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RESEARCH ARTICLE

Spatial variations in surface water methane super-saturation and emission in Lake Lugano, southern Switzerland

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Abstract We measured methane concentrations in the surface water of the northern basin of Lake Lugano in spring (May 2012) and autumn (October 2011, 2012), and calculated turbulent diffusive methane fluxes to the atmosphere. Surface water methane concentrations were highly variable in space and time but always exceeded atmospheric equilibrium. Methane concentrations were significantly lower in spring (on average 16 nmol L^{-1}) than during the autumn sampling campaigns (on average 57 nmol L^{-1} in 2011 and 45 nmol L^{-1} in 2012). This suggests methane accumulation in the surface mixed layer during the summer productive season. The origin of the methane in the lake's surface waters requires further assessment, but the observed concentration profiles indicate that the excess methane originates from a near-surface source, rather than from the large deep-water methane pool in the anoxic monimolimnion. As a consequence of the higher surface water methane concentrations and increased buoyancy turbulence caused by autumnal cooling of the surface boundary layer, diffusive fluxes were much higher in October (average ~ 97 μmol m^{-2} day^{-1}, compared to 7 μmol m^{-2} day^{-1} in May 2012). The increase in methane concentration in the surface water between spring and autumn suggests links between methane accumulation and the annual biological cycle, yet seasonal changes in wind and temperature forcing of methane emission likely play an important modulating role. While the relative importance of biological versus physical controls on methane emission in Lake Lugano awaits further investigations, our study underscores that lakes can act as an important source of methane to the atmosphere, even when the lake-internal microbial methane filter in the water column seems to work efficiently.

Keywords Methane · Methanogenesis · Surface water · Methane emission · Lake Lugano

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Introduction

Methane (CH_4) is a powerful greenhouse gas with a global warming potential ~ 21 times that of carbon dioxide (CO_2) on a hundred year time horizon (Manne and Richels 2001), accounting for ~ 20 % of the radiative forcing induced by long-lived greenhouse gases (Wuebbles and Hayhoe 2002; IPCC 2013). Atmospheric CH_4 concentrations have almost tripled since the start of industrialisation (Blasing 2008; Dlugokencky et al. 2009), but the absolute contribution of individual sources to the atmospheric budget is still a matter of debate (Kirschke et al. 2013). Natural sources of atmospheric CH_4 mainly originate from the anaerobic degradation of organic matter by specialised methanogenic *Archaea* (Liu 2010; Sieber et al. 2010). In lakes and other freshwater bodies, the activity of these microbes often leads to CH_4 excess in anoxic water layers and sediments. CH_4 is oxidised by methanotrophic bacteria in oxic surface sediments or in the water column (Rudd et al. 1974; Hanson and Hanson 1996; Blees et al. 2014a, b), but a significant fraction of CH_4 may bypass this microbial CH_4 filter (IPCC 2013; Kirschke et al. 2013). When CH_4

production exceeds microbial CH_4 consumption, sedimentary porewaters may become super-saturated with respect to CH_4, and CH_4 can occur as a free gas, which further reduces its biodegradability. Indeed, lakes are very important sources of CH_4, accounting for around 20 % of the total natural flux to the atmosphere (Bastviken et al. 2004; Kirschke et al. 2013). Vegetation in littoral zones may furthermore enhance CH_4 efflux because CH_4 is transported through the roots, stems and leaves of aerenchymatous plants (Laanbroek 2010). In small and shallow lakes, on average only ~ 30 % of lacustrine CH_4 evasion is diffusive, and advective, bubble and plant-mediated transport are more effective (Bastviken et al. 2004). The diffusive component becomes more important with increasing lake surface area and depth (Bastviken et al. 2004) because the relative importance of littoral (mostly non-diffusive) effects and the probability of CH_4 loss by ebullition decrease with increasing surface area and depth, respectively.

The turbulent diffusive CH_4 flux from lacustrine water bodies to the atmosphere depends greatly on the surface water CH_4 concentration and mixing behaviour (Bastviken et al. 2004). During episodic turnover of lakes, CH_4 efflux can transiently be very high, because CH_4 stored in anoxic bottom waters reaches the surface in a short time, allowing only incomplete consumption by the methanotrophic microbial community (Schmid et al. 2005; Walter et al. 2007; Schubert et al. 2012). Yet, also in the absence of a significant CH_4 flux from deeper parts of lacustrine water columns, elevated CH_4 concentrations in surface waters have been reported (Murase et al. 2005; Hofmann et al. 2010; Grossart et al. 2011; Tang et al. 2014), including Lake Lugano (Blees et al. 2014a). The source of this surface water CH_4 is not well understood, but shallow sediments on the lake shores (Murase et al. 2005; Hofmann et al. 2010), or in situ CH_4 production in anoxic microenvironments (Karl and Tilbrook 1994; Rusanov et al. 2004; Grossart et al. 2011) have been suggested. In analogy to non-classical CH_4 production pathways proposed for marine environments, oxic degradation of methylated substances may also account for CH_4 accumulation in surface waters (Karl et al. 2008; Damm et al. 2010; Carini et al. 2014).

Our knowledge of the dynamics of CH_4 fluxes is often based on point measurements that are extrapolated in space and time. This approach has recently been called into question, as significant heterogeneity in surface water CH_4 concentration was found in lakes (Hofmann 2013; Schilder et al. 2013). In this study, we investigated the spatial variability of CH_4 concentrations and C-isotope ratios in surface and subsurface waters of the deep meromictic northern basin of Lake Lugano in spring and autumn, in order to (1) determine spatial fluctuations of the CH_4
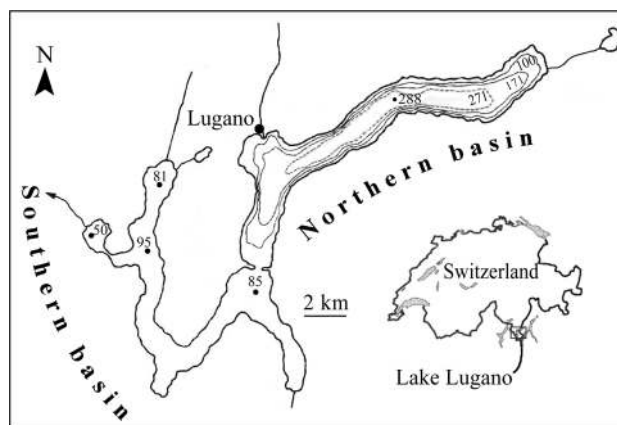

Fig. 1 Map of Lake Lugano and its location in Switzerland. Water depths are shown in m (map adapted from Barbieri and Polli (1992))

source strength, and 2) gain insight into the possible origin(s) of excess CH_4 in the surface waters.

