On the methane paradox: Transport from shallow water zones rather than in situ methanogenesis is the major source of CH₄ in the open surface water of lakes

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Abstract

Estimates of global methane (CH₄) emissions from lakes and the contributions of different pathways are currently under debate. In situ methanogenesis linked to algae growth was recently suggested to be the major source of CH₄ fluxes from aquatic systems. However, based on our very large data set on CH₄ distributions within lakes, we demonstrate here that methane-enriched water from shallow water zones is the most likely source of the basin-wide mean CH₄ concentrations in the surface water of lakes. Consistently, the mean surface CH₄ concentrations are significantly correlated with the ratio between the surface area of the shallow water zones and the entire lake, fₐ/s, but not with the total surface area. The categorization of CH₄ fluxes according to fₐ/s may therefore improve global estimates of CH₄ emissions from lakes. Furthermore, CH₄ concentrations increase substantially with water temperature, indicating that seasonally resolved data are required to accurately estimate annual CH₄ emissions.

1. Introduction

Lakes are considered to be major natural sources of methane (CH₄), contributing a large fraction of the global CH₄ emissions to the atmosphere [Michmerhuizen and Stiegl, 1996; Luysaert et al., 2012; Bastviken et al., 2011]. However, the quantification of the global CH₄ emissions from lakes and the controls and contributions of the different CH₄ pathways from aquatic systems to the atmosphere are currently studied worldwide [Bastviken et al., 2011; Hofmann, 2013; Grossart et al., 2011; Prairie and del Giorgio, 2013; Bogard et al., 2014; Tang et al., 2014; Blees et al., 2015; Encinas Fernández et al., 2014].

Global emissions of CH₄ are typically estimated by categorizing CH₄ emissions per unit surface area according to lake size and multiplying these areal CH₄ emissions by the global surface area of lakes within the respective size category [Bastviken et al., 2011; Bastviken et al., 2004; Kirschke et al., 2013]. Therefore, global CH₄ emissions from lakes depend on the estimated global surface area of lakes in different size categories [Bastviken et al., 2011; Cole et al., 2007; Conrad, 2009; Downing et al., 2006; McDonald et al., 2012]. Furthermore, the estimates of areal CH₄ emissions are complicated by the large spatial heterogeneity of CH₄ emissions [Hofmann, 2013; Blees et al., 2015; Murase et al., 2005] and the multiple pathways and sources that can contribute to CH₄ emissions [Grossart et al., 2011; Prairie and del Giorgio, 2013; Bogard et al., 2014; Bastviken et al., 2004; Karl and Tilbrook, 1994; Walter et al., 2007; DeSontro et al., 2011; Carmichael et al., 2014; Carini et al., 2014].

CH₄ in lakes mainly originates from anaerobic carbon mineralization in anoxic sediments [Segers, 1998]. Most of the CH₄ produced in anoxic sediments is oxidized by methanotrophic bacteria at anoxic-oxic interfaces [Conrad, 2009; Bastviken et al., 2002; Utsumi et al., 1998; Utsumi et al., 1998b]. Observations from several lakes show that in the oxic epilimnion, CH₄ concentrations are typically oversaturated and higher than in the oxic hypolimnion [Luysaert et al., 2012; Bogard et al., 2014; Blees et al., 2015; Schulz et al., 2001]. This phenomenon, called the “methane paradox” [Reeeburgh, 2007], has been taken as an indication of the in situ production of CH₄ in oxic waters [Bogard et al., 2014; Schulz et al., 2001]. Anoxic microzones were proposed as sites of in situ CH₄ production in generally oxic waters [Schulz et al., 2001]. Methanogenic Archaea attached to photoautotrophs were detected and identified as possible candidates responsible for causing elevated CH₄ concentrations in the oxic metalimnion [Grossart et al., 2011]. Recently, it has been suggested that methanogenesis in oxic surface waters is closely linked to algal dynamics and driven by acetoclastic production [Bogard et al., 2014]. A positive correlation between CH₄ and Chl-α concentrations across diverse open-water aquatic ecosystems was presented as support of this hypothesis [Bogard et al., 2014]. The possible metabolic pathways for CH₄ production in oxic waters and field evidence of oxic methane production have recently been
reviewed by Tang et al. [2016]. These authors conclude that oxic methane production may be an important source of CH₄ in lakes but the fate of the produced methane and its relevance for the overall methane emissions from lakes requires additional research. According to Bogard et al. [2014], “oxic water methanogenesis is a significant component of the overall CH₄ budget in a small, shallow lake” and “this pathway (oxic water methanogenesis) may be the main CH₄ source in large, deep lakes …”

