

RESEARCH ARTICLE

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Key Points:

- Shallow water zones are the most likely source of the basin-wide mean CH<sub>4</sub> concentrations in the surface water of lakes
- The categorization of CH<sub>4</sub> fluxes according to the fraction of shallow water zones may improve global estimates of CH<sub>4</sub> emissions from lakes

Supporting Information:

- Supporting Information S1

Correspondence to:

J. Encinas Fernández,  
[jorge.encinas@uni-konstanz.de](mailto:jorge.encinas@uni-konstanz.de)

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## On the methane paradox: Transport from shallow water zones rather than in situ methanogenesis is the major source of CH<sub>4</sub> in the open surface water of lakes

Jorge Encinas Fernández<sup>1</sup>, Frank Peeters<sup>1</sup>, and Hilmar Hofmann<sup>1</sup>

<sup>1</sup>Environmental Physics, Limnological Institute, University of Konstanz, Konstanz, Germany

**Abstract** Estimates of global methane (CH<sub>4</sub>) 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 CH<sub>4</sub> fluxes from aquatic systems. However, based on our very large data set on CH<sub>4</sub> distributions within lakes, we demonstrate here that methane-enriched water from shallow water zones is the most likely source of the basin-wide mean CH<sub>4</sub> concentrations in the surface water of lakes. Consistently, the mean surface CH<sub>4</sub> concentrations are significantly correlated with the ratio between the surface area of the shallow water zone and the entire lake,  $f_{A,s/t}$ , but not with the total surface area. The categorization of CH<sub>4</sub> fluxes according to  $f_{A,s/t}$  may therefore improve global estimates of CH<sub>4</sub> emissions from lakes. Furthermore, CH<sub>4</sub> concentrations increase substantially with water temperature, indicating that seasonally resolved data are required to accurately estimate annual CH<sub>4</sub> emissions.

### 1. Introduction

Lakes are considered to be major natural sources of methane (CH<sub>4</sub>), contributing a large fraction of the global CH<sub>4</sub> emissions to the atmosphere [Michmerhuizen and Striegl, 1996; Luysaert et al., 2012; Bastviken et al., 2011]. However, the quantification of the global CH<sub>4</sub> emissions from lakes and the controls and contributions of the different CH<sub>4</sub> 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; Brees et al., 2015; Encinas Fernández et al., 2014].

Global emissions of CH<sub>4</sub> are typically estimated by categorizing CH<sub>4</sub> emissions per unit surface area according to lake size and multiplying these areal CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> emissions are complicated by the large spatial heterogeneity of CH<sub>4</sub> emissions [Hofmann, 2013; Brees et al., 2015; Murase et al., 2005] and the multiple pathways and sources that can contribute to CH<sub>4</sub> 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; DelSontro et al., 2011; Carmichael et al., 2014; Carini et al., 2014].

CH<sub>4</sub> in lakes mainly originates from anaerobic carbon mineralization in anoxic sediments [Segers, 1998]. Most of the CH<sub>4</sub> produced in anoxic sediments is oxidized by methanotrophic bacteria at anoxic-oxic interfaces [Conrad, 2009; Bastviken et al., 2002; Utsumi et al., 1998a; Utsumi et al., 1998b]. Observations from several lakes show that in the oxic epilimnion, CH<sub>4</sub> concentrations are typically oversaturated and higher than in the oxic hypolimnion [Luysaert et al., 2012; Bogard et al., 2014; Brees et al., 2015; Schulz et al., 2001]. This phenomenon, called the “methane paradox” [Reeburgh, 2007], has been taken as an indication of the in situ production of CH<sub>4</sub> in oxic waters [Bogard et al., 2014; Schulz et al., 2001]. Anoxic microzones were proposed as sites of in situ CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> and Chl-*a* concentrations across diverse open-water aquatic ecosystems was presented as support of this hypothesis [Bogard et al., 2014]. The possible metabolic pathways for CH<sub>4</sub> production in oxic waters and field evidence of oxic methane production have recently been

