headspace over the incubation time, respectively. Concentration of CH_4 was determined by gas chromatography; the chromatograph was equipped with a flame ionization detector and FID detector (Shimadzu 2014 in Alaska and Germany, and Perkin Elmer Clarus 500 in Mexico). Potential rates of methanogenesis and methanotrophy were accepted when the linear regression models presented a $P < 0.001$ and a $R^2 > 0.7$ (data from at least 4 measurements in each triplicate temperature). PMP and PMox rates are reported as mass of CH_4 produced per mass of dry weight of sediment per day (mg CH_4 g_{dw}^{-1} d^{-1}) and mass of CH_4 oxidized per volume of water per day (mg CH_4 L^{-1} d^{-1}), respectively.

We used temperature dependence to explore the effect of trophic state and latitude on the potential rates of PMP and PMox. The observed temperature maxima (T'_{opt}) is the temperature at which the highest PMP or PMox rates were observed for each lake (Svensson, 1984). PMox assays were conducted without substrate limitation (*i.e.*, O_2 and CH_4), and PMP assays were conducted without substrate addition, but under well mixed conditions, which reduce potential local limitations of mass transfer, although mixing may disturb microbial consortia present in the natural environment. These conditions were selected to restrain additional factors from influencing T'_{opt}.

2.3. Q_{10} and activation energy

The sensitivity of PMP and PMox to temperature was assessed through the Q_{10} coefficient, which corresponds to the magnitude of PMP or PMox rate change as the result of a 10 °C temperature increase (Eq. (1)); where r_a and r_b are the PMP (mg CH_4 g_{dw}^{-1} d^{-1}) or PMox (mg CH_4 L^{-1} d^{-1}) rates at the incubation temperatures T_a and T_b (°C), respectively:

$$Q_{10} = \left(\frac{r_b}{r_a}\right)^{\left(\frac{10}{T_b - T_a}\right)} \tag{1}$$

Additionally, the sensitivity of PMP and PMox to temperature was also assessed through the apparent activation energy (E'_a; kJ mol^{-1}) described by the Arrhenius equation (Duc et al., 2010). The apparent activation energy was calculated from the positive exponential section of the PMP and PMox temperature dependence curves. For this purpose, the Arrhenius equation was linearized by applying natural logarithm

Table 2
E'_a and Q_{10} values (mean ± SE) for: potential methanotrophic production (PMP) and potential aerobic oxidation of CH_4 (PMox). The summary of the statistical analysis outputs (REML) is also presented. A is the Arrhenius constant, which is a pre-exponential factor that expresses the dependence of the rate coefficient to temperature.

Assay	Lake	Trophic state	E'_a (kJ mol^{-1})	Q_{10}	A
PMP					
	Otto	Oligotrophic	92.6 ± 6.6	3.5 ± 0.6	6.12×10^{16}
	Stechlin	Oligotrophic	105.5 ± 1.1	4.9 ± 0.0	1.33×10^{19}
	L. Llano	Oligotrophic	127.9 ± 16.1	6.2 ± 0.7	1.53×10^{23}
	Goldstream	Mesotrophic	142.8 ± 10.6	8.5 ± 0.1	7.70×10^{25}
	Dagow	Eutrophic	77.3 ± 1.7	2.9 ± 0.0	1.03×10^{14}
	L. Guadalupe	Hypereutrophic	72.4 ± 2.6	2.5 ± 0.0	1.33×10^{13}
	Encanto	Hypereutrophic	194.4 ± 14.3	5.2 ± 1.4	1.74×10^{25}
	Tezozomoc	Hypereutrophic	230.1 ± 2.6	18.9 ± 0.6	5.17×10^{41}
	Olmeca	Hypereutrophic	243.2 ± 30.2	4.3 ± 0.5	1.22×10^{44}
	San Julian	Hypereutrophic	274.1 ± 57.7	7.1 ± 1.1	4.89×10^{49}
PMox					
	Otto	Oligotrophic	103.7 ± 8.3	4.6 ± 0.4	3.78×10^{18}
	Stechlin	Oligotrophic	77.8 ± 13.4	3.4 ± 0.6	7.62×10^{13}
	L. Llano	Oligotrophic	64.9 ± 6.3	2.4 ± 0.1	3.50×10^{11}
	Goldstream	Mesotrophic	74.6 ± 3.9	2.7 ± 0.3	2.00×10^{13}
	Dagow	Eutrophic	71.4 ± na	2.9 ± na	5.27×10^{12}
	L. Guadalupe	Hypereutrophic	144.3 ± 17.5	3.1 ± 0.2	8.65×10^{25}
	Encanto	Hypereutrophic	101.5 ± 7.8	3.4 ± 0.2	1.51×10^{18}
	Tezozomoc	Hypereutrophic	70.6 ± 2.4	3.0 ± 0.1	3.77×10^{12}
	Olmeca	Hypereutrophic	149.8 ± 27.3	3.8 ± 0.4	8.60×10^{26}
	San Julian	Hypereutrophic	110.1 ± 13.2	7.4 ± 2.2	5.46×10^{19}

Summary of statistical analyses for E'_a and Q_{10} in PMP and PMox[a,b]

		F	df	*P*
E'_a				
PMP-PMox		22.4	1,74	<0.001
PMP	Trophic state	7.1	3,32	<0.001
	Latitude	6.7	3,32	<0.001
PMox	Trophic state	4.1	3,37	<0.013
	Latitude	0.9	3,37	n.s.
Q_{10}				
PMP-PMox		12.8	1,75	<0.001
PMP	Trophic state	1.28	3,32	n.s.
	Latitude	0.59	3,32	n.s.
PMox	Trophic state	1.75	3,37	n.s.
	Latitude	2.97	3,37	0.04

[a] E'_a and Q_{10} values were log_{10} transformed to fulfil the homogeneity of variance requirements of the REML.

[b] n.s. = not significant (>0.05).