However, elevated CH₄ concentrations in oxic surface waters of the pelagic zone do not necessarily originate from the in situ production of CH₄ but could alternatively be explained by the lateral transport of CH₄ from littoral zones [Hofmann, 2013; Bastviken et al., 2004; Rudd and Hamilton, 1978; Murase et al., 2003]. CH₄ concentrations in the littoral zone (here, the shallow water zone) can be expected to be particularly high because the production rate of CH₄ in anoxic pore waters of sediments increases with temperature [Murase et al., 2005; Bastviken et al., 2008], and temperatures are higher in littoral than profundal sediments. Furthermore, CH₄-rich pore water in littoral sediments is regularly released into the water column during resuspension events associated with surface waves [Hofmann et al., 2010]. In this study, we utilize one of the world’s largest data sets on CH₄ distributions within lakes to test whether CH₄ from shallow water zones (hypothesis A) or the in situ production of CH₄ in oxic surface water, i.e., production within the anoxic microzones and production due to methanogenic bacteria (hypothesis B), is the more likely explanation for the methane paradox. If CH₄ from the shallow water zone is the major source of the CH₄ in the surface water of the deepwater zone, (a) CH₄ concentrations in the shallow water zone must be higher than in the deepwater zone and (b) the ratio of CH₄ from the shallow water zone to CH₄ from the deepwater zone, \( f_{\text{CH}_4,\text{s/d}} \), should increase with increasing surface area of the deepwater zone because CH₄ introduced from the shallow water zone is more strongly diluted in a larger deepwater zone. In contrast, if the dominant source of CH₄ in the surface water is in situ production, one does not necessarily expect significant differences between CH₄ in shallow water and deepwater zones, and an increase in the ratio \( f_{\text{CH}_4,\text{s/d}} \) with increasing surface area of the deepwater zone cannot be easily explained. If the in situ production of CH₄ is linked to Chl-\( a \) [Bogard et al., 2014], CH₄ concentrations in individual lakes should vary with seasonal changes in Chl-\( a \), whereas the trophic state of a lake, i.e., the annual mean biomass, may influence both the oxic in situ production of CH₄ and the CH₄ concentrations in the shallow littoral zone via production in the sediments.

2. Methods

2.1. Study Sites

Sampling was conducted in nine basins in seven lakes (Königseggsee, Rohrsee, Illmensee, Mindelsee, Lower Lake Constance (LLC), Lake Ammer, and Upper Lake Constance (ULC)) located in southwest Germany (Table 1). The total surface areas of the studied basins range from 0.16 to 64.69 km², and shallow areas with water depths of less than 6 m represent between 9% and 100% to the total surface area of the different basins.

2.2. Field Measurements

Between April 2011 and June 2014, the horizontal distributions of CH₄ concentrations in the surface water (1 m water depth) were measured in each of the basins, in some cases multiple times. Details of the sampling stations and water sample analysis are provided in Table S1 and Figures S4–S12 in the supporting information. In three
lakes (Königseggsee: March 2013 to October 2014, Illmensee: March 2013 to October 2014, and Mindelsee: May 2012 to October 2013), the vertical profiles of CH₄ concentration were measured with a 1 m vertical resolution at least once a month at the deepest station of the lake (Table S2 and Figures S4, S6, and S7).

All water samples for CH₄ analysis were collected with a 2 L sampler (Limnos, Rossinkatu 2 E17, Turku, Finland) and then transferred into 122 mL serum bottles [Hofmann et al., 2010]. The vertical profiles of Chl-α were measured with a multispectral Fluoroprobe (Moldenke FluoroProbe, MFP). Additionally, vertical profiles of depth and temperature were measured with a multiparameter probe (CTD probe, RBR Ltd., Ottawa, Canada) at a sampling frequency of 6 Hz.

