Variability in methane emissions from West Siberia's shallow boreal lakes on a regional scale and its environmental controls

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Abstract. Small lakes represent an important source of atmospheric CH_4 from northern wetlands. However, spatio-temporal variations in flux magnitudes and the lack of knowledge about their main environmental controls contribute large uncertainty into the global CH_4 budget. In this study, we measured methane fluxes from small lakes using chambers and bubble traps. Field investigations were carried out in July-August 2014 within the West Siberian middle and south taiga zones. The average and median of measured methane chamber fluxes were 0.32 and 0.30 $mgCH_4\ m^{-2}\ h^{-1}$ for middle taiga lakes and 8.6 and 4.1 $mgCH_4\ m^{-2}\ h^{-1}$ for south taiga lakes, respectively. Pronounced flux variability was found during measurements on individual lakes, between individual lakes and between zones. To analyze these differences and the influences of environmental controls we developed a new dynamic process-based model. It shows good performance with emission rates from the south taiga lakes and poor performance for individual lakes in the middle taiga region. The model shows that, besides well-known controls such as temperature, pH and lake depth, there are significant variations in the maximal methane production potential between these climatic zones. In addition, the model shows that variations of gas-filled pore space in lake sediments are capable to control the total methane emissions from individual lakes. The CH_4 emissions exhibited distinct zonal differences not only in absolute values but also in their probability density functions: the middle taiga lake fluxes were best described by a lognormal distribution while the south taiga lakes followed a power law distribution. The latter suggests applicability of self-organized criticality theory for methane emissions from the south taiga zone, which could help to explain the strong variability within individual lakes.

Keywords: controls of methane emission, mathematical modeling

1 Introduction

Due to its higher global warming potential, methane contributes about 20% of the overall greenhouse effect (Cicerone and Oremland, 1988; Wuebbles and Hayhoe, 2002; IPCC, 2013). Lakes and wetland ponds have strong potential impacts on the methane budget (Travnik et al., 2009) due to their anoxic sediment conditions and often high organic matter content (Zehnder, 1978). Lake methane fluxes and their temporal patterns are still poorly constrained, and form a major gap in the northern C budget (Rasilo et al., 2015). Over the past decade, new evidence has demonstrated that these systems have been underestimated in their contribution to the northern carbon balance (Kortelainen et al., 2006; Juutinen et al., 2009; Holgerson and Raymond, 2016; Wik et al., 2016b). Lakes and wetlands ponds can form high CH_4 emission hotspots that contribute largely to landscape-scale CH_4 budgets but create uncertainty for bottom-up regional CH_4 emission estimates due to their small size (Bubier et al., 2005). For example current global methane assessment estimate methane emission in a wide range from 37 to 112 $TgCH_4$ $year^{-1}$ (Saunois et al., 2016). Thus, more data are needed to resolve the divergence between top-down and bottom-up estimates, including the generation of flux measurement that is more representative in time and space (Nisbet et al., 2014; Saunois et al., 2016).

Small shallow lakes have high methane emission potential for several reasons. First, methanogenesis is sensitive to temperature conditions (Zeikus and Winfrey, 1976; Dunfield et al., 1993; Schulz et al., 1997; Yvon-Durocher et al., 2014) and shallow lakes are warmed up quickly during the summer season. Second, small water volume coupled with high organic carbon content promotes the formation of anoxic hypolimnion and is related to increased concentrations and fluxes of CH_4 (Juutinen et al., 2009). Third, these lakes occupy significant areas in waterlogged regions (Downing et al., 2006) where they receive large inputs of substrate for methanogenesis in the form of terrigenous dissolved organic matter (Segers, 1998).

Methane fluxes from small lakes have great spatial variability (e.g., Casper et al., 2000; Dzyuban, 2002; Kankaala et al., 2004; Bergström et al., 2007), which hampers flux upscaling and modeling of the processes required for making regional and global estimations. This high variability results from multiple environmental controls, including biological (system productivity, organic matter loading and its mineralization, methane production and oxidation by different groups of microorganisms), physical (temperature, mixing rate, stratification, diffusion and bubble transport rate) and chemical factors (such as concentrations of methane, oxygen, inhibitors and pH) (Rudd and Hamilton, 1978; Bastviken et al., 2004; Lofton et al., 2013; DelSontro et al., 2011; 2015; 2016). Due to these variations, the effect of different control factors is complicated and still insufficiently known. In particular we must develop robust relationships between lake CH_4 emissions and their potential controlling factors to facilitate both prediction and spatial extrapolation (Rasilo et al., 2015).

The excess water supply and flat topography with impeded drainage provides favorable conditions for wetland and lake formation in West Siberia (Terentieva et al., 2016). A few conducted studies of methane emission from lakes of this region (Gal'chenko et al., 2001; Repo et al., 2007; Glagolev et al., 2011; Sabrekov et al., 2013) indicate that the methane flux from middle taiga lakes is ten times lower in magnitude than from south taiga lakes. It is in an agreement with data showing strong latitude gradient of methane release from permafrost lakes in the Northern Hemisphere (Holgerson and Raymond, 2016). Despite there are a lot of studies about local spatial variability in methane emission from lakes, there is still a gap of knowledge about methane emission from lakes and, even more rare, their environmental controls on a regional scale (West et al., 2015). An understanding of the nature of this difference is important for modeling and reliably estimating regional methane emission from lakes. In this study, we have the following objectives:

- To estimate methane fluxes from small lakes of the middle and southern taiga;
- To detect key environmental controls of methane emissions on both regional (between zones) and local (within each zone) scale;
- To improve the precision of methane emission modeling.

In order to complete these tasks the following methodology was applied. The best way to take into account the key processes is to construct a process-based model founded on established physical, chemical and biological dependences. Regression procedures, commonly used for identification of environmental controls, cannot fully reflect complicated interactions between different controls, and thus mask a lot of important details. Rather, with process-based modeling, it is possible to test which dependences and which parameters are reliable (at least, for a certain climate zone), and which are not. After taking into account well-known dependences a comparison of predicted and measured values can help to find new potentially important controls.

Since the focus of our work is on lake methane emissions, it is necessary to examine their huge temporal variability and episodic peaks attributed to bubbling, which is challenging to quantify (Walter et al., 2006; Wik et al., 2013). It can be suggested that these stochastic emissions can be modeled using self-organized criticality (SOC) theory (for details on this theory see, e.g., Bak et al., 1988; Bak, 1996; Turcotte, 1999) which can simplify scaling the flux measurements across larger areas. Bubbling is similar to systems showing SOC behavior, where constant external force leads to rapid changes in non-linear interactions after the reaching of a certain threshold (Bak et al., 1988). Systems with SOC behavior occur in many disciplines, including physics, biology, and economics (Bak et al., 1988). It has been argued that earthquakes, landslides, forest fires, and species extinctions, are examples of SOC in nature (Bak, 1996). To the best of our knowledge, no applications of SOC to bubbling in lakes have been previously published. However, such a behavior of gas bubbles in foam (Kawasaki and Okuzono, 1996) and in different artificial systems (see, for example, Juodis et al., 2006; Petrashenko et al., 2005) is well-known. Therefore we test whether the measured flux values demonstrate SOC behavior and examine the consequences for upscaling.

2 Materials and methods

2.1 Study sites

The studied lakes are located in two different boreal zones (both with subarctic climate according to Köppen climate classification) of the Western Siberia Lowland (Russian Federation) (Figure 1). The northern study area is in the middle taiga zone (referred to hereafter as 'MT') about 20–30 km south-west from Khanty-Mansiysk (61° N, 69 °E). Mean (range for 1979–2014) temperature is 18.4 (14.0–23.1) °C in July and -18.9 (-22.9 – -14.9) °C in January, mean annual temperature and precipitations are -0.8 (-4.7–3.5) °C and 530 (308–762) mm respectively (All Russian Research Institute of Hydrometeorological Information - World Data Center, Khanty-Mansiysk). The southern study area is in the south taiga (referred to hereafter as 'ST') zone about 100-200 km north-west from Tomsk (57° N, 83 °E), approximately 900 km southeast of the MT study area. Mean (range for 1979–2014) temperature is 18.7 (13.7–24.8) °C in July and -17.1 (-20.9 – -13.0) °C in January, mean annual temperature and precipitations are 0.9 (-3.5–6.2) °C and 567 (292–768) mm respectively (All Russian Research Institute of Hydrometeorological Information - World Data Center, Tomsk). The climate in both regions is continental with moderate annual rainfall, long and cold winters, and warm summers. Permafrost is absent in both study regions.

The MT lakes are mostly acid, have low ionic strength and are surrounded by wetlands (Figure 1; Table 1). Four lakes were selected to cover the range of sediment properties in this zone. Lake Muhrino has peaty sediments with high mineral content (sandy bedrock), Lakes Babochka and Lebedinoe both have mineral-free peaty sediments and Lake Bondarevskoe has sapropel (flocculated humic material) sediments. The ST lakes are more diverse due to high ground water mineralization. Lakes Bakchar.ryam, Plotnikovo and the three Bakchar.forest Lakes (1–3) represent mesotrophic or eutrophic lakes surrounded by soils rich in clay and grasslands. Lakes Gavrilovka.1 and Gavrilovka.2 represent lakes with low nutrient concentrations and influenced by ground waters with high pH. Lakes Bakchar.bog.1 and Bakchar.bog.2 represent acidic humic wetland lakes with low pH, low ionic strength and low nutrient concentrations. Finally, lake Ob' Floodplain represents floodplain lakes (oxbows) with extremely high nutrient concentrations.

2.2 Methods

2.2.1 Field measurements

Field investigations were carried out during summer 2014. We conducted 190 methane flux and 170 carbon dioxide flux measurements, with 70 and 60 in MT and 120 and 110 in the ST respectively. The total field measurement time varied from 4 to 10 hours per lake, while the average was 6 hours. All measurements were carried out between 10 am and 8 pm; each lake was visited one time. All measurements were conducted using a boat to prevent any influence on the lake vegetation or sediments. CH_4 emissions were measured from the lakes using closed floating chambers. CO_2 fluxes were also measured as a background data. The plexiglas chambers were equipped with plastic bottles to ensure a 5 cm floating depth, and had dimensions of 40×40×30 cm (length×width×height) creating a headspace volume of 0.048 m^3. Chambers were covered by aluminum foil to prevent changes of temperature inside due to solar heating. Four gas samples for both CH_4 and CO_2 were taken from the fan-mixed chamber headspace at 10–15 min intervals during a chamber closure period of 30–45 min with 12 or 20 ml polypropylene syringes ("SFM", Germany). Prior to sampling, chamber air was used to flush the sampling tube several times. Until the chromatographic analysis, the syringes with the CH_4 samples had been kept in salt solution to prevent methane leakage. Boiled water was used for this purpose, because it does not contain methane in the amounts capable of affecting the measurement. The sample CH_4 concentration was measured on a calibrated gas chromatograph "Crystall-5000" ("Chromatec" Co., Ioshkar-Ola, Russia) with a flame-ionization detector (FID) and column (3 m) filled by HayeSep Q (80-100 mesh) at 70 °C with nitrogen as a carrier gas (flow rate 30 mL min^{-1}) or on a calibrated gas chromatograph "KhPM-4" ("Hromatograf" Co., Moscow, Russia) with an FID and column (1 m) filled by Sovpol at 40 °C with hydrogen as a carrier gas (flow rate 10 mL min^{-1}) within 72 h after sampling. Uncertainty of individual concentration measurement averaged ±0.03 ppm. The CH_4 concentrations were corrected for leakages as described in (Glagolev et al 2011). CO_2 concentrations were measured within 4 hours of sampling on an infrared gas analyzer (DX-6100; "RMT Ltd.", Moscow, Russia). The uncertainty of individual CO_2 concentration measurements averaged ±2.1 ppm. Each gas sample for both methane and carbon dioxide was analyzed in a three replicates. Fluxes were calculated from linear regression between chamber headspace CO_2 and CH_4 concentration versus measurement time using weights inverse to the measurement of gas concentration uncertainty (Kahaner et al., 1989). Fluxes are reported following the sign-convention that exchange from the landscape to the atmosphere are positive.

During the chamber measurements, near-surface water (10 cm depth) was sampled for dissolved CH_4. The 10 ml water samples were taken with a polypropylene syringe and vigorously shaken for 3 min with a 10 ml headspace of known CH_4 concentration (taken from ambient air where methane concentration was 1.88 ppm). The headspace CH_4 concentrations were then analyzed in a field laboratory on a gas chromatograph as described above within 24 h after lake water sampling. Samples were kept in a refrigerator before analysis. The dissolved CH_4 concentrations were calculated with Henry's law accounting for the temperature dependence of solubility (Sander, 2015). Due to logistical problems these measurements were only conducted for three ST lakes (Bakchar.forest.2, Gavrilovka.1 and Plotnikovo).

We tested for potential diurnal variability of stratification and vertical mixing due to the difference between day and night temperatures that can occur in shallow lakes by examining the lake temperature and oxidation-reduction potential profiles. We found that in this study's lakes these terms do not show strong vertical gradients, and the lakes all belong to the class of "continuous cold polymictic lakes" (Wetzel, 2001). We are therefore confident that our single daytime measurements will not generate a bias in the measured flux estimates (Ford et al., 2002). During flux measurements there were no periods with strong thermal stratification, as temperature gradients between surface and bottom water never exceeded 2°C. In this concern the studied West Siberian lakes do not correspond to the "summer pattern", described by Ford et al. (2002), when diurnal flux cycles are coupled with afternoon stratification and night mixing, but rather correspond to the "autumn pattern", when there are neither strong gradients nor pronounced diurnal flux variability. We also neglected the storage flux, because it is important only for stratified lakes, while all study lakes were mixed and no stratification was found during field campaign (Bastviken et al., 2004).

