# Greenhouse gas emissions (CO2, CH4, and N2O) from several perialpine and alpine hydropower reservoirs by diffusion and loss in turbines

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RESEARCH ARTICLE

# Greenhouse gas emissions (CO$_2$, CH$_4$, and N$_2$O) from several perialpine and alpine hydropower reservoirs by diffusion and loss in turbines

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**Abstract** We investigated greenhouse gas emissions (CO$_2$, CH$_4$, and N$_2$O) from reservoirs located across an altitude gradient in Switzerland. These are the first results of greenhouse gas emissions from reservoirs at high elevations in the Alps. Depth profiles were taken in 11 reservoirs located at different altitudes between the years 2003 and 2006. Diffusive trace gas emissions were calculated using surface gas concentrations, wind speeds and transfer velocities. Additionally, methane entering with the inflowing water and methane loss at the turbine was assessed for a subset of the reservoirs. All reservoirs were emitters of carbon dioxide and methane with an average of $970 \pm 340$ mg m$^{-2}$ day$^{-1}$ (results only from four lowland and one subalpine reservoir) and $0.20 \pm 0.15$ mg m$^{-2}$ day$^{-1}$, respectively. One reservoir (Lake Wohlen) emitted methane at a much higher rate ($1.8 \pm 0.9$ mg m$^{-2}$ day$^{-1}$) than the other investigated reservoirs. There was no significant difference in methane emissions across the altitude gradient, but average dissolved methane concentrations decreased with increasing elevation. Only lowland reservoirs were sources for N$_2$O ($72 \pm 22$ μg m$^{-2}$ day$^{-1}$), while the subalpine and alpine reservoirs were in equilibrium with atmospheric concentrations. These results indicate reservoirs from subalpine/alpine regions to be only minor contributors of greenhouse gases to the atmosphere compared to other reservoirs.

**Keywords** Greenhouse gases · Emissions · Reservoirs · Methane · Alpine

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## Introduction

In the early 1990s artificial lakes and reservoirs were discovered as potential greenhouse gas emitters (Rudd et al. 1993; Kelly et al. 1994). The question was put forward whether hydroelectric reservoirs, especially in the tropics, could still be considered cleaner energy sources compared to fossil alternatives (Fearnside 1997, 2002; Delmas et al. 2001; Pacca and Horvath 2002). Estimates suggest total emissions from reservoirs of about 70 Tg CH$_4$ year$^{-1}$ and 1,000 Tg CO$_2$ year$^{-1}$, accounting for 7 % of the anthropogenic emissions of these gases (St. Louis et al. 2000). Based on a much larger dataset, Barros et al. (2011) recently estimated reservoirs to emit only 176 Tg CO$_2$ year$^{-1}$ and 4 Tg CH$_4$ year$^{-1}$. There is, however, a high variability of trace gas emissions between different reservoirs, which leads to large uncertainties in quantification of global emissions and the available amount of data is still small compared to the number of reservoirs. So far there is limited information about emissions from reservoirs in the temperate climate zone (e.g. Soumis et al. 2004; DelSontro et al. 2010), which account for approximately 40 % of all reservoirs (Barros et al. 2011), and to our knowledge none from alpine reservoirs. In total, Swiss reservoirs cover an area of nearly 120 km$^2$ (approximately 0.01 % of the area

of temperate hydroelectric reservoirs), 60 % of which are situated at an elevation above 1,000 m a.s.l. (http://www.bfe.admin.ch/php/modules/publikationen/stream.php?extlang=de&name=de_242311927.pdf).

The main emission pathways for greenhouse gases from reservoir surfaces are the diffusive flux across the air–water interface and bubble flux (ebullition) resulting from supersaturation in the sediment. Bubbles mainly transport methane and only small amounts of carbon dioxide. The strong temperature dependence of methane production (e.g. Zeikus and Winfrey 1976; Kelly and Chynoweth 1981; Nguyen et al. 2010) suggests a decrease of methane emissions with decreasing temperatures at higher elevations. Besides emissions from the reservoir surface, other emission pathways that can significantly contribute to total gas emissions have recently drawn attention, i.e. gas release immediately below the turbine and emissions further downstream (Abril et al. 2006; Roehm and Tremblay 2006; Kemenes et al. 2007). Emissions from these two pathways contribute methane amounts similar to reservoir surface loss (Guérin et al. 2006; Kemenes et al. 2007) and are thus highly relevant for greenhouse gas (especially methane) emissions from reservoirs.

Besides sediments, other relevant sources of surface water greenhouse gases in lakes or estuaries are rivers and inflows (de Angelis and Lilley 1987; Upstill-Goddard et al. 2000; Murase et al. 2005). Thus reservoir inflows could contribute a considerable amount of dissolved greenhouse gases to the epilimnion of the reservoir and therewith the water layer is significant for diffusive surface flux. Inflowing water that has not yet completely mixed in a reservoir can be identified by hydrographic data (for example temperature and conductivity) or by the isotopic composition of methane, which can also be used to distinguish between different sources (for example inflows and sediment flux) of methane. However, when using the isotopic composition of methane, one has to keep in mind that methane oxidation can significantly alter $\delta^{13}C$ values (Barker and Fritz 1981; Whiticar 1999). In stratified oxic waters, methane oxidation is limited to a narrow zone at the oxic–anoxic interface (Rudd et al. 1976). Changes in isotopic signature caused by methane emission are small (Knox et al. 1992), while turbulent diffusion has no effect.

With this study, we provide the first data on greenhouse gas emissions from hydropower reservoirs across an altitude gradient in the Swiss Alps (Central Europe). We calculated diffusive fluxes of $CO_2$, $CH_4$ and $N_2O$ from the surface concentrations of several Swiss reservoirs at different times of the year. Eleven reservoirs at different altitudes were sampled and compared for diffusive greenhouse gas emissions over an altitude gradient, assuming conditions for greenhouse gas production and emission to decrease with altitude. Furthermore, we examined the importance of river inflows for the methane content of reservoirs at different altitudes and the contribution of methane loss to total methane emissions.

## Study sites

Between September 2003 and August 2006, 11 Swiss reservoirs from different regions and elevations were sampled for greenhouse gases (Table 1; Fig. 1 for reservoir properties and locations, Table 3 for sampling dates). The reservoirs are distributed along an elevation gradient from 481 to 2,368 m a.s.l. and climate varies accordingly between the different reservoirs. For example, average yearly air temperatures range from ∼8 °C at Lake Wohlen (lowland) to nearly 0 °C at Lake Oberaar (alpine). Average precipitation differs by a factor of 3 between the reservoirs and is listed in Table 1 together with the geology of the watershed and other reservoir characteristics. Unfortunately, nutrient data was only available for some reservoirs (supplementary Table A).

There are several specific features concerning reservoirs in alpine Switzerland. Reservoirs set in alpine valleys with steep slopes are rather deep (up to 230 m) with small littoral zones, due to the rapid increase of water depth. This is especially important and distinguishes those reservoirs from lowland reservoirs and lakes where littoral zones are very important for overall greenhouse gas emissions of oligotrophic lakes (Thebrath et al. 1993; Casper 1996). Another feature is that water is pumped from neighbouring valleys into the reservoirs, enlarging the reservoir catchment area in some cases quite substantially. Electricity production uses the elevation difference between mountain reservoirs and power stations in the valley. A drop of reservoir water of several hundred meters through pipes and tunnels before it reaches the turbines is the result. A second water outflow (called residual water) is a legally established amount of water that has to be released from the reservoirs to provide the river ecosystem downstream with a minimum amount of water. A last characteristic of these reservoirs is that the majority of the water filling the reservoirs is available from spring to autumn when the snow stored in winter melts. Thus, water level declines in winter and reaches its minimum in early spring with, in some cases, less than 10 % of the maximum water volume left.