Methods

Study site

Lake Lugano is a deep south-alpine lake at an elevation of 271 m above mean sea level. The lake consists of two basins, which are connected through a shallow strait across a natural dam (Fig. 1). The northern basin has a maximum water depth of 288 m and a surface area of 27.5 km^2. Due to the fjord-like bathymetry, the sidewalls of the basin are steep, with little or no accumulation of sediments. This basin has an east–west orientation, and is surrounded by mountains, shielding it from the prevailing southern wind directions. As a result of eutrophication, the basin has been meromictic for more than 4 decades (with the exception of two mixing events in the winters of 2004–2005 and 2005–2006, Holzner et al. 2009), featuring a deep (~ 135 m) oxic-anoxic interface, with accumulation of CH_4 in the hypolimnion below (Liu et al. 1996; Blees et al. 2014a). The annual average wind speed at 10 m above the lake is ~ 1.6 m s^{-1} with little seasonal variation (Source MeteoSwiss, http://gate.meteoswiss.ch/idaweb, station Lugano-Biblioteca). Nevertheless, peak wind speeds reached 30 m s^{-1} during gusts recorded less than 100 m from the lake shore in Lugano between October 2011 and October 2012.

Sampling

Sampling campaigns were performed in October 2011, May 2012, and October 2012 (Table 1). During each campaign, we collected water samples in 5-L Niskin bottles from 0.4 m water depth throughout the northern basin. A

Table 1 Average surface water CH_4 concentration (± 1 standard deviation), wind speed and calculated daily diffusive fluxes of CH_4 into the atmosphere for the northern basin of Lake Lugano

Date	$[CH_4]$ (nM)	U_{10} (m s^{-1})	Average diffusive flux (μmol m^{-2} day^{-1})			Whole lake basin diffusive flux (mol day^{-1})		
			C&W	C&C	MacIntyre	C&W	C&C	MacIntyre
13 Oct. 2011	57 ± 19	5.5	133	76	168	3664	2080	4607
14 May 2012	16 ± 2	3.7	7	11	17	202	301	466
15 May 2012		3.2	6	9	14	163	257	384
16 Oct. 2012	45 ± 5	1.1	7	19	35	181	530	968
17 Oct. 2012		0.5	3	18	25	82	487	689

U_{10} is the wind speed in m s^{-1} at 10 m above the lake surface. Diffusive fluxes were calculated according to the parameterisations of Crusius and Wanninkhof (2003) (C&W), Cole and Caraco (1998) (C&C) and MacIntyre et al. (2010) (MacIntyre)
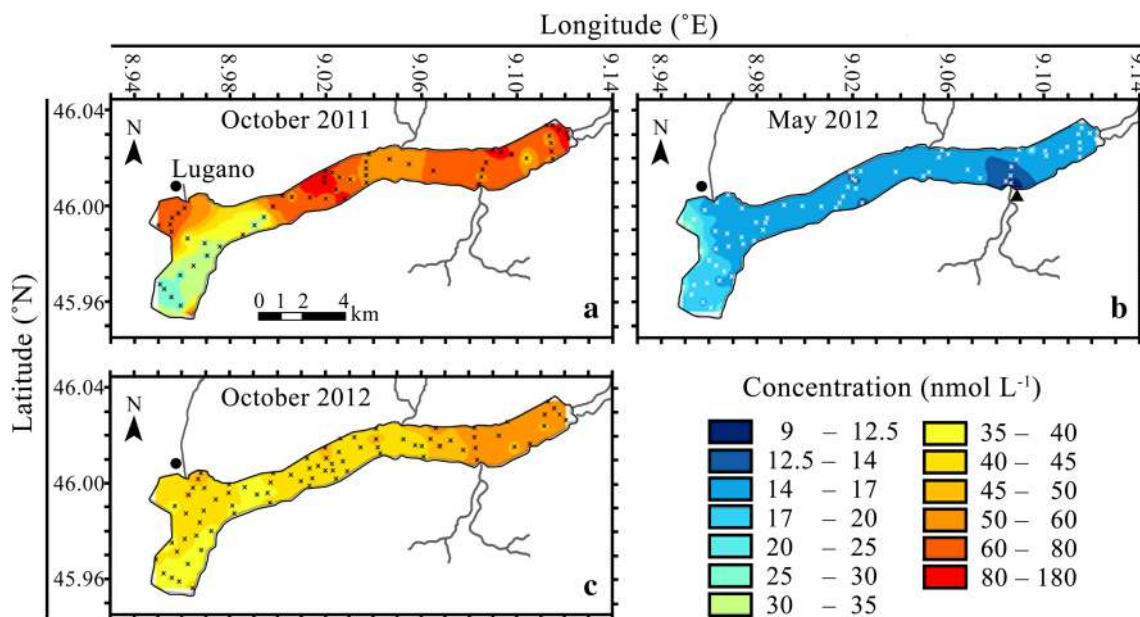

Fig. 2 Surface water CH_4 concentration in the northern basin of Lake Lugano determined in October 2011 (**a**), May 2012 (**b**), and October 2012 (**c**). *Crosses* indicate sampling locations. Tributary streams are shown as *grey lines*. The river delta where anomalously low CH_4 concentrations were found in May 2012 is indicated with a *black triangle* in (**b**), and the city of Lugano is shown as a *black dot*

total of 59, 77 and 79 surface water samples were collected in October 2011, May 2012, and October 2012, respectively (Fig. 2). Additional samples were taken by hydrocast sampling down to 40 m water depth (0.4, 2.5, 5, 7.5, 10, 12.5, 15, 20, 30 and 40 m) along two transects and at selected sites (Figs. 3, 4, 5). At each sampling site, temperature, conductivity, O_2 concentration, pH and turbidity were measured with a CTD device (Idronaut Ocean Seven 316 Plus, Idronaut S.r.l., Italy). Subsamples for CH_4 concentration and $\delta^{13}C$ measurements were taken directly from the Niskin bottle through silicon tubing and fixed with NaOH in glass vials (final concentration 1 %) (Blees et al. 2014a). Vial volumes of 120 to 1000 mL were used. A small headspace of 1–2 % of the sample volume was added to facilitate outgassing of all CH_4 into the headspace, and the vials were stored upside down until analysis in our

home laboratories. The smaller vials were then used for concentration analysis, while the larger volumes were used for isotopic analysis.

