Higher late summer methane emission from central than northern European lakes

Päivi RINTA,[1*] David BASTVIKEN,[2] Jos SCHILDER,[1] Maarten VAN HARDENBROEK,[1] Tabea STÖTTER,[1] Oliver HEIRI[1]

[1]Institute of Plant Sciences and Oeschger Centre for Climate Change Research, University of Bern, Altenbergrain 21, CH-3013 Bern, Switzerland; [2]Department of Thematic Studies - Environmental Change, Linköping University, 581 83 Linköping, Sweden

*Corresponding author: paivi.rinta@gmail.com

ABSTRACT

Quantifying methane (CH_4) emissions from lakes is important for regional and global greenhouse gas emission inventories. However, regional and global estimates suffer from methodologically inconsistent data sets and from the situation that systematic flux measurements are presently available only for some regions in the world. In particular, many temperate regions dominated by agricultural land use, like central Europe, lack regional multi-lake studies of lacustrine CH_4 emissions. We compare estimates of diffusive and ebullitive flux from 30 small central European and 17 small boreal lakes based on standardized measurements during a single visit per lake in late summer. Furthermore, we assess the amount of CH_4 accumulated in the hypoxic deep-water layers in late summer. This provides an estimate of the potential release of CH_4 from these lakes during autumn mixing (storage flux). The results show that emissions per unit area of lake surface from central European lakes are significantly higher than those from boreal lakes, with average estimates of diffusive and ebullitive flux being as much as six and 27 times higher, respectively. CH_4 concentration in the surface water was significantly related with lake area and maximum depth in the boreal lakes. However, no significant relationships between diffusive and ebullitive fluxes and lake basin morphometry were found in central European or boreal lakes, as proposed in earlier studies, although the short measurement period (6 h) may not have been adequate for reliably quantifying ebullition in our study. As expected, storage flux was related to relative depth and relative volume of the hypoxic water layer in both regions. We discuss the relevance of the higher observed diffusive and ebullitive fluxes for regional estimates in central Europe based on an example of previous emission estimates from small lakes in Switzerland. Our results suggest that diffusive and ebullitive CH_4 emissions from these lakes may be considerably higher than estimated based on widely applied relationships for predicting lacustrine CH_4 emissions developed in northern European and North American regions. The results also confirm that modifications are necessary when applying these relationships to central European lakes. Our study highlights the inter-regional variability in lacustrine CH_4 emissions and the need for regionally developed calibration data for validating and developing predictive models for estimating CH_4 emissions from lakes at the landscape scale.

Key words: Greenhouse gases; methane; ebullition; diffusive flux; temperate lakes; upscaling.

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INTRODUCTION

Methane (CH_4) is an important greenhouse gas, accounting for approximately 20% of the radiative forcing by well-mixed greenhouse gases (Myhre *et al.*, 2013). Freshwaters including lakes, reservoirs, streams, and rivers, are estimated to contribute 12 to 18% of the natural CH_4 sources to the atmosphere (Kirschke *et al.*, 2013). Quantifying these natural greenhouse gas emissions is important for understanding the mechanisms controlling atmospheric CH_4 concentrations on decadal to millennial time scales (Loulergue *et al.*, 2008; Kirschke *et al.*, 2013; Nisbet *et al.*, 2014). Furthermore, inventories of emissions are also needed at the regional and local scale to support national greenhouse gas management strategies (Ciais *et al.*, 2014). However, large uncertainties are involved in the estimates of global CH_4 emissions from freshwaters due to scarce measurements and inconsistent methodology in available data sets (Schulze *et al.*, 2010; Bastviken

et al., 2011; Holgerson and Raymond, 2016). Furthermore, while lakes in some regions have been intensively studied, some other lake types have received little attention in global and regional studies. For example, small lakes in the heavily populated temperate zone are understudied regarding their role as a source of CH_4 (Bastviken *et al.*, 2011; Ortiz-Llorente and Alvarez-Cobelas, 2012). Even though the total area of lakes in these regions is lower than, for example, in the boreal zone (Verpoorter *et al.*, 2014), anthropogenic pressures on these lakes (*e.g.,* eutrophication or organic pollution) may strongly affect their carbon cycles (Juutinen *et al.*, 2009; Schrier-Uijl *et al.*, 2011) and make them relevant for estimates of regional and global CH_4 emissions.

Due to the lack of regional multi-lake studies of lacustrine CH_4 emissions in many regions of the world, flux estimates in the better studied boreal zone have been used as a basis for upscaling emissions in other regions (Bastviken *et al.*, 2004; Saarnio *et al.*, 2009; Schulze *et*

al., 2010; Hiller *et al.*, 2014). For example, in the recent inventory of anthropogenic and natural CH_4 emissions in Switzerland (Hiller *et al.*, 2014), lacustrine CH_4 emissions were estimated based on regression equations developed by Bastviken *et al.* (2004). These authors analysed CH_4 flux data, predominantly measured during the summer period, from 73 lakes situated mainly in boreal northern Europe and continental northern temperate North America, with only few sites included from central Europe. The study concluded that the different components of open-water CH_4 emissions can be predicted for the studied lakes based on lake surface area. However, Bastviken *et al.* (2004) and several other authors (Huttunen *et al.*, 2003; Juutinen *et al.*, 2009; Duc *et al.*, 2010; Marotta *et al.*, 2014; Rasilo *et al.*, 2014; Yvon-Durocher *et al.*, 2014; Yang *et al.*, 2015) have pointed out that additional variables, such as lake productivity and temperature, are expected to strongly affect lacustrine CH_4 emissions. Higher emissions in heavily populated central Europe compared with the regions mainly covered by the data set of Bastviken *et al.* (2004) were anticipated in the Swiss CH_4 inventory (Hiller *et al.*, 2014). Based on the restricted CH_4 emission data available for Swiss lakes, Hiller *et al.* (2014) estimated that the emissions per unit area of lake surface from small Swiss lakes are three times higher than based on the equations by Bastviken *et al.* (2004). Hiller *et al.* (2014) emphasized that this represents a coarse estimate and point out that more calibration data are needed to validate this assumption. However, so far no multi-lake studies are available to confirm this assumed difference between CH_4 emissions from lakes located in densely populated central Europe and the lakes from northern Europe or North America studied by Bastviken *et al.* (2004).

Recently, Schilder *et al.* (2013) and Rinta *et al.* (2015) studied diffusive CH_4 fluxes and concentrations in different parts of the water column in 32 small lakes in central and western Europe and Fennoscandia and observed clear differences between the regions. Schilder *et al.* (2013) focused on describing within-lake patterns of diffusion but also noted that diffusive fluxes were apparently higher in central and western European lakes than in Fennoscandian lakes. However, the authors did not discuss the implications of these measurements for regional upscaling. Rinta *et al.* (2015) measured higher CH_4 concentrations in the surface water of central and western European lakes confirming systematic differences in CH_4 cycling between the two regions. However, the relatively small number of non-Fennoscandian lakes in these studies did not allow a rigorous assessment of the extent to which diffusive CH_4 fluxes differ between lakes in western and central Europe compared with Fennoscandian lakes. Furthermore, it remains unclear if the higher diffusive CH_4 flux and CH_4 concentrations in the surface water of western and central European lakes reported by these studies are also indica-

tive for other CH_4 emission pathways. In previous studies (Bastviken *et al.*, 2004; Wik *et al.*, 2016b), open-water CH_4 emissions have been separated into diffusive flux, ebullition, and storage flux. The latter represents the CH_4 that is accumulated under ice cover or in the hypoxic deep-water layers and can potentially be released to the atmosphere during ice melt or water column mixing (Encinas Fernández, *et al.*, 2014; Ducharme-Riel *et al.*, 2015). The fourth potential emission pathway, not examined in the present study, consists of plant-mediated flux from littoral zones with emergent vegetation (Juutinen *et al.*, 2003).

