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Journal Article**Author(s):**

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Publication date:

2017-10

Permanent link:

<https://doi.org/10.3929/ethz-b-000218541>

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Originally published in:

Environmental Science: Processes & Impacts 19(10), <https://doi.org/10.1039/c7em00232g>

Cite this: DOI: 10.1039/xxxxxxxxxx

Minor methane emissions from an Alpine hydropower reservoir based on monitoring of diel and seasonal variability

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Received Date

Accepted Date

DOI: 10.1039/xxxxxxxxxx

www.rsc.org/journalname

We monitored CH₄ emissions during the ice-free period of an Alpine hydropower reservoir in the Swiss Alps, Lake Klöntal, to investigate mechanisms responsible for CH₄ variability and to estimate overall emissions to the atmosphere. A floating eddy-covariance platform yielded total CH₄ and CO₂ emission rates at high temporal resolution, while hydroacoustic surveys provided no indication of CH₄ ebullition. Higher CH₄ fluxes (2.9 ± 0.1 mg CH₄ m⁻² d⁻¹) occurred during the day when surface water temperatures were warmer and wind speeds higher than at night. Piston velocity estimates (k_{600}) showed an upper limit at high wind speeds that may be more generally valid also for other lakes and reservoirs with limited CH₄ dissolved in the water body: above 2.0 m s⁻¹ a further increase in wind speed did not lead to higher CH₄ fluxes, because under such conditions it is not the turbulent mixing and transport that limits effluxes, but the resupply of CH₄ to the lake surface. Increasing CH₄ fluxes during the warm season showed a clear spatial gradient once the reservoir started to fill up and flood additional surface area. The warm period contributed 27% of the total CH₄ emissions (2.6 t CH₄ yr⁻¹) estimated for the full year and CH₄ accounted for 63% of carbonic greenhouse gas emissions. Overall, the average CH₄ emissions (1.7 to 2.2 mg CH₄ m⁻² d⁻¹ determined independently from surface water samplings and eddy covariance, respectively) were small compared to most tropical and some temperate reservoirs. The resulting greenhouse gas (GHG) emissions in CO₂-equivalents revealed that electricity produced in the Lake Klöntal power plant was relatively climate-friendly with a low GHG-to-power output ratio of 1.24 kg CO_{2,eq} MWh⁻¹ compared to 6.5 and 8.1 kg CO_{2,eq} MWh⁻¹ associated with the operation of solar photovoltaics and wind energy, respectively, or about 980 kg CO_{2,eq} MWh⁻¹ for coal-fired power plants.

Environmental Impact

Hydropower plants provide renewable energy, but their carbon footprint depends on their greenhouse gas emissions. In this case study of an Alpine storage reservoir, we focus on the pathways of CH₄ emissions, their spatial gradients and their variability over diel and seasonal cycles. Observations during 13 months reveal that CH₄ and CO₂ emissions are restricted to diffusive pathways. The lack of an emission pathway via gas bubbles is one factor why specific emissions of CO₂ equivalents per megawatt-hour are almost three orders of magnitude smaller than for typical coal-fired power plants. This high resolution study confirms earlier surveys that estimated smaller carbon footprints for Alpine storage reservoirs compared to run-of-the river plants in the lowlands.

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1 Introduction

Hydropower plants are important sources of renewable energy and they are often considered “green energy”¹. However, over the last two decades, studies have shown that reservoirs can be significant greenhouse gas (GHG) emitters². Recent studies estimated the GHG strength of methane (CH₄) and carbon dioxide (CO₂) emissions from reservoirs globally as 0.5–1.2 Pg CO_{2,eq} yr⁻¹³. A recent global synthesis of reservoir emissions suggests that CH₄ contributes up to 80% of the total radiative forcing by reservoirs³. The primary reason that CH₄ dominates the radiative forcing of reservoirs and other aquatic sources is linked to the fact that the global warming potential (GWP) of CH₄ is 34 times larger than that of CO₂, on a 100 year time-scale, including positive climatic feedbacks⁴. In addition, the low solubility of CH₄ in water favors the direct transfer to the atmosphere via bubbles^{5,6}. In contrast to slower emissions via diffusion, this ebullitive pathway bypasses the effective methane oxidation by bacteria that can substantially limit atmospheric emissions^{7–9}. Importantly, when ebullitive emissions are included in more comprehensive estimates of inland water carbon emissions, it appears that aquatic carbon emissions may partially offset the global continental carbon sink¹⁰. Ultimately, improving our mechanistic understanding of CH₄ emissions from different types of water bodies has been identified as an important research priority, particularly for man-made hydroelectric reservoirs^{10,11} given that global hydropower capacity is estimated to increase by 73% over the coming decades¹².

A large uncertainty in global CH₄ emission estimates from reservoirs is partially linked to the lack of detailed emission studies, particularly ones with rigorous analysis of the contributions by both ebullitive and diffusive pathways which requires detailed considerations of temporal and spatial coverage of total emissions depending on methodology³. Such data gaps were mostly due to the methods chosen for gas emission surveys, which were typically floating chambers and gas traps that merely report point measurements of gas flux^{13–15}. Fortunately, several measurement techniques are now available to help better constrain the role of reservoirs as global CH₄ sources. Hydroacoustic techniques via an echosounder can easily detect the presence or absence of bubble plumes as well as quantify ebullitive emissions following certain calibration procedures^{6,16–18}. The eddy-covariance (EC) technique is best suited to monitor seasonal cycles and short-term changes of total surface CH₄ emissions^{19–24}. These methods, however, remain costly and, thus, most surveys are still performed with low cost alternative methods such as floating chambers¹⁴, air–water exchange calculations using measured dissolved gas concentrations and wind speed²⁵, and depth profiles for gas budgets that include storage or turnover emissions^{13,26}.

Therefore, here, we combine several different gas emission observation techniques, including high resolution ones, in order to constrain and present a comprehensive and annual CH₄ emission budget for Lake Klöntal, a medium-sized 60 MW hydropower scheme in the Swiss Alps. An EC flux tower was deployed throughout the ice-free season to evaluate diel and seasonal changes in CH₄ and CO₂ emissions, which was compli-

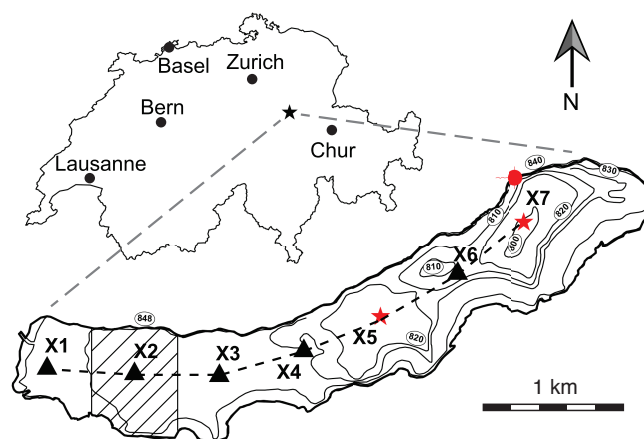


Fig. 1 Location of Lake Klöntal and sampling locations. Symbols show the surface (triangles) and profile (stars) sampling locations, while the circle shows the location of the EC system close to the dam outlet. The shaded area is an example, how CH₄ emissions measured at X2 were weighed for lake total efflux estimates.

mented by surface sampling along the reservoir to assess how representative the EC flux measurements were for the entire reservoir. In addition, hydroacoustic surveys for CH₄ ebullition were conducted. Combining these spatial and temporal observations, we calculate the specific emission rate of this Alpine storage reservoir to approximate the carbon footprint in kg CO_{2,eq} MWh⁻¹ of this high-mountain hydropower reservoir.

2 Material and methods

2.1 Study sites

Lake Klöntal is a hydropower reservoir located in the northern Swiss Alps (47°01'32"N, 8°58'50"E, Fig. 1) that has a maximum water depth of 45 m, a volume of 39.8·10⁶ m³ and a maximum water level of 847 m a.s.l. It is surrounded by two high mountain ranges (> 2000 m a.s.l.) running from east to west. The climate (Fig. 2) is cold temperate with a mean annual temperature (MAT) of 10.9 and 9.4°C in 2011 and 2012, respectively. Absolute minimum (maximum) temperatures were -9.6 and -18.1°C (30.5 and 30.6°C). Annual precipitation was 2125 mm in 2011 and 2600 mm in 2012, of which 40% and 58% was snowfall in 2011 and 2012, respectively. A rain gauge of the Swiss national weather service MeteoSwiss with hourly-resolving data collection was only installed in 2013. From this site located at the west end of Lake Klöntal we used precipitation intensity data from 29 August 2013 until 31 December 2016 at hourly resolution. During this period, 86.3% was rainfree, 90% of the time precipitation intensity was ≤0.4 mm h⁻¹, 95% ≤1 mm h⁻¹, 99% ≤7.8 mm h⁻¹, and the maximum was 34.8 mm h⁻¹.