### 2.3. Laboratory Measurements

The CH₄ concentrations of the water samples were analyzed using the headspace method [Hofmann et al., 2010] and a gas chromatograph with a flame ionization detector (GC 6000, Carlo Erba Instruments). The GC was calibrated every five water samples using gas standards of 10, 50, and 100 ppm (Air Liquide). On average, the concentration measurements of replicate samples varied by ~5%.

### 2.4. Numerical Analysis and Statistics

In our analysis, we separated each basin into a shallow water zone (water depth ~6 m) and a deepwater zone (water depth ~2 m). The ratio between the surface area of the shallow water zone (Aₛ) and the total surface area of the lake, a, is the aspect ratio defined as f₃ₛₚ = Aₛ / Aₐ. The surface water CH₄ concentrations in the shallow water zone (CH₄ₛ), deepwater zone (CH₄ₜₚ), and entire lake (CH₄ₜₚ) were determined using the standard chemical sampling method of CH₄ concentration was measured with a 1 m vertical resolution at 2010. The vertical profiles of CH₄ were determined using a surface-area weighted average of CH₄ from shallow water and deepwater zones: CH₄ₛ = (Aₛ · CH₄ₚₚ + Aₜₚ CH₄ₜₚ) / Aₚₚ, where Aₚₚ is the surface area of the deepwater zone. The variance of all the CH₄ concentrations measured during an individual horizontal survey (V_WS) is taken as a measure of the horizontal heterogeneity of CH₄.

Linear regression and t tests were used to investigate the relationship between morphometric properties and CH₄, as well as the ratio f₃ₛₚₚ = CH₄ₛ / CH₄ₜₚ measured during different campaigns and in different basins.

Multiple linear models (MLMs) were applied to assess the relationships between the basin-wide mean surface CH₄ concentration (CH₄ₛ) as a dependent variable and the total surface area of the lake (Aₚₚ), the aspect ratio (f₃ₛₚ), and the water temperature at a water depth of 1 m (T) as independent variables. Additionally, MLMs were used to investigate the relationship between the seasonal development of CH₄ concentrations, temperature, and Chl-α concentrations within the lakes using time series of averaged data from the first 6 m of the water column as measured at the deepest station in Königseggsee, Illmensee, and Mindelsee. In the latter analysis, we only considered data from the stratified period from May to October and thereby deliberately excluded time periods of fall overturn. In all applications using MLM, the data on CH₄ and Chl-α concentrations were logarithmized prior to analysis.

The statistical analyses were performed using MATLAB.

### 3. Results

#### 3.1. Properties of Methane Concentration Distributions as Measured in Different Basins

In all the basins, surface CH₄ concentrations were horizontally heterogeneous and sensitive to the 1 m deep surface water temperature (Figure 1 and Table S1). The median values and the range of CH₄ concentrations in the horizontal distributions differ substantially between lake basins and for different surface water temperatures (Figure 1). In the comparatively small lakes, Königseggsee, Illmensee, and Mindelsee, the CH₄ concentrations ranged between ~0.06 and ~3.9 μM (Figures 1a, 1b, and 1d). In the similarly sized but very shallow Rohrsee, the CH₄ concentrations exhibited the greatest variability (~0.4 and ~20 μM; Figure 1c) and the highest maximum lake-wide median concentration (~8.7 μM). In the three basins of LLC and in Lake Ammer, which have larger surface areas than that of Rohrsee, the CH₄ concentrations were lower than those in Rohrsee and ranged between 0.5 and 16 μM (Figures 1e–1h). The lowest CH₄ concentrations (median 0.14 μM) and the lowest horizontal heterogeneity in the CH₄ concentrations (V₃ₛₚₚ < 0.05 μM²) of all basins were measured in ULC (Figure 1i), the largest and deepest basin with the smallest f₃ₛₚ. In the basins in which
several surveys were conducted at different temperatures, the greatest variability and the highest median CH4 concentrations were observed during the summer season, when temperatures were high (Figures 1a, 1c, 1e, and 1f). An exception is the horizontal heterogeneity in the CH4 concentrations in Illmensee, which peaked in late fall ($V_{CH4} \approx 0.48 \mu M^2$) during overturn (Figure 1b).

