

Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate

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Received 12 February 2004; revised 12 August 2004; accepted 9 September 2004; published 20 October 2004.

[1] Lake sediments are “hot spots” of methane production in the landscape. However, regional and global lake methane emissions, contributing to the greenhouse effect, are poorly known. We developed predictions of methane emissions from easily measured lake characteristics based on measurements for 11 North American and 13 Swedish lakes, and literature values from 49 lakes. Results suggest that open water methane emission can be predicted from variables such as lake area, water depth, concentrations of total phosphorus, dissolved organic carbon, and methane, and the anoxic lake volume fraction. Using these relations, we provide regional estimates from lakes in Sweden and the upper midwest of the United States. Considering both open water and plant-mediated fluxes, we estimate global emissions as 8–48 Tg CH₄ yr⁻¹ (6–16% of total natural methane emissions and greater than oceanic emission), indicating that lakes should be included as a significant source in global methane budgets. **INDEX TERMS:** 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4806 Oceanography: Biological and Chemical: Carbon cycling; 4810 Oceanography: Biological and Chemical: Corrosion; 4845 Oceanography: Biological and Chemical: Nutrients and nutrient cycling; **KEYWORDS:** methane emission, lakes, greenhouse gases, ebullition, regional, global

Citation: Bastviken, D., J. Cole, M. Pace, and L. Tranvik (2004), Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate, *Global Biogeochem. Cycles*, 18, GB4009, doi:10.1029/2004GB002238.

1. Introduction

[2] Methane is an important radiative trace gas, accounting for about 20% of the green house effect [Cicerone and Oremland, 1988; Wuebbles and Hayhoe, 2002]. Inland waters are thought to be important sources of methane, but documentation of emissions from these sources has been limited. Nevertheless, *St. Louis et al.* [2000] estimate that 7% of anthropogenic global warming equivalents comes from methane emitted from man-made reservoirs alone. Estimating emissions from lakes and reservoirs is difficult, since there are at least four emission pathways which may be regulated differently: ebullition flux, diffusive flux, storage flux, and flux through aquatic vegetation. Present evidence from lakes suggests that the majority of methane production occurs in anoxic sediment [Bartlett *et al.*, 1988; Rudd and Hamilton, 1978]. Methane can be exported from the sediment either by ebullition or by diffusion (Figure 1). Ebullition results in direct flux of methane from the sedi-

ment to the atmosphere, with limited impact of methane oxidation in the water column. Hence the ebullition flux component should be related primarily to the net methane production rate in the sediments (i.e., the gross methane production rate minus potential methane oxidation) and the hydrostatic pressure which has to be overcome for the bubbles to leave the sediment [Fendinger *et al.*, 1992; Mattson and Likens, 1990].

[3] As a result of the diffusive export from anoxic sediment, methane eventually enters the water column. As soon as the methane reaches oxic sediment or water, a large proportion is likely oxidized by methane-oxidizing bacteria [Bastviken *et al.*, 2002]. Most of the methane that escapes oxidation and reaches the upper mixed layer of the water column will be emitted by diffusive flux. This flux component depends on the difference in methane concentration between the water and the atmosphere, and on the physical rate of exchange between the air and water, usually expressed as a piston velocity [Stumm and Morgan, 1996]. The piston velocity is the result of turbulence and therefore depends on the wind speed, while the methane concentration in the surface water is a function of methane

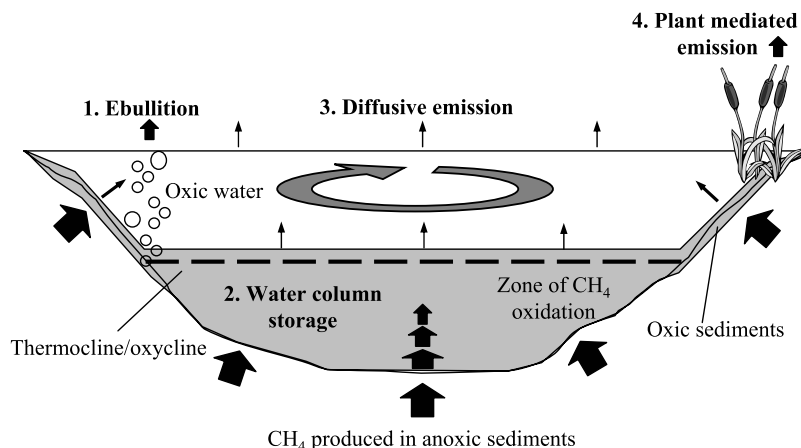


Figure 1. Illustration of emission pathways and methane dynamics in stratified lake. See text for details.

production, methane oxidation, rates and pattern of methane fluxes within the lake, and the piston velocity since it affects the rate of methane removal from the water.

[4] For stratified lakes, there can be a buildup of methane in the anoxic layer, resulting in methane storage in the water column. This storage will be emitted rapidly by diffusion during periods of lake overturn, for example, during spring and fall in dimictic temperate lakes [Michmerhuizen *et al.*, 1996; Riera *et al.*, 1999]. The “storage flux” component is likely a function of methane production rates, the volume of the anoxic water layer, and the losses by methane oxidation and diffusion to upper layers.

[5] The fourth potential flux component includes plant-mediated emission in littoral zones with emergent vegetation. This flux component depends on methane production and oxidation in the sediments, and vegetation characteristics, and has been extensively studied in wetlands [e.g., Segers, 1998].

[6] Most previous estimates of methane emissions from individual lakes include only one or two of these flux components, and the few current global estimates include only ebullition [Ehalt, 1974], or ebullition, diffusive flux and plant mediated emission [Smith and Lewis, 1992]. In addition, the accuracy of these estimates is highly uncertain as they are calculated from the average emission of all included studies, a global lake area estimate without considering lake-area-dependence of emission, and the assumption that only 10–50% of the lake surfaces emit methane.

[7] In this study we combine measurements of ebullition, diffusive flux, and storage from 11 Wisconsin and 13 Swedish lakes with available literature estimates from 49 other temperate and boreal lakes, and present relationships between emission and lake characteristics. These relationships provide a basis for predicting methane emissions, and with data on the number, size, and distribution of lakes, we derive estimates of regional and global methane emissions.

2. Methods

2.1. Study Sites

[8] The 11 North American lakes are located at the University of Notre Dame Environmental Research Center

(UNDERC) near Land O’ Lakes, Wisconsin (89°32’W, 46°13’N). These lakes are situated in one of the most lake rich districts in the United States, and the lakes are representative of a large area [Marin *et al.*, 1990]. The topography consists of rolling hills with extensive bogs and low-lying forests [Webster *et al.*, 1996]. Many of the lakes have been well studied in terms of hydrology and chemistry [Cole and Pace, 1998]; see also Table 1 for water chemistry. Three of the lakes (Paul, Peter, and Hummingbird) were sampled repeatedly (4–12 times), and the other lakes (Crampton, East Long, Morris, Roach, Brown, North Gate Bog, Tuesday, and Ward) were sampled once or twice from early June to late August 2001.

[9] Diffusive emissions and water column storage were estimated for 13 Swedish lakes. These lakes were situated in southern or central Sweden (six and seven lakes, respectively), in the provinces of Småland and Dalarna. All the lakes are representative of the boreal oligotrophic lake type [Sobek *et al.*, 2003]. Sampling occurred in July 2000.