(Eq. (2)); where r_T is the PMP or PMox rates at T; A is the Arrhenius constant, which is a pre-exponential factor that expresses the dependence of the rate coefficient on temperature; R is the universal gas constant (8.314 J mol^{-1} K); T is the absolute incubation temperature expressed in Kelvin (K), and E'_a /R is determined from the slope of the Ln(r_T) *vs* 1/T graph:

$$\ln(r_T) = \ln(A) - \left(\frac{E'_a}{R}\frac{1}{T}\right) \quad (2)$$

2.4. Impact of a temperature increase scenario on lake CH_4 emissions

To evaluate the effect of a potential temperature increase caused by climate warming in CH_4 production and oxidation in lakes, we considered a model lake in which CH_4 production and oxidation comply with the following assumptions: (i) the lake has a homogeneous reference temperature (T) assumed to be 15 °C (present temperature assumption) and is subjected to a temperature increase that affects equally the water column and sediments (ΔT); (ii) at T, the total CH_4 production rate in the lake ($R_{MP,T}$; kg CH_4 d^{-1}) is a fixed and arbitrary rate, while the total CH_4 oxidation rate in the lake ($R_{MOX,T}$; kg CH_4 d^{-1}) is considered to be 60% of $R_{MP,T}$, which is a conservative estimation (Bastviken et al., 2008; Kankaala et al., 2007; Thauer et al., 2008); and (iii) the net CH_4 emission from the lake is exclusively the result of the balance between $R_{MP,T}$ and $R_{MOX,T}$. From these assumptions, we estimated the impact of ΔT on the balance between CH_4 production and oxidation (Eq. (3)); where ΔCH_4 (%) is the modeled increase in net methane emission and $R_{MP,T}$ and $R_{MOX,T}$ were determined with the Arrhenius equation (Eq. (2)).

$$\Delta CH_4(\%) = \left(\frac{R_{MP,T+\Delta T} - R_{MOX,T+\Delta T}}{R_{MP,T} - R_{MOX,T}} - 1\right) \times 100 \quad (3)$$

2.5. Statistical analysis

We used linear mixed models to assess the effect of the trophic state and latitude on the temperature dependence of PMP and PMox. The models were fitted using residual maximum likelihood (REML) due to the unbalanced nature of the data, a consequence of the experimental program with different number of lakes at each latitude and under distinct trophic states. To analyse the effect of trophic state and latitude on Q_{10} and E'_a from PMP and PMox, trophic state and latitude were used as fixed factors and the individual lakes as random factor. PMP and PMox rates were $\log_{10}$ transformed to fulfil the normality condition of the REML. Level of significance of the differences between the fixed effects was estimated by Wald tests using an F distribution; significance was attributed at $P < 0.05$. To explore the relationship between PMP and PMox rates at T'_{opt} against trophic state and physicochemical parameters we used linear regression analyses. Statistical analyses were performed

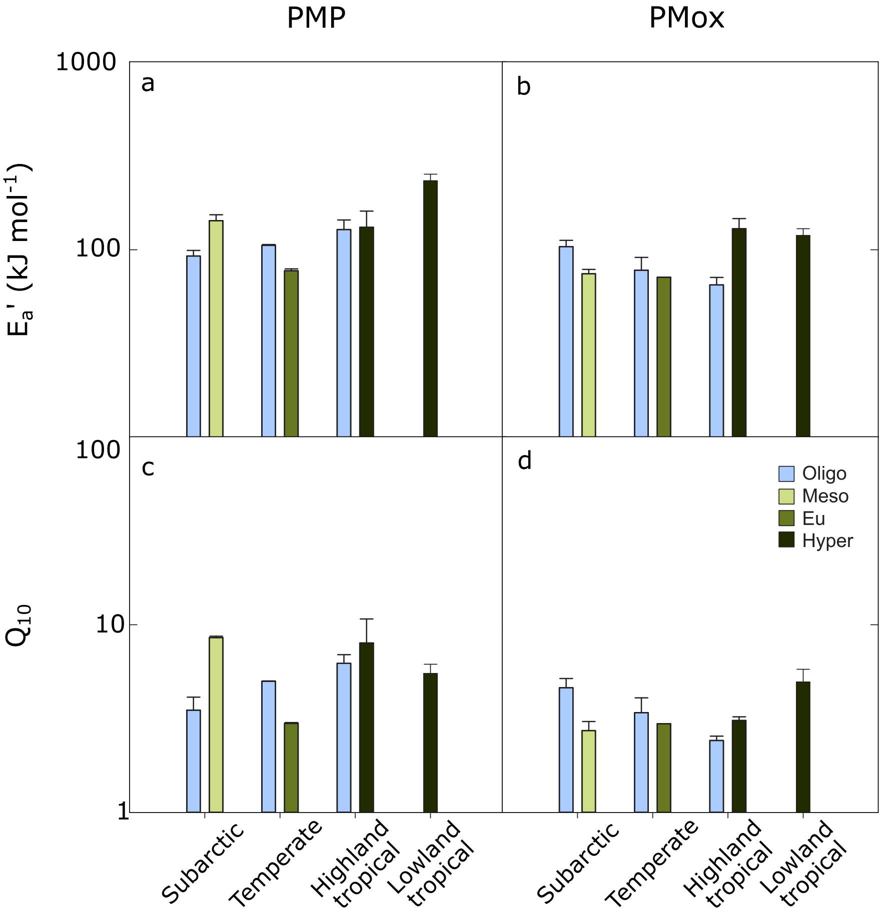


Fig. 2. Temperature sensitivity of the potential CH_4 production-PMP in sediments (a and c) and the potential CH_4 oxidation- PMox in water column (b and d) expressed as the apparent activation energy (E'_a) and Q_{10} coefficient. Colour bars represent trophic state of the lake; oligotrophic (blue), mesotrophic (light green), eutrophic (medium dark green) and hypereutrophic (dark green). The y axis is represented in a Log_{10} scale. Errors bars indicate standard error of incubation set of triplicate incubation; two subarctic, two temperate, three highland tropical and three lowland tropical lakes analyzed.

with NCSS 11 Statistical Analysis System software (NCSS LLC, Kaysville UT, USA).