**Table 1.** Morphometric Properties of the Investigated Lakes and Lake Basins

Lake	Total Area $A_t$ (km <sup>2</sup> )	Shallow Area $A_s$ (km <sup>2</sup> )	Deep Area $A_d$ (km <sup>2</sup> )	Ratio of Areas $f_{A_s/t}$ (%)	Maximum Depth $D_{max}$ (m)
Königseggsee	0.16	0.06	0.10	36	9.6
Rohrsee	0.55	0.55	0	100	2
Illmensee	0.64	0.16	0.49	24	16.5
Mindelsee	1.05	0.29	0.76	28	13.5
Lower Lake Constance northern basin	13.44	6.18	7.26	46	21.34
Lower Lake Constance central basin	16.92	6.13	10.79	36	23.6
Lower Lake Constance southern basin	31.46	12.56	18.9	40	42.64
Lake Ammer	45.99	6.91	39.08	15	81
Upper Lake Constance	64.69	6.00	58.68	9	175

reviewed by Tang *et al.* [2016]. These authors conclude that oxic methane production may be an important source of CH<sub>4</sub> 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 CH<sub>4</sub> budget in a small, shallow lake” and “this pathway (oxic water methanogenesis) may be the main CH<sub>4</sub> source in large, deep lakes ...”

However, elevated CH<sub>4</sub> concentrations in oxic surface waters of the pelagic zone do not necessarily originate from the in situ production of CH<sub>4</sub> but could alternatively be explained by the lateral transport of CH<sub>4</sub> from littoral zones [Hofmann, 2013; Bastviken *et al.*, 2004; Rudd and Hamilton, 1978; Murase *et al.*, 2003]. CH<sub>4</sub> concentrations in the littoral zone (here, the shallow water zone) can be expected to be particularly high because the production rate of CH<sub>4</sub> 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, CH<sub>4</sub>-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 CH<sub>4</sub> distributions within lakes to test whether CH<sub>4</sub> from shallow water zones (hypothesis A) or the in situ production of CH<sub>4</sub> in oxic surface water, i.e., production within the anoxic micro-zones and production due to methanogenic bacteria (hypothesis B), is the more likely explanation for the methane paradox. If CH<sub>4</sub> from the shallow water zone is the major source of the CH<sub>4</sub> in the surface water of the deepwater zone, (a) CH<sub>4</sub> concentrations in the shallow water zone must be higher than in the deepwater zone and (b) the ratio of CH<sub>4</sub> from the shallow water zone to CH<sub>4</sub> from the deepwater zone,  $f_{CH_4,s/d}$ , should increase with increasing surface area of the deepwater zone because CH<sub>4</sub> introduced from the shallow water zone is more strongly diluted in a larger deepwater zone. In contrast, if the dominant source of CH<sub>4</sub> in the surface water is in situ production, one does not necessarily expect significant differences between CH<sub>4</sub> in shallow water and deepwater zones, and an increase in the ratio  $f_{CH_4,s/d}$  with increasing surface area of the deepwater zone cannot be easily explained. If the in situ production of CH<sub>4</sub> is linked to Chl-*a* [Bogard *et al.*, 2014], CH<sub>4</sub> 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 CH<sub>4</sub> and the CH<sub>4</sub> 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 km<sup>2</sup>, 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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-*a* 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 CH<sub>4</sub> 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 ≥6 m). The ratio between the surface area of the shallow water zone ( $A_s$ ) and the total surface area of the lake,  $A_t$ , is the aspect ratio defined as  $f_{A,s/t} = A_s/A_t$ . The surface water CH<sub>4</sub> concentrations in the shallow water zone ( $CH_{4,s}$ ), deepwater zone ( $CH_{4,d}$ ), and entire lake ( $CH_{4,t}$ ) were determined for each individual horizontal survey by averaging all of the measurements available for the respective zone. Furthermore, an additional estimator of the basin-wide mean CH<sub>4</sub> concentration ( $CH_{4,w}$ ) was determined using a surface-area weighted average of CH<sub>4</sub> from shallow water and deepwater zones:  $CH_{4,w} = (A_s \cdot CH_{4,s} + A_d \cdot CH_{4,d})/A_t$ , where  $A_d$  is the surface area of the deepwater zone. The variance of all the CH<sub>4</sub> concentrations measured during an individual horizontal survey ( $V_{CH_4}$ ) is taken as a measure of the horizontal heterogeneity of CH<sub>4</sub>.