2.2. Methane Concentrations

[10] For both the Swedish and North American lakes, water samples for methane concentration were collected in 118-mL infusion bottles capped with 10-mm-thick, gas tight butyl rubber septa (Apodan, Copenhagen, Denmark). The bottles were capped prior to sampling in the laboratory after the addition of preservative (0.2 mL of 2.5 M H₂SO₄). Residual air in the bottles was replaced with He by repeated evacuation using a vacuum pump, followed by addition of He through tubing connected to syringe needles (0.6 × 25 mm, Becton-Dickinson) piercing the septa. The gas replacement procedure was ended with evacuation. Evacuation efficiency was 78%, leaving 25 mL of He in the bottles. A final addition of 25 mL He was made using a syringe (Plastipak, Becton-Dickinson).

[11] To retrieve surface water samples, a prepared infusion bottle (above) was lowered just below the water surface. A syringe needle was then inserted through the septum, and water was thereby sucked into the bottle. After 6 min, equilibrating the pressures in the bottle and in the surrounding water, the needle was removed, sealing the bottle at the sampling depth. To retrieve samples from

deeper water, prepared infusion bottles were attached to a 2-m-long plastic rod at desired distances using rubber bands. The rod was attached to a 2-kg weight at one end and a rope at the other end. To open and close the bottles at desired depths, we used two-way hypodermic needles (Venoject MultiSample 22G1 TW, Terumo Medical Corporation). To prepare for sampling, one end of such a needle was first inserted halfway through an additional stopper capping the needle, while the other end was inserted into the infusion bottle. Then the rod with bottles and needles was lowered to the desired depth. The capping stoppers, as well as the needles, were attached to separate lines, so to start the sampling, the capping stoppers were pulled away from the needles, and to seal the bottles at the in situ depth after 6 min, the needles were pulled away from the bottles.

[12] Since He was already present in the bottle, the headspace extraction occurred in the infusion bottles. After confirming the volume of water sampled by weighing the bottles, allowing all bottles to reach room temperature, and agitating the bottles thoroughly, methane concentration in the headspace was measured by gas chromatography using a flame ionization detector (GC-FID; Shimadzu GC-8, Poropack N column). When calculating the in situ concentration, we corrected for the headspace-water partitioning of methane using Henry's Law, and the pressure in the bottles as well as the volume sampled, which both differed with depth due to hydrostatic pressure. In this way, we obtained concentration measurements at all depths that varied 3.7% on an average between replicate samples, and that were not biased by the pressure changes induced if water is transferred to the surface by pumping or the use of a water sampler.

2.3. Ebullition and Diffusive Flux

[13] The ebullition and diffusive flux components for the North American lakes were estimated using floating chambers (0.03 m², 5 L, polyethylene/Plexiglas). Gas samples were withdrawn by syringe through a butyl rubber stopper on the top of the chambers right after placing them on the lake, and at the end of the measurement period. A 24-hour measurement set with 15 chambers, arranged in three different transects from the shore to the center of the lake, was performed for all lakes once during the sampling period. Additional measurements on seven of the lakes were carried out with two to six chambers, and included 3- to 24-hour measurements. Short-term measurements revealed that the length of the measurement period did not bias the measurements and that there was a substantial diurnal variation in methane emissions, with 9–158% greater emissions during the day (average and median of 69 and 53%, respectively). Therefore we report only the 24-hour measurements. The gas samples were analyzed within 24 hours as above. In total, 242 chambers were deployed for these analyses. Simultaneous, independent measurements of diffusive gas transfer across the lake surface using SF₆ additions and the CO₂ mass balance obtained by additions of ¹³C confirmed that chamber technique did not bias flux estimates [Cole et al., 2004].

[14] The surface water methane concentration and temperature were measured at the location of each chamber.

The diffusive flux across the water surface into the floating chamber can be described by the equation

$$F = k \times (C_w - C_{fc}), \quad (1)$$

where F is the flux (moles m⁻² d⁻¹), k is the piston velocity (m d⁻¹), and C_w is the measured methane concentration in the water (moles m⁻³), and C_{fc} is the methane concentration in the water given equilibrium with the methane partial pressure in the floating chamber [Cole and Caraco, 1998]. This equation implies that the flux is partly driven by the concentration difference which will decrease with time in the chambers. Hence a simple calculation of the total amount of methane that entered the chambers divided with the time of measurement will underestimate the instantaneous flux rate. To estimate the instantaneous flux, we therefore solved for k . Equation (1) was rewritten as

$$\frac{(P_t - P_0)V}{RTA} = k(P_w K_h - P_0 K_h), \quad (2)$$

where P_t and P_0 are the partial pressure of methane in the chamber (Pa) at times t and 0, respectively, V is the chamber volume (m³), R is the gas constant (8.314 m³ Pa K⁻¹ mol⁻¹), T is the temperature (K), A is the bottom area of the chamber (m²), P_w is the partial pressure of methane in the chamber at equilibrium with C_w (Pa), and K_h is the Henry's Law constant for methane (moles m⁻³ Pa⁻¹). Hence

$$\frac{dP}{dt} = K(P_w - P), \quad (3)$$

where

$$K = k \frac{K_h RTA}{V}. \quad (4)$$

The solution for equation (3) is

$$(P_w - P) = C e^{(-Kt)}, \quad (5)$$

where C is a constant determined by setting $t = 0$. After solving for k , the instantaneous flux was calculated using equation (1). The temperature dependence of K_h was calculated from the Bunsen coefficients given by Wiesenburg and Guinasso [1979].

[15] Some chambers received methane by both diffusive flux and ebullition. We used the distribution and variance in the apparent piston velocities to determine which chambers received ebullition flux. The calculated k values for each chamber were transformed into k_{600} values. Here k_{600} is k for a gas with a Schmidt number of 600 and allows k values to be compared for any gas and temperature [Jahne et al., 1987; Wanninkhof, 1992]. Where ebullition into a chamber is significant, a k value, strictly speaking, has no meaning, but ebullition makes calculated apparent k_{600} values substantially higher than for chambers receiving methane only by diffusive flux, allowing the two flux components to be estimated separately. For each chamber the calculated k_{600} was divided by the minimum k_{600} for the same lake and sampling period, which we attributed solely to diffusive flux. The frequency distribution of this ratio for all chambers clearly indicated that there were two distinct groups of chambers having ratios of 1–1.8 and >2, respectively

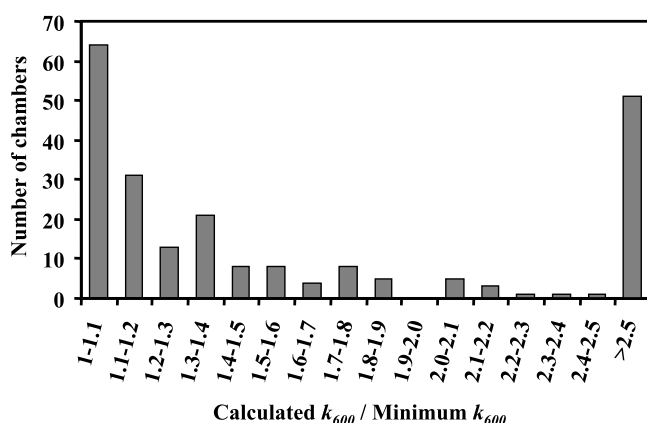


Figure 2. Frequency distribution for floating chamber measurements of the ratios of calculated k_{600} for each chamber to the minimum k_{600} for the specific lake and measurement period. The calculated k_{600} was similar to the minimum k_{600} for most chambers, indicating only diffusive flux into the chamber, but for chambers with a high calculated k_{600} relative to the minimum k_{600} , ebullition contributed to the methane flux as well. On the basis of the frequency distribution, we assumed that ebullition into a chamber occurred only if the calculated k_{600} was more than twice the minimum k_{600} . See text for details.

