Biogeosciences Discuss., 5, 3457–3496, 2008
www.biogeosciences-discuss.net/5/3457/2008/

Biogeosciences Discussions

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Methane dynamics in different boreal lake types

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Received: 30 July 2008 – Accepted: 5 August 2008 – Published: 1 September 2008

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

This study explores the variability in concentrations of dissolved CH_4 and annual flux estimates in the pelagic zone in a statistically defined sample of 207 lakes in Finland. The lakes were situated representatively in the boreal zone, where the mean annual air temperature ranges from −2.8 to 5.9°C. We examined how lake CH_4 dynamics related to regional lake types assessed according to the EU water framework directive. Ten lake types were defined on the basis of water chemistry, color, and size. Lakes were sampled for dissolved CH_4 concentrations four times per year, at four different depths at the deepest point of each lake. We found that CH_4 concentrations and fluxes to the atmosphere tended to be high in nutrient rich calcareous lakes, and that the shallow lakes had the greatest surface water concentrations. CH_4 content in the hypolimnion was related to oxygen and nutrient concentrations, and lake depth or area. The surface water CH_4 concentration was related to the depth or area of lake. Methane close to the bottom can be viewed as proxy of lake status in terms of frequency of anoxia and nutrient levels. Median CH_4 release from randomly selected lakes was 45 mmol m^{-2} a^{-1}. Shallow lakes had the highest median CH_4 effluxes, with the clear shallow lake type having the smallest median. Our data, combined with other studies, suggest that lake surface area could be used for an approximation of CH_4 release from lakes. Shallow small lakes common in boreal and arctic landscapes may have disproportional significance with respect to CH_4release.

1 Introduction

With accumulating information, lakes have grown in significance as regional and global sources of atmospheric methane (CH_4). Most recent annual lake CH_4 emission estimates are 8–48 Tg, i.e 6–16% of the global natural CH_4 emissions (Bastviken et al., 2004), and 24.2±10.5 Tg (Walter et al. 2007). In the European region, large lakes were estimated to contribute 24% of all wetland CH_4 emissions (Saarnio et al., 2008).

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The current study contributes to the fact that small lakes may have proportionally high significance in element fluxes in the landscapes (see Cole et al., 2007). The smallest lakes are shown to have high sedimentation rates and large CO_2 and CH_4 emissions per unit area in samples of arctic, boreal and temperate lakes (Michmerhuizen et al., 1996; Kortelainen et al., 2000; Bastviken et al., 2004; Kortelainen et al., 2004 and 2006; Walter et al., 2007). Particularly small lakes in areas of thawing permafrost form significant spot sources of atmospheric CH_4 (Hamilton et al., 1994; Walter et al., 2007). The new estimate of number and area of global lakes emphasized the very high number of small lakes in the boreal and arctic regions (Downing et al., 2006). These small water bodies are susceptible to ongoing changes in climate or land use, which may notably alter the lake environment and their CH_4 fluxes. Increasing or decreasing lake areas as a consequence of warming and shifts in water balance have been documented recently for northern lakes (e.g. Smith et al., 2005; Smol et al., 2007). In order to better understand the drivers behind the variability in the observed emissions, to reduce uncertainty in global estimates, and to estimate the anthropogenic influence on lake derived CH_4 emissions, comparison of CH_4 dynamics and net emissions in different types of lakes is required.

The production of CH_4 in freshwater lake sediments is a microbial process, regulated by the presence of anoxia, temperature, and the amount and quality of substrates (Rudd and Hamilton, 1978; Strayer and Tiedje, 1978; Kelly and Chynoweth, 1981; Liikanen et al., 2003). A large proportion of CH_4 produced in the sediment can be consumed at the sediment surface or water column by methanotrophs, a process that contributes to oxygen deficiency (e.g. Rudd and Hamilton, 1978; Bastviken et al., 2002; Liikanen et al., 2002; Kankaala et al., 2006). Besides these biological controls, abiotic factors also contribute. Stratification and seasonal overturns of the water mass, driven by wind and temperature, respectively, control the retention of CH_4 in the water column, while diffusion along the concentration gradient, boundary layer dynamics, bubble formation and plant mediated transport determine the rate of gas transport and liberation of CH_4 from the surface (Dacey and Klug, 1979; Chanton et al., 1989; Mac-

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Intyre et al., 1995; Michmerhuizen et al., 1996; Bastviken et al., 2004; Bastviken et al., 2008). Generally, high micro- and macrophyte production rate, small lake area, and high organic carbon content all promote the formation of anoxic hypo- and epilimnion and are related to increased concentrations and fluxes of CH_4 (Michmerhuizen et al., 1996; Riera et al., 1999; Huttunen et al., 2003; Bastviken et al., 2004).

