Fates of methane from different lake habitats: Connecting whole-lake budgets and CH$_4$ emissions

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[1] Methane (CH$_4$) represents a major product of organic matter decomposition in lakes. Once produced in the sediments, CH$_4$ can be either oxidized or emitted as a greenhouse gas to the atmosphere. Lakes represent an important source of atmospheric CH$_4$, but the relative magnitudes of the internal pathways that lead to CH$_4$ emissions are not yet clear. We quantified internal cycling and methane emissions in three lakes during summer stratification. These methane budgets included: sediment release of CH$_4$ at different depths; water column transport patterns and methane oxidation; methane storage in the water column; and methane emissions to the atmosphere by diffusion and ebullition. The contribution of CH$_4$ carbon, via oxidation by methanotrophic bacteria, to pelagic food webs was also estimated. Despite the very low concentration of CH$_4$ in surface waters, shallow, epilimnetic sediments were major contributors of CH$_4$ to the atmosphere. While 51–80% of the CH$_4$ produced in deep sediments was oxidized in the water column, most of the CH$_4$ released from shallow sediment escaped oxidation and reached the atmosphere. Epilimnetic sediments accounted for 100% of CH$_4$ emitted during summer stratification, and 14–76% considering the release of CH$_4$ stored in deep water layers during lake circulation after the stratification period; diffusive emission accounted for 26–48% and ebullition the remainder. These results indicate that it is important to address transport rates of CH$_4$ from the shallow sediment along with the production-consumption processes when trying to understand methane dynamics and the regulation of lake methane emissions.

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1. Introduction

[2] Methane (CH$_4$) is a major product of carbon metabolism in lakes. It has been suggested that anaerobic carbon mineralization accounts for as much as 20–60% of the overall mineralization in freshwater environments [*Boon and Mitchell*, 1995; *Hamilton et al.*, 1995; *Hessen and Nygaard*, 1992; *Mattson and Likens*, 1993; *Utsumi et al.*, 1998b], and that methanogenesis corresponds to 30–80% of anaerobic C mineralization in waters and sediments [*Bédard and Knowles*, 1991; *Fallon et al.*, 1980; *Kuivila et al.*, 1988; *Rudd and Hamilton*, 1978]. Hence, methanogenesis could account for 10–50% of the overall carbon mineralization. Similarly, several studies indicate that 20–59% of the total contribution of sestonic carbon to sediments is converted to CH$_4$ [see *Wetzel*, 2001].

[3] The proportion of the CH$_4$ produced in lakes that is oxidized can be large (30–99%), and oxidation is believed to be performed by methanotrophic bacteria at oxic water or sediment interfaces [*Bastviken et al.*, 2002; *Fallon et al.*, 1980; *Frenzel et al.*, 1990; *Kankaala et al.*, 2006a; *Kuivila et al.*, 1988; *Liikanen et al.*, 2002; *Rudd and Taylor*, 1980; *Utsumi et al.*, 1998b]. One important role of CH$_4$ oxidation is that it reduces CH$_4$ emissions to the atmosphere. Recent studies indicate that CH$_4$ emissions from lakes account for 6–16% of the non-anthropogenic emissions, and that reservoirs contribute 18% of the anthropogenic emissions, on a global basis [*Bastviken et al.*, 2004; *St. Louis et al.*, 2000]. Hence, the internal CH$_4$ cycling in lakes is potentially important for the global CH$_4$ budget, and highly significant in the pre-industrial CH$_4$ budget.

[4] To date many studies on CH$_4$ cycling have focused largely on profundal sediments as the source of CH$_4$ and oxidation in the water column as a sink [*Bastviken et al.*, 2002; *Bédard and Knowles*, 1991; *Casper*, 1992; *Huttunen et al.*, 2006; *Kankaala et al.*, 2006a; *Liikanen et al.*, 2002; *Matthews et al.*, 2005; *Rudd and Taylor*, 1980; *Strayer and Tiedje*, 1978; *Utsumi et al.*, 1998b]. Further work has examined the role of methane oxidizing bacteria in the water column as a potential carbon source for zooplankton [*Bastviken et al.*, 2003; *Jones et al.*, 1999; *Kankaala et al.*, 2006b; *Taipale et al.*, 2008]. Water column CH$_4$ oxidation also affects aquatic organisms indirectly by the associated O$_2$ consumption, contributing to the O$_2$ depletion of isolated

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water layers [*Rudd and Taylor*, 1980]. There has also been a considerable interest in CH_4 production in profundal sediments since CH_4 accumulating in anoxic hypolimnia can be released to the atmosphere rapidly upon lake circulation resulting in significant emissions [*Michmerhuizen et al.*, 1996; *Riera et al.*, 1999].

[5] While less work has examined epilimnetic sediments, there are indications that these shallow areas may be important in both the internal CH_4 cycle and to atmospheric emissions. It is well recognized that CH_4 produced in sediments along lake margins accounts for most of the ebullition (bubble flux) and plant mediated flux to the atmosphere [e.g., *Bastviken et al.*, 2004; *Smith and Lewis*, 1992; *Walter et al. 2006, Wang et al.*, 2006]. The diffusive flux of CH_4 from shallow oxygenated sediment has generally been considered minor compared to the CH_4 flux from anoxic profundal sediments. Although this notion has support from measurements of CH_4 flux from oxic versus anoxic sediments in closed environments (e.g., sediment cores [*Frenzel et al.*, 1990; *Liikanen et al.*, 2002]), uncertainties remain about relative fluxes among habitats. For example, substantially higher CH_4 production can occur in littoral relative to profoundal sediments [*Michmerhuizen et al.*, 1996; *Murase et al.*, 2005], and several studies suggest that epilimnetic dissolved CH_4 may be derived from epilimnetic sediments rather than from hypolimnetic waters [*Murase et al.*, 2005; *Rudd and Hamilton*, 1978; *Schmidt and Conrad*, 1993]. Experimental work also indicates that turbulence and bottom shear stress enhance sediment flux rates [*Bussmann*, 2005; *Murase et al.*, 2005]. A rapid turbulence-enhanced flux from shallow sediments allows less time for CH_4 oxidation to act. Thereby a larger proportion of the CH_4 produced in epilimnetic sediments could escape CH_4 oxidation, resulting in a turbulence induced "shortcut" of dissolved CH_4 from shallow sediments to the atmosphere.

[6] Here we provide field-scale estimates of the relative contribution of CH_4 from sediments at different depths to CH_4 emissions. Such information is vital for our understanding of climate impacts on lake emissions. For example, changes in temperature will affect CH_4 production in shallow sediments much more than in deeper sediments in temperate and boreal stratified lakes. Hence, the larger relative contribution of emitted CH_4 from shallow sediments – the greater temperature sensitivity of overall lake emissions. Our estimates are based on whole-lake CH_4 budgets for three lakes during summer stratification. Budget calculations were based on measurements of CH_4 concentrations and CH_4 oxidation in the water column, as well as CH_4 emissions. Additional measurements of stable carbon isotopes ($\delta^{13}C$ signatures) were used to constrain rate estimates in the budgets. The stratification pattern allowed separate estimates of sediment flux from epilimnetic sediments (high turbulence, oxic conditions), metalimnetic sediments (low turbulence, oxic conditions) and hypolimnetic sediments (intermediate turbulence, anoxic conditions). Altogether, our mass balance approach yielded estimates of both sediment CH_4 flux, and quantitative information about the overall CH_4 cycling and its regulation within the studied lakes. In general, few such budgets have been presented and even fewer have (1) differentiated between epilimnetic and metalimnetic sediments, (2) accounted for different types of emissions (in this case diffusive flux, ebullition – i.e., bubble flux directly from sediment to atmosphere, and emission of water column CH_4 upon lake circulation), and (3) considered the possibility of turbulence enhanced transport across the sediment-water interface based on in situ observations.

2. Methods

2.1. Study Sites

[7] The three studied lakes (Paul, Peter, and Hummingbird) are located at the University of Notre Dame Environmental Research Centre (UNDERC) near Land O' Lakes, WI, U.S.A. ($89°32'W, 46°13'N$). These lakes are situated in one of the most lake rich districts in the United States and the lake sizes are close to the average size of northern temperate water bodies [*Marin et al.*, 1990; *Downing et al.*, 2006]. The topography consists of rolling hills with extensive bogs and low-lying forests [*Webster et al.*, 1996]. The studied lakes are small, steep-sided and surrounded by forest typical for the upper Great Lakes region. These lakes have been well studied in terms of hydrology, chemistry, and ecology [*Carpenter and Kitchell*, 1993; *Cole and Pace*, 1998].