Two of the reservoirs investigated (Lakes Oberaar, alpine and Sihl, lowland) are pump-storage reservoirs, which receive water from a reservoir or lake located at lower altitude (Lake Grimsel for Lake Oberaar and Lake Zurich for Lake Sihl). While the water volume of Lake Oberaar is replaced up to ten times every year by pumping, it only contributes a minor part to Lake Sihl. Lake Wohlen (lowland) on the other hand is a run-of-the-river reservoir,

**Table 1** Properties of the sampled reservoirs

| Lake | Location (latitude/longitude) | Elevation (m) | Classification | Year of construction | Volume (Mio m³) | Surface (km²) | Greatest depth (m) | Average depth (m) | Retention time (days) | Geology of watershed | Average yearly precipitaion (mm) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. Lake Wohlen | 46°58'N/7°19'E | 481 | Lowland[a] | 1920 | 25 | 3.65 | 20 | 7 | 2–3 | Sedimentary rocks (marl, sandstone, limestone, clay) | 1,000–1,200 |
| 2. Lake Gruyère | 46°39'N/7°06'E | 677 | Lowland[a] | 1947 | 200 | 9.6 | 75 | 21 | 75 | Fluvial deposits, limestone | 1,200–1,600 |
| 3. Lake Lungern | 46 48'N/8°10'E | 689 | Lowland[a] | 1920 | 65 | 2.01 | 68 | 32 | 100–200 | Sedimentary rocks (lime, marl) | 1,400–2,000 |
| 4. Lake Sihl | 47°08'N/8°48'E | 889 | Lowland[a] | 1936 | 96.5 | 10.85 | 23 | 9 | 140[d] | Sedimentary rocks (limestone, marl) | 1,200–1,600 |
| 5. Lake Luzzone | 46°34'N/8°58'E | 1,591 | Subalpine[b] | 1963 | 88 | 1.44 | 181 | 61 | 230 | Deformed sedimentary, metamorphic and igneous rocks | 1,600–2,000 |
| 6. Lake Zeuzier | 46°21'N/7°26'E | 1,777 | Subalpine[b] | 1957 | 51 | 0.85 | 140 | 60 | 120 | Sedimentary rocks | 2,000–2,400 |
| 7. Lake Santa Maria | 46°34'N/8°48'E | 1,908 | Subalpine[b] | 1968 | 67 | 1.17 | 86 | 57 | 100–200[e] | Granite, gneiss and paragneiss | 2,000–2,400 |
| 8. Lake Grimsel | 46°34'N/8°20'E | 1,908 | Alpine[c] | 1932 | 101 | 2.72 | 100 | 37 | 20–50[f] | Igneous rocks (granite) | 2,400–3,000 |
| 9. Lago Bianco | 46°24'N/10°01'E | 2,234 | Alpine[c] | 1912 | 21 | 1.5 | 53 | 14 | 100–200[g] | Igneous rocks (granite) | 2,000–2,400 |
| 10. Lake Oberaar | 46°33'N/8°16'E | 2,303 | Alpine[c] | 1953 | 61 | 1.46 | 90 | 42 | 30–60[f] | Igneous rocks (granite) | 2,400–3,000 |
| 11. Lake Dix | 46°04'N/7°24'E | 2,368 | Alpine[c] | 1961 | 401 | 4.3 | 227 | 93 | 30–50 | Igneous rocks (granite) | 1,600–2,400 |

[a] Lowland reservoirs is used for reservoirs below 1,000 m a.s.l

[b] Subalpine reservoirs is used for reservoirs between 1,000 and approximately 1,900 m a.s.l., which do not have a whitish water color due to a high amount of particles from glacial melt water

[c] Alpine reservoirs are is used for reservoirs above 1,900 m a.s.l., which do have a whitish water color due to a high amount particles from glacial melt water

[d] About 10 % of the water in the lake are pumped from Lake Zurich

[e] Is connected with two other reservoirs to one power station

[f] Water from Lake Grimsel is pumped into Lake Oberaar at night and released back to Lake Grimsel during the day for energy production; this way the volume of Lake Oberaar gets replaced about ten times every year

[g] Is a storage reservoir for Lake Palü, no direct energy production

**Fig. 1** Locations of the sampled reservoirs (for numbers see Table 1)

which has a steady inflow from a river, a small capacity (as well as a small water retention time) and has water flowing through it all the time. All other reservoirs are conventional reservoirs, which use the dam to create a large water storage capacity, produce electricity during times of demand or store the water in the meantime.

Reservoirs were selected to roughly include the whole extent of reservoir depths (4–227 m), sizes (0.1–10.9 km$^2$), volume (0.4–401 Mio m$^3$) and altitude distributions (459–2,446 m a.s.l.) of the reservoirs. Sampling time was restricted to late spring until autumn, as access to the high altitude reservoirs was limited due to weather conditions and water content was low after ice-melt.

## Methods

### Sampling

A SBE 19 CTD probe (Sea Bird Electronics) equipped with an oxygen and pH sensor was used to collect hydrographic data (conductivity, temperature, depth, light transmission, pH and dissolved oxygen). The water column was sampled with a 5 L Niskin bottle and aliquots were immediately transferred into bottles with a tube, avoiding bubbles (Winkler bottles for oxygen, 200 mL plastic bottles for alkalinity and 600 mL glass bottles for methane and nitrous oxide concentration). Samples were taken at different depths for each reservoir, usually below the surface, above the sediment and every 10 or 20 m in between. Sample sites are at the deepest point of the dam basin and for some reservoirs a second site was examined closer to the inlet. Replicates were taken for dissolved gas concentrations.

Winkler samples were used to correct the offset in the oxygen sensor. Unfiltered water was titrated with 0.1 M HCl for alkalinity. Samples for dissolved gas analysis were flushed with 2–3 times the bottle volume before the samples were preserved with NaOH (pH > 12) or Cu(I)Cl, then closed with a butyl septa while carefully avoiding air bubbles in the bottles. To calibrate the pH sensor (SBE 18 pH sensor, SeaBird, measurement range 0–14, accuracy 0.1 pH units), solutions of known pH (pH = 4, 7 and 9) were used before each sampling date. The accuracy of the pH sensor was not sufficient for low conductivity lakes, thus $CO_2$ concentrations and fluxes for reservoirs with conductivities below 100 μS cm$^{-1}$ were not calculated.

## Inflows, outflows

Methane concentrations were measured in the in- and outflowing water of six reservoirs. If possible the CTD probe was used, but if depth of the river was not sufficient, temperature and conductivity were measured with a WTW LF 330 conductivity meter, pH with a Metrohm 704 pH-meter and oxygen with a WTW Multi 340i multi probe. Water samples for methane measurements were sampled as described below. Only major inflows (Number 1 in Fig. 2) were sampled, as well as residual water (3) from the river right below the reservoir and water after passage of the turbine (4), but before re-entering the river further downstream.

Methane loss at the turbine was calculated using the difference between the measured methane concentration at the sampling point closest to the depth of the reservoir outlet and methane concentrations measured after the turbine.

## Dissolved gases

### $CO_2$

Dissolved $CO_2$ (DIC) was calculated using the measured alkalinity, temperature, pH, and the dissociation constants of $H_2CO_3$ and $HCO_3^-$ (Plummer and Busenberg 1982). Samples for alkalinity were taken at the surface and at the bottom of the water column.

According to Neal et al. (1998), the error of $CO_2$ concentration calculations using temperature and pH is less than 2 % for pH values <9. The error of pH in our measurement was 0.1 pH units, resulting in a total error of 23 % when calculating DIC from pH and alkalinity.

### $CH_4$ and $N_2O$

Concentrations of dissolved methane and nitrous oxide were measured by the headspace technique similar to McAuliffe (1971). A sample volume of 50 mL was replaced by an inert gas (helium or nitrogen) and equilibrated in an ultra-sonic bath for about 30 min. Nitrous oxide was measured with a Dani 86.10 HT gas chromatograph (GC) with a Porapak Q column (Supelco) and an electron capture detector (ECD). The oven temperature was kept constant at 70 °C and the detector temperature was 340 °C.

Methane concentrations were measured on a HRGC 5160 Mega Series (Carlos Erba Instruments) with a flame ionization detector (FID), a GS-Q P/N 115-3432 column (J&W Scientific) and hydrogen as a carrier gas. Temperatures were 40 °C for the oven and 200 °C for the detector. Gas volumes of 2 mL for $N_2O$ and 200 μL for $CH_4$ were injected. Replicate measurements yielded an accuracy of ±5 % for methane and ±10 % for nitrous oxide.

