

# Extreme Methane Emissions from a Swiss Hydropower Reservoir: Contribution from Bubbling Sediments

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Received October 14, 2009. Revised manuscript received February 3, 2010. Accepted February 15, 2010.

Methane emission pathways and their importance were quantified during a yearlong survey of a temperate hydropower reservoir. Measurements using gas traps indicated very high ebullition rates, but due to the stochastic nature of ebullition a mass balance approach was crucial to deduce system-wide methane sources and losses. Methane diffusion from the sediment was generally low and seasonally stable and did not account for the high concentration of dissolved methane measured in the reservoir discharge. A strong positive correlation between water temperature and the observed dissolved methane concentration enabled us to quantify the dissolved methane addition from bubble dissolution using a system-wide mass balance. Finally, knowing the contribution due to bubble dissolution, we used a bubble model to estimate bubble emission directly to the atmosphere. Our results indicated that the total methane emission from Lake Wohlensee was on average  $>150 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ , which is the highest ever documented for a midlatitude reservoir. The substantial temperature-dependent methane emissions discovered in this 90-year-old reservoir indicate that temperate water bodies can be an important but overlooked methane source.

## Introduction

There is growing interest and concern regarding greenhouse gas emissions, mainly carbon dioxide ( $\text{CO}_2$ ) and methane ( $\text{CH}_4$ ), from lakes and reservoirs (1–4). Organic-rich sediments in lakes and reservoirs are thought to be ‘hot spots’

of methanogenesis in particular, from which  $\text{CH}_4$  can escape to the atmosphere via four major pathways - ebullition (bubbling), surface diffusion, advection through plants, and exposure of anoxic  $\text{CH}_4$ -rich deep waters to the atmosphere during convective mixing events (turnover) (1). Additionally, gas is emitted from  $\text{CH}_4$ -saturated dam releases (5). Typically, surface diffusion is the dominant atmospheric emission pathway for  $\text{CO}_2$  and for  $\text{CH}_4$  from deep water bodies ( $>50 \text{ m}$ ) (6, 7). The low solubility of  $\text{CH}_4$  relative to  $\text{CO}_2$  means that  $\text{CH}_4$  bubbles form more readily with typical diameters ranging from 2 to 8 mm (7–9). While these bubbles typically dissolve in deep systems, in shallow waters ( $<50 \text{ m}$ ) ebullition is the dominant  $\text{CH}_4$  emission pathway because limited dissolution occurs during bubble ascent (9, 10). Microbial oxidation depletes  $\text{CH}_4$ , mainly at the intersection of  $\text{CH}_4$  and  $\text{O}_2$  gradients near sediment-water interfaces and oxyclines (11, 12).

$\text{CH}_4$  bubble formation and transport to the atmosphere, combined with  $\text{CH}_4$ 's large global warming potential ( $\sim 25$  times more than that of  $\text{CO}_2$  over a 100 year period) (13), suggests that  $\text{CH}_4$  emissions are important to understand and monitor. The methane fluxes from reservoirs reported in the literature, however, are very discordant and range over an order of magnitude (2, 3).

The aquatic methane fluxes are difficult to accurately estimate because measuring all the different flux pathways is complicated and time-consuming, particularly due to the high degree of spatial and temporal variability. Therefore, the goal of this study was to quantify the methane emission pathways within a relatively small run-of-river reservoir over a full year and then apply a system analytical mass balance approach to better calculate the methane diffusion and ebullition from sediments using basin-wide dissolved methane concentrations. Finally, all estimates were compared and validated based on actual observations, and seasonal methane pathways and associated fluxes from the reservoir were calculated.

## Materials and Methods

**Study Site.** Lake Wohlensee, a run-of-river hydropower reservoir located on the Aare River downstream of the city of Bern (Switzerland), was studied because of extensive ebullition observed during a previous campaign. Completed in 1920, the reservoir has a surface area of  $\sim 2.5 \text{ km}^2$  and holds  $22 \times 10^6 \text{ m}^3$  of water with a maximum depth of 18 m near the dam (mean depth  $\sim 10 \text{ m}$ ). Located in a temperate region, the reservoir experiences seasonal water temperatures ranging from  $\sim 5 \text{ }^\circ\text{C}$  in winter up to nearly  $20 \text{ }^\circ\text{C}$  in summer (Figure 1a) (14). The turbine release is  $\sim 10\text{--}14 \text{ m}$  below the lake surface. The yearly average discharge ( $Q$ ) of  $\sim 122 \text{ m}^3 \text{ s}^{-1}$  ( $\sim 40\text{--}400 \text{ m}^3 \text{ s}^{-1}$ ; Figure 1a) results in a mean water residence time of  $\sim 2$  days ( $7.2\text{--}0.7$  days) (15). Due to the short residence time and energetic mixing, the entire water column of Lake Wohlensee is oxic year round.