[8] Paul Lake had low nutrient concentrations and low to moderate concentrations of dissolved organic carbon (DOC; Table 1). Peter Lake shared most characteristics with Paul Lake with the main difference that it is larger and deeper (Table 1). Hummingbird is the smallest of the studied lakes and had higher concentrations of both nutrients and DOC relative to Paul and Peter. Paul and Peter were subjected to experimental additions of $NaH^{13}CO_3$ to the mixed surface water layer (0–approximately 2.5 m depth) from June 11 to July 27, 2001 (see *Carpenter et al.* [2005] and *Pace et al.* [2004] for details).

[9] Paul and Peter lakes were sampled 11 times at weekly intervals for CH_4 and dissolved inorganic carbon (DIC) concentration profiles; 5 times for $^{13}CH_4$ profiles; 2 times for water column CH_4 oxidation; and 12 (Paul) and 2 times (Peter) for CH_4 emissions from June 4 to August 28, 2001. Hummingbird Lake was sampled 6 times for CH_4 concentration profiles, once for $^{13}CH_4$ profiles, once for water column CH_4 oxidation, and 4 times for CH_4 emissions. Measurements of temperature and O_2 profiles were performed using an YSI Model 58 O_2 probe along with the CH_4 concentration measurements. Depth profile measurements were performed at the deepest site of the lake while emission and surface water CH_4 concentration measurements were distributed over the entire lake surface.

2.2. Concentration Profiles of CH_4 and DIC

[10] CH_4 concentrations were measured at depth intervals of 0.5 or 1 m as described in detail previously [*Bastviken et al.*, 2004]. Briefly, partially evacuated and pre-capped 118 ml infusion bottles holding 0.2 ml 2.5 M H_2SO_4 as preservative and 50 ml He added by syringe prior to sampling, were lowered to desired depths. The bottles were opened by a remote open/close mechanism [see *Bastviken et al.*, 2004] allowing water to enter the bottles due to the difference in pressure between the bottles and the outside water. After allowing time for the pressure inside and outside the bottle to equilibrate in the bottles were closed in situ. When the bottles

Table 1. Lake Characteristics and Surface Water Chemistry in the Studied Lakes[a]

Lake	Paul	Peter	Hummingbird
Total surface area, m^2	17458	26417	7622
Total volume, m^3	65109	150742	28083
Epilimnetic sediment area, m^2	7879	9132	1366
Epilimnetic volume, m^3	33581	53252	10746
Mean depth, m	3.7	5.7	3.7
pH	6.4	6.9	4.9
Color, G440, m^{-1}	1.5	1.3	19.8
Chlorophyll a, $\mu g\ L^{-1}$; surface water	4.31	3.55	17.72
Dissolved organic carbon, $mg\ L^{-1}$	3.65	4.51	22.01
Total phosphorous, $\mu g\ P\ L^{-1}$	10	8	28
Total nitrogen, $mg\ N\ L^{-1}$	0.38	0.42	0.82
Dissolved inorganic carbon, $mg\ C\ L^{-1}$	1.12	1.69	0.96
Particulate organic nitrogen, $mg\ N\ L^{-1}$	0.05	0.05	0.12
Particulate organic carbon, $mg\ C\ L^{-1}$	0.44	0.41	0.79

[a]Values are simple means from numerous measurements performed 2001–2002 in the studied lakes [*Carpenter et al.*, 2005].

were pulled up from the water they were already tightly sealed and ready for either storage if necessary or for immediate head space analysis after equilibration between the water and the headspace. CH_4 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 CH_4 using Henry's law (Henry's law constants based on *Wiesenburg and Guinasso* [1979]), and accounted for the pressure in the bottles as well as the volume sampled, which both differed with depth due to hydrostatic pressure. Concentration measurements at all depths varied 3.7% on average between replicate samples, and were not biased by the pressure changes induced when water is transferred to the surface by other sampling methods such as pumping or the use of a water sampler.

[11] The gas chromatograph was equipped with a methanizer allowing the determination of dissolved inorganic carbon (DIC) in the same samples that were used for CH_4 analysis. Since the water samples were acidified, the CO_2 measurements followed by water-headspace partitioning calculations according to Henry's law, yielded concentrations of DIC in the water. The DIC values were used primarily for comparing the CH_4 budget with parts of the net DIC budget (see Discussion).

2.3. $^{13}CH_4$ Profiles

[12] CH_4 concentration analysis required less than 10 ml of the 50 ml headspace in the 118 ml infusion bottles. Subsamples from the remainder of the headspace were transferred to 10-mL evacuated exetainers (Labco Limited, High Wycombe, UK) for later $^{13}CH_4$ analysis. Samples from selected depths and dates were analyzed at the UC Davis Stable Isotope Facility (Department of Agronomy and Range Science, Davis, California, USA). Measurements were made using a PDZ Europa (Cheshire, UK) TGII trace gas analyzer and online continuous-flow Europa 20/20 isotope ratio mass spectrometer (IRMS). Isotopic data are reported in δ units (‰) relative to the PDB standard (Pee Dee belemnite) according to $\delta^{13}C = [(R_{sample}/R_{standard}) - 1] \times 10^3$ where R is the $^{13}C/^{12}C$ ratio.

[13] $\delta^{13}C$ CH_4 values were used to qualitatively validate the CH_4 oxidation measurements. This was possible since CH_4 oxidation strongly fractionates against $^{13}CH_4$. As a result, CH_4 oxidation of biogenic CH_4 which is ^{13}C depleted results in enrichment of ^{13}C in the residual CH_4 pool. Hence, shifts in $\delta^{13}C$ signatures can be used to estimate the fraction of the CH_4 oxidized (see *Bastviken et al.* [2002] for more information), and differences in $\delta^{13}C$ signatures among depths were used to confirm the location and relative magnitude of the water column CH_4 oxidation.

2.4. Water Column CH_4 Oxidation

[14] CH_4 oxidation was measured as the CH_4 concentration decline over time in closed vessels as in many previous studies [e.g., *Utsumi et al.*, 1998a], but with the main difference that we used containers with flexible walls instead of rigid glass vials. This allowed repeated sampling from the same containers without pressure changes or the introduction of gas or water to compensate for the sampled volumes. Measurements were performed at 11, 12, and 9 depths in Paul, Peter, Hummingbird lakes, respectively. Water from each depth was pumped into 3–4 replicate medical blood bags (Theruflex transfer bags, Terumo Medical Corporation, volume 1000 ml) equipped with luer-lock fittings, using a battery driven peristaltic pump. The bags were thoroughly flushed with water and care was taken to prevent gas bubbles in the bags. Initial samples for CH_4 concentration (60 mL) were withdrawn with a plastic syringe and transferred to 118 ml infusion vials prepared as described in the CH_4 concentration profiles section above. Subsequently, the transfer bags were lowered to the actual depth for incubation. Additional samples were withdrawn from the bags at approximately 6, 18 and 30 h from the start of the incubation. CH_4 oxidation rates were calculated from the decline in CH_4 concentration in the bags over time. Separate measurements of CH_4 concentrations in the surrounding water were made upon the start of the lake incubations. To account for possible diffusive CH_4 leakage through the bag walls, the diffusion coefficient for such leakage was determined in the laboratory by monitoring concentration changes over time in bags filled with sterile CH_4 saturated water and placed in water with a lower CH_4 concentration. The measured diffusion coefficients and the difference between CH_4 concentrations inside and outside the bags were used to correct CH_4 oxidation rates. CH_4 leakage was negligible relative to CH_4 oxidation at all depths where CH_4 oxidation could be detected. CH_4 oxidation rates were normalized to initial CH_4 concentrations yielding specific CH_4 oxidation rates (in units d^{-1} and corresponding to the fraction of the standing stock of CH_4 being oxidized each day), which were used in mass balance calculations.