3.2. CH4 Concentrations in the Shallow Water and Deepwater Zones of the Different Basins

The CH4 distributions of the individual surveys in all the basins, as shown in Figure 1, were analyzed further by distinguishing between measurements in shallow water and deepwater zones and averaging the respective CH4 concentrations to obtain $CH4_s$, $CH4_d$, $CH4_t$, and $CH4_w$. The two different estimates of the mean basin-wide methane concentrations, $CH4_t$ and $CH4_w$, are highly correlated ($p$ value $<0.001$, $R^2 = 99.96\%$) and have essentially the same values (the coefficients of the regression line are $a = -0.009 \mu M$ and $b = 0.999$; Figure 2a and Table 2a). Therefore, statistical analyses involving mean basin-wide CH4 concentrations provide the same results regardless of whether they use $CH4_t$ or $CH4_w$. The excellent agreement between $CH4_t$ and $CH4_w$ indicates that the sampling stations associated with the different surveys of the different basins provide representative coverage, with the number of samples from shallow water and deepwater zones being proportional to their respective surface areas.

Across diverse lake morphologies and seasons (as indicated by water temperature), the horizontal heterogeneity in the CH4 concentration increases with the lake-wide average CH4 concentration; i.e., log($V_{CH4}$) and log ($CH4_t$) are positively correlated ($p$ value $<0.001$, $R^2 = 80\%$). According to the regression model, $V_{CH4}$ increases

Figure 1. Properties of the horizontal distributions of CH4 concentrations in different basins and seasons. Box plots of the CH4 concentrations (μM) measured at 1 m water depth in (a) Königseggsee, (b) Rohrsee, (c) Illmensee, (d) Mindelsee, (e) Lower Lake Constance (northern basin), (f) Lower Lake Constance (central basin), (g) Lower Lake Constance (southern basin), (h) Lake Ammer, and (i) Upper Lake Constance. Multiple surveys conducted in a single basin are sorted according to the average surface water temperature (°C). The box plots indicate the median value and the 5% and 95% percentiles of the CH4 concentrations measured during the survey. The outliers are indicated by grey dots. For more detailed information on the sampling dates and the sampling stations in each lake, see Table S1 and Figures S4–S12.
Table 2. Assessment of the Relationship Between \( CH_4 \) Concentrations and Lake Morphology, Temperature, and Chl-\( a \) Concentrations

<table>
<thead>
<tr>
<th>Linear Models</th>
<th>( a ) (( \mu M ))</th>
<th>( b )</th>
<th>( p ) Value</th>
<th>( R^2 ) (%)</th>
<th>NRMSE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CH_{4,w} = a + b \cdot CH_{4,t} )</td>
<td>-0.009</td>
<td>0.999</td>
<td>&lt;0.001</td>
<td>100</td>
<td>0.5</td>
</tr>
<tr>
<td>( \ln(CH_{4,w}) = a + b \cdot CH_{4,t} )</td>
<td>-1.80</td>
<td>2.22</td>
<td>&lt;0.001</td>
<td>80.9</td>
<td>11.99</td>
</tr>
<tr>
<td>( f_{CH4,sid} = a + b \cdot A_d )</td>
<td>1</td>
<td>3.03 ( \times 10^{-8} )</td>
<td>&lt;0.01</td>
<td>71.0</td>
<td>19.21</td>
</tr>
<tr>
<td>MLM considering ( CH_{4,t}, A_p, f_{A,s/t} ), and ( T )</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>( \ln(CH_{4,t}) = a + b \cdot A_d )</td>
<td>0.17</td>
<td>-7.47 ( \times 10^{-9} )</td>
<td>0.57</td>
<td>0.01</td>
<td>26.26</td>
</tr>
<tr>
<td>( \ln(CH_{4,t}) = a + b \cdot A_d + c \cdot T )</td>
<td>-0.94</td>
<td>-1.49 ( \times 10^{-8} )</td>
<td>0.08</td>
<td>0.24</td>
<td>17.4</td>
</tr>
<tr>
<td>( \ln(CH_{4,t}) = a + b \cdot f_{A,s/t} )</td>
<td>-0.99</td>
<td>2.27</td>
<td>&lt;0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \ln(CH_{4,t}) = a + b \cdot f_{A,s/t} + c \cdot T )</td>
<td>-2.61</td>
<td>2.66</td>
<td>0.1</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>MLM applied to seasonal data of ( CH_{4,0-6 \text{m}}, Chl-a_{0-6 \text{m}}, ) and ( T_{0-6 \text{m}} )</td>
<td></td>
<td></td>
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<tr>
<td>( \ln(CH_{4,0-6 \text{m}}) = a + b \cdot \ln(Chl-a_{0-6 \text{m}}) + c \cdot T_{0-6 \text{m}} )</td>
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<td></td>
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Figure 2. Relationship between the basin-wide mean \( CH_4 \) concentration and two different variables. (a) Basin-wide areal weighted average \( CH_4 \) concentration (\( CH_{4,w} \)) versus basin-wide mean \( CH_4 \) concentration (\( CH_{4,t} \)). The line represents the linear model considering the \( CH_{4,w} \) as a dependent variable and the \( CH_{4,t} \) as an independent variable (Table 2a). (b) Basin-wide variance of surface concentrations (\( VCH_4 \)) versus the basin-wide mean \( CH_4 \) concentration (\( CH_{4,t} \)). The line represents the results from the application of a linear model with \( VCH_4 \) and \( CH_{4,t} \) as independent variables (Table 2b).