3. Results and discussion

3.1. Influence of eutrophication and latitude on optimum of temperature response

The PMP and the PMox rates showed a clear dependence with temperature (Fig. 1). Minimum PMP and PMox rates of 0.53 ± 0.14 μg g_{dw}^{-1} d^{-1} and 0.13 ± 0.01 mg L^{-1} d^{-1}, respectively were observed at the lowest tested temperatures (2 °C) (PMP-Temperature of assay: $F_{7,210} = 210.1$, $P < 0.001$); PMox-Temperature of assay: $F_{7,181} = 93.9$, $P < 0.001$). These rates gradually increased until reaching an optimum rate, at different temperatures (T'_{opt}), according to the latitude and trophic state (Fig. 1). The PMP presented higher mean T'_{opt} values (34.98 ± 0.47 °C) in comparison with PMox (29.09 ± 0.70 °C; T'_{opt}: $F_{1,88} = 85$, $P < 0.001$). The T'_{opt} for PMP was independent of the trophic state and latitude of the lakes (T'_{max} -trophic state: $F_{3,2.3} = 1.4$, $P > 0.05$; T'_{opt} -latitude: $F_{3,2.3} = 2.8$, $P > 0.05$) (Fig. 1 a-d). This might be caused by the relatively low sensitivity of the methanogenic community composition to temperature variations, as previously reported (Cui et al., 2015). The mean T'_{opt} value for methanogenesis (34.98 ± 0.47 °C) is consistent with mesophilic methanogenesis activity, with optimal temperatures ranging between 30 and 42 °C (Blake et al., 2015; Schulz et al., 1997; Zeikus and Winfrey, 1976). This range of temperature suggests that, in most of our assays, methanogenesis was conducted by heterotrophic and hydrogenotrophic (H_2/CO_2) pathways, since these temperatures favor the production of the necessary precursors for syntrophic H_2 production (Schulz et al., 1997). Despite the fact that T'_{opt} for PMP was independent of the latitude of the lakes, a CH_4 maximum production rate was observed at 15 °C in the sediments from subarctic lakes under oligotrophic conditions (Fig. 1a), but not in lakes located in lower latitudes, suggesting the presence of an active psychrotolerant/psychrophilic methanogenic community in some northern lakes (Nozhevnikova et al., 2003). By contrast, the T'_{opt} for PMox rates varied with trophic state and latitude (T'_{opt} -Trophic state: $F_{3,7.4} = 6.2$, $P < 0.05$; T'_{opt}-latitude: $F_{3,5} = 9$, $P < 0.05$), increasing parallel to the trophic state index and decreasing as latitude increased (Fig. 1 e-h). Under oligotrophic conditions the mean T'_{opt} for PMox rates was 25.40 ± 1.95 °C, whereas under hypereutrophic conditions, the mean T'_{opt} for PMox rates was 31.17 ± 0.83 °C. The mean T'_{opt} for PMox rates in subarctic lakes was 22.17 ± 2.61 °C, which is lower in comparison with the 31.26 ± 0.81 °C observed in lowland tropical lakes. This can be explained by distinct methanotrophic consortia, whose composition is dependent on the average annual temperature in the lake, as an adaptive response to environmental conditions (Martineau et al., 2010; Trotsenko and Murrell, 2008; Wartiainen et al., 2006). Thus, in subarctic lakes, and temperate lakes the T'_{opt} corresponded to a methanotroph community rich in psychrotolerant and psychrophilic microorganisms, compared to the mesophilic methanotrophs found in tropical lakes. Indeed, psychrotolerant and psychrophilic methanotrophs exist in the environment, and many ecosystems produce large quantities of CH_4 in cold regions (Ricao Canelhas et al., 2016; Martinez-Cruz et al., 2015; reviewed in Semrau et al., 2010).

Comparing all PMP and PMox rates observed at T'_{opt} ($r_{opt,PMP}$ and $r_{opt,PMox}$, respectively), we found that both were influenced by the latitude ($r_{opt,PMP}$-latitude: $F_{3,2.4} = 13.2$, $P < 0.05$; $r_{opt,PMox}$ -latitude: $F_{3,4} = 45.5$, $P < 0.01$), with highest values observed in lakes located at lowland tropical regions, whereas subarctic lakes presented the lowest $r_{opt,PMP}$ and $r_{opt,PMox}$ (Fig. 1). The $r_{opt,PMP}$ were also influenced by the trophic state ($r_{opt,PMP}$ -Trophic state: $F_{3,2.4} = 28.9$, $P < 0.05$), and were 14-fold lower in oligotrophic lakes (0.005 ± 0.001 mg CH_4 g_{dw}^{-1} d^{-1}), compared to hypereutrophic lakes (0.068 ± 0.003 mg CH_4 g_{dw}^{-1} d^{-1}) (Fig. 1 a-d). Similarly, the $r_{opt,PMox}$ were influenced by the trophic state ($r_{opt,PMox}$ -Trophic state: $F_{3,6} = 145.8$, $P < 0.001$), and were 20-fold lower under oligotrophic conditions (0.344 ± 0.019 mg CH_4 L^{-1} d^{-1}), than those observed in hypereutrophic lakes (6.843 ± 0.287 mg CH_4 L^{-1} d^{-1}) (Fig. 1 e-h).

The PMP presented higher activation energy (E'_a) values than PMox, with mean values of 165.34 ± 13.59 kJ mol^{-1} and 110.92 ± 7.30 kJ mol^{-1}, respectively (Table 2; Fig. 2a-b). The highest E'_a values for PMP and PMox were observed in hypereutrophic lakes (Fig. 2) (PMP, E'_a – trophic state: $F_{3,32} = 7.1$, $P < 0.001$; PMox, E'_a – trophic state: $F_{3,37} = 4.1$, $P < 0.001$), suggesting that PMP and PMox sensitivity to temperature is increased in highly eutrophic ecosystems. However, E'_a values were similar in ecosystems ranging from oligotrophic to eutrophic, discarding a linear response of temperature sensitivity to eutrophication. The Q_{10} coefficient, which corresponds to the magnitude of rate change as result of a 10 °C temperature increase, revealed the same tendency, with values of 5.92 ± 0.68 for PMP and 4.01 ± 0.44 for PMox (Table 2; Fig. 2c-d). The differences between Q_{10} values for methanogenesis and methanotrophy, as well as their magnitude, are consistent with previous reports; with values of up to 28 for methane