Linear regression and *t* tests were used to investigate the relationship between morphometric properties and  $CH_{4,t}$  as well as the ratio  $f_{CH_{4,s/d}} = CH_{4,s}/CH_{4,d}$  measured during different campaigns and in different basins.

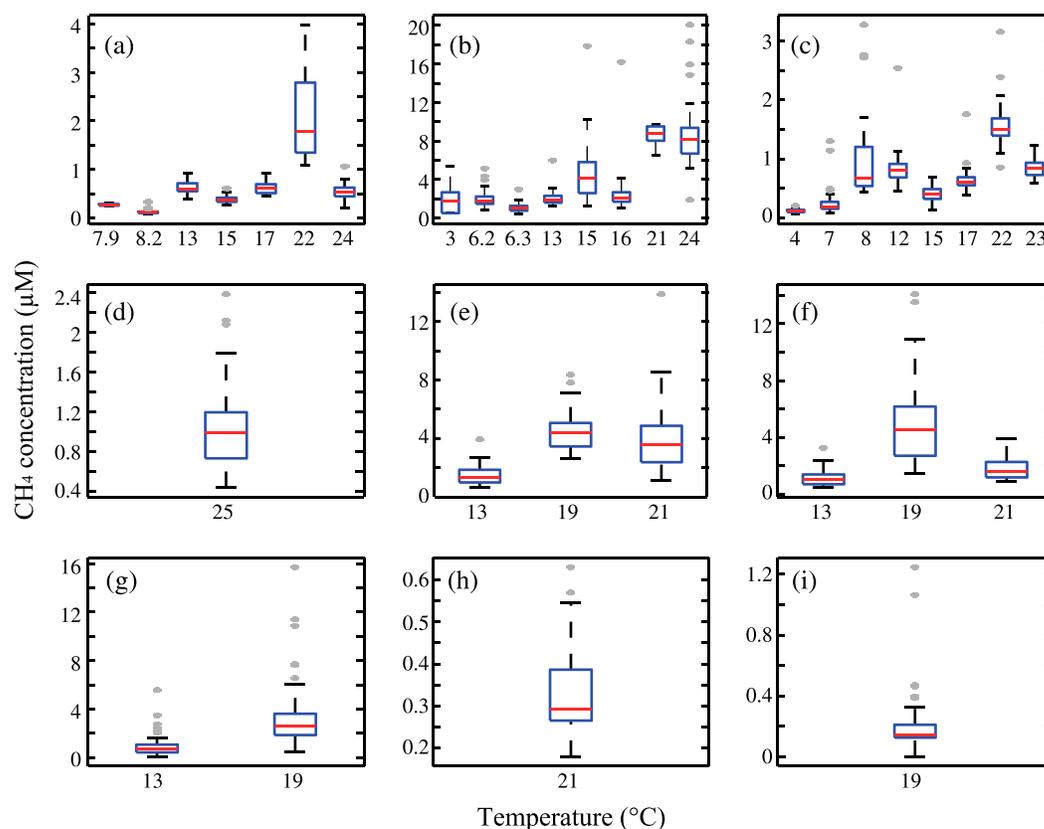
Multiple linear models (MLMs) were applied to assess the relationships between the basin-wide mean surface CH<sub>4</sub> concentration ( $CH_{4,t}$ ) as a dependent variable and the total surface area of the lake ( $A_t$ ), the aspect ratio ( $f_{A,s/t}$ ), and the water temperature at a water depth of 1 m (*T*) as independent variables. Additionally, MLMs were used to investigate the relationship between the seasonal development of CH<sub>4</sub> concentrations, temperature, and Chl-*a* 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 CH<sub>4</sub> and Chl-*a* 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> concentrations ranged between ~0.06 and ~3.9 μM (Figures 1a, 1b, and 1d). In the similarly sized but very shallow Rohrsee, the CH<sub>4</sub> 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 CH<sub>4</sub> concentrations were lower than those in Rohrsee and ranged between 0.5 and 16 μM (Figures 1e–1h). The lowest CH<sub>4</sub> concentrations (median 0.14 μM) and the lowest horizontal heterogeneity in the CH<sub>4</sub> concentrations ( $V_{CH_4} < 0.05 \mu M^2$ ) of all basins were measured in ULC (Figure 1i), the largest and deepest basin with the smallest  $f_{A,s/t}$ . In the basins in which