Lake Wohlensee receives a relatively large amount of organic and nutrient loading as it is located directly downstream of Bern, Switzerland and three wastewater treatment plants. Total organic carbon (TOC) concentration in the inflow is  $\sim 2.4 \text{ mg L}^{-1}$ , while  $\sim 1.9 \text{ mg L}^{-1}$  is in the form of dissolved organic carbon (DOC). Total phosphorus and nitrogen are on average  $30 \text{ } \mu\text{g P L}^{-1}$  and  $1 \text{ mg N L}^{-1}$ , respectively (16). Sediment dissolved oxygen uptake was determined to be around  $35\text{--}40 \text{ mmol m}^{-2} \text{ d}^{-1}$  (17), which is typical for mesotrophic-eutrophic reservoirs. Macrophytes are largely absent. Sediments consist mainly of clay and fine silt and contain about 2% organic carbon, except in the upstream region where they tend to be much coarser and enriched in mineral particles (18).

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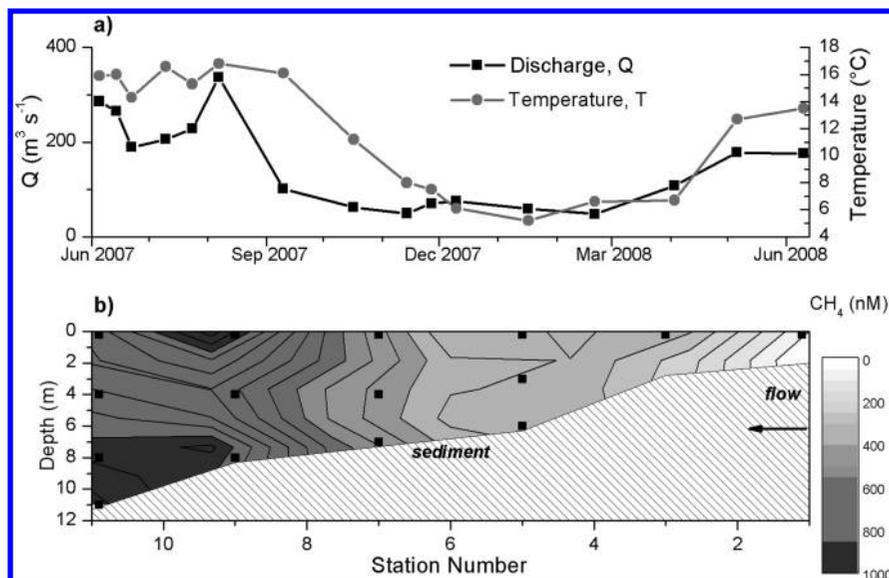
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**FIGURE 1.** a) Temperature and discharge,  $Q$ , in Lake Wohlen during samplings.  $Q$  ranges from  $\sim 400 \text{ m}^3 \text{ s}^{-1}$  in summer (residence time,  $R_t$ ,  $\sim 1$  day) to  $50 \text{ m}^3 \text{ s}^{-1}$  in winter ( $R_t \sim 7$  days). b) Contour plot of dissolved methane distribution in Lake Wohlen on June 21, 2007. Black squares - actual samplings. Water flows in from right to the dam (left). Profiles were taken every kilometer at a vertical resolution of 3–4 m. The figure suggests that methane is vertically homogeneous, while concentrations can increase five times horizontally.

**Sampling Summary.** Methane fluxes were assessed based on multiple sampling campaigns and are reported as areal fluxes in  $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1} \pm 1$  standard deviation. Dissolved  $\text{CH}_4$  concentrations ( $[\text{CH}_4]_d$ ) were measured at the inflow ( $M_{\text{IN}}$ ) and outflow ( $M_{\text{OUT}}$ ) of the reservoir approximately monthly from June 2007 until June 2008 (total, 14 campaigns). The longitudinal and vertical distribution of  $[\text{CH}_4]_d$  were measured during three additional surveys in June, July, and December of 2007. Diffusion from the sediment to the water column ( $M_{\text{SD}}$ ) was estimated from Fick's First Law of diffusion and  $\text{CH}_4$  gradients in the porewater from 15 cores taken in September and November of 2006 and July, November, and December of 2007. Gas exchange of  $\text{CH}_4$  at the water–air interface ( $M_{\text{WD}}$ ) was calculated as described below based on  $[\text{CH}_4]_d$  measurements taken on 20 sampling days between June 2007 and July 2008, as well as directly measured with anchored floating chambers (AC) in July 2008. Gas trap funnels were used to measure bubble flux from the sediment ( $M_{\text{BF}}$ ) during surveys conducted in August and October 2007. The remaining pathways - bubble dissolution ( $M_{\text{BD}}$ ) and bubble emission to the atmosphere ( $M_{\text{BE}}$ ) - were estimated using a bubble dissolution model. Finally, drifting chambers (DC) were deployed in July 2008 to measure total atmospheric emissions via diffusion and ebullition over the lake surface.

**Methane Inflow, Outflow, and Distribution.**  $[\text{CH}_4]_d$  inflow samples were collected monthly  $\sim 6$  km upstream of the dam (Figure S1a of the Supporting Information, right star) at a shallow ( $< 5$  m) area with relatively fast-flowing conditions. The  $[\text{CH}_4]_d$  outflow samples were taken at 0, 4, 8, 12, and 16 m depths on the reservoir-side of the dam before turbine passage (Figure S1a, left star). Average profile concentrations were used for the discharge. The three longitudinal surveys conducted for  $[\text{CH}_4]_d$  distribution included profiles every kilometer through the center of the  $\sim 7$  km long reservoir at a vertical resolution of 3–4 m (e.g., Figure 1b). From the inflow ( $[\text{CH}_4]_{\text{IN}}$ ) and outflow ( $[\text{CH}_4]_{\text{OUT}}$ ) concentration results of the monthly and longitudinal surveys (sampling method details can be found in the Supporting Information), the mass of dissolved methane increase along the reservoir was calculated as

$$\frac{\Delta[\text{CH}_4]}{\Delta t} \times V = Q \times [\text{CH}_4]_{\text{OUT}} - Q \times [\text{CH}_4]_{\text{IN}} \quad (1)$$

where  $V$  is the volume of the reservoir, and  $Q$  is the discharge.