Dissolved methane

CH_4 concentrations were determined using a gas chromatograph (GC) equipped with a flame ionisation detector (FID), and $\delta^{13}C$ values were measured with a GC with a pre-concentration cryo-trap coupled to an isotope ratio mass spectrometer (GC-IRMS, Isoprime TraceGas) (Blees et al. 2014a). Corrections were made for linearity effects and instrument drift. Stable C-isotope ratios are reported in the common δ-notation (in ‰) relative to the Vienna Pee Dee Belemnite standard. $\delta^{13}C$ values reported here have an analytical error of ± 1 ‰.

Fig. 3 Temperature and CH_4 concentration profiles in the upper 40 m of the water column in north–south transects in the centre of the lake in October 2011 (**a–c**), May 2012 (**d–h**), and October 2012 (**i–m**), and $\delta^{13}C$ of CH_4 (**k**, *open symbols*). The location of the transect is indicated by a *black line* in the map. The concentration axis for (**b**) and (**c**) is shown at the top (up to 200 nmol L^{-1}), and for **e–h** and **j–m** at the bottom (up to 75 nmol L^{-1})
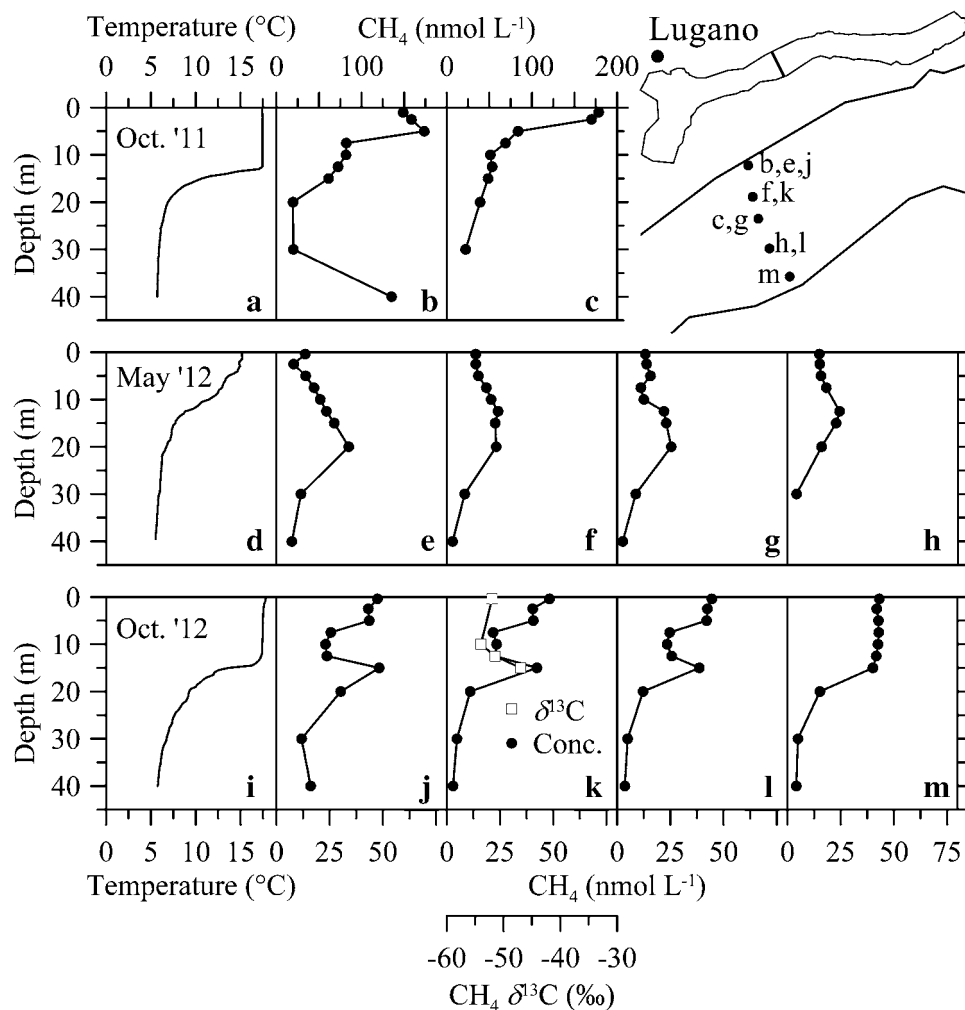
Flux calculations

Diffusive CH_4 fluxes (F) were calculated according to the boundary layer model of Liss and Slater (1974) (for a review see also Wanninkhof et al. 2009):

$$F = k(C_w - C_{eq}) \tag{1}$$

where k is the transfer velocity (see below) and C_w and C_{eq} are the CH_4 concentration in the surface water (here at 0.4 m depth) and the equilibrium CH_4 concentration, respectively. C_{eq} was calculated following Wiesenburg and Guinasso (1979), based on the average atmospheric CH_4 concentration (1874 ppbv) in the northern hemisphere (Dlugokencky et al. 2009), lake surface temperature (14–21 °C) and salinity (0.3 ‰) as measured with the CTD device. The k-value, which is determined by wind speed and buoyancy flux (Cole and Caraco 1998; Crusius and Wanninkhof 2003; MacIntyre et al. 2010), was calculated according to:

$$k_{CH_4} = k_{600}\left(\frac{Sc_{CH_4}}{600}\right)^c \tag{2}$$

where Sc is the dimensionless Schmidt number, i.e., the ratio between kinematic viscosity of water and the gas diffusion coefficient, which relates the respective k-values for different gases. k_{600} denotes the transfer velocity of CO_2 at 20 °C, corresponding to an Sc of 600, and is used for comparison of different gases (Cole et al. 2010). c is a wind speed-dependent conversion factor, for which we used $-2/3$ for $U_{10} < 3.7$ m s^{-1}, and $-1/2$ for all other wind speeds (Jähne et al. 1987). U_{10} stands for the wind speed at 10 m above the surface, in m s^{-1}.