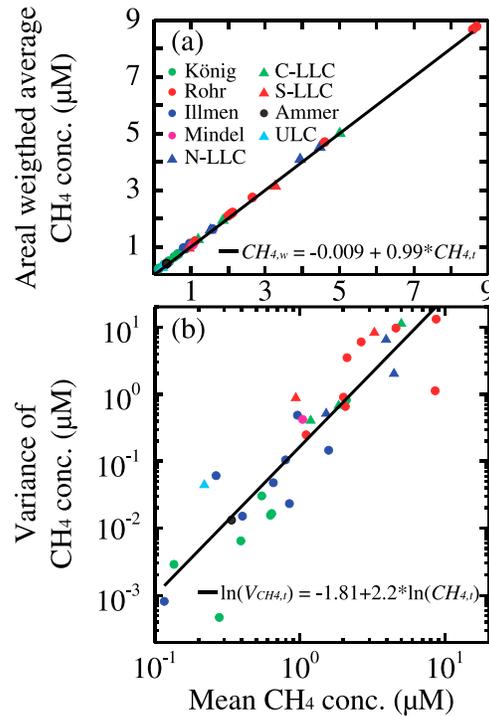
**Figure 1.** Properties of the horizontal distributions of CH<sub>4</sub> concentrations in different basins and seasons. Box plots of the CH<sub>4</sub> concentrations (µM) measured at 1 m water depth in (a) Königseggsee, (b) Rohrsee, (c) Illmensee, (d) Mindelsee, (e) Lower Lake Constance (northern 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 CH<sub>4</sub> 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.

several surveys were conducted at different temperatures, the greatest variability and the highest median CH<sub>4</sub> 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 CH<sub>4</sub> concentrations in Illmensee, which peaked in late fall ( $V_{CH_4} \sim 0.48 \mu M^2$ ) during overturn (Figure 1b).

### 3.2. CH<sub>4</sub> Concentrations in the Shallow Water and Deepwater Zones of the Different Basins

The CH<sub>4</sub> 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 CH<sub>4</sub> concentrations to obtain  $CH_{4,sr}$ ,  $CH_{4,dr}$ ,  $CH_{4,tr}$  and  $CH_{4,wr}$ . The two different estimates of the mean basin-wide methane concentrations,  $CH_{4,t}$  and  $CH_{4,w}$  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 CH<sub>4</sub> concentrations provide the same results regardless of whether they use  $CH_{4,t}$  or  $CH_{4,w}$ . The excellent agreement between  $CH_{4,t}$  and  $CH_{4,w}$  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 CH<sub>4</sub> concentration increases with the lake-wide average CH<sub>4</sub> concentration; i.e.,  $\log(V_{CH_4})$  and  $\log(CH_{4,t})$  are positively correlated ( $p$  value < 0.001,  $R^2 = 80\%$ ). According to the regression model,  $V_{CH_4}$  increases