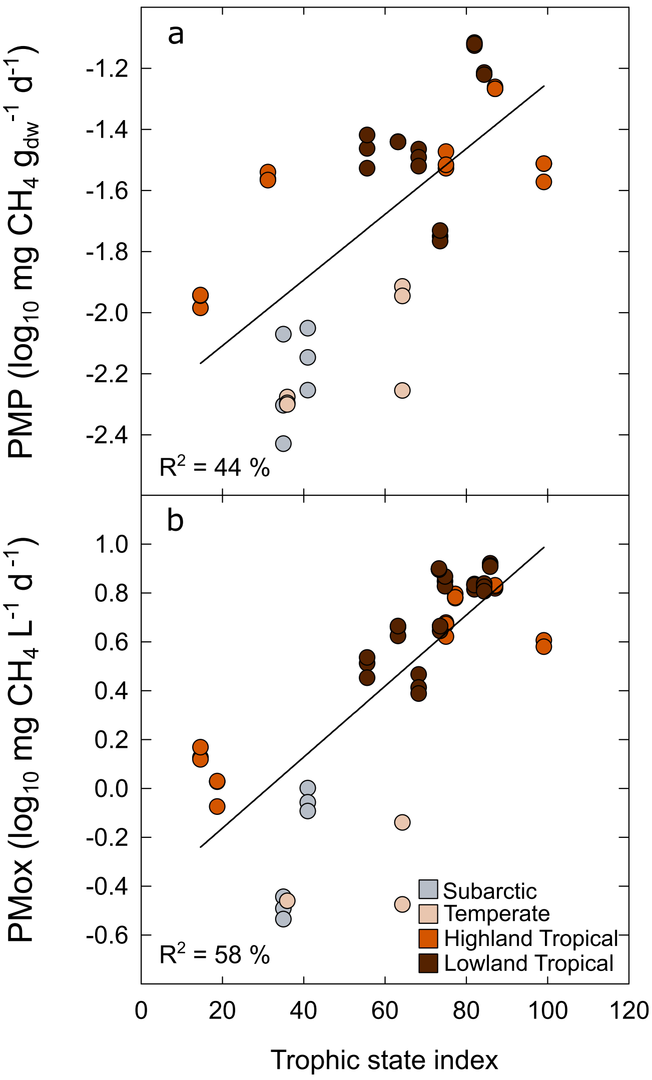


Fig. 3. The potential CH_4 production-PMP at T'_{opt} in sediments (a) and the potential CH_4 oxidation- PMox T'_{opt} in water column (b) in relation to trophic state index. Circles colour represents latitude location of the lake; subarctic (gray), temperate (pale orange), highland tropical (orange) and lowland tropical (brown). The fitted solid lines correspond to the linear regression estimates for a semi logarithmic data transformation.

production, and 4.1 for methane oxidation (Duc et al., 2010; Dunfield et al., 1993; Segers, 1998).

Our findings further support previous evidence that methanotrophy is less sensitive to temperature increments than methanogenesis, with a systematic approach encompassing, for the first time, methanogenic and methanotrophic processes at four different latitudes and in lakes with contrasting trophic states. As it will be developed hereafter, the main corollary of the lower thermal sensitivity of methanotrophy is that with climate warming a larger net CH_4 emission from lakes is expected. However, it is important to highlight that, in the present work, the results obtained, and their derived conclusions were based on a single time point, without considering seasonal variations. Whereas the results obtained from PMP incubations may be considered poorly sensitive to seasonal variations, as suggested by Yvon-Durocher et al. (2014), for instance Martinez-Cruz et al. (2015) observed strong variations of PMox in subarctic lakes among seasons. Therefore, due to the limited amount of lakes included in our experimental approach, the results presented in this study should be considered with caveats. Additional research including a larger number of lakes and a multi-seasonal approach is required to fully understand the effect of trophic state on the sensitivity of PMP and PMox to temperature changes.

3.2. Potential methanogenesis and methanotrophy in relation to eutrophication

When exploring the relationship between $r_{opt,}$for both methanogenesis and methanotrophy and trophic state, lowland tropical lakes were clearly located in the higher cluster of the data regression, while the rates for subarctic and temperate lakes were located in the lower cluster (Fig. 3). Physicochemical parameters such as TOC, TN, NH_4^+ and SRP were also positively correlated to $r_{opt,PMP}$ and $r_{opt,PMox}$; these physicochemical parameters explained 13 to 34% and 15 to 46% of the variance in $r_{opt,PMP}$ and $r_{opt,PMox}$, respectively (Table 3). Moreover, $r_{opt,PMP}$ and $r_{opt,PMox}$ were inversely correlated with the Secchi disk depth (Table 3). The relationship observed between the rates of PMP and PMox at T'_{opt} and the degree of eutrophication or the physicochemical parameters (apart from chlorophyll-a), is consistent with literature, where the dominant role of nutrients and substrates availability on methanogenesis and methanotrophy rates has been reported (Martinez-Cruz et al., 2015; Schulz et al., 1997; Yvon-Durocher et al., 2017). For example, lakes rich in nutrients produce substantial amounts of labile organic matter from primary production, that can be readily transformed into precursors of CH_4, triggering large CH_4 emission to the atmosphere (Davidson et al., 2018; Vonk et al., 2015; West et al., 2016; Yvon-Durocher et al., 2017).

3.3. Potential effect of climate warming on PMP and PMox rates in lakes

Given that present-day lake temperatures are lower than the T'_{opt} determined for methanotrophy and methanogenesis in this study, a temperature increase caused by climate warming should stimulate both processes. Furthermore, being that methanogenesis is more sensitive to temperature than methanotrophy, CH_4 production should increase in a larger proportion than CH_4 consumption, affecting CH_4 balance in lakes, ultimately increasing their CH_4 emission to the atmosphere. To illustrate such effect, we considered a model lake in which CH_4 production and oxidation are affected by a potential increase in temperature, using a reference temperature of 15 °C (present temperature assumption); Fig. 4 shows the results of ΔCH_4 estimation with respect to ΔT, calculated from the mean A and E'_a of two trophic state classes; hypereutrophic ($n = 6$) and oligotrophic lakes ($n = 3$; Table 2). It is relevant to mention that this model does not pretend to simulate what the impact of global warming would be at the global lake ecosystem scale but aims to illustrate the trend of net CH_4 emission in a model lake subject to temperature increase, using an average A and E'_a, experimentally determined. In our model, ΔCH_4 does not depend on the fixed $R_{MP,T}$ selected, but is marginally related to the reference T and the percentage of CH_4 oxidized assumed at that T. For instance, with a reference T of 10 °C or 15 °C, the differences between the estimated ΔCH_4 would not exceed 4%. Similarly, if the percentage of CH_4 oxidized is 70% instead of 60%, the difference in ΔCH_4 would range between 16 and 24%.