Here we provide a detailed assessment of open water CH_4 flux from the 32 lakes studied by Schilder *et al.* (2013) and Rinta *et al.* (2015) and from an additional 15 lakes in central Europe. For each lake, CH_4 concentration and flux were measured during a single sampling visit in late summer. We used a consistent methodology to separate different open-water flux components, including diffusive flux, ebullition, and the potential storage flux released from these lakes during autumn overturning. Since we measured diffusive flux and ebullition in both shallow and pelagic zones of the lake basins, we can provide upscaled estimates accounting for the relative importance of these two zones in individual lakes (Schilder *et al.*, 2013). This large data set allows us to assess if and to what extent 1) the magnitude of open-water CH_4 flux and 2) the environmental variables related to different flux components differ between western and central European lakes and boreal lakes in late summer. In addition, we examine how the observed differences affect regional CH_4 emission estimates from small lakes in central and western Europe. We assessed, as an example, how our revised flux estimates from central European lakes potentially influence the approach used to assess CH_4 emissions from Swiss lakes in the CH_4 emission inventory of Hiller *et al.* (2014).

METHODS

Study sites

Data from a total of 47 small lakes in Europe are available for this study (Fig. 1, Supplementary Tab. 1). Seventeen of these lakes are located in the boreal/hemiboreal zone in southern Finland and Sweden (referred to as boreal lakes). They are situated on non-calcareous Precambrian bedrock covered by Quaternary deposits and generally characterized by humic water with a naturally low pH (Supplementary Tab. 2). Two Swedish lakes (Hargsjön and Illersjön) are exceptions as they are situated on alkaline carbonate-rich soils. The Swedish lakes were studied in August and September 2010 and the Finnish lakes in August 2011. Thirty of the studied lakes are situated in western and central Europe (here referred to as central European lakes). They are located in lowland or

subalpine regions dominated by agriculture or grasslands in the Netherlands, Germany, and Switzerland. The lakes are located on mainly calcareous sedimentary bedrock or Quaternary deposits. The Dutch, German and 10 of the

Fig. 1. Geographical location of the 47 study lakes. In the upper figure, dark grey symbols indicate boreal lakes (n=17) and light grey symbols indicate central European lakes (n=30). Source of digital elevation model: Swiss Federal Office of Topography (2005).

Swiss lakes were studied in August and September 2011. CH_4 concentration and diffusive flux measurements from these and the Fennoscandian lakes are described in detail in Schilder *et al.* (2013) and Rinta *et al.* (2015). Fifteen additional Swiss lakes were sampled in August 2012.

Gas sampling and flux measurements

The field sampling was conducted at each lake during a single day in late summer. For the analysis of CH_4 concentrations in water, samples from the surface water (ca. 0.5 m below the surface) and from the bottom water (ca. 0.5-1 m above the sediment) were collected using a 5 L water sampler (Uwitec, Austria) in the deepest part of the basin. Sampling and storage of gas samples in acidified N_2-filled glass vials are described in detail in Rinta *et al.* (2015).

The ebullition and diffusive flux components were estimated using the floating chamber design and methodology described by Bastviken *et al.* (2004; 2010). Four groups of three chambers were deployed for approximately 6 h (ca. 10 a.m. - 4 p.m.) on a transect from the near-shore zone to the central part of the lake (see Schilder *et al.*, 2013 for details). After 6 h, 30 ml gas were taken from each chamber with a syringe and injected into a glass vial (10 mm thick butyl rubber stopper; Apodan, Denmark) or into a 10 ml exetainer (Labco Limited, UK) pre-filled with saturated NaCl solution. The exetainers were stored upside down with a small amount of NaCl solution covering the septa. Samples for determining CH_4 concentration in the surface water and in the ambient air were collected at each group of chambers following Bastviken *et al.* (2010).

CH_4 concentrations in the headspace of the storage vials were quantified using a GC-FID equipped with a methanizer (Agilent 6890 N with a PlotQ capillary column for the samples from the Finnish lakes, Shimadzu GC-2014 with a ShinCarbon ST column for the samples taken from the Swiss lakes in August 2012, and Shimadzu GC-8 with PoropackN column for the others). The analytical error (σ) based on repeated measurements of standards (n ≥3) was less than 1.7%.

Concentration and flux calculations

Concentrations of CH_4 in the lake water were calculated using the headspace equilibration method (McAuliffe, 1971) by applying Henry's law describing gas-water partitioning (Stumm and Morgan, 1996; see methods in Bastviken *et al.*, 2010). The total flux into the floating chambers, including both diffusion and ebullition, was estimated using simple flux calculation based on the accumulated CH_4 divided by chamber area and time (Bastviken *et al.*, 2010). Flux estimates were expressed per m^2 and per day rather than per hour for comparison with values reported in the literature. The diffusive flux
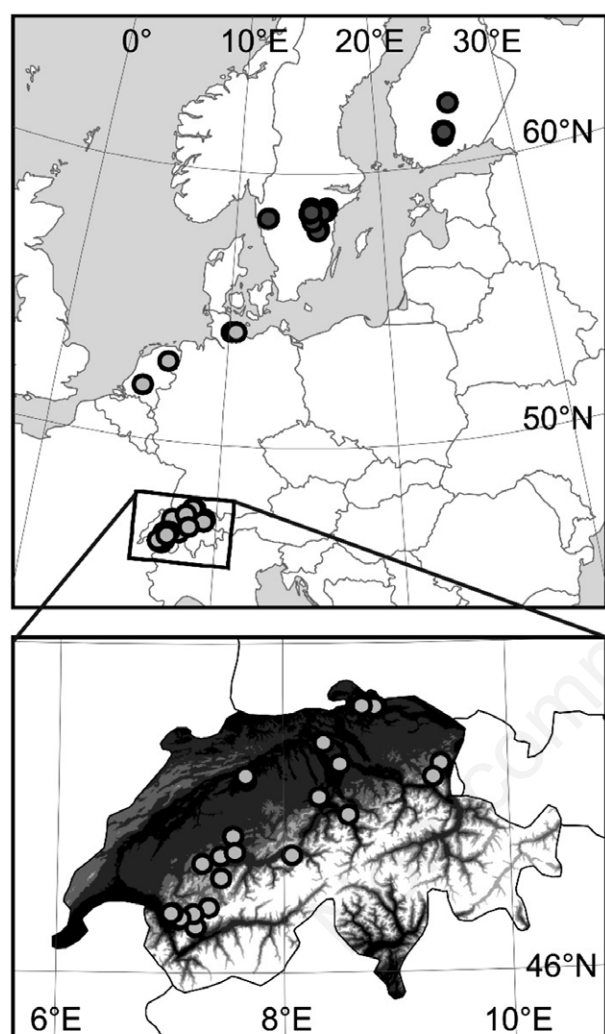
into the chambers was calculated based on measured CH_4 concentration in the surface water, the calculated theoretical CH_4 concentration in the surface water when in equilibrium with the CH_4 partial pressure in the chamber, and the estimated piston velocity (k). The k value was estimated based on the CH_4 accumulation in the chamber corrected for the chamber area, volume, and deployment duration and for the decreasing concentration gradient due to increasing CH_4 concentration in the chamber as described by Bastviken *et al.* (2004). Chambers having received ebullition were eliminated from these calculations. They were identified based on having unrealistically high calculated k values indicating that more CH_4 entered the chamber than could be explained by diffusion only. This method is described in detail by Bastviken *et al.* (2004) and Schilder *et al.* (2013). In short, chambers returning k values at a Schmidt number of 600 (k_{600}; see definition in Bade, 2009) higher than the mixing depth of the water column, or k_{600} values higher than 2.1 times the lowest k_{600} within the group were considered to have received both diffusive flux and ebullition.

Chamber groups were classified into two zones based on water depth: chamber groups located in shallower water than the thermocline depth were defined as belonging to the shallow water zone and chamber groups in deeper water than the thermocline depth belonged to the pelagic zone. In six non-stratified lakes, all chamber groups were classified as belonging to the shallow water zone (Supplementary Tab. 3). In two lakes, the thermocline depth was so shallow that all chamber groups were defined as pelagic. This approach differs from the procedure of Schilder *et al.* (2013), who classified chamber groups for whole-lake upscaling of diffusive flux into near-shore and central areas based on the distance to the shoreline.

Average total flux into the chambers and average diffusive flux in the shallow and pelagic zone was calculated for each lake. Due to the high ebullition rates in some lakes, diffusive flux both in the shallow and pelagic zone could be separated only for 33 out of 47 lakes (Supplementary Tab. 3). To estimate the diffusive flux in the zones where no separation of diffusive and ebullitive flux was possible, we used the diffusive flux of the other zone if diffusive flux estimates were available. In two lakes where these were not available, we estimated the diffusive flux based on the wind speed and CH_4 concentration in the surface water as described in Schilder *et al.* (2013). Local wind speed data for these two lakes were obtained from the nearest weather station (data downloaded from Swiss Federal Office of Meteorology and Climatology, https://gate.meteoswiss.ch/idaweb and from Royal Netherlands Meteorological Institute, http://www.knmi.nl /climatology/daily_data).