Submerged funnel gas collectors analogous to those in other measurement campaigns (Huttunen et al., 2001; Repo et al., 2007) were used to monitor CH_4 ebullition in the lakes. The gas collectors were 20 and 50 cm diameter funnels feeding into a graduated 500 ml polypropylene cylinder ("Thermo Fisher Scientific", USA), which was fitted with a PVC-tube to a 20 ml polypropylene syringe for sampling. One or two gas collectors were installed randomly near to the study sites in the same day as the chamber measurements for 1–2 days in MT and 3–4 days in ST lakes. The net CH_4 ebullition was determined from the released gas bubble's volume and its concentration as analyzed on the GC-FID described above. Short period of sampling used in our study does not allow to obtain high-accuracy flux estimates because ebullitive methane flux showed strong temporal and within-lake spatial variability defined by weather events (Shilder et al., 2016; Wik et al., 2016a). These data used only for comparison in a first approximation.

At each lake site environmental characteristics were measured at three depth levels – 20 cm below water surface, the lake profile mid-point, and 10 cm above sediment depth. At each level, we measured air and water temperatures (T) with "TERMOCHRON" iButton loggers (DS 1921-1922, DALLAS Semiconductor, USA), pH and oxidation-reduction potential (Eh) by a "SG-8" ("Mettler Toledo", USA) and electrical conductivity (EC) by an "SG-7" ("Mettler Toledo", USA). At the same three depth levels water samples were collected using PVC tube and immediately filtered in pre-washed 30-mL PP Nalgene® flacons through single-use 0.45 µm filter units Minisart (Sartorius, acetate cellulose filter) having a diameter of 25 mm . After discarding the first 20 to 50 mL of filtrate, the filtered solutions for cation analyses were acidified (pH ~ 2) with ultrapure double-distilled HNO_3 and stored in pre-cleaned HDPE bottles. The sample storage bottles were prepared in a clean bench room (ISO A 10,000) and blank samples were used to check the level of pollution induced by sampling and filtration. Major anion (Cl^-, SO_4^{2-}) concentrations were measured by ion chromatography (HPLC, Dionex ICS 2000) with an uncertainty of 2%. DOC and DIC were analyzed using a Carbon Total Analyzer (Shimadzu TOC VSCN) with uncertainty below 3%. Special calibration of the instrument for analysis of both form of dissolved carbon in organic-rich, DIC-poor waters was performed as described elsewhere (Prokushkin et al., 2011). Major cations (Ca, Mg, Na, K), Si and trace metal (Fe, Cu, Ni, Co) concentrations were measured with an ICP-MS Agilent ce 7500 with In and Re as internal standards and 3 various external standards, measured as check samples between each run of ten lake water samples. Further details about analysis, uncertainties and detection limits are given elsewhere (Pokrovsky et al., 2015; 2016). Sediment layer depth was determined using a peat auger (accuracy is ±0.2 m). It should be noted that bottom pH served as a pH in a whole sediment layer since no data were available on latter. It bears the risks of misinterpretation because in some cases lake water pH can strongly differ from lake sediment pH especially for acidic lakes (Casper et al., 2003). All studied acidic lakes have secondary origin, they have the same oligotrophic sphagnum peat in the bottom (at least – several upper meters which are only important for lake emission) as peat in wetlands around. Bottom water pH of acidic lakes in our study is very close to pH of surrounding wetland according to available data for ST (Kotsyurbenko et al., 2004; 2007) and MT (Sabrekov et al., 2011) wetlands. This peat has very low ash content (Turunen et al., 2001) and unlikely able to strongly regulate pH. Therefore it could be suggested that bottom pH is fair proxy of pH in a whole sediment layer.

It is important to notice that obtained flux and supporting data gives only an actual snapshot of methane emission from a certain lake section. Considering the spatio-temporal variability in CH_4 fluxes is critical when making whole lake or annual budgets (Natchimuthu et al., 2015; Wik et al., 2016a) while our target is actual variability on a regional spatial scale. As it was mentioned above, the best way to take into account complicated and non-linear key processes is to construct a process-based model. Modern lake methane emission models tend to operate not with whole lake and seasonal budgets but on a much smaller temporal (days or hours) and spatial (with subsequent averaging) scale (Stepanenko et al., 2011, 2016; Tan et al., 2015) because it allows to resolve small-scale heterogeneity of such important controls as lake depth or water temperature. Considering not the whole lake but the certain lake sections can also improve aquatic greenhouse gas emission estimates (Shilder et al., 2016). Therefore it should be mentioned that in our study not the whole lake but lake section (area about 10 m^2) is the studied object.

2.2.2 Statistical analysis

All statistical analyses were performed using the STATISTICA 8 software ("StatSoft", USA). Ordinary-least square regression ($\alpha = 0.05$) is used to find the significance of the relationship between each environmental variable and the measured CH_4 flux (for average and median values across all the individual fluxes for each lake). Stepwise multiple regressions ($\alpha = 0.05$) included parameters such as air temperature (°C), lake depth (LD, m), sediment depth (m), area (ha), CO_2 flux (mgCO_2 m^{-2} h^{-1}), and on three water depths (surface, middle, bottom): temperatures (°C), pH, oxidation-reduction potential (Eh, mV), electrical conductivity (EC, µS cm^{-1}), concentrations of DOC, DIC, SO_4^{2-}, Cl^-, P, Fe, Cu, Ni, Co, and K (mg l^{-1}). To estimate the power law distribution parameters C and α in $f(x) = Cx^{-\alpha}$ (where $f(x)$ is a probability density function, and x is a flux) a maximum-likelihood estimate was used (Newman, 2005). The minimum chi-square estimation test was used to check how different probability density functions fit the flux data. In order to test the linearity between flux rank and absolute value of this flux value in doubly logarithmic coordinates (which is typical for systems having SOC behavior (Bak et al., 1987; 1988; Jensen, 1998; Turcotte, 1999)), the sample of methane fluxes was sorted (where rank 1 indicates the highest magnitude flux). The Levenberg–Marquardt algorithm was used to define coefficients of empirical dependences for methane production on pH and temperature.

2.2.3 Model description

To analyze the zonal difference between fluxes, a process-based model reproducing the effect of main environmental controls that are well-known from literature (such as temperature, pH, lake area and depth, DOC concentration etc.) was developed. The model is designed to couple the processes of production, consumption and transport of methane and consumption and transport of oxygen in water column and sediments of shallow boreal lakes. The model structure is similar to other methane emission models for wetlands (Walter and Heimann, 2000; Tian et al., 2010; Meng et al., 2012) and lakes (Stepanenko et al., 2011, 2016; Tan et al., 2015). The model structure is represented in Figure 2, and a full description is given in Appendix A. Input model parameters include the temperature profile of the lake, concentrations of DOC, total phosphorous and the pH value where these values are measured in the near-bottom water and assumed to be representative for the sediment layer, lake and sediment depth, latitude and wind speed at the 10 m height. The model outputs are methane and oxygen concentration profiles, methane ebullition rate and diffusive flux of methane to the atmosphere.

The model is constructed similarly to other modern models that have shown good ability to predict methane emissions from lakes and ponds (Stepanenko et al., 2011, 2016; Tan et al., 2015). There are several differences between our approach and these models. First, in our model, the necessary parameters were each obtained from published literature for the appropriate climate zone (where possible) and averaged across different sources. There was no calibration of model parameters, because we try to test how current scientific knowledge about the methane cycle in boreal lakes can simulate the chamber-measured methane fluxes. In order to avoid using different calibrated constants relating the dependence of methane production from substrates (Stepanenko et al., 2011; Tan et al., 2015) DOC was selected as a single proxy for substrate of methane emission (Tian et al., 2010). In order to avoid calibrating the strongly variable temperature dependence of methane production and to take into account its potential climatic differences, a climate-sensitive approach was used (see Appendix B). Second, unlike previous models (Stepanenko et al., 2011, 2016; Tan et al., 2015) we have added the influence of pH (Appendix B). Third, gaseous molecular methane diffusion in lake sediments is included in contrast with the previous models (Stepanenko et al., 2011, 2016; Tan et al., 2015). It was introduced because initial numerical experiments demonstrated that taking into account only liquid CH_4 molecular diffusion in the pore space of lake sediments leads to a concentration of dissolved methane in lake water more than an order of magnitude lower than observed in several ST lakes in this study (see Sect. 3 and Table 2) and in other temperate and boreal lakes according to the literature (see Sect. 4.2 for details). Data regarding the gas-filled pore space in shallow lake sediments are very sparse (see Appendix A). Wetland gas-filled pore space occupies from 3% to 18% of total peat volume (Fechner-Levy and Hemond, 1996; Rosenberry et al., 2003; Strack et al., 2005). Close values (7-18%) were obtained in laboratory experiments with muddy lake sediments (Flury et al., 2015). Therefore we assume that the lake sediment value of this parameter has the same order of magnitude.

This choice of the model framework is based on the data availability, which covers a mix of both spatial and seasonal variations. Recent models for lake methane emissions (Stepanenko et al., 2011; 2016; Tan et al., 2015) are validated mostly against seasonal time series taken at singular locations. Thus, it is not clear whether the influence of spatial variability can be explained according to modern knowledge about environmental controls of methane emission or there are controls which are valuable on different spatial scales, but not included into models. For example, controls that are relatively stable for a single lake and on a seasonal scale (climate, lake pH and trophic state, sediment porosity) may not be relevant at greater spatial scales. Since this paper's obtained flux data cover regional and local spatial variability, we use simple empirical relationships for controls that are known to be important on these scales: temperature (on a climate-sensitive basis), pH and DOC concentration (Le Mer and Roger, 2001; Nazaries et al., 2013; Serrano-Silva et al., 2014). The microbial communities of methanogens and methanotrophs and their dynamics were not simulated (as performed, for example, in Grant and Roulet, 2002; Kettunen, 2003) despite their importance because it is currently not possible to obtain reliable estimates of microbiological parameters for lakes with different pH and trophic state. Therefore, we compromise between the model's complexity (which cannot be overly detailed due to the challenge of obtaining reliable data for validation) and data availability (i.e., that the model should describe the influence of important and measured controls on the scale of the data that are present).

The partial differential equations were solved with MATLAB v. 7.8.0 ("MathWorks", USA). A bootstrap method (Efron and Tibshirani, 1986) was implemented to find the uncertainty bounds on the modeled fluxes, as follows. First, artificial errors were introduced for each model parameter using their given standard deviations and a normal distribution. Then, 1000 iterations of these "noisy" parameter values were used to generate "noisy" flux estimates, and the uncertainty on the predicted flux value was derived as the standard deviation of these outputs.

3 Results

A summary of methane flux measurements is presented in Table 3. The median methane fluxes were 0.3 and 4.1 $mgCH_4\ m^{-2}\ h^{-1}$ for MT and ST lakes, respectively. For MT lakes the median relative uncertainty of the individual measurements was 10%. For ST lakes the median relative uncertainty of the individual measurements was 20% for fluxes higher than 1 $mgCH_4\ m^{-2}\ h^{-1}$ and 50% for fluxes lower than 1 $mgCH_4\ m^{-2}\ h^{-1}$. The higher relative uncertainty for smaller flux observations may be caused by the fact that smaller fluxes are potentially influenced by single rare bubbles. This impact creates higher scatter in the measured gas concentrations than the relatively constant bubbling driving higher fluxes. The median fluxes for individual lakes vary from 0.1 to 0.5 $mgCH_4\ m^{-2}\ h^{-1}$ for MT and from 0.8 to 7.4 $mgCH_4\ m^{-2}\ h^{-1}$ for ST. Methane fluxes in both zones differ significantly (Wilcoxon test, $p < 0.00001$). Average values of pH, EC, P differed between the two zones with the confidence level of 0.05 in contrast to average DOC, DIC, temperatures, Eh, Fe, and CO_2 flux, which were not significantly distinguished. Variability amongst repeated measurements for individual lakes in ST was higher than in MT: the coefficients of variation were 1.68 and 0.71, respectively. The average dissolved methane concentration for three ST lakes (Bakchar.forest.3, Gavrilovka.2 and Plotnikovo) is 8.3 ± 6.3 $mgCH_4\ m^{-3}$ (see Table 2).

Simple regression showed that there were no strong correlations ($R^2 > 0.5$) between environmental variables and either average or median CH_4 flux. The average CH_4 flux for all data faintly ($0.5 > R^2 > 0.3$) positively correlates with CO_2 flux ($R^2 = 0.43$, $p = 0.012$) and surface [P] ($R^2 = 0.30$, $p = 0.042$). The average CH_4 flux for ST lakes correlates faintly negatively with pH-middle ($R^2 = 0.48$, $p = 0.022$), pH-bottom ($R^2 = 0.51$, $p = 0.020$) and lake depth ($R^2 = 0.39$, $p = 0.052$). Median CH_4 flux for all data faintly positively correlates with surface [Cu] ($R^2 = 0.33$, $p = 0.030$) and CO_2 flux ($R^2 = 0.30$, $p = 0.043$). Median CH_4 flux for ST lakes only correlates faintly negatively with bottom [Cu] ($R^2 = 0.44$, $p = 0.037$). Multiple linear regression by flux median and average with two or more independent variables did not show any reliable dependences ($p \leq 0.05$).