According to our model (Fig. 4), a temperature increase would have a positive impact on the net CH_4 emission from the lake, which will be intensified by the trophic state. Considering the temperature dependence of CH_4 production and oxidation determined in the present work, a 2 °C temperature increase in hypereutrophic lakes would result in a 101–183% increase of the net CH_4 emission; whereas in oligotrophic lakes, the increase would be limited to 47–56%; both ranges estimated with a confidence interval of 95%.

We have several reasons to consider that our ΔCH_4 estimations are conservative. First, as previously mentioned, an increase in CH_4 production would fuel methanotrophy by increasing CH_4 availability, but would also reduce O_2 availability throughout the water column. This would be beneficial to anaerobic methanogenesis and detrimental to methanotrophy, but has not been considered in our model. Such sequence of reciprocal cause and effect has been observed in subarctic

Table 3
Linear regression models for PMP and PMox[a]: physicochemical characteristics of water column.

		Intercept	s.e.	*P*	Slope	s.e.	*P*	R^2
PMP								
Secchi disk	(m)	−1.495	0.052	<0.001	−0.123	0.021	<0.001	0.43
Chlorophyll a	($mg\ L^{-1}$)			n.s.			n.s.	–
Trophic state index		−2.322	0.117	<0.001	0.0107	0.001	<0.001	0.44
TOC	($mg\ L^{-1}$)	−1.872	0.080	<0.001	0.006	0.001	<0.001	0.23
TN	($mg\ L^{-1}$)	−1.920	0.069	<0.001	0.055	0.011	<0.001	0.34
NH_4^+	($mg\ L^{-1}$)	−1.688	0.062	<0.001	0.071	0.027	<0.05	0.13
NO_3^-	($mg\ L^{-1}$)			n.s.			n.s.	–
SRP	($mg\ L^{-1}$)	−1.801	0.060	<0.001	0.431	0.113	<0.001	0.23
PMox								
Secchi disk	(m)	−0.701	0.049	<0.001	−0.228	0.028	<0.001	0.55
Chlorophyll a	($mg\ L^{-1}$)			n.s.			n.s.	–
Trophic state index		−0.453	0.116	<0.001	0.014	0.001	<0.001	0.58
TOC	($mg\ L^{-1}$)	−0.218	0.084	<0.05	0.007	0.001	<0.001	0.26
TN	($mg\ L^{-1}$)	0.087	0.073	>0.05	0.071	0.010	<0.001	0.46
NH_4^+	($mg\ L^{-1}$)	0.418	0.063	<0.001	0.074	0.021	<0.001	0.20
NO_3^-	($mg\ L^{-1}$)	0.325	0.094	<0.001	0.387	0.188	<0.05	0.05
SRP	($mg\ L^{-1}$)	0.347	0.069	<0.001	0.441	0.139	<0.01	0.15

n.s. = Not significant ($P > 0.05$).

[a] PMP and PMox values at T'_{opt} were transformed ($\log_{10}$) to fulfil the homogeneity of variance requirement.

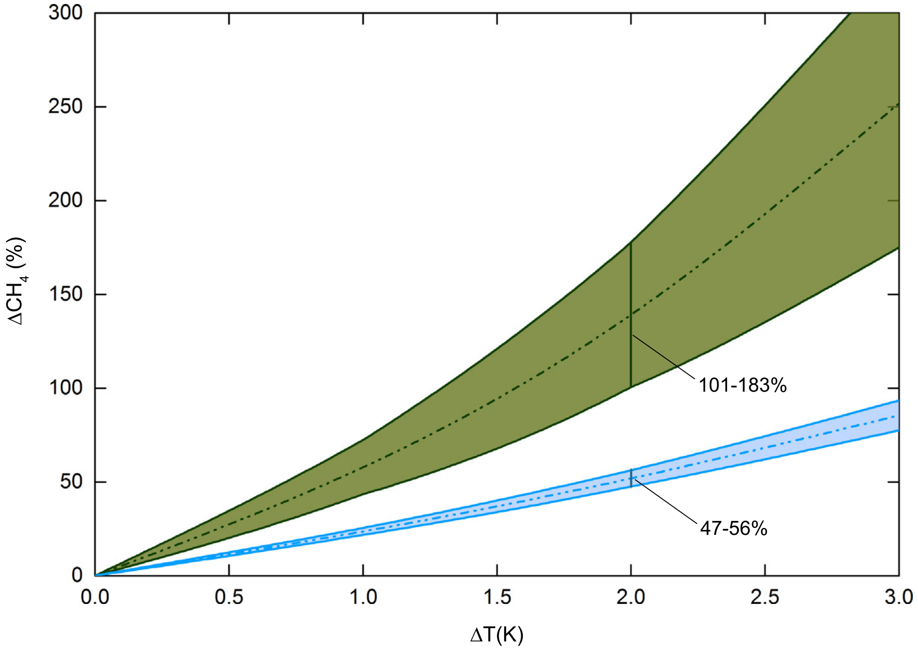


Fig. 4. Impact of a temperature increase scenario on hypereutrophic (green dotted lines) and oligotrophic lakes (blue dotted lines) over the net CH_4 emission balance (ΔCH_4). Blue and green areas show the confidence intervals ($P = 0.05$). The model considers a reference temperature of 15 °C and a percentage of CH_4 oxidized at that temperature of 60%.

lakes, where higher CH_4 concentrations were well correlated with lower dissolved O_2 concentrations (Martinez-Cruz et al., 2015). Second, our model did not consider the particular conditions of high-latitude lakes, which are covered each year by a thick layer of ice for several months. This ice layer impedes gas transfer between water-atmosphere; *e.g.* oxygen supply to the water and affects photosynthesis by reducing light penetration (Clilverd et al., 2009; Vonk et al., 2015), accentuating anoxic conditions and thus further enhancing methanogenesis. Third, our ΔCH_4 estimation did not consider the mixing regime of lakes. Climate warming may increase epilimnion temperature, favoring thermal stratification for longer periods and reducing O_2 availability for methanotrophy in the hypolimnion (DelSontro et al., 2016; Kirillin, 2010; West et al., 2016). Finally, our model does not consider ebullitive emission, which is expected to increase by 6 to 20% per each 1 °C temperature increase (Aben et al., 2017; Davidson et al., 2018; DelSontro et al., 2016) and reduced the accessibility of CH_4 for methanotrophs in the water column.