In 2006, measurements were made on an Agilent GC using a GS-Carbonplot column (Agilent) for nitrous oxide and a Carboxen 1010 Plot column (Supelco) for methane. The temperature was kept constant at 40 °C for 5 min and then raised to 110 °C at the rate of 10 °C/min. The GC had a 1 mL sample loop for nitrous oxide and a 500 μL sample loop for methane. Accuracy on this GC improved to ±3 % for methane and ±5 % for nitrous oxide.
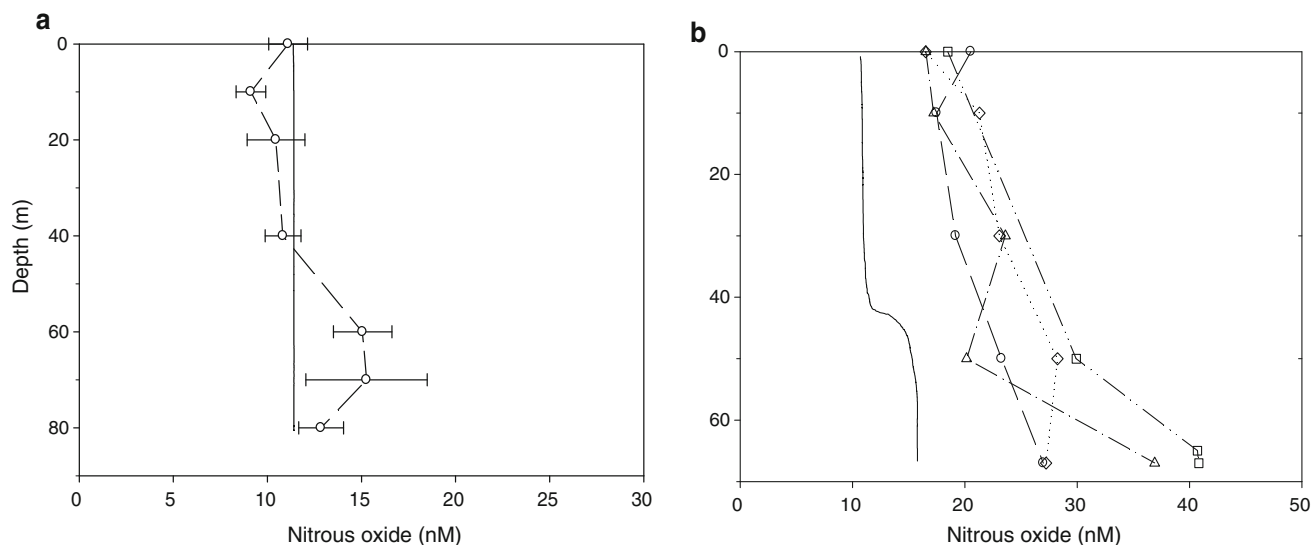


Fig. 2  a $N_2O$ concentrations (*circles*) and atmospheric equilibrium concentration (*solid line*) of Lake Grimsel on 9 October 2003. b $N_2O$ concentrations in Lake Lungern on 19 October 2005 (*diamonds*), 1 September (*circles*), 14 September (*squares*), and 21 September 2006 (*triangles*) and atmospheric equilibrium concentration (*solid line*) of Lake Lungern

Standards used for calibration were supplied from Scott Specialty Gases. Concentrations were 15 ppm, 1,000 ppm and 1 % for methane and 1 and 10 ppm for nitrous oxide.

Dissolved gas concentrations were calculated using solubility data from Wiesenburg and Guinasso (1979) for methane, from Weiss and Price (1980) for nitrous oxide, and from Weiss (1974) for carbon dioxide.

### Stable isotopes

The carbon isotopic signature of methane was determined similar to the method described by Sansone et al. (1997). Measurements were done with an IsoPrime mass spectrometer connected to a TraceGas preconcentrator (GV Instruments, UK). The amount of injected gas depended on the methane concentration in the sample, ranging from a few μL to several mL. Samples were measured twice. Results are noted in the standard $\delta$-notation relative to Vienna PeeDee Belemnite (VPDB):

$$\delta^{13}C = \left( \frac{R_{sample}}{R_{reference}} - 1 \right) \times 1000, \quad (1)$$

where $R_{sample}$ is the ratio of $^{13}C/^{12}C$ of the sample, $R_{reference}$ is the ratio of the reference material, and $\delta^{13}C$ is the isotopic signature of methane in ‰ versus VPDB. A standard (1 % $CH_4$ in argon) of known isotopic composition was injected between every two or three sample runs. The precision of the method was ±0.7 ‰.

### Gas fluxes

Greenhouse-gas fluxes were calculated using the boundary layer model as described by Liss and Slater (1974).

$$F = k \cdot f \cdot \left( C_w - C_{eq} \right) \quad (2)$$

The model estimates the air–water flux F [mg m$^{-2}$ day$^{-1}$] using the water saturation concentration $C_{eq}$ [M], the measured water concentration $C_w$ [M] of the greenhouse-gas, the transfer velocity k [cm h$^{-1}$] and a unit conversion factor f. For the calculation of the transfer velocity k we used the bi-linear relationship given by Crusius and Wanninkhof (2003):

$$\begin{aligned} \text{for } U_{10} < 3.7 \text{ m s}^{-1} \quad k_{600} &= 0.72 \cdot U_{10} \\ \text{for } U_{10} > 3.7 \text{ m s}^{-1} \quad k_{600} &= 4.33 \cdot U_{10} - 13.3 \end{aligned} \quad (3)$$

and the power function given by Cole and Caraco (1998):

$$k_{600} = 0.228 \cdot U_{10}^{2.2} + 0.168 \quad (4)$$

where $k_{600}$ is the transfer velocity for the Schmidt number Sc = 600, and $U_{10}$ the wind speed 10 m above the ground. To convert $k_{600}$ to the actual transfer velocity k of the gas, we used

$$k = k_{600}(Sc/600)^c \quad (5)$$

where Sc is the Schmidt number of the greenhouse gas ($CH_4$, $CO_2$ and $N_2O$) at water surface temperature and c is $-2/3$ for $U_{10} < 3.7$ m s$^{-1}$ and $-1/2$ for higher wind speeds (Liss and Merlivat 1986).

Atmospheric equilibrium concentrations ($C_{eq}$) were determined using an air concentration of 1.77 ppm $CH_4$, 379 ppm $CO_2$ and 319 ppb $N_2O$ (Forster et al. 2007), corrected to the reduced pressure of the lake elevation and measured water temperatures. Schmidt numbers were calculated for the measured water temperatures according to Wanninkhof (1992) and the authors cited therein. Wind data were supplied by MeteoSwiss from the ANETZ- or ENET-Station closest to the lake in question. Results are given as flux for the measured surface concentration or the average flux, if more than one site was sampled.

## Results

### $CO_2$ concentrations and emissions

Surface concentrations of $CO_2$ were supersaturated in all five reservoirs for which data are available (Table 2) with concentrations ranging from 40–280 μmol L$^{-1}$. In nearly all lakes, alkalinity measured above at the bottom of the lake was nearly 0.5 units higher than at the lake surface, except for Lake Luzzone (subalpine) and Lake Wohlen (lowland), where values were similar (data not shown).

The calculated fluxes were on average 970 ± 340 mg $CO_2$ m$^{-2}$ day$^{-1}$ (median 920 mg $CO_2$ m$^{-2}$ day$^{-1}$, range 132–2,516 mg $CO_2$ m$^{-2}$ day$^{-1}$) for all dates. Diffusive fluxes are highest during May, with an average of 1,800 ± 500 mg $CO_2$ m$^{-2}$ day$^{-1}$ (three sites) and decrease towards September to 520 ± 290 mg $CO_2$ m$^{-2}$ day$^{-1}$ for lowland sites. At the lone subalpine site in Lake Luzzone (subalpine), emissions nearly double from July to August to reach 2,520 mg $CO_2$ m$^{-2}$ day$^{-1}$.

### Nitrous oxide concentrations and emissions

Minimum $N_2O$ concentration in the five reservoirs sampled for $N_2O$ was 6 nmol L$^{-1}$ (55 % saturation) in Lake Zeuzier (subalpine) and maximum concentration 41 nmol L$^{-1}$ (260 % saturation) at the bottom of Lake Lungern (lowland). Figure 2a, b show a typical profile for an alpine reservoir (Lake Grimsel) and for a lowland reservoir (Lake Lungern).