2.5. CH_4 Emission

[15] CH_4 emissions were measured using floating chambers as described in detail previously [*Bastviken et al.*, 2004]. Chambers were placed along transects from the shore to the center of the lakes, and we used flux estimates based on a 24 h measurement period. By simultaneously using up to 15 chambers we could separate diffusive flux from ebullition since many of the chambers always showed a relatively low flux with very low between chamber

variability representing diffusive flux, while the other chambers showed much higher flux and greater between chamber variability indicating ebullition (see *Bastviken et al.* [2004] for details). The diffusive flux across the water surface into the floating chamber can be described by the equation $F = k \times (C_w - C_{fc})$, where F is the flux (moles m^{-2} d^{-1}), k is the piston velocity (m d^{-1}), and C_w is the measured CH$_4$ concentration in the water (moles m^{-3}), and C_{fc} is the CH$_4$ concentration in the water given equilibrium with the CH$_4$ partial pressure in the floating chamber [*Cole and Caraco*, 1998]. We used our emission measurements to empirically determine the piston velocity (k; see *Bastviken et al.* [2004] for details). This approach to estimating k yielded similar results to multiple, other approaches including SF$_6$ additions in these and similar lakes [*Cole et al.*, 2006]. The estimated k values and the surface water CH$_4$ concentrations were used to drive diffusive emissions in the mass balance calculations (see below).

2.6. Mass Balance Calculations

[16] Mass balance calculations were made to estimate the flux of dissolved CH$_4$ from the sediments and to compare the magnitudes of different fluxes and fates of lake CH$_4$. Based on information from temperature, O$_2$, and CH$_4$ profiles, the water column of each lake was described as a number of different water strata. The uppermost stratum (referred to as the surface layer or epilimnion) was completely mixed extending to 2.5 m depth in Paul and Peter, but to only 1 m in Hummingbird. The water below the surface layer was divided into 1-m thick strata. Within each stratum instantaneous horizontal mixing was assumed. All profile data were linearly interpolated relative to depth to yield one representative value per stratum for each sampling occasion. CH$_4$ concentration values for each stratum were then interpolated over time using a linear regression, polynomial function, or constant value, depending of best fit. Due to the similarity between CH$_4$ oxidation measurements performed approximately one month apart in Paul and Peter, the specific CH$_4$ oxidation rate was assumed to be constant over time in each stratum. We additionally tested the effect of variability in CH$_4$ oxidation values by making calculations with not only average CH$_4$ oxidation values but also using maximum and minimum values for each stratum for each lake. The piston velocity variability was low compared to surface water concentrations, so we used a constant average k value for each lake. As a consequence, the calculated temporal variation in diffusive CH$_4$ emissions was driven solely by the variation in the surface water CH$_4$ concentration. The total amounts of CH$_4$ in each stratum were calculated iteratively from the time interpolated concentration data and strata volumes. The total amount of CH$_4$ oxidized at each time step was calculated from specific CH$_4$ oxidation rates multiplied by the amount of CH$_4$, and the total diffusive emission per time step was estimated from surface CH$_4$ concentrations and the piston velocity.

[17] The data regarding CH$_4$ concentrations, temperatures and O$_2$ profiles, as well as eddy diffusion calculations according to *Jassby and Powell* [1975] indicated that CH$_4$ transport between some strata was negligible compared to sediment flux, CH$_4$ oxidation, and atmospheric emission (which occurs only in the surface layer). To simplify our analysis, we defined water layers between which negligible
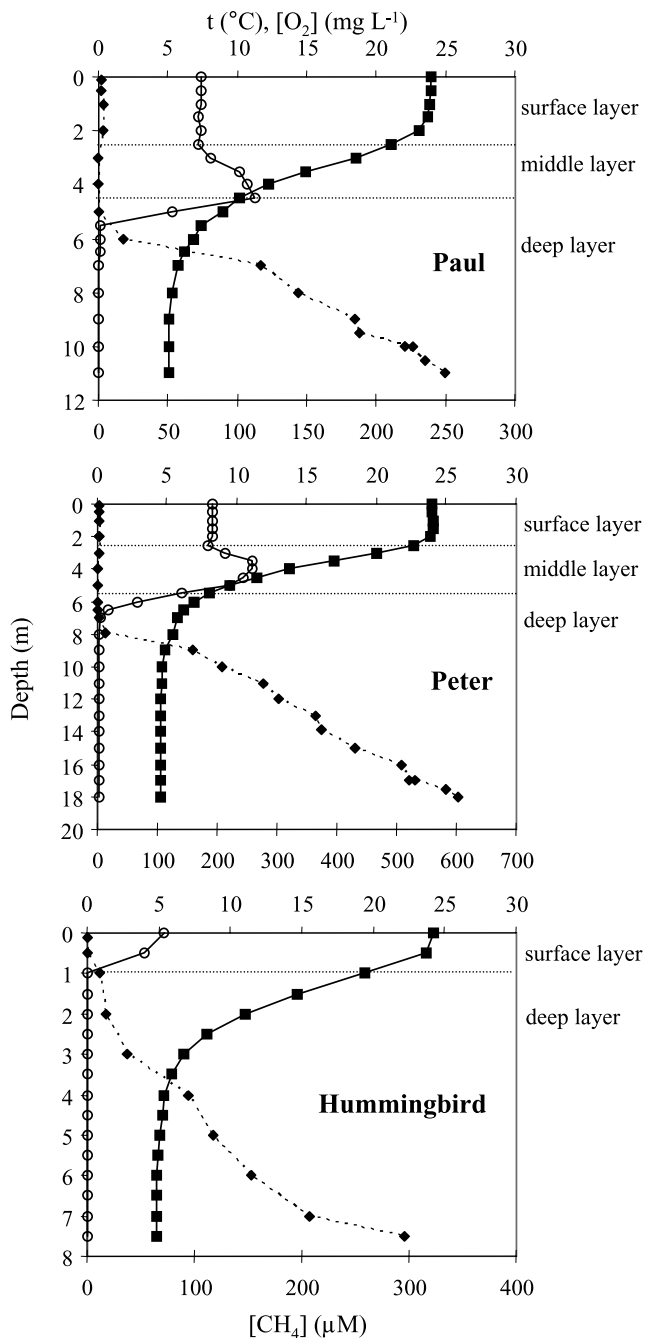

Figure 1. Depth profiles from July of temperature (squares), O$_2$ (circles) and CH$_4$ (diamonds) in Paul, Peter and Hummingbird. The different layers defined in the Methods section for Paul and Peter are shown (see text for details).

CH$_4$ transport occurred. This resulted in two layers below the surface layer in Paul and Peter, and one layer below the surface layer in Hummingbird (Figure 1). We assume no CH$_4$ transport occurred between these layers (discussed below) and thus were able to apply mass balance calculations separately for each layer. The deep layer in Paul and Peter comprised the hypolimnion and the lower metalimnion where CH$_4$ oxidation rates were highest. The lower metalimnion was oxic, while the rest of the deep layer was

anoxic and had high CH_4 concentrations. The middle layer comprised all strata between the deep zone and the surface layer (i.e., the upper metalimnion), and was characterized by having the lowest CH_4 concentration and by a strong temperature gradient. The deep layer in Hummingbird corresponded to the deep layer in Paul and Peter; no obvious middle layer could be identified for Hummingbird. Over time during the summer, the water temperature in the epilimnion and the metalimnion increased slightly, but based on O_2 and CH_4 profiles this did not affect the depth distribution of the mixing pattern. Therefore the depths separating the surface, middle, and deep layers, and thereby also water volumes, were kept constant over time in the calculations.