**Sediment Methane Emissions.** The methane gradient was measured in the porewater of the top 10 cm of 15 cores from different locations along the reservoir (18) (see the Supporting Information for sampling details). Methane gas exchange at the sediment surface was calculated using Fick's First Law of diffusion and the molecular diffusivity given by Furrer and Wehrli (19). Oxidation partially controls the dissolved  $\text{CH}_4$  concentrations near the sediment–water interface (12, 20); however, the 1 cm vertical sampling resolution did not allow us to resolve dissolved  $\text{CH}_4$  within the top boundary layer. In most of the cores sediment methane concentrations decreased linearly from  $\sim 10$  cm sediment depth toward the sediment–water interface, likely due to methane oxidation (18), and since the fine-scale details of the methane gradient at the surface were unknown, we used the  $\text{CH}_4$  concentration difference between the top sediment layer and the sediment layer at 1 cm depth to calculate a first estimate of the sediment diffusive  $\text{CH}_4$  flux.

Sediment methane ebullition was measured with custom-made gas traps, which are inverted funnels with an opening of  $\sim 0.785 \text{ m}^2$  surface area (see Figure S1b and the extended methods section in the Supporting Information for design and sampling procedures). August gas trap surveys (Figure S1a, filled triangles) covered almost the entire length of the reservoir in random locations. The October surveys (Figure S1a, empty triangles) focused on the more active bubbling areas of the reservoir. In total, 38 measurements of ebullition were obtained from 26 different locations that varied from 2 to 16.5 m water depth.

**Bubble Dissolution and Atmospheric Emission.**  $\text{CH}_4$  bubbles exchange gases with the surrounding water (e.g., a pure  $\text{CH}_4$  bubble will gain oxygen and nitrogen and lose  $\text{CH}_4$ ) as they rise in the water column, thus a bubble gas exchange/dissolution model was used to predict the fractions of methane that dissolve in the water column and the fraction that reaches the atmosphere (see ref 7 for details). The model was run for each funnel measurement. The water was assumed to be saturated with nitrogen and oxygen, while actual measured values of temperature and dissolved methane were used. Finally, for the purpose of this calculation, the initially released bubble was assumed to be pure methane

**TABLE 1. Point Measurements and System-Wide Estimates from System Analysis of Methane Fluxes**

pathway (methods)	notation	point measurements <sup>a</sup> (mg CH <sub>4</sub> m <sup>-2</sup> d <sup>-1</sup> )	system-wide estimates <sup>a</sup> (mg CH <sub>4</sub> m <sup>-2</sup> d <sup>-1</sup> )
sediment diffusion (porewater cores)	$M_{SD}$	41 ± 42	15 ± 9
surface diffusion (anchored chambers - AC)	$M_{WD}$	12 ± 7	--
surface diffusion ([CH <sub>4</sub> ] <sub>d</sub> , wind speed, BLE)	$M_{WD}$	1.5 ± 1.0	--
bubble flux (average of all gas trap measurements)	$M_{BF}$	~1000 ± 1300 <sup>b</sup>	--
bubble flux (gas traps spatially weighted)	$M_{BF}$	~700 <sup>b</sup>	470 <sup>b</sup>
bubble dissolution (bubble model and gas traps spatially weighted)	$M_{BD}$	~220 <sup>b</sup>	140 <sup>b</sup>
surface bubble emission - (bubble model and gas traps spatially weighted)	$M_{BE}$	~480 <sup>b</sup>	330 <sup>b</sup>
outflow ([CH <sub>4</sub> ] <sub>d</sub> )	$M_{OUT}$	~59 <sup>b</sup>	~58 <sup>c,d</sup>
CH <sub>4</sub> oxidation	$M_{OX}$	negligible	--
total atmospheric emission (drifting chambers - DC)	$M_{ATM}$	855 ± 824 <sup>b</sup>	~156 <sup>c</sup>

<sup>a</sup> Values are means ± SD. <sup>b</sup> At 17 °C. <sup>c</sup> Annually integrated daily average. <sup>d</sup> Calculated as  $M_{SD} + M_{BD} +$  measured  $M_{IN}$  - measured  $M_{WD}$ ; [CH<sub>4</sub>]<sub>d</sub>, dissolved CH<sub>4</sub> concentration; BLE, boundary layer equation.

and have a diameter of 6 mm, which is an average size often reported in the literature (7–9).