Ebullition was estimated by subtracting the average diffusive flux from the average total flux into the chambers in the respective zone. Due to the differences in methodology for calculating total flux and diffusive flux (total flux calculations do not take into account the decreasing concentration gradient due to increasing CH_4 concentration in the chambers), subtraction returned negative values for ebullition in some cases. These negative ebullitive fluxes were corrected to 0. Average estimates for total flux, diffusive flux, and ebullition for the entire lake surface were corrected for the fraction of shallow and pelagic zones of the lake surface area to produce whole-lake estimates. The fractions of shallow and pelagic zones were calculated based on the thermocline depth and lake bathymetry (see below).

The dissolved CH_4 that accumulated in the hypoxic deep-water layers during the summer and that was potentially released to the atmosphere during water column mixing in the autumn (referred to as storage flux) was estimated by multiplying the CH_4 concentration in the bottom water by the volume of the hypoxic layer (see below).

Environmental variables

We explored relationships between CH_4 fluxes and lake characteristics which have been identified as relevant for predicting CH_4 emissions from lakes in earlier studies. These variables include lake morphology, relative volume of the hypoxic layer, temperature, dissolved organic carbon (DOC) concentration, and nutrient concentrations (Michmerhuizen *et al.*, 1996; Bastviken *et al.*, 2004; Juutinen *et al.*, 2009; Schrier-Uijl *et al.*, 2011; Ouellet *et al.*, 2012; Kankaala *et al.*, 2013; Rasilo *et al.*, 2014).

Bathymetric maps were obtained from municipal or regional authorities or from the literature. They were digitized and the volumes of the whole lake, the hypolimnion, and the hypoxic water layer were calculated using the 3D Analyst tool in ArcMap 9.3 (Esri). The hypolimnion was defined as the water layer below the depth from the surface where the temperature gradient first reached 1°C m[1] (Huotari *et al.*, 2009) and the hypoxic water layer as below the depth were oxygen saturation first reaches hypoxic conditions (oxygen saturation <5%) in the temperature and oxygen profile created in the field (WTW, Oxi 1970i, Germany). Relative depth (z_r) (%) of the lake basin was calculated according to following equation (Wetzel, 2001):

$$z_r = \frac{50 z_m \sqrt{\pi}}{\sqrt{A_0}}$$

where z_m is the maximum depth and A_0 the lake surface.

Estimates of mean annual and July air temperatures and precipitation for the closest weather station or interpolated for the lake location were obtained from national meteorological services for the reference period 1981-2010 (except for Switzerland 1981-2006) and land use in the catchment from the CORINNE Land Cover database

(Nippel and Klingl, 1998; European Environmental Agency, 2007). Conductivity, pH, total phosphorus (TP) and total nitrogen (TN) concentration, and absorbance at 420 nm as an indicator for coloured dissolved organic matter concentration were analysed as described in Rinta *et al.* (2015). Volume-weighted average nutrient conditions in the water column were calculated based on the TN and TP concentration in the bottom water and in the surface water and corresponding hypolimnion and mixing layer volumes.

Numerical analyses

Statistical analyses of CH_4 concentrations, fluxes, and environmental variables were made using R (R Core Team, 2013). Each variable was tested for normal distribution using the Shapiro-Wilk test, and skewed distributions were log_{10}-transformed. All reported averages of concentration and flux data represent back-transformed values of averages calculated on log_{10}-transformed data (marked using term "log-average"). Statistically significant differences between the regions were detected using Student's *t*-test and a simple linear regression model was used to examine relationships between variables. When examining relationships between CH_4 concentrations or emissions and environmental variables, p-values were adjusted for multiple testing according to the FDR method (Benjamini and Hochberg, 1995) within the sub-data sets separated by region and flux component.

Influence on lacustrine CH_4 emission estimates from Switzerland

For assessing the relevance of our CH_4 flux measurements in central European lakes for regional upscaling, we compared emission estimates from small Swiss lakes: i) based on the area-dependent regression equations by Bastviken *et al.* (2004) as described in the original publication; ii) based on the area-dependent regression equations by Bastviken *et al.* (2004) as modified for the Swiss CH_4 inventory (Hiller *et al.*, 2014); and iii) based on area-dependent regressions we developed by following the methodology of Bastviken *et al.* (2004) but using our new late-summer CH_4 flux measurements from 30 central European lakes. For comparison, the regressions were developed for our boreal lakes as well.

For the estimation based on our measurements, we first extrapolated our flux measurements per m² and day to emissions per lake and year following Bastviken *et al.* (2004). Annual emission estimates per lake were expressed in grams carbon rather than mols CH_4 for comparison with values reported in the previous studies. Bastviken *et al.* (2004) extrapolated diffusive flux per day obtained from single or multiple measurements during the open-water period to flux per year by multiplying the val-

ues by the number of ice-free days of each lake (90-150 ice-cover days per year). For estimating annual emissions from our studied lakes, we assumed that ice cover in lakes in southern Finland lasts for 150 days (Korhonen, 2005), in southern and central Sweden 110 days (Swedish Meteorological and Hydrological Institute, 2014), and in Switzerland above 1500 m asl for six months (Guthruf *et al.*, 1999). In central European lowland lakes, we assumed no ice cover, since in Swiss lowland lakes permanent ice cover only develops during cold winters (Guthruf *et al.*, 1999). Following Hiller *et al.* (2014), ebullition was assumed to occur during the warmest half of the year only.

Based on the annual emission estimates per lake, we then calculated regression equations using the linear model function (lm) in R (R Core Team, 2013) for log_{10}-transformed area and emission data. Equations for ebullition were calculated excluding the zero values. Due to the sporadic nature of ebullition in lakes, it can be expected that a longer measurement period than possible in our campaign would have revealed ebullition in most lakes. For calculating equations for the storage emission, we replaced zero values by 1 (log_{10}-transformed 0). As a last step, the regression equations were used to estimate emissions from small Swiss lakes in the size range of 0.5 to 75 ha. Following Hiller *et al.* (2014), we calculated ebullition only for lakes located lower than 1500 m asl. Distribution of lakes (including reservoirs and artificial ponds) in Switzerland, their surface areas, and altitudes were obtained from the Primary surface layer of the landscape model VECTOR25 (Swiss Federal Office of Topography, 2007) and from the digital elevation model of Switzerland (Swiss Federal Office of Topography, 2005). Hiller *et al.* (2014) did not apply correction factors for back-transformation bias of log-transformed data (Newman, 1993). We therefore also present uncorrected back-transformed values, since our aim was to compare how our CH_4 emission estimates affect regional upscaling based on this earlier study. However, we do briefly report how much our estimates would have to be corrected as a consequence of back-transformation.

RESULTS

Environmental conditions

Environmental conditions in the two study regions, boreal Fennoscandia and central Europe, are clearly different (Tab. 1). Mean annual air temperature and precipitation as well as water temperature during the sampling were significantly higher in central Europe than in the boreal regions (P<0.001). Also, TN concentrations were significantly higher (P=0.03-0.04) and absorbance was lower for the central European lakes (P=0.0003). Different geology is reflected in significantly different conductivity

and pH in the surface water (P<0.0001). However, no significant difference in lake size (lake surface area, maximum depth), fraction of the hypoxic volume relative to the total volume (Supplementary Tab. 1), or TP concentrations was observed between the central European and boreal lakes of our data set (P=0.2-0.5).

CH$_4$ fluxes

CH$_4$ concentrations in the surface water varied between 0.1 and 17.6 µmol L^{-1} (Fig. 2a). They were significantly higher in the central European lakes than in the boreal lakes (P<0.0001). In the boreal lakes, log-average concentration in the surface water was 0.4 µmol L^{-1} (range 0.1-3.9 µmol L^{-1}) and in central European lakes 1.8 µmol L^{-1} (range 0.3-17.6 µmol L^{-1}).

In the boreal lakes, log-average total CH$_4$ flux into the chambers in the shallow zone was 0.3 mmol m^{-2} day^{-1} (range 0.02-2.0 mmol m^{-2} day^{-1}) and in the pelagic zone 0.2 mmol m^{-2} day^{-1} (range 0.04-1.3 mmol m^{-2} day^{-1}) (Fig. 3). In the central European lakes, log-average total CH$_4$ flux into the chambers in the shallow zone was 3.6 mmol m^{-2} day^{-1} (range 0.2-54.9 mmol m^{-2} day^{-1}) and in the pelagic zone 2.7 mmol m^{-2} day^{-1} (range 0.05-35.7 mmol m^{-2} day^{-1}).