The ST lake methane flux is more variable (both for individual lakes and for data combined for all lakes) than the MT lake fluxes (see Table 3). For example, the median coefficient of variation for average flux values from ST lakes (0.87) is more than twice the value from MT lakes (0.36). CH_4 flux values in MT and ST lakes are also from different continuous probability density distributions (two-sample Kolmogorov-Smirnov test, $p < 0.00001$). The combined ST lake flux values correspond to a power law distribution with parameters $C = 0.86 \pm 0.05$ and $\alpha = 1.71 \pm 0.07$ (minimum chi-square estimation test, $p = 0.46$, Figure 3a) and do not correspond to a lognormal distribution ($p < 0.00001$). On the contrary, the fluxes sampled from MT lakes have a lognormal distribution (mean = -1.46 ± 0.19, variance = 0.72 ± 0.12, $p = 0.25$, Figure 3b) and do not have a power law distribution ($p < 0.00001$). A linear dependence of flux rank on the absolute flux magnitude in doubly logarithmic coordinates (with the exception of a few points at the bounds) is also observed for methane fluxes from ST lakes (Figure 3c), and is not observed for fluxes from MT lakes (Figure 3d). Both power law probability distributions and linearity in doubly logarithmic coordinates are typical for systems having self-organized criticality (SOC) (Bak et al., 1988). Hence SOC can be used to describe dynamic of methane emission from lakes.

Since multiple linear regression did not reveal statistically significant dependences with two or more independent variables from the environmental factors listed in the Sect. 2.2.2, the multiple effect of environmental controls is confounding. Further analysis was provided using a process-based model (see Sect. 2.2.3 and Appendix A) that reproduced the methane and oxygen production, consumption and transport in lake water and lake sediments.

The modeling results are presented in Figure 4 and in Table 4. The predicted fluxes fit the observed values for ST lakes quite well ($R^2 = 0.76$); however, the model overestimates MT lake fluxes by more than one order of magnitude. Modeled concentrations of dissolved methane in ST lakes vary in a wide range from 0.35 to 21.52 mgCH$_4$ m^{-3} with an average value 7.63 mgCH$_4$ m^{-3} (recall our observations, where for three ST lakes, the dissolved methane had mean 8.3 ± 6.3 mgCH$_4$ m^{-3}). The modeled fraction of oxidized methane varies from 12% to 40% with an average value 22%. Linear regression analysis of the residual differences between modeled and measured fluxes did not reveal statistically significant dependences from factors listed in the Sect. 2.2.2.

Methane concentrations appear to be strongly underestimated (4–6-fold) for those ST lakes where it was measured (Table 2). Our numerical experiments showed that the CH$_4$ molecular diffusion in liquids within the pore space of lake sediments by itself could not generate a surface CH$_4$ concentration close to the observed values. These modeled values are very sensitive to the gas-filled porosity of the sediments (Table 2).

Thus, the main differences between observed and predicted methane emissions are that the model:

- overestimated fluxes for MT lakes by more than one order of magnitude;
- underestimated concentration of dissolved methane in both MT and ST lakes (4–6-fold);

Additionally, the data showed extremely high variability of fluxes from ST lakes. Without additional flux monitoring and a greater focus on the driving process mechanisms it may be that this experimental dataset is not suitable for a model comparison or validation effort. In the discussion section we try to suggest where these discrepancies have come from and how they can be explained.

4 Discussion

The obtained data indicates that CH$_4$ fluxes are distinctly higher in the ST than MT lakes. They are also in good correspondence with the data reported in these West Siberian zones by other researchers. Fluxes from the MT lakes agree with Repo et al. (2007) data from near Khanty-Mansiysk sites, where medians for two individual lakes were 0.2 and 1.0 mgCH$_4$ m^{-2} h^{-1}. They are also similar to the previously defined flux median of 0.6 mgCH$_4$ m^{-2} h^{-1} (across 51 flux measurements) for MT wetland lakes and ponds (Glagolev et al., 2011; Sabrekov et al., 2013). The median flux for ST lakes corresponds to the wide interval between 1st and 2nd quartile (4.3 – 23.9 mgCH$_4$ m^{-2} h^{-1}, across 82 flux measurements) reported earlier for the wetland lakes and ponds of the same climate zone (Glagolev et al., 2011; Sabrekov et al., 2013).

Comparison with measurements from small (<100 ha) boreal lakes beyond West Siberia is presented in Table 5. Data for MT lakes are in the range of data from other regions in all parameters. Alternatively, methane flux (8.3 versus 1.3 mgCH$_4$ m^{-2} h^{-1} as average sum of diffusive and ebullitive fluxes for lakes from Table 5) and DOC concentration (30 versus

11 mg l^{-1}) in ST lakes are considerably higher, but the concentration of dissolved methane is lower (8.3 versus 15.0 mgCH_4 m^{-3}). A comparison between the model and observational results can produce information on which controls and processes should be measured and examined to improve predictions of boreal lake methane emissions.

4.1 Differences in methane production between ST and MT lakes

The significant differences in measured CH_4 flux between MT and ST lakes can be explained with the help of the model results. Modeled fluxes from MT lakes are overestimated by one to one and a half orders of magnitude. However, for ST lakes the model meets close to the observations in both the mean level of emissions (where the intercept of the observed vs. predicted flux linear regression is close to zero in comparison with average flux, Figure 4) and the representation of controls (where the slope is close to unity). Hence the question is what model parameter(s) should be changed for MT lakes to reach good correspondence as well. A first choice could be the potential controlling environmental parameters of CH_4 exchange. But pH, DOC, and temperature are in the same range in both zones (although their average values vary) and if the model interprets these values correctly in one zone it is unlikely to shift their interpretation in the other zone. Thus differences in measured emissions between zones could come from parameters that we had modeled as unchanging between zones: the maximal methane production rate (MMPR, Eq. A14 in Appendix A) and/or the maximal intensity of methane oxidation (Eq. A15). It is doubtful that the key parameters of methane oxidation are different between the zones, because the methanotrophic microbial community is assumed be adaptable to any climate and pH conditions and so the oxidation rate is not heavily influenced by these factors (Le Mer and Roger, 2001; Nazaries et al., 2013; Serrano-Silva et al., 2014). Additionally, methane oxidation is proportional to methane production in lakes where there is no influence of plant methane and oxygen transport (Bastviken et al., 2008; Duc et al., 2010). Therefore, differences in methane flux between zones are likely caused by differences in MMPR.

We therefore focus on MMPR, which may actually be lower in MT lakes compared to ST lakes due to substrate availability. While the mean difference in DOC between zones is not significant (15 mg l^{-1} versus 30 mg l^{-1} for MT and ST lakes respectively, $p = 0.142$), if two low-DOC and low emitting Gavrilovka lakes would be excluded from the ST sample, the difference becomes significant (15 mg l^{-1} versus 36 mg l^{-1} for MT and ST lakes respectively, $p = 0.028$). The DOC concentration is taken into account in calculations in Michaelis-Menten equation (see Appendix A for details) and it can also influence the MMPR. MMPR implicitly reflects the abundance of methanogenic microbia. Higher substrate availability leads to higher methanogenic biomass and consequently to higher MMPR as simulated explicitly in previous research (Grant and Roulet, 2002; Kettunen, 2003). Greater substrate availability may be caused by higher plant productivity. Methane production correlates positively with plant productivity because root exudates provide additional fresh organic substrates for methanogens (Whiting and Chanton, 1993; Aulakh et al., 2001; Mitra et al., 2005). Net primary production (NPP) in the MT wetlands that surround MT lakes is 40% less than in ST wetlands (Peregon et al., 2008). This mechanism is extremely important for lakes with low level of nutrients where a greater fraction of organic matter is allochthonous. The lower trophic state in MT lakes may also lead to a decrease in the MMPR. It is well known that higher trophic states generate both higher methane production and emission (Bubier, 1995; Segers, 1998; Duc et al., 2010). As a result, a critical concentration for bubble formation is either not attained at all or is attained at a lower depth in lakes with a lower MMPR. Therefore, a greater fraction of methane diffuses through the water column and is oxidized, further decreasing the flux.

This low-production, low-ebullition hypothesis is supported in this study by measurements with bubble traps (see Table 3): the ebullition flux in MT lakes is less or equal to the diffusion flux calculated as the difference between the flux measured by static chambers and the flux measured by bubble traps. Meanwhile, the ebullition flux in ST lakes is many times higher than the diffusive flux by both model predictions and measurements. Certainly, our field experiments covered a relatively short period and were insufficient for exhaustively estimating methane emission pathways because we lacked time to catch more bubbles. However, data by Repo et al. (2007) obtained in similar lakes with bubble traps during month or more in a summer are in good correspondence with our measurements: no caught bubbles in lake with a peat bottom (similar to lakes Lebedinoe and Babochka in the current study where bubble were also not detected) and small fluxes in lakes with sandy bottom (0.04–0.4 mgCH_4 m^{-2} h^{-1} in (Repo et al., 2007) and 0.01–0.1 mgCH_4 m^{-2} h^{-1} in the current study).

One can try to estimate the impact of these two possible reasons – “climatic” and “trophic”. There are no data about the MMPR in lake sediments in Western Siberia but we can estimate the “climatic” impact driving MMPR differences using data for ST and MT wetlands. According to Kotsyurbenko et al. (2004), the methane production under optimal temperature conditions and without substrate limitation measured in ST wetlands is 110 mgCH_4 m^{-3} h^{-1}. The same parameter for MT wetlands can be estimated from Kotsyurbenko et al. (2008) as 38 mgCH_4 m^{-3} h^{-1}. So, taking into account that both sites have similar pH conditions (because both wetlands are acidic, and pH is 4.8 and 4.4 respectively) and trophic state (both wetlands are ombrotrophic *Sphagnum* bogs), the “climatic” methane production in MT wetlands is 3 times lower than in ST wetlands. The “trophic” impact can be estimated using average values of methane production for two groups of Swedish lakes (Duc et al., 2010). These groups were situated within the same region (so, had no “climatic” effect) and approximately correspond in phosphorous concentration to our MT (in (Duc et al., 2010) this group of lakes is labeled “low methane formation”, P = 0.011 mg l^{-1}) and ST (“high methane formation”, P = 0.064 mg l^{-1}) lakes. Since phosphorous is known as a main control of methane production in lakes (Bastviken et al., 2004; Juutinen et al., 2009), in the first approximation it represents a difference in the trophic state between groups. For the low methane producing lakes at optimal temperature, methane production is approximately 4 times lower than for the second.

Therefore, the sum of the “climatic” and “trophic” impacts gives a 12-fold reduction for the MMPR value for MT lakes in comparison with ST lakes. If we presume that the model’s MMPR value is typical for ST lakes, the MMPR for MT lakes should be 2.60 mgCH_4 m^{-3} h^{-1}. Model experiments shows that MMPR fitted to the corresponding measured methane fluxes from MT lakes is in the range 1.5–3.7 mgCH_4 m^{-3} h^{-1}. Hence it can be expected that accounting for both climatic and trophic differences can help to adequately predict MMPR in a variety of lakes and reach a correspondence between measured and modeled fluxes for the MT zone. For these calculations and extrapolations cross-ecosystem comparisons to evaluate the potential effects of both climate and local biogeochemistry on MMPR are needed.

4.2 Effect of diffusivity in the lake sediments

Model calculations show that only on average 22% (12-40%) of total produced methane is oxidized (see Table 3). The latter value is lower than the experimentally measured oxidized CH_4 fraction from Bastviken et al. (2008) reaching 22–40% for the epilimnion of stratified lakes, similar to this study’s lakes because this layer is both oxic and have high turbulence. Both modeled and measured concentrations of dissolved methane in ST lakes are also less than the literature values for different temperate and boreal lakes (Table 5) including the West Siberian MT lakes (Repo et al., 2007); at the same time total methane flux in ST was considerably higher. This situation is in disagreement with the typical pattern where higher methane concentration correlates with greater fluxes (as sum of diffusive and ebullition flux). So, both the oxidized fraction of methane and concentration of dissolved methane seem to be underestimated.

The first possible reason for these differences is that the model has underestimated methane oxidation. Indeed, a comparison of half saturation constants for methane oxidation from different studies showed that this constant for highly producing CH_4 samples was greater than for samples with low production rates (Segers, 1998). But the model parameters of methane oxidation, estimated based on several different sources (see Appendix A), correspond to measured and literature data on concentration of dissolved methane for studied lakes. Model experiments also show that increased oxidation leads to much less concentrations of dissolved methane, moving them even further from the measured values. Methane oxidation can also vary strongly depending on water chemistry or availability of different metals, such as Ni and Cu which are main micronutrients necessary for enzyme production in both methanogens and methanotrophs (Krüger et al., 2003; Sazinsky and Lippard, 2015). Linear regression revealed that higher copper concentration in bottom waters corresponds to lower fluxes in

ST lakes. It could be suggested that at higher copper concentration enhance methane oxidation in bottom waters, decreasing total emission. The known mechanism of this possible enhancement is a “copper switch”: at Cu concentration in water <50 μg l^{-1} soluble methane monooxygenase dominates activity while Cu concentration >250 μg l^{-1} is necessary to fully activate much more effective (for methane oxidation) particulate methane monooxygenase (Hakemian and Rosenzweig, 2007). Measured Cu concentration in MT and ST lakes does not exceed 2.5 μg l^{-1} making “copper switch” hypothesis not relevant in this situation. In observed range copper bottom water concentration shows no significant effect on methane oxidation (Schnell and King, 1995; Scheutz and Kjeldsen, 2005; Van der Ha et al., 2013).