[18] In this paper the flux of dissolved methane from sediment to the water column will be denoted "DMSF" (dissolved methane sediment flux), while total methane sediment flux (denoted TotMSF) includes both DMSF and the flux due to ebullition. We assumed that the DMSF into the water column was affected by the O_2 concentrations in the water above the sediments and by potential bottom shear stress (induced by turbulence in the water). Oxic bottom water indicated oxic surface sediment in which substantial CH_4 oxidation could occur reducing the DMSF into the water. In turn, the higher potential shear stress in the surface mixed layers could enhance the flux rate through the surface sediment resulting in less time for CH_4 oxidation in the sediment. Thereby, we designed our calculations to allow three different DMSF rates in Paul and Peter. The DSMF per m^2 and time step in the surface layer ($DMSF_{surface}$) was calculated according to $DMSF_{surface} = (\Delta X_{surface} + MOX_{surface} + E_{diff})/S_{surface}$, where $\Delta X_{surface}$ is the change in the total amount of CH_4 in the layer calculated from the concentration change times the volume of the water layer, $MOX_{surface}$ is the total CH_4 oxidation per time step, E_{diff} is the diffusive CH_4 emission to the atmosphere per time step, and $S_{surface}$ is the total sediment surface area in the surface layer. Similarly, in the middle layer the sediment flux per m^2 and time step ($DMSF_{middle}$) was calculated as $DMSF_{middle} = (\Delta X_{middle} + MOX_{middle})/S_{middle}$. The deep layer in Paul and Peter included both oxic and anoxic sediments (Figure 1). The flux from the oxic sediments in the deep layer was assumed to be equal to $DMSF_{middle}$. The flux from sediment overlain with anoxic water ($DMSF_{anox}$) could be calculated from $DMSF_{anox} = (\Delta X_{deep} + MOX_{deep} - DMSF_{middle} \cdot S_{oxdeep})/S_{anoxdeep}$, where ΔX_{deep} and MOX_{deep} are the change in the total amounts of CH_4 and CH_4 being oxidized, respectively, in the deep layer, S_{oxdeep} is the sediment area in the deep layer having oxygenated surface sediments (i.e., overlain by oxic water), and $S_{anoxdeep}$ is the area having anoxic surface sediment. The validity of the assumptions regarding the definition of the layers and the transport of CH_4 between them is addressed in the discussion section below.

[19] According to above, DMSF was estimated from mass balance calculations based on measurements in the water column and of diffusive fluxes from the lake surface. This approach was recommended by *Rudd and Taylor* [1980] and does not rely on assumptions associated with attempts to calculate diffusion or advective transport in sediments or across the sediment water interface based equations in the literature. For example, our approach simply quantifies the flux of dissolved methane regardless of whether diffusion or advective or turbulent flux dominates, so assumptions about the dominating flux mode are not required. The mass balance approach also provides a spatially integrated value and does not rely on local measurements of sediment characteristics affecting flux rates.

3. Results
3.1. CH_4 Concentration and ^{13}C Profiles

[20] CH_4 concentrations ranged from 0.1 to several hundred μM in all studied lakes (Figure 2). Surface water concentrations were typically between 0.5 and 2.6 μM with temporal variability being greater than the spatial variability (up to eightfold and twofold, respectively). In Paul and Peter the minimum CH_4 concentrations were always found in the middle layer. Concentrations in this minimum zone were nearly constant over time. In the deep layer CH_4 concentrations increased with depth and with time over the summer period. As a consequence, the standing stock of CH_4 in the whole water column increased linearly by 75, 29, and 170% in Paul, Peter, and Hummingbird, respectively, during the sampling period (r^2 of 0.96, 0.84, and 0.97, respectively). There was a sharp CH_4 concentration gradient in the upper part of the deep layer corresponding to a decline in O_2 concentrations (Figure 1).

[21] The $\delta^{13}C$ of CH_4 in the deep anoxic part of the water column was stable over time at a level close to $-70‰$ in all lakes (Figure 3). A marked shift to values between $-40‰$ and $-20‰$ occurred in the zone with steep O_2 and CH_4 concentration gradients. Further up in the water column slightly lower $\delta^{13}C$-CH_4 values between $-55‰$ and $-40‰$ were detected. Variability over time (data from Paul and Peter only) was substantial in the middle and surface layers. There was a tendency toward increasing values during the first part of the sampling period followed by a decline. These trends reflect the ^{13}C labeling of the inorganic and particulate organic carbon in these lakes with a time delay. The ^{13}C enrichment of epilimnetic methane in Paul and Peter lakes indicates that some of the methane production arose from recent primary production resulting from fixation of the enriched ^{13}C- in DIC (Figure 4).

3.2. Water Column CH_4 Oxidation

[22] The total CH_4 oxidation rates, ranged from 2.25 to 3.55 mmol m^{-2} (whole lake) d^{-1} and were similar in Paul and Hummingbird and somewhat higher in Peter (Table 2). On a whole-lake basis most of the CH_4 oxidation occurred in the upper hypolimnion and lower metalimnion (80–90%; Figure 5). Comparing CH_4 oxidation on a volumetric basis in individual water layers, average rates in the layer showing highest CH_4 oxidation were 5.57, 6.30, and 2.42 mmol m^{-3} d^{-1} in Paul, Peter, and Hummingbird, respectively. Corresponding rates in the surface layer were 0.25, 0.22, and 0.17 mmol m^{-3} d^{-1}. Over the whole measurement period (84 d), 3602, 7043, and 1295 moles of CH_4 were oxidized in Paul, Peter, and Hummingbird, respectively. This corresponds to 57.6, 112.7, and 20.7 kg CH_4 or 52–55% of the CH_4 released from the sediments (Table 2).

[23] CH_4 oxidation measurements from Paul and Peter indicate highest specific rates in the zone with the steepest CH_4 and O_2 gradients, i.e., in the upper part of the deep
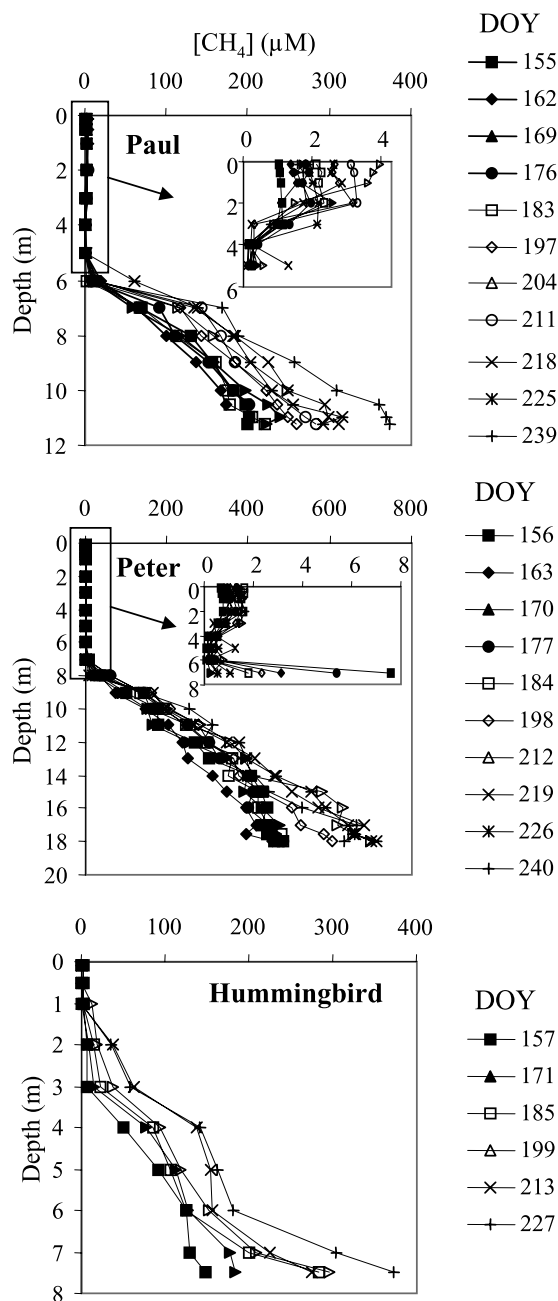
Figure 2. Measured methane concentration profiles in Paul, Peter, and Hummingbird. DOY shown in the legend denotes day of year and refers to the day of sampling.

sive in the oxycline, but the very shallow depth of the oxycline (0.5 m) made the profile look different in Hummingbird relative to Paul and Peter. Both CH_4 oxidation measurements and $\delta^{13}C$ signatures indicate that some CH_4 may have been oxidized below the oxycline and thereby that anaerobic CH_4 oxidation may have occurred in this lake.