For parameterisation of k_{600} we compared the following three common empirical relationships previously used in other studies (e.g., Schubert et al. 2012):

1. The bilinear relationship of Crusius and Wanninkhof (C&W) (2003): for

$$U_{10} < 3.7 \text{ m s}^{-1} : k_{600} = 0.72U_{10} \tag{3}$$

Fig. 4 Temperature and CH$_4$ concentration profiles in the upper 40 m of the water column at isolated stations (**a–c**) and in a north–south transect (**d–h**), and δ^{13}C of CH$_4$ (**c**, *open symbols*). **b** October 2011; **c** October 2012; **d–h** May 2012. Locations of profiles **b** and **c** are indicated with *dots*, and the transect **e–h** is indicated as a *black line* in the map. The concentration axis for (**b**) goes up to 150 nmol L^{-1}, whereas for **c** and **e–h** it goes up to 75 nmol L^{-1}
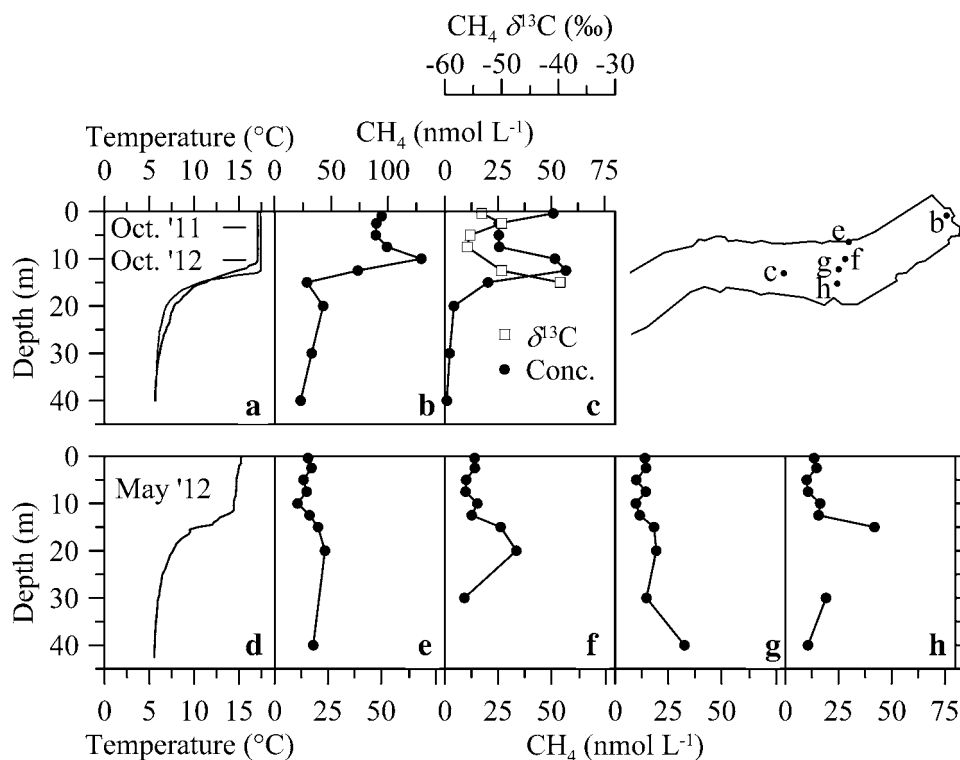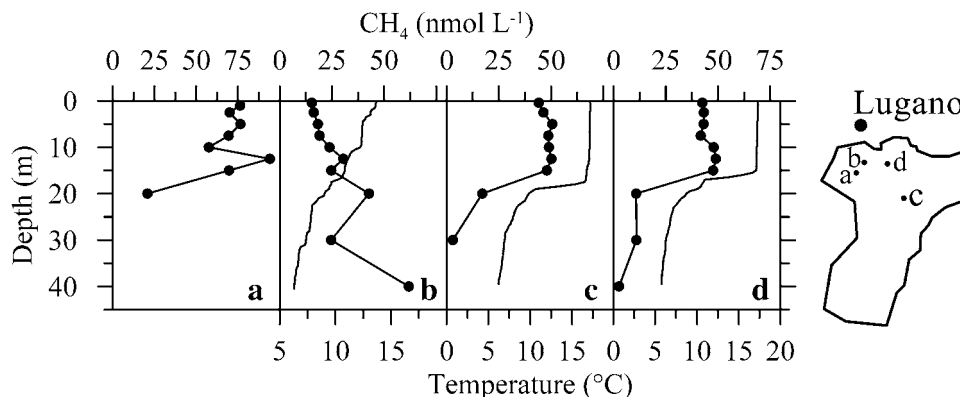

Fig. 5 Temperature (*lines*) and CH$_4$ concentration (*symbols*) profiles in the upper 40 m of the water column in the vicinity of Lugano, in October 2011 (**a**), May 2012 (**b**) and October 2012 (**c**, **d**). Profile locations are indicated in the map on the *right*. The concentration axis for (**a**) goes up to 100 nmol L^{-1}, whereas for (**b–d**) it goes up to 75 nmol L^{-1}