This pattern could also be explained by the underestimated gas-filled porosity in lake sediments, which is an important control of dissolved CH_4 concentration influencing its diffusion through sediments (see Table 2). Literature data about gas-filled porosity in shallow lake sediments are sparse, while its variability is very high (Valsaraj et al., 1998; Brennwald et al., 2005). However, it is well known that higher silt and mineral content as well as higher bulk density sediments have lower diffusion coefficients for the same values of gas-filled porosity (Clapp and Hornberger, 1978; Moldrup et al., 2003). This mechanism may explain why ebullition was not observed in MT lakes with peat bottoms and higher diffusion fluxes (Babochka, Lebedinoe) but was observed in lakes with lower organic content in their sediments and lower diffusion fluxes (Muhrino, see Table 3). The same situation was revealed by Repo et al. (2007), who found no ebullition and high diffusive fluxes in lake “MTPond” with peat sediments of several meters. Alternately, the lake “MTlake” of non-wetland origin was characterized by higher mineral content in sediments and lower diffusive flux. As a consequence there was significant ebullition flux in this lake.

Accumulation of free gas affects the tortuosity of the sediment and leads to an underestimated diffusion coefficients for dissolved gas species (Flury et al., 2015). The gas-filled porosity influence on methane cycling in lakes could be tested with a quick numerical experiment. Consider doubling the gas-filled porosity for ST lakes to 0.05. This value is still typical for natural shallow lake sediments. For example, according to Valsaraj et al. (1998) the maximal gas-filled porosity is 0.07, a value more than 2 times higher than the 0.025 used by default in our model. In this higher-porosity case the oxidized fraction of produced methane will increase to average 49% (over a wide range from 19-90%). The concentration of dissolved methane will increase to average 27.7 $mgCH_4\ m^{-3}$, becoming 4 times higher than calculated using the default value of gas-filled porosity. Linearity between the observed and predicted fluxes under this experiment still remains high: $\text{Predicted} = 1.02 \cdot \text{Observed} - 1.47\ mgCH_4\ m^{-2}\ h^{-1}$, $R^2 = 0.73$. Thus, both the underestimated fraction of oxidized CH_4 and concentrations of dissolved CH_4 can reach literature and measured values through natural variability in gas-filled porosity.

It could be concluded that natural variability of gas-filled porosity in the sediments can strongly influence the ratio between diffusive transport and ebullition and, hence, on the fraction of oxidized methane and total emissions. This variation may result from the extremely non-linear influence of relatively low values of gas-filled porosity on gas diffusivity (Sallam et al., 1984; Flury et al., 2015). This non-linearity is related to interconnected water films causing disconnectivity in gas-filled pore space and, thus, reducing gas diffusivity (Moldrup et al., 2003). Unfortunately, data about gas-filled porosity in lake sediments are very sparse and it is difficult to provide a comprehensive analysis of this parameter’s influence on methane emission from lakes.

4.3 Emission uncertainty and self-organized criticality

The power-law dynamics of methane emission from ST lakes (Figure 3) are similar with dynamic system behavior in the SOC theory (Bak et al., 1987; 1988; Jensen, 1998; Turcotte, 1999). SOC is based upon the idea that complex behavior can develop spontaneously in certain multicomponent systems whose dynamics vary abruptly. The paper by Bak et al. (1987) contained the hypothesis that systems that i) are driven by some external force and ii) consist of non-linear interactions amongst their components, may generate a characteristic self-organized behavior. The self-organized state into which systems organize themselves has similar properties as equilibrium systems at their critical point, so they are described as having SOC behavior (Bak et al., 1987). SOC dynamics are assumed to evolve through the contribution of processes at different time scales. The processes driven externally are typically much slower than the internal relaxation processes. A prototypical example is an earthquake, driven by stress that has slowly accumulated in the earth's crust due to tectonic activity. This slowly built stress is subsequently released very quickly (in seconds or minutes) in an earthquake (Jensen, 1998). There is an analogous situation in lake sediments, as they become saturated by methane. Methane molecules and energy input continue much longer and more continuously than the release of bubbles and relaxation to the new steady state (Scandella et al., 2011).

The separation of relevant time scales is generated by the threshold responses – which build up over time - and metastability, which awaits a triggering event. In lake sediments, the situation is generated by microorganisms that produce and emit methane molecules into the surrounding lake water. The methane concentrations increase slowly until a solubility limit is reached. In this moment a new phase in the form of a bubble is produced. Then the methane concentration inside the bubble slowly continues to increase until the moment when pressure in the bubble is high enough to do work against forces preventing its release to the atmosphere (Scandella et al., 2011). When a critical pressure is exceeded, bubbles very quickly leave sediments via the previously formed channel. The applied force – the buildup of the CH_4 concentration - has to accumulate in order to overcome the critical threshold. This buildup occurs over a much longer time scale than the short time interval it takes the bubble to be released. The release of accumulated energy is nearly instantaneous in the moment the bubble moves. If the CH_4 molecules were produced very slowly by microorganisms and diffuse in water without ebullition then no threshold for motion would exist. In this situation the dissolved methane would be continuously released and its energy dissipated at the same rate as it was produced by the system.

The actual force that the generated bubble of CH_4 must overcome depends on the molecular details of how the bubble interlocks with the sediment particles. As a result, there are a multitude of states where the bubble will remain immobile even in response to an applied force. When these forces do not pass the release threshold, these states are metastable. The forces induce strain in the sediment material, corresponding to a certain amount of stored elastic energy. Thus, despite the bubble-sediment material system existing in an apparently stable, time-independent state, the system is not actually in its lowest energy state. A small increase in applied force can lead to a number of different responses from no motion of the bubble to a large jump and removal of the bubble from the sediment matrix (Scandella et al., 2011; 2016).

There are several practical consequences of SOC behavior of methane emission in lakes. The high values of SD in Figure 4 show not the low accuracy of measurements but natural spatial and temporal variability of methane emissions from lakes. Short-term measurements can produce uncertainty if they are extrapolated on a long period or a season. Controls found to be important from short term measurements may be unreliable on other spatial or temporal scales. Whole season multiyear measurements in three lakes of Northern Sweden, made by Wik et al. (2013; 2014), confirm this hypothesis. Each season of their measurements has a unique type of seasonal dynamic with a unique pattern of peaks and falls related to temperature and atmospheric pressure dynamics (Wik et al., 2013). But the whole season methane budget clearly linearly correlates with seasonal energy input to lakes (Wik et al., 2014).

Another practical consequence is in the upscaling of flux measurements in lakes for large regions. Once we determine that the probability distribution law is relevant across all the ST lakes, we can use it for upscaling. The mean value for a power law distribution is (Newman, 2006):

$$x_{mean} = \left(\frac{C}{2-\alpha} \cdot \left(x^{-\alpha+2}\right)\right)\Big|_{x_{min}}^{x_{max}} \qquad (1)$$

where x_{mean} is an mean flux value, x_{min} is the minimal flux value, x_{max} is the maximal flux value, and the other parameters were described in the Sect. 2.2.2. While x_{min}, C and α can be easily calculated based on our flux measurement campaign, it is more complicated to give a reliable estimate of x_{max}, because we cannot be sure that in our sample set we have obtained the maximal possible flux value. In SOC theory x_{max} is infinite, but in real conditions of lakes it is a function of methane production (as a measure for the applied external force) and sediment diffusivity (as a measure of energy dissipation). The maximal measured flux in ST lakes in our previous work (Glagolev et al., 2011; Sabrekov et al., 2013) is 359 mgCH$_4$ m^{-2} h^{-1}. If we assume this value is the $x_{max,}$ then the mean flux value according to Eq. (1) would be 13.2 mgCH$_4$ m^{-2} h^{-1}. This value is 50% higher than the simple average and 220% higher than the median obtained from the flux dataset for ST lakes of the current study. Therefore, use of simple average and median statistics can lead to substantial underestimation of the total methane amount emitted from lakes.

Despite this stochastic behavior of emission, our modeled flux values are in good correspondence with measured fluxes. There are several reasons for this agreement. According to the probability law distribution identified for ST, ten or more flux measurements, as we have performed, allow detection of high flux moments (for example, for our ST flux power-law function the probability to detect a flux with magnitude from 10 to 20 mgCH$_4$ m^{-2} h^{-1} is 0.095) and represent the total emission in the first approximation. The wide range of fluxes and relatively high number of studied lakes also help to obtain good correspondence.

4.4 Other important controls for regional model development

Comparison of observed and predicted fluxes can help to reveal other important methane emission controls on a spatial scale. There are two strong site discrepancies for our model: CH$_4$ emission for the Ob’ floodplain oxbow lake is strongly underestimated, while the model generates a large overestimation for the Bakchar.forest.1 lake. Both these model-data disagreements can be considered in a context of organic matter quality. In our model it is assumed that organic matter in form of DOC has the same quality for all lakes, but in reality the quality depends on its origin. There are generally two possible sources of this organic matter – plant and algae exudations and decomposition of organic matter (dead plants, different types of peat, gyttja, sapropel etc.); both of them can be autochthonous and allochtonous (Whiting and Chanton, 1993; Cao et al., 1996; Segers, 1998). As a rule, fresh, labile and/or rich in nitrogen organic matter leads to higher methane fluxes (Segers, 1998; Duc et al., 2010).

The Ob’ floodplain lake has the highest trophic state (in terms of P concentration) in our sample (see Table 1). So, it is natural to suggest that higher trophic states produce higher MMPR (in this case approximately on 50%) and hence higher emissions for this lake. Phosphorous does not directly influence methane production but strongly positively correlates with concentration of chlorophyll, indicating productivity of algae, and with sediment respiration, indicating higher intensity of organic matter decomposition and higher oxygen consumption by sediments, as reviewed by Pace and Prairie (2005). Higher algae productivity (West et al., 2015) and peat decomposition supply methanogenesis with fresh organic substances, while lower oxygen concentration leads to decreasing of methane oxidation. Moreover, temperature dependency of CH$_4$ fluxes actually increases with the overall system productivity (DelSontro et al., 2016). The Bakchar.forest.1 lake is mesotrophic, but the highest DOC concentration between studied lakes and 2 and more times lower CO$_2$ flux than other lakes with relatively high methane flux (see Table 3). DOC in lake water positively correlates with both plankton and sediments respiration (Pace and Prairie, 2005). It can be suggested that the highest DOC and the lowest CO$_2$ flux for the same lake together demonstrate that this DOC is formed from recalcitrant organic matter leading to lower CH$_4$ production. This hypothesis is in correspondence with findings of Duc et al. (2010) where the similar values of MMPR correlate not with DOC concentration but with the quality of organic matter in form of C:N ratio.

We decided not to compare residuals for the MT lakes because of the small sample size and, as mentioned in Sect. 4.2, possible differences in gas-filled porosity. The latter parameter needs special investigation since now, without further datasets, it requires near arbitrary selection. It is interesting to compare our CO$_2$ and CH$_4$ flux data with data of Repo et al. (2007) for the same region. It was obtained that the “MTlake” site corresponds with our dataset’s CO$_2$ and CH$_4$ flux values and ebullition-to-diffusive flux ratio. At the same time, much higher diffusive CH$_4$ flux and no ebullition were found for lake “MTPond” of 0.5 ha (see Table 5). The DOC concentration for this lake is not higher than in MT lakes studied by us, but 3-

fold higher CO_2 flux can indicate better quality of this substrate for methanogenesis, as mentioned earlier in this section. The latter finding can be explained by the fact that "MTPond" is located in a through-flow poor fen and is partly vegetated (Repo et al., 2007). This setting means that methanogenesis in this lake is supplied by both autochthonous and allochtonous organic matter. In contrast, our study's MT lakes are surrounded by a pine-shrub-sphagnum community that prevents any through-flowing, and are not even partly covered with any vegetation. Therefore, carbon dioxide flux can be useful to predict methane fluxes from shallow lakes, as shown in other studies (Rasilo et al., 2015). Regression dependences of CO_2 flux from different controls reliable on a large scale (as obtained, for example, by Kortelainen et al., 2006) can increase the precision of global models of methane emission from lakes.

Another possible important control of CH_4 emission is presence of chemical inhibitors. It is well-known that a number of alternative electron acceptors (such as dissolved NO_3^-, Fe^{3+}, Mn^{4+} and SO_4^{2-}) inhibits methane production (Conrad, 1989; Nealson and Saffarini, 1994). But only in one studied lake (the Ob' Floodplain) did the concentration of an inhibitor (SO_4^{2-}) in the near bottom water exceed the threshold value 1.92 mg l^{-1} reported in previous research (Kuivila et al., 1989). Despite this fact, emission from this lake is even underestimated by model. The discrepancy can be explained by the fact that an amount of sulfate can prevent methanogenesis only in a small part of sediment layer, as discovered previously by Kuivila et al. (1989). The mechanism of inhibition corresponds with Sabrekov et al. (2016), where two groups of wetlands were distinguished in the forest-steppe zone (next to the south climatic zone after ST) of Western Siberia: one where pore water EC is about 600–800 $\mu S\ cm^{-1}$ and CH_4 fluxes are 2–4 $mgCH_4\ m^{-2}\ h^{-1}$, and one where EC is more than 2000 $\mu S\ cm^{-1}$ and fluxes are not higher than 0.1 $mgCH_4\ m^{-2}\ h^{-1}$. The maximal EC in the studied lakes is 500 $\mu S\ cm^{-1}$. Therefore we can suppose that in the humid climate of the West Siberia taiga zone, there is a small probability of methane inhibition in lakes. This mechanism can be important for regions where evaporation exceeds precipitation, leading to a higher concentration of mineral components in lake water. Certain trace elements can be beneficial for methane production (Basiliko and Yavitt, 2001), but linear regression did not reveal significant correlation between concentrations of these elements in the lake water and model residuals.

5 Conclusion

A study of small-size bodies of water in the non-permafrost region of Western Siberia has demonstrated that lake and pond methane fluxes vary on both regional and local spatial scales. Based on the presented model's calculations it can be suggested that it is possible to predict fluxes for individual lakes within the same climate zone with a fair correspondence by taking into account such established controls as temperature, pH and substrate availability. Individual characteristics of lake origin and development, such as sediment gas-filled porosity, trophic state and organic matter quality can also have crucial effects on methane emission.