The Klöntal hydropower plant (Fig. 1) was finished in 1908 and produces on average 114 GWh of electricity annually. The reservoir surface varies between 1.2 km² (minimum water level, 829 m a.s.l.) and 3.3 km² (maximum water level, 847 m a.s.l.) and is covered by snow and ice during three months of the year (mid-December until mid-March). After snowmelt, the water level generally rises by ca. 15 m from May through July. During this pe-

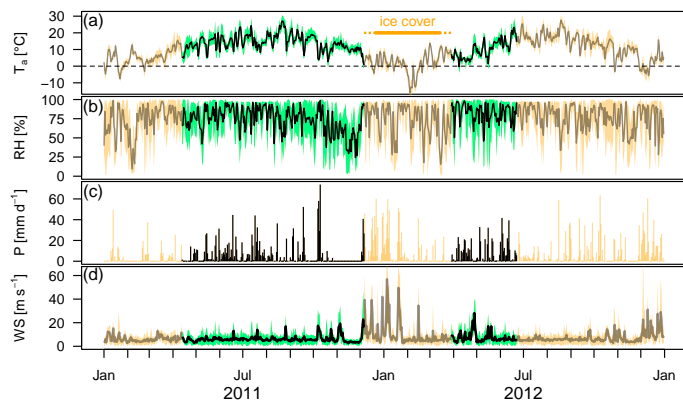


Fig. 2 Meteorological conditions in years 2011 and 2012, (a) air temperature; (b) relative humidity; (c) daily precipitation; (d) wind speed at 10 m above ground. The periods with EC flux measurements on the lake are plotted with green color and bold lines, and the periods not covered by this study are shown with orange color and opaque lines. Data retrieved from Meteoblue.com.

riod, the surface area of the reservoir almost doubles and then decreases again in winter.

2.2 CH₄ and CO₂ flux monitoring using the eddy covariance technique

During the ice-free period from April until December 2011 and from March until June 2012, we continuously measured the CH₄ flux using an EC system. The EC system consisted of an FMA-100 fast CH₄ analyzer (Los Gatos Research Inc., Mountain View, CA, USA) and a Solent R2A ultrasonic anemometer (Gill Instruments Ltd., Lymington, UK) as described in detail by Eugster and Plüss²⁷. The sensor head was placed 1.49 m above the water surface on a floating aluminum frame in 2011 (1.72 m in 2012). The analyzer was protected by a water trap to prevent dust, moisture and droplets from penetrating the sample cell. The analyzer and gas inlet were moored on a skeleton raft roughly 50 m off the shore of the reservoir, almost identical to an earlier deployment at Rotsee²⁰. A high-performance vacuum pump was used for carrying gas through an 8 mm inner diameter Synflex-1300 hose (Eaton Performance Plastics, Cleveland, OH, USA) to the analyzer on shore, and raw data were recorded at 20.8 Hz²⁷. This allowed us to measure fluxes at high frequency for further analysis of the diel and seasonal variability. The platform was removed for winter before ice-on, but replaced again by the end of March 2012 to continue the experiment for an additional three months.

In 2012, additional water vapor and CO₂ flux measurements were performed with an infra-red gas analyser (Li-Cor 7500, Lincoln, NE, USA) since CH₄ fluxes were surprisingly low compared to earlier deployments elsewhere^{19,20} and thus a flux correction for density fluctuations associated with water vapor fluctuations was needed²⁸. The closed-path FMA-100 measured CH₄ concentrations with respect to moist air, not dry air, and hence density fluctuations caused by concurrent water vapor fluctuations may bias CH₄ flux measurements²⁸. Since no such additional measurements were available in 2011, the density flux correction in 2011 was approximated by an empirical relationship obtained

from 2012 flux data. For this, a stepwise elimination multiple regression approach was used in which all time series variables that were also measured in 2011 were used as candidate predictor variables for the density fluctuation correction term (*DFC*). In each step the variables with insignificant explanatory power (t-test yielded $p > 0.05$) were eliminated. The final model for *DFC* was

$$DFC \approx \alpha_1 \cdot \sqrt{w^2} + \alpha_2 \cdot \overline{w^2} + \alpha_3 \cdot \sqrt{m^2} + \alpha_4 \cdot H, \quad (1)$$

where w^2 and m^2 are the variance of the vertical and horizontal (scalar) wind velocity components ($\text{m}^2 \text{s}^{-2}$), and H is a cyclical hour variable derived from hour of day CET (hh) as $H = |\text{hh} - 13|$. Overbars denote averaging over standard 30-minute periods, and α_1 – α_4 are regression coefficients determined via least-squares fitting. Adjusted r^2 was 0.637 ($p < 0.0001$) with $\alpha_1 = (1.62 \pm 0.07) \cdot 10^{-10}$, $\alpha_2 = (-1.54 \pm 0.08) \cdot 10^{-10}$, $\alpha_3 = (6.4 \pm 1.7) \cdot 10^{-12}$, and $\alpha_4 = (-6.7 \pm 0.7) \cdot 10^{-13}$. The empirically determined *DFC* has units of $\text{kg CH}_4 \text{ m}^{-2} \text{ s}^{-1}$ and was added to the measured CH₄ flux. These additional measurements in 2012 also provided CO₂ fluxes, which were corrected for density fluctuations by both sensible and latent heat fluxes in the standard way described by Webb et al.²⁸.

The data collection and processing closely followed the recommendations for EC flux measurements over lakes²¹ using our in-house eth-flux software²⁹. Unrealistic spikes in raw data were filtered out, and the quality of the remaining fluxes was assessed using Foken's quality flags³⁰ for steady-state conditions during each 30-minute averaging interval. Fluxes did not require a special correction for the oscillation of the platform as was shown in detail by Eugster et al.³¹. During the two measurement periods in 2011 and 2012 the data coverage was 89.9% with 6334 hours of valid data. Of these 83.7% can be considered of good or best quality (with 26.4% best quality) and 16.3% of poor quality that are useful for monthly and annual averages but not good enough for in-depth investigations of half-hour intervals. The flux footprint analysis with the Kljun model³² shows that the flux footprint in all wind directions almost perfectly covers lake surface and is not affected directly by the surrounding terrain (Fig. 3).

2.3 Hydroacoustical determination of ebullition

Ebullition surveys were conducted during two campaigns in July and September 2011, two months of warmest weather in which ebullition would occur if at all. We used a split-beam echosounder (Simrad EK60, 7° beam angle) with a 120 kHz transducer pinging at 5 Hz, as described by DelSontro et al.⁶, along a grid of 50×50 m throughout the reservoir surface.

2.4 Spatial explicit water sampling and flux estimates

From April–December 2011 water samples were taken monthly at two locations (X5 & X7, Fig. 1). As the first samplings in April 2011 showed substantial differences in surface water concentrations at X5 and X7, additional measurements (X1–4 and X6, Fig. 1) were carried out starting in August 2011 so that a sample was taken about every 500 m along the reservoir. Water was col-

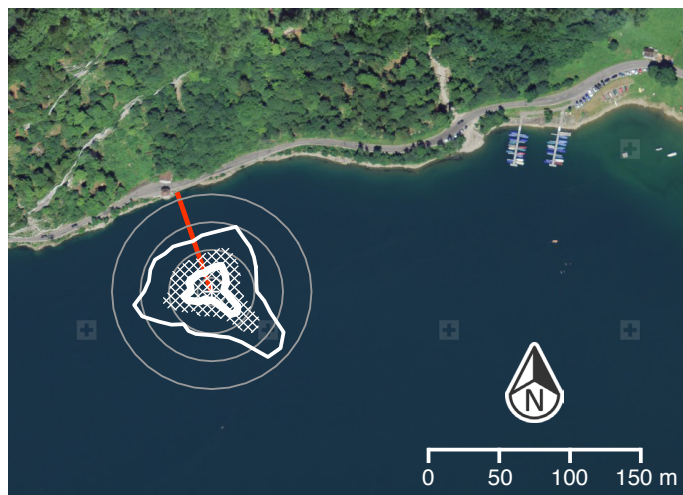


Fig. 3 Flux footprint area covered by the eddy covariance system. Bold line: median of wind direction-specific footprint area; outer thick line: 90% extent of the footprint area; hashed area: 50% of the direction specific footprint area. Red line: intake hose and electrical cables connecting sensors on floating platform with analyser and data acquisition in the building on shore. Gray circles around the eddy covariance system are drawn at 30, 50 and 70 m distance for reference. Background image © swisstopo, reprint permission JD100042.

lected in 120 ml glass vials and poisoned with CuCl to prevent microbial activity. The samples were sealed bubble-free using butyl stoppers and aluminum caps. Gas samples were analyzed for CH₄ concentrations by gas chromatography (Agilent 6890 gas chromatograph equipped with a flame ionization detector (FID), Agilent Technologies Inc., Santa Clara, USA). Conductivity-temperature-depth (CTD) casts and vertical CH₄ profiles were conducted at locations X5 and X7 down to maximum summer depths of 30 and 45 m, respectively.