Slightly more rapidly than quadratic with \( CH_{4,t} \) (Figure 2b and Table 2b). Thus, the standard deviation of the \( CH_4 \) concentrations measured during individual surveys (\( \sqrt{VCH_4} \)) is approximately proportional to \( CH_{4,t} \), which supports the suitability of using the logarithm of \( CH_{4,t} \) in correlation analyses and MLM.

In all the basins, the ratio \( f_{CH4,sid} \) is on average larger than 1, suggesting that the mean \( CH_4 \) concentration in the shallow water zone is typically larger than the mean \( CH_4 \) concentration in the deepwater zone. The values of \( f_{CH4,sid} \) in the different surveys in each basin range from (in brackets are mean values) 0.72 to 1.14 (1.03), 0.78 to 2.08 (1.17), and 1.35 in Königseggsee, Illmensee, and Mindelsee, respectively. Larger values of \( f_{CH4,sid} \) were observed in the northern, central, and southern basins of LLC and in Lake Ammer: 0.87–1.41 (1.16), 0.97–1.45 (1.23), 2.02–2.08 (2.05), and 1.38, respectively. The deepest and largest basin, ULC, has the largest value of \( f_{CH4,sid} \) = 3.18 of all the lakes. According to a test, the mean \( f_{CH4,sid} \) for the different basins is significantly larger than 1 (\( p \) value <0.05). Furthermore, the mean \( f_{CH4,sid} \) value significantly increased with the surface area of the deepwater zone (\( p \) value <0.05, \( R^2 = 68\% \)). Rohrsee was not included in this analysis because it does not have a deepwater zone. If \( A_d \) becomes very small, i.e., \( A_d \to 0 \), \( f_{CH4,sid} \) is expected to approach 1 because transport and mixing will readily remove differences in \( CH_4 \) concentrations between the deepwater zone and the adjacent shallow water zone. Considering the mean \( f_{CH4,sid} \) value from all basins except Rohrsee and forcing the linear regression through \( f_{CH4,sid} = 1 \) at \( A_d = 0 \) (Table 2c) reveals a significant positive relationship between \( f_{CH4,sid} \) and \( A_d \) (\( p \) value <0.005, \( R^2 = 71\% \)).
3.3. Relationship Between CH₄, Morphometry, Chl-α, and Water Temperature