Zone-weighted diffusive and ebullitive fluxes were significantly higher in the central European lakes than in the boreal lakes (P<0.0001-0.002) (Fig. 2 b,c). These differences between the regions are not related to the lake size distribution, since they are still apparent when only the boreal lakes in the same range of surface areas as the central European lakes are examined (P<0.0001 and P=0.01, respectively). The log-average daily diffusive flux was six times higher in central European lakes than in boreal lakes. In the boreal lakes, it was 0.2 mmol m^{-2}

day^{-1} (range 0.02-1.3 mmol m^{-2} day^{-1}) and in the central European lakes 1.2 mmol m^{-2} day^{-1} (range 0.06-8.5 mmol m^{-2} day^{-1}). Diffusive flux was significantly related to CH$_4$ concentrations in the surface water both in the boreal and the central European lakes (P=0.02, R^2=0.33 and P<0.0001, R^2=0.76, respectively) (Fig. 4). The log-average daily ebullitive flux was 27 times higher in central European lakes than in boreal lakes. In the boreal lakes, it was 0.03 mmol m^{-2} day^{-1} (range 0-1.8 mmol m^{-2} day^{-1}) and in the central European lakes 0.8 mmol m^{-2} day^{-1} (range 0-45.4 mmol m^{-2} day^{-1}) (Fig. 2c). The storage flux did not differ significantly between the regions (P=0.1) (Fig. 2d). In the boreal lakes, the estimated storage flux varied from zero up to 11910 mmol m^{-2} and in the central European lakes up to 3476 mmol m^{-2}.

CH$_4$ fluxes related to environmental variables

Within each of the two study regions, we explored relationships between late summer CH$_4$ concentration in the surface water and diffusive, ebullitive, and storage flux with the following environmental variables: lake area, maximum depth, relative depth, relative volume of the hypoxic water layer, mean annual air temperature, absorbance in the surface water, TN concentration in the surface water, and average TN concentration in the water column (Tab. 2). We tested only TN concentrations, since TN and TP concentrations were correlated both in the surface water (P<0.0001, R^2=0.50) and in the water column (P<0.0001, R^2=0.60) in our data set. In addition, TN concentration in the surface water was more strongly related to the fraction of managed land (incl. agricultural land and artificial surfaces) in the catchment (P<0.0001, R^2=0.54).
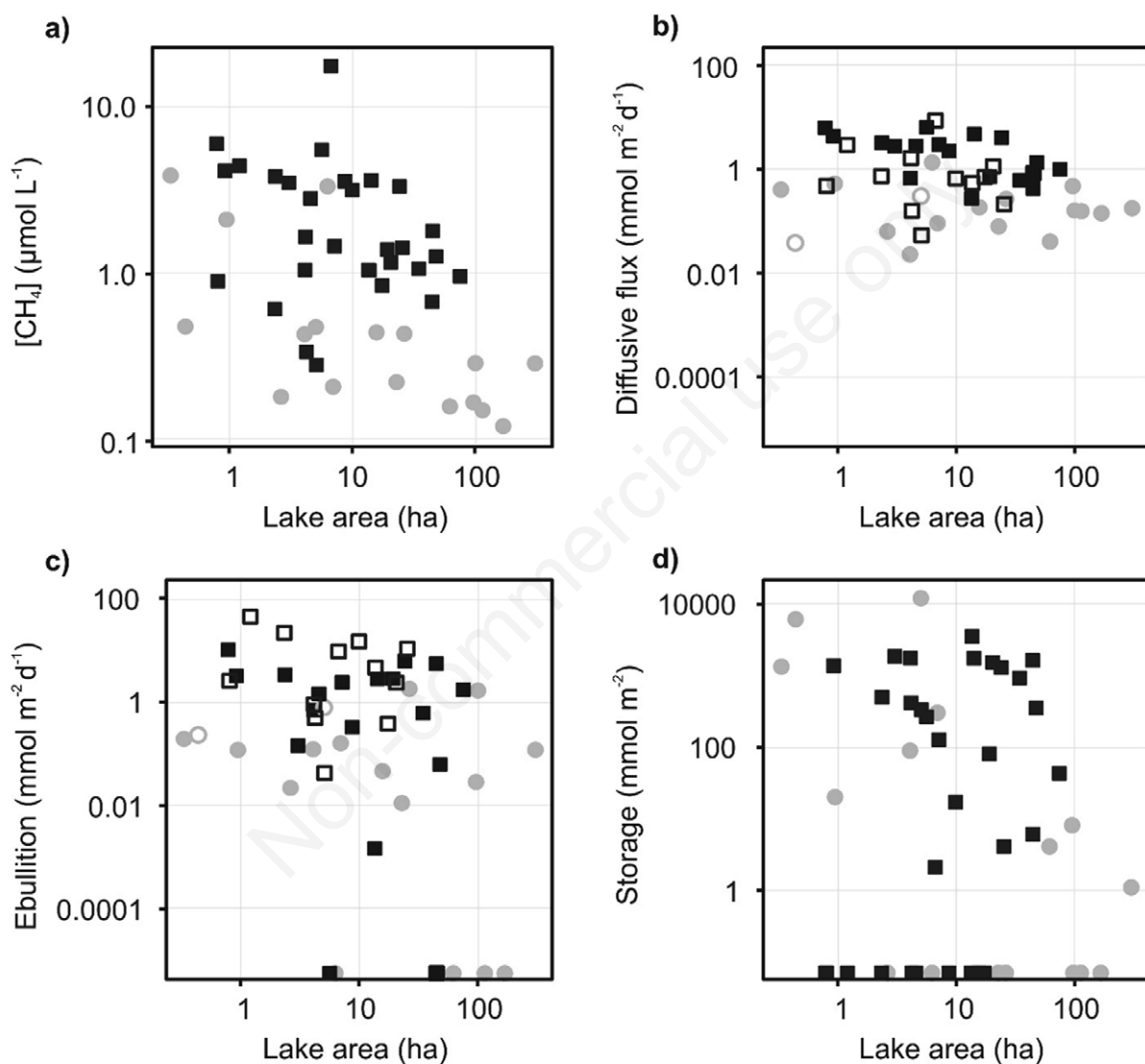
Only CH$_4$ concentration in the surface water and stor-

Tab. 1. Environmental characteristics of the study regions and water chemistry of the studied lakes.

		Boreal		Central European	
		Mean	Range	Mean	Range
Mean annual air temperature	°C	5.6	3.2-6.9	8.7	4.9-11.8
Annual precipitation	mm	695	620-902	1506	742-2323
Forests in the catchment	%	76	23-100	18	0-100
Managed land in the catchment (incl. agricultural areas and artificial surfaces)	%	13	0-58	38	0-100
Temperature of surface water	°C	17	14-18	20	11-25
Conductivity of surface water	µS cm^{-1}	95	24-311	256	54-462
pH of surface water		6.6	5.4-7.8	8.3	6.6-9.3
Absorbance of surface water	at 420 nm	0.045	0.006-0.104	0.019	0.003-0.121
TP in surface water	µg L^{-1}	19	3-45	35	7-260
Average TP in water column	µg L^{-1}	185	5-2247	109	9-985
TN in surface water	µg L^{-1}	585	200-1172	949	290-2900
Average TN in water column	µg L^{-1}	1259	250-6549	1657	403-4137

TP, total phosphorus; TN, total nitrogen.

age flux were significantly related to environmental variables in our data set (Tab. 2). CH_4 concentration in the surface water was negatively related to lake area and maximum depth in boreal lakes. In the central European lakes, the relationships were not statistically significant. No significant relationships between diffusive flux or ebullition

and environmental variables were found. Storage flux was related to morphological parameters (*e.g.*, positively to relative depth and relative volume of the hypoxic water layer) and positively correlated with average TN concentration in the water column both in the boreal and in the central European lakes.