(Figure 2). Hence a ratio of 2 was chosen as a threshold where we inferred significant methane flux into the chamber had occurred by ebullition. In these chambers the diffusive flux was estimated from equation (1) using the lake average k_{600} from the chambers receiving diffusive flux only, and all the remaining methane flux into the chambers was attributed to ebullition. When calculating yearly fluxes, we assumed that ebullition occurred 365 days per year while the diffusive flux only occurred during the open water season, i.e., during, on an average, 224 days per year (http://www.limnology.wisc.edu/lter_lake.html).

[16] For the Swedish lakes the diffusive flux was estimated from equation (1) using surface methane concentrations only. Since both the Swedish and the North American lakes are of similar size and surrounded by forest, we assumed that the average k_{600} value from the North American lakes would give a reasonable estimate of the piston velocity in the Swedish lakes.

2.4. Storage

[17] Depth profiles of methane concentrations were measured in each lake. The distance between the samples in the profiles were 0.5 m or less in lakes shallower than 6 m, and 1 m or less in the deeper lakes. In three lakes (Paul, Peter, and Hummingbird), concentration profiles were obtained weekly or biweekly throughout the whole sampling period to monitor how the methane storage in the water column changed over time. The concentration at each depth was multiplied by the volume of that water layer, yielding the total methane content at different depths. The total storage per lake was estimated as the sum of the methane in all strata. This number divided with the lake surface area yielded storage per m^2 . The linear increase in storage with

time found in the three lakes sampled intensively ($r^2 = 0.84\text{--}0.97$; $n = 6\text{--}10$), and the relation between the slope of the linear increase and the anoxic proportion of the lake water volume (slope in $mg\ C\ m^{-2}\ d^{-1} = 9.92 \times \ln[\text{anoxic lake volume fraction}] + 29.7$; $r^2 = 0.99$; $n = 3$) was used to estimate the storage at fall lake overturn assumed to occur 1 November. This was used as a yearly estimate for the North American lakes, since the stratified lakes most likely did not mix completely following ice melt prior to the first sampling in spring. The Swedish lakes mixed both during spring and fall, but since all these lakes were oligotrophic, we assumed that the water column remained oxic throughout the winter, and hence that no methane accumulated in the water column under ice.

2.5. Other Measurements

[18] O_2 concentrations and temperature was measured along depth profiles in all lakes using a YSI 5000 oxygen-temperature meter. In addition, pH, and concentrations of dissolved organic carbon (DOC), chlorophyll *a*, and total phosphorus were measured in surface water samples. The pH was measured using a Orion pH meter with ATC gel-filled electrode. Concentrations of DOC, chlorophyll *a*, and total phosphorus were analyzed according to Pace and Cole [2002].

2.6. Statistical Methods and Synthesis of Literature Values

[19] Relationships between methane emission and lake characteristics were investigated graphically, and by linear univariate or multiple regression analysis in SPSS 11.0 for Windows. Proportions were arcsin-transformed, while other variables were \log_{10} -transformed prior to analyses [Sokal and Rohlf, 1995]. To make general estimates, we included literature estimates of methane emission from 49 temperate and boreal lakes in addition to our own measurements (Table 1). Studies that clearly separated the different flux components were selected. We analyzed the annual flux per lake, as well as per unit lake area (per m^2).

3. Results

3.1. Methane Concentrations

[20] Average surface water methane concentrations for both the 11 UNDERC lakes (0.27 to $2.32\ \mu\text{mol}\ L^{-1}$) and the 13 Swedish lakes (0.08 to $1.89\ \mu\text{mol}\ L^{-1}$) are within the range of previously reported surface water methane concentrations (Table 1). Methane concentration in surface waters was positively related to the fraction of the lake volume being anoxic and negatively related to DOC concentration and lake area (Table 2). There was no significant relation between surface methane concentrations and estimates of within-lake productivity, such as total phosphorus or chlorophyll *a*.

3.2. Ebullition

[21] Ebullition was highly variable within and between lakes (Table 1, Figure 3). The frequency of ebullition was nonlinearly related to water depth, with ebullition occurring in 25–80% of the chambers in locations where water depths

Table 1. Characteristics of Lakes Sampled in the Present Study Along With Lakes Where Methane Fluxes Were Previously Reported in the Literature^a