To successfully predict CH_4 fluxes in several zones different values of MMPR should be used. The climate and trophic state may be primary controls of MMPR variability on inter-zonal scale. Searching for simple governing relationships for MMPR on all spatial scales may be the most feasible manner to improve the precision of methane emission modeling.

The constructed ab initio model is much more primitive than more complex recent models (Tan et al., 2015; Stepanenko et al., 2016), but it does not include calibrated parameters, because all parameters can be adopted from the literature as average values from several literature sources for the suitable climate zone. It can be assumed that this approach can be effective for analysis of spatial variability of methane emission which appears to be higher than the temporal (Treat et al., 2007; Olefeldt et al., 2012; Sabrekov et al., 2014). Additionally, controls of spatial variability seem to have lower predictive ability (for example in terms of R^2 for regression models) than for temporal variability (Treat et al., 2007; Olefeldt et al., 2012; Wik et al., 2013; 2014; Rasilo et al., 2015).

For global modeling it is important to know, which lakes and with what kind of ecological features and on what season there exists SOC behavior. These lakes can emit significantly more methane because methane bypasses the oxidation filter through ebullition. The most interesting question in this concern is about limits of environmental controls in time and space that define the switch between ebullitive and non-ebullitive regimes. Because of variability of MMPR and diffusivity of lake sediments, the presence of such methane emission “hot spots” as small shallow lakes is expected in any climate zone. However because of their great extent in the taiga and tundra regions, small lakes in those zones are particularly relevant for the global CH_4 budget.

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Appendix A. Model description

The functional forms of process controls were chosen in order to obtain reliable estimates of the governing parameters using publically available information from the appropriate climatic zone. There was no calibration of any model parameters.

Oxygen and methane dynamics in the water column from the water-atmosphere border to the lower boundary of sediments was modelled using the following equations according to (Tang and Riley, 2014):

$$0 = -\frac{\partial F_{CH_4}(z)}{\partial z} + Prod(z) - Ebul(z) - Ox(z) \tag{A1}$$

$$0 = -\frac{\partial F_{O_2}(z)}{\partial z} - 4 \cdot Ox(z) - Resp(z) + Phot(z) \tag{A2}$$

where $F_{CH_4}(z)$ and $F_{O_2}(z)$ (mg m^{-2} h^{-1}) are the transport terms, $Prod(z)$, $Ebul(z)$ and $Ox(z)$ (mg m^{-3} h^{-1}) are the rates of methane production by methanogens, ebullition and consumption by methanotrophs respectively, $Resp(z)$ (mg m^{-3} h^{-1}) is oxygen consumption by plankton and sediment respiration, $Phot(z)$ (mg m^{-3} h^{-1}) is the oxygen production via photosynthesis, z (m) is the spatial coordinate (positive downward) and t (h) is the time. The coefficient 4 reflects the stoichiometric relationship for oxidation, where for each 1 gram of methane, 4 grams of oxygen are necessary according to the equation $CH_4 + 2O_2 = CO_2 + 2H_2O$.

Oxygen and methane diffusion can be written as (Stepanenko et al., 2011; Tan et al., 2015):

$$F_{CH_4}(z) = -D_{CH_4}(z) \cdot \frac{\partial C_{CH_4}}{\partial z} \tag{A3}$$

where $D_{CH_4}(z)$ is the diffusivity for methane and C_{CH_4} (mg m^{-3}) is the methane concentration in liquid phase. The resultant diffusion coefficient was calculated as either the sum of molecular diffusivity coefficient within a liquid and eddy diffusivity in the water column or as the sum of molecular transport within both liquid and gas phases in the lake sediment layer (Tang and Riley, 2014):

$$D_{CH_4}(z) = \begin{cases} D_{0,liq,CH_4} \cdot \left(\frac{T(z)}{273} + 1\right)^{1.82} + D_{tur}(z) & \text{if} \quad z \le z_{bot} \\ \left(\Phi(z) - \varepsilon_a(z)\right) \cdot D_{mol,liq,CH_4}(z) + \left(\frac{\varepsilon_a(z)}{\alpha_{CH_4}}\right) \cdot D_{mol,gas,CH_4}(z) & \text{if} \quad z > z_{bot} \end{cases} \tag{A4}$$

where D_{0,liq,CH_4} (m^2 h^{-1}) is the molecular diffusivity of methane in lake water at 0°C, $T(z)$ (°C) is the water/sediment temperature from field observations, $D_{tur}(z)$, $D_{mol,liq,CH_4}(z)$ and $D_{mol,gas,CH_4}(z)$ (m^2 h^{-1}) are the wind-induced turbulent diffusivity in water column, molecular diffusivity of methane in sediment pore water and molecular diffusivity of methane through gas-filled pore space of lake sediments, respectively, $\Phi(z)$ (m^3 m^{-3}) is the total sediment porosity, $\varepsilon_a(z)$ (m^3 m^{-3}) is the gas-filled porosity, α_{CH_4} (non-dimensional) is the Bunsen solubility coefficient for methane and z_{bot} (m) is the depth to lake bottom. Molecular diffusion both in liquid and gas phase was taken into account in the sediment layer as it is performed for wetlands (Walter and Heimann, 2000; Zhu et al., 2014). The Penman equation was used for molecular diffusion in the liquid phase, because the fraction of pores in sediments filled with water was high (0.6–0.9), so the equation is quite precise under observed porosity (Moldrup et al., 2000):

$$D_{mol,liq,CH_4}(z) = 0.66 \cdot \left(\Phi(z) - \varepsilon_a(z)\right) \cdot D_{0,liq,CH_4} \cdot \left(\frac{T(z)+273}{298}\right)^{1.82} \tag{A5}$$

Because gas-filled porosity in sediments is very low (0.015–0.07 according to (Valsaraj et al., 1998; Brennwald et al., 2005)), the Penman equation is not accurate in these conditions (Moldrup et al., 2000). As a result, we used the Millington–Quirk equation (Jin and Jury, 1996) which generates a diffusion coefficient similar to experimentally measurements conducted under low gas-filled porosity (Salam et al., 1984; Moldrup et al., 2000):

$$D_{mol,gas,CH_4}(z) = D_{0,gas,CH_4} \cdot \left(\frac{\varepsilon_a{}^{3.3}(z)}{\Phi^2(z)}\right) \cdot \left(\frac{T(z)}{273} + 1\right)^{1.82} \tag{A6}$$

where D_{0,gas,CH_4} ($\mathrm{m^2\,h^{-1}}$) is the molecular diffusivity of methane in air at 0°C. We neglected the solubility effect in consistency with Stepanenko et al. (2011). The depth profile of $\Phi(z)$ was adopted from (Gadzhiev and Kovalev, 1982) and used for all lakes. The same value of $\varepsilon_a(z) = 0.025$ was chosen for all lakes as an average (Valsaraj et al., 1998; Brennwald et al., 2005). Since gas-filled porosity does not vary strongly with depth for the first 1–3 meters of sediments (Brennwald et al., 2005), it was assumed to be depth-independent. α_{CH_4} was calculated as in (Tang et al., 2010):

$$\alpha_{CH_4} = K_{H,CH_4}\big(T(z)\big)\cdot\frac{T(z)}{12.2} \tag{A7}$$

where $K_{H,CH_4}\big(T(z)\big)$ ($\mathrm{mg\,m^{-3}\,atm^{-1}}$) is temperature-dependent Henry's law constant for methane, calculated as (Sander, 2015):

$$K_{H,CH_4}\big(T(z)\big) = K_{0,H,CH_4}\cdot\exp\left(B_{CH_4}\left(\frac{1}{T(z)+273}-\frac{1}{298}\right)\right) \tag{A8}$$

where K_{0,H,CH_4} ($\mathrm{mg\,m^{-3}\,atm^{-1}}$) is Henry's law constant for methane at 25°C, B_{CH_4} (K) is a coefficient of Henry's law constant temperature dependence for methane. For calculation of turbulent diffusivity in water in non-neutral conditions, the following scheme (Henderson-Sellers, 1985) was used:

$$D_{tur}(z) = 3600\cdot\frac{k\cdot w_S\cdot z}{Pr\cdot(1+37Ri^2)}\cdot\exp(k^*\cdot z) \tag{A9}$$

$$w_s = 0.0012\cdot U_{10} \tag{A10}$$

$$k^* = 6.6\cdot\sqrt{\sin(Lat)}\cdot {U_{10}}^{-1.84} \tag{A11}$$

$$Ri = \frac{1}{20}\cdot\left(-1+\left(1+\frac{40\cdot N^2\cdot k^2\cdot z^2}{{w_S}^2\cdot\exp(-2\cdot k^*\cdot z)}\right)^{0.5}\right) \tag{A12}$$

All parameters of Eq. (A9-A12) are specified in the original study (Henderson-Sellers, 1985). Input data include latitude (Lat, Rad), Brunt–Väisälä frequency (N, $\mathrm{s^{-1}}$), and wind speed at 10 m height (U_{10}, $\mathrm{m\,s^{-1}}$). Calculations were carried out using wind speed data from closest meteorological stations: Khanty-Mansiysk for MT lakes and Bakchar for ST lakes (Russian Federal Service, 2016). Brunt–Väisälä frequency (a measure of lake stratification stability) calculated basing on experimental temperature data from surface and bottom of the lake:

$$N = \sqrt{-\frac{g}{\rho_w}\cdot\frac{\rho_s(T(0))-\rho_b(T(z_{bot}))}{z_{bot}}} \tag{A13}$$

where g ($\mathrm{m\,s^{-2}}$) is the acceleration of gravity, ρ_w ($\mathrm{kg\,m^{-3}}$) is the mean water density, $\rho_s\big(T(0)\big)$ and $\rho_b\big(T(z_{bot})\big)$ ($\mathrm{kg\,m^{-3}}$) are the water density on the surface and the bottom of the lake, respectively, as a function of water temperature, $T(0)$ and $T(z_{bot})$ (°C) at the lake surface and bottom, respectively. Water densities at different temperature were taken from (Weast, 1983). The same Eq. as (A3–A13) but with different Henry's law and molecular diffusivity constants were used for calculating oxygen molecular and turbulent diffusion.

Methane production in lake sediments was taken into account by multiplying maximal methane production rate (MMPR) $V_{prod,max}$ ($\mathrm{mg\,m^{-3}\,h^{-1}}$), obtained using an average value according to the review of Segers (1998), and the dimensionless empirical functions. These functions are allowed to vary between 0 to 1 for the following factors:

- pH ($f_{prod,pH}$) obtained using extensive data given in (Meng et al., 2012) (see Appendix B for details);
- temperature ($f_{prod,T}$) obtained using set of literature data (see Appendix B for details);
- substrate availability, DOC ($\mathrm{g\,m^{-3}}$) by Michaelis-Menten kinetics (Tian et al., 2010) with $K_{prod,DOC}$ ($\mathrm{g\,m^{-3}}$) – Michaelis constant for DOC:

$$Prod(z) = V_{prod,max}\cdot f_{prod,pH}\cdot f_{prod,T}\cdot\frac{DOC}{K_{prod,DOC}+DOC} \tag{A14}$$

Methane oxidation within the profile was calculated based on oxygen and methane concentrations (Michaelis-Menten kinetics) and temperature. The maximal intensity of methane oxidation $V_{ox,max}(z)$ ($\mathrm{mg\,m^{-3}\,h^{-1}}$) was selected using literature data separately for the water column $V_{wc,ox,max}$ (Striegl and Michmerhuizen, 1998; Utsumi et al., 1998a, 1998b; Bastviken et al., 2008) and sediment layer $V_{sed,ox,max}$ (Rudd and Hamilton 1975; Lidstrom and Somers 1984; Kuivila et al., 1988):

$$Ox(z) = V_{ox,max}(z) \cdot f_{ox,T} \cdot \frac{C_{CH_4}}{K_{ox,CH_4}+C_{CH_4}} \cdot \frac{C_{O_2}}{K_{ox,O_2}+C_{O_2}} \tag{A15}$$

$$V_{ox,max}(z) = \begin{cases} V_{wc,ox,max} & \text{if} \quad z \leq z_{bot} \\ V_{sed,ox,max} & \text{if} \quad z > z_{bot} \end{cases} \tag{A16}$$

where $f_{ox,T}$ (non-dimensional) is function of the methane oxidation temperature dependency varying from 0 to 1, K_{ox,CH_4} and K_{ox,O_2} (mg m^{-3}) are the Michaelis constants (the methane and oxygen concentrations at which the methane oxidation rate is at half-maximum). The temperature dependence of methane consumption was also derived as a dimensionless coefficient ranging between 0 and 1:

$$f_{ox,T} = \frac{\exp\left(b_2 \cdot \left(T(z)\right)^2 + b_1 \cdot T(z) + b_0\right)}{b_{max}} \tag{A17}$$

where $b_{\max}$ (non-dimensional), b_0 (non-dimensional), b_1 (°C^{-1}), b_2 (°C^{-2}) are the empirical coefficients.