Fig. 2. a) CH_4 concentration ($[CH_4]$) in the surface water, b) zone-weighted average diffusive flux, c) zone-weighted average ebullitive flux, and d) storage flux relative to lake area. In b and c, open symbols indicate lakes where separation of diffusive and ebullitive flux was not possible in all zones and values needed to be estimated based on diffusive flux in the other zone or based on $[CH_4]$ in the surface water and wind speed (see Supplementary Tab. 3 for details). In c and d, values plotted on the x-axis represent zero values.

Influence on lacustrine CH_4 emission estimates from Switzerland

Annual diffusive, ebullitive, and storage emissions per lake based on our flux measurements in late summer relative to lake area are presented in Fig. 5. In boreal lakes, significant relationships were found between lake area and annual diffusive emission per lake and annual ebullition per lake (Tab. 3). In central European lakes, significant relationships were found between lake area and annual diffusive emission per lake and storage emission

per lake. The relationship between lake area and annual ebullition per lake was nearly significant.

The total number of Swiss lakes in the size range of 0.5 to 75 ha is estimated to be 2161, and they cover in total 8310 ha (Swiss Federal Office of Topography, 2007). Forty-five% of the lakes in this size range were located higher than 1500 m asl. The original area-dependent regression equation by Bastviken *et al.* (2004) and the modified equation applied for the Swiss CH_4 emission inventory of Hiller *et al.* (2014) (Fig. 5) return a total annual diffusive emission of 0.06 and 0.18 Gg year^{-1}, ebul-

Tab. 2. Relationships of the environmental variables with CH_4 concentration in the surface water and diffusive, ebullitive, and storage CH_4 flux per unit area of lake surface.

	Boreal				**Central Europe**			
	P not corrected	Significance after FDR correction	R^2		P not corrected	Significance after FDR correction	R^2	
$\log_{10}$ CH_4 concentration in surface water								
$\log_{10}$ lake area	0.004	*	0.44	-	0.2		0.07	-
$\log_{10}$ maximum depth lake	0.006	*	0.40	-	0.4		0.03	-
$\log_{10}$ relative depth	0.2		0.13	+	0.9		0.00	+
$\log_{10}$ fraction hypoxic volume	0.7		0.01	+	0.3		0.04	+
Mean annual air temperature	0.09		0.18	-	0.9		0.00	-
$\log_{10}$ absorbance of surface water	0.5		0.04	+	1.0		0.00	-
$\log_{10}$ TN in surface water	0.7		0.01	-	0.9		0.00	-
$\log_{10}$ average TN in water column	0.5		0.03	+	0.3		0.03	+
$\log_{10}$ diffusive flux								
$\log_{10}$ lake area	1		0.00	+	0.1		0.07	-
$\log_{10}$ maximum depth lake	0.2		0.10	-	0.7		0.01	-
$\log_{10}$ relative depth	0.4		0.04	-	0.5		0.02	+
$\log_{10}$ fraction hypoxic volume	0.3		0.08	-	0.2		0.06	+
Mean annual air temperature	0.8		0.00	+	1		0.00	-
$\log_{10}$ absorbance of surface water	0.5		0.03	-	0.7		0.01	+
$\log_{10}$ TN in surface water	0.6		0.02	-	1		0.00	-
$\log_{10}$ average TN in water column	0.6		0.02	-	0.1		0.07	+
$\log_{10}$ ebullition								
$\log_{10}$ lake area	0.2		0.12	-	0.2		0.06	-
$\log_{10}$ maximum depth lake	0.2		0.13	-	0.1		0.07	-
$\log_{10}$ relative depth	0.5		0.03	+	0.5		0.02	-
$\log_{10}$ fraction hypoxic volume	0.2		0.10	+	0.9		0.00	+
Mean annual air temperature	0.07		0.20	-	0.06		0.13	+
$\log_{10}$ absorbance of surface water	0.8		0.00	+	0.5		0.01	+
$\log_{10}$ TN in surface water	0.7		0.01	+	0.008		0.23	+
$\log_{10}$ average TN in water column	0.2		0.13	+	0.02		0.17	+
$\log_{10}$ storage								
$\log_{10}$ lake area	0.01	*	0.37	-	0.08		0.10	+
$\log_{10}$ maximum depth lake	0.8		0.00	-	0.0001	**	0.41	+
$\log_{10}$ relative depth	0.003	**	0.45	+	0.003	**	0.27	+
$\log_{10}$ fraction hypoxic volume	<0.0001	***	0.82	+	<0.0001	***	0.85	+
Mean annual air temperature	0.004	**	0.44	-	0.02	*	0.17	+
$\log_{10}$ absorbance of surface water	0.8		0.01	+	0.9		0.00	+
$\log_{10}$ TN in surface water	0.9		0.00	+	0.9		0.00	+
$\log_{10}$ average TN in water column	0.003	**	0.46	+	0.0002	***	0.41	+

P-values represent uncorrected values, asterisks show the significance after correction for multiple testing using the false discovery rate method (FDR) by Benjamini and Hochberg (1995), ***P<0.001, **P<0.01, *P<0.05). Negative or positive correlations are indicated by plus or minus symbols.
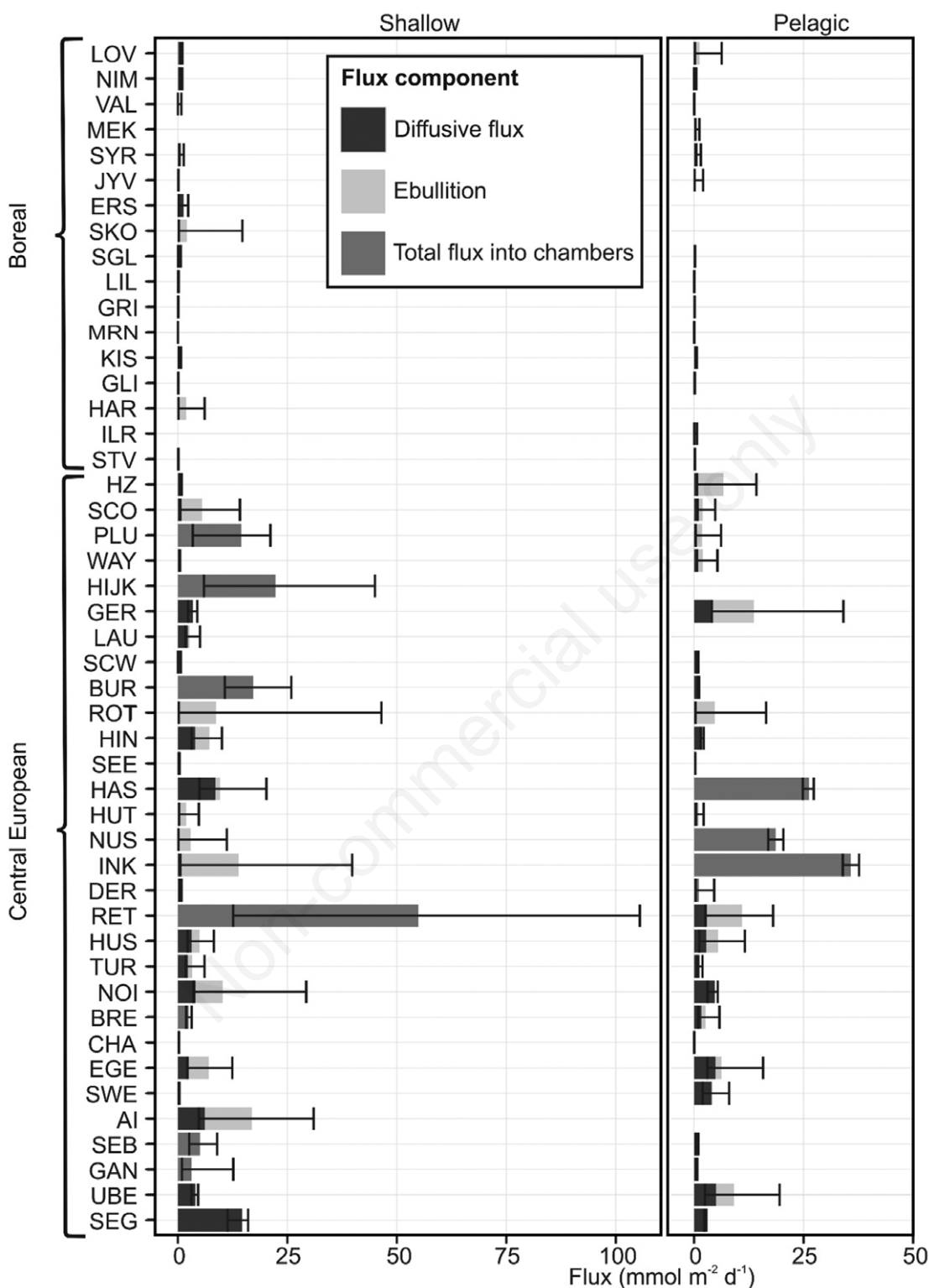
Fig. 3. Average open-water CH$_4$ flux estimated from flux measurements during fieldwork in the shallow and pelagic zone of the studied lakes. Estimates are provided for diffusive (dark grey) and ebullitive flux (light grey) where it was possible to separate these two flux components (see text for details). In lakes where this was not possible (*i.e.*, in lakes where all chambers within a given depth zone received ebullition), we provide total flux into chambers instead (medium grey). In some small lakes, all chamber groups were classified to the shallow or the pelagic zone and flux estimates for only one of these zones are provided (see Supplementary Tab. 3). Error bars show the range of the total flux in the chambers in the respective zone.