Concentrations in the three alpine reservoirs were close to the atmospheric equilibrium concentration throughout most of the water column. While Lake Grimsel (alpine)

**Table 2** Diffusive fluxes of $CH_4$, $CO_2$ and $N_2O$ in the studied reservoirs

| Reservoir | Date | Number of stations | $CH_4$ Inflow Concentration (nmol l$^{-1}$) | $CH_4$ Inflow $\delta^{13}C$ (‰) | $CH_4$ Surface concentration (nmol l$^{-1}$) | $CH_4$ Diffusive flux (µg m$^{-2}$ day$^{-1}$) | $CH_4$ Outflow[a] (nmol l$^{-1}$) | Loss at turbine[b] (%) | DIC Inflow (mmol l$^{-1}$) | DIC Reservoir (mmol l$^{-1}$) | $CO_2$ Surface concentration (µmol l$^{-1}$) | $CO_2$ Diffusive flux (mg m$^{-2}$ day$^{-1}$) | $N_2O$ Surface concentration (nmol l$^{-1}$) | $N_2O$ Diffusive flux (µg m$^{-2}$ day$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lake Wohlen | 5/24/2005 | 2 | 97 | −52 | 516 ± 527 | 1,239 ± 1,341 | 870 | Not observed | 2.3 | 2.3 | 279 ± 98 | 1,558 ± 613 | | |
| | 6/14/2005 | 3 | 71 | −51 | 572 ± 333 | 1,672 ± 666 | 1,412 | Not observed | 2.2 | 2.2 | 140 ± 10 | 1,053 ± 72 | | |
| | 8/10/2005 | 3 | 102 | −53 | 498 ± 256 | 1,183 ± 605 | 653 | Not observed | 1.9 | 1.9 | 52 ± 6 | 276 ± 57 | | |
| | 9/28/2006 | 2 | | | 1,039 ± 302 | 2,025 ± 569 | | | | | | | 23 ± 4 | 72 ± 22 |
| Lake Gruyére | 5/24/2005 | 1 | 42; 189 | −43; −53 | 48 | 142 | 102 | Not observed | 2.8; 2.6 | 3.6 | 185.0 | 1,518 | | |
| | 6/15/2005 | 2 | 15; 84 | −48; −53 | 42 ± 16 | 135 ± 55 | 23 | Not observed | 2.7; 2.7 | 3.2 ± 0.3 | 88 ± 17 | 707 ± 170 | | |
| | 8/10/2005 | 2 | 12; 27 | −49; −39 | 49 ± 16 | 179 ± 63 | 15 | Not observed | 2.9; 3.0 | 3.4 ± 0.3 | 80 ± 18 | 712 ± 182 | | |
| Lake Lungern | 10/25/2005 | 1 | | | 104 | 163 | | | | | | | | |
| | 8/1/2006 | 2 | | | 101 ± 23 | 340 ± 80 | | | | 2.0 | 50 ± 14 | 353 ± 136 | | |
| | 9/1/2006 | 2 | | | 48 ± 11 | 86 ± 20 | | | | 2.0 | 40 ± 0 | 132 ± 2 | 18 ± 3 | 47 ± 16 |
| | 9/14/2006 | 2 | | | 62 ± 13 | 147 ± 32 | | | | | | | 19 ± 0 | 69 ± 1 |
| | 9/21/2006 | 2 | | | 22 ± 9 | 35 ± 15 | | | | | | | 17 ± 1 | 38 ± 4 |
| | 10/19/2006 | 2 | | | 22 ± 7 | 30 ± 10 | | | | | | | 20 ± 5 | 46 ± 24 |
| Lake Sihl | 5/14/2005 | 2 | 416; 172 | −66; −64 | 67 ± 1 | 286 ± 11 | 53 | 16 | 2.6; 2.5 | 2.3 | 203 ± 23 | 2,391 ± 362 | | |
| | 6/17/2005 | 2 | 128; 102 | −55; −59 | 51 ± 10 | 133 ± 29 | 23 | 73 | 2.4; 2.6 | 2.4 | 74 ± 14 | 460 ± 960 | | |
| | 8/9/2005 | 2 | 367; 102 | −39; −63 | 72 ± 9 | 205 ± 25 | 32 | 46 | 2.4; 3.2 | 2.6 | 68 ± 30 | 451 ± 249 | | |
| Lake Luzzone | 7/21/2005 | 1 | 91; 20; 14 | −59; −40; −38 | 12 | 122 | 13 | 46 | 1.2; 1.8; 0.6 | 1.1 | 53 | 1,313 | | |
| | 8/22/2005 | 1 | 272; 24; 23 | −61; −36; −40 | 27 | 140 | 33 | 45 | 1.2; 1.8; 0.8 | 1.0 | 72 | 2,516 | | |
| Lake Zeuzier | 9/10/2003 | 1 | | | 15 | 65 | | | | | | | 6 | −27 |
| Lake Santa Maria | 6/7/2005 | 1 | 31; 26; 24 | −35; −35; −36 | 55 | 650 | | | | | | | | |
| | 7/6/2005 | 1 | 29; 23; 21 | −37; −28; −28 | 16 | 189 | | | | | | | | |
| | 8/23/2005 | 1 | 10; 19; 11 | −38; −42; −22 | 15 | 108 | | | | | | | | |
| Lake Grimsel | 10/9/2003 | 1 | | | 34 | 212 | 20 | 57 | | | | | 11 | −11 |
| | 7/5/2005 | 1 | | | 18 | 355 | | | | | | | | |
| | 7/28/2005 | 1 | | | 13 | 532 | | | | | | | | |
| Lago Bianco | 9/28/2004 | 1 | | | 3 | −1 | | | | | | | | |
| Lake Oberaar | 7/5/2005 | 1 | 18 | −36 | 13 | 254 | 18 | | | | | | | |
| | 7/28/2005 | 1 | 15 | −37 | 9 | 313 | 15 | | | | | | | |
| | 8/24/2005 | 1 | 31 | −35 | 25 | 262 | 31 | | | | | | | |
| Lake Dix | 9/10/2003 | 1 | | | 31 | 48 | | | | | | | 17 | 65 |

[a] Measured after water passed the turbine

[b] Calculated from the difference of methane concentration closest to the depth of the water outlet and the outflow concentration

and Lake Zeuzier (subalpine) were small sinks (−11, resp. −27 µg $N_2O$ m$^{-2}$ day$^{-1}$), Lake Dix (alpine) was a small source (65 µg $N_2O$ m$^{-2}$ day$^{-1}$) of $N_2O$. Both lowland reservoirs were supersaturated with $N_2O$ throughout the water column and concentrations increased towards the sediment. Both were small nitrous oxide sources of 72 ± 22 µg $N_2O$ m$^{-2}$ day$^{-1}$ (Lake Wohlen, lowland) and 50 ± 13 µg $N_2O$ m$^{-2}$ day$^{-1}$ (Lake Lungern, lowland).

## Methane concentrations, $\delta^{13}C$ isotopic composition and emissions

### Concentrations and isotopic composition

In the 11 reservoirs sampled, three characteristic types of methane profiles were identified. In the following, one example for each profile type will be illustrated. Profiles of the remaining reservoirs are documented in the electronic supplement (Figs. A1–A3).

The categories are: (1) uniform methane profile, (2) increasing methane concentrations towards the sediment, (3) profiles with methane maxima in the water column.

#### (1) Uniform methane profiles

Constant methane concentrations very close to the atmospheric equilibrium concentration were found for example in the water column of Lake Bianco (alpine, Fig. 3a). Concentrations varied between 1 and 3 nmol L$^{-1}$ for the whole lake with the maximum at 40 m depth. Variation is greater in the $\delta^{13}C$ values due to the low concentrations and the higher error in the measurements associated with that. Values range from −40 to −36 ‰.

#### (2) Increasing methane concentrations from the surface towards the sediment

Profiles of this category had a more or less steady increase of methane concentrations from the water surface to the sediment surface and a stable stratification during summer. Methane diffusing from the sediment was responsible for the higher concentrations at the lake bed.

In Lake Santa Maria (subalpine), methane concentrations on all three sampling dates (June, July, and August) increased towards the bottom (Fig. 3b). In June, surface concentrations were 55 nmol L$^{-1}$, while on the other two dates concentrations were about 15 nmol L$^{-1}$. Concentrations right above the sediment decreased from June to August, from 100 to 63 nmol L$^{-1}$. The carbon isotopic signal of methane decreased on all sampling dates from the surface down to the bottom of the reservoir. The rapid temporal change in the isotopic composition from June to July is reflected in temperature and other hydrographic

**Fig. 3 a** *Left* Methane concentration (*open triangles*) and isotopic composition (*full triangles*) in Lake Bianco on 28 September 2004. *Right* Temperature (*black line*), light transmission (*yellow line*), conductivity (*green line*) and dissolved oxygen concentration (*red*) profiles of Lake Bianco. **b** *Left* Methane concentrations (*open symbols*) and isotopic composition (*full symbols*) in Lake Santa Maria on 7 June (*squares*), 6 July (*triangles*) and 23 August 2005 (*circles*). *Right* Temperature (*black line*), light transmission (*yellow line*), conductivity (*green line*) and dissolved oxygen (*red line*) profiles of Lake Santa Maria on 23 August 2005. **c** *Left* Methane concentrations (*open symbols*) and isotopic composition (*full symbols*) in Lake Luzzone on 21 July (*triangles*) and 22 August 2005 (*circles*). *Right* Temperature (*black line*), light transmission (*yellow line*), conductivity (*green line*), dissolved oxygen (*red line*) and pH (*short dash*) profiles of Lake Luzzone on 22 August 2005 (color figure online)

parameters as well (Fig. 3b and supplementary material 1c, d).