For

$$U_{10} \geq 3.7 \text{ m s}^{-1} : k_{600} = 4.33U_{10} - 13.3 \quad (4)$$

2. The power function by Cole and Caraco (C&C) (1998):

$$k_{600} = 2.07 + 0.215U_{10}^{1.7} \quad (5)$$

3. The relationship given by MacIntyre et al. (2010) for a cooling lake

$$k_{600} = 2.04U_{10} + 2.0 \quad (6)$$

and for a heating lake

$$k_{600} = 1.74U_{10} - 0.15 \quad (7)$$

The MacIntyre relationships (Eqs. 6 and 7) distinguish between cooling and heating of the surface water, because heating and cooling changes the buoyancy flux. When the surface layer starts losing heat to the atmosphere, the water starts to sink and eddy turbulence will bring water from below with higher CH$_4$ concentrations to the surface (MacIntyre et al. 2001). Thus, the CH$_4$ flux from the surface mixed layer to the atmosphere is greater when the surface water is cooling than when it is heating. Although we recognise that heating and cooling cycles also take place on a diurnal basis, we only considered seasonal trends, assuming a heating mode of the lake when monthly average air temperature was higher than surface water

temperature (March–August), and a cooling mode when the monthly average air temperature was lower (September–February). Data of wind speeds at 10 m above the lake surface were made available by MeteoSwiss, which operates a measurement station at the shore in Lugano (station Lugano-Biblioteca), without obstructions between the station and the lake. These wind speeds are most representative for the Bay of Lugano area, which is relatively open. The narrower central part of the basin, however, is well shielded from the prevailing southern and northern winds, and is therefore rarely exposed to high wind speeds. In the following, we therefore use a relatively low average wind speed of 2 m s^{-1}, which is more representative for the entire basin (personal observation). Integration of concentration and flux data was performed in the ArcMap module of the ArcGIS 10 software package (ESRI) by inverse distance squared weighting.

Results

Dissolved methane concentration and stable isotope composition

Surface water CH$_4$ concentrations were above saturation concentration (~ 3 nmol L^{-1}) at all times and considerably higher during the autumn samplings than in spring. In October 2011, surface water concentrations generally ranged between 26 and 96 nmol L^{-1} (Fig. 2a). During this campaign we only observed higher concentrations at one sampling location close to the shore at a river delta at the eastern end of the basin (132 nmol L^{-1}) and at three sampling locations along the Swiss-Italian border on the northern side of the basin (128–178 nmol L^{-1}). In October 2012, lowest surface water concentrations were ~ 35 nmol L^{-1}, in the western part of the basin (Fig. 2c), and highest concentrations (~ 60 nmol L^{-1}) were found in the eastern part of the lake. Unlike in 2011, we did not measure exceptionally high concentrations (>100 nmol L^{-1}). Surface water concentrations in May 2012 ranged between 9 and 30 nmol L^{-1} (Fig. 2b). Notably, concentration differences between spring and autumn were strongest in the eastern part of the lake (east of 9.10°E), i.e., 3 to fivefold higher in October (70 $\pm$ 27 nmol L^{-1} in 2011 and 52 $\pm$ 2.6 nmol L^{-1} in 2012) than in May (15 $\pm$ 0.6 nmol L^{-1}). In contrast, concentration differences were comparably small in the western part of the lake, close to the town of Lugano (west of 8.96°E), i.e., twofold higher in October (43 $\pm$ 18 and 41 $\pm$ 3.1 nmol L^{-1} in October 2011 and 2012, respectively) than in May (19 $\pm$ 4.3 nmol L^{-1}).

In autumn, we generally found the highest CH$_4$ concentrations close to the surface (Figs. 3, 4, 5), and often we

found an additional concentration maximum at the depth of the thermocline, i.e., at ~ 15 m depth. In contrast, no surface maximum was present in May 2012, but again we detected a subsurface maximum at 15–20 m water depth. The highest CH$_4$ concentration in May 2012 (62 nmol L^{-1}) was found at 40 m depth, close to the bottom in the Bay of Lugano (Fig. 5b).

In October 2012, CH$_4$ in the surface mixed layer was depleted in ^{13}C relative to CH$_4$ from below the thermocline (Figs. 3k, 4c). Contrary to expectation, the lowest CH$_4$ concentrations in the mixed layer were paralleled by the greatest ^{13}C depletion in the CH$_4$. In contrast, CH$_4$ from the water mass below the thermocline (Fig. 4c) had the least negative δ^{13}C. Similarly, in October 2009, January and August 2010, CH$_4$ in the surface mixed layer was associated with relatively low CH$_4$ δ^{13}C (Blees et al. 2014a).

In order to investigate further whether the conspicuous isotope differences within the mixed layer were linked to microbial CH$_4$ consumption, we investigated CH$_4$ oxidation rates with ex situ radio isotope assays (Blees et al. 2014a; Niemann et al. 2015) in samples from a hydrocast in the centre of the lake in January 2010 and in October 2011 (at the location of the profile in Fig. 3c). Our measurements revealed that CH$_4$ oxidation rates in surface and subsurface waters were negligible (<0.1 % CH$_4$ turnover day^{-1}, i.e., $\ll 0.1$ nmol L^{-1} day^{-1}), without any noticeable depth trends. In agreement with the negligible oxidation rates, we could not detect any cells of type 1 or type 2 methanotrophic bacteria by epifluorescence microscopy of subsurface water samples stained by fluorescence in situ hybridisation with specific gene probes for alpha and gamma proteobacterial methanotrophs (Mγ84, Mγ705 and Mα450; Eller et al. 2001) (Blees et al. 2014b) (data not shown).