litive emission of 0.11 and 0.17 Gg year^{-1}, and storage emission of 0.06 and 0.17 Gg year^{-1}, respectively, from Swiss lakes in the given size range. The equations based on our measurements return a total annual diffusive emission of 0.35 Gg C year^{-1} and ebullitive emission 0.16 Gg C year^{-1}. Applying correction factors for back-transformation bias of log-transformed data (10$^\varepsilon$; Newman, 1993) in our equations would have led to 40% higher total annual diffusive emission and more than 400% higher ebullitive emission for the estimates based on our measurements (10$^\varepsilon$ values 1.4 and 2.7, respectively). We did not estimate total annual storage emission using our equations due to the high variability of storage emission estimates for Swiss lakes (Fig. 5). The 10$^\varepsilon$ value being higher than 200, this would have led to a major bias of emission values when back-transforming log-values.

DISCUSSION

CH$_4$ flux in late summer

Higher CH$_4$ concentrations in the surface water of central and western European lakes than in Fennoscandia have been reported in previous studies based on measurements in some of the same lakes as we examined in this study (Schilder *et al.* 2013; Rinta *et al.* 2015). Therefore, we also expected to find higher diffusive fluxes from central European lakes than from boreal lakes in our analysis. Using standardized measurements in late summer, we were able to confirm that both the measured daily diffusive and ebullitive flux were significantly higher in the central European lakes than in the boreal lakes (Fig. 2).

The factors responsible for the observed differences between the regions are difficult to identify since several environmental variables recognized as important for lacustrine CH$_4$ emissions in earlier studies, such as temperatures (Liikanen *et al.*, 2002; Marotta *et al.*, 2014; Yvon-Durocher *et al.*, 2014) and nutrient concentrations (Juutinen *et al.*, 2009; Schrier-Uijl *et al.*, 2010; Rasilo *et al.*, 2014; Yang *et al.*, 2015), but also geology and land use differ significantly between the regions (Tab. 1). Some of the reasons for the higher CH$_4$ concentrations in the surface water of central European lakes compared to those in the boreal lakes are discussed by Rinta *et al.* (2015), and these arguments can also be extended to explain higher diffusive and ebullitive flux in the central European lakes. In short, higher CH$_4$ production in the littoral zone is likely in the central European lakes due to warmer *in situ* temperature and more suitable substrates for methanogenesis (Duc *et al.*, 2010). Lateral transport of CH$_4$ from the littoral zone might be an important process in small central European lakes, as indicated by the CH$_4$ concentrations and stable carbon isotopic composition (δ^{13}C) profiles in the water column reported by Rinta *et al.* (2015), and may provide a source for high diffusive fluxes in the pelagic zone as well (Hofmann, 2013). The quality of the organic matter (OM) in the central European lakes may be more suitable for methanogenesis than in the boreal lakes, since autochthonous OM tends to be a better substrate for methanogenesis than OM of terrestrial origin (Duc *et al.*, 2010; West *et al.*, 2012; Guillemette *et al.*, 2013). In-lake primary production is expected to be higher in the central European lakes due to the higher nutrient inputs from non-forested catchments dominated by arable land, pastures, and alpine grasslands often used for seasonal summer pasturing than from the more forested catchments in the boreal regions (Tab. 1). Furthermore, humic substances and acid conditions have been observed to inhibit methanogenic activity in lake sediments (Casper *et al.*, 2003). The boreal lakes of our study are located in forest-dominated landscapes, and the water of these lakes is characterized by higher concentrations of DOC and lower pH than in central European lakes (Tab. 1).

Besides higher temperatures and more suitable substrate for methanogenesis, higher CH$_4$ emissions from the central European lakes might also be related to differences in landscape structure. Six times higher estimates of log-average daily diffusive flux values in the central European

Tab. 3. Regression equations for diffusive, ebullitive, and storage CH$_4$ emission (g C lake^{-1} year^{-1}) as a function of lake area (m^2) based on the daily flux estimates of this study.

|	Equation	P	R^2
Boreal			
log$_{10}$ (diffusion)°	1.0258 * log$_{10}$ (lake area) - 0.4739	0.000001	0.80
log$_{10}$ (ebullition)#	0.9974 * log$_{10}$ (lake area) - 0.4809	0.001	0.64
log$_{10}$ (storage)	8.1026-1.0335 * log$_{10}$ (lake area)	0.1	0.14
Central European			
log$_{10}$ (diffusion)°	0.8981 * log$_{10}$ (lake area) + 1.1317	0.00002	0.48
log$_{10}$ (ebullition)#	0.6392 * log$_{10}$ (lake area) + 2.2962	0.06	0.13
log$_{10}$ (storage)	2.2161 * log$_{10}$ (lake area) - 6.8225	0.006	0.24

°*Diffusion assumed to be relevant only during open-water season;* #*ebullition assumed to be relevant during half of the year, zero values excluded.*

lakes than for the boreal lakes cannot only be explained by differences in the CH_4 concentrations in the surface water. Based on the model used to calculate diffusive flux into the floating chamber (see Methods), the observed flux values are only possible if the gas exchange rates at the water-atmosphere boundary of the central European lakes are also higher (Bade, 2009). This is supported by the significantly higher *k* values in the central European lakes (P=0.04) (Fig. 4b). In our data set, higher wind-induced turbulence in the surface waters of the central European lakes cannot be explained by lake size (Schilder *et al.*, 2013; Vachon and Prairie, 2013) since no significant difference in lake areas between the regions was observed. However, the central European lakes are mainly located in open landscape, whereas most of our boreal lakes are

sheltered by forests, which may have led to higher wind-induced turbulence in the surface water of the central European lakes (Markfort *et al.*, 2010) (Tab. 1). Unfortunately, systematic differences in wind speeds near lake surfaces cannot be detected by the wind speed estimates at 10 m height obtained from meteorological monitoring networks.