**Surface Methane Emissions.** Gas exchange at the air–water interface was measured using ACs as well as by the boundary layer equation (e.g., ref 21)

$$J_L = K_x \times (C_w - C_{eq}) \quad (2)$$

where  $K_x$  is the gas exchange coefficient,  $C_w$  is the average surface [CH<sub>4</sub>]<sub>d</sub>, which was directly measured, and  $C_{eq}$  is the atmospheric equilibrium concentration of CH<sub>4</sub> calculated according to Wiesenburg and Guinasso (22) and the 2005 estimate for atmospheric CH<sub>4</sub> concentration (1774 ppb) (13).  $K_x$  was calculated using eqs 3 and 5 of Crusius and Wanninkhof (23) and incorporates wind speed data that were measured ~2 km away (24).

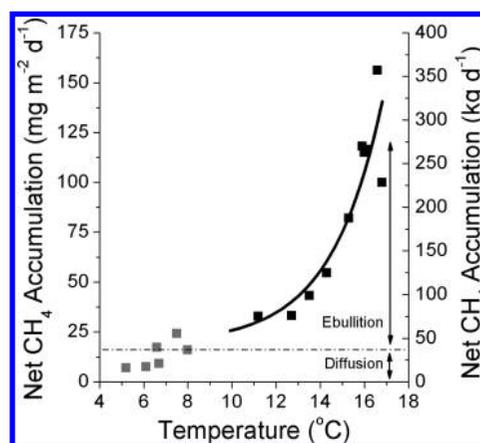
ACs were anchored at bubble-free locations in the dam basin and used to measure CH<sub>4</sub> diffusion to the atmosphere during two 2-day campaigns. For chamber design and gas sampling details, see Figure S1c and the extended methods section of the Supporting Information. Gas flux was calculated from the increase in methane concentration during the measuring period. Surface water samples for [CH<sub>4</sub>]<sub>d</sub> were taken next to the AC at each gas sampling.

DCs were constructed nearly the same way as ACs (see the Supporting Information) but were not anchored. DC surveys yielded total surface methane emissions due to both ebullition and diffusion and therefore account for the intermittency and spatial variability of ebullition. Two 2-day campaigns were conducted in which transects lasted up to an hour covering ~0.5 km. See the Supporting Information for sampling and analysis details.

**Methane Oxidation.** Two 2-day methane oxidation experiments were conducted in July 2008 according to the method of Bastviken et al. (11), in which flexible airtight containers were moored at 4.5 and 8.5 m depths in the reservoir. Water temperature was ~17 °C during both campaigns. Enclosed waters were sampled every few hours for 2 days, corresponding to the average water residence time of the reservoir, and poisoned and analyzed using the same sampling procedure described in the Supporting Information for other water samples.

## Results

**Longitudinal and Temporal Changes of Methane.** Dissolved methane at the upstream sampling station ([CH<sub>4</sub>]<sub>IN</sub>) ranged throughout the year from 50 to 290 nM (average ~170 nM; Table S1 in the Supporting Information). At the dam, [CH<sub>4</sub>]<sub>d</sub> before turbine passage ([CH<sub>4</sub>]<sub>OUT</sub>) ranged from 280 nM in winter to 2200 nM in summer (yearly average ~850 nM; Table



**FIGURE 2.** Dissolved methane accumulation (net flux [kg d<sup>-1</sup>] =  $Q \times ([CH_4]_{OUT} - [CH_4]_{IN})$  or areal flux in mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> when divided by the lake area) in Lake Wohlen is very strongly and exponentially correlated with temperature. Methane sediment diffusion flux (gray points and dashed line) is treated as relatively constant through the year at ~15 mg m<sup>-2</sup> d<sup>-1</sup>, while the exponential increase at temperatures >10 °C (black points) is attributed to contributions from bubble dissolution.

S1). Each longitudinal survey of [CH<sub>4</sub>]<sub>d</sub> revealed immense increases of dissolved methane (up to 5×) along the reservoir and relatively well-mixed conditions vertically (e.g., Figure 1b). The average daily [CH<sub>4</sub>]<sub>d</sub> discharge was estimated by integral averaging the product of the monthly [CH<sub>4</sub>]<sub>d</sub> release and  $Q$  over the sampling year and dividing by reservoir surface area, thus yielding ~59 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> (Table 1). The mass accumulation calculated for each survey was positively and exponentially correlated with water temperature ( $r^2 = 0.92$ ; Figure 2).

**Sediment Methane Emissions.** Sediment diffusion calculated from the 15 cores ranged from ~1 to 150 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> (Table S1) with an average of 41 ± 42 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> (Table 1).

Gas traps that were deployed to capture sediment bubble flux (Figure S1a) measured extremely variable ebullition rates (Table S2, Supporting Information). The overall average was ~1000 ± 1300 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> (Table 1), and ~29% recovered no detectable ebullition. The standard deviation of the bubble flux measurements highlights the stochastic nature of ebullition over space and time. However, the mean fluxes and 95% confidence levels of the October 2007 survey measurements, in which locations were biased toward bubbling areas, were similar to those of the August 2007 survey when random locations were chosen (Figure S2, Supporting Information). Gas samples contained on average

74% CH<sub>4</sub>, and bubbles typically traveled <2 m through the water column before being collected in the funnel cylinder.