CH$_4$ fluxes

Average wind speeds during our sampling campaigns were variable with values between 0.5 m s^{-1} (17 October 2012) and 5.5 m s^{-1} (13 October 2011) (Table 1). Depending on the k-value parameterisation according to C&W, C&C or MacIntyre, the Liss and Slater model yielded diffusive fluxes of CH$_4$ to the atmosphere of 3–168 μmol m^{-2} day^{-1} (Table 1; Fig. 6). Extrapolating to the whole-lake scale, the fluxes calculated from discrete concentration measurements translate into a system-flux of 2080–4607 mol day^{-1} in October 2011, 163–466 mol day^{-1} in May 2012 and 82–968 mol day^{-1} in October 2012. Despite the uncertainties associated with k value parameterisation, flux calculations thus revealed considerable temporal variability in CH$_4$ emission from the lake surface to the atmosphere, with overall higher CH$_4$ fluxes during fall (Fig. 6). The C&W and C&C relationships were developed from datasets with relatively low wind speeds (5.5 m s^{-1}), i.e., lower than
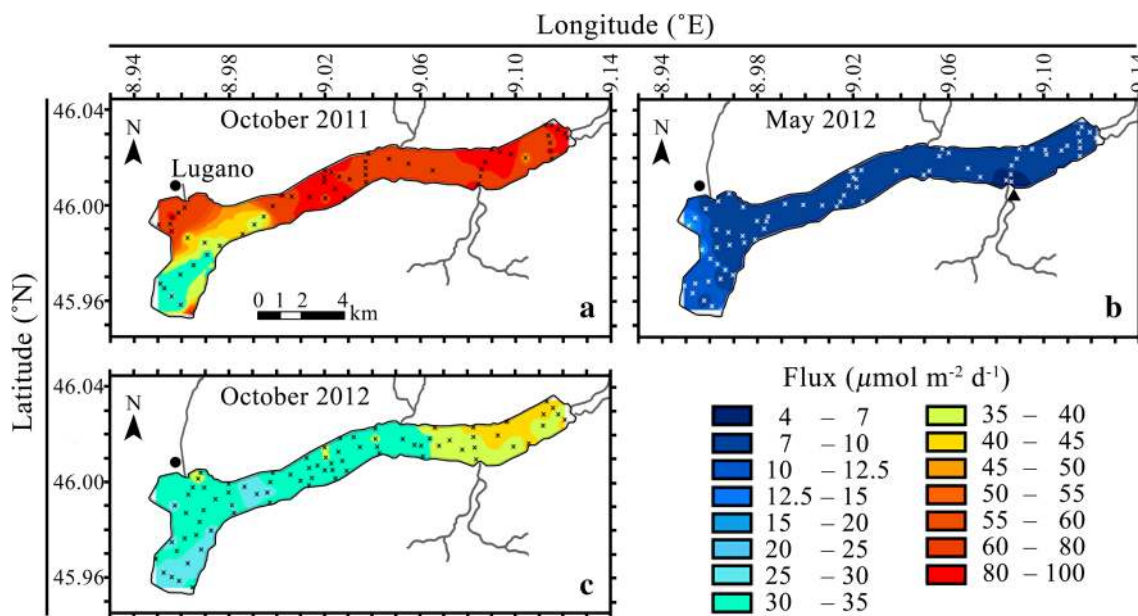
Fig. 6 Diffusive fluxes across the water–air boundary layer in October 2011 (**a**), May 2012 (**b**), and October 2012 (**c**). Fluxes were calculated using the transfer velocity according to MacIntyre (2010) and an average wind speed of 2 m s^{-1}. *Crosses* indicate sampling locations. Tributary streams are shown as *grey lines*. The river delta where anomalously low CH$_4$ concentrations were found in May 2012 is indicated with a *black triangle* in (**b**), and the city of Lugano is shown as a *black dot*

wind speeds recorded in Lugano (often >10 m s^{-1} and up to 30 m s^{-1}, MeteoSwiss). The MacIntyre model, on the other hand, is based on wind data more similar to Lake Lugano, with its variable wind regime, including wind speeds >10 m s^{-1}, which we decided not to exclude from the outset. Furthermore, the MacIntyre model considers the influence of heating and cooling on the buoyancy flux, which has a profound influence on the change in efflux between spring and autumn. Given these arguments, we believe that the MacIntyre model yields the most reliable results, and therefore, we used this model for the comparison of the three sampling campaigns (Fig. 6).

Discussion

Modes of CH$_4$ emission

The CH$_4$ emission flux from lakes can be broadly subdivided into four components: (1) plant-mediated emission in littoral zones, (2) ebullition, (3) a storage flux during lake turnover, and (4) diffusion across the lake surface-atmosphere boundary driven by a partial pressure gradient (Bastviken et al. 2004). (1) As a result of the geometry of the northern basin, comprising steep sidewalls along most of the lake's periphery, the majority of the lacustrine sedimentary deposits are located at great depth. Therefore, the littoral zone, where submerged plants such as reed could grow, is very small relative to the surface area of the lake.

This likely reduces the impact of plant-mediated emissions to the total CH$_4$ budget. (2) Similarly, a substantial CH$_4$ flux through ebullition is unlikely in a deep lake such as the northern basin of Lake Lugano, since the probability of bubble formation decreases with increasing hydrostatic pressure (Bastviken et al. 2004). CH$_4$ concentrations in the sediment reach 5 mmol L^{-1}, but decrease linearly towards the sediment–water interface (Blees et al. 2014a), implying diffusive rather than bubble transport out of the sediment into the water column. At the depths where the sediment surface area is greatest, i.e. below 200 m (see Fig. 1), the CH$_4$ concentration within the sediments is below saturation. Furthermore, gas exchange between rising bubbles and the surrounding water rapidly decreases the CH$_4$ concentration within the bubble, limiting the potential for CH$_4$ ebullition from the deep parts of Lake Lugano. For example, a bubble with a diameter of up to 20 mm released at 200 m water depth would have virtually no CH$_4$ left upon reaching the surface (McGinnis et al. 2006). (3) In lakes that experience a yearly overturn, a storage flux, i.e., release of CH$_4$ stored in the anoxic hypolimnion, can be important (Bastviken et al. 2004; Schubert et al. 2010). However, although the monimolimnion in the meromictic northern basin of Lake Lugano is CH$_4$-rich (Blees et al. 2014a), this deep water CH$_4$ reservoir is decoupled from the surface waters. Indeed, since the onset of meromixis in 1967 (Barbieri and Mosello 1992), the northern basin only mixed fully in the winters of 2004–2005 and 2005–2006 (Holzner et al. 2009). We consequently argue that plant

mediated emission, ebullition and storage flux during lake turnover are unlikely to contribute substantially to CH_4 emission from Lake Lugano's northern basin. Given the arguments above, our results indicate that partial-pressure-gradient-driven CH_4 diffusion from a shallow CH_4 source across the surface water – atmospheric boundary layer constitutes the prime mechanism of CH_4 emission from Lake Lugano, at least during the sampling campaigns in 2011 and 2012.