Environmental variables affecting CH_4 flux in late summer

Within the regions, no significant relationships between daily diffusive or ebullitive fluxes and variables related to temperature and nutrients were found (Tab. 2). Similarly, the relationships to morphological parameters (*e.g.*, lake area, maximum depth, relative depth), which
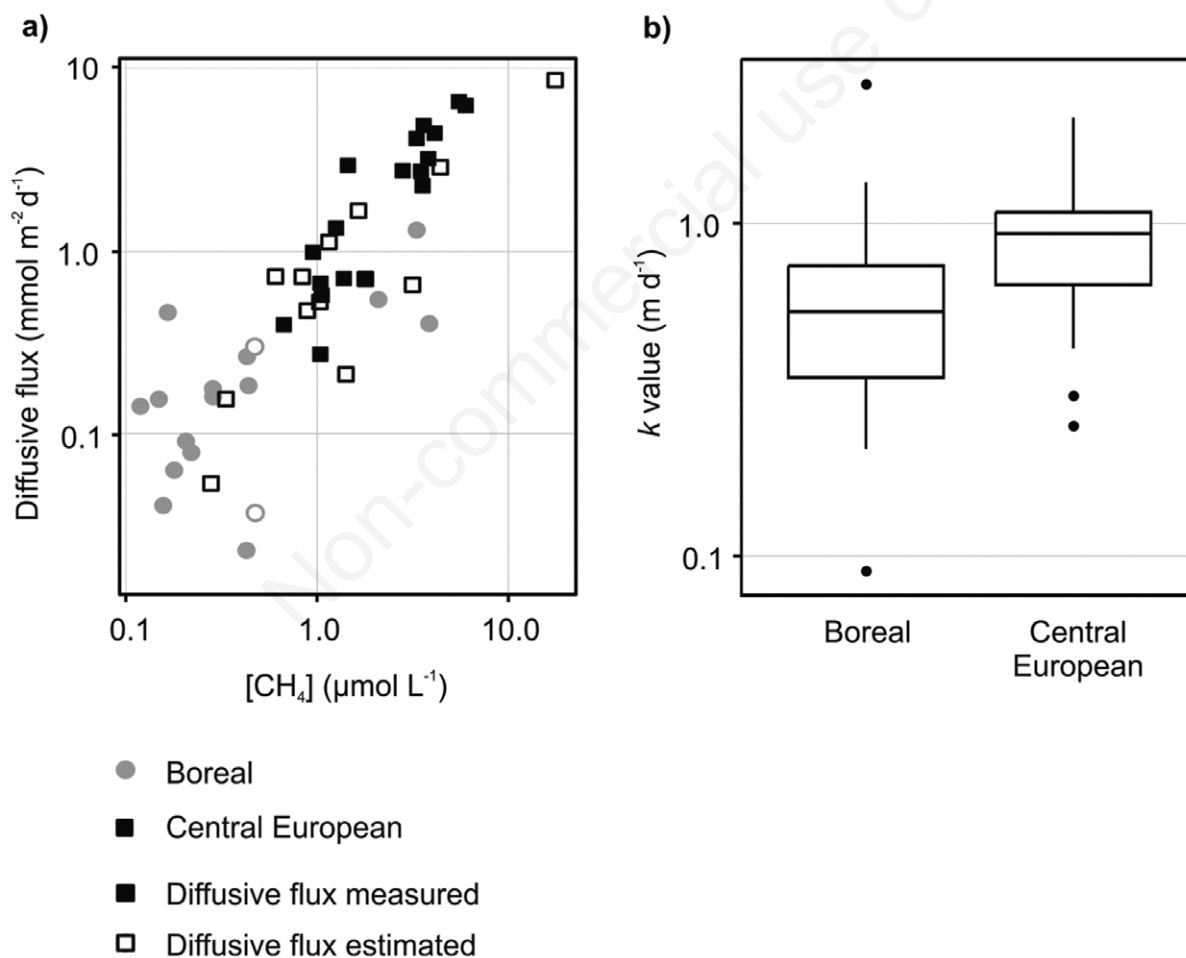
Fig. 4 a) Zone-weighted average diffusive flux plotted against CH_4 concentration ($[CH_4]$) in the surface water (P=0.02, R^2=0.33 and P<0.0001, R^2=0.76, for boreal and central European lakes, respectively). Open symbols indicate lakes where separation of diffusive and ebullitive flux was not possible in all zones and diffusive flux was estimated based on diffusive flux in the other zone or surface water $[CH_4]$ and wind speed (see Methods for details). b) *k* values representing zone-weighted lake averages for chambers having received diffusive flux only. Whiskers of the boxplots show data points less than 1.5 times the interquartile range from the box, circles indicate more extreme data points.

have been recognized as one of the most important controls of the open-water CH$_4$ emissions in lakes in the boreal regions and in northern temperate regions in North America (Bastviken *et al.*, 2004; Juutinen *et al.*, 2009; Kankaala *et al.*, 2013; Rasilo *et al.*, 2014), were not significant.

However, the absence of significant relationships between diffusive or ebullitive flux and environmental variables can be explained by the relatively short exposition of flux chambers (ca. 6 h) in our study. Ebullition from lakes is characterized by large temporal and spatial variability (Mattson and Likens, 1990; Wik *et al.*, 2013, 2016a). Therefore, our ebullition measurements may not have adequately captured regional patterns of between-lake variability in ebullition, as is also evident in our data set in the form of very variable ebullition estimates within and between lakes (Fig. 3). Many floating chambers on lakes where no ebullition was detected during the six-hour measurement would likely have received some ebullition during a longer measurement period. Similarly, diffusive flux rates can be strongly impacted by variations in wind speed and water turbulence (Cole and Caraco, 1998; Bade, 2009). When CH$_4$ concentrations in the surface water are examined instead of the measured diffusive flux estimates, relationships to morphometric variables are stronger in the boreal lakes (Tab. 2). In line with earlier studies (Bastviken *et al.*, 2004; Kankaala *et al.*, 2013), CH$_4$ concentration in the boreal lakes of our data set are related to lake area and maximum depth (Fig. 2, Tab. 2). However, in the central European lakes the relationships between morphometric variables and CH$_4$ concentration in the surface water are not evident (Fig. 2, Tab. 2), although they would have been significant without FDR correction for testing multiple relationships. The weaker relationship between lake area and CH$_4$ concentrations in the surface water in the central European lakes might be a consequence of higher wind exposure causing more efficient mixing in the surface waters (see above). Also, the smaller range of lake area covered by the central European lakes than by the boreal lakes in our data set (Fig. 2) or the lakes studied by Bastviken *et al.* (2004) may have obscured relationships between lake area and CH$_4$ concentrations.

As expected, the storage flux estimates are controlled by the relative depth and the relative volume of the hypoxic water layer in both regions (Tab. 2). The correlation between storage flux and average TN concentration in the water column can be explained by the effects of stratification stability on both of these variables. Strong stratification in the water column promotes accumulation of both CH$_4$ and nutrients in the hypolimnion, which leads to larger storage flux values and may lead to higher TN concentrations averaged over the water column. The apparent relationships between storage flux and mean annual air temperature can be explained by the lake size distribution in our data set. In the boreal region, most of the lakes with

relatively large hypoxic water layer are located in Finland, with lower mean annual air temperatures than in southern and central Sweden, and in central Europe at low altitudes (Supplementary Tab. 1).

Influence on lacustrine CH$_4$ emission estimates from Switzerland

To examine how relevant the higher observed flux estimates from central European lakes are for estimating regional emissions, we compared, as an example, total annual emission values from small Swiss lakes estimated based on the original area-dependent regression equations by Bastviken *et al.* (2004) and those estimated following the procedure used in the Swiss CH$_4$ inventory (Hiller *et al.*, 2014) with those calculated using the relationships between lake area and CH$_4$ emissions based on our measurements in 30 central European lakes.

The comparison shows that estimates based on the equations developed mainly in northern European and North American lakes (Bastviken *et al.*, 2004), and even those previously modified for Swiss conditions (Hiller *et al.*, 2014), might underestimate the emissions from small central European lakes. Total annual diffusive emission from small Swiss lakes using the modified regression equations based on our measurements are estimated to be 5.7 times the value derived from the relationships by Bastviken *et al.* (2004) and 1.9 times the value estimated based on the relationships used by Hiller *et al.* (2014). Total annual ebullitive emission using our modified regression equations are 1.4 times the value estimated based on the equations by Bastviken *et al.* (2004) but similar to the value derived from the relationships used Hiller *et al.* (2014). For these calculations, we follow Hiller *et al.* (2014) in assuming that ebullition occurs only during the warmest half of the year and is not a relevant process in subalpine and alpine lakes due to their low organic accumulation rates. However, we observed high ebullitive fluxes also in small high-altitude lakes. In five out of eight lakes situated higher than 1500 m asl, ebullitive fluxes higher than 2 mmol m^{-2} day^{-1} were measured in the shallow zone (Fig. 3). This indicates that the ebullition should be also included in estimates of total emissions of subalpine lakes surrounded by seasonal summer pastures or other agricultural activities, which may result in high sedimentation of organic matter in the lakes. Similarly, a recent study indicates that ebullitive flux in small Swiss lowland lakes can be significant even during the winter months (Schilder *et al.*, 2016).