Dissolved CH₄ concentration measurements in surface waters carried out between April and November 2011 at location X7 were used in combination with EC flux measurements during the same time period to estimate a piston or gas exchange velocity (k) that could be used to estimate CH₄ flux at other locations on the reservoir where the EC footprint (Fig. 3) could not account for but surface concentrations were taken (i.e., locations X1–X6). The governing flux equation is³³

$$F_{CH_4} = k_{CH_4} \cdot (C_w - C_{eq}), \quad (2)$$

where CH₄ flux, F_{CH_4} (mg CH₄ m⁻² d⁻¹) is the product of the piston velocity, k_{CH_4} (cm h⁻¹ or m d⁻¹), and the CH₄ concentration gradient across the air–water interface that is equal to the difference between dissolved CH₄ in the water, C_w (nM), and surface water in equilibrium with atmospheric CH₄ concentrations, C_{eq} (nM). C_w was found as described above and measurements at location X7 were used because it was directly upwind of the eddy covariance flux system during typical daytime conditions with winds from the southeast (Fig. 4a). C_{eq} was calculated according to Wiesenburg and Guinasso³⁴ using an atmospheric CH₄ concentration of 1.803 ppm³⁵.

We used five different published models proposed for k_{600} , the

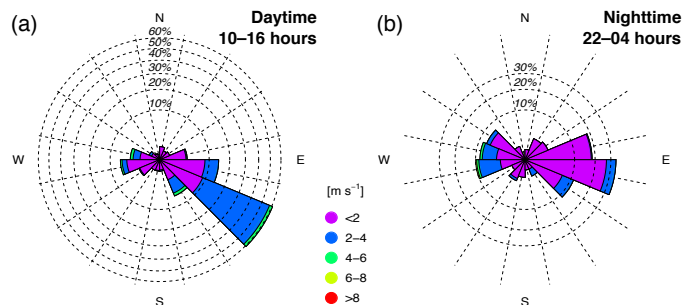


Fig. 4 Windroses observed by the EC system during (a) daytime and (b) nighttime. The dominant southeasterly direction is typically associated with slightly higher wind speeds (>2 m s⁻¹) than those observed from other directions. Calm conditions with wind speeds <1 m s⁻¹ were excluded.

piston velocity normalized to a Schmidt number of 600 (Table 1, models 1–5), to determine the CH₄ flux with equation (2) and

$$k_{CH_4} = k_{600} \left(\frac{600}{Sc_{CH_4}} \right)^{-n}. \quad (3)$$

k_{600} is parametrized for constant oversaturation at the water–air interface at variable wind speeds. This condition is usually met in oceans, where most of these parametrizations have been done, because of intense surface mixing and rather limited gradients of dissolved gas. In the Klöntal case the difference between the five models was very large, and thus the average k_{600} from all five models was used for the spatial integration, thereby keeping this estimate independent of the EC flux measurements.

2.5 Validation of piston velocity

For validation of this approach, we however also back-calculated k_{600} using EC fluxes and concentration measurements in the water interpolated over time (see below). In this way, equation (2) was solved for k_{CH_4} , which then was normalized to a k for CO₂ at 20°C in freshwater (k_{600}) using the following equation^{33,41},

$$k_{600} = k_{CH_4} \left(\frac{600}{Sc_{CH_4}} \right)^n, \quad (4)$$

where Sc_{CH_4} is the Schmidt number for CH₄, which was calculated here according to Wanninkhof⁴², and n is a constant that depends on the roughness of the water surface, which was set to $-2/3$ when wind speeds were below 3.7 m s⁻¹ and set to $-1/2$ when wind speeds were above 3.7 m s⁻¹⁴³. As we had the ability for continuous flux measurements via the EC system, C_w and Sc_{CH_4} were estimated from measured surface concentrations at location X7 for each 30-min averaging interval using a local polynomial regression fit (loess function⁴⁴) of second order with a span of 0.7 for both C_w and water temperature T_w , from which Sc_{CH_4} was calculated with

$$Sc_{CH_4} = 1897.8 - 114.28 T_w + 3.2902 T_w^2 - 0.039061 T_w^3. \quad (5)$$

As most k_{600} models are expressed according to wind speed at 10 m height, U_{10} , we converted EC wind speed (measured at

Table 1 Empirical relationships between wind (U_{10}) and piston velocity (k_{600}) based on a threshold depending on either U_{10} or buoyancy flux (β). Models 1–5 were averaged to compute spatially averaged fluxes, and model 6 was derived from eddy covariance flux data on Lake Klöntal for comparison.

| Nr. | k_{600} [cm h ⁻¹] | Condition | Source |
|------|--|---|--|
| 1. | $0.215U_{10}^{1.7} + 2.07$ $0.45U_{10}^{1.64}$ | $U_{10} < 4.0$ m s ⁻¹ $U_{10} \geq 4.0$ m s ⁻¹ | Cole and Caraco (1998) ³⁶ |
| 2. | $0.72U_{10}$ $4.33U_{10} - 13.3$ | $U_{10} < 3.7$ m s ⁻¹ $U_{10} \geq 3.7$ m s ⁻¹ | Crusius and Wanninkhof (2003) ³⁷ |
| 3. | $2.04U_{10} + 2.0$ $1.74U_{10} - 0.15$ | $\beta > 0$ $\beta < 0$ | MacIntyre et al. (2010) ³⁸ |
| 4. | $1.03 + 0.129U_{10}^2 + 19.99R_n$ | $R_n =$ rainfall rate [cm h ⁻¹] | Frost and Upstill-Goddard (2002) ³⁹ |
| 5. L | $(1.05 \pm 0.17)U_{10} + (0.74 \pm 0.67)$ | bin averaged data | Guerin et al. (2007) ⁴⁰ , linear model |
| 5. P | $(1.76 \pm 0.77) + (0.23 \pm 0.32)U_{10}^{1.78 \pm 0.72}$ | bin averaged data | Guerin et al. (2007) ⁴⁰ , power model |
| 5. E | $(1.66 \pm 0.34)e^{(0.26 \pm 0.04)U_{10}}$ | bin averaged data | Guerin et al. (2007) ⁴⁰ , exponential model |
| 6. | $(0.25 \pm 0.08)U_{10}^{(4.92 \pm 0.49)} + (1.53 \pm 0.09)$ 9.12 ± 0.37 | $U_{10} < 2.0$ m s ⁻¹ $U_{10} \geq 2.0$ m s ⁻¹ | This study |

z=1.49 m and 1.72 m in 2011 and 2012, respectively) to U_{10} using the logarithmic wind profile,

$$U_{10} = U(z) + \frac{u_*}{k_a} \cdot (\ln 10 - \ln z) \quad (6)$$

2.6 Total annual CH₄ emission estimate

Finally, we integrated CH₄ flux derived at all locations to estimate total emissions from the lake (see Fig. 1). Each local flux measurement i was weighted by the surface area S_i of the lake section for which it was considered representative. Section boundaries were chosen mid-way between two sampling points as depicted for section X2 in Figure 1. Annual CH₄ emission E_{tot} (t yr⁻¹) was estimated as follows:

$$E_{tot} = \alpha \sum_{j \in M_y} D_j \cdot \sum_{i \in X_m} F_{i,j} \cdot S_i \quad (7)$$

with M_y month of year y (2011, 2012), X_m sampling location X1–X7, D_j the number of days in month M_y , and $F_{i,j}$ the CH₄ flux (in mg m⁻² d⁻¹). The sum over all S_i corresponds to the maximum lake surface area (in m²), and $\alpha = 10^{-9}$ t mg⁻¹ converts from mg CH₄ yr⁻¹ to t CH₄ yr⁻¹. The sampling lasted for eight months during the ice-free period and reduced effluxes were assumed from December to March due to ice cover. Thus, the measured flux in April is expected to contain the signal of the CH₄ that may have accumulated under the ice during winter and is released to the atmosphere once the ice has disappeared. This spatial explicit approach was then compared with the EC fluxes measured near location X7, which provide a better temporal, but much lower spatial representativity.

3 Results

In order to disentangle diffusive and potential ebullitive pathways, we combined different surveys. The eddy covariance instrument allowed for an analysis of total diel emissions at one spot with a flux footprint area of ≈ 100 m². The long observation period also provided a basis for quantifying the seasonal variability. The monthly surveys of surface CH₄ and its depth distribution allowed us to determine spatial gradients and the response of CH₄ emissions to water-level changes. Interestingly, ebullition

could be ruled out as a major emission pathway in Lake Klöntal. We conducted two hydroacoustic surveys during the warmest period and at maximum water level but we did not detect any CH₄ ebullition nor were any bubbles seen rising to the lake surface. This does not imply that ebullition never occurred in Lake Klöntal, but indicates that this process contributes little to the overall CH₄ emissions. The sonar surveys therefore indicated that the main emission pathway in this reservoir was via diffusion, and so the following analysis and discussion will focus on diffusive emissions.

3.1 Variations of gas concentrations in the water and the air

Diel variations in hourly median atmospheric CH₄ concentration (Fig. 5a) only varied between 1.875 and 1.891 ppm, thus only by $\approx 1\%$, with peak concentrations being synchronous with CH₄ effluxes (Fig. 5b). This indicates, that the increase in local atmospheric CH₄ concentrations is a result of the CH₄ losses from the lake, and hence the average CH₄ concentration was clearly above the global background of 1.803 ppm³⁵.