Potential sources of surface water CH_4

Typically, CH_4 in aquatic systems can be attributed to a biogenic (i.e., microbial methanogenesis in anoxic environments) or, to a lesser extend, a thermogenic (fossil) source. The oxic degradation of methylated substrates was additionally found to contribute to surface water maxima in marine environments (Karl et al. 2008; Damm et al. 2010; Carini et al. 2014). The isotopic composition of CH_4 can be used to trace CH_4 sources and consumption (e.g., Whiticar 1999). Microbial methanogenesis is associated with a strong isotope effect, so that microbial CH_4 is characterised by $\delta^{13}C$ values typically below −50 ‰. Thermogenic CH_4 on the other hand is comparatively ^{13}C-enriched, with values of −20 ‰ to −50 ‰. The low $\delta^{13}C$ values of CH_4 in the surface water of Lake Lugano, above the thermocline (between −50 ‰ and −56 ‰ in October 2012 (Figs. 3k, 4c), indicate isotopic disequilibrium with atmospheric CH_4 (−47 ‰, Dlugokencky et al. 2009) and suggest a biogenic rather than a thermogenic origin. In contrast, $\delta^{13}C$ of CH_4 in the water below the thermocline was distinctly more ^{13}C-enriched (>−40 ‰), which is consistent with our previous measurements (Blees et al. 2014a). Upward-diffusing CH_4 from the lake bottom is efficiently consumed by aerobic methanotrophs at the permanent redoxcline in 135 m water depth, and only traces of strongly ^{13}C-enriched CH_4 escape this microbial filter (Blees et al. 2014a). Indeed, CH_4 concentrations in intermediate waters between 135 and 30 m water depth never exceed 20 nmol L^{-1} and $\delta^{13}C$-values are about −30 ‰. CH_4 accumulation in the surface water of the Lake Lugano North Basin, as well as the generally encountered subsurface peak at the thermocline (Figs. 3, 4, 5), thus seems to be independent of the deep water CH_4 reservoir. The surface water concentrations in Lake Lugano's northern basin (between 26 and 178 nmol L^{-1} in October, and between 9 and 30 nmol L^{-1} in May) were supersaturated with respect to atmospheric equilibrium (∼3 nmol L^{-1}) and in a range similar to other lakes (e.g. Bastviken et al. 2004; Murase et al. 2005; Schubert et al. 2010; Diem et al. 2012).

Similar CH_4 concentration maxima have been found previously in other lakes (Murase et al. 2005; Hofmann et al. 2010; Grossart et al. 2011) and in marine surface waters (Karl and Tilbrook 1994; Rusanov et al. 2004; Karl et al. 2008; Damm et al. 2010). The subsurface CH_4 maximum was explained by lateral turbulent-diffusive transport of sediment-derived, biogenic CH_4 (Hofmann and Roussy 2002; Murase et al. 2005), by in situ production in anoxic microenvironments (Rusanov et al. 2004; Grossart et al. 2011), or aerobic processes such as decomposition of methylphosphonate and dimethylsulfoniopropionate (Karl et al. 2008; Damm et al. 2010; Carini et al. 2014).

The subsurface CH_4 peak in the Lake Lugano North Basin could originate from epilimnetic sediments, particularly in the shallow Bay of Lugano. Turbulence at the sediment–water interface as a result of wind-induced surface and internal waves in lake basins (MacIntyre et al. 1999; Hofmann et al. 2010) can lead to the release of CH_4 from the sediments (Sakai et al. 2002), which can subsequently be transported laterally by advection. Such a mechanism has previously been invoked as an explanation for CH_4 accumulation in lake surface water during stratified conditions (Murase et al. 2005). Mean monthly wind speeds 10 m above Lake Lugano were relatively low (1.6 ± 0.2 m s^{-1} between October 2011 and October 2012, MeteoSwiss), but maximum wind speeds during gusts were as high as 30 m s^{-1} in the same period, which indeed could have caused internal waves at the pycnocline. On the other hand, with the exception of the Bay of Lugano and the SW and NE ends of the basin, the shores of Lake Lugano are generally steep. Particularly in the central part of the basin, where we observed elevated subsurface CH_4 concentrations during all sampling campaigns (Fig. 3), the sediment cover at the depth of the thermocline is thin, if present at all (unpublished seismic data). It is thus difficult to invoke shallow benthic methanogenesis as the main source of surface water CH_4. Similarly, tributary rivers, e.g. as suggested by Murase et al. (2005) for Lake Biwa, are an unlikely source of the CH_4 in the upper Lake Lugano water column. Here river inputs are small, and the CH_4 concentration in the river entering the eastern part of the basin was low (∼4 nmol L^{-1}), leading to a plume of lowered CH_4 concentrations in the surface water in front of the outflow (Fig. 2b). A more likely source of CH_4 in the surface water of the northern basin of Lake Lugano may be in situ production in the oxic water column, as was found in other lakes (Grossart et al. 2011) and in marine environments (Karl et al. 2008; Damm et al. 2010; Carini et al. 2014). To date, little is known about CH_4 production rates in oxygenated surface waters, but in a speculative sense, the CH_4 production rates found in Lake Stechlin (43–58 μmol m^{-3} day^{-1}; Grossart et al. 2011) could, if maintained over a depth range of around 1 m, and accounting for an efflux of 4–18 μmol m^{-2} day^{-1} in May 2012 (see Table 1; Fig. 6b), support the CH_4 accumulation observed in the surface water of Lake Lugano during

spring. A biological origin of the CH_4 peak in the subsurface waters is suggested by its low (and, compared to CH_4 $\delta^{13}C$-values at the surface and at the oxycline, anomalous) $\delta^{13}C_{CH4}$. Nevertheless, the observed C-isotope signatures are ambiguous with regards to the actual source of the biological CH_4. Both CH_4 from methanogenesis in shallow littoral sediments and anoxic microenvironments likely display similarly low $^{13}C/^{12}C$ ratios. Moreover, the C-isotope effects associated with methylation and de-methylation pathways under oxic conditions are still unknown.