It was evident by the flux measurements and visual observations along the reservoir that there was considerable spatial heterogeneity in ebullition. Therefore, we used both the bathymetry and the similarity in flux measurements to divide the reservoir into 4 regions (Figure S1a) with average rates of ebullition calculated for each region. Thus, a spatially weighted ebullition flux from the sediment into the water column for the late summer/early fall season (~700 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>, Table 1) was found by summing the ebullition fluxes from the different regions.

**Bubble Dissolution and Atmospheric Emission.** As it is impossible to accurately measure bubble dissolution and emission to the atmosphere, we performed a system mass balance described later in the System Analysis section. The first step, however, was to estimate which fraction of sediment-released bubbles dissolves in the water column and which fraction escapes to the atmosphere. These values were estimated using a bubble dissolution model (7) with boundary background [CH<sub>4</sub>]<sub>d</sub> profiles, which ranged from 5 nM to 3500 nM, along with the parameters previously described. As bubbles typically contain mostly CH<sub>4</sub> and perhaps some nitrogen as they exit the sediment (8), and as this calculation was to determine what fraction of the initial methane content of a bubble would reach the surface, we assumed 100% CH<sub>4</sub> concentration in the bubble model and found that ~70% of the initial methane in a bubble reaches the atmosphere with the remaining 30% dissolving in the water column upon ascent. In addition, selecting CH<sub>4</sub> compositions ranging from 70–100% did not significantly affect the results in terms of atmospheric CH<sub>4</sub> emissions (e.g., using 74% CH<sub>4</sub> composition in the model results in 65% of the initial CH<sub>4</sub> reaching the atmosphere).

As a first estimate using the gas trap volumetric measurements and the same regional subdivisions mentioned above, we calculated a spatially weighted average for bubble dissolution as ~220 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> and ~480 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> as bubble emission to the atmosphere (Table 1).

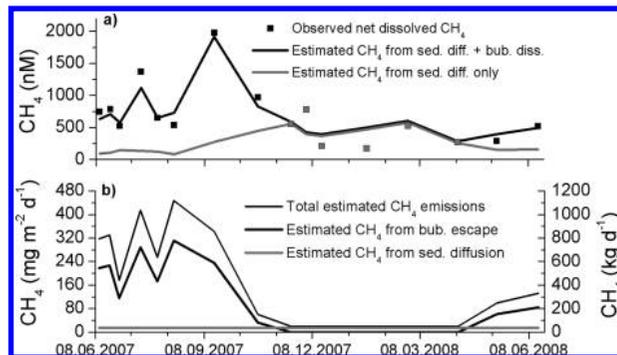
**Surface Methane Emissions.** Based on the average surface [CH<sub>4</sub>]<sub>d</sub>, diffusion across the air–water interface was calculated with eq 2 and ranged from ~0.1 to ~4 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> (Table S3 in the Supporting Information) with an average of 1.5 ± 1.0 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> (Table 1). The average directly measured methane diffusion using all AC values was 12 ± 7 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> (Table 1 and Table S3) and was higher than the calculated fluxes, as also observed in other studies (21, 25). All DC samplings were used to estimate total CH<sub>4</sub> emissions from the reservoir surface (i.e., diffusion and ebullition), and the results varied greatly (Table S3) with an average of 855 ± 824 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> (Table 1).

**Methane Oxidation.** The results from the methane oxidation experiments did not indicate significant, if any, methane oxidation over the residence time of water in the reservoir (data not shown). At no point during the course of the two oxidation experiments was a loss of methane observed.

## Discussion

**System Analysis.** We used a system analytical mass balance approach to deduce the internal sources of methane to the water column and the CH<sub>4</sub> emission to the atmosphere based on the following considerations:

- The mass of CH<sub>4</sub> accumulating in the water as it passes through the reservoir is only from sediment diffusion ( $M_{SD}$ ) and bubble dissolution ( $M_{BD}$ ).
- Methane oxidation in the water column is negligible, as suggested by conducted experiments. Diffusion at the air–water interface represents the only sink for dissolved methane and is nearly negligible.



**FIGURE 3.** Lake Wohlen system analysis results. a) Squares indicate measured dissolved methane in Lake Wohlen (out-flow - inflow). Black squares indicate measurements at water temperatures,  $T > 10$  °C when ebullition is occurring, gray squares when  $T < 10$  °C (see Figure 2). Gray line - best fit of predicted concentration due to sediment diffusion (sed. diff.) only. Black line - model results for predicted CH<sub>4</sub> concentration using exponential fit for methane bubble dissolution (bub. diss.) as a function of temperature plus the constant sediment diffusion of 15 mg m<sup>-2</sup> day<sup>-1</sup> (Figure 2). b) CH<sub>4</sub> emission rates: Gray line - constant sediment diffusion input. Thick black line - predicted methane emission due to methane bubbles reaching the atmosphere (bub. escape). Thin black line - total predicted methane flux including dam discharge emissions.

• The only methane source to the water column during the winter was  $M_{SD}$ . Seasonal observations, measurements, and sonar surveys of Lake Wohlen (Del Sontro, unpublished data) indicate that ebullition is severely diminished during the colder winter months.

Thus, Lake Wohlen represents a relatively simple system for deducing the methane source fluxes - ebullition and sediment diffusion.