Seasonal variations also remained in the narrow range from 1.774 to 2.225 ppm with the minimum and maximum concentration observed on 27 June and 7 November 2011, respectively (data not shown). Thus, on average, 2011 atmospheric CH₄ concentrations translated into a surface water equilibrium concentration of 3.10 ± 0.34 nM (Fig. 6), which was ≈ 2 orders of magnitude less than 2011 observed surface water CH₄ concentrations and implied a constant outgassing of CH₄ from the reservoir surface.

CO₂ concentration measurements were only added in 2012 without parallel measurements of concentrations in the water since CO₂ effluxes were initially considered much less important than CH₄ effluxes. The daily averaged CO₂ concentrations ranged from 433 to 599 ppm (data not shown), which is clearly higher than the global average of 390.5 ppm in 2011³⁵. The diel variations of hourly medians varied from 439 to 461 ppm (Fig. 5c), but were inversely related to CO₂ fluxes from the lake ($r = -0.7027$ for hourly medians shown in Fig. 5d). This indicates that the lake most likely is only a weak source of CO₂ and that the diel CO₂ concentration variations are more affected by larger-scale emissions, atmospheric mixing, and plant uptake during daytime.

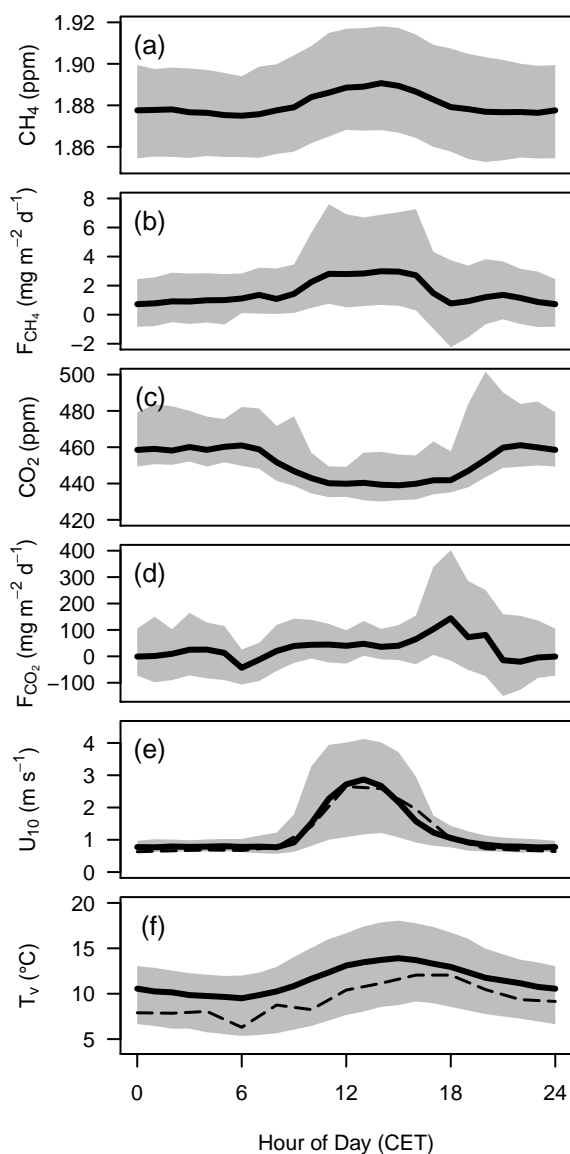


Fig. 5 Hourly median (bold line) and inter-quartile range (gray band) of a) atmospheric CH₄ concentration (CH₄), b) eddy covariance measured CH₄ flux (F_{CH_4}), c) atmospheric CO₂ concentration (CO₂), c) eddy covariance measured CO₂ flux (F_{CO_2}), e) wind speed (U_{10}), and f) virtual temperature (T_v) measured between 13 April 2011 and 22 June 2012 (excluding months with ice cover before 13 April 2011 and between 6 December 2011 and 29 March 2012). The dashed lines in panels (e) and (f) show the hourly medians for the period with CO₂ concentration and flux measurements (29 March to 22 June 2012).

3.2 Validation of piston velocity estimation

The spatially averaged CH₄ fluxes computed from gas concentrations in the surface water (equation 2) strongly depend on the assumptions made for k_{CH_4} piston velocity, hence a validation with direct EC flux measurements as a function of wind speed was done. Figure 7 shows the result of 7.5 months of computed gas exchange coefficients, converted to k_{600} using equation (4), which was excellently correlated with U_{10} . To account for the non-uniform distribution of wind speeds, data were grouped in 50 wind speed classes with equal number of flux measurements (50 groups with $N = 212$ half-hourly flux records each). For each

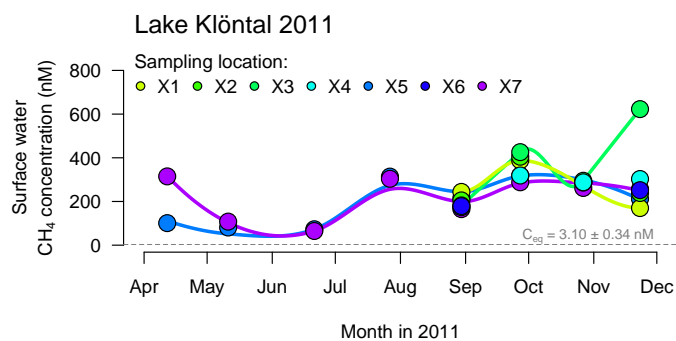


Fig. 6 Seasonal evolution of surface water CH₄ concentrations in 2011 determined by the headspace equilibration method. At all times the water was supersaturated with CH₄ with respect to atmospheric concentration C_{eq} (gray horizontal dashed line).

group the median U_{10} and median k_{600} was calculated (circles in Fig. 7). A logistic curve fit well to these group medians. Note the logarithmic display of the U_{10} axis in Figure 7 to show the details at low wind speeds, which were dominant during the entire deployment of the system. The logistic approach has two important benefits for this application: (1) it has a lower and upper asymptote which agree much better with the empirical data than a simple exponential (or power law) or even a polynomial fit; and (2) in the central range of the logistic fit, the typical exponential increase of k_{600} with increasing U_{10} is still correctly reflected³⁷. The best fit for k_{600} (in $cm\ h^{-1}$) derived from EC-CH₄ flux measurements was

$$k_{600} = 2.1 + \frac{7.0 \pm 0.2}{1 + \exp\left(\frac{1.70 \pm 0.04 - U_{10}}{0.11 \pm 0.03}\right)}, \quad (8)$$

where the parameter estimates are given with their respective standard error of the best estimate. For practical applications, this equation was also approximated by a simplified approach with two U_{10} regimes given in Table 1 (model 6).

At low wind speeds $< 1\ m\ s^{-1}$ the C1998 model³⁶ almost perfectly agrees with k_{600} calculated from our EC flux measurements, whereas most other models predicted lower k_{600} . Under conditions with positive buoyancy fluxes, the M2010 model³⁸ also predicted k_{600} correctly at wind speeds $< 0.4\ m\ s^{-1}$, but at U_{10} exceeding this threshold, M2010 leads to a substantial overestimation of k_{600} , unless the buoyancy flux is negative. The most important difference between published k_{600} models and measurements from Lake Klöntal, however, are (a) the narrow range of wind speeds ($1\text{--}2\ m\ s^{-1}$) where k_{600} visibly increases in an exponential way similar to all other models, and (b) the upper limit of k_{600} at $U_{10} > 2\ m\ s^{-1}$ when k_{600} remains constant at $9.12 \pm 0.37\ cm\ h^{-1}$ irrespective of U_{10} .

3.3 Seasonal flux variations

The comparison of the methane profiles at the deepest site (X7) with the shallower location (X5) reveals rather low methane levels at the end of the winter season (black profiles in Fig. 8). In summer and autumn sediments at warm-water intermediate depths, 10–20 m, act as an important methane source and pro-

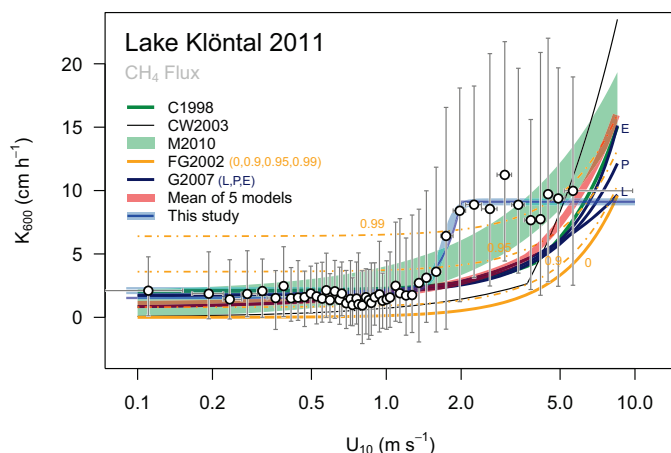


Fig. 7 Piston velocity k_{600} determined from CH_4 EC fluxes and air-water concentration gradients. 30-min averages were binned in 50 groups of equal number of samples. For each group the median (open circles) and the inter-quartile ranges (horizontal and vertical whiskers) are shown. A logistic fit was calculated for all median U_{10} values (bold blue curve), and a simplified power fit (thin blue line; see Table 1). Parametrizations used for the spatial flux estimations are shown for reference: C1998³⁶, CW2003³⁷, M2010³⁸, FG2002³⁹, and G2007⁴⁰, and the mean of all five models (bold red curve), which uses FG2002 under absence of rainfall and the exponential version (E) of the G2007 model (L = linear; P = power). The dashed orange lines of the FG2002 model show the values for rainfall intensities that correspond to the 0.90, 0.95 and 0.99 percentiles measured at a nearby rainfall gauge. The broad band shown for M2010 shows the range depending on the buoyancy flux.

duce maxima in the profiles. The low concentrations in the deep waters indicate that the cold conditions at the lake bottom prohibit intense methane release from sediments.