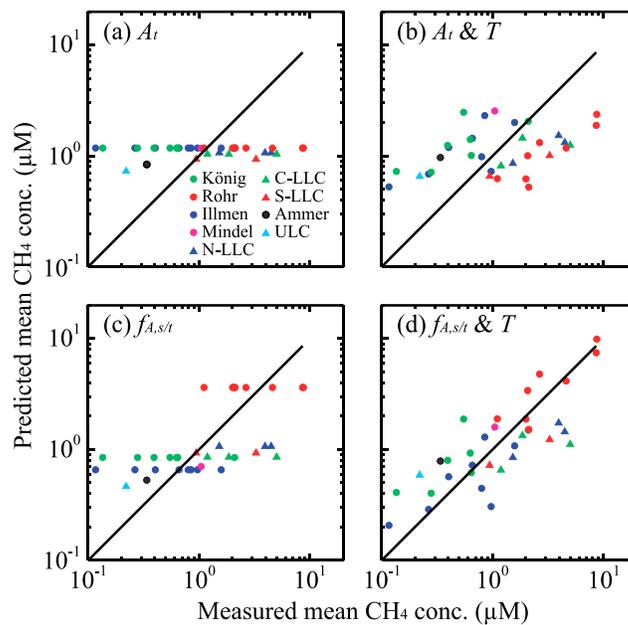
**Figure 2.** Relationship between the basin-wide mean CH<sub>4</sub> concentration and two different variables. (a) Basin-wide areal weighted average CH<sub>4</sub> concentration ( $CH_{4,w}$ ) versus basin-wide mean CH<sub>4</sub> concentration ( $CH_{4,t}$ ). The line represents the linear model considering 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 ( $V_{CH_4}$ ) versus the basin-wide mean CH<sub>4</sub> concentration ( $CH_{4,t}$ ). The line represents the results from the application of a linear model with  $V_{CH_4}$  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<sub>4</sub> concentrations measured during individual surveys ( $\sqrt{V_{CH_4}}$ ) 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  $f_{CH_4,s/d}$  is on average larger than 1, suggesting that the mean CH<sub>4</sub> concentration in the shallow water zone is typically larger than the mean CH<sub>4</sub> concentration in the deepwater zone. The values of  $f_{CH_4,s/d}$  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 Königsegsee, Illmensee, and Mindelsee, respectively. Larger values of  $f_{CH_4,s/d}$  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  $f_{CH_4,s/d} = 3.18$  of all the lakes. According to a *t* test, the mean  $f_{CH_4,s/d}$  for the different basins is significantly larger than 1 (*p* value < 0.05). Furthermore, the mean  $f_{CH_4,s/d}$  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.,  $A_d \rightarrow 0$ ,  $f_{CH_4,s/d}$  is expected to approach 1 because transport and mixing will readily remove differences in CH<sub>4</sub> concentrations between the deepwater zone and the adjacent shallow water zone. Considering the mean  $f_{CH_4,s/d}$  value from all basins except Rohrsee and forcing the linear regression through  $f_{CH_4,s/d} = 1$  at  $A_d = 0$  (Table 2c) reveals a significant positive relationship between  $f_{CH_4,s/d}$  and  $A_d$  (*p* value < 0.005,  $R^2 = 71\%$ ).

**Table 2.** Assessment of the Relationship Between CH<sub>4</sub> Concentrations and Lake Morphology, Temperature, and Chl-*a* Concentrations

Linear Models							
	<i>a</i> (μM)	<i>b</i>	<i>p</i> Value	<i>R</i> <sup>2</sup> (%)	NRMSE (%)		
(a) $CH_{4,w} = a + b \cdot CH_{4,t}$	-0.009	0.999	<0.001	100	0.5		
(b) $V_{CH_4} = a + b \cdot CH_{4,t}$	-1.80	2.22	<0.001	80.9	11.99		
(c) $f_{CH_4,s/d} = a + b \cdot A_d$	1	$3.03 \times 10^{-8}$	<0.01	71.0	19.21		
MLM considering $CH_{4,t}$ , $A_t$ , $f_{A,s/t}$ and <i>T</i>							
	<i>a</i>	<i>b</i> (m <sup>-2</sup> )	<i>c</i> (°C <sup>-1</sup> )	<i>p</i> value for $A_t$ or $f_{A,s/t}$	<i>p</i> value for <i>T</i>	<i>R</i> <sup>2</sup> (%)	NRMSE (%)
(d1) $\ln(CH_{4,t}) = a + b \cdot A_t$	0.17	$-7.47 \times 10^{-9}$		0.57		0.01	26.26
(d2) $\ln(CH_{4,t}) = a + b \cdot A_t + c \cdot T$	-0.94	$-1.49 \times 10^{-8}$	0.08	0.24	0.02	17.4	24.37
(e1) $\ln(CH_{4,t}) = a + b \cdot f_{A,s/t}$	-0.99	2.27		<0.01		38.1	20.77
(e2) $\ln(CH_{4,t}) = a + b \cdot f_{A,s/t} + c \cdot T$	-2.61	2.66	0.1	<0.01	<0.01	63.7	16.16
MLM applied to seasonal data of $CH_{4,0-6m}$ , $Chl-a_{0-6m}$ and $T_{0-6m}$							
(f) $\ln(CH_{4,0-6m}) = a + b \cdot \ln(Chl-a_{0-6m}) + c \cdot T_{0-6m}$	<i>a</i>	<i>b</i> (-)	<i>c</i> (°C <sup>-1</sup> )	<i>p</i> value for $Chl-a_{0-6m}$	<i>p</i> value for $T_{0-6m}$	<i>R</i> <sup>2</sup> (%)	NRMSE (%)
Königsegsee	-1	-0.6	0.13	0.05	<0.01	76.1	18.15
Illmensee	-3.14	0.7	0.09	0.04	<0.01	83.7	13.38
Mindelsee	-2.9	-0.05	0.13	0.91	0.05	29.4	21.62