3.3. CH₄ Emissions

[24] The measured gas piston velocities (k_{600} in m d^{-1}) were 0.42 ± 0.09, 0.47 ± 0.08, and 0.35 ± 0.06 (average ± 1SD) in Paul, Peter, and Hummingbird, respectively. As expected the piston velocities were positively related with lake size. Within lake variability considering all measurements was less than 22% and remarkably similar in spite of the different sampling frequency among the lakes (see Methods section). We used the average values in the mass balance calculations. Diffusive CH_4 emissions were thereby driven solely by surface CH_4 concentrations according to the equation given in the Methods section. Surface CH_4 concentrations and hence also diffusive emissions could vary up to eightfold between individual sampling days (i.e., much greater variability then for the piston velocity) indicating a considerable variation in the supply of CH_4 from epilimnetic sediments. Diffusive emissions were lowest in Hummingbird, followed by Peter, and the largest diffusive emissions were found in Paul (Table 2).
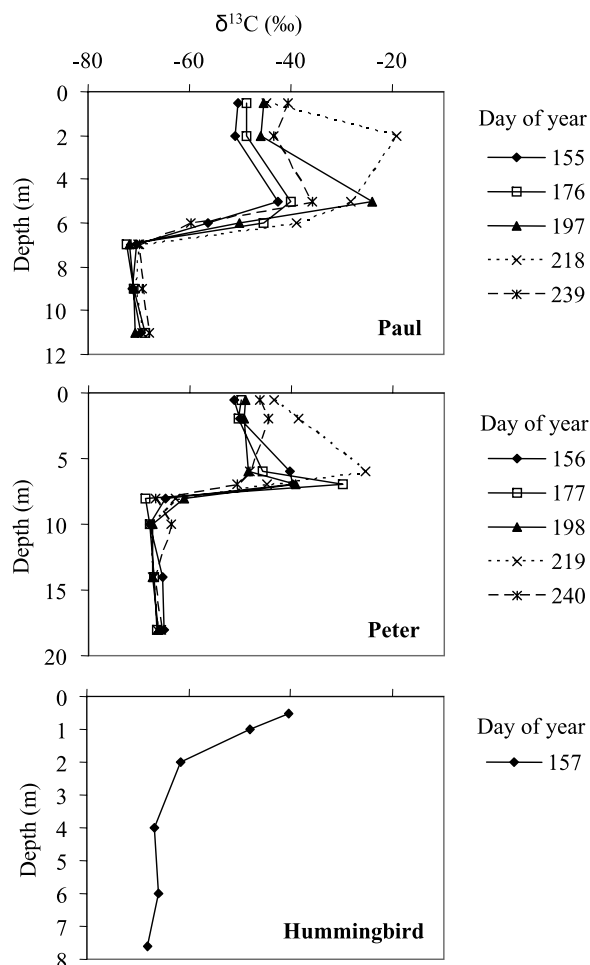

Figure 3. Depth profiles of $\delta^{13}C$ values of CH_4 in Paul, Peter and Hummingbird at different dates.

layer (Figure 5). As much as 80% of the standing stock CH_4 could be oxidized on a daily basis in this layer. The large shifts in $\delta^{13}CH_4$ in this part of the water column of approximately 30‰ (from −70‰ to −40‰) support the estimated rates of oxidation. In the deep anoxic water, CH_4 oxidation was typically not significantly different from zero as indicated both by the CH_4 oxidation measurements and by the lack of a strong gradient of $\delta^{13}CH_4$ (Figures 3 and 5). Specific oxidation rates were also quite low in the middle layer in Peter and Paul – the layer which also had the lowest CH_4 concentrations. Intermediate specific CH_4 oxidation rates were found in the surface layer of Paul and Peter. In Hummingbird, specific CH_4 oxidation was also most exten-
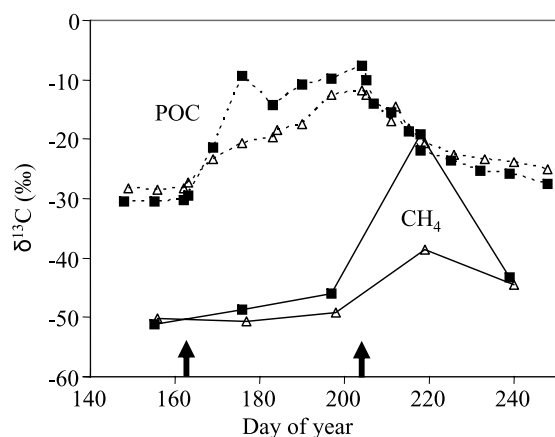
Figure 4. ^{13}C signatures of CH_4 at 2 m depth (solid lines) and particulate organic matter (POC; striped lines) in Paul (solid squares) and Peter (open triangles) over time. POC data from the surface mixed layer obtained from *Carpenter et al.* [2005]. The arrows indicate start and stop date for $NaH^{13}CO_3$ addition to the lake.

3.4. CH_4 Flux From the Sediment

[25] The dissolved methane sediment flux (DMSF) from the sediment into the water column was very similar in Paul and Peter (Table 2). There was a clear difference among depth zones with highest areal flux from sediments overlain with anoxic water. The areal flux from the surface mixed layer was fourfold lower, but still substantial. Very low fluxes were found for the middle layer. Results from Hummingbird showed a similar pattern but with somewhat lower flux rates (Table 2), and the extremely steep gradients of temperature and CH_4 concentration profiles made it impossible to separate out a middle layer in Hummingbird. The flux differences between depths were also reflected by the calculated residence times, corresponding to 4−5 d in the surface layer, 10−19 d in the middle layer, and 36−127 d in the deep layer (Table 2). Hence, 20−25% of the standing stock CH_4 in the surface layer was lost per day due to CH_4 oxidation or emission, and simultaneously replaced by flux from the sediment.

[26] The DMSF only accounts for dissolved CH_4 export from the sediment. To estimate the total CH_4 flux from the sediment (TotMSF), information about CH_4 ebullition from the sediments is also needed. Including ebullition the TotMSF was estimated to range between 4.5 and 6.1 mmol m^{-2} d^{-1} for the studied lakes (Table 2). Ebullition was much more frequent at shallow depths in these lakes [*Bastviken et al.*, 2004], and primarily occurred from sediment in the surface layer. Considering DMSF only, the surface layer sediments accounted for 37, 20, and 10% of the CH_4 flux to the water column in Paul, Peter, and Hummingbird, respectively. Including ebullition the proportion of the TotMSF from the surface layer sediments was 46, 34, and 11%, respectively (Table 3).

4. Discussion

4.1. Evaluation of Assumptions

[27] Our rate estimates depend on the assumption that CH_4 from deep water layers did not (or only in negligible

amounts) reach the surface layer by diffusive or advective processes in Paul and Peter. This assumption was based on concentration gradients which consistently showed lower concentrations in the middle layer than in the surface
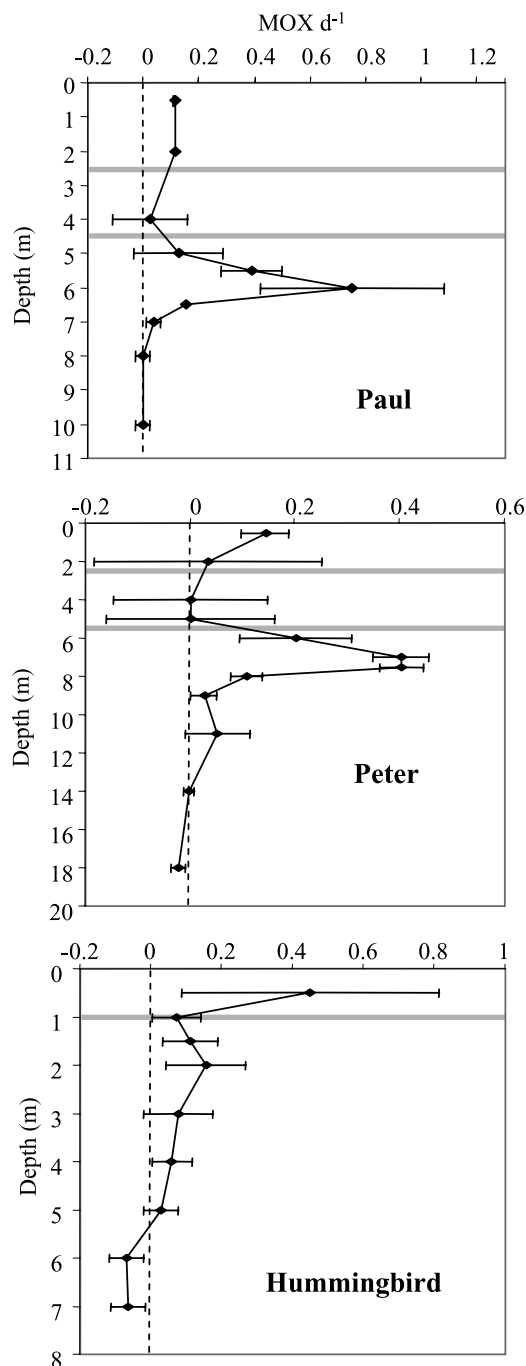

Figure 5. Specific methane oxidation (MOX) rates at different depths in Paul, Peter, and Hummingbird. Averages ± 1 SD are shown. In Paul and Peter data from measurements in both July and August (n = 4 in July and n = 3 in August) are included. In Hummingbird measurements were performed in July only (n = 4). The striped line denotes the zero line for the methane oxidation. The gray horizontal lines show the demarcation of the surface middle and deep layers, respectively (see Figure 1).