The period until end of June 2011 was characterized by rising lake levels that filled the entire reservoir by early summer (Fig. 9b, blue line). While bottom water temperatures in the deep Eastern locations remained cold, the shallow inundation zone at the western locations warmed completely to the bottom (Fig. 9a). The rapid inflow of snowmelt enhanced the lake volume substantially, but the lake remained highly supersaturated with CH_4 (Fig. 6). EC-derived CH_4 fluxes aggregated at a monthly resolution (Fig. 10) follow the pattern of CH_4 concentrations in surface waters (Fig. 6), except for November 2011 with the lowest median fluxes despite high CH_4 supersaturation in the water due to exceptionally low wind speeds (Fig. 2). From mid-December 2011 until early March 2012, ice cover prevented EC deployment and, hence, flux measuring. For this period we assumed zero effluxes of CH_4 and CO_2 , assuming that the accumulated gas in the ice covered water will not evade until ice-out in spring. In March 2012, when the EC system could be again deployed on the lake, median fluxes were slightly higher compared to December 2011 before the onset of ice. This may be related to CH_4 accumulating in the water under the ice cover, which is slowly emitted during and following ice melt. In contrast to 2011, the seasonal evolution of CH_4 fluxes showed a pronounced decrease from $4.6 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ in March 2012 to $0.4 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ in June 2012 (monthly median values; Fig. 10 and Table 2). During the same

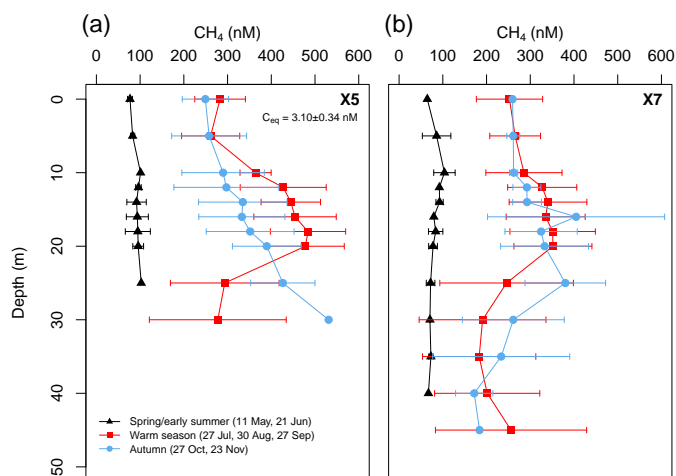


Fig. 8 Mean CH_4 concentration profiles (with standard deviation bars) at a) site X5 and b) site X7 in spring/early summer (11.05.2011; 21.06.2011), warm season (27.07.2011; 30.08.2011; 27.09.2011), and autumn (27.10.2011; 23.11.2011). C_{eq} is the mean (\pm SD) CH_4 equilibrium concentration with the atmosphere for both sites using the atmospheric CH_4 concentration measured at the eddy covariance flux site near X7.

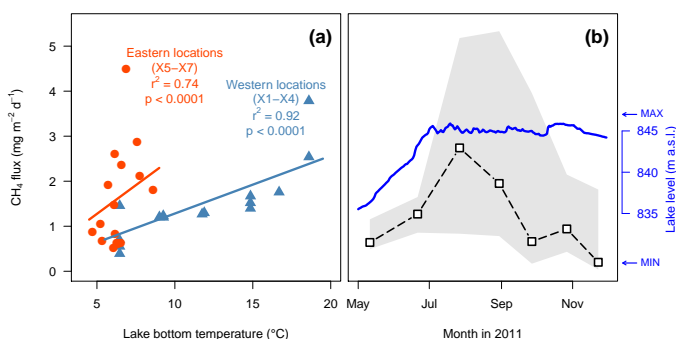


Fig. 9 a) Relationship between lake bottom water temperatures and surface CH_4 fluxes at the eastern (red line) and western (blue line) locations. b) Median seasonal variations of CH_4 fluxes (squares) from water sampling at all seven locations using five different models to calculate k_{600} . Grey shaded area shows the inter-quartile range of all fluxes (left y-axis), and the blue line shows the water level (right y-axis).

months, CO_2 fluxes exhibited an opposite trend starting with a net uptake of $56 \text{ mg CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ to a net efflux of $103 \text{ mg CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ (Table 4).

3.4 Diel flux variations

The fine temporal resolution of the EC technique enables analysis of the diel variations in CH_4 fluxes from the reservoir surface, which were rather pronounced over Lake Klöntal (Fig. 5b). The median reservoir fluxes determined for each hour of the day yielded a maximum that remained rather constant at $2.9 \pm 0.1 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ during peak daytime (11–16 hours CET)—which was roughly 3 times the typical nighttime CH_4 efflux observed ($0.9 \pm 0.2 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$, 23–07 hours CET). During peak daytime, more than 75% of the eddy covariance flux measurements indicated a CH_4 efflux from the lake, whereas at night ef-

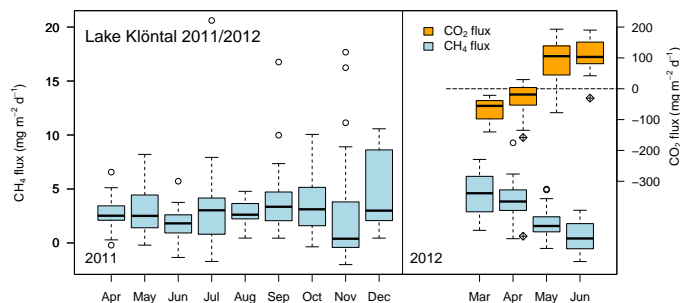


Fig. 10 Seasonal variability of CH_4 and CO_2 fluxes ($\text{mg m}^{-2} \text{d}^{-1}$) in 2011 (CH_4 measurements only) and 2012 measured by the EC system. Boxes, whiskers and dots show the inter-quartile range (IQR), the data range up to 1.5 times the IQR, and outlier values, respectively. The EC system was installed during the ice-free period, from 13 April until 6 December 2011, and from 29 March 2012 until 22 June 2012.

Table 2 Annual CH_4 emission estimate from Lake Klöntal based on eddy covariance flux measurements in 2011 and 2012 near the deepest spot of the reservoir. For January and February 2012 with ice cover we assumed an efflux (numbers in italics) of 23% the average magnitude measured under ice free conditions following Wik et al.¹⁵.

| Lake Klöntal 2011/2012 | | | Methane flux densities | | | Methane emissions | | |
|------------------------|-------------|------|--|-------------|------------|-------------------------------------|-------------|------------|
| Eddy Covariance | | | [$\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$] | | | [$\text{t CH}_4 \text{ yr}^{-1}$] | | |
| Month | Year | Days | Median | Lower | Upper | Total | Lower | Upper |
| Mar | 2012 | 3 | 4.6 | 1.6 | 7.6 | 5.6 | 2.0 | 9.2 |
| Apr | 2011 | 18 | 2.5 | 2.0 | 3.0 | 3.1 | 2.5 | 3.7 |
| Apr | 2012 | 29 | 3.8 | 3.3 | 4.4 | 4.7 | 4.0 | 5.3 |
| May | 2011 | 31 | 2.5 | 1.6 | 3.4 | 3.1 | 2.0 | 4.1 |
| May | 2012 | 22 | 1.6 | 1.1 | 2.0 | 1.9 | 1.3 | 2.5 |
| Spring | | | 3.0 | 1.9 | 4.1 | 3.7 | 2.4 | 5.0 |
| Jun | 2011 | 30 | 1.8 | 1.3 | 2.3 | 2.2 | 1.6 | 2.8 |
| Jun | 2012 | 22 | 0.4 | -0.4 | 1.2 | 0.5 | -0.4 | 1.5 |
| Jul | 2011 | 31 | 3.0 | 2.1 | 4.0 | 3.7 | 2.5 | 4.8 |
| Aug | 2011 | 31 | 2.6 | 2.2 | 3.0 | 3.2 | 2.7 | 3.7 |
| Summer | | | 2.0 | 1.3 | 2.6 | 2.4 | 1.6 | 3.2 |
| Sep | 2011 | 30 | 3.4 | 2.6 | 4.1 | 4.1 | 3.1 | 5.0 |
| Oct | 2011 | 31 | 3.1 | 2.1 | 4.1 | 3.8 | 2.6 | 5.0 |
| Nov | 2011 | 30 | 0.4 | -0.8 | 1.6 | 0.5 | -1.0 | 2.0 |
| Autumn | | | 2.3 | 1.3 | 3.3 | 2.7 | 1.6 | 3.8 |
| Dec | 2011 | 6 | 3.0 | -1.2 | 7.2 | 3.6 | -1.5 | 8.8 |
| Jan | (ice cover) | | 0.6 | 0.5 | 0.9 | 0.7 | 0.6 | 1.1 |
| Feb | (ice cover) | | 0.6 | 0.5 | 0.9 | 0.7 | 0.6 | 1.1 |
| Winter | | | 1.4 | -0.1 | 3.0 | 1.7 | -0.1 | 3.7 |
| Annual average | | | 2.2 | 1.1 | 3.3 | 2.6 | 1.4 | 3.9 |

flux dropped to between 50 and 75% of the observed fluxes.