Source	Lake	Area, ha	Ebullition, ^b mg C m ⁻² yr ⁻¹	Diffusive Flux, ^c mg C m ⁻² yr ⁻¹	Storage, ^d mg C m ⁻² yr ⁻¹	DOC, ^e mg L ⁻¹	TP, ^e μmol L ⁻¹	[CH ₄], ^e μmol L ⁻¹
<i>North America</i>								
Bastviken et al. (present study)	Brown	32.9	1428	1161	501	7.9	1.13	0.82
Bastviken et al. (present study)	Crampton	25.8	841	508	8	3.7	0.24	0.41
Bastviken et al. (present study)	East Long	2.3	2649	940	730	12.1	1.22	0.66
Bastviken et al. (present study)	Hummingbird	0.8	1152	592	4623	22.0	1.09	0.68
Bastviken et al. (present study)	Morris	5.9	16284	1730	2434	12.7	0.62	1.22
Bastviken et al. (present study)	North Gate	0.3	896	618	6454	21.3	0.46	0.34
Bastviken et al. (present study)	Paul	1.7	2680	2489	1792	3.1	0.38	2.15
Bastviken et al. (present study)	Peter	2.7	4452	1603	5536	4.5	0.25	1.31
Bastviken et al. (present study)	Roach	45.0	93	395	11	2.7	0.19	0.27
Bastviken et al. (present study)	Tuesday	0.9	1171	2346	4498	7.6	0.29	2.32
Bastviken et al. (present study)	Ward	2.7	9983	1484	3344	6.5	0.86	1.22
Chau et al. [1977]	Ontario	1896000	533			12	0.26	
Fallon et al. [1980]	Lake Mendota	3937.0		2180	12346	10.0	3.81	0.50
Howard et al. [1971]	Erie	2570000		190		2.7	0.39	0.013
Kling et al. [1992]	Toolik	150.0		1120				1.10
Kling et al. [1992]	N2-cont	1.8		582				0.57
Kling et al. [1992]	N2-fert	1.8		253				0.25
Kling et al. [1992]	N1	0.5		88			0.16	0.09
Mattson and Likens [1993]	Mirror	15.0	876			4.0		
Michmerhuizen et al. [1996]	Little Shingboee	2.7			5751			
Michmerhuizen et al. [1996]	11th Crow Wing	299.7			1191			
Michmerhuizen et al. [1996]	Leech	57340.0			283			
Michmerhuizen et al. [1996]	Allequash	161.2			358	3.9	0.95	
Michmerhuizen et al. [1996]	Big Muskellunge	384.1			289	3.9	0.73	
Michmerhuizen et al. [1996]	Trout	1561.0			12	2.9	0.55	
Michmerhuizen et al. [1996]	Glacier pond	7.2			578			
Michmerhuizen et al. [1996]	Tofte	50.6			749			
Michmerhuizen et al. [1996]	Jasper	75.8			211			
Michmerhuizen et al. [1996]	Ojibway	152.1			1701			
Michmerhuizen et al. [1996]	Snowbank	2004.0			50			
Michmerhuizen et al. [1996]	Hiawatha	21.7			3233			
Michmerhuizen et al. [1996]	Nokomis	80.6			28			
Michmerhuizen et al. [1996]	Harriet	119.5			47			
Michmerhuizen et al. [1996]	Calhoun	172.0			72			
Michmerhuizen et al. [1996]	Minnetonka	5301.0			165			
Michmerhuizen et al. [1996]	Crystal	37.9		104	224	1.8		0.10
Riera et al. [1999]	Crystal Bog	0.5				9.3		1.50
Riera et al. [1999]	Trout Bog	1.1				20.7		1.50
Riera et al. [1999]	Sparkling	63.9				3.2		0.10
Rudd and Hamilton [1978]	Lake 227	5.5		743	5257	9.0	1.13	
Smith and Lewis [1992]	Dillon	1300.0		2681				0.74
Smith and Lewis [1992]	Red Rock	2.1		5883		10.0		1.60
Smith and Lewis [1992]	Rainbow	1.0		3602				1.02
Smith and Lewis [1992]	Long	16.0		140				0.10
Smith and Lewis [1992]	Pass	1.6		2556				0.65
Strayer and Tiedje [1978]	Wintergreen	15.0	91980	43920				
Striegl and Michmerhuizen [1998]	Williams	37.1			3000			
Striegl and Michmerhuizen [1998]	Shingboee	65.5			1920			
<i>Eurasia</i>								
Bastviken et al. [2002]	Illersjön	3.9		2058	3613	9.4	1.25	0.55
Bastviken et al. [2002]	Mårn (south sub-basin)	4.5		222	789	17.9	1.68	0.10
Bastviken et al. [2002]	Lillsjön	2.0		92	539	19.8	0.50	0.10
Bastviken et al. (present study)	Bisen	43.3		110		8.3	0.28	0.11
Bastviken et al. (present study)	L Sångaren	24.0		184	10	7.4	0.39	0.18
Bastviken et al. (present study)	Ljustjärn	13.0		495	98	4.4	0.27	0.47
Bastviken et al. (present study)	Lövtjärn	8.5		637		6.6	0.31	0.61
Bastviken et al. (present study)	Rågåstjärn	4.0		1153		5.8	0.28	1.10
Bastviken et al. (present study)	Skottjärn	2.8		1917		20.5	0.48	1.84
Bastviken et al. (present study)	Svartjärn	0.7		1974		18.8	0.45	1.89
Bastviken et al. (present study)	Fiolen	150.0		95	4	6.8	0.42	0.08
Bastviken et al. (present study)	Gransjön	4.5		568		11.6	0.74	0.48
Bastviken et al. (present study)	Grunnen	48.0		543		17.2	0.71	0.46
Bastviken et al. (present study)	Gyslätasjön	26.3		459		13.4	0.65	0.38
Bastviken et al. (present study)	Klintsjön	10.0		373	17	4.7	0.21	0.31
Bastviken et al. (present study)	Skärshultssjön	29.2		201	5	15.9	0.71	0.17

Table 1. (continued)

Source	Lake	Area, ha	Ebullition, ^b mg C m ⁻² yr ⁻¹	Diffusive Flux, ^c mg C m ⁻² yr ⁻¹	Storage, ^d mg C m ⁻² yr ⁻¹	DOC, ^e mg L ⁻¹	TP, ^e μmol L ⁻¹	[CH ₄], ^e μmol L ⁻¹
Casper et al. [2000]	Priest Pot	1.0	54312	1489	3316		19.35	1.10
Huttunen et al. [2003]	Postilampi	3.0	6750	3750	1575			
Huttunen et al. [2003]	Kevätön	407.0	983	983	194			
Huttunen et al. [2003]	Vehmasjärvi	41.0		230				
Huttunen et al. [2003]	Mäkijärvi	20.0		197				
Miyajima et al. [1997]	Biwa	67400		1181			0.19	0.07
Schultz et al. [2001]	Constance	54000		173		1.5	0.48	0.012
Utsuimi et al. [1998a]	Kasumigaura	16800		1150			0.13	0.3
Utsuimi et al. [1998b]	Nojiri	440		274				0.15

^aFor units, mg C m⁻² yr⁻¹ refer to mg C emitted per m² of lake per year.

^bEbullition assumed to occur 365 d per yr.

^cDiffusion assumed to occur under ice free conditions only.

^dWhen only spring values of storage in dimictic lakes were reported we assumed similar water column accumulation rate during summer stratification as during winter.

^eSurface water concentrations.

were 4 m or less (Figure 4). In deeper water, ebullition occurred in less than 10% of the chambers. Owing to this depth dependence, the annual ebullition per lake, as well as per m², was corrected for the area of the lake having shallow water with a high probability of ebullition, in accordance with Figure 4. The fraction of the lake area at particular depths was estimated from mean and maximum depth using equations given by Carpenter [1983] for all lakes in Table 1 for which ebullition estimates were available.

[22] Annual ebullition per lake was clearly related to lake area (Figure 5; Table 2). This relationship was improved when total phosphorous was added as a second

variable. The pH, being correlated with lake area ($p < 0.001$, $n = 35$), was also significantly related to the annual ebullition per lake, but with a lower r^2 ($p = 0.001$, $r^2 = 0.67$, $n = 12$). Annual ebullition per m² was best predicted from total phosphorous concentrations and surface methane concentrations (Table 2), and the relation with chlorophyll *a* was weaker ($p = 0.034$, $r^2 = 0.29$, $n = 13$).