The relationship between the surface water CH₄ concentrations and lake morphometry was assessed using MLM that consider the basin-wide mean CH₄ concentrations at a 1 m water depth (CH₄₁), the morphometric parameters Aₜ and fₐ,s, and the basin-wide mean water temperature at 1 m water depth (T). The application of MLM reveals that ln(CH₄₁) is not correlated with the total surface area Aₜ (p value > 0.5) and that Aₜ could only explain less than 1% of the variance in ln(CH₄₁) (Table 2d and Figure 3a). Including T as an additional independent variable in the model (Table 2d and Figure 3b) increases the explained variance to ~17%. However, this increase in explained variance results from a significant correlation between ln(CH₄₁) and T (p value < 0.02), whereas ln(CH₄₁) and Aₜ remain uncorrelated (p value > 0.2; Table 2d and Figure 3b). In contrast to the morphometric parameter Aₜ, the ratio fₐ,s is significantly correlated with ln(CH₄₁) (p value < 0.01), explaining 38% of the variance in ln(CH₄₁) (Table 2e and Figure 3c). The MLM considering fₐ,s and T as independent variables (Table 2e and Figure 3d) even explains 64% of the variance in ln(CH₄₁) and indicates a significant correlation between ln(CH₄₁) and both of the independent variables fₐ,s and T (p value < 0.01 in both cases; Table 2e and Figure 3d). The coefficient c describing the dependence of ln(CH₄₁) on T is positive (c = 0.1°C⁻¹; Table 2e), suggesting that the average basin-wide surface CH₄ concentrations increase exponentially with the surface water temperature.

The relationship between CH₄ and Chl-α concentrations was investigated with MLM separately considering individual lakes, i.e., Königseggsee, Illmensee, and Mindelsee, and using seasonally resolved and vertically averaged (mean of the top 6 m) data on CH₄ concentrations (CH₄₀–₆ m), Chl-α concentrations (Chl-α₀–₆ m), and water temperatures (T₀–₆ m).

According to the MLM applied to the data from Königseggsee, ln(CH₄₀–₆ m) is significantly correlated with ln(Chl-α₀–₆ m) and with T₀–₆ m (p value ~ 0.05 and p value ~ 0.01, respectively; Table 2f and Figure 4a). The MLM explains ~76% of the variance of ln(CH₄₀–₆ m) (Table 2f). Coefficient b describing the slope of the relationship between ln(CH₄₀–₆ m) and ln(Chl-α₀–₆ m) is negative (b = −0.60; Table 2f), suggesting that the CH₄ concentrations increase with T₀–₆ m but decrease with increasing Chl-α concentrations.

In the case of the data from Illmensee, the MLM also indicate that ln(CH₄₀–₆ m) is significantly correlated with ln(Chl-α₀–₆ m) and with T₀–₆ m (p value = 0.04 and p value < 0.01, respectively; Table 2f and Figure 4b). The MLM explains ~84% of the variance in ln(CH₄₀–₆ m) (Table 2f). However, coefficient b is positive in Illmensee (b = 0.69; Table 2f), suggesting that the CH₄ concentrations increase with increasing Chl-α concentrations, which is the opposite of the results for Königseggsee.

In Mindelsee, ln(CH₄₀–₆ m) is not significantly correlated with ln(Chl-α₀–₆ m) (p value > 0.9; Table 2f and Figure 4c) but is with T (p value ~ 0.05; Table 2f). Temperature explains ~30% of the variance in the ln(CH₄₀–₆ m) time series (Table 2f).
Hence, the MLMs provide three opposing results with respect to the relationship between CH$_4$ and Chl-a concentrations: a significant negative correlation in Königseggsee, a significant positive correlation in Illmensee, and no correlation in Mindelsee.

With respect to the relationship between ln(CH$_4$,0–6m) and T$_{0–6m}$, the MLMs provide consistent results for the three lakes: the coefficient $c$ describing the slope of the relationship between ln(CH$_4$,0–6m) and T$_{0–6m}$ is positive in all the three lakes ($c=0.13^\circ$C$^{-1}$, $c=0.09^\circ$C$^{-1}$, and $c=0.13^\circ$C$^{-1}$, respectively), indicating that the CH$_4$ concentrations increase exponentially with water temperature.

4. Discussion
The CH$_4$ concentration distributions as measured in the surface water of all basins are spatially heterogeneous (Figure 1), supporting the findings of earlier studies [Hofmann, 2013; Blees et al., 2015; Murase et al., 2005] that demonstrated that individual measurements from lakes may result in misleading estimates of mean basin-wide CH$_4$ concentrations and emissions [Hofmann, 2013]. The heterogeneity of the CH$_4$ concentrations in the horizontal distributions increases with increasing CH$_4$,$t$ (Figure 2b). Therefore, spatially resolved measurements are required to reduce uncertainties in the estimate of the mean basin-wide CH$_4$ concentration, especially in lakes with high CH$_4$ concentrations.