Lake typology could provide a tool to deal with the complexity of lake ecosystems, and to find a reasonable basis for spatial extrapolation. For example, the European Union water framework directive (Directive 2000/60/EC) requires the Member States to typify lakes in order to recognize and improve the ecological status of lakes to meet the unspoiled status of the each lake type. Regional typology is based on morphometry and water chemistry. In addition, the North-American ecosystem-specific framework for nutrient criteria was recently presented by Sorrano et al. (2008). This approach could link the studies of greenhouse gas methane to overall environmental monitoring of lakes.

We report the variability in dissolved CH_4 concentrations and CH_4 fluxes as derived from the concentrations in a statistically defined sample of 207 boreal lakes in Finland. These data are distributed according to regional lake typology (Vuori et al., 2006), based on simple water quality and morphometric measurements. We examine

1. use a lake type as an indicator of the CH_4 concentrations and fluxes,
2. quantitative relationships among CH_4 concentrations and fluxes, oxygen, nutrient and organic carbon concentrations, and lake area and depth among and within the lake types, and
3. the relationship between the occurrence of anoxia, nutrient content and CH_4 accumulation.

Our aim is to evaluate the generalization tools for CH_4 release from the northern lakes. The same water samples have been analyzed for CO_2 and those results are published by Kortelainen et al. (2006).

2 Materials and methods

2.1 Study lakes and lake typology

Dissolved methane concentrations were examined from 207 Finnish lakes (Fig. 1). Data consisted of a random sample, including 177 lakes, and 30 additional lakes with the highest total phosphorous content, from the Finnish Lake Survey database (for details see Mannio et al., 2000; Rantakari and Kortelainen, 2005; Kortelainen et al., 2006). The 30 lakes were included in order to balance the distribution of oligotrophic and eutrophic lakes in this study. In all, the Finnish Lake Survey database contains 874 lakes larger than four hectares (0.04 km^2), but the random sample was restricted to lakes smaller than 100 km^2. The sample includes one eutrophic lake having larger area.

The study lakes were situated representatively in an area reaching from the margin of hemi/south boreal zone over the north boreal vegetation zone in Finland. Within this region the annual mean temperature ranges from −2.8 to 5.9°C, annual precipitation from 449 to 879 mm (Finnish Meteorological Institute, 1999, 2000), and the ice covered period lasts about 5 months in the south and about 7 months in the north (Hyvärinen and Korhonen, 2003). Lakes in Finland are mostly of glacial origin, and set in non-calcareous granite bedrock or till. Shallow and small humic lakes are the most numerous. The catchments are largely forested, and peatlands are common. Generally, nitrogen and phosphorous concentrations are greatest in southern and western Finland and lowest in northern Finland (Mannio et al., 2000; Rantakari et al., 2004).

Lakes were typified according to the Finnish lake typology required for ecological lake status classification governed by the EU water framework directive (Directive 2000/60/EC; Vuori et al., 2006). At first the naturally nutrient rich and/or calcareous lakes were distinguished on the basis of alkalinity and winter turbidity (Table 1). The rest of the lakes were first divided into three groups according to their humic content using water color as a criterion, and then grouped according to the surface area and mean depth. This sample did not include any lakes above the northern tree line. Fur-

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thermore the lakes with very short residence times were not identified. Some lakes were already typified by Finnish Regional Environmental Centres on the basis of long term observations and registered (HERTTA register). For those lakes that had no pre-registered type, the type was derived on the basis of morphological and chemical data from this study. The surface water chemistry in autumn was used in typification. Winter turbidity was needed to determine the nutrient rich and calcareous type.

2.2 Sampling and gas and water chemistry analyzes

Each lake was sampled four times during either year 1998 or year 1999 in order to capture CH_4 concentrations during potential winter and summer stratification and after spring and autumn overturn periods. Timing of sampling was thus as follows:

1. before thaw in March–April,
2. after thaw in May–June,
3. during late summer in the end of August–early September, and
4. in October.