3.3. Diffusion

[23] Although the areal annual diffusive flux showed lower variability than other measures, it still varied sixfold among the UNDERC lakes and 20-fold among the Swedish

Table 2. Selected Regression Equations for Surface CH₄ Concentration, Ebullition, Diffusive Flux, and Storage Based on Data From Table 1^a

Regression Equation ^b	<i>n</i>	Adjusted <i>r</i> ²	<i>p</i>
<i>Surface CH₄ Concentration</i>			
Log(CH ₄) = 0.781 - 0.227log(AREA)	47	0.38	<0.001
Log(CH ₄) = 0.228 + 1.209arcsin(√VFAN) - 1.042log(DOC)	18	0.55	0.001/0.002
<i>Ebullition^c</i>			
Log(EPL) = 1.190 + 0.841log(AREA)	17	0.78	<0.001
Log(EPL) = 0.838 + 0.934log(AREA) + 0.881log(TP)	13	0.89	<0.001/0.016
Log(EPM) = 0.523 + 0.950log(TP)	13	0.46	0.006
Log(EPM) = 0.601 + 0.821log(TP) + 1.169log(CH ₄)	13	0.65	0.007/0.024
<i>Diffusive Flux^d</i>			
Log(DPL) = 0.234 + 0.927log(AREA)	53	0.86	<0.001
Log(DPM) = 0.083 + 0.282log(SPM)	27	0.44	<0.001
<i>Storage</i>			
Log(SPL) = 1.546 + 0.649log(AREA)	45	0.41	<0.001
Log(SPL) = 7.068 + 3.304log(TP) - 1.904log(DOC)	24	0.59	<0.001/0.007
Log(SPM) = -1.098 + 1.553log(CH ₄) + 1.365log(DOC)	23	0.46	0.001/0.029
Log(SPM) = 0.305 + 1.590log(CH ₄) + 1.003log(TP)	21	0.49	0.002/0.023
Log(SPM) - 1.609 + 3.475arcsin(√VFAN) ^e	15	0.72	<0.001

^aThe *p* values are given for each variable in order of appearance in the equation. Abbreviations used: AREA, lake area (m²); CH₄, surface water concentration of methane (μmol L⁻¹); DOC, concentration of dissolved organic carbon (mg C L⁻¹); DPL, diffusive flux per lake (g C lake⁻¹ yr⁻¹); DPM, diffusive flux per m² (g C m⁻² yr⁻¹); EPL, ebullition per lake (g C lake⁻¹ yr⁻¹); EPM, ebullition per m² (g C m⁻² yr⁻¹); TP, concentration of total P (μmol L⁻¹); SPL, storage per lake (g C lake⁻¹ yr⁻¹); SPM, storage per m² (g C m⁻² yr⁻¹); VFAN, volume fraction being anoxic.

^bValid ranges of the equation variables can be found in Table 1.

^cProbability of ebullition at different water depths (see Figure 4), and the relative area of different depth zones [see Carpenter, 1983] was accounted for when calculating EPL and EPM.

^dDPM was well predicted by CH₄ (Adj. $R^2 = 0.627$, $n = 47$, $p < 0.001$), but since [CH₄] was used to calculate DPM in many studies, this equation is excluded in the table.

^eLakes for which VFAN was used to estimate storage was excluded.

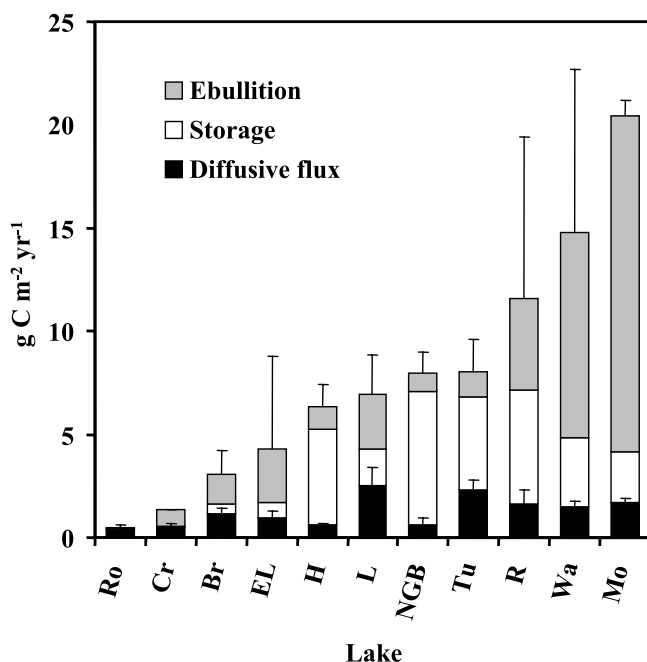


Figure 3. Estimated yearly methane emission by different flux pathways from the studied UNDERC lakes. Error bars denote ± 1 SD. The lakes are Roach (Ro), Crampton (Cr), Brown (Br), East Long (EL), Hummingbird (H), Paul (L), North Gate Bog (NGB), Tuesday (Tu), Raspberry (R), Ward (Wa), and Morris (Mo); see Table 1.

lakes (Table 1, Figure 3). The annual diffusive flux per lake was well predicted by lake area (Figure 5; Table 2). Areal annual diffusion (e.g., per m^2) was best predicted by the storage per m^2 (Table 2).

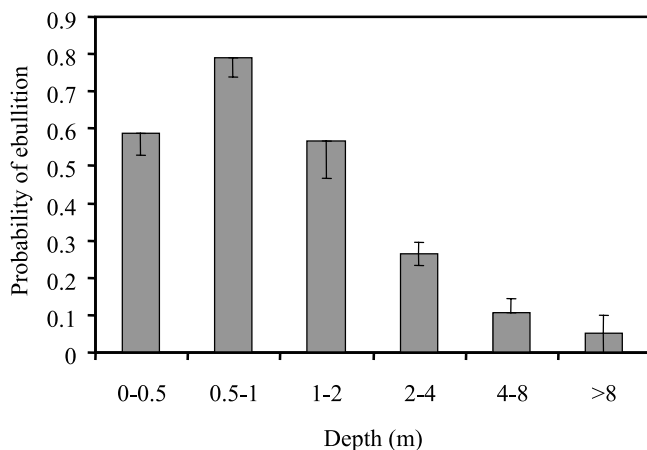


Figure 4. Probability of ebullition (i.e., fraction of the floating chambers receiving ebullition) at different depths. Ebullition was assumed to occur in chambers for which $(\text{calculated } k_{600})/(\text{minimum } k_{600}) > 2$ (see text for details). The error bars denote how the distribution is affected by changing this threshold ratio to 1.8 or 2.2, and illustrate that the distribution is not very sensitive to the chosen threshold value to distinguish between ebullition and diffusive flux.

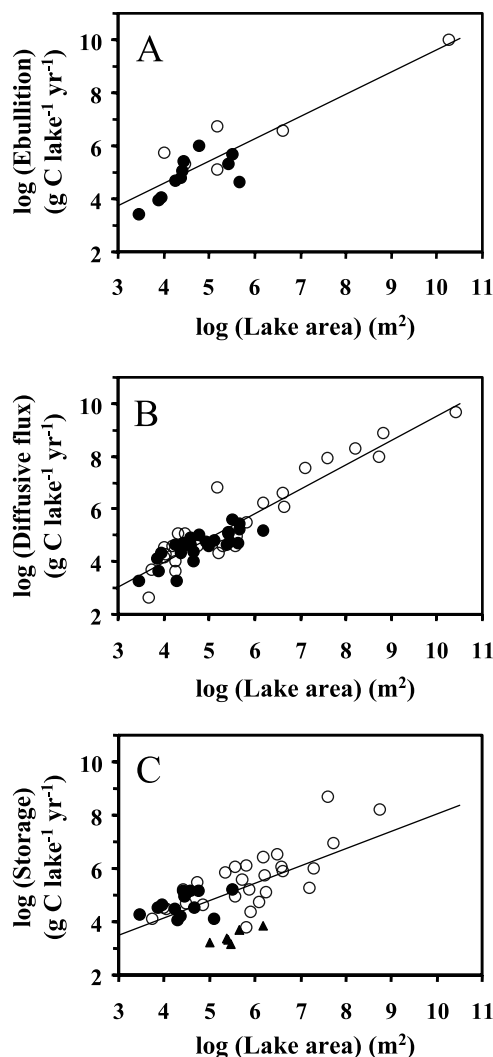


Figure 5. (a) Ebullition, (b) diffusive flux, and (c) water column methane storage during stratification periods for lakes of different size. The solid symbols represent the UNDERC lakes and the Swedish lakes investigated in this study. The open circles denote the other lakes in Table 1. The solid triangles in Figure 5c represent lakes without anoxic parts of the water column. Linear regression lines are given in the graphs. For regression statistics, see Table 2.