The spatial distributions of CH$_4$ concentrations confirm that in all the basins, the average surface CH$_4$ concentrations are higher in the shallow water zone than in the deepwater zone (Table S1). Thus, a fundamental requirement of hypothesis A, i.e., that CH$_4$ from shallow water zones is a major source of the CH$_4$ concentrations in the surface water of the deepwater zone, is fulfilled. The comparatively high CH$_4$ concentrations in the shallow water zones can be explained by the frequent release of CH$_4$-rich pore water during resuspension events (Figure S2) associated with hydrodynamic forcing in shallow waters [Hofmann et al., 2010] and by high anaerobic CH$_4$ production in the sediments due to the comparatively high temperatures at shallow water depths [Murase et al., 2005; Bastviken et al., 2008; Thebrath et al., 1993]. Moreover, since temperature dependence of CH$_4$ production is larger than the one from CH$_4$ oxidation [Dunfield et al., 1993], the input of CH$_4$ from the shallow anoxic sediments and thus from the shallow water zone would be even more pronounced with increasing temperature.

According to hypothesis A, CH$_4$-rich water is transported from the shallow water zone to the deepwater zone and diluted within the deepwater zone. Because vertical mixing across the thermocline is greatly
resolved under stratified conditions (Figures S1 and S2a), the lateral transport of CH4-rich water from shallow water to deepwater zones should lead to elevated near-surface CH4 concentrations in the deepwater zone, thus explaining the methane paradox. The dilution of CH4 in the deepwater zone increases with increasing horizontal extent of the deepwater zone. Therefore, the ratio between the CH4 concentrations in the shallow water and deepwater zones should increase with the surface area of the deepwater zone. This implication of hypothesis A is supported by the significant positive correlation between \( f_{CH4,s,d} \) and \( A_d \) (Table 2c).

According to hypothesis B, the dominant source of CH4 in surface waters of lakes is the in situ production of CH4 within the oxic water column. In situ production in the deepwater zone could explain the methane paradox if the in situ production of CH4 is larger near the lake surface than in deeper layers. However, the observation of significant differences between \( CH4,s \) and \( CH4,d \) cannot be easily explained if hypothesis B is true because near the water surface, the distribution of both, the anoxic microzones and the methanogenic Archaea, is expected to be similar in the shallow water and deepwater zones. Even more difficult to explain is why the ratio \( f_{CH4,s,d} \) increases with \( A_d \) if the CH4 production in the water column is responsible for the CH4 concentrations in the surface water of the deepwater zone.

To support the link between oxic water column methanogenesis and algal dynamics, Bogard et al. [2014] presented a positive correlation between the logarithms of CH4 and Chl-a concentrations. However, the correlation analysis was based on a data set combining measurements from open oceans, several freshwater lakes, and mesocosm experiments. Considering only their data for freshwater lakes, the logarithms of CH4 and Chl-a concentrations are not correlated (\( p \) value > 0.01; \( R^2 = 10\% \) using all the data for freshwater lakes from Bogard et al. [2014]). The data therefore do not provide evidence for the link between in situ production of CH4 and algal dynamics in lakes. Furthermore, a correlation between CH4 and Chl-a concentrations is not conclusive to support such a link because sediment-borne CH4 may also be correlated with Chl-a concentrations, as organic material is the source of anaerobic CH4 production in the sediments. However, in contrast to CH4 production in sediments, methanogenesis in oxic waters linked to algal dynamics should depend not only on the annual mean concentrations of Chl-a but also on the seasonal changes in Chl-a, e.g., increases during spring bloom development and decreases thereafter during the clear water phase. However, our seasonally resolved data from three lakes do not show a consistent relationship between CH4 and Chl-a concentrations (Figure 4 and Table 2f).