Table 2. CH$_4$ Budgets for Paul, Peter, and Hummingbird Lakes During Summer Stratification[a]

	Paul	Peter	Hummingbird
Diffusive emission, mmol m^{-2} d^{-1}; total range in parentheses	0.90 (0.40–1.1)	0.58 (0.36–0.71)	0.22 (0.07–0.55)
Ebullition,[b] mmol CH$_4$ m^{-2} d^{-1}	0.61	1.02	0.27
Average water column CH$_4$ oxidation,[c] mmol m^{-2} d^{-1}	2.45 (2.25–2.62)	3.17 (2.92–3.55)	2.42
Storage in water column, mmol m^{-2} d^{-1}	0.48	1.31	1.81
Average DMSF at different depths,[c] mmol m^{-2} sediment d^{-1}:			
Epilimnion (oxic, high turbulence)	3.21 (3.19–3.23)	3.02	2.36
Metalimnion (oxic, low turbulence)	0.12	0.40 (0.38–0.49)	No middle layer
Hypolimnion (anoxic, intermediate turbulence)	12.87 (11.77–13.83)	12.99 (12.06–14.27)	4.86
Average lake DMSF,[c] mmol m^{-2} d^{-1}	3.87 (3.68–4.04)	5.05 (4.81–5.43)	4.43
Average TotMSF, mmol m^{-2} d^{-1}	4.48	6.07	4.70
Percentage of TotMSF oxidized within the water column during stratification[d]	55%	52%	52%
CH$_4$ residence time, days			
Surface layer (Epilimnion)	4.6	4.3	4.0
Middle layer (Upper metalimnion)	19.9	10.4	Nd
Deep layer (Hypo- and lower metalimnion)	35.7	127.1	74.6
Deep layer DIC accumulation, mmol m^{-2} d^{-1}	*1.46*	*1.72*	*4.02*

[a]Mean ±1 SD. Note that DMSF denotes dissolved methane sediment flux into the water column (see text for details). TotMSF denotes total methane sediment flux and includes both DMSF and ebullition. Unless otherwise noted, average values are given. The net accumulation rate of dissolved inorganic carbon (DIC) in the deep layer is included to for comparison.

[b]Values are normalized to flux per whole lake area to allow comparison in spite of spatially heterogonous distribution of ebullition being related to water depth.

[c]Ranges are based on calculations using maximum and minimum specific CH$_4$ oxidation when measurements were performed at two occasions (only one occasion for Hummingbird).

[d]Note that CH$_4$ oxidation in oxic surface sediments most likely consumes large amounts of CH$_4$, but were not accounted for in this study.

layer (Figure 2). The assumption seems valid because it would be unrealistic for diffusion of CH$_4$ to occur against the prevailing concentration gradient. There may even have been a small flux along the concentration gradient from the surface layer to the middle layer in Paul and Peter. If such a flux occurred, it would make the difference between sediment release from surface and middle layer sediments even greater, but since this flux was very small based on estimates of eddy diffusion coefficients we did not account for it in our calculations. Diurnal measurements of water temperatures showed that day-night advective mixing did not reach below 2.5 m depth down in the water and thereby were not likely to affect CH$_4$ transport patterns across the water layers used in the CH$_4$ mass balance calculations. Significant episodic transport of CH$_4$ from the deep layer to the middle and surface layers due to internal waves should have resulted in lowered deep water accumulation between adjacent measurement dates, but there were no such indications of sudden major transport across the layers in these small lakes. In Hummingbird we could not identify any middle layer with a minimum CH$_4$ concentration. Either such a layer did not exist, or it occurred over finer depth intervals than 0.5 m. Hence, the data supporting our assumptions is less clear-cut for Hummingbird. Finally, the basic assumption is supported by independent studies showing that advective mixing across the aggregated layers in lakes in this area is very small [*Cole and Pace*, 1998; *Houser et al.*, 2003].

4.2. CH$_4$ Concentration and ^{13}C Profiles

[28] The measured CH$_4$ concentrations were in the range of stratified lakes with anoxic hypolimnia [*Bédard and Knowles*, 1997; *Fallon et al.*, 1980; *Rudd and Hamilton*, 1978]. Hypolimnetic CH$_4$ concentrations (up to 700 μM;

Figure 2) were at the high end of this range. Given the low productivity of the studied lakes, the high concentrations may indicate incomplete water column mixing during spring circulation, with some CH$_4$ stored in the deep waters from the previous winter. The highly depleted ^{13}C signatures found for CH$_4$ in anoxic water layers (Figure 3) were consistent with biogenic CH$_4$ production and indicate little or no oxidation [*Whiticar*, 1999]. ^{13}CH$_4$ values higher up in the water column are consistent with significant rates

Table 3. Fates of the Released CH$_4$ in the Studied Lakes During the Sampling Period (82 Days During Summer Stratification)[a]

	Surface	Middle	Deep
Paul			
TotMSF,[b] mol	3027	41	3562
Percentage oxidized	24%	100%	80%
Percentage emitted	76%	0%	0%
Percentage stored in water column	<1%	0%	20%
DIC accumulation, mol			*2140*
Peter			
TotMSF,[b] mol	4577	228	8675
Percentage oxidized	22%	92%	67%
Percentage emitted	77%	0%	0%
Percentage stored in water column	1%	8%	33%
DIC accumulation, mol			*3816*
Hummingbird			
TotMSF,[b] mol	308	-	2296
Percentage oxidized	40%	-	51%
Percentage emitted	60%	-	4%
Percentage stored in water column	0%	-	45%
DIC accumulation, Mol			*2146*

[a]Surface, middle, and deep denote the different layers as indicated in Figure 1 and explained in the text. The total net accumulation of dissolved inorganic carbon (DIC) in the deep layer is included for comparison.

[b]Total methane sediment flux including both flux of dissolved CH$_4$ from sediments to the water and ebullition.

of methane oxidation [*Bastviken et al.*, 2002; *Murase et al.*, 2005; *Whiticar*, 1999] (Figure 3).

4.3. CH$_4$ Oxidation in the Water Column

[29] The methane oxidation profiles we observed are typical for stratified periods in lakes with anoxic hypolimnia [e.g., *Bédard and Knowles*, 1997; *Rudd and Taylor*, 1980] and fall within the range previously reported for water columns (0–17.3 mmol m^{-3} d^{-1} [*Bastviken et al.*, 2002; *Harrits and Hanson*, 1980; *Jannasch*, 1975; *Rudd and Hamilton*, 1975; *Striegl and Michmerhuizen*, 1998; *Utsumi et al.*, 1998a, 1998b]). Decreasing CH$_4$ oxidation rates with decreasing CH$_4$ concentrations near the oxycline are consistent with previous suggestions that both CH$_4$ and O$_2$ concentrations jointly regulate CH$_4$ oxidation rates [e.g., *Sundh et al.*, 2005]. From a methodological point of view, it should be noted that the sensitivity of CH$_4$ oxidation measurements based on concentration changes over time in closed vessels declines with decreasing CH$_4$ concentrations. Hence, large variability in specific CH$_4$ oxidation rates in strata where CH$_4$ concentrations are low (see Figure 5) is probably related to methodological limitations. However, due to the low concentrations, the variability in specific CH$_4$ oxidation at these depths had a minor impact on the total CH$_4$ budget. This was confirmed since mass balance calculations with minimum and maximum CH$_4$ oxidation values only had minor effects on the CH$_4$ sediment flux estimates (Table 2).