3.4. Storage

[24] The storage component varied 800-fold among UNDERC lakes (Figure 3, Table 1). Storage per lake and year was significantly related to lake area and to total phosphorous and dissolved organic carbon (Figure 5; Table 2). Storage per m^2 was best predicted by the anoxic volume fraction of the lake, but could also be predicted from surface methane concentrations and total phosphorous, or surface methane concentrations and dissolved organic carbon (Table 2).

4. Discussion

[25] The results of this study clearly indicate that methane emissions are predictable from easily measured lake char-

acteristics. Most variables produced significant relationships with at least one flux component, and in the following we focus on the relationships with greatest explanatory power (i.e., lowest p values and highest r^2). Regressions based on all available data suggest that lake area, along with total phosphorous and dissolved organic carbon concentrations, were the most useful variables for describing methane emissions (Table 2). This indicates that lake morphology, lake productivity, and the load of allochthonous organic carbon influence methane dynamics. Significant relationships with some of the flux components were also obtained with the anoxic volume fraction, representing an interaction between lake morphology, lake metabolism, and the mixing regime (Table 2). Other variables, such as pH and chlorophyll a concentrations, showed weaker relationships with methane emissions. Relationships with chlorophyll a were generally found in accordance with the relationships with total phosphorous concentrations, supporting the result that autochthonous production stimulates emission. Interestingly, areal diffusive flux was also significantly correlated with lake latitude (Spearman rho, $p = 0.02$, $R^2 = -0.32$, $n = 53$), indicating that temperature may affect methane dynamics in lakes, but information from more lakes are needed to validate that hypothesis.

[26] Total methane emission in the 11 UNDERC lakes, including all three pathways, ranged from 0.5 to 20 g C m⁻² yr⁻¹ among lakes (Figure 3; Table 1). The relative contribution of the different pathways differed substantially between lakes, and the proportion of the flux attributed to ebullition or storage increased with increasing total areal flux. The diffusive flux was least variable both within and among lakes, while ebullition was most variable (Figure 3). These differences between the flux pathways confirm that each flux component should be considered separately in measuring and predicting methane emissions from lakes.

4.1. Methane Concentrations

[27] Conceptually, surface water methane concentration can be described as a function of sources and losses. The sources include methane fluxes into the mixed surface layer from sediments and from the water column below the mixed layer. These fluxes should be constrained by methane production and methane oxidation rates in the sediment and water column. The losses comprise diffusive emission from the lake surface, which depends on the piston velocity (see above), and potential methane oxidation within the mixed surface layer. Hence the negative relation between concentration and lake area probably reflects a higher piston velocity in larger lakes or, due to the larger volume and longer residence time, more extensive methane oxidation in the mixed layer of large lakes.

[28] The positive relation of methane concentration to the anoxic volume fraction (Table 2) may indicate (1) that a substantial proportion of the methane in the surface water comes from methane that is stored in anoxic parts of the water column below the mixed surface layer, or (2) that the export of methane to the atmosphere is smaller in lakes with a high anoxic volume fraction simply because such lakes are less well mixed, resulting in a low piston velocity. The first

alternative is interesting since the flux of methane from deeper parts of the water column to surface waters is often considered highly constrained by both methane oxidation and restricted diffusion across the thermocline [Bastviken *et al.*, 2003].

[29] The negative relation between surface methane and DOC concentrations (Table 2) may indicate that lakes with high DOC concentration generally develop a stable and shallow stratification causing the surface methane to rapidly vent due to the small volume of the mixed layer of such lakes. Another potential interpretation of the negative relation to DOC concentrations is that less methane is formed and transported to the mixed layer in lakes rich in DOC, since they are also often oligotrophic. However, the absence of relations with estimates of lake productivity contradicts this hypothesis. Even if methane production rate increases with lake primary productivity, so may the methane oxidation which potentially decouples surface methane concentrations from methane production rates.

4.2. Ebullition

[30] The depth-dependence of ebullition (Figure 4) relates to the previously observed connection between ebullition and air pressure [Casper *et al.*, 2000; Mattson and Likens, 1990]. Bubbles in sediments under a shallow water column have less hydrostatic pressure to overcome before release to the atmosphere, and changes in the air pressure, observed to induce ebullition, will have a proportionally greater impact on shallow sediments. In addition, wave-induced pressure changes in the littoral zones may facilitate the release of bubbles from shallow sediments. The connection between ebullition and water depth has been discussed [e.g. Fendinger *et al.*, 1992; Mattson and Likens, 1990], but not quantified previously.

[31] Ebullition per lake increased with lake area (Table 2), indicating that the total area of the shallow sediments are of major importance in spite of possible differences in the methane production between sediments of different lakes. The relations between ebullition per lake, as well as the areal ebullition, and total phosphorus concentration (Table 2) probably reflect a positive effect of nutrient load and lake primary productivity on methane production. The relation between methane concentration and areal ebullition is surprising and more difficult to interpret. One possible connection is that the methane concentration indirectly reflects the magnitude of the methane production and overall cycling in the lake.

[32] It should be noted that there are fewer measurements of ebullition than of the other two open water flux components, and existing measurements were primarily made in small lakes (Figure 5). Hence our results need further validation, particularly with measurements from large lakes.

4.3. Diffusion

[33] Lake area was a good predictor of annual diffusive flux per lake (Figure 5; Table 2). This is to be expected, even if surface methane concentrations decrease with lake size. This decline is compensated for by increased fetch and thereby increased gas piston velocity. The relation between areal annual diffusion (e.g., per m²) and the storage per m²

(Table 2) indicates that one source of the surface water methane leaving the lake by diffusive emission is methane from deeper water layers (see also paragraph about methane concentration above).

4.4. Storage

[34] The storage was highly variable among lakes (Table 1), reflecting low storage in lakes without anoxic water layers. The effect of water column anoxia is illustrated in Figure 5c by the comparison between partly anoxic lakes and lakes without anoxic water layers. The relation between annual storage flux per lake and lake area (Table 2, Figure 5) reflects that the volume in which methane can be stored increases with lake area. The positive relation with total phosphorous (Table 2) may indicate a greater production of methane and a greater anoxic volume fraction in productive lakes, while the simultaneous negative relation with dissolved organic carbon reflects the small size of lakes with high DOC concentrations with consequent smaller volume in which methane can be stored.

[35] As expected, the storage per m^2 and year was best predicted by the anoxic volume fraction of the lake. In addition, the areal storage could also be predicted from surface methane concentrations and total phosphorous, or surface methane concentrations and dissolved organic carbon (Table 2). In these cases, concentrations of both total phosphorus and dissolved organic carbon showed a positive relationship with storage per m^2 (Table 2), indicating that the supply of substrates for microbial metabolism is important for methane production and by promoting anoxic conditions in the water column. The surface methane concentration component in the above relations probably reflects the relation between surface methane concentrations and the anoxic volume fraction, and may be useful for predicting storage if data on the anoxic volume fraction are not available.