Water samples were drawn from

1. 1 m below the surface,
2. in the middle of the water column,
3. 1 m above the sediment surface, and
4. 0.2 m above the sediment surface, all at the deepest point of each lake.

In very shallow lakes the amount of samples was smaller. Water samples of 30 ml for CH_4 concentration determination were drawn from the silicone tube of the Ruttner water sampler using a hypodermic needle and 60 ml polypropylene syringes equipped

with three-way stopcocks. In addition, water temperature was recorded and water samples for chemical analyses were collected.

Water samples were transported in coolers to the laboratories of the universities of Kuopio and Joensuu, where analyses of dissolved CH_4 concentrations were conducted the day after sampling. According to the headspace equilibration technique (McAuliffe, 1971), 30 ml ultra pure N_2 gas was added to each syringe and shook vigorously for 3 min. The headspace gas CH_4 concentration was quantified with a gas chromatograph (Hewlett Packard Series II and Shimadzu GC-14-A) equipped with an FI -detector. The CH_4concentration dissolved in water was calculated from the headspace gas concentration according to Henry's law using the values after Lide and Fredrikse (1995).

Oxygen, alkalinity, turbidity, pH, water color, total nitrogen (Ntot), NO_3, NH_4, total phosphorous (Ptot), PO_4-P, and total organic carbon (TOC) were analyzed from unfiltered samples in the laboratories of the Regional Environment Centres (National Board of Waters, 1981). Oxygen was determined by adding H_3PO_4 to the sample in the field and titration of the acidified sample in the laboratory with the Winkler method. Alkalinity was measured by Gran titration. Conductivity was measured conductometrically with temperature compensating cell. The values of pH were obtained electrometrically at 25°C with a pH meter. Water color (milligrams platinium per liter) was measured by optical comparison with standard platinum cobalt chloride disks. Total nitrogen was determined by oxidation with $K_2S_2O_8$, reduction of NO_3 to NO_2 in Hg-Cd (Cu-Cd) column and colorimetric determination of azo-colour. The sum of NO_3 and NO_2 was measured by reduction of NO_3 to NO_2 in Hg-Cd (Cu-Cd) column and colorimetric determination of azo-color. NH_4 was measured using spectrophotometer after adding hypochlorite and phenol. Total phosphorus and phosphate phosphorus were measured with spectrophotometer. Total organic carbon was determined by oxidizing the sample by combustion and measuring C using IR-spectrophotometry.

2.3 Morphometric and catchment characteristics

Data on area, mean depth, total volume and volume of water layers for the lakes in the sample were either collected from the register or measured directly in this study. If lake basin volume was not available in the register, it was estimated using regressions based on representative lake data (n=1831) available in the Finnish Environment Institute. The catchment boundaries were interpreted using topographic maps, and were digitized. We used a Landsat TM grid and digital elevation model with ArcView georeferencing software to obtain catchment and lake areas, catchment to lake ratios, and proportions of agricultural land, peatlands, and forests on upland soil, and areas of water and human settlements. The peatland category included both pristine and forestry drained areas.

2.4 Calculation of CH_4 fluxes and CH_4 storage in water

Annual CH_4 flux from the lake pelagic zone was estimated by summing the diffusive flux during the ice-free period, and the "storage change" fluxes associated with spring and autumn overturn periods. The diffusion rate between the water and the atmosphere was estimated on the basis of surface water CH_4 concentration.

The diffusive flux F (mol m^{-2} d^{-1}) between the water surface and the atmosphere was calculated as:

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

where k is the gas transfer coefficient, i.e. piston velocity (m d^{-1}), and C_w the measured CH_4 concentration (mol m^{-3}) in the surface water, i.e. at the depth of 1 m, and C_{eq} the methane concentration in water that is in equilibrium with the atmosphere at in situ temperature. The CH_4 concentration in the lake water in equilibrium with the atmosphere was calculated assuming the atmospheric CH_4 concentration of 1.72 μL L^{-1} for the year 1994 and taking into account the annual increase of 0.01% (Houghton et al., 1996). Gas transfer coefficient k was estimated according to Cole and Caraco (1998).

They determined experimentally k for tracer gas SF6 in small sheltered lake and normalized it to Schmidt number 600 (CO_2 at temperature of 20°C). An empirical relationship between wind speed and k_{600} value based on several tracer studies (Cole and Caraco, 1998), was used to determine k_{600}(cm h^{-1}):

$$k_{600}=2.07+0.215\times U_{10}^{1.7} \quad (2)$$

where U_{10} denotes the wind speed at 10 m height. We applied a value of 3 m s^{-1}, which is the average wind speed at 10 m height in the inland stations of Finnish Meteorological Institute during the open water period.