#### (3) Enhanced methane concentrations in an intermediate layer

These profiles showed a local maximum of methane concentrations in intermediate water layers. Below the intermediate layer, concentrations had another minimum and increased again towards the sediment. We suggest methane entering the reservoir with inflowing water during the filling stage and stratifying at intermediary depth to be the reason for this profile shape.

Lake Luzzone (subalpine) was sampled twice in July and August 2005 (Fig. 3c). Both times methane concentrations in the enhanced intermediate layer were about twice as much as the upper and lower minimum. Concentrations increase again towards the sediment and reach the highest concentrations above the sediment at 100 nmol L$^{-1}$ in August. The carbon isotopic composition followed the concentration profile with values between −38 and −40 ‰ at the minima and −50 to −52 ‰ at higher concentrations. The existence of an intermediate layer also is supported by profiles of conductivity and dissolved oxygen (Fig. 4c; supplementary material 1e).

### Emissions

Concentrations in Lake Bianco (alpine) were at saturation (∼3 nmol L$^{-1}$), therefore the methane emissions were negligible (Table 2; Fig. 4). The three other alpine reservoirs—Lake Dix, Oberaar and Grimsel—emitted methane at 0.05, 0.28 ± 0.03, and 0.37 ± 0.16 mg CH$_4$ m$^{-2}$ day$^{-1}$, respectively.

For subalpine reservoirs (reservoirs between 1,000 and 1,900 m a.s.l. in this manuscript; Lake Santa Maria is included due to its obvious profile differences from that of the alpine reservoirs) diffusive methane emission was lowest in Lake Zeuzier at 0.07 mg CH$_4$ m$^{-2}$ day$^{-1}$, two times higher in Lake Luzzone at 0.15 ± 0.06 mg CH$_4$
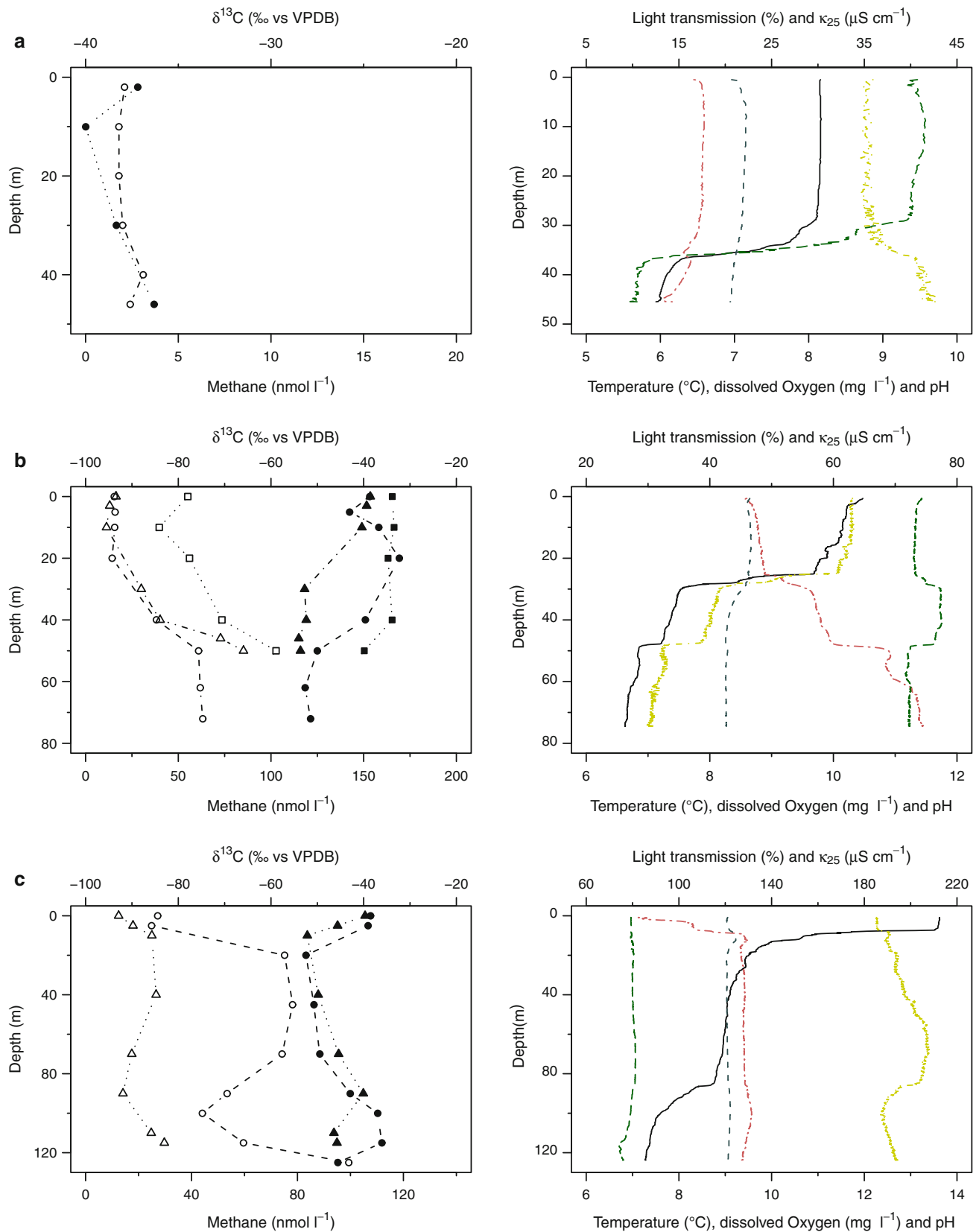
m$^{-2}$ day$^{-1}$ and still higher in Lake Santa Maria at 0.32 ± 0.29 mg CH$_4$ m$^{-2}$ day$^{-1}$. Emissions in Lake Santa Maria were highest in June 2005 with 0.65 mg CH$_4$ m$^{-2}$ day$^{-1}$, while in July and August values were similar to the ones in Lake Luzzone for the same time span.

Diffusive methane emissions for lowland lakes were 0.15 ± 0.02, 0.13 ± 0.12, and 0.21 ± 0.08 mg CH$_4$ m$^{-2}$ day$^{-1}$ for Lake Gruyère, Lake Lungern and Lake Sihl, respectively. Changes during the sampling period were small in Lake Gruyère and Lake Luzzone, while in Lake Lungern emissions decreased in the year 2006 from 0.34 ± 0.08 mg CH$_4$ m$^{-2}$ day$^{-1}$ in early August to 0.07 ± 0.06 mg CH$_4$ m$^{-2}$ day$^{-1}$ for four sampling dates in September and October. Diffusive fluxes in Lake Wohlen were one order of magnitude higher than in the other lowland reservoirs at an average of

1.8 ± 0.9 mg CH$_4$ m$^{-2}$ day$^{-1}$ for all sampling campaigns confirming results by DelSontro et al. (2010).

## Inflows and outflows

In- and outflows were supersaturated with methane at all sampling dates, with concentrations between 10 and 420 nmol L$^{-1}$ with $\delta^{13}$C values between −22 and −66 ‰. Concentrations tend do decrease later in the year, but this is not a common trend for all reservoirs. There were no concentration differences between the turbine inlet concentrations and the concentration after the turbine in lowland Lakes Wohlen and Gruyère, while at Lakes Sihl (lowland), Luzzone (subalpine) and Grimsel (alpine) concentrations are between 16 and 73 % lower after the water passed the turbine (Table 2).