[36] In a previous study of the potential springtime emission of methane from northern temperate lakes, Michmerhuizen *et al.* [1996] found a significant negative relationship between potential emission per m^2 and lake area ($r^2 = 0.38$, $p = 0.01$, $n = 16$). With our data set, including the lakes studied by Michmerhuizen *et al.* [1996], we obtained a similar significant regression ($p = 0.006$, $n = 43$), but the r^2 was much lower ($r^2 = 0.152$). Better predictions of the storage per m^2 could be made using other variables (Table 2).

4.5. Comparison of Different Flux Components

[37] As indicated in Figure 3, the relative contribution of fluxes differs among lakes. The relationships between emissions and lake area (Table 2) indicate that ebullition contributes 40–60% of total emissions from open water (i.e., not considering plant mediated emissions; Figure 6). The storage component can contribute up to 45% in the smallest lakes, but this contribution diminishes with increasing lake size. The diffusive flux, on the other hand, increases in importance with increasing lake size and can account for as much as 50% in the largest lakes (Figure 6).

[38] Data from the literature suggest that plant mediated flux ranges from 8 to 262 $\text{mg C m}^{-2} \text{d}^{-1}$ [Chanton *et al.*, 1993; Juutinen *et al.*, 2003; Kankaala *et al.*, 2003; Sebach

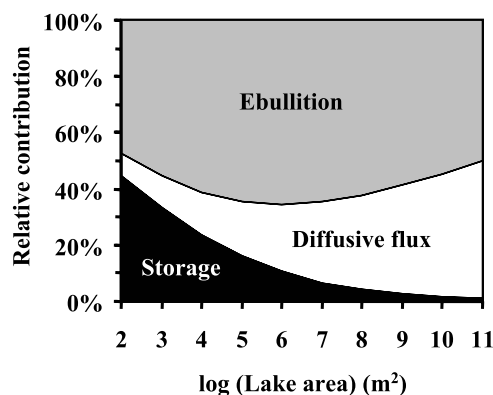


Figure 6. Relative contribution of the different methane flux components from open water versus lake area based on equations in Table 2. See text for details.

et al., 1985; Smith and Lewis, 1992; Sugimoto and Fujita, 1997; Walter *et al.*, 2001; Whiting and Chanton, 1993]. If emergent plants primarily grow at water depths less than 1.5 m [Kalff, 2002], plant-mediated flux primarily occurs over 1–15% of the lake surface for most lakes [Carpenter, 1983]. Given this, literature estimates of plant mediated flux correspond to 0.4–6 $\text{g C m}^{-2} \text{lake yr}^{-1}$, using the average value of 150 $\text{mg C m}^{-2} \text{d}^{-1}$ (median value was 143 $\text{mg C m}^{-2} \text{d}^{-1}$) and assuming that the vegetation period is 240 d yr^{-1} for 50% of the lakes and 365 d yr^{-1} for the remaining lakes based on the distribution of lakes at different latitudes [Kalff, 2002]. For comparison, the ebullition range between 0.09 and 92 $\text{g C m}^{-2} \text{yr}^{-1}$, and average and median ebullition in our data set is 8.3 and 1.4 $\text{g C m}^{-2} \text{yr}^{-1}$, respectively (Table 2). In comparison with the open water flux components, the contribution of the plant-mediated flux decreases with increasing lake size, since the proportion of the lake area covered by emergent plants declines with increasing lake area.

4.6. Regional Estimates

[39] The relationships between the different components of emission and easy-to-obtain lake state variables allows a new approach to estimating emissions at a larger scale. For the Northern Highlands area of Wisconsin, there is a complete data set based on satellite images with area information for all lakes larger than 0.008 ha (unpublished data provided courtesy of the North Temperate Lakes LTER site, URL <http://lter.limnology.wisc.edu>). Applying the equations in Table 2 for the 6930 lakes in this data set, we estimate that the open water methane emission is 4.0 $\text{Gg CH}_4 \text{ yr}^{-1}$ from this region, with ebullition, diffusive emission, and storage accounting for 65, 24, and 12%, respectively. Lakes with an area smaller than 0.01 km^2 contributed 3.4% and lakes larger than 1 km^2 accounted for 52% of the total methane emission.

[40] Using information from Swedish Meteorological and Hydrological Institute about average lake sizes and number of lakes in different size categories (available at www.smhi.se), we performed a similar calculation of methane emissions from Swedish lakes. The sum of ebullition, diffusive flux, and storage was 105 $\text{Gg CH}_4 \text{ yr}^{-1}$

Table 3. Comparison Between Global Estimates of Methane Emissions From Lakes

Study	Number of Lakes	Flux Components Considered	Estimated Global Methane Emission, Tg CH ₄ yr ⁻¹	Percent of Estimated Total Natural CH ₄ Emissions ^a
Ehlt [1974]	2	ebullition	1–25	1–8
Smith and Lewis [1992]	17	ebullition, diffusive flux, plant-mediated flux	11–55	8–18
This study	73	ebullition, diffusive flux, storage, plant-mediated flux	6–25 (open water) ^b 2–23 (through plants) ^c 8–48 (total)	6–16

^aAccording to Table 1 of *Wuebbles and Hayhoe* [2002]. Average and maximum emissions estimated to 145 and 304 Tg CH₄ yr⁻¹, respectively. Lakes are not considered as a significant CH₄ source in this table.

^bEbullition, diffusive flux, and storage combined. See text for details.

^cOn the basis of literature values and the assumption that 1–15% of the lake area is covered by emergent plants. See text for details.

based on a total number of 95,721 lakes in Sweden (total area of Sweden is 449,964 km²). The relative contribution of the different flux components was similar as for the Northern Highlands. Methane emissions from areas with *Phragmites* sp. and *Typha* sp. in Sweden was recently estimated to be 15–40 Gg CH₄ yr⁻¹, and this flux probably accounts for 5–10% of the total methane emissions from wetlands in Sweden [Kasimir-Klemedtsson *et al.*, 2001]. Accordingly, emissions from lakes can be significant, even compared to total wetland emissions, and therefore should be included in regional estimates of greenhouse gas emissions.

[41] Ebullition, representing the major flux from open water in the regional estimates above, occurs as discrete events and large fluxes are often associated with changes in local air pressure [Casper *et al.*, 2000; Mattson and Likens, 1990]. In spite of this, the majority of the ebullition data available is based on short-term measurements (0.5–24 hours) that probably do not capture the true variation in ebullition events. With such measurements, there is a high probability of missing the less frequent events with extremely high fluxes, and hence many of the studies used for creating the equations in Table 2 probably underestimate ebullition. Therefore the regional estimates above are likely conservative. It should also be noted that the regional estimates, as well as all results in this study, rely on single-season emission measurements due to lack of long-term data. Hence variability between years is presently unknown.