CO_2 fluxes (2012 only, Fig. 5d) were also highest during the day, but not primarily during peak daytime ($46 \pm 10 \text{ mg CO}_2 \text{ m}^{-2} \text{ d}^{-1}$) as for CH_4 . Rather, peak CO_2 fluxes occurred at the end of the day when the sun set below the mountains and left Lake Klöntal in full shadow prior to nightfall (hourly median $144 \text{ mg CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ at 18 hours). The corresponding time period in the morning, before the sun reached the valley bottom, was a short period of negative CO_2 fluxes (i.e., net CO_2 uptake), while nocturnal fluxes were basically zero ($1 \pm 20 \text{ mg CO}_2 \text{ m}^{-2} \text{ d}^{-1}$). Both minimum and maximum hourly median CO_2 fluxes occurred shortly before the clear transition of atmospheric CO_2 concentrations from night to day (i.e., high to low concentrations) and day to night (i.e., low to high concentrations), respectively (Fig. 5d). Ultimately, the diel course of CO_2 concentration showed the inverse of CH_4 concentrations.

The diel cycles of concentrations and fluxes of both gases were tightly linked to horizontal wind speed (Fig. 5e). Its diel pattern was very distinctive and reflects the narrowly channeled flow in a deeply incised mountain valley where only the diurnal up-valley wind typically exceeds 1 m s^{-1} , whereas nocturnal winds are rather calm in the range of 1 m s^{-1} . Thus, the typical daytime wind system is not along the valley but across the valley (from the southeast; see Fig. 4a), which is easily explained by the steepness of the topography that allows the sun to heat up the southern rock face and produce updrafts that mix the air above Lake Klöntal in a vortices roll along the lake. This means that eddy covariance flux measurements during the day should be closely related to conditions measured at locality X7 (Fig. 1) where the deepest spot of the lake bathymetry is found.

Methane fluxes increased exponentially with wind speed U_{10} up to $\approx 3 \text{ m s}^{-1}$, above which the flux remained relatively constant—although with considerable scatter—at around $5.24 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ (Fig. 11). At low wind speeds (i.e., below 0.67 m s^{-1}), CH_4 fluxes also remained constant at around $0.8 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$. In the transition range between 0.67 and 3 m s^{-1} , the best estimate of CH_4 fluxes relative to wind speed was $F_{\text{CH}_4} = (0.29 \pm 0.07) + U_{10}(1.69 \pm 0.04)$, with U_{10} in m s^{-1} and F_{CH_4} in $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$.

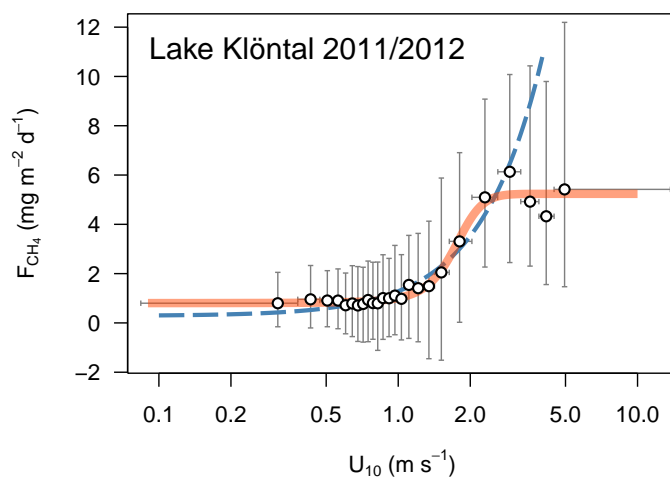


Fig. 11 Eddy covariance CH_4 flux as a function of 10-m wind speed U_{10} . 30-min flux averages were binned in 25 groups of equal number of samples. For each group the median (open circle) and the inter-quartile ranges (horizontal and vertical whiskers) are shown. A power law was fit to median $U_{10} \leq 3 \text{ m s}^{-1}$ (blue dashed curve, $F_{\text{CH}_4} = (0.29 \pm 0.07) + U_{10}^{(1.69 \pm 0.04)}$). The leveling off at high U_{10} , however, can only be modeled with a logistic fit (bold orange curve, $F_{\text{CH}_4} = 0.8 + (4.44 \pm 0.15)/[1 + \exp\{(1.72 \pm 0.06) - U_{10}/(0.24 \pm 0.04)\}]$).

Virtual air temperature, T_v , as measured by the ultrasonic anemometer–thermometer (Fig. 5f), indicated a rather small diel temperature range (DTR), which is characteristic for a local climate with a strong influence from the cool water surface of the reservoir.

3.5 Along-lake flux variations

Since the additional sampling locations were not added until August 2011, we could only evaluate the spatial variability in surface CH_4 from August to November. There was no persistent spa-

tial pattern observed during those months (Fig. 6), but rather a subgrouping of locations could be made based on dissolved CH₄ concentrations. Similarities in concentrations in the western locations (X1–X4), which were nearer the shallow inlet of the reservoir, differed from concentrations in the eastern locations (X5–X7) closer to the outlet and deepest parts of the lake. At the western sites, where shallower depths translated into a large gradient in lake bottom water temperatures (T_{LB}) throughout the year (6.4 to 18.6°C), a strong relationship between CH₄ effluxes and T_{LB} was observed ($F_{CH_4} = (0.13 \pm 0.01) T_{LB}$, $r^2 = 0.92$, $p < 0.0001$; Fig. 9a). In the eastern part of the reservoir, a relationship between T_{LB} and F_{CH_4} was also observed, although the more limited monthly T_{LB} range (4.7 to 8.6°C) resulted in a slightly weaker relationship ($F_{CH_4} = (0.25 \pm 0.04) T_{LB}$, $r^2 = 0.74$, $p < 0.0001$). Note that in both cases the regression intercept was insignificantly different from zero ($p=0.37$) and thus the regression was forced through the origin.

3.6 Annual CH₄ emissions from Lake Klöntal and its global warming potential

Annual CH₄ emissions and their uncertainties from the entire lake surface as derived via surface samples along the reservoir and from EC measurements are shown in Tables 3 and 2, respectively. Several assumptions were made to calculate these values, however, and will be discussed in detail below. First, potential losses off-site, such as degassing during pipeline passage, were not included in our estimates. Second, both surface sample-derived and EC based annual estimates suffered from a lack of direct winter emission estimates. Unlike natural lakes in frozen regions, ice covers on Alpine hydropower storages are not safe enough to walk on or deploy instruments because of the substantial vertical displacement of water level below the ice during hydroelectric production. Thus, we assumed 23% of the average CH₄ emissions from months that we could survey, the percentage found by Wik et al.¹⁵. In this way we assume that CH₄ supersaturation accumulates under the ice which then leads to increased fluxes after the ice has disappeared. This assumption was made for December to March (Table 3). As for the EC estimate, the few days with measurements in December 2011 and March 2012 were considered the best estimates for these two months, so that a reduced flux only had to be assumed for January and February 2012 (Table 2).

Finally, for the surface sample-derived estimate, flux data from each sampling location representing an entire month were weighted according to the surface area of the segment that they represent using equation (7). In the case when a location was not measured, the average flux of the measured locations obtained on that date was used in the weighted average. Ultimately, the annual CH₄ emissions from the lake were estimated at 2.6 (range 1.4 to 3.9) t CH₄ yr⁻¹ and 1.8 (range 0.5 to 7.4) t CH₄ yr⁻¹ with the EC (Table 2) and the gas-sampling approaches (Table 3), respectively.

Because CO₂ was not of interest at the beginning of the study, more assumptions had to be made to obtain a realistic annual CO₂ emission estimate: July–October were assumed to produce CO₂ emissions of the same magnitude as measured during June.