Fig. 4 Methane emissions in mg m$^{-2}$ day$^{-1}$ from 11 Swiss reservoirs calculated with transfer velocity k calculated from the bi-linear relationship of Crusius and Wanninkhof (2003, dark grey bars) and the relationship given by Cole and Caraco (1998, white bars), as well as the average diffusive emissions listed in St. Louis et al. (2000, light grey bar, diffusive emissions only) for comparison
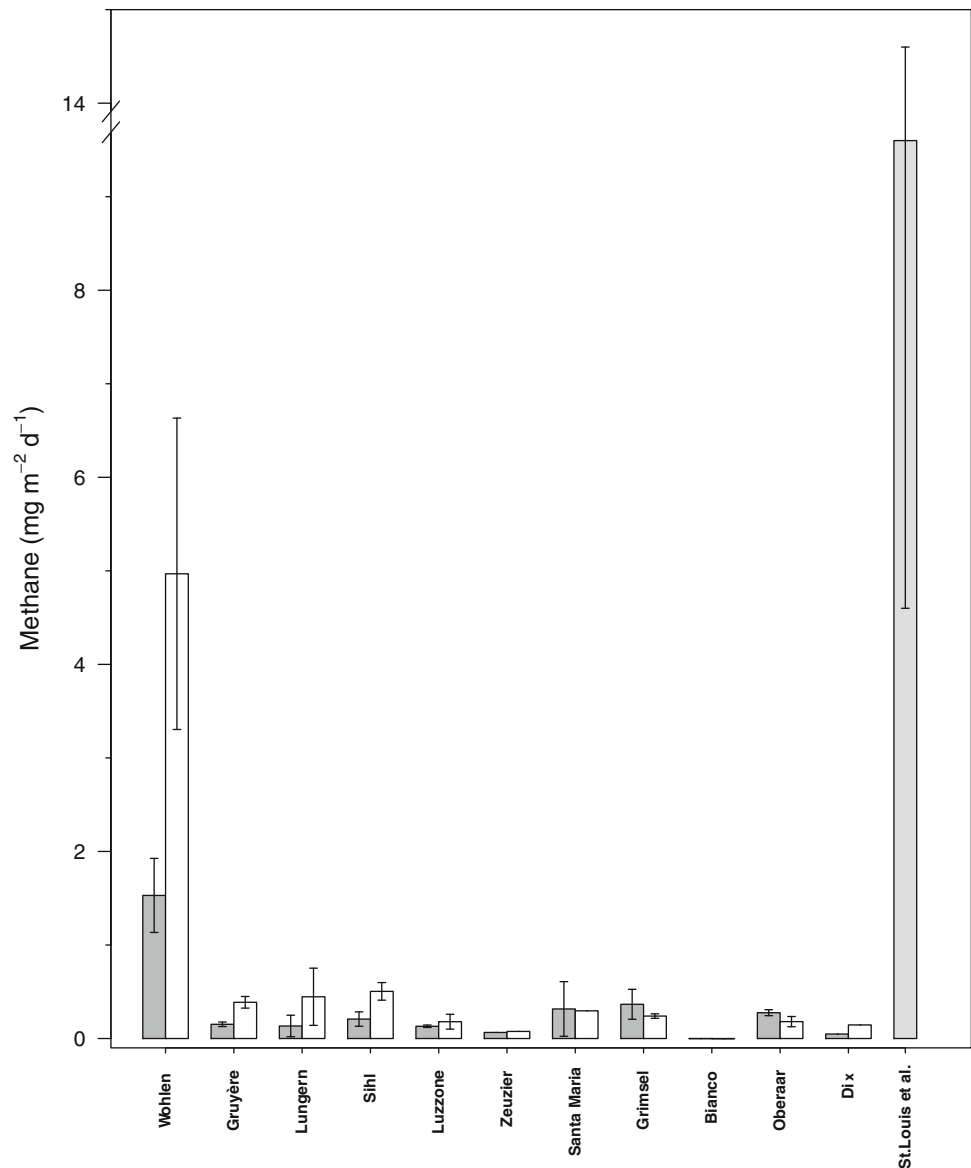
## Discussion

### Carbon emissions

In comparison to reservoirs from other regions, methane emissions from the 11 Swiss reservoirs are more than one order of magnitude lower than methane emissions from temperate reservoirs ($10 \pm 5$ mg $CH_4$ m$^{-2}$ day$^{-1}$; St. Louis et al. 2000, only diffusive fluxes were considered) and up to two orders of magnitude lower than emissions from tropical reservoirs ($72 \pm 44$ mg $CH_4$ m$^{-2}$ day$^{-1}$, Abril et al. 2006), while $CO_2$ emissions are only slightly smaller than, but within the range, of the ones from other temperate and boreal reservoirs ($970 \pm 340$ mg $CO_2$ m$^{-2}$ day$^{-1}$ in this study compared to $1{,}150 \pm 990$ mg $CO_2$ m$^{-2}$ day$^{-1}$, St. Louis et al. 2000) and about one-fourth of emissions from the tropics ($1{,}150 \pm 990$ mg $CO_2$ m$^{-2}$ day$^{-1}$, St. Louis et al. 2000).

One reason the $CH_4$ emissions we measured are low compared to diffusive fluxes from other reservoirs in general could be that they have been measured at deep sites of the reservoirs where emissions are lower compared to shallow, littoral areas (Duchemin et al. 1995, 1999; Bastviken et al. 2004). Thus our results could underestimate total diffusive emissions, especially for lowland reservoirs. These are less steep and have a higher amount of littoral areas, whereas the subalpine/alpine reservoirs in this study have almost no littoral zone and our emissions are more likely to represent the whole of the reservoir. For example, methane concentrations measured at several sites near the shore of Lake Oberaar (alpine) were not higher than at the deep station in the reservoir (data not shown), suggesting that fluxes are similar all over the reservoir.

Differences in $CO_2$ emissions between deep/shallow locations are negligible (Duchemin et al. 1999) resulting in more reliable $CO_2$ emissions for subalpine and lowland reservoirs. The higher $CO_2$ emissions found in May are not the result of changes in DIC, whose largest difference over the sampling period is 0.4 mmol L$^{-1}$ and which even increases in Lake Sihl from May to September, but from increasing pH values at the reservoir surfaces. This increase causes a shift away from DIC and $H_2CO_3$ towards $CO_3^{2-}$ causing lower concentration differences between water and the atmosphere and thus smaller fluxes. Increasing pH is a common occurrence in lakes during stratification in summer caused, among others, when photosynthetic activity is larger than respiratory activity (Maberly 1996).

There are no differences found between methane emissions and altitude (Shapiro–Wilk, $p < 10$–6 to test for normal distribution of emissions; Kruskal–Wallis, $p = 0.5803$), and none were found between emission and date, although methane is supposed to show a similar behaviour

to $CO_2$ with high emissions after ice-melt (Michmerhuizen et al. 1996; Duchemin et al. 2006) and during lake turnover in autumn (Kankaala et al. 2007). Potentially our sampling started too late and it definitely ended too early, with the reservoir water bodies still stratified, to catch these two events. For alpine reservoirs, we assume autumn turnover to be of minor importance, as total amounts of methane in the water column are small due to low dissolved methane concentrations found in these reservoirs. Importance will probably increase for reservoirs at lower altitudes, as methane concentrations, especially above the sediment, are higher here, resulting in higher potential emissions. But further studies are needed to address these potential fluxes, as well as the influence of water drawdown during winter for ice-covered reservoirs.

The lack of differences between reservoirs at different altitudes (and thus different temperatures) is somewhat astonishing as methane production was shown to be temperature dependent (e.g. Zeikus and Winfrey 1976; Nguyen et al. 2010) as did $CO_2$ emissions from lakes (Kosten et al. 2010). With our data, we are only able to discuss $CH_4$ emissions which did not have significant differences between emissions and altitude. When looking at the methane profiles of reservoirs (Fig. 3; supplementary material 1–3), there is an obvious difference between alpine reservoirs which have dissolved methane concentrations below 60 nmol L$^{-1}$ and subalpine/lowland reservoirs which have maximum concentrations above 100 nmol L$^{-1}$ and up to 6,500 nmol L$^{-1}$. These differences are not reflected in the methane emissions for several reasons. The first is the much smaller difference in surface methane concentrations, which we used to calculate emissions with the turbulent boundary layer model resulting in smaller differences for fluxes at the same wind speed. Secondly wind speeds are generally higher (data not shown) at higher elevations, leading to higher emissions for similar surface methane concentrations. These two combined even out much of the differences between the reservoirs, with the lowland reservoirs having in general higher surface methane concentrations and lower wind speed than alpine reservoirs. A third reason is that ebullition, a potential pathway for methane emission, is not included in our calculations. Assuming that higher temperatures lead to higher methane production and thus to a higher rate of ebullition for lower lying reservoirs, the total rate of methane emission (diffusive + ebullition) could be significantly higher than for reservoirs at higher elevations (as for example the very high ebullition rates of Lake Wohlen in DelSontro et al. 2010).