When piston velocity is known for one gas and temperature, it can be applied to another gas and temperature by the ratio of the Schmidt numbers. To calculate k for CH_4 we used

$$k\mathrm{CH}_4=k_{600}\times(Sc_{\mathrm{CH4}}/600)^{-0.5}, \quad (3)$$

where Schmidt numbers for CH_4 (Sc_{CH4}) evaluated for particular temperature and water density were calculated from empirical third-order polynomial fit with water temperature as an independent variable (Jähne et al., 1987). For the exponent we used value −0.5 according to Hamilton et al. (1994) and MacIntyre et al. (1995).

To calculate the diffusive flux over the whole ice-free period, the before ice-out concentration was extrapolated over 0.5 months after the ice-out. Similarly, the after ice-out concentration was assumed to last for 1.5 months, the summer time concentration for 3 months, and the autumn concentration over 2 months of the ice-free period of 7 months. These same periods were used when estimating the CO_2 emissions from our lakes (Kortelainen et al., 2006). In the current study time spans were proportionally the same for lakes having shorter ice free period.

The CH_4 storage was calculated for the water column (m^2) at sampling points and for whole lakes by multiplying concentration values by the volume of each layer assuming horizontal mixing of CH_4. Storage change fluxes were calculated from the differences in CH_4 storage between winter and spring, and between late summer and autumn.

This flux compared with the estimate of potential flux i.e. CH_4 storage exceeding the equilibrium concentration in the water column during late winter and late summer. This storage was assumed to be released to the atmosphere during circulation (Michmerhuizen et al., 1996). Methane storage in the water column at sampling point (m^2) was calculated by extrapolating the measured dissolved CH_4 concentration over depth ranges 0–0.5 m above the sediment, 0.5–2 m above sediment, 2 m above sediment to 2 m below the lake surface, and 2–0 m below the lake surface. The weighted estimate was produced by calculating storage in the whole volume of lake, integrating storage in the above depth ranges and dividing it by lake area.

2.5 Data analyses

Statistical distributions of CH_4 concentrations and fluxes are presented for the different lake types. We used multiple linear regression analysis (SPSS 15.0 for Windows) to quantify relationships between oxygen, total phosphorous, and total organic carbon concentrations and lake area, depth and the CH_4concentration, i.e. the residual of production and oxidation, during different phases of the lake annual cycles. Our objective was to examine patterns within and between the lake types. Near bottom and surface water samples were analyzed independently during both the late summer (summer stratification) and the late winter (winter stratification). Lake types of different size categories but with same humic content (Table 1) were pooled into one group in order to increase the number of observations in the group and to facilitate the statistical analyzes. $\log_e$ and angular transformations were used for unevenly distributed data.

We also examined the connection between the CH_4 concentration in near bottom water in winter or summer and nutrient and oxygen saturation making use of the practical Finnish lake usability classification (Vuori et al., 2006). For this purpose the lakes were divided in groups according to their total phosphorus concentration and occurrence of anoxia in the near bottom water, thus simplifying the classification criteria. Three groups were identified according to total phosphorous:

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1. good (Ptot<30 μg L^{-1}),
2. satisfactory (30≤Ptot≤50 μg L^{-1}), and
3. poor (Ptot>50 μg L^{-1}).

Four groups were identified according to anoxia: Lakes never facing anoxia, and the lakes in which the near bottom water was anoxic either in winter or summer, or more often. The water was considered anoxic if O_2 saturation was below 5%. Differences in mean CH_4 concentrations between the categories were tested using the Mann-Whitney *U*-test. Differences in catchment land cover between these groups were similarly tested. We also show central CH_4 emissions estimates for lake size classes 0.04–<0.1, 0.1–<0.5, 0.5–<1, 1–<100, and >100 km^2.