Annual emission estimates per lake as estimated by Bastviken *et al.* (2004), Hiller *et al.* (2014), and this study are sensitive to several assumptions regarding the annual variability of flux. First, ice-cover length is critical for extrapolating diffusive flux values measured during open-water season to annual flux. Bastviken *et al.* (2004) assumed 90-150 days of ice cover for northern European

and North American lakes, when no diffusive flux occurred. For the comparison presented here, we used a rough estimate of six months of ice-cover in lakes located above 1500 m asl but these estimates could be refined if more accurate data on ice-cover length in different altitudes would be

available. Second, the extrapolation of our estimations of daily diffusive or ebullitive flux to annual flux assumes that measurements during a single day in late summer are representative for daily flux during the entire year. Diurnal variations in CH_4 fluxes from the lake surface to the atmos-
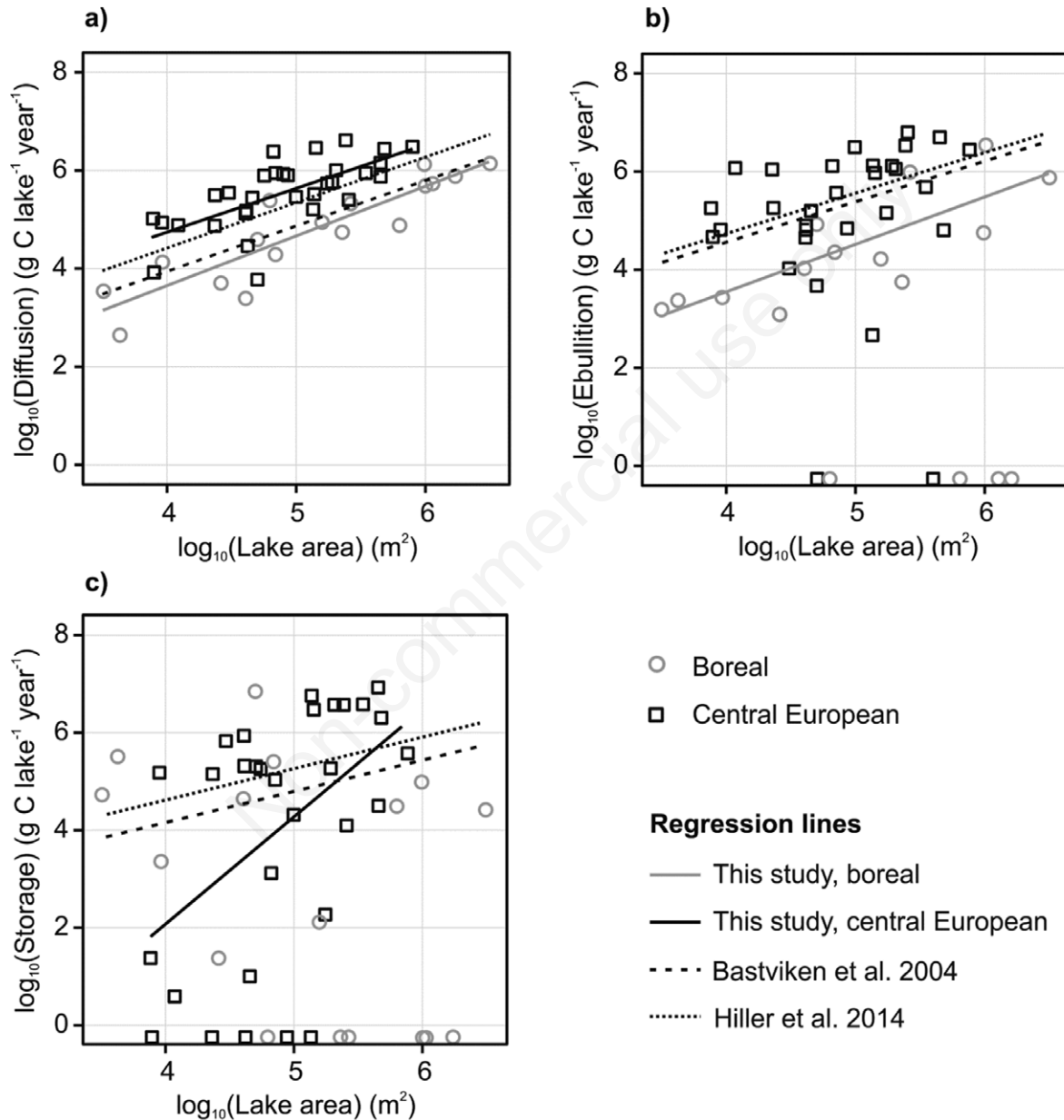
Fig. 5 a) Diffusive CH_4 emission assuming ice-free conditions during 215 days for Finnish lakes, 255 days for Swedish lakes, and during 182.5 days above 1500 m asl and during 365 days below 1500 m asl for central European lakes, b) ebullitive, and c) storage emission relative to lake area. Values on the x-axis represent zero values. Where significant, linear regression lines for the boreal lakes and central European lakes are provided. For ebullition in c, zero values were not included in the regression equations. Additionally, the linear regression lines used by Bastviken *et al.* (2004) and Hiller *et al.* (2014) are indicated. Bastviken *et al.* (2004): diffusion=$10^{0.234 + 0.927 * \log10(Lake\ area)}$, ebullition=$10^{1.190 + 0.841 * \log10(Lake\ area)}$, and storage=$10^{1.546 + 0.649 * \log10(Lake\ area)}$. Hiller *et al.* (2014): diffusion=$3 * 10^{0.234 + 0.927 * \log10(Lake\ area)}$, ebullition=$3 * 0.5 * 10^{1.190 + 0.841 * \log10(Lake\ area)}$, and storage=$3 * 10^{1.546 + 0.649 * \log10(Lake\ area)}$.

phere have been observed in several surveys (Keller and Stallard, 1994; Podgrajsek *et al.*, 2014; Natchimuthu *et al.*, 2014), and many studies have reported higher fluxes during summer than in other seasons (Casper *et al.*, 2000; Martinez and Anderson, 2013), presumably due to higher temperature and in-lake productivity. In addition, high fluxes during ice thaw in spring, as a result of accumulation of CH$_4$ under the ice, have been observed in several studies (Michmerhuizen *et al.*, 1996; Karlsson *et al.*, 2013; Miettinen *et al.*, 2015). However, due to a general lack of studies describing diurnal and seasonal variations in CH$_4$ flux from a wide range of lakes, it is presently not possible to use correction factors for our measurements during the morning-afternoon period and in late summer to make them more representative for daily or annual mean values.

Nevertheless, our regression equations are methodologically comparable with those of Bastviken *et al.* (2004) and hence able to show relative differences between annual diffusive and ebullitive emission estimates based on the earlier and our modified relationships between lake surface area and CH$_4$ emissions. The comparability of our flux measurements with those reviewed by Bastviken *et al.* (2004) is strongly supported by the very similar relationship between lake area and diffusive and ebullitive emissions calculated for boreal lakes in our data set and the mainly boreal and northern temperate lakes presented by Bastviken *et al.* (2004) (Fig. 5). Our regression equations based on the measurements in boreal lakes in late summer even return lower annual diffusive emission per lake than based on the data of Bastviken *et al.* (2004), which indicates that our late summer measurements do not systematically overestimate the mean daily fluxes during open-water season compared to measurements reviewed by Bastviken *et al.* (2004). Our example on emissions from small Swiss lakes confirms the order of magnitude of correction factors used in the Swiss CH$_4$ inventory (Hiller *et al.*, 2014). However, our estimates also suggest that the total annual emissions from Swiss lakes might be even higher than estimated in the inventory.

CONCLUSIONS

In this study, we quantified open-water CH$_4$ emissions using standardized methods for small lakes in Sweden, Finland, Germany, the Netherlands, and Switzerland in late summer. The measurements demonstrate that average late summer diffusive flux is significantly higher in central European lakes than in boreal lakes as indicated by the six-fold higher log-average diffusive flux observed for central European lakes. This difference is even more pronounced for ebullitive flux, with a 27 times higher log-average flux recorded for central European lakes, although due to the high temporal variability of ebullition in lakes and the short measurement period in our campaign we are likely underestimating ebullitive flux in our

study. In contrast to earlier studies, we did not find significant relationships between diffusive or ebullitive flux and environmental variables. Storage flux was similar between the regions and was related to the relative depth of the lake basin, relative volume of the hypoxic water layer, and average TN concentration in the water column.

Despite the many uncertainties still involved in the upscaling of open-water CH$_4$ emissions at regional scales, we were able to show that the significantly higher diffusive and ebullitive flux values observed in the central European lakes than in the boreal lakes of this study are relevant for inventories of lacustrine CH$_4$ emissions in central European regions. As suggested by Hiller *et al.* (2014), modifications are needed for regression equations developed in northern European and North American regions before they can be used in central European conditions. Especially, detailed seasonal studies of both diffusive and ebullition flux, for the latter including observations during winter ice cover and at different elevations, are therefore necessary to further refine CH$_4$ emission rates from small central European lakes.

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