### Carbon sources in reservoirs

Studies of newly impounded reservoirs reported a peak of carbon emissions shortly after flooding, caused by the degradation of the labile organic material in submerged

soils (Kelly et al. 1997). Emissions decline significantly after 2–3 years and were estimated to reach a steady state at a much lower emission level after approximately 20 years (Galy-Lacaux et al. 1999). All reservoirs in this study are more than 35 years old and have thus reached their "base level" emission. A study of boreal reservoirs showed this base level is maintained by respiration of both allochthonous and autochthonous carbon, while contributions from carbon in the soil are less important (Huttunen et al. 2003a).

Autochthonous carbon is the result of autotrophic and heteroptropic productivity in the reservoir, which is dependent, among others, on temperature, light and nutrient availability. Nutrient content (nitrogen and phosphorus) in alpine lakes was shown to be low and the lakes can be classified as oligotrophic (e.g. Barbieri et al. 1999; Hinder et al. 1999; Sommaruga et al. 1999). Additionally, increased UV-radiation at higher elevations reduces primary productivity (Sommaruga et al. 1999), as do low temperatures (Eppley 1972), having an effect on the overall amount of autochthonous carbon available. On the other hand, snowmelt and glacial meltwater increase the input of allochthonous material to alpine reservoirs and higher UV radiation, compared to lower altitude reservoirs, photomineralizes dissolved organic material to $CO_2$ (Miller and Moran 1997; Soumis et al. 2007) adding an additional source of $CO_2$ for alpine reservoirs.

Lower concentrations of DIC (only Lake Luzzone, subalpine) and $CH_4$ in reservoirs of higher elevations (Table 2; Fig. 3 and supplementary material 1) reflect the less favourable conditions for internal productivity and respiration (lower temperatures, shorter ice-free periods, less nutrients) compared to lower elevations. Another hint to low productivity in subalpine/alpine reservoirs is given by missing oxygen gradients towards the sediment. Organic material is respired, consuming oxygen first with hypoxic and later anoxic conditions evolving if high amounts of organic material are present in the sediments. However, in the subalpine/alpine reservoirs we studied, oxygen concentration above the sediment, which never decreased below 6 mg L$^{-1}$ (Fig. 3; supplementary material 1 and 2) and only very shallow gradients were visible. Only in Lake Gruyère and Lake Lungern (both lowland) anoxic and hypoxic conditions, respectively, were detected (supplementary material 2i–l and 3a–g), with resulting oxygen concentrations of 6.7, resp. <0.1 µmol L$^{-1}$.

*Methane sources*

Generally, the carbon cycle in oxic lakes and reservoirs assumes methane production in the sediments followed by methane oxidation during the diffusion into the water column (e.g. Kuivila et al. 1988). This oxidation is indicated by increasing $\delta^{13}$C values of methane (Barker and

Fritz 1981; Whiticar 1999). Concentration and isotopic composition profiles in the lowland reservoirs agree well with this trend [profiles described in "Methane concentrations, $\delta^{13}$C isotopic composition and emissions" (ii) and (iii)], where methane concentrations decline from the sediment surface upwards, while $\delta^{13}$C increases, resulting in a concentration decline from the sediment surface upwards, unless the water layer above the sediment is very well mixed. On the other hand, alpine reservoirs did not show this behaviour (similar to profile described in "Methane concentrations, $\delta^{13}$C isotopic composition and emissions" (i) with uniform and rather low methane concentrations above the sediment), thus indicating these sediments to be only small sources of methane and the existence of possible relevant methane sources besides sediments in these reservoirs, which could explain increased methane concentrations in the water column.

Many alpine reservoirs collect additional water from neighbouring valleys to increase their catchment areas. This water is transported via pipes or pumped up from lower altitude, where it is sometimes stored in small storage reservoirs. As more favourable conditions for methane production exist at lower altitude (e.g. higher temperatures, nutrients, less UV radiation), this can be a potential source for methane input to alpine reservoirs [which can lead to enhanced methane concentrations in intermediate layers as described for the profiles in "Methane concentrations, $\delta^{13}$C isotopic composition and emissions" (iii)]. This assumption could, for example, explain the deviations in the methane concentrations and $\delta^{13}$C values we found in Lake Dix (alpine, supplementary material 1k, l). Elevated concentrations are related to small perturbations in the temperature profile at these depths. A possible explanation is inflowing water from lower altitudes carrying elevated methane concentrations of a deviating isotopic composition stratifying at these depths. Other potential sources for methane in alpine reservoirs could be glacial meltwater (Tung et al. 2005; Price 2007; Wadham et al. 2008) and glacial forefields (Bárcena et al. 2010).

Not only in alpine reservoirs are inflows important for the methane content in and emissions from the reservoirs. Estimating methane inflow by rivers and comparing it to diffusive emissions shows ratios of 0.1 (methane inflow contributes 10 % to diffusive flux) to 5.7 (methane inflow is 5.7 times higher than diffusive flux; Table 3). An exception is Lake Oberaar (alpine), which is a pump-storage reservoir and receives substantial amounts of water from Lake Grimsel (alpine), and thus is more likely controlled by the methane inflow from Lake Grimsel than by the inflow of glacial melt water. However, during the measurements in July, methane concentrations and $\delta^{13}$C in the inflows were similar to the ones in the water column of the reservoir (see Table 2; supplementary material 1h–j).

**Table 3** Methane inflow compared to diffusive emissions in four Swiss reservoirs

| Reservoir | Date | Depth of mixed layer (m) | Reservoir surface area (km²) | Volume of mixed layer[a] (Mio m³) | Average methane concentration (nM) | Methane content in mixed layer (kg CH₄) | Diffusive emission for the whole lake (g CH₄ day⁻¹) | Mixed layer loss[b] (days) | Average daily water inflow (Mio m³ day⁻¹) | Average daily methane inflow (g CH₄ day⁻¹) | Mixed layer inflow[c] (days) | Ratio of inflow/ diffusive flux |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Luzzone | Jul-05 | 5 | 1.4 | 7 | 15 | 2 | 176 | 10 | 0.5 | 305 | 6 | 1.7 |
|  | Aug-05 | 10 | 1.4 | 14 | 26 | 6 | 202 | 30 | 0.5 | 778 | 8 | 3.9 |
| Oberaar | Jul-05 | 6 | 1.5 | 9 | 13 | 2 | 371 | 5 | 0.2 | 47 | 37 | 0.1 |
|  | Jul-05 | 6 | 1.5 | 9 | 11 | 1 | 457 | 3 | 0.2 | 39 | 38 | 0.1 |
|  | Aug-05 | 20 | 1.5 | 29 | 24 | 11 | 383 | 30 | 0.2 | 81 | 141 | 0.2 |
| Sihl | May-05 | 6 | 10.9 | 65 | 67 | 70 | 3,103 | 23 | 0.7 | 3,093 | 23 | 1.0 |
|  | Jun-05 | 6 | 10.9 | 65 | 57 | 60 | 1,443 | 41 | 0.7 | 1,210 | 49 | 0.8 |
|  | Aug-05 | 7 | 10.9 | 76 | 73 | 88 | 2,224 | 40 | 0.7 | 2,467 | 36 | 1.1 |
| Gruyère | May-05 | 8 | 9.6 | 77 | 59 | 72 | 1,363 | 53 | 3.0 | 7,821 | 9 | 5.7 |
| Sarine[d] |  |  |  |  |  |  |  | 42 | 2.9 | 1,974 |  | 1.4 |
|  | Jun-05 | 7 | 9.6 | 67 | 45 | 49 | 1,296 | 38 | 3.0 | 2,339 | 21 | 1.8 |
| Sarine[d] |  |  |  |  |  |  |  | 23 | 1.8 | 668 |  | 0.5 |
|  | Aug-05 | 6 | 9.6 | 58 | 58 | 53 | 1,718 | 31 | 3.0 | 921 | 58 | 0.5 |
| Sarine[d] |  |  |  |  |  |  |  | 6 | 1.1 | 101 |  | 0.1 |

[a] To calculate the volume the mixed layer was assumed to be a rectangle

[b] Time until all methane in mixed layer would be lost by diffusive flux

[c] Time it takes for inflowing methane to reach mixed layer content

[d] For the river Sarine (one of the two major inflows of Lake Gruyère) flow rates were available from BAFU

Methane inflow is highest during spring for the two lowland reservoirs (Lakes Sihl and Gruyère), while these reservoirs are refilling. We assume that at these times methane inflow is more important for methane emissions (or methane content in the reservoir) than sediment diffusion as temperature and organic matter input are important factors for methane production in sediments (Kelly and Chynoweth 1981). For the subalpine reservoir Lake Luzzone, the ratio of methane inflow to surface diffusion actually increases later in the year suggesting that methane related to inflows plays a more important role in this reservoir later in the year. This means that methane inflows are an important contribution to the amount of methane stored in the reservoir during summer. A rough estimate using average inflow concentrations has about 20 % of the total methane originating from inflowing methane. Given our limited data of two inflow measurements and one reservoir, further studies are necessary to determine the exact contribution of inflows to subalpine/alpine reservoirs and if this is a common occurrence or only limited to several reservoirs.