4.4. CH$_4$ Flux From the Sediment

[30] The DMSF per unit area of sediment was highest from sediment overlain by anoxic water in all lakes (Table 2). In contrast, the middle layer sediments, characterized by oxic surface sediments and strong temperature gradients had very low areal DMSF (Table 2). The most likely reason is very slow CH$_4$ diffusion and thereby substantial CH$_4$ oxidation within surface sediments. Conditions in the epilimnetic sediments should have also favored extensive CH$_4$ oxidation, but higher water turbulence in the epilimnion presumably transports CH$_4$ from the sediment faster, allowing less time for CH$_4$ oxidation to occur within surface sediments. Consequently, net release rates of dissolved CH$_4$ from the epilimnetic sediments were more than 26 times higher than in the middle layer in Paul and Peter (Table 2). Less extensive CH$_4$ oxidation in sediments of the surface layer was also indicated by lower ^{13}CH$_4$ signatures relative to the CH$_4$ in the middle layer (Figure 3). Independent evidence of turbulence in the surface water layer causing rapid horizontal mixing in the studied lakes has been demonstrated by tests with additions of rhodamine or SF$_6$ [*Cole and Caraco*, 1998; *Cole and Pace*, 1998]. The importance of turbulence for sediment release of CH$_4$ has previously been addressed experimentally [*Bussmann*, 2005; *Murase et al.*, 2005] as well as in the field study of [*Sakai et al.*, 2002]. In the latter study increased release of CH$_4$ was observed following a rapid shift in the thermocline depth probably due to an internal wave. Hence, the present study adds new in situ field indications of continuously enhanced transport through epilimnetic sediments reducing the impact of CH$_4$ oxidation. In large lakes, significant contributions from epilimnetic sediments may result in higher surface water CH$_4$

concentrations along the shore than in the central lake [*Larmola et al.*, 2004; *Schmidt and Conrad*, 1993]. However, our study illustrates that proportionally large contributions from epilimnetic sediments can be the case also when CH$_4$ concentrations are similar in the whole epilimnion possibly due to rapid horizontal mixing.

[31] Assuming that wind induced turbulence can explain the enhanced sediment flux from epilimnetic sediments, this also means that high wind events does not only enhance emissions by the increase in the piston velocity during the wind event itself. The wind event may also substantially increase surface water CH$_4$ concentrations which can sustain elevated emissions for several days after the actual wind event. Such a delayed effect on concentrations could be more important than the short-term effect on the piston velocity for emissions, and could also explain why we found much higher variability for surface water concentrations than for the piston velocity. Very short high wind events could potentially increase water concentrations substantially while having a minor effect on the average daily piston velocity which we measured.

[32] The DMSF rates we observed are within the range of previously reported values (Table 4). Note that our estimates of DMSF from sediments represent net release since we did not account for the CH$_4$ oxidation occurring in oxic surface sediments. Therefore the total CH$_4$ production in surface sediment may have exceeded our estimates. Likewise, the total CH$_4$ oxidation, including sediment methane oxidation, must have exceeded the water column methane oxidation reported here.

4.5. Shallow Sediments and CH$_4$ Emissions

[33] In spite of potentially extensive CH$_4$ oxidation in oxygenated sediments, the TotMSF from surface layer sediments, including both dissolved CH$_4$ flux and ebullition, was 46, and 34% in Paul, and Peter, respectively, of the total whole lake sediment release during the measurement period (Table 3). The corresponding percentage in Hummingbird – a lake with very small sediment area in the shallow surface layer - was 11%. Almost all CH$_4$ emitted from the lakes to the atmosphere by diffusion or ebullition during the stratified period was released from surface layer sediments (Table 3). The result that not only ebullition but also diffusive fluxes depend primarily on shallow sediment processes further illustrates the importance of littoral, and sub-littoral sediments for lake CH$_4$ dynamics and emissions.

[34] CH$_4$ had a short residence time in the surface water layer (4–5 days; Table 2). This explains the high contribution of CH$_4$ from oxic surface sediments in spite of low CH$_4$ concentrations in the epilimnion. Such a situation, with extensive CH$_4$ production in shallow sediments in combination with enhanced transport to the water and the atmosphere due to turbulence, results in an "epilimnetic shortcut" to the atmosphere for CH$_4$. This is in sharp contrast to the long residence time and high CH$_4$ oxidation efficiency for the CH$_4$ released from deep layer sediment. Most of the CH$_4$ being oxidized in the water column in this study was derived from deep profundal sediments (Table 3). Thus the potential of CH$_4$ oxidation to limit CH$_4$ emissions from lakes to the atmosphere can be overestimated in lakes where the epilimnetic shortcut is not considered.

[35] Ebullition, diffusive flux, and the emission of stored CH$_4$ in the water column upon water column circulation

Table 4. Previously Reported Rates of CH_4 Production and Oxidation in Sediment, or Net Flux From Sediment to Water in Lakes[a]

Reference	Lake	Trophic State	Method	Sediment Origin	O_2 Regime in Water Above Sediment	Sediment CH_4 Production, mmol m^{-2} d^{-1}	CH_4 Oxidation in Surface Sediment, % of production	Net CH_4 Flux From Sediment to Water, mmol m^{-2} d^{-1}
Casper [1992]	Fuchskuhle	Acid	Slurry incubation	Profundal		0.42–1.17		
Casper [1992]	Dagow	Eu	Slurry incubation	Profundal		0.67–13		
Liikanen et al. [2002]	Kevätön	Eu	Slurry incubation	Profundal		27–68		
Roy et al. [1994]	Ontario	Meso	Slurry incubation	Prof+Litt		0–42.5		
Casper [1992]	Stechlin	Oligo	Slurry incubation	Profundal		0.25–1.17		
Gal'chenko et al. [2001]	Two Siberian lakes	Dys	Radioisotopes	Prof+Litt		0.006	67%	
Kuivila et al. [1988]	Washington	Meso	Benthic chamber	Profundal	oxic	0.56	50%	0.2–0.3
Huttunen et al. [2006]	Tuusulanjärvi	Eu	Conc gradient calc	Profundal	oxic	4.5		
Huttunen et al. [2006]	Postilampi	Eu	Conc gradient calc	Profundal	anoxic	6.6		
Huttunen et al. [2006]	Soiviojärvi	Eu	Conc gradient calc	Profundal	oxic	0.54		
Huttunen et al. [2006]	Takajärvi	Eu	Conc gradient calc	Profundal	oxic	0.3		
Huttunen et al. [2006]	Ranuanjärvi	Eu	Conc gradient calc	Profundal	oxic	4.75		
Huttunen et al. [2006]	Lokka	Eu	Conc gradient calc	Profundal	oxic	0.03		
Huttunen et al. [2006]	Luiminkajärvi	Meso	Conc gradient calc	Profundal	oxic	1.69		
Huttunen et al. [2006]	Porttipahta	Meso	Conc gradient calc	Profundal	oxic	1.56		
Iversen et al. [1987]	Big Soda Lake	Saline	Conc gradient calc	Profundal	anoxic			2.9
Oremland et al. [1987]	Mono Lake	Saline	Conc gradient calc	Profundal	anoxic			1.32
Liikanen et al. [2002]	Kevätön	Eu	Intact cores	Profundal	oxic	1.9–9.4	66–95%	0.1–3.2
Frenzel et al. [1990]	Constance	Meso	Intact cores	Profundal	oxic	0.5	93%	0.04
Murase et al. [2005]	Biwa	Meso	Intact cores	Profundal	oxic	0.002–1.2	90%	
Murase et al. [2005]	Biwa	Meso	Intact cores	Littoral	oxic	1–8.8	90%	
Kelly and Chynoweth [1980]	Frain's Lake	Eu	Hypolimnion budget	Profundal	anoxic			3.8–9.8
Strayer and Tiedje [1978]	Wintergreen	Eu	Hypolimnion budget	Profundal	anoxic			10–46
Bédard and Knowles [1991]	St George	Meso	Hypolimnion budget	Profundal	anoxic			4.95–14.8
Kelly and Chynoweth [1980]	Third Sister	Meso	Hypolimnion budget	Profundal	anoxic			3.2–4.5
Matthews et al. [2005]	Onodaga	Meso	Hypolimnion budget	Profundal	anoxic			5.6–11.9
Fallon et al. [1980]	Mendota	Eu	Whole lake budget	Profundal	anoxic			35.8
Rudd and Hamilton [1978]	Lake 227	Eu	Whole lake budget	Profundal	oxic			10.8
Rudd and Hamilton [1978]	Lake 227	Eu	Whole lake budget	Littoral	anoxic			0.8
This study	Hummingbird	Dys	Whole lake budget	Littoral	oxic			2.4
This study	Hummingbird	Dys	Whole lake budget	Profundal	anoxic			4.9
This study	Paul	Oligo	Whole lake budget	Littoral	oxic			3.2
This study	Paul	Oligo	Whole lake budget	Profundal	anoxic			12.9
This study	Peter	Oligo	Whole lake budget	Littoral	oxic			3
This study	Peter	Oligo	Whole lake budget	Profundal	anoxic			13