**Figure 3.** Comparison of measured basin-wide mean CH<sub>4</sub> concentrations with results from MLM using morphometric parameters and temperature as independent variables. The different plots depict the results from MLM considering the logarithm of CH<sub>4,t</sub> (μM) from the different basins as a dependent variable and (a) A<sub>t</sub>, (b) A<sub>t</sub> and T, (c) f<sub>A,s/t</sub> and (d) f<sub>A,s/t</sub> and T as independent variables. The coefficients and the performance of the different MLM are provided in Tables 2d and 2e.

Figure 3b). In contrast to the morphometric parameter A<sub>t</sub>, the ratio f<sub>A,s/t</sub> is significantly correlated with ln(CH<sub>4,t</sub>) (p value <0.01), explaining 38% of the variance in ln(CH<sub>4,t</sub>) (Table 2e1 and Figure 3c). The MLM considering f<sub>A,s/t</sub> and T as independent variables (Table 2e2 and Figure 3d) even explains 64% of the variance in ln(CH<sub>4,t</sub>) and indicates a significant correlation between ln(CH<sub>4,t</sub>) and both of the independent variables f<sub>A,s/t</sub> and T (p value <0.01 in both cases; Table 2e2 and Figure 3d). The coefficient c describing the dependence of ln(CH<sub>4,t</sub>) on T is positive (c = 0.1°C<sup>-1</sup>; Table 2e2), suggesting that the average basin-wide surface CH<sub>4</sub> concentrations increase exponentially with the surface water temperature.

The relationship between CH<sub>4</sub> and Chl-a concentrations was investigated with MLM separately considering individual lakes, i.e., Königseggeesee, Illmensee, and Mindelsee, and using seasonally resolved and vertically averaged (mean of the top 6 m) data on CH<sub>4</sub> concentrations (CH<sub>4,0-6 m</sub>), Chl-a concentrations (Chl-a<sub>0-6 m</sub>), and water temperatures (T<sub>0-6 m</sub>).

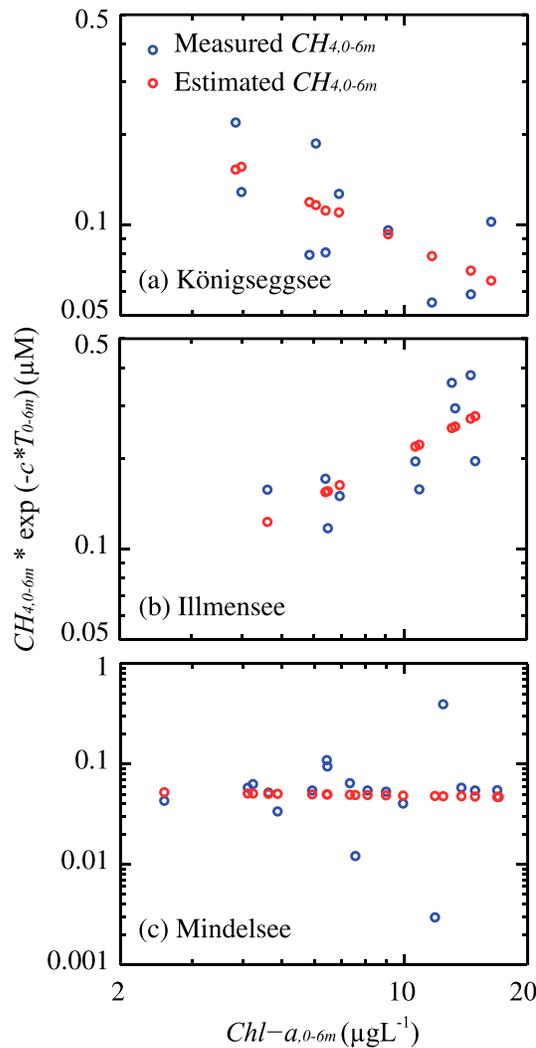
According to the MLM applied to the data from Königseggeesee, ln(CH<sub>4,0-6 m</sub>) is significantly correlated with ln(Chl-a<sub>0-6 m</sub>) and with T<sub>0-6 m</sub> (p value ~0.05 and p value <0.01, respectively; Table 2f and Figure 4a). The MLM explains ~76% of the variance of ln(CH<sub>4,0-6 m</sub>) (Table 2f). Coefficient b describing the slope of the relationship between ln(CH<sub>4,0-6 m</sub>) and ln(Chl-a<sub>0-6 m</sub>) is negative (b = -0.60; Table 2f), suggesting that the CH<sub>4</sub> concentrations increase with T<sub>0-6 m</sub> but decrease with increasing Chl-a concentrations.