3 Results

3.1 Distribution of lake types

The most numerous lake types were very humic shallow (VHSh), humic shallow (HSh) and nutrient rich and calcareous (NRC) (Table 2). The surface area of lakes ranged from 0.04 to 119.8 km^2. The median lake area was 0.28 km^2 and only 25% of the sample exceeded 1.6 km^2. Most of those were typified into the three shallow types (Table 2). NRC lakes were also commonly shallow and had a small area. Defined by color (Pt mg L^{-1}), proportions of lakes with clear, humic or very humic water were 22%, 40%, or 38%, respectively. The type of NRC lakes also included many highly humic lakes. Nutrient rich and calcareous lakes, and very humic lakes were more common in the southern part of the study region, while the distributions of humic large, clear shallow, and humic small were more northern. Catchments of NRC lakes had the greatest proportional cover of agricultural land, while proportional peatland cover was largest in the catchments of larger humic lakes and very humic lakes. Very humic lakes

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and NRC lakes had small water area in catchments and large catchments relative to the lake size. Those lake types had the greatest total nutrient concentrations; in humic lakes the nutrients are largely bound in organic matter (Table 2).

3.2 CH_4 concentration dynamics

The CH_4 accumulation in the water column showed strong seasonality (Fig. 2). Generally, the storage of dissolved CH_4 in the water column was greatest late in the winter and during the summer stratification, i.e. prior to ice-out and the fall overturn periods. Methane storage decreased dramatically during the overturn periods, indicating a gas release to the atmosphere. The water column CH_4 storage reached its maximum during winter in 52% of the lakes, and during summer in 33% of the lakes. In some lakes the largest storage was recorded during spring (6.3%) or in autumn (8.7%). Median proportions of CH_4 storage lost during water column mixing were 96% and 66% in spring and fall, respectively.

The difference in dissolved concentrations of CH_4 between the surface and bottom was generally most pronounced during the late winter (Table 3, Fig. 2). Under the ice cover, median concentration in the bottom was 113 times the surface concentration. In the late summer, the median bottom concentration was 1.6 times the median concentration in the surface. In turn, the surface water concentrations were most often the largest during the late summer, the median value being 0.17 μmol L^{-1}. Generally, greatest CH_4 concentrations were found in water layer closest to the sediment during late winter (md 7.9 μmol L^{-1}), and during late summer (md 0.27 μmol L^{-1}). Some large concentrations were occasionally measured (3×>1000 μmol L^{-1}).

Seasonal and vertical distribution patterns of dissolved CH_4 reflected the chosen lake typology to some degree (Fig. 2) as expected. Within each type the variation in CH_4 concentration was, however, considerable. Over the whole annual cycle, nutrient rich calcareous lakes (NRC) had commonly high CH_4 concentrations in their water column, whereas shallow lakes had the greatest surface water concentrations. During the late winter, greatest CH_4 concentrations in bottom water typically occurred in the

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larger lakes (types HM and HL), and shallow lakes (types NRC and CSh), i.e. medians were from 28.4 to 47.9 μmol L^{-1}. High CH_4 concentrations in bottom water were also common in very humic lakes (10.4–12.7 μmol L^{-1}). Greatest surface water concentrations were found in the shallow type NRC and in the shallow humic types VHSh and HSh. During the late summer, bottom water concentrations were highest in very humic (VH) and NRC lakes, 1.1 and 0.6 μmol L^{-1} Greatest surface water CH_4 concentrations in late summer were found in the shallow types VHSh, CSh, NRC, and HSh, medians being from 0.18 to 0.31 μmol L^{-1}, respectively. Corresponding median values for other lake types varied from 0.02 to 0.09 μmol L^{-1}.

Patterns of CH_4 concentrations indicated the effects of factors associated with CH_4 production, oxidation, and transport between the sediment and the atmosphere. The relationships between CH_4 concentrations and O_2 concentration, Ptot concentration, TOC concentration, depth of sampling point and lake surface area were quantified by stepwise linear regression analyzes. These independent variables were chosen for the analysis, because they are used as lake type criteria and in lake status classification.

Under the ice cover in the late winter, the surface water CH_4concentration was related to the depth, the concentrations being the greatest when the depth was smallest (Table 4, Fig. 3). Secondarily, CH_4 concentration was related to lake water Ptot and oxygen concentrations, and large Ptot and small O_2 accompanied high CH_4 concentration. In the NRC lakes winter-time surface CH_4 concentration had a positive correlation with TOC concentration. Bottom water CH_4 concentration was, in turn, firstly explained by O_2 concentration. The highest CH_4 concentrations occurred predominantly when O_2 saturation was under 5% (Fig. 3). There was group of deeper lakes having poor oxygen saturation. Additionally, variation in the bottom water CH_4concentration was explained by variations in Ptot and lake area.