4. Conclusions

The empirical and theoretical results of this study suggest that the severe eutrophication of lakes may exacerbate the net CH_4 emission from lakes in response to climate warming. Further approaches should consider the complex impact of climate warming on oxygen availability for methanotrophy, which depends on many parameters, such as: mixing regime, primary productivity, seasonality, morphology and bathymetry of the lakes. Moreover, additional factors like the mechanisms of CH_4 transport within the water column (*e.g.*, diffusion *vs* bubbling), quality and quantity of the organic matter available for the syntrophic processes associated to methanogenesis, and the availability of nutrients (*e.g.*, N, S and P) could further improve the current estimates. Nevertheless, even with the partial picture depicted in the present work, most of the parameters that may be affected by climate warming suggest a negative impact on methanotrophy together with a positive impact on methanogenesis, pointing out to a net increase in global CH_4 emissions from lakes.

Acknowledgments

We thank A. Strom, G. Idoate Santaolalla, M. Rodriguez, for field and lab assistance. We gratefully acknowledge the financial support to J.H.-S. (grant #211962), A.S.-J. (grant #232083 and 206621/203709), K.M.-C. (grant #330197/233369), Y.B.-I. (grant #243319) by the Consejo Nacional de Ciencia y Tecnología (CONACyT). This study was funded by SEMARNAT-CONACyT (23661) and by the Leibniz Association within the projects “Climate driven changes in biodiversity of microbiota – TemBi” (SAW-2011-IGB-2), “Aquatic Boundaries and Linkages – Aqualink” (SAW 2012-IGB 4167). Additional support for A.S.-J. and K.M.-C. was provided by Fondo Nacional de Desarrollo Científico y Tecnológico (Fondecyt-Conicyt; grant #11170134 and grant #11160391, respectively). Support for K. W. A. was provided by NASA NNX15AU49A and NSF-1500931.

References

Aben, R.C.H., Barros, N., van Donk, E., Frenken, T., Hilt, S., Kazanjian, G., et al., 2017. Cross continental increase in methane ebullition under climate change. Nat. Commun. 8 (1682). https://doi.org/10.1038/s41467-017-01535-y.

Adrian, R., Hessen, D.O., Blenckner, T., Hillebrand, H., Hilt, S., Jeppesen, E., et al., 2016. Environmental impacts—lake ecosystems. In: Quante, M., Colijn, F. (Eds.), North Sea Region Climate Change Assessment. Springer International Publishing, Cham, pp. 315–340.

APHA (Ed.), 2005. Standard Methods for the Examination of Water and Wastewater, 21st ed. APHA, AWWA, WPCF, Whashingon DC, USA.

Audet, J., Neif, É.M., Cao, Y., Hoffmann, C.C., Lauridsen, T.L., Larsen, S.E., et al., 2017. Heatwave effects on greenhouse gas emissions from shallow lake mesocosms. Freshw. Biol. 62:1130–1142. https://doi.org/10.1111/fwb.12930.

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.J., Pace, M.L., Van de Bogert, M.C., 2008. Fates of methane from different lake habitats: connecting whole-lake budgets and CH4 emissions. J. Gephy. Res. 113:G0204. https://doi.org/10.1029/2007JG000608.

Bastviken, D., Tranvik, L.J., Downing, J.A., Crill, P.M., Enrich-Prast, A., 2011. Freshwater methane emissions offset the continental carbon sink. Science 331. https://doi.org/10.1126/science.1196808.

Blake, L.I., Tveit, A., Øvreås, L., Head, I.M., Gray, N.D., 2015. Response of methanogens in Arctic sediments to temperature and methanogenic substrate availability. PLoS One 10, e0129733. https://doi.org/10.1371/journal.pone.0129733.

Casper, P., 1992. Methanhaushalt in baltischen Seen untershiedlicher Trophiestufe (methane metabolism in Baltic Lakes of different trophic state). Limnologica 22, 121–128.

Casper, P., Adams, D., Furtado, A., Chan, O., Gonsiorczyk, T., Koschel, R., 2005. Greenhouse gas cycling in aquatic ecosystems – methane in temperate lakes across an environmental gradient in NE Germany. Int. Ver. The. Ange. Limnol. 29, 564–566.

Clilverd, H., White, D., Lilly, M., 2009. Chemical and physical controls on the oxygen regime of ice-covered arctic lakes and reservoirs. J. Am. Water Resour. Assoc. 45: 500–511. https://doi.org/10.1111/j.1752-1688.2009.00305.x.

Conrad, R., 1999. Contribution of hydrogen to methane production and control of hydrogen concentrations in methanogenic soils and sediments. FEMS Microbiol. Ecol. 28: 193–202. https://doi.org/10.1111/j.1574-6941.1999.tb00575.x.

Cui, M., Ma, A., Qi, H., Zhuang, X., Zhuang, G., Zhao, G., 2015. Warmer temperature accelerates methane emissions from the Zoige wetland on the Tibetan plateau without changing methanogenic community composition. Sci. Rep.-UK 5:11616. https://doi.org/10.1038/srep11616.

Davidson, T.A., Audet, J., Jeppesen, E., Landkildehus, F., Lauridsen, T.L., Søndergaard, M., Syväranta, J., 2018. Synergy between nutrients and warming enhances methane ebullition from experimental lakes. Nat. Clim. Chang. 8:156–160. https://doi.org/10.1038/s41558-017-0063-z.