In the case of the data from Illmensee, the MLM also indicate that ln(CH<sub>4,0-6 m</sub>) is significantly correlated with ln(Chl-a<sub>0-6 m</sub>) and with T<sub>0-6 m</sub> (p value = 0.04 and p value <0.01, respectively; Table 2f and Figure 4b). The MLM explains ~84% of the variance in ln(CH<sub>4,0-6 m</sub>); Table 2f). However, coefficient b is positive in Illmensee (b = 0.69; Table 2f), suggesting that the CH<sub>4</sub> concentrations increase with increasing Chl-a concentrations, which is the opposite of the results for Königseggeesee.

In Mindelsee, ln(CH<sub>4,0-6 m</sub>) is not significantly correlated with ln(Chl-a<sub>0-6 m</sub>) (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(CH<sub>4,0-6 m</sub>) time series (Table 2f).

### 3.3. Relationship Between CH<sub>4</sub>, Morphometry, Chl-a, and Water Temperature

The relationship between the surface water CH<sub>4</sub> concentrations and lake morphometry was assessed using MLM that consider the basin-wide mean CH<sub>4</sub> concentrations at a 1 m water depth (CH<sub>4,t</sub>), the morphometric parameters A<sub>t</sub> and f<sub>A,s/t</sub> and the basin-wide mean water temperature at 1 m water depth (T). The application of MLM reveals that ln(CH<sub>4,t</sub>) is not correlated with the total surface area A<sub>t</sub> (p value >0.5) and that A<sub>t</sub> could only explain less than 1% of the variance in ln(CH<sub>4,t</sub>) (Table 2d1 and Figure 3a). Including T as an additional independent variable in the model (Table 2d2 and Figure 3b) increases the explained variance to ~17%. However, this increase in explained variance results from a significant correlation between ln(CH<sub>4,t</sub>) and T (p value <0.02), whereas ln(CH<sub>4,t</sub>) and A<sub>t</sub> remain uncorrelated (p value >0.2; Table 2d2 and



**Figure 4.** Illustration of the relationship between  $CH_{4,0-6m}$  and  $Chl-a_{0-6m}$ . This figure compares  $CH_4$  concentrations normalized for temperature effects ( $CH_{4,0-6m} e^{-cT_{0-6m}}$ ) with  $Chl-a_{0-6m}$  concentrations measured in 2 years during the stratified period (March to October) in (a) Königseggsee, (b) Illmensee, and (c) Mindelsee. Normalized  $CH_4$  concentrations were calculated from measured  $CH_{4,0-6m}$  concentrations (blue circles) and from  $CH_4$  concentrations estimated (red circles) from the results of a MLM considering the logarithm of measured  $CH_{4,0-6m}$  as a dependent variable and the logarithm of  $Chl-a_{0-6m}$  and  $T_{0-6m}$  as independent variables (Table 2f). The temperature normalization was based on the relationship between  $\ln(CH_{4,0-6m})$  and  $T_{0-6m}$  obtained from this MLM (coefficient  $c$ ; Table 2f).

(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

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; Bles 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  $CH_4$  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

reduced under stratified conditions (Figures S1 and S2a), the lateral transport of CH<sub>4</sub>-rich water from shallow water to deepwater zones should lead to elevated near-surface CH<sub>4</sub> concentrations in the deepwater zone, thus explaining the methane paradox. The dilution of CH<sub>4</sub> in the deepwater zone increases with increasing horizontal extent of the deepwater zone. Therefore, the ratio between the CH<sub>4</sub> 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  $f_{CH_4,s/d}$  and  $A_d$  (Table 2c).