Spatio-temporal variability in CH_4 concentrations in the surface mixed layer

CH_4 concentrations in the surface waters and the efflux to the atmosphere were highly variable in space and time (Figs. 2, 6). On average, surface water concentrations were higher in October (57 nmol L^{-1} in 2011 and 45 nmol L^{-1} in 2012) than in May 2012 (16 nmol L^{-1}). Based on the depth profiles taken throughout the lake, we calculated an average CH_4 content of 487 μmol m^{-2} within the mixed layer in May 2012, and 687 μmol m^{-2} in October 2012 (upper 17.5 m of the water column). Given a surface area of 27.5 km^2, this translates into a total CH_4 content in this layer of 14×10^3 mol (May 2012) and 19×10^3 mol (October 2012). In general, microbial CH_4 production is probably higher in late summer/early autumn compared to spring because the water temperature is higher, and increased primary production leads to higher substrate availability for methanogens. Since the pycnocline becomes more pronounced with warming of the surface water, turbulence at the sediment–water interface as a result of internal waves acting on the density interface is also expected to increase (MacIntyre et al. 1999). This increased turbulence would promote the release of sedimentary CH_4, which could specifically explain the accumulation of CH_4 at the thermocline (Figs. 3, 4, 5). Similarly, increased biological production in the warmer summer surface waters, in combination with O_2 consumption through respiration, also increases the number of potential anoxic microenvironments, both in detrital aggregates and in the digestive tracts of zooplankton. Thus, regardless of whether the source of CH_4 to the surface water in Lake Lugano is sedimentary or located in the surface water itself, the source strength is expected to increase during the summer season.

The observed spatial heterogeneity in CH_4 concentration, which indicates a spatial imbalance of sources and sinks of CH_4, is more difficult to explain. An epilimnetic sedimentary CH_4 source would probably lead to a concentration decrease with distance from the sedimentary sources, which are restricted to the shallower parts of the basin in the west (Bay of Lugano) and the eastern end. However, in these areas, i.e., the eastern (May 2012, Fig. 2b) and western part of the basin (October 2011 and 2012, Fig. 2a,c) we encountered comparably low CH_4 concentrations. Alternatively, the fact that we do not observe a spatial correlation with sedimentary deposits may indicate a water column source that is more evenly distributed laterally, such as methylphosphonate and dimethylsulfoniopropionate degradation.

Absence of CH_4 oxidation in the surface water

An important factor constraining the efflux of CH_4 from the surface mixed layer to the atmosphere, besides CH_4 production leading to CH_4 excess concentrations (see previous section), is the extent of biological CH_4 consumption. Since CH_4 oxidation leaves the residual CH_4 enriched in ^{13}C relative to ^{12}C, such an enrichment in the surface water, coupled to a concentration decrease, could be regarded as evidence of a microbial CH_4 sink. In October 2012, several profiles showed a distinct CH_4 concentration minimum between the concentration peaks at the thermocline and at the surface (Figs. 3j–m, 4c). The corresponding $\delta^{13}C$ values between −50 and −56 ‰ (10 m water depth, Fig. 3k) stand in contrast to what would be expected for biological consumption (which discriminates against $^{13}CH_4$) of the CH_4 in the mixed surface layer. Although we still lack a plausible explanation for the local CH_4 concentration minimum, the fact that we did not see any characteristic ^{13}C-isotopic enrichment is consistent with our CH_4 oxidation rate measurements in January 2010 and October 2011, which, despite O_2 concentrations in excess of 240 μmol L^{-1}, showed very low ($\ll 0.1$ nmol L^{-1} day^{-1}) rates within the upper 15 m of the water column without any systematic variation with depth. These results are in agreement with previously reported low rates of CH_4 oxidation in limnetic (Murase et al. 2005) and marine surface waters (Mau et al. 2013; Steinle et al. 2015), possibly caused by sunlight-inhibition of microbial CH_4 oxidation (Murase and Sugimoto 2005). Low turbidity of around 3 FTU in Lake Lugano surface waters from autumn until spring indicates strong light penetration.

Spatio-temporal variability of CH_4 loss from the surface mixed layer

The calculated diffusive fluxes of CH_4 to the atmosphere (between 168 μmol m^{-2} day^{-1} in October 2011 and 17 μmol m^{-2} day^{-1} in May 2012; MacIntyre equation, Table 1; Fig. 6) are low but comparable to other lakes in the northern hemisphere (e.g., Bastviken et al. 2004). Although we cannot with the present dataset determine temporal trends, the temporal variation in the CH_4 pool in

the surface water described above could in part be caused by the differential rates of CH_4 emission. The accumulation of CH_4 in the upper water column in summer is probably aided by an increase in methanogenesis and/or methylation/de-methylation reactions as the water warms. Since the buoyancy flux in a warming water column is reduced, and the transfer velocity depends on the buoyancy flux (Eqs. 6, 7) (MacIntyre et al. 2010), the emission is dampened in spring and early summer, thus reinforcing the accumulation of CH_4 in the near-surface water. On the other hand, in late summer and autumn the cooling water body, with an increased buoyancy flux (at elevated CH_4 concentrations), is prone to emitting more CH_4. CH_4 efflux is thus retarded during spring and early summer (Fig. 6b) when warming of the surface water outweighs nocturnal cooling, and enhanced in autumn (Fig. 6a,c) when heat loss from the water to the atmosphere is more important. Indeed, surface water warming and cooling, and therewith the buoyancy flux, show a much more distinct seasonality than do average wind speeds. Also the probability of high wind speeds is similar for all seasons (MeteoSwiss). We thus argue that the observed seasonal variability of surface water CH_4 concentration is driven by temperature-driven differences in the strength of both sources and sinks, underlining that biological as well as physical aspects are relevant for CH_4 fluxes from lake environments to the atmosphere.

Conclusion

Lake Lugano surface waters are supersaturated with CH_4 with respect to atmospheric equilibrium and thus represent an important source of atmospheric CH_4. The absence of CH_4 oxidation in the surface waters shows that CH_4 produced in the surface water or in shallow-water sediments is eventually outgassed to the atmosphere. The outgassing of CH_4 seems to undergo distinct seasonal variation, with peak fluxes in autumn and substantially lower fluxes in spring. Annual flux variations are modulated by seasonal changes in CH_4 production and temperature-related changes in the buoyancy flux associated with the warming and cooling of the surface water during spring and autumn, respectively. The source of the surface water CH_4, and the exact mechanisms behind observed spatial patterns in surface water CH_4 concentration and fluxes remains unclear, but the lack of any clear spatial correlation with sedimentary deposits tentatively suggests in situ CH_4 production in the oxic water column itself. The low $\delta^{13}C$ values of CH_4 in the surface waters and at the thermocline support a biological origin. Since the C-isotope effects of de-methylation pathways in the water column are as yet unknown, we cannot rule out these pathways. These isotope effects will have to be elucidated in future work.

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