Oxygen is consumed not only by methane oxidation but also by the plankton respiration in the lake water $V_{pl,resp}(z)$ and sediment respiration $V_{sed,resp}(z)$, both in (mg m^{-3} h^{-1}):

$$Resp(z) = \begin{cases} V_{pl,resp}(z) & \text{if} \quad z \leq z_{bot} \\ V_{sed,resp}(z) & \text{if} \quad z > z_{bot} \end{cases} \tag{A18}$$

Respiration of plankton in lake water is calculated according to (Pace and Prairie, 2005) as a function of concentration of dissolved phosphorous $C_P(z)$ (mg m^{-3}):

$$V_{pl,resp}(z) = 10^{-1.27+0.81 \cdot \lg\left(C_P(z)\right)} \tag{A19}$$

This empirical function was derived from a number of sources for a range of temperature from 11 to 22.5 °C ($R^2 = 0.81$), and thus a temperature correction for this dependence is not required. $V_{sed,resp}(z)$ was calculated using Michaelis-Menten kinetics (Arah and Stephen, 1998; Walter and Heimann, 2000):

$$V_{sed,resp}(z) = \frac{V_{sed,resp,max} \cdot C_{O_2}}{K_{sed,resp}+C_{O_2}} \tag{A20}$$

where $K_{sed,resp}$ (mg m^{-3}) is the Michaelis constant for sediment respiration, $V_{sed,resp,max}$ (mg m^{-3} h^{-1}) is maximal sediment respiration rate. The temperature dependence of sediment respiration can be presented in the following form (Arah and Stephen, 1998):

$$V_{sed,resp,max} = V_{10} \cdot \exp\left(\frac{\Delta E}{R} \cdot \left(\frac{1}{283} - \frac{1}{273+T(z)}\right)\right) \tag{A21}$$

where V_{10} (mg m^{-3} h^{-1}) is maximal sediment respiration rate at 10°C, ΔE (J mol^{-1}) is activation energy of respiration, R (J K^{-1} mol^{-1}) is universal gas constant. Since no data about solar radiation are available, photosynthesis is not taken into account. However, numerical tests show that oxygen does not limit methane oxidation in water column.

Photosynthesis is the only process producing O_2 in a water column. For its calculation parameterization from Stefan and Fang (1994) was used. This parameterization assumes the rates of biogeochemical processes to depend on temperature, photosynthetic active radiation (PAR) and be proportional to chlorophyll *a* concentration. PAR was calculated for a period of chamber measurements with a help of simple model SPLASH v.1.0 (Davis et al., 2017) using latitude, date and cloudiness (Russian Federal Service, 2016) as input parameters. Chlorophyll *a* concentration was calculated from total phosphorous concentration based on empirical function from (Pace and Prairie, 2005). For more details an interested reader may refer to the original paper.

Ebullition was calculated under the assumption that emitted methane bubbles immediately reach the surface (Stepanenko et al., 2011, Tan et al., 2015).

$$Ebul(z) = \max\left\{0; c_e \cdot \left(C_{CH_4}(z) - \alpha_e \cdot C_{cr,CH_4}(z)\right)\right\} \tag{A22}$$

where c_e (h^{-1}) and α_e (non-dimensional) are empirical parameters, $C_{cr,CH_4}(z)$ (mg m^{-3}) is the critical methane concentration of bubble formation that has been estimated according to Stepanenko et al. (2011):

$$C_{cr,CH_4}(z) = \Phi(z) \cdot K_{H,CH_4}\big(T(z)\big) \cdot \Big(p_a + \rho_w \cdot g \cdot z - C_{N_2}(z)/K_{H,N_2}\big(T(z)\big)\Big) \qquad \text{(A23)}$$

where $C_{N_2}(z)$ (mg m^{-3}) is the nitrogen concentration in the sediments according to depth profile from (Bazhin, 2001), $K_{H,N_2}\big(T(z)\big)$ (mg m^{-3} atm^{-1}) is the temperature-dependent Henry constant for nitrogen, p_a (Pa) is the atmospheric pressure. Methane flux through the bubbles was calculated by integration within the sediment layer:

$$Flux_{ebul} = \int_{z_{bot}}^{z_{sed}} Ebul(z)\,dz \qquad \text{(A24)}$$

where z_{sed} (m) is the depth of lower bound of sediments. Gas exchange between bubbles and ambient water was neglected because its relative impact to methane transport is very small for relatively shallow lakes (Stepanenko et al., 2011; Tan et al., 2015).

As the boundary conditions, we specify zero flux for both gases at the lower bound:

$$\left.\frac{\partial c_{CH_4}}{\partial z}\right|_{z=z_{sed}} = 0; \ \left.\frac{\partial c_{O_2}}{\partial z}\right|_{z=z_{sed}} = 0 \qquad \text{(A25)}$$

At the upper bound, we specified diffusive methane flux calculated according to (Riera et al., 1999; Bastviken et al., 2004; Rasilo et al., 2015):

$$\left.\frac{\partial c_{CH_4}}{\partial z}\right|_{z=0} = k_{CH_4} \cdot \big(C_{CH_4}(0) - C_{eq,CH_4}\big) \qquad \text{(A26)}$$

where k_{CH_4} (m h^{-1}) is the so-called “piston velocity”, an empirical gas exchange coefficient and C_{eq,CH_4} (mg m^{-3}) is concentration of dissolved methane, corresponding to atmosphere concentration of methane by Henry's Law:

$$C_{eq,CH_4} = P_{CH_4,atm} \cdot K_{H,CH_4}\big(T(0)\big) \qquad \text{(A27)}$$

where $P_{CH_4,atm}$ (atm) is the partial pressure of methane in the atmosphere above the lakes, calculated via concentration using ideal gas law. k_{CH_4} was calculated as follows (Rasilo et al., 2015):

$$k_{CH_4} = 0.01 \cdot k_{600} \cdot \left(\frac{Sh_{CH_4}\big(T(0)\big)}{600}\right)^n \qquad \text{(A28)}$$

where k_{600} (cm h^{-1}) and n (non-dimensional) are empirical parameters, $Sh_{CH_4}\big(T(0)\big)$ (non-dimensional) is the temperature-dependent Schmidt number. k_{600} was calculated according to best fit from (Crusius and Wanninkhof, 2003):

$$k_{600} = \begin{cases} 0.72 \cdot U_{10} & \text{if} \quad U_{10} < 3.7 \\ 4.33 \cdot U_{10} - 13.3 & \text{if} \quad U_{10} \geq 3.7 \end{cases} \qquad \text{(A29)}$$

Temperature sensitivity of Schmidt number was calculated using interpolation of experimental data from (Jähne et al., 1987) by third-order polynomial function. Parameter n was assumed –2/3 for wind speed < 3.7 m·s^{-1} and –1/2 for wind speed ≥ 3.7 m·s^{-1} (Crusius and Wanninkhof, 2003). Upper boundary condition for oxygen was calculated in the same way.

Appendix B: pH and temperature effect on methane production

Since data about the temperature and pH sensitivity of methane production are highly variable (Dunfield et al., 1993; Segers, 1998; Meng et al., 2012) special consideration is required for these important controls.

$f_{prod,pH}$ is a non-dimensional multiplier reflecting the decrease of methane production under real, non-optimal pH conditions. $f_{prod,pH}$ was calculated using data and the functional form from Meng et al. (2012) but with other coefficient values:

$$f_{prod,pH} = 10^{(a_2 \cdot pH^2 + a_1 \cdot pH + a_0)} / a_{max} \tag{B1}$$

We preferred not to use the coefficients given in Meng et al. (2012), because they strongly underestimate production in acidic conditions. Data obtained in a number of Russian lakes (Gal'chenko et al., 2001; Kotsyurbenko et al., 2004; Sabrekov et al., 2012) has shown that both production and emission can be very high even when pH is about 4 and lower. We suppose that this underestimation is caused mainly by lack of CH_4 production data for acidic wetlands. The coefficient of determination, R^2 for this dependence, given in Meng et al. (2012), is quite low (0.44) due to scatter in data. This scatter can be explained by variations in other methane production controls. In order to avoid both of these problems we have obtained an empirical function of CH_4 production's pH dependence using data binned into 0.5 of pH unity intervals (Figure B1). In order to obtain a function varying from 0 to 1, the fitted function was divided by its maximal value. Therefore we have the term $f_{prod,pH}$ in the form of Eq. (B1). Fitted parameters are given in Table A1.

$f_{prod,T}$ is a non-dimensional multiplier reflecting the decrease of methane production under real, non-optimal temperature conditions. $f_{prod,T}$ was calculated using the empirical function suggested by O'Neill et al. (1972) (presented within Strashkraba and Gnauk, 1985) for describing the effect of temperature change on photosynthesis:

$$f_{prod,T} = \begin{cases} S^X \cdot \exp\big(X \cdot (1-S)\big) & \text{if} \quad T(z) < T_{max} \\ 0 & \text{if} \quad T(z) \geq T_{max} \end{cases} \tag{B2}$$

$$S = \big(T_{max} - T(z)\big)/T_\Delta \tag{B3}$$

$$T_\Delta = T_{max} - T_{opt} \tag{B4}$$

$$X = Y^2 \cdot \big(1 + (1 + C_1/Y)^{1/2}\big)^2 / C_2 \tag{B5}$$

$$Y = \ln(Q_{10}) \cdot T_\Delta \tag{B6}$$

where T_{max} (°C) is a maximal temperature (when the process rate drops to zero); C_1 (°C) and C_2 (°C^2) are parameters equal to 40°C and 400°C^2, respectively in the original O'Neil model (for photosynthesis) and fitted for methanogenesis; T_{opt} (°C) is optimal temperature (i.e., when the process intensity is maximal); Q_{10} (non-dimensional) is a parameter showing how many times the process rate will grow for each 10°C increase of temperature (for low temperatures).

To constrain the C_1 and C_2 parameters, we used literature data (Svensson, 1984; Moore et al., 1990; Sass et al., 1991; Dunfield et al., 1993; Parashar et al., 1993; Klinger et al., 1994; Kotsyurbenko et al., 2004) about methanogenesis intensity under different temperature conditions in different climatic zones. T_{opt} was calculated using linear regression from the average number of days per year with average day temperature higher than 10°C ($N_{T>10}$, days):

$$T_{opt} = 0.055 \cdot N_{T>10} + 13.08 \tag{B7}$$

This empirical function (B7) was found using the studies cited above as well as others (Cicerone and Shetter, 1981; King et al., 1981; Whalen and Reeburgh, 1988; Frolking and Crill, 1994; Best and Jacobs, 1997). The average annual number of days with average day temperature higher than 10°C had better correlation with T_{opt} ($R^2 = 0.62$, $p = 0.002$) than other climatic parameters such as average daily air temperatures, average daily air temperature minimums and maximums of January, July or the whole year.

T_{max} was calculated as a function of T_{opt} using linear regression ($R^2 = 0.74$, $p < 0.001$), carried out with a help of data from a variety of sources (Van den Berg et al., 1976; Zeikus and Winfrey, 1976; Williams and Crawford, 1984; Svensson, 1984; Sass et al., 1991; Miyajima et al., 1997; Kotsyurbenko et al., 2001; 2004):

$$T_{max} = 1.023 \cdot T_{opt} + 15.29 \qquad \text{(B8)}$$

When C_1 = 590°C, C_2 = 1000°C^2, Q_{10} = 2, the empirical functions (B2-B6) fit almost all the experimental data (Figure B2). The only exception (Figure B2c) can be explained by the fact that emission was measured at a site with low water table depth (10 cm below moss surface) and as a consequence the influence of temperature on methane oxidation confounds with methane production. Usually the temperature optimum of methane oxidation is lower than that for methane production (Segers, 1998). Therefore, the left shoulder of experimental data in Fig. B2c lays below the expected, modeled values.

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Table 1. Basic characteristics of study lakes (mean values of three measured values – bottom, middle, surface)

№ on map	Lake	Date in 2014	Lake depth	Area	T	pH	EC	Eh	DOC	Total P	Cu
			m	ha	°C		µS cm^{-1}	mV	mg l^{-1}	µg l^{-1}	
MT lakes											
1	Bondarevskoe	24 Aug	3.7	39.15	18.4	5.3	10	103	5	11	0.28
2	Lebedinoe	22 Aug	2.5	7.80	17.6	4.2	35	165	25	11	0.40
3	Babochka	21 Aug	2.2	1.77	16.7	4.4	19	150	18	9	0.33
4	Muhrino	20 Aug	1.5	536.4	19.0	5.4	14	95	11	6	0.57
ST lakes											
5	Bakchar.ryam	19 Aug	1.4	0.45	21.1	8.3	79	59	48	76	1.31
6	Bakchar.forest.1	28 Jul	1.6	1.84	20.1	7.3	200	132	56	38	2.45
	Bakchar.forest.2	30 Jul	2.1	1.04	14.2	7.3	271	132	49	39	1.63
	Bakchar.forest.3	18 Aug	2.3	0.70	14.5	7.3	283	39	26	13	1.05
7	Gavrilovka.1	15 Aug	4.7	0.93	20.7	8.2	217	102	8	11	1.19
	Gavrilovka.2	16 Aug	2.5	0.19	18.4	8.3	261	75	10	11	1.19
8	Bakchar.bog.1	6 Aug	0.9	0.05	22.9	4.5	36	311	38	16	1.04
	Bakchar.bog.2	10 Aug	2.2	0.20	21.2	4.8	46	270	34	13	1.09
9	Plotnikovo	31 Jul	1.8	0.90	19.5	7.1	183	95	24	20	0.84
10	Ob’.Floodplain	1 Aug	1.7	4.50	18.9	7.5	260	102	12	188	0.64

Table 2. Surface dissolved water CH_4 concentration ($mgCH_4$ m^{-3}) in three ST lakes, both measured and calculated assuming a range of values of gas-filled porosity

Lake	Surface dissolved water CH_4 concentrations ($mgCH_4$ m^{-3})				
	Calculated when gas-filled porosity (m^3 m^{-3}) is				Measured
	0	0.025[a]	0.05	0.075	
Bakchar.forest.3	1.51	2.35	8.24	35.68	10.3
Gavrilovka.2	0.13	0.21	0.73	2.43	1.20
Plotnikovo	1.98	2.98	9.42	36.16	13.4

[a] Value used in model by default (see Appendix A for details)

Table 3. Summary of field flux observations (empty cells indicate no data)

Lake	CH_4 flux (static chambers)		Ebullition CH_4 flux[b]	Median CO_2 flux (static chambers)
	Average ± SD (N[a])	Median		
		$mgCH_4\ m^{-2}\ h^{-1}$		$mgCO_2\ m^{-2}\ h^{-1}$
		MT lakes		
Bondarevskoe	0.5 ± 0.2 (24)	0.5	0.1 ± 0.2	17.5
Lebedinoe	0.3 ± 0.1 (16)	0.3	Not found	22.3
Babochka	0.1 ± 0.03 (14)	0.1	Not found	24.9
Muhrino	0.2 ± 0.2 (15)	0.1	0.01	16.5
		ST lakes		
Bakchar.ryam	3.2 ± 2.8 (6)	1.9		10.2
Bakchar.forest.1	7.4 ± 12.5 (10)	3.1	6.8 ± 4.3	63.2
Bakchar.forest.2	2.6 ± 1.2 (12)	2.2		87.4
Bakchar.forest.3	5.1 ± 2.0 (7)	5.1	3.5 ± 3.1	141.4
Gavrilovka.1	1.5 ± 1.8 (14)	0.8		10.1
Gavrilovka.2	2.7 ± 2.2 (10)	1.9		14.0
Bakchar.bog.1	8.9 ± 9.5 (12)	4.7	5.2	116.8
Bakchar.bog.2	8.2 ± 14.1 (14)	4.1		136.8
Plotnikovo	7.2 ± 2.5 (8)	7.4		116.4
Ob’ Floodplain	8.8 ± 7.3 (16)	5.7		302.8

[a] Number of individual flux measurements

[b] Measured using bubble traps; if there were two replicate traps, standard deviation is given.