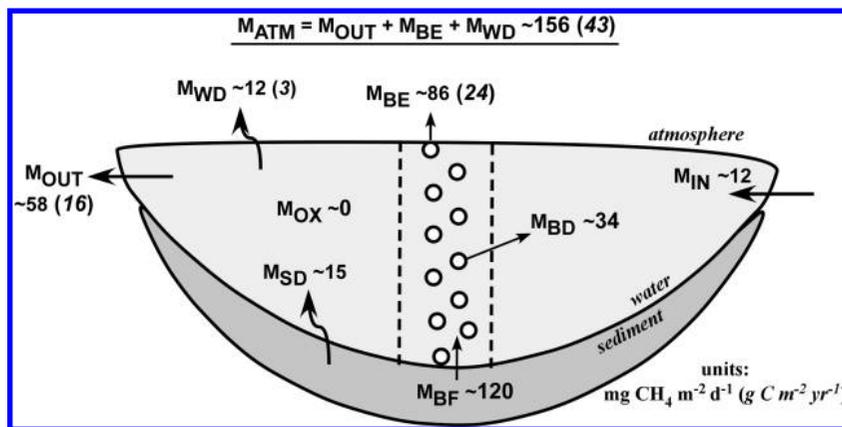
We began by calculating the  $M_{SD}$  values required to account for the observed [CH<sub>4</sub>]<sub>d</sub> during the 6 winter samplings (water temp <10 °C, November 2007 through April 2008) using  $Q$  for each day. This was performed by adjusting the sediment flux value until it most closely matched the observed concentration values ([CH<sub>4</sub>]<sub>d</sub> =  $M_{SD}/Q$ ; see Figure 3a). The average of these calculated values (15 ± 9 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>, Table 1) was used as the baseline  $M_{SD}$  in the subsequent calculations (Figure 3a), meaning that  $M_{SD}$  represents a rather seasonally constant source of CH<sub>4</sub> to the water column, as demonstrated below.

Next,  $M_{BD}$  could be determined as the difference between the measured [CH<sub>4</sub>]<sub>d</sub> accumulation and the amount contributed by the baseline  $M_{SD}$  for the  $Q$  at the time of sampling, i.e., any observed CH<sub>4</sub> accumulation in the water that cannot be attributed to  $M_{SD}$  must be due to the dissolution of CH<sub>4</sub> bubbles escaping the sediment. In fact, once the baseline  $M_{SD}$  was subtracted from the observations, the remaining CH<sub>4</sub> increases were exponentially correlated with temperature (Figure 2).  $M_{BD}$  can therefore be estimated as a function of temperature  $T$  (in °C) using

$$M_{BD} = 0.16e^{0.40T} \quad (3)$$

( $r^2 = 0.92$ ) for temperatures in the range 10–17 °C. Estimated  $M_{BD}$  ranged from ~13 mg m<sup>-2</sup> d<sup>-1</sup> at 11 °C to ~140 mg m<sup>-2</sup> d<sup>-1</sup> at 17 °C (the maximum temperature observed during sampling, Table 1). The estimated [CH<sub>4</sub>]<sub>d</sub> values fit the observed seasonal pattern of [CH<sub>4</sub>]<sub>d</sub> well, reproducing both seasonal patterns and the magnitude of net dissolved CH<sub>4</sub> in the reservoir (Figure 3a).

Finally, we used the estimated  $M_{BD}$  and the average fraction of CH<sub>4</sub> escaping rising bubbles (30%), as calculated from the bubble dissolution model, to determine the ebul-



**FIGURE 4.** Average basin scale methane fluxes and pathways in L. Wohlen in  $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  ( $\text{g C m}^{-2} \text{ yr}^{-1}$ ) derived from the system analysis or, if not available, from measurements. Pathways are as follows:  $M_{\text{ATM}}$ , emission to atmosphere;  $M_{\text{WD}}$ , water surface diffusion;  $M_{\text{BE}}$ , bubble emission to atmosphere;  $M_{\text{BD}}$ , bubble dissolution;  $M_{\text{SD}}$ , sediment surface diffusion;  $M_{\text{IN}}$ , dissolved methane input;  $M_{\text{OUT}}$ , methane discharge passed dam;  $M_{\text{BF}}$ , sediment bubble flux driving the entire methane balance. Dashed lines outline bubble pathway. The main portion of methane is directly released to the atmosphere, and the second part is dissolved to the water phase.

lition flux from the sediment ( $M_{\text{BF}}$ , 100%) and to the atmosphere ( $M_{\text{BE}}$ , 70%). Thus, we determined that  $M_{\text{BF}}$  ranges from  $\sim 40 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  at  $11^\circ \text{C}$  up to  $\sim 470 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  at  $17^\circ \text{C}$  resulting in a  $M_{\text{BE}}$  of  $\sim 30$  to  $\sim 330 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  to the atmosphere between  $11$  and  $17^\circ \text{C}$  (Table 1).

**Reservoir Surface Methane Emissions.** Ebullition emissions to the atmosphere at  $17^\circ \text{C}$ , as estimated by the system analysis ( $330 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ ), agrees remarkably well with the spatially integrated  $M_{\text{BE}}$  from gas trap surveys ( $480 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ ), which were conducted throughout the reservoir also at  $\sim 17^\circ \text{C}$  water temperature (Table 1). DCs measured both diffusion and ebullition at the surface in  $\sim 17^\circ \text{C}$  water but resulted in much higher emissions ( $\sim 855 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ ) than the system analysis  $M_{\text{BE}}$  plus measured diffusion ( $330 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1} + 12 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ ). The DC surveys, however, were not conducted throughout the reservoir but rather only in a highly active ebullition region  $\sim 1$ – $2 \text{ km}$  from the dam. Ultimately, the system analysis provides a more reliable estimate as it averages emissions over space and time, while DC and gas trap measurements are spatially and/or temporally limited in resolution.