According to hypothesis B, the dominant source of CH<sub>4</sub> in surface waters of lakes is the in situ production of CH<sub>4</sub> within the oxic water column. In situ production in the deepwater zone could explain the methane paradox if the in situ production of CH<sub>4</sub> is larger near the lake surface than in deeper layers. However, the observation of significant differences between  $CH_{4,s}$  and  $CH_{4,d}$  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  $f_{CH_4,s/d}$  increases with  $A_d$  if the CH<sub>4</sub> production in the water column is responsible for the CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 oxic in situ production of CH<sub>4</sub> and algal dynamics in lakes. Furthermore, a correlation between CH<sub>4</sub> and Chl-*a* concentrations is not conclusive to support such a link because sediment-borne CH<sub>4</sub> may also be correlated with Chl-*a* concentrations, as organic material is the source of anaerobic CH<sub>4</sub> production in the sediments. However, in contrast to CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> production in oxic waters linked to algal dynamics in lakes. Hypothesis A assumes that the shallow water zone is a major source of CH<sub>4</sub> in lakes and consequently implies that basin-wide mean surface CH<sub>4</sub> 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  $CH_{4,t}$  is not correlated with  $A_t$  but with the aspect ratio  $f_{A,s/t}$ , thus further indicating that the shallow water zones contribute a major fraction of the overall CH<sub>4</sub> concentrations in lakes.

The flux of CH<sub>4</sub> to the atmosphere depends on the gas exchange velocity  $k$ , the atmospheric equilibrium concentration of CH<sub>4</sub> at the surface water's temperature and salinity ( $CH_{4,eq}$ ), and the surface water concentration of CH<sub>4</sub>. Distinguishing between shallow water and deepwater zones suggests that the average CH<sub>4</sub> flux is given by  $F_{CH_4} = (k_s A_s \cdot (CH_{4,s} - CH_{4,eq}) + k_d A_d \cdot (CH_{4,d} - CH_{4,eq})) / A_t$ , 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  $CH_{4,w} \approx CH_{4,t}$  (Table 2a),  $F_{CH_4} = k_s (CH_{4,t} - CH_{4,eq})$ . Thus, the conclusion that  $f_{A,s/t}$  rather than  $A_t$  is a better predictor of  $CH_{4,t}$  also applies to the average basin-wide diffusive flux of CH<sub>4</sub> into the atmosphere. Note that not only CH<sub>4</sub> 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 CH<sub>4</sub>. Thus, ebullition may also be related to  $f_{A,s/t}$  and the estimates of lake-wide CH<sub>4</sub> fluxes due to diffusion and ebullition may benefit from a categorization according to the aspect ratio  $f_{A,s/t}$  rather than using  $A_t$ , 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 CH<sub>4</sub> concentrations and water temperature, consistent with Marotta *et al.* [2014] and Yvon-Durocher *et al.* [2014]. Neglecting temperature compilations in CH<sub>4</sub> 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 CH<sub>4</sub> concentrations increase exponentially with *T* at a rate of 0.09–0.13°C<sup>-1</sup>. This increase implies that an increase of *T* from 4 to 20°C would change the CH<sub>4</sub> concentrations by a factor of 4 to 8. Undersampling in the cold winter season and averaging the available data on CH<sub>4</sub> emissions may therefore lead to an overestimation of the annual mean CH<sub>4</sub> emission.

## 5. Conclusion

In summary, the correlation analysis of CH<sub>4</sub> and Chl-*a* 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 CH<sub>4</sub> emissions as recently suggested [Bogard *et al.*, 2014]. CH<sub>4</sub> from shallow water zones in lakes is an important source of CH<sub>4</sub> 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 CH<sub>4</sub> concentrations than the total surface area itself. CH<sub>4</sub> concentrations increase exponentially with water temperature, which implies that compilations of CH<sub>4</sub> 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 CH<sub>4</sub> emissions from lakes require seasonally and spatially resolved CH<sub>4</sub> data and that methanogenesis in oxic water columns is not linked to algal growth. Furthermore, the CH<sub>4</sub> generated in shallow water zones is a major source of basin-wide diffusive CH<sub>4</sub> emissions from lakes. Statistical analyses of our data consistently suggest that a categorization of CH<sub>4</sub> 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 CH<sub>4</sub> emissions from lakes.

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