During the late summer, surface water CH_4 concentration had a negative correlation with depth and lake area (Fig. 3). The greatest CH_4 concentrations occurred in lakes with intermediate depth but small area. There was negative correlation between TOC and CH_4 concentration when all lakes were analyzed as one group. As in late win-

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ter, oxygen concentration was the primary factor behind the variation in summer-time bottom water CH_4 concentration, which was additionally explained by depth and Ptot.

The regression models captured more of the variation in the CH_4 concentrations near the bottom than near the surface where gas exchange occurs between the water and the atmosphere, varying in intensity according to mixing forces. Environmental gradients were wider when all lakes were included and typically regression coefficients were also larger for those models. With few exceptions, regulatory factors were the same. The most extreme cases (CH_4>1000μmol L^{-1}) were not associated with anoxic water, and possibly sediment interstitial water was mixed with the lower water layers during sampling in those cases.

3.3 Dissolved CH_4 and lake status

Methane concentration of bottom close water could be viewed as an indicator of lake status in terms of oxygen and nutrients. In the late winter the CH_4 concentrations were significantly greater in the lakes suffering anoxia and having the highest Ptot levels (Md 151.1 μmol L^{-1}) than in the lakes in which bottom water stayed oxic and Ptot levels were low (Md 0.1 μmol L^{-1}) (Fig. 4A, Table 5). The difference in CH_4 concentrations was smaller although statistically significant during the late summer (Md 6.4 vs. 0.1 μmol L^{-1}). Within any category of anoxia, the CH_4 concentrations increased with increasing Ptot level (Fig. 4). The lakes where the near bottom water stayed oxic over the whole annual cycle had significantly smaller CH_4 concentrations than the lakes where near bottom water turned anoxic at least once during the annual cycle (Table 5). Among the lakes where near bottom water was anoxic at least once or more during a year, the lakes having the lowest Ptot level had also significantly smaller CH_4 concentrations than lakes with higher Ptot levels (p<0.01) during winter. Difference in CH_4 concentrations between these lake groups was not significant during the summer (p=0.985).

Oxygen saturation, Ptot and CH_4 concentrations also reflected land cover patterns (Table 6). The catchments of lakes having poor status (prevailing anoxia and high

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Ptot levels) had significantly larger proportions of settlement and agricultural land, and significantly smaller proportions of peatland and water than the catchments of the good status lakes ($p<0.05$). The large proportions of agricultural land and settlements in the catchments were particularly related to high Ptot levels.

3.4 Estimated methane effluxes to the atmosphere

Annual release of CH_4 from the lakes ranged from very low emissions of 2.4 to high rates of 3606 mmol m^{-2} a^{-1}. Median CH_4 release of the 177 statistically selected lakes was 45 mmol m^{-2} a^{-1} (Fig. 5). These annual emissions represent the sampling point and were estimated by summing the spring and fall storage change fluxes and the diffusive efflux over the open water period. Proportional storage flux varied from a minute percentage to 99.8% of the annual CH_4 emission and it corresponded to more than 1/3 of the annual CH_4 release in half of the randomly selected lakes (Fig. 5). The largest CH_4 flux estimates resulted from the release of large CH_4 storage, which occurred in larger or deeper lakes with substantial volume of deep water. The most extreme sample point CH_4 flux estimates, smallest and highest, were found in lakes that were quite deep in our data (ca. 11 m). However, they were different in area: the lakes with the smallest fluxes were deep and larger than the average lake, while the greatest fluxes were found in deeper lakes with smaller surface area.

The humic middle size and NRC lakes had the greatest median annual CH_4 emissions expressed for the sampling point, 98 and 95 mmol m^{-2} a^{-1}, respectively (Fig. 5). Besides the NRC, the other shallow lakes also had typically large CH_4 emissions, medians for the types VHSh, HSh, and CSh were 65, 62 and 44 mmol m^{-2} a^{-1}. Storage flux contributed typically more than 1/3 to the annual CH_4 release in HM lakes, in the other HL lake, CSh, VH, and NRC lakes (Fig. 5). This indicates that the proportional storage flux can be a significant part of total annual CH_4 efflux both in deeper and shallow lakes.