Table 3 Annual CH₄ emission estimate from Lake Klöntal based on monthly gas sampling surveys in 2011 (locations X1–X7, see Fig. 1). Bold numbers are the best estimates for seasonal and annual averages. Number in italics show estimated fluxes (see text for details).

| Lake Klöntal | Methane flux densities | | | Methane emissions | | |
|-----------------------|---|------------|------------|---------------------------------------|------------|-------------|
| | [mg CH ₄ m ⁻² d ⁻¹] | | | [t CH ₄ yr ⁻¹] | | |
| 2011 | | | | | | |
| Gas Sampling | Mean | Min | Max | Total | Min | Max |
| Mar | <i>0.5</i> | <i>0.4</i> | <i>0.8</i> | <i>0.6</i> | <i>0.5</i> | <i>0.9</i> |
| Apr | 3.5 | 0.9 | 9.8 | 3.3 | 0.9 | 9.1 |
| May | 0.9 | 0.5 | 1.5 | 1.0 | 0.6 | 1.7 |
| Spring | 2.2 | 0.4 | 9.8 | 1.6 | 0.5 | 9.1 |
| Jun | 3.3 | 0.9 | 9.1 | 1.5 | 0.9 | 2.4 |
| Jul | 1.0 | 0.6 | 1.7 | 4.9 | 1.5 | 13.3 |
| Aug | 2.8 | 2.7 | 8.8 | 3.2 | 0.9 | 9.6 |
| Summer | 2.3 | 0.6 | 9.1 | 3.2 | 0.9 | 13.3 |
| Sep | 2.3 | 0.2 | 5.8 | 2.5 | 0.2 | 6.4 |
| Oct | 1.6 | 0.4 | 3.2 | 1.8 | 0.5 | 3.5 |
| Nov | 1.2 | 0.1 | 4.3 | 1.4 | 0.1 | 5.0 |
| Autumn | 1.7 | 0.1 | 5.8 | 1.9 | 0.1 | 6.4 |
| Dec | <i>0.5</i> | <i>0.4</i> | <i>0.8</i> | <i>0.6</i> | <i>0.5</i> | <i>0.9</i> |
| Jan | <i>0.5</i> | <i>0.4</i> | <i>0.8</i> | <i>0.6</i> | <i>0.5</i> | <i>0.9</i> |
| Feb | <i>0.5</i> | <i>0.4</i> | <i>0.8</i> | <i>0.6</i> | <i>0.5</i> | <i>0.9</i> |
| Winter | 0.5 | 0.4 | 0.6 | 0.6 | 0.5 | 0.9 |
| Annual average | 1.7 | 0.4 | 6.3 | 1.8 | 0.5 | 7.4 |

In contrast to CH₄ there was a net CO₂ uptake measured when the surface water was cold in March and April, hence we assumed that November and December may yield similar uptake rates as April and March, respectively. With these assumptions an annual CO₂ emission of 53 t CO₂ yr⁻¹ was obtained (Table 4).

Table 4 Net CO₂ fluxes from Lake Klöntal, March–June 2012, and estimate for annual total CO₂ emissions. Numbers in italics denote estimates without direct measurements (see text for details).

| Lake Klöntal 2012 | | | CO ₂ flux densities | | | CO ₂ emissions | | |
|-----------------------|-------------|------|---|------------|------------|---------------------------------------|------------|------------|
| Eddy Covariance | | | [mg CO ₂ m ⁻² d ⁻¹] | | | [t CO ₂ yr ⁻¹] | | |
| MONTH | YEAR | Days | Median | Lower | Upper | Total | Lower | Upper |
| Mar | 2012 | 3 | -56 | -110 | -1 | -68 | -133 | -2 |
| Apr | 2012 | 29 | -19 | -35 | -2 | -23 | -43 | -2 |
| May | 2012 | 22 | 106 | 74 | 137 | 129 | 90 | 167 |
| Spring | | | 10 | -24 | 45 | 13 | -29 | 54 |
| Jun | 2012 | 22 | 103 | 79 | 127 | 125 | 97 | 154 |
| Jul | | | | | | 130 | 100 | 159 |
| Aug | | | | | | 125 | 97 | 154 |
| Summer | | | 103 | 79 | 127 | 127 | 98 | 156 |
| Sep | | | | | | 125 | 97 | 154 |
| Oct | | | | | | 125 | 97 | 154 |
| Nov | | | | | | -23 | -43 | -2 |
| Autumn | | | | | | 76 | 50 | 102 |
| Dec | | | | | | -68 | -133 | -2 |
| Jan | (ice cover) | | | | | 30 | 21 | 39 |
| Feb | (ice cover) | | | | | 30 | 21 | 39 |
| Winter | | | | | | -3 | -30 | 25 |
| Annual average | | | 57 | 28 | 86 | 53 | 22 | 84 |

To address the carbon footprint associated with hydropower generation, we normalized our emission results by electrical energy produced, which amounts to 114 GWh yr⁻¹. To allow for a comparison with other hydropower reservoirs, a factor of 34⁴ was used to convert CH₄ emissions to CO₂-equivalents (CO_{2,eq}). Our surface sample-derived estimates suggest a carbon cost of 0.54 (range 0.15–2.2) kg CO_{2,eq} associated with each MWh of electri-

cal energy produced. If EC flux estimates are used as a basis, this number is considerably higher (0.78 (range 0.42–1.16) kg CO_{2,eq} MWh⁻¹). An additional ≈0.46 kg CO₂ MWh⁻¹ is expected from the CO₂ emissions (Table 4). With only four months of CO₂ fluxes (Fig. 10, Table 4) an annual estimate is more difficult to obtain than that for CH₄, but a CO₂ estimate is provided because measured CH₄ fluxes were substantially lower than expected.

4 Discussion

4.1 Diel cycles of CH₄ and CO₂ fluxes

CH₄ fluxes—at least at night—are rather small compared to other reservoirs^{14,19}, or lakes²⁰, and within the detection limit for EC flux measurements, hence the random scatter around zero which also includes apparent negative fluxes.

On short time-scales the diel cycles of CH₄ and CO₂ fluxes provide some additional insights into the processes leading to GHG emissions. CH₄ fluxes (Fig. 5a) are almost a factor 3 larger during the daytime hours than during the night. This is in agreement with the diel cycle of horizontal wind speed U_{10} (Fig. 5e) that shows almost calm conditions at night and a pronounced effect of the diurnal up-valley wind system. This affects the piston velocity k_{600} (Fig. 7) and hence CH₄ efflux. While typical models assume an exponential increase of k_{600} and thus CH₄ fluxes (as shown in Fig. 11), we observed an upper limit for k_{600} of 9.12 ± 0.37 cm h⁻¹ irrespective of wind speeds ≥ 2 m s⁻¹ (Table 1, Fig. 7; midpoint of logistic fit at 1.70 ± 0.04 m s⁻¹). The highest wind speeds were observed during a few storms that probably completely mixed the reservoir, thereby exhausting the CH₄ water pool; hence, under high-wind conditions the CH₄ concentration gradient between water and air became the limiting factor for gas efflux, and more turbulent atmospheric mixing no longer increased the CH₄ efflux. This effect is also seen in Figure 11: CH₄ effluxes levelled off around 5.24 mg CH₄ m⁻² d⁻¹ at $U_{10} > 3$ m s⁻¹.

The good agreement between the two efforts to estimate annual emissions by taking into account spatial gradients and diel as well as seasonal changes (Tables 3 and 2) is reassuring. In comparison, the EC method offers the advantage of a much richer set of data that can resolve driving factors such as temperature, wind-speed and mixing.

4.2 Validation of piston velocity models

Our determination of k_{600} from EC flux measurements in comparison with published models (Fig. 7, Table 1) reveals the general dilemma of how fluxes are estimated from concentration gradients and U_{10} alone. The selection of a single model can substantially affect flux estimates, and even our approach in which we take the average of various published models (Table 1) would not have led to very robust estimates without the direct EC flux measurements. Our finding that k_{600} showed an upper limit at high wind speeds may be more generally valid for other lakes and reservoirs with limited CH₄ dissolved in the water body: above a specific U_{10} threshold (2.0 m s⁻¹ in the case of Lake Klöntal)—which may depend on local conditions such as lake dimensions and depth, sheltering effect by surrounding topography, and sta-

tistical distribution of wind speeds—a further increase in U_{10} does not lead to higher CH₄ fluxes because under such conditions it is not the turbulent mixing and transport that limits effluxes, but the resupply of CH₄ to the lake surface.

Although all five models (Table 1) assume an exponential increase even at high wind speeds, the overall effect on our spatially integrated annual flux estimates was not detrimental since U_{10} very rarely exceeded the threshold above which exponential models would heavily overestimate k_{600} . It is however also important to note that there is a bit of a mismatch between the monthly data interpolated as in Figure 6 and the high-resolution EC data. On a diel timescale the surface temperature changes and therefore also the solubility, which could not be taken in account in equation (5). In addition, convective mixing will change surface temperature by mixing in cold deeper water, thereby also shifting the oversaturation at the surface. Thus, water concentration measurements at hourly or better intervals would be required to further reduce the uncertainty in k_{600} derived from EC fluxes in our study.

4.3 Estimating the carbon footprint

To evaluate the contribution of this reservoir as an anthropogenic CH₄ source, we compared the spatially integrated monthly CH₄ diffusion rates (Table 3) with the integrated time-series of 2011–2012 EC fluxes measured near position X7 (Table 2). We had to adopt slightly different boundary conditions for the ice-covered period: For the spatial integration we assumed that the flux was low (≈23% the flux under absence of ice¹⁵) during the period from December to February (Table 3). In reality, the ice cover did not start on the first of December and hence some days in early December 2011 could still be covered with eddy covariance flux measurements. In addition, last few days of March 2012 already allowed the re-installation of the EC system, hence we used the December and March measurements as representative for the whole months and only assumed low fluxes (≈23% the flux under absence of ice¹⁵) during permanent ice cover in January and February for the annual estimates derived from EC measurements (Table 2).