Table 4. Summary of modeling results

Lake	$[CH_4]$ (at 1 m depth)	Modeled diffusive CH_4 flux	Modeled ebullition CH_4 flux	Modeled total CH_4 flux	Difference with real CH_4 flux[a]	Oxidized fraction
	$mgCH_4\ m^{-3}$	$mgCH_4 \cdot m^{-2} \cdot h^{-1}$				%
			MT lakes			
Bondarevskoe	0.55	0.01	6.25	6.26	5.74	19
Lebedinoe	0.95	0.02	7.23	7.25	6.95	18
Babochka	2.82	0.06	6.84	6.90	6.80	18
Muhrino	28.05	0.70	5.50	6.21	6.02	16
			ST lakes			
Bakchar.ryam	10.36	0.31	2.70	3.01	-0.15	26
Bakchar.forest.1	21.52	0.65	9.93	10.57	3.08	13
Bakchar.forest.2	3.45	0.14	1.22	1.36	-1.25	36
Bakchar.forest.3	2.95	0.06	5.62	5.68	0.56	23
Gavrilovka.1	0.35	0.01	1.63	1.64	0.15	35
Gavrilovka.2	0.76	0.02	0.84	0.85	-1.86	40
Bakchar.bog.1	15.60	0.16	9.47	9.78	0.87	12
Bakchar.bog.2	4.71	0.09	7.99	8.08	-0.16	22
Plotnikovo	12.63	0.38	7.33	7.71	0.50	17
Ob' Floodplain	10.49	0.23	5.07	5.30	-3.49	20

[a] Difference between modelled total flux (as a sum of diffusive and ebullition flux) and measured average flux

Table 5. Summary for temperate and boreal lakes with area <100 ha. Empty cells mean no data, storage fluxes are not shown and do not have values more than 1 $mgCH_4\ m^{-2}\ h^{-1}$

Reference	Coordinates	MAT[a]	MJT[b]	DOC	Total P	Surface $[CH_4]$	Average CH_4 flux	
							Diffusive	Ebullition
		°C		$mg \cdot l^{-1}$		$mgCH_4 \cdot m^{-3}$	$mgCH_4 \cdot m^{-2} \cdot h^{-1}$	
Juutinen et al., 2009 (3 groups of lakes)	Finland	-2.8	12.3	5	0.006	5.1	0.06[d,e]	
		–	–	9	0.014	6.4	0.14[d,e]	
		5.9	17.2	17	0.024	4.0	0.12[d,e]	
Repo et al., 2007	66° N, 75° E	-4.7	16.3	11	0.044	4.6	0.25	0.09
Huttunen et al., 2003	63° N, 28° W	3.4	17.5		0.056		0.61	1.7
Repo et al., 2007 (two lakes)	61° N, 70° E	-0.8	18.2	17	0.005	41.6	1.71	Not found
				10	0.006	4.5	0.34	0.25
Casper et al., 2000	59° N, 3° W	13.0	19.9		0.60	17.6	0.30	8.3
Bastviken et al., 2004[c]	59° N, 15° E	5.8	16.5	11	0.014	10.7	0.11	
Rudd and Hamilton, 1978	50° N, 95° W	3.1	19.7	9	0.035		0.91[d]	
Bastviken et al., 2008 (3 lakes)	46° N, 90° W	4.3	18.3	22	0.028		0.15	0.18
		4.3	18.3	4	0.010	30.4	0.60	0.41
		4.3	18.3	5	0.008	20.8	0.39	0.68
Bastviken et al., 2004[c]	46° N, 90° W	4.3	18.3	10	0.020	17.8	0.35	0.63
Smith and Lewis, 1992	40° N, 106° W	1.7	13.7	10		16.3	1.1	
This study, MT lakes	61° N, 69° E	-0.8	18.2	15	0.009		0.32[f]	0.28
This study, ST lakes	57° N, 83° E	1.0	18.7	30	0.043	8.3	8.60[f]	4.30

[a] Mean annual temperature

[b] Mean July temperature

[c] Average values according to Table 1 data for central Sweden (59° N, 15° E) and Land O'Lakes, Wisconsin, USA (46° N, 90° W) are given

[d] Sum of diffusion and storage flux

[e] Medians are given. There are no average values in original work.

[f] Static chamber values, presenting sum of diffusive and ebullition flux values, are given.

Table A1. List of the model parameters.

Parameter	Description	Value	Units	Reference
a_0	Coefficients of the dependency of the methane production on pH, $f_{prod,pH}$	-3.5172		Recalculated data from (Meng et al., 2012) (see Appendix B)
a_1		1.1217	pH^{-1}	
a_2		-0.0921	pH^{-2}	
a_{max}		0.7905		
b_0	Coefficients of the dependency of methane oxidation on temperature, $f_{ox,T}$	-3.6945		Glagolev, 2006; $b_{\max}$ was chosen so that the function ranges between 0 and 1
b_1		0.1486	$^oC^{-1}$	
b_2		-0.0029	$^oC^{-2}$	
b_{max}		0.1668		
B_{CH_4}	Coefficient of Henry's law constant temperature dependence for methane	1700	K	Sander, 2015
B_{N_2}	Coefficient of Henry's law constant temperature dependence for nitrogen	1300	K	Sander, 2015
B_{O_2}	Coefficient of Henry's law constant temperature dependence for oxygen	1500	K	Sander, 2015
C_1	Empirical coefficients for temperature dependence of methane production, $f_{prod,T}$	590	^oC	see Appendix B
C_2		1000	$^oC^2$	
c_e	Parameter, defining velocity of bubble formation	1.008	h^{-1}	Walter and Heimann 2000
D_{0,gas,CH_4}	Diffusion coefficient for CH_4 in the air at 0 °C	0.068	$m^2\ h^{-1}$	Arah and Stephen 1998
D_{0,gas,O_2}	Diffusion coefficient for O_2 in the air at 0 °C	0.065	$m^2\ h^{-1}$	Arah and Stephen 1998
D_{0,liq,CH_4}	Diffusion coefficient for CH_4 in the water at 25 °C	$5.4 \cdot 10^{-6}$	$m^2\ h^{-1}$	Arah and Stephen 1998
D_{0,liq,O_2}	Diffusion coefficient for O_2 in the water at 25 °C	$8.6 \cdot 10^{-6}$	$m^2\ h^{-1}$	Arah and Stephen 1998
g	Gravitational acceleration	9.81	$m \cdot s^{-2}$	Weast, 1983
K_{0,H,CH_4}	Henry's law constant for methane at 25 °C	0.021	$mg\ m^{-3}\ atm^{-1}$	Sander, 2015
K_{0,H,N_2}	Henry's law constant for nitrogen at 25 °C	0.017	$mg\ m^{-3}\ atm^{-1}$	Sander, 2015
K_{0,H,O_2}	Henry's law constant for oxygen at 25 °C	0.040	$mg\ m^{-3}\ atm^{-1}$	Sander, 2015
K_{ox,CH_4}	Michaelis CH_4-constant for methane consumption	116 ± 39	$mg\ m^{-3}$	Rudd and Hamilton 1975; Lidstrom and Somers 1984; Kuivila et al., 1988
K_{ox,O_2}	Michaelis O_2-constant for methane consumption	1019 ± 1019	$mg\ m^{-3}$	Bender and Conrad 1994
$K_{prod,DOC}$	Michaelis DOC-constant for soil methane production	10 ± 7	$g\ m^{-3}$	Lokshina et al., 2001 (review); Tian et al., 2010
$K_{sed,resp}$	Michaelis constant for sediment respiration	7040 ± 2500	$mg\ m^{-3}$	Frenzel et al., 1990; Arah and Stephen 1998;
$P_{CH_4,atm}$	Atmospheric partial pressure of CH_4	$1.9 \cdot 10^{-6}$	atm	measured value
$P_{O_2,atm}$	Atmospheric partial pressure of O_2	0.2095	atm	Weast, 1983
Q_{10}	Empirical coefficient for temperature dependence of methane production, $f_{prod,T}$	2		see Appendix B
R	Universal gas constant	8.314	$J \cdot K^{-1} \cdot mol^{-1}$	Weast, 1983
V_{10}	Maximal respiration rate at 10°C	27000 ± 12000	$mg\ m^{-3}\ h^{-1}$	Yavitt et al., 1987; Arah and Stephen 1998; Thamdrap et al., 1998
$V_{prod,max}$	Maximal rate of methane production	31.3 ± 24.4	$mg\ m^{-3}\ h^{-1}$	Segers, 1998 (review)
$V_{sed,ox,max}$	Maximal rate of CH_4 consumption in the sediments	228 ± 153	$mg\ m^{-3}\ h^{-1}$	Rudd and Hamilton 1975; Lidstrom and Somers 1984; Kuivila et al., 1988
$V_{wc,ox,max}$	Maximal rate of CH_4 consumption in the water column	4 ± 2.4	$mg\ m^{-3}\ h^{-1}$	Striegl and Michmerhuizen, 1998; Utsumi et al., 1998a, 1998b; Bastviken et al., 2008
α_e	Coefficient describing concentration when bubble formation starts	0.4		Wania, 2007

ε_a	Gas-filled porosity	0.025	$m^3\ m^{-3}$	Valsaraj et al., 1998; Brennwald et al., 2005
ρ_w	Water density	1000	$kg\ m^{-3}$	Weast, 1983
ΔE	Activation energy of respiration	50000	$J\ mol^{-1}$	Arah and Stephen 1998; Thamdrap et al., 1998;

Figure 1. Studied lakes in MT (left panel; shades of yellow corresponds to floodplain, brown – to forests, green – to pine-shrub-sphagnum communities, purple – to ridge-hollow complexes) and ST (right panel; shades of green corresponds to forests and grasslands, blue – to wetlands) on Landsat satellite images.

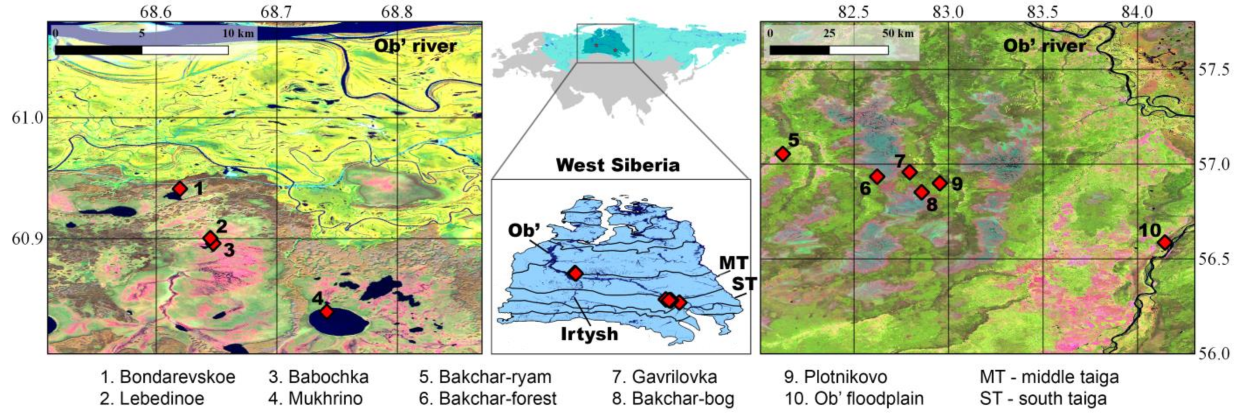

Figure 2. Schematic representation of the model structure. The one-dimensional column is divided into lake water and sediments. The forcing consists of lake and sediment depths, the water $T_{water}(z)$ and sediment $T_{sed}(z)$ temperature, DOC and phosphorous concentration [P] and pH. CH_4 production occurs only in the sediments. The methane production rate $R_{prod}(z)$ is a function of the sediment temperature, the DOC, which is taken as a measure for substrate availability, and pH. CH_4 oxidation is calculated in the different way for sediments and for lake water. The CH_4 oxidation rate $R_{oxid}(z)$ follows Michaelis-Menten kinetics for both methane and oxygen and is a function of the water and sediment temperature. The water respiration rate WaterResp(z) is a function of the water temperature, the phosphorous concentration, which is taken as a measure for abundance of phytoplankton. The sediment respiration rate SedResp(z) is a function of the sediment temperature. Both water and sediment respiration follows Michaelis-Menten kinetics for oxygen uptake. Transport of CH_4 in lake sediments proceeds by (1) molecular diffusion through gas-filled and water-filled pores, (2) ebullition, which is the formation of gas bubbles in the sediment layer and their immediate ascent to the water surface. Transport of CH_4 in lake water proceeds by (1) wind-induced turbulent diffusion (2) molecular diffusion in water. Transport of O_2 is the same except ebullition. The model calculates methane fluxes to the atmosphere and CH_4 and O_2 concentration profiles in the lake water and sediments.