The daily  $\text{CH}_4$  ebullition emission from Lake Wohlen at  $17^\circ \text{C}$  ( $330 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ ) is comparable to most values reported for tropical reservoirs and much higher than the few values reported for temperate and boreal reservoirs (2, 3), except for a Finnish reservoir with comparable emissions (26). Lake Wohlen exhibits a large degree of seasonality in its emissions, therefore reporting a yearly integrated average is more convenient for comparing methane emissions from other reservoirs.

On average throughout the year Lake Wohlen emits  $\sim 86 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  via ebullition alone ( $M_{\text{BE}}$ , Figure 4), which still compares with or exceeds average estimates of ebullition from tropical, boreal and temperate reservoirs (2, 3, 6, 26). However, total surface emissions (diffusion plus ebullition) from some of the larger tropical reservoirs, such as Petit Saut in French Guiana (6) and Balbina in Brazil (27), far exceed Lake Wohlen's emissions, mostly due to the difference in surface area ( $\sim 120$ – $700$  times larger).

**System Analysis Constraints and Limitations.** One of the major assumptions needed for the system analysis is that methane oxidation in the water column is negligible, as our oxidation experiments confirmed. The lack of oxidation is most likely explained by the short residence time and well-mixed conditions in Lake Wohlen that (1) do not allow enough time for methane-oxidizing bacteria to colonize, and (2)

contain relatively low levels of methane compared to the oxyclines of stratified waters where most oxidation occurs (11, 28, 29).

The average baseline  $M_{\text{SD}}$  calculated from the system analysis model ( $15 \pm 9 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ ) is well within the error of the average  $M_{\text{SD}}$  calculated from sediment cores ( $41 \pm 42 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ ). The variability between the results is likely because the baseline  $M_{\text{SD}}$  from the system analysis is a basin-wide estimate accounting for potential methane oxidation at the sediment surface since the observed  $[\text{CH}_4]_d$  in the water column was the basis of the estimation. The core-obtained values are point estimates that possibly underestimate oxidation near the sediment-water interface, which could lower the diffusive  $\text{CH}_4$  flux by up to an order of magnitude (12).

The net methane increase estimated from the system analysis mostly agrees with the observed seasonal values, except for the December 2007 and January 2008 sampling that fall below the estimated  $[\text{CH}_4]_d$  (Figure 3a). Some possible explanations are that (1) methane oxidation occurs in the water column, and/or (2) the outflow sample should have been matched with an inflow sample several days earlier in order to account for the residence time of up to one week during the winter season.

Because the temporal resolution of  $M_{\text{SD}}$  calculated from sediment cores was limited (July through December),  $M_{\text{SD}}$  throughout the temperature range of the reservoir ( $5^\circ \text{C}$  –  $20^\circ \text{C}$ ) was calculated using  $\text{CH}_4$  diffusivity and solubility constants (details in ref 7) to determine if there is any seasonality in diffusion. For this coarse calculation, we assumed that  $[\text{CH}_4]_d$  in the water column was negligible compared to porewater concentrations and that methane saturation was reached by  $10 \text{ cm}$  depth, which is roughly consistent with Lake Wohlen cores (18), and found that the diffusive  $\text{CH}_4$  flux would be  $31 \pm 2 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  and largely independent of temperature. Increasing the temperature from  $5$  to  $20^\circ \text{C}$  led to a  $\sim 30\%$  decrease in  $\text{CH}_4$  solubility (Figure S3 in the Supporting Information) and a concomitant  $\sim 30\%$  increase in  $\text{CH}_4$  diffusivity, resulting in seasonally stable diffusion. Hence, three independent estimates (cores, system analysis, and the saturation calculation) point toward a consistently low and seasonally stable sediment diffusion.

The sediment bubble flux approximation at  $17^\circ \text{C}$  ( $470 \text{ mg m}^{-2} \text{ d}^{-1}$ ) is  $\sim 2/3$  the gas trap-measured bubble flux ( $\sim 700 \text{ mg m}^{-2} \text{ d}^{-1}$ ) but is well within the variability of the measurements. This small variability can be attributed to

sampling bias toward active bubbling sites during some funnel surveys and the fact that funnel measurements only covered a very small fraction ( $10^{-5}$ ) of the reservoir area. Overall, the bubble flux approximation derived from the system analysis is more accurate because it is based on a spatially and temporally integrated data set (i.e., the monthly  $[\text{CH}_4]_d$  samplings and  $Q$ ).