The seasonal integration of EC fluxes yielded an estimated overall CH₄ emission from the Klöntal reservoir of 2.6 t CH₄ yr⁻¹ (Table 2), of which 27% can be attributed to the warm season (July–September) when the reservoir is filled to its maximum. These losses are due to diffusion alone as no ebullition was detected during our hydroacoustic surveys.

The EC fluxes provide a more coarse spatial resolution but a much better temporal coverage of fluxes compared to surface sampling considering measurements were continuously recording at 0.05 s resolution, from which EC-derived CH₄ and CO₂ fluxes were calculated in 30-minute intervals. Aggregated to daily and then monthly fluxes for upscaling, these measurements provide a more robust estimate of the fluxes near position X7. The best estimate for the annual CH₄ emissions from EC flux measurements is 29% higher than the spatially weighted estimate obtained from monthly samplings, and thus outside the range of variability of the spatial sampling. Although the relationship between reser-

voir bottom water temperatures and CH₄ flux differs between the shallower western part and the deeper eastern part (Fig. 9a) where the EC measurements were performed, the CH₄ fluxes between the two parts of the lake did not differ significantly (t-test, p=0.624).

We thus used the EC flux measurements for an assessment of the GWP of GHG fluxes from the Lake Klöntal reservoir and included a best annual estimate of concurrent CO₂ fluxes from the first half of 2012 (Table 4). The study of Diem et al.⁴⁵ has shown that N₂O only provides a negligible contribution to GHG emissions in alpine reservoirs.

Following conversion to CO₂-equivalents, we can compare annual Lake Klöntal GHG emissions and the contribution of CH₄ to total emissions to that of other reservoirs. Klöntal emits 88.4 t CO_{2,eq} yr⁻¹ as CH₄, which is roughly 63% of the total global warming forcing when our best estimate for CO₂ emissions is included in the total (141 t CO_{2,eq} yr⁻¹). Compared to a meta-analysis from global reservoirs³, the relevance of CO₂ effluxes from Lake Klöntal (≈37%) was higher than expected. Deemer et al.³ estimated the average breakdown of GHG contribution to be 79% from CH₄ and 18% from CO₂, but note their dataset was dominated by low altitude reservoirs and may not be representative of Alpine reservoirs. In addition, reservoirs with active CH₄ ebullition significantly increased the contribution of that GHG to the average carbon emissions in the Deemer et al.³ synthesis.

In a multi-reservoir study on other Alpine hydropower plants across Switzerland, Diem et al.⁴⁵ found even lower CH₄ emission rates than those measured in our study. The reservoirs from that study that provide the best comparison with Lake Klöntal (L. Sihl and L. Lungern) emitted only 6–10% of the CH₄ emissions observed from Lake Klöntal. Perhaps the better spatiotemporal resolution and use of EC measurements improved CH₄ estimates in our study as we would not necessarily expect an order of magnitude difference between Alpine reservoirs of similar altitudes. Regardless, this Lake Klöntal study and that of Diem et al.⁴⁵ suggest that high altitude, seasonally frozen reservoirs do not likely contribute substantially to global anthropogenic GHG emission budgets, at least not in the form of CH₄. Diem et al.⁴⁵ found that CO₂ dominated carbon emissions from those Alpine reservoirs (up to 99%), while Demarty et al.⁴⁶ found the same in three boreal reservoirs. Demarty et al.⁴⁶ suggested that seasonal exposure of shallow reservoir sediments to the atmosphere could limit CH₄ production and prevent the CH₄ buildup in sediment porewaters necessary to fuel ebullition, which is the pathway that significantly enhances overall CH₄ emissions. Together these studies suggest that measurements of CO₂ fluxes from boreal and high Alpine reservoirs are necessary in combination with CH₄ in order to accurately estimate carbon footprints. At the same time, measurement techniques or sampling strategies that provide higher spatiotemporal resolution of CH₄ fluxes may find that CH₄ emissions from such reservoirs are higher than expected, as was the case for Lake Klöntal.

GHG emission normalized by mean annual electricity production of the Klöntal hydropower scheme (114 GWh yr⁻¹) indicated that 1.24 kg CO_{2,eq} MWh⁻¹ are produced from this Alpine reservoir, which is more than one order of magnitude smaller than the

25 kg CO_{2,eq} MWh⁻¹ for the run-of-the-river hydropower scheme of Lake Wohlen on the Swiss plateau (T. DelSontro, pers. comm.) or the 36 kg CO_{2,eq} MWh⁻¹ reported as the upper range of tropical reservoirs by Demarty and Bastien⁴⁷, and far below the range of 10–550 kg CO_{2,eq} MWh⁻¹ for some high-emission reservoirs in tropical regions of Brazil⁴⁸.

As an upper limit for GHG emissions, a recent review proposed an average carbon footprint of 980 kg CO_{2,eq} MWh⁻¹ for coal-fired power plants⁴⁹. Lower average GHG emissions of renewable electricity systems have been documented in a recent meta-analysis as 34 and 50 kg CO_{2,eq} MWh⁻¹ for wind energy and solar photovoltaics, respectively⁵⁰. Depending on the boundary conditions, plausible estimates span two orders of magnitude. The operation of a power plant alone is responsible for 23.9% and 13.0% of the carbon footprint of wind energy and solar photovoltaics, respectively⁵⁰, which is 8.1 and 6.5 kg CO_{2,eq} MWh⁻¹ that can be compared with our estimates.

The situation is similar in the case of hydroelectricity: The existence and operation of a hydropower reservoir alters the CH₄ and CO₂ fluxes, and thus hydroelectricity is not perfectly carbon neutral relative to the conditions that would have prevailed had the dam never been built^{51,52}.

Low nutrient inputs and changing water levels might contribute to the rather small observed emissions of Lake Klöntal. Apart from two campgrounds, there are no major settlements in the partially forested catchment area of the lake and therefore nutrient inputs remain low. Reactive phosphate concentrations in the river⁵³ downstream of Lake Klöntal are consistently below 5 mg P m⁻³. Therefore, the lake is oligotrophic with very high recreational water quality as assessed by local authorities⁵³. Low productivity correlates with low methane emissions according to a recent meta-analysis³. In addition, large water level fluctuations aerate the littoral sediments during winter months and block methane production close to the sediment surface. Finally, we might have missed additional emission pathways in our study because it was not possible to monitor the period of drawdown during harsh snow and ice in winter. Decreasing water levels could theoretically trigger ebullition⁵⁴ and freshly exposed sediment surfaces during drawdown could release methane at significant rates⁵⁵.

5 Conclusions

Hydropower electricity is a renewable energy source that is valued positively in the context of climate change mitigation as compared to fossil fuel-based electricity generation. Our best estimate for the Lake Klöntal reservoir as derived from EC flux measurements during 2011 and 2012 suggests that average CH₄ and CO₂ emissions are on the order of 2.2 (range 1.1 to 3.3) mg CH₄ m⁻² d⁻¹ (Table 2) and 57 (range 28 to 86) mg CO₂ m⁻² d⁻¹ (Table 4). For the entire lake, converted to CO₂-equivalents, the GHG emissions (from CH₄ and CO₂) associated with the electrical power generation of 114 GWh yr⁻¹ was on the order of 1.24 kg CO_{2,eq} MWh⁻¹, of which 63% could be attributed to CH₄ emissions. The best estimate of CH₄ emissions derived from area-weighted surface water concentration measurements in 2011 yielded a carbon footprint of electricity of 0.54 kg CO_{2,eq} MWh⁻¹ from CH₄,

roughly 31% less than the EC-derived estimate of 0.78 kg CO_{2,eq} MWh⁻¹. Both estimates indicate that electricity from the Lake Klöntal reservoir produces a non-negligible carbon footprint and thus contributes to climate change; however, the effect per energy unit is rather small compared to warmer reservoirs at lower elevations and the majority of the reservoirs in the tropical climate zone. It's carbon footprint is roughly 15–20% that associated with the operation of wind energy and solar photovoltaic plants.

Conflicts of interest: There are no conflicts of interest to declare

Acknowledgments

This study was funded by Eawag and ETH Zurich. W.E. acknowledges funding received from ETH Zurich scientific equipment grants 0-43350-07 and 0-43683-11 for components of the EC flux instrumentation. We thank Christian Capello, Kurt Steiner, Bruno Steiger and Urs Beitela from the energy Axpo group who helped us with the logistics and coordination. Additional acknowledgments go to Christian Dinkel and Michael Schurter for technical support and Gijs Nobbe for lab assistance. We also thank Ines Bamberger, Sandro Brunner, Sandra Ogorka, Clío Sideri and Chrysanthi Tsimitri for fieldwork assistance. We are grateful for the technical support provided by Peter Plüss and Thomas Baur.

Data availability: Data collected by the authors are made available via doi:10.3929/ethz-b-000169083

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