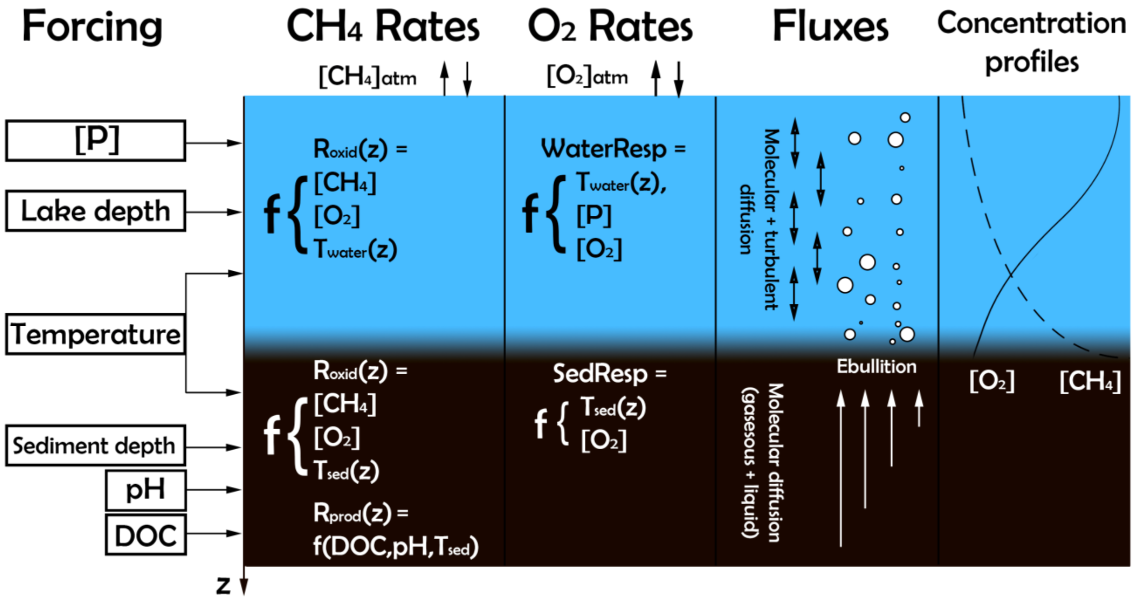

Figure 3. Flux data for (a) ST and (b) MT lakes in log-log scale and probability distribution fitting: (c) power law for ST lakes fluxes and (d) log-normal for MT lakes fluxes. Rank 1 indicates the highest magnitude flux. Note the strong difference in the y-axis scaling between the two regions.

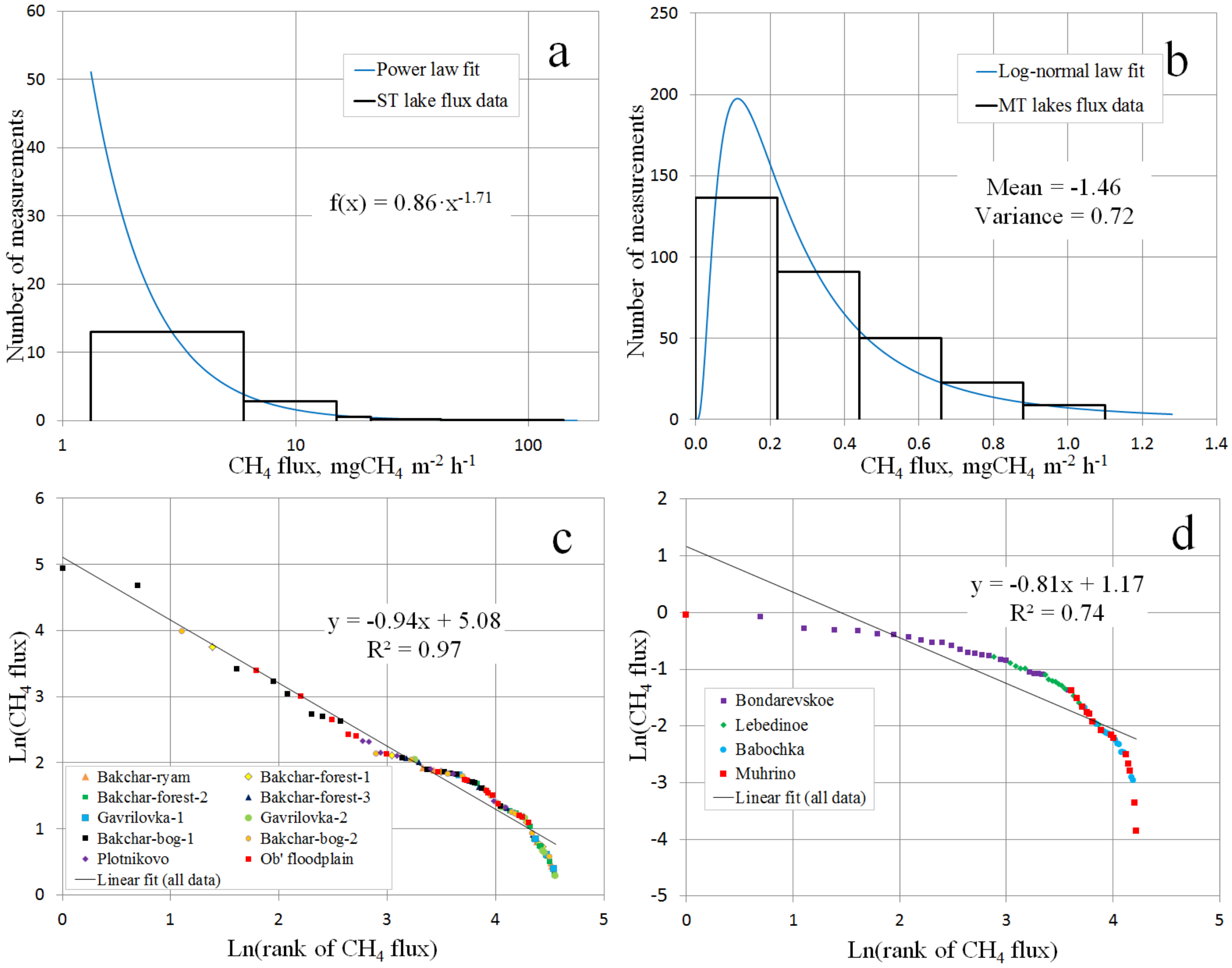

Figure 4. Observed versus predicted values of methane flux. Whiskers denote ±1SD. Predicted flux uncertainties are calculated from bootstrapping (see Sect. 2.2.3) and are explained by high uncertainty in model parameters adopted from literature (see Appendix A). High magnitudes of observation SD's may be explained by ebullition and SOC behavior of lakes as methane sources (see Sect. 4.3). Note that predicted flux uncertainties are higher than the magnitude of observation SD's for the MT lakes but less for the ST lakes.

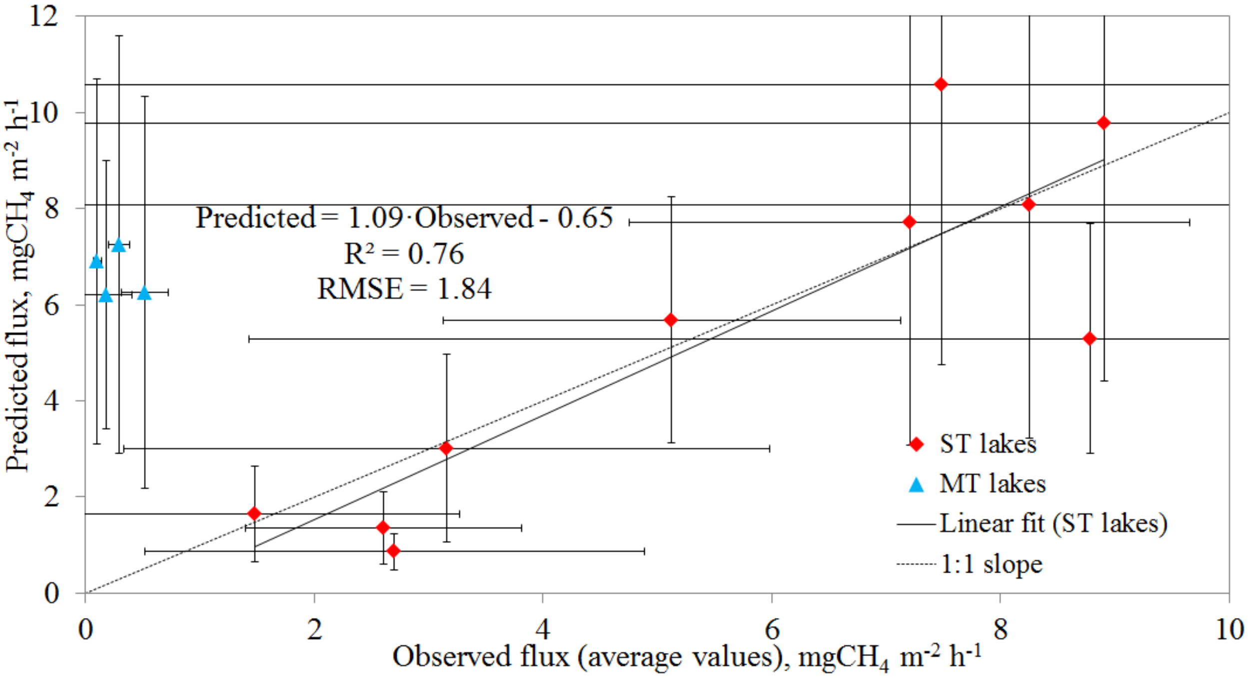

Figure B1. Empirical function of relative methane production dependence on pH. The function from Meng et al. (2012) is given for comparison. Whiskers denote ±1SD for binned values of production, according to data presented in Meng et al. (2012).

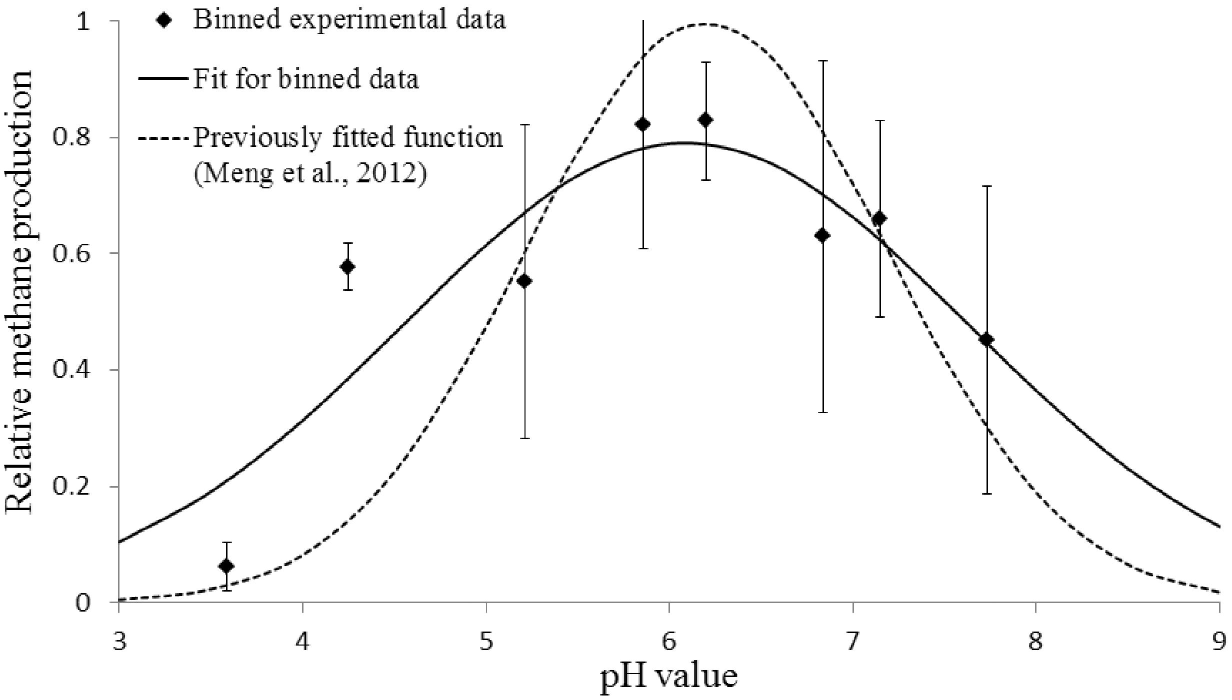

Figure B2. Empirical function of relative methane emission (a-c) and production (d-h) dependence on temperature. Black squares are experimental data, solid lines represent the fitted empirical function using Eq. (B2-B8). Standard deviations are given as whiskers for investigations where they have been presented.