The above discussion indicates that our data are consistent with hypothesis A but are comparatively difficult to explain with hypothesis B and do not provide evidence for in situ CH4 production in oxic waters linked to algal dynamics in lakes. Hypothesis A assumes that the shallow water zone is a major source of CH4 in lakes and consequently implies that basin-wide mean surface CH4 concentrations do not necessarily depend on the surface area of the lake but rather on the relative contribution of the surface area of the shallow water zone to the surface area of the entire lake. This implication of hypothesis A is confirmed by our results from MLM. The MLMs indicate that the logarithm of \( CH4,t \) is not correlated with \( A_d \) but with the aspect ratio \( f_{A,s/d} \), thus further indicating that the shallow water zones contribute a major fraction of the overall CH4 concentrations in lakes.

The flux of CH4 to the atmosphere depends on the gas exchange velocity \( k \), the atmospheric equilibrium concentration of CH4 at the surface water’s temperature and salinity (\( CH4,eq \)), and the surface water concentration of CH4. Distinguishing between shallow water and deepwater zones suggests that the average CH4 flux is given by \( F_{CH4} = k_s \cdot A_s \cdot (CH4,s - CH4,eq) + k_d \cdot A_d \cdot (CH4,d - CH4,eq)/A_w \), where \( k_s \) and \( k_d \) are the gas exchange velocities in the shallow water and deepwater zones, respectively. Assuming that \( k_s \) and \( k_d \) are approximately the same and using \( CH4,s \approx CH4,t \) (Table 2a), \( F_{CH4} = k_t (CH4,t - CH4,eq) \). Thus, the conclusion that \( f_{A,s/d} \), rather than \( A_d \), is a better predictor of \( CH4,t \) also applies to the average basin-wide diffusive flux of CH4 into the atmosphere. Note that not only CH4 concentrations but also ebullition fluxes are elevated in the shallow water zone [Bastviken et al., 2004]. In shallow sediments, the oversaturation required for the development of gas bubbles is less than in deep sediments because of the differences in hydrostatic pressure. Furthermore, the high temperatures in shallow water zones support a higher production of CH4. Thus, ebullition may also be related to \( f_{A,s/d} \) and the estimates of lake-wide CH4 fluxes due to diffusion and ebullition may benefit from a categorization according to the aspect ratio \( f_{A,s/d} \) rather than using \( A_d \), as is commonly done in estimations of global emissions from lakes [Bastviken et al., 2004; Bastviken et al., 2011].
Our data indicate a significant correlation between CH₄ concentrations and water temperature, consistent with Marotta et al. (2014) and Yvon-Durocher et al. (2014). Neglecting temperature compilations in CH₄ data sets and their statistical analysis [e.g., Bogard et al., 2014] may lead to unreliable conclusions. The application of MLM to the surface data from several basins and to the seasonal data from individual lakes suggests that CH₄ concentrations increase exponentially with T at a rate of 0.09–0.13°C⁻¹. This increase implies that an increase of T from 4 to 20°C would change the CH₄ concentrations by a factor of 4 to 8. Undersampling in the cold winter season and averaging the available data on CH₄ emissions may therefore lead to an overestimation of the annual mean CH₄ emission.

5. Conclusion

In summary, the correlation analysis of CH₄ and Chl-α does not provide evidence for methanogenesis in oxic water columns linked to algal production in lakes, indicating that this process is not as important for lacustrine CH₄ emissions as recently suggested [Bogard et al., 2014]. CH₄ from shallow water zones in lakes is an important source of CH₄ concentrations in the surface water of deepwater zones [Hofmann, 2013; Bastviken et al., 2004; Murase et al., 2005]. Consistent with this finding, the ratio of the surface area of shallow water zones to the overall surface area is a better predictor of basin-wide CH₄ concentrations than the total surface area itself. CH₄ concentrations increase exponentially with water temperature, which implies that compilations of CH₄ data in large data sets and their statistical analysis must consider water temperature in order to provide meaningful results.

Our data indicate that global estimates of CH₄ emissions from lakes require seasonally and spatially resolved CH₄ data and that methanogenesis in oxic water columns is not linked to algal growth. Furthermore, the CH₄ generated in shallow water zones is a major source of basin-wide diffusive CH₄ emissions from lakes. Statistical analyses of our data consistently suggest that a categorization of CH₄ fluxes according to the ratio between the surface area of the shallow water zone and the total surface area may help to improve global estimates of CH₄ emissions from lakes.

References

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