Another estimate of annual CH_4 release averages the total storage change flux of

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CH_4 from whole lake per unit area. Consequently, it gave greater weight to the surface layers of the lakes resulting in much smaller values than the sampling point estimate due to smaller proportion of storage change flux. The statistical sample of lakes had median emission of 21 mmol m^{-2} a^{-1} and the share of storage change flux was only 5% of the total amount (Fig. 5). When results are expressed in this way, the role of the shallow lakes is pronounced. Among the four shallow types, the clear shallow lakes tended to have the smallest annual CH_4 emissions. Median CH_4 emission estimates for the shallow lakes varied from 19 to 47 mmol m^{-2} a^{-1}, and for the small to large lakes from 2 to 9 mmol m^{-2} a^{-1} (Fig. 5). It is to be noted that the shallow lakes typically had much smaller area than the small lake type (area <5 km^2).

Within-type variation in the annual CH_4 release estimates was commonly large (Fig. 5). Coefficient of variation within types CSm and M, CSh, and VH exceeded the coefficient of variation within all 207 lakes (174%, weighted estimate). Small area and shallow depth, however, indicated high CH_4 emissions (Fig. 6). Maximum depth alone explained 24% of variation in annual CH_4 efflux in the linear regression model. Including Ptot and lake area in the model improved the regression coefficient to 0.30 and to 0.38, respectively (Table 7).

4 Discussion

4.1 Lake types and CH_4 concentrations

We collected data from a representative set of small and medium size boreal lakes, which are typical in the region, to determine levels and variation of CH_4 concentrations and factors that could be used for estimation of pelagic CH_4 fluxes for boreal lakes. Methane concentrations were expected to relate with the regional lake types (Directive 2000/60/EC; Vuori et al., 2006; Table 2), because the type determinants, size, nutrient content, and humic content have been found to associated with CH_4 dynamics in the boreal and temperate lakes (Riera et al., 1999; Kortelainen et al., 2000; Huttunen et al.,

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2003; Bastviken et al., 2004). Consequently, we found that in nutrient rich, humic, and shallow lake types CH_4 concentrations and concurrently CH_4 fluxes to the atmosphere likely are high. However, high CH_4 concentrations also occurred in some clear and large lakes (Fig. 2). The advantage of a large data set is showing common patterns, but also the exceptions.

Among and within the lake types oxygen, Ptot, and TOC concentrations, area and depth all explained part of variation in CH_4 concentration in regression analyses. CH_4 concentrations in the sediment close water were more dependent on the absence or presence of oxygen, and secondarily of Ptot concentration and depth or area (Table 4, Fig. 3). Nutrient rich and calcareous lake type had high CH_4 concentrations both in the surface and close to the sediment (Fig. 2), and indicated a response to a typically high autotrophic organic matter production, and tendency to have anoxia. Further, as expected, very humic deeper lakes had high CH_4 concentrations in the bottom water during the late summer. Strong stratification of dark waters combined with the decay of organic matter often lead to oxygen deficiency (see also Kankaala et al., 2007). One third of the studied lakes showed the largest total water column CH_4 storage during the late summer, a result of the commonness of brown waters in our study region. Concentration of TOC, however, was not a statistically significant factor explaining bottom water concentration. This suggests that high TOC concentration enhances stratification and oxygen consumption, and does not indicate a substrate for the methanogenesis (Riera et al., 1999; Huttunen et al., 2002a; Kankaala et al., 2007).

Surface water CH_4 concentration is dependent on the sedimentary CH_4 production, but connections between the sediment – water column – fluxes and the water surface – atmosphere – fluxes can be poor (e.g. Huttunen et al., 2006). Firstly, oxidation of CH_4 in the water column typically reduces the CH_4 emissions from the surface (e.g. Rudd and Hamilton, 1978; Kankaala et al., 2006, 2007). Secondly, surface water CH_4 concentration can be largely determined by the CH_4 production and release in shallow littoral areas of the lake, and to a lesser extent in the deepest hypolimnetic sediments below the surface sample (Bastviken et al., 2004; Murase et al., 2005; Bastviken et al.,

2008).