[a]Lake trophic states denoted are acidotrophic (Acid), eutrophic (Eu), mesotrophic (Meso), oligotrophic (Oligo), and dystrophic (Dys) (see *Wetzel* [2001] for definitions). The different methods used have been grouped based on the general approach, and we refer to original references for method details. Mean values or ranges are given.
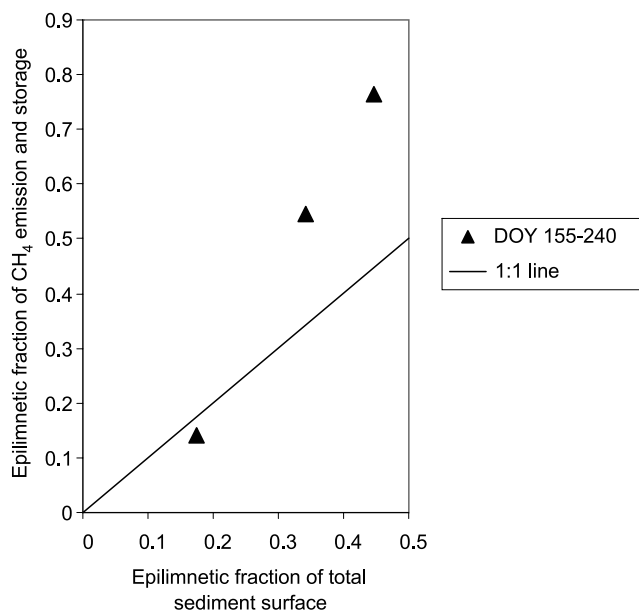
Figure 6. Contribution of epilimnetic CH_4 to total potential emissions to the atmosphere (here diffusive flux, ebullition, and water column storage) versus the proportion of the total sediment area belonging to the epilimnion. CH_4 from epilimnetic sediments accounted for the diffusive flux and most of the ebullition, while CH_4 from hypolimnetic sediments was responsible for the water column storage eventually being released upon lake circulation. Triangles represent the results of the present study based on the measurement period only (DOY 155–240), while the line denotes the 1:1 line.

together comprise the total emission from the studied lakes (emergent plants were nearly absent). Over the measurement period (DOY 155–240) the fraction of ebullition, diffusive emission and water column storage which was accounted for by CH_4 from epilimnetic sediments was 76% in Paul Lake, 55% in Peter Lake, and 14% in Hummingbird. In this calculation it was assumed that methane being stored in the deep layer was eventually emitted during fall lake turnover and this was the primary non-epilimnetic contribution to emissions. The contribution of epilimnetic CH_4 to total emissions appeared proportional to the fraction of the total surface sediment area within the epilimnion (Figure 6). Accordingly, based on data from the three studied lakes, epilimnetic sediments contribute more than 50% of the total CH_4 emitted if the epilimnetic sediment area is above 30% of the total sediment area. Littoral zones have previously been identified as important for CH_4 emissions via aquatic emergent macrophytes [e.g., *Juutinen et al.*, 2003]. Here we show that littoral zones are also of primary importance for non-plant mediated fluxes.

[36] Altogether, shallow (epilimnetic) sediments not only contribute a large proportion of the CH_4 flux to the water, but also seem to contribute most of the CH_4 being emitted to the atmosphere from lakes. Our results indicate that shallow sediments are key sites for lake CH_4 cycling and illustrate the importance of turbulence in influencing biogeochemical transport processes in aquatic ecosystems. In addition, the result that processes in shallow sediments regulate CH_4 emissions from lakes has important implica-

tions for the effects of global warming on future lake emissions. The temperature in shallow sediments is likely to increase with the predicted increase in air and surface water temperatures [*IPCC*, 2007]. Temperature is a main limiting factor for methanogenesis while methane oxidation seems to depend more on factors other than temperature [*Kiene*, 1991; *King*, 1992; *Segers*, 1998]. Consequently, the already considerable lake CH_4 emissions [*Bastviken et al.*, 2004] may increase with increasing temperatures due to the direct temperature effect on methanogenesis rates in shallow sediments. Dramatic increases in CH_4 emissions due to climate warming in Siberian thaw lakes has been proposed by *Walter et al.* [2006]. In such lakes, surrounded by organic rich soils, very high rates of ebullition were observed as a result of thermokarst erosion along lake margins transporting previously frozen labile organic material to lake sediments. In boreal or temperate lakes, such as the lakes in the present study, such dramatic effects on CH_4 emissions following increasing temperatures are not to be expected, but a smaller increase in CH_4 emissions could be significant on a larger scale given the large number of lakes in these climate zones.

4.6. CH_4 as a Potential Food Web Carbon Source

[37] CH_4 oxidation transforms CH_4 carbon to microbial biomass. Several previous studies have addressed the potential use of CH_4 as a carbon or energy source for lake food webs via grazing on methanotrophic bacteria [e.g., *Bastviken et al.*, 2003; *Kankaala et al.*, 2006b, *Taipale et al.*, 2008]. In the studied lakes CH_4 oxidation ranged from 2.4 to 3.6 mmol m^{-2} d^{-1} (Table 2). Comparing with previous studies, *Rudd and Taylor* [1980] and *Striegl and Michmerhuizen* [1998] reported methane oxidation of 2.8 and 0.8–58 mmol m^{-2} d^{-1}, respectively. Assuming an average growth efficiency of 0.4 for methanotrophic bacteria [*Bastviken et al.*, 2003], approximately 1–1.4 mmol C m^{-2} d^{-1} or 12–17 mg C m^{-2} d^{-1} could have been produced as methanotrophic biomass in the water columns of Paul, Peter and Hummingbird. This corresponds to about 4–6% of net primary production (approximately 300 mg C m^{-2} d^{-1} [*Carpenter et al.*, 2001]) and was similar to the pelagic bacterial production in the surface layer [*Kritzberg et al.*, 2006]. Most of the methanotrophic biomass production (80–90%) occurred in the upper part of the deep layer, and the rest (10–20%) in the surface layer. Hence, methanotrophic bacteria and thereby CH_4 carbon, probably contributed only a small quantity of carbon to organisms feeding in surface water layers, but could have represented a significant food source for organisms feeding on bacteria in the oxycline, deeper in the water column.

4.7. CH_4 Versus DIC

[38] The CH_4 production and flux from sediments in the studied lakes was substantial compared to the inorganic carbon fluxes. In the deep layer, the TotMSF of CH_4 was equal to, or up to more than twice as large as the DIC accumulation (Table 3). The accumulation of CH_4 in the deep layer corresponded to 33–76% of the DIC accumulation (Table 2). Since 51–80% of the CH_4 entering the deep layer was oxidized (Table 3) sediment methanogenesis must have been the source for a large share of the DIC in the hypolimnia. Similarly, a previous study of lakes in the same

area report that CH_4 accounted for more than 25% of the DIC and CH_4 accumulation in 14 out of 21 studied lakes [*Houser et al.*, 2003]. Hence, a large proportion of the organic matter mineralization in the deep layer must have occurred through methanogenesis during stratification.

5. Conclusion

[39] Epilimnetic sediments represent a key element for understanding CH_4 dynamics and fluxes based on our study of whole lake CH_4 budgets. Physical factors such as turbulence have an important influence on transport patterns and process rates at the ecosystem scale. Thereby, this study suggests that low CH_4 environments (oxic surface sediments and oxic water) are important for CH_4 cycling and emissions. Many previous studies on CH_4 in lakes have focused on lakes with anoxic hypolimnia having high CH_4 concentration, and on the often extensive CH_4 oxidation in stratified water columns. This study indicates that future studies should also focus on areas in lakes of low CH_4 concentrations in combination with short CH_4 residence times where a major routing of CH_4 to the atmosphere occurs.

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