Dean, J.F., Middelburg, J.J., Röckmann, T., Aerts, R., Blauw, L.G., Egger, M., et al., 2018. Methane feedbacks to the global climate system in a warmer world. Rev. Geophys. 56: 207–250. https://doi.org/10.1002/2017RG000559.

DelSontro, T., Boutet, L., St-Pierre, A., del Giorgio, P.A., Prairie, Y.T., 2016. Methane ebullition and diffusion from northern ponds and lakes regulated by the interaction between temperature and system productivity. Limnol. Oceanogr. 61:S62–S77. https://doi.org/10.1002/lno.10335.

Duc, N.T., 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.

Dunfield, P., Knowles, R., Dumont, R., Moore, T.R., 1993. Methane production and consumption in temperate and sub-arctic peat soils – response to temperature and pH. Soil Biol. Biochem. 25:321–326. https://doi.org/10.1016/0038-0717(93)90130-4.

Gonzalez-Valencia, R., Sepulveda-Jauregui, A., Martinez-Cruz, K., Hoyos-Santillan, J., Dendooven, L., Thalasso, F., 2014. Methane emissions from Mexican freshwater bodies: correlations with water pollution. Hydrobiologia 721:9–22. https://doi.org/10.1007/s10750-013-1632-4.

Grasset, C., Mendonça, R., Villamor Saucedo, G., Bastviken, D., Roland, F., Sobek, S., 2018. Large but variable methane production in anoxic freshwater sediment upon addition of allochthonous and autochthonous organic matter. Limnol. Oceanogr. in press. https://doi.org/10.1002/lno.10786.

Holgerson, M.A., Raymond, P.A., 2016. Large contribution to inland water CO2 and CH4 emissions from very small ponds. Nat. Geosci. 9:222–226. https://doi.org/10.1038/NGEO2654.

Hoyos-Santillan, J., Lomax, B.H., Large, D., Turner, B.L., Boom, A., Lopez, O.R., et al., 2016. Quality not quantity: organic matter composition controls of CO2 and CH4 fluxes in neotropical peat profiles. Soil Biol. Biochem. 103:86–96. https://doi.org/10.1016/j.soilbio.2016.08.017.

Jenny, J.-P., Francus, P., Normandeau, A., Lapointe, F., Perga, M.-E., Ojala, A., et al., 2016. Global spread of hypoxia in freshwater ecosystems during the last three centuries is caused by rising local human pressure. Glob. Chang. Biol. 22:1481–1489. https://doi.org/10.1111/gcb.13193.

Kankaala, P., Taipale, S., Nykanen, H., Jones, R.I., 2007. Oxidation, efflux, and isotopic fractionation of methane during autumnal turnover in a polyhumic, boreal lake. J. Geophys. Res. Biogeosci. 112, G02003. https://doi.org/10.1029/2006JG000336.

Kirillin, G., 2010. Modeling the impact of global warming on water temperature and seasonal mixing regimes in small temperate lakes. Boreal. Environ. Res. 15 (2), 279–293.

Lewis, W.M., 1996. Tropical lakes: how latitude makes a difference. In: Schiemer, F., Boland, K.T. (Eds.), Perspectives in Tropical Limnology. SPB Academic Publishing, Amsterdam, pp. 44–64.

Lofton, D.D., Whalen, S.C., Hershey, A.E., 2014. Effect of temperature on methane dynamics and evaluation of methane oxidation kinetics in shallow Arctic Alaskan lakes. Hydrobiologia 721:209–222. https://doi.org/10.1007/s10750-013-1663-x.

Marotta, H., Pinho, L., Gudasz, C., Bastviken, D., Tranvik, L.J., Enrich-Prast, A., 2014. Greenhouse gas production in low-latitude lake sediments responds strongly to warming. Nat. Clim. Chang. 4:467–470. https://doi.org/10.1038/NCLIMATE.

Martineau, C., Whyte, L.G., Greer, C.W., 2010. Stable isotope probing analysis of the diversity and activity of methanotrophic bacteria in soils from the Canadian high arctic. Appl. Environ. Microbiol. 76:5773–5784. https://doi.org/10.1128/AEM.03094-09.

Martinez-Cruz, K., Sepulveda-Jauregui, A., Anthony, K.W., Thalasso, F., 2015. Geographic and seasonal variation of dissolved methane and aerobic methane oxidation in Alaskan lakes. Biogeosciences 12:4595–4606. https://doi.org/10.5194/bg-12-4595-2015.

Martinez-Cruz, K., Gonzalez-Valencia, R., Sepulveda-Jauregui, A., Plascencia-Hernandez, F., Belmonte-Izquierdo, Y., Thalasso, F., 2017. Methane emission from aquatic ecosystems of Mexico City. Aquat. Sci. 79:159–169. https://doi.org/10.1007/s00027-016-0487-y.

Moore, T.R., Dalva, M., 1997. Methane and carbon dioxide exchange potentials of peat soils in aerobic and anaerobic laboratory incubations. Soil Biol. Biochem. 29: 1157–1164. https://doi.org/10.1016/S0038-0717(97)00037-0.

Moss, B., Kosten, S., Meerhoff, M., Battarbee, R.W., Jeppesen, E., Mazzeo, N., et al., 2011. Allied attack: climate change and eutrophication. Inland Waters 1:101–105. https://doi.org/10.1002/2013GL057669.

Negandhi, K., Laurion, I., Lovejoy, C., 2016. Temperature effects on net greenhouse gas production and bacterial communities in arctic thaw ponds. FEMS Microb. Ecol. 92, fiw117. https://doi.org/10.1093/femsec/fiw117.

Nozhevnikova, A.N., Zepp, K., Vazquez, F., Zehnder, A.J.B., Holliger, C., 2003. Evidence for the existence of psychrophilic methanogenic communities in anoxic sediments of deep lakes. Appl. Environ. Microbiol. 69:1832–1835. https://doi.org/10.1128/AEM.69.3.1832-1835.2003.

Nürnberg, G.K., 1996. Trophic state of clear and colored, soft- and Hardwater Lakes with special consideration of nutrients, anoxia, phytoplankton and fish. Lake and Reserv. Manage. 12:432–447. https://doi.org/10.1080/07438149609354283.