Methane loss at the turbines

Another important emission pathway for reservoirs is the loss caused by the turbulence and reduced pressure during and after turbine passage. Of the five lakes sampled to investigate methane loss at the turbine, two lowland lakes (Lake Wohlen and Lake Gruyère) did not lose methane during passage (Table 2). The average loss for the three other lakes (Lake Sihl, Lake Luzzone and Lake Grimsel) was $46 \pm 18$ % (range 16–73 %), which matches the findings of Kemenes et al. (2007). Whereas at Lake Wohlen, the water drops only a few meters down to the river and at Lake Gruyère it is transported through a pipe over an elevation of nearly 100 m, the height difference between the dam and the downstream river for the other three reservoirs is several hundred meters. While this drop creates enough turbulence for the water to degas on its way down the pipe, the shorter drops of Lake Wohlen and Gruyère do not seem to be sufficient for a measurable loss of gas. Further research is needed to clarify the factors relevant for gas loss from water dropping through the turbines and why for some reservoirs gas is not lost when leaving the reservoir.

If we compare the importance of average methane loss at the turbine to methane loss by surface diffusion, for Lake Grimsel and Lake Luzzone both are nearly equal in size (loss at turbine accounts for $44 \pm 12$ % of the sum of both loss by diffusion + turbine), while for Lake Sihl gas loss at the turbine accounts for $14 \pm 7$ % of the total emissions at the time of the measurement (Table 4). This implies that methane loss from water passing the turbine could be equally important as methane loss via the reservoir surface

in alpine and subalpine reservoirs, while being of less importance for lowland reservoirs. As methane loss by ebullition (bubbles rising from the sediment) is definitely a factor in lowland reservoirs (DelSontro et al. 2010) the importance of loss at the turbines will even decrease. The conditions in subalpine/alpine reservoirs (e.g. large depth, steep slopes, low productivity) could be unfavourable for ebullition, resulting in little to no gas loss via this pathway. But to our knowledge, so far no ebullition measurements have been published in these kinds of reservoirs to date, necessitating further studies to determine the exact importance of methane loss via turbines for subalpine/ alpine reservoirs.

Nitrous oxide emissions

Similar to previous findings, fluxes of $N_2O$ in lakes and reservoirs are small in open water areas (Huttunen et al. 2002). While emissions from the two lowland reservoirs are in the same range as previous results (Huttunen et al. 2003a; Tremblay et al. 2005; measurements in both studies were done with static chambers) and nitrous oxide is supersaturated in the whole water column, in the alpine reservoirs concentrations throughout the water column are very close to atmospheric equilibrium (Fig. 2a). Only $N_2O$ concentrations at the surface deviate from the equilibrium concentrations. $N_2O$ production has not been measured, but we assume the conditions in high alpine lakes are not favourable for $N_2O$ production, as low oxygen concentrations (Mengis et al. 1996) or steep oxygen gradients are required (Huttunen et al. 2003b) for $N_2O$ production in lakes. Both prerequisites are absent in the reservoirs we investigated. Thus, the concentrations above atmospheric equilibrium in high alpine lakes are probably connected to inflowing water and not to internal production (see discussion on "Methane sources").

Conclusions

The most important greenhouse gas emitted from the perialpine and alpine reservoirs we sampled in Switzerland is $CO_2$. On average, reservoir emissions are $970 \pm 340$ mg $CO_2$ m$^{-2}$ day$^{-1}$ and therefore only slightly smaller than emissions from boreal and temperate reservoirs in other parts of the world.

Alpine reservoirs were in equilibrium with atmospheric $N_2O$ concentrations throughout most of their water column, whereas two lowland reservoirs were oversaturated and emitted small amounts of $N_2O$ at $0.07 \pm 0.02$ mg $N_2O$ m$^{-2}$ day$^{-1}$. Methane emissions were an order of magnitude smaller than values published for reservoirs in temperate and boreal climates. Average emissions were

**Table 4** Methane emissions via turbine for Lake Luzzone, Lake Grimsel and Lake Sihl

| Reservoir | Date | Average discharge ($10^3$ m³ day⁻¹) | Methane concentration closest to outlet (nmol L⁻¹) | Methane loss via turbine (g CH₄ day⁻¹) | Reservoir surface area (km²) | Emission via turbine[a] (µg m⁻² day⁻¹) | Diffusive flux (µg m⁻² day⁻¹) | Ratio[b] | Fraction of total emission (surface + turbine) (%) |
|---|---|---|---|---|---|---|---|---|---|
| Luzzone | June-05 | 427 | 25 | 79 | 1.44 | 55 | 122 | 0.45 | 31 |
| Luzzone | July-05 | 427 | 60 | 189 | 1.44 | 131 | 140 | 0.94 | 48 |
| Grimsel | Sep-03 | 1,918 | 46 | 649 | 2.72 | 239 | 212 | 1.13 | 53 |
| | | | | | | | | Average | 44 ± 12 |
| Sihl | May-05 | 644 | 63 | 299 | 10.85 | 28 | 286 | 0.10 | 9 |
| Sihl | June-05 | 644 | 84 | 398 | 10.85 | 37 | 133 | 0.28 | 22 |
| Sihl | Aug-05 | 644 | 60 | 284 | 10.85 | 26 | 205 | 0.13 | 11 |
| | | | | | | | | Average | 14 ± 7 |

Emissions are compared to diffusive surface flux

[a] Equals methane emissions at the turbine divided by lake surface

[b] Turbine flux divided by diffusive flux

$0.2 \pm 0.15$ mg CH₄ m⁻² day⁻¹ for all reservoirs, except Lake Wohlen, which emitted $1.8 \pm 0.9$ mg CH₄ m⁻² day⁻¹ via surface diffusion. Though there were no significant differences between methane emissions from different altitudes, methane concentrations are lower in alpine reservoirs compared to lowland reservoirs. Factors like reservoir age, DOC input and latitude (equivalent to temperature) have been investigated by Barros et al. (2011). Temperature and organic matter input are presumably the most important factors for the decrease we found, while reservoir morphology of the predominantly steep and deep subalpine/alpine reservoirs could be an important factor as well. The higher dissolved methane concentrations and clearly visible oxygen gradients towards the sediment suggest high methane concentrations in the sediments of lowland reservoirs. This would lead to higher total methane emissions via bubble flux from the sediment (DelSontro et al. 2010 for Lake Wohlen) and in the end make lowland reservoirs significantly more important emitters of methane to the atmosphere. Further studies are needed to support this and determine up to which altitude bubble flux plays a role in reservoirs of the Alps.

The amount of external methane entering via inflows is sufficient to explain the emission rates found in some reservoirs in spring and early summer, while contributions from other sources (e.g. sediments) increase towards autumn for two lowland reservoirs. In one subalpine reservoir input from inflows remained important throughout the summer. As a result the reservoir stores methane from rivers, which otherwise would probably emit on the way down the mountain, and exposes it to potential methane oxidation inside the reservoir.

Methane loss at the turbine accounted for nearly 50 % of total emissions (diffusive surface flux + gas loss at the turbine) in a subalpine and an alpine reservoir. This emission pathway seemed to be less important in lowland reservoirs, where it contributed only 14 % of the total CH₄ flux to the atmosphere (e.g. Lake Sihl). This is related to the higher surface area/volume-ratio of lowland reservoirs compared to the subalpine/alpine reservoirs which increases emissions via the surface and thus decreases the relevance of methane loss at the turbine.

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