4.7. Global Estimate

[42] In addition to the regional estimates above, we estimated methane emissions from lakes on a global basis using the equations in Table 2 and data on lake area and lake numbers given by Kalff [2002]. This data set contains five very broad size classes of lakes. To reduce the error when estimating the average lake area within each size class, we divided the data into 19 smaller size classes, assuming that the global distribution of lake areas was similar to the Northern Highland distribution. The number of lakes and the geometric mean lake area of each of these narrower size classes were then used in the equations in Table 2 to calculate emissions (excluding the Caspian Sea). This yielded a total global open water flux estimate of 6 Tg CH₄ yr⁻¹ from lakes, with the ebullition, diffusive flux, and storage contributing 62%, 31%, and 7%, respectively, of

the emissions. Lakes smaller than 0.01 km² accounted for about 3% of the total emissions, while lakes larger than 1 km² contributed 67%. Lakes larger than 100 km² contributed 14% of the total emissions.

[43] The open water flux estimate of 6 Tg CH₄ yr⁻¹ should be regarded as our best estimate. A possible range of 2–25 Tg CH₄ yr⁻¹ was calculated by changing the intercepts and slopes in the equations by ± 0.5 SD. Our best estimate, however, most likely underestimates actual global emission from lakes for two major reasons. First, the equations used are based on flux measurements in subarctic, boreal, and temperate regions, averaging 12 g C m⁻² yr⁻¹ (median of 3 g C m⁻² yr⁻¹), while limited studies to date indicate average emissions from tropical lakes are 19 g C m⁻² yr⁻¹ (median of 12 g C m⁻² yr⁻¹). Hence tropical lake emissions may be 58% higher than from subarctic, boreal, and temperate regions based on averages, or even up to 400% higher considering median values [Bartlett *et al.*, 1988; Boon and Mitchell, 1995; Crill *et al.*, 1988; Devol *et al.*, 1988; Engle and Melack, 2000; Smith *et al.*, 2000]. Therefore, including tropical emissions in the calculations would increase the global emission estimate. Second, ebullition accounts for the major part of the flux from open water, ranging from 1 to 19 Tg CH₄ yr⁻¹ in the ± 0.5 SD scenario above, and as discussed previously, the ebullition is most likely underestimated. Hence, considering that the equations in Table 2 likely underestimate the global flux, we conclude that the global emission from the open water of lakes is most likely somewhere between 6 and 25 Tg CH₄ yr⁻¹ (Table 3).

[44] To estimate the plant-mediated flux, we rely on previous studies. Given the previous assumptions concerning the area fraction of lakes covered with emergent plants and the vegetation period, along with information about the global number of lakes of different sizes, we estimate the global plant mediated flux as 2–23 Tg CH₄ yr⁻¹. Hence the total methane flux from lakes to the atmosphere should be 8–48 Tg CH₄ yr⁻¹ globally (Table 3). On a global basis this indicates that ebullition and plant-mediated flux accounts for most of the emissions, followed by diffusive flux, which is substantial from lakes larger than 1 km². The storage flux, being substantial only from small lakes, most likely accounts for a minor part of the total global lake emissions. Natural lakes with an area >0.01 km² cover approximately 3×10^6 km² [Kalff, 2002], and for compari-

son, methane emissions of $70 \text{ Tg CH}_4 \text{ yr}^{-1}$ globally have been estimated from reservoirs (not included in our estimates) covering $1.5 \times 10^6 \text{ km}^2$ [St. Louis *et al.*, 2000].

4.8. Comparison to Previous Estimates

[45] The first estimate of global lake methane emissions was made by *Ehalt* [1974] and is based on two extremely high ebullition measurements (90 and $480 \text{ g C m}^{-2} \text{ yr}^{-1}$) much higher than the range of 0.09 – $92 \text{ g C m}^{-2} \text{ yr}^{-1}$ for the 17 ebullition estimates in Table 1), along with the assumption that emission occur from only 1–10% of the lake area. This study also concluded that diffusive flux does not significantly contribute to emissions. In contrast, we found that approximately 31% of the open water emission is due to diffusive flux. Hence this early estimate of 1 – $25 \text{ Tg CH}_4 \text{ yr}^{-1}$ [Ehalt, 1974] (see also Table 3) was a result of a number of assumptions in combination with very limited data. This range has been frequently cited, directly or indirectly, in contemporary global analyses [e.g., Cicerone and Oremland, 1988] and may explain why emissions from lakes are not considered in current global methane budgets [e.g., Wuebbles and Hayhoe, 2002].

[46] A later global estimate considered more flux components and is based on more data [Smith and Lewis, 1992]. This estimate is much closer to our estimate (Table 3), but still relies on assumptions that a certain percentage of the lake surface emits methane, and for extrapolation, the average emissions from all lakes was multiplied by the total global lake area, without considering lake-size effects on flux.

[47] Our estimate of the total global emission, 8 – $48 \text{ Tg CH}_4 \text{ yr}^{-1}$, corresponds to 6–16% of global nonanthropogenic emissions, and 1.6–9.6% of total emissions [Wuebbles and Hayhoe, 2002]. Although lakes appear to be a significant component of the nonanthropogenic methane flux, they are rarely considered. For example, Wuebbles and Hayhoe [2002] omit lakes altogether, even though lakes contribute more nonanthropogenic methane to the atmosphere than does the ocean. There are still unresolved questions concerning the global methane budget, including a discrepancy between extrapolations of small-scale measurements from specific environments and inverse modeling relying on atmospheric methane concentrations. For wetlands, all small-scale estimates indicate emissions below 156 Tg yr^{-1} , while inverse approaches indicate emissions of 200 – 260 Tg yr^{-1} [Walter *et al.*, 2001]. One explanation for this discrepancy is that additional sources of atmospheric methane such as lakes are important.

5. Conclusions

[48] We conclude that the open water methane emissions from lakes are predictable, and that emission per lake is mainly related to lake area. Thus methane flux per unit area of lake is less variable than is lake area. On the other hand, the mechanisms behind the fluxes vary substantially among lakes of different sizes, and key variables for predicting areal emission include concentrations of total phosphorus, dissolved organic matter, and methane, as well as the anoxic volume fraction for storage and water depth for ebullition.

Ebullition is quantitatively most important, accounting for 40–60% of the open water emission from the average lake, but ebullition is also variable, represented by fewer measurements, and more difficult to measure than the other emission components. The relative importance of diffusive flux and the storage component increases and decreases, respectively, with increasing lake area (Figure 6). On a regional to global scale, lakes larger than 1 km^2 contribute most of the methane emission, which makes the general lack of measurements in large lakes a significant limitation to providing more robust regional and global estimates. More studies of lake methane emissions in tropical areas would also greatly improve the global estimate. This study indicates that lakes, which occupy a small portion of the Earth's surface, contribute more methane to the atmosphere than does the much larger ocean. Hence lakes constitute a substantial but largely overlooked source of methane to the atmosphere that should be included in regional and global methane budgets.

[49] **Acknowledgments.** We are deeply grateful to Darren Bade, Matt Van de Bogert, Emma Kritzbeg, Sebastian Sobek, Grete Algesten, Stephen Carpenter, James Kitchell, and James Hodgson for valuable assistance and support. We thank Gary Belovsky for facilitating our research at the University of Notre Dame Environmental Research Center. The study was funded by the Swedish Research Council, the Sweden-America Foundation, the Magnus Bergvall Foundation, and the National Science Foundation. This study is a contribution to the Institute of Ecosystem Studies.

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