Peura, S., Nykanen, H., Kankaala, P., Eiler, A., Tiirola, M., Jones, R.I., 2014. Enhanced greenhouse gas emissions and changes in plankton communities following an experimental increase in organic carbon loading to a humic lake. Biogeochemistry 118:177–194. https://doi.org/10.1007/s10533-013-9917-2.

Ricao Canelhas, M., Denfeld, B.A., Weyhenmeyer, G.A., Bastviken, D., Bertilsson, S., 2016. Methane oxidation at the water-ice interface of an ice-covered lake. Limnol. Oceanogr. 61:S78–S90. https://doi.org/10.1002/lno.10288.

Saunois, M., Bousquet, P., Poulter, B., Peregon, A., Ciais, P., Canadell, J.G., et al., 2016. The global methane budget 2000–2012. Earth Syst. Sci. Data 8:697–751. https://doi.org/10.5194/essd-8-697-2016.

Schilder, J., van Hardenbroek, M., Bodelier, P., Kirilova, E.P., Leuenberger, M., Lotter, A.F., et al., 2017. Trophic state changes can affect the importance of methane-derived carbon in aquatic food webs. P. Roy. S. B Biol. Sci. 284. https://doi.org/10.1098/rspb.2017.0278.

Schindler, D.W., 2012. The dilemma of controlling cultural eutrophication of lakes. P. Roy. S. B Biol. Sci. 279:4322. https://doi.org/10.1098/rspb.2012.1032.

Schulz, S., Matsuyama, H., Conrad, R., 1997. Temperature dependence of methane production from different precursors in a profundal sediment (Lake Constance). FEMS Microbiol. Ecol. 22:207–213. https://doi.org/10.1016/S0168-6496(96)00091-8.

Segers, R., 1998. Methane production and methane consumption: a review of processes underlying wetland methane fluxes. Biogeochemistry 41:23–51. https://doi.org/10.1023/A:1005929032764.

Semrau, J.D., DiSpirito, A., Yoon, S., 2010. Methanotrophs and copper. FEMS Microbiol. Rev. 34:496–531. https://doi.org/10.1111/j.1574-6976.2010.00212.x.

Sepulveda-Jauregui, A., Hoyos-Santillan, J., Gutierrez-Mendieta, F.J., Torres-Alvarado, R., Dendooven, L., Thalasso, F., 2013. The impact of anthropogenic pollution on limnological characteristics of a subtropical highland reservoir "Lago de Guadalupe", Mexico. Knowl. Manag. Aquat. Ec. (410):04 https://doi.org/10.1051/kmae/2013059.

Sepulveda-Jauregui, A., Anthony, K.M.W., Martinez-Cruz, K., Greene, S., Thalasso, F., 2015. Methane and carbon dioxide emissions from 40 lakes along a north-south latitudinal transect in Alaska. Biogeosciences 12:3197–3223. https://doi.org/10.5194/bg-12-3197-2015.

Svensson, B.H., 1984. Different temperature optima for methane formation when enrichments from acid peat are supplemented with acetate or hydrogen. Appl. Environ. Microbiol. 48, 389–394.

Thauer, R.K., Kaster, A.K., Seedorf, H., Buckel, W., Hedderich, R., 2008. Methanogenic archaea: ecologically relevant differences in energy conservation. Nat. Rev. Microbiol. 6:579–591. https://doi.org/10.1038/nrmicro1931.

Trotsenko, Y.A., Murrell, J.C., 2008. Metabolic aspects of aerobic obligate methanotrophy. Adv. Appl. Microbiol. 63:183–229. https://doi.org/10.1016/S0065-2164(07)00005-6.

Utsumi, M., Nojiri, Y., Nakamura, T., Nozawa, T., Otsuki, A., Seki, H., 1998. Oxidation of dissolved methane in a eutrophic, shallow lake: Lake Kasumigaura, Japan. Limnol. Oceanogr. 43:471–480. https://doi.org/10.4319/lo.1998.43.3.0471.

Verpoorter, C., Kutser, T., Seekell, D.A., Tranvik, L.J., 2014. A global inventory of lakes based on high-resolution satellite imagery. Geophys. Res. Lett. 41:6396–6402. https://doi.org/10.1002/2014GL060641.

Vonk, J.E., Tank, S.E., Bowden, W.B., Laurion, I., Vincent, W.F., Alekseychik, P., et al., 2015. Reviews and syntheses: effects of permafrost thaw on Arctic aquatic ecosystems. Biogeosciences 12:7129–7167. https://doi.org/10.5194/bg-12-7129-2015.

Wartiainen, I., Hestnes, A.G., McDonald, I.R., Svenning, M.M., 2006. Methylobacter tundripaludum sp. nov., a methane-oxidizing bacterium from Arctic wetland soil on the Svalbard islands, Norway (78° N). Int. J. Syst. Evol. Microbiol. 56:109–113. https://doi.org/10.1099/ijs.0.63728-0.

West, W.E., Creamer, K.P., Jones, S.E., 2016. Productivity and depth regulate lake contributions to atmospheric methane. Limnol. Oceanogr. 61:S51–S61. https://doi.org/10.1002/lno.10247.

Wik, M., Varner, R.K., Anthony, K.W., MacIntyre, S., Bastviken, D., 2016. Climate-sensitive northern lakes and ponds are critical components of methane release. Nat. Geosci. 9: 99–105. https://doi.org/10.1038/NGEO2578.

Yvon-Durocher, G., Allen, A.P., Bastviken, D., Conrad, R., Gudasz, C., St-Pierre, A., et al., 2014. Methane fluxes show consistent temperature dependence across microbial to ecosystem scales. Nature 507:488–491. https://doi.org/10.1038/nature13164.

Yvon-Durocher, G., Hulatt, C.J., Woodward, G., Trimmer, M., 2017. Long-term warming amplifies shifts in the carbon cycle of experimental ponds. Nat. Clim. Chang. 7: 209–213. https://doi.org/10.1038/NCLIMATE3229.

Zeikus, J.G., Winfrey, M.R., 1976. Temperature limitation of methanogenesis in aquatic sediments. Appl. Environ. Microbiol. 31, 99–107.