Sediment ebullition was estimated via the bubble dissolution model and the relationship between temperature and  $[\text{CH}_4]_d$  accumulation, implying that seasonal changes in  $[\text{CH}_4]_d$  accumulations were best described by temperature (Figure S3 in the Supporting Information) (30, 31). However, lake level changes have been shown to strongly influence ebullition rates (9, 32, 33) and hence  $[\text{CH}_4]_d$  values. Lake Wohlen does experience slight seasonal and moderate daily water level changes of less than 10 cm, which are due to hydropower operations. We performed a principal component analysis on water level fluctuation, temperature, and  $[\text{CH}_4]_d$  accumulation and found that temperature was much more strongly correlated with  $[\text{CH}_4]_d$  than was any parameter describing the extent or rate of water level fluctuation (data not shown). While the <1% daily difference in hydrostatic pressure probably impacts the hourly variability in emission rates, longer-term average rates should be relatively unaffected.

**Extreme Methane Emissions - Maximum Potential Output.** The  $[\text{CH}_4]_d$  input from sediment diffusion and bubble dissolution within the water column is discharged through the turbines and what is not degassed there will eventually be released further downstream. Thus, total methane emission from the reservoir can be up to  $500 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  (>1 ton per day) on warm summer days (Figure 3b). On average throughout the year Lake Wohlen emits  $>150 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  corresponding to  $>40 \text{ g C m}^{-2} \text{ y}^{-1}$  ( $M_{\text{ATM}}$ , Figure 4). While this annual carbon emission is several orders of magnitude lower than that of the large tropical reservoirs (6, 27), it is the highest recorded for a temperate reservoir to date, and, in contrast to the tropical reservoirs, the majority of the emission is due to ebullition (~80%,  $M_{\text{BF}}$ , Figure 4). In addition, Saarnio et al. (34) estimated  $\text{CH}_4$  from European water bodies, and the  $\text{CH}_4$  emission rate of Lake Wohlen is well above that of the average small lake.

Finally, at the current yearly average water temperature of  $11^\circ\text{C}$  the reservoir emits ~0.2 tons of  $\text{CH}_4$  per day via surface emissions and discharge. The projected temperature increase of  $3^\circ\text{C}$  in the coming century (13) could result in a doubling of  $\text{CH}_4$  emission from Lake Wohlen, given the exponential dependence of  $\text{CH}_4$  emission on temperature (Figure 2). Even if this statement is highly speculative, it clearly illustrates the need for further investigations on the temperature dependence of  $\text{CH}_4$  emissions from lakes and reservoirs.

**Implications.** Our findings indicate that this 90-year-old, temperate reservoir is a very significant  $\text{CH}_4$  source, almost entirely due to bubbling sediments. In addition, we found that  $[\text{CH}_4]_d$  accumulation was highly temperature-dependent in Lake Wohlen and allowed us to estimate methane emissions using the  $[\text{CH}_4]_d$  accumulation and flow rate of the reservoir. Even though the results of this study clearly point to a relationship between temperature and methane emission, many questions remain open regarding what is causing such intense methane production and subsequent ebullition in this small oxic reservoir, especially since the 10-year high emission period following damming that has been observed in newly dammed reservoirs is long over (6).

A potential explanation is the combination of reservoir characteristics that made Lake Wohlen an easy system to analyze - a flow-through reservoir with a short residence time and minimal oxidation - as well as its high organic carbon load (~25 tons per day) and fast sedimentation rate (18) all leading to an exceptional rate of methanogenesis, super-

saturation, and subsequent ebullition. The high organic carbon load comes from several sources - (1) passage of the Aare River through the capital city, Bern (population >100,000), including input from several wastewater treatment plants; (2) drainage of the large Alpine and agricultural river basin (35) yielding terrigenous carbon; and (3) the input from two large Prealpine lakes, Brienz and Thun. Consequently, similar run-of-river reservoirs lying downstream of such organic carbon sources may also be large  $\text{CH}_4$  producers. Therefore, the sampling and system analysis methods outlined in this paper are quite appropriate for studying other similar systems and could even be adapted for use in more complex ones. Depending on access to the reservoir, monthly inflow/outflow samplings are not too time-consuming and essential to this method. More detailed campaigns could include coring, funnel, and chamber surveys conducted seasonally when water temperature differences are obvious.

On a global scale of methane emissions from reservoirs, temperate ones are often overlooked because the largest reservoirs reside in tropical regions where warm temperatures support methanogenesis year round (2, 3, 36). Our findings indicate that temperate reservoirs with high carbon inputs and burial rates (37) as well as the sources of these carbon inputs should be given some consideration in current greenhouse gas budgets, especially in a changing climate. A more detailed analysis of the biogeochemical and geographic setting of reservoirs in temperate areas is needed when assessing global methane emissions from water bodies.

## Acknowledgments

A thank you goes to D. Bastviken, M. Schmid, K. Wallmann, and A. Wuest for helpful suggestions and special thanks go to K. Ashe, T. Diem, C. Dinkel, S. Flury, A. Jullian, L. Rovelli, M. Schurter, N. Wongfun, J. Yuen, and A. Zwysig for help in the lab and field. Also thanks go to T. Schneider and BKW for allowing dam and data access and three reviewers who helped improve this manuscript. This study was supported by the Swiss National Science Foundation (Nr. 200020-112274 and 200021-120112).

## Supporting Information Available

An extended methods section, three tables containing measurements from various surveys, and three figures showing gas trap and floating chamber details and temperature relationship with  $\text{CH}_4$  saturation concentrations and production. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ES9031369