In our data, the surface water CH_4 concentrations were primarily related to the depth (Table 4, Fig. 3). Consequently, the three shallow lake types had the highest surface water CH_4 concentrations both during the late winter and the late summer (Fig. 2). In these shallow lakes the epilimnion and productive littoral sediments have a large proportional contribution to the total sediment area and gas exchange in the water column. Littoral areas tend to have greater CH_4 production rates, but the sedimentary gases are also easily mixed to the water column in shallow turbulent conditions (den Heyer and Kalf, 1998; Bastviken et al., 2004; Murase et al., 2005; Bastviken et al., 2008). In other studies of boreal and temperate lakes, small area has been found to indicate high potential spring emissions of CH_4 and surface water CH_4concentration, respectively (Michmerhuizen et al., 1996; Bastviken et al., 2004). Bastviken et al. (2004) improved the model by predicting surface water CH_4 concentrations using the fraction of anoxic water volume and DOC as explanatory variables. A negative correlation between DOC and surface water CH_4 was explained by the stratification of stained waters that hinder mixing of CH_4 from deeper layers to the surface. We found a similar trend in the summer when all lakes were included in analysis (Table 4). A positive correlation in the late winter data between TOC and surface water CH_4 concentrations in lakes of NRC type might indicate that TOC corresponds to the oxygen deficiency in the ice covered water column and/or is a substrate. Anoxia and small variation in the area and depth in this lake type likely caused the fact that oxygen concentration and depth were not statistically correlated with CH_4 concentrations within the type. Other types were pooled according to humus class and thus had wider size gradients (Table 4).

Carbon dioxide concentrations in the lakes of our study also had strong negative correlation with O_2 saturation and positive correlation with nutrient concentrations in water (Kortelainen et al., 2006). Processes and factors leading to accumulation of CO_2 in the water column are related with those affecting CH_4 accumulation, i.e. load of organic matter and oxygen consumption in decomposition. Average CH_4 concentrations in surface waters, 0.2–1.8 μmol L^{-1} (Table 3) in the current study, were compa-

rable to average surface water concentrations of CH_4 in 13 oligotrophic Swedish lakes of 0.1–1.9 μmol L^{-1} and in 11 Wisconsin lakes of 0.3–2.3 μmol L^{-1} (Bastviken et al., 2004). The highest dissolved CH_4 concentrations measured close to the sediment in our study, up to >3000 μmol L^{-1}, were similar with, for example, those reported for the eutrophic Lakes 277 and Wintergreen (Rudd and Hamilton, 1978; Strayer and Tiedje, 1978).

4.2 Lake status and CH_4 concentrations

Lake types are defined for assessing the ecological status of Finnish lakes in relation to each type's natural conditions (Directive 2000/60/EC; Vuori et al., 2006). Human impact has changed the ecological status of many lakes due to the increased matter fluxes to the lakes, which is indicated by changes in e.g. abundance and primary production of aquatic macrophyte or planctic species, and more frequent periods of oxygen deficiency (Mannio et al., 2000; Dodson et al., 2005; Vuori et al., 2006). All these changes may relate to CH_4 production and oxidation conditions, and might explain some of the variability observed in CH_4 concentrations within the lake types. At the time being we could not relate CH_4 data with ecological status categories, because the work by the environmental authorities is still continuing.

Methane flux from the sediment to the water column is by definition an indicator of serious oxygen depletion within the sediment (Huttunen et al., 2006), but does not necessarily reflect the efflux of CH_4 to the atmosphere. Thus the amount of CH_4 in the sediment close water might serve as a classification measure that integrates oxygen and nutrient status. In our data the CH_4 concentrations in bottom close water during winter were significantly higher in lakes having frequently anoxic bottom water and highest Ptot levels than in lakes having lower Ptot levels or oxygen in the water (Table 5). This is a result of higher CH_4 production rates in nutrient rich conditions supporting autotrophic production of organic matter and lower CH_4 oxidation rates in anoxic sediment and water (e.g. Rudd and Hamilton, 1978; Huttunen et al., 2003).

Anoxia and high nutrient levels are typically correlated due to both oxygen consumption by decomposition and nutrient release from the sediment in anoxic conditions. However, factors affecting the water column mixing and gas exchange, i.e. depth and area (Fee et al., 1996), cause some deviations from the typical trend. Concentration of CH_4 indicates a combination of the two factors.

4.3 Estimated methane fluxes from lakes

The uncertainty in our flux estimates follows from assumptions concerning the use of concentration data and boundary layer models, and those of horizontal and vertical scaling up over the whole lake. The estimate of annual CH_4 release includes two parts, CH_4 diffusion from the surface during the open water season and the release of CH_4 storage during the overturn periods. The boundary layer diffusion method often gives values lower than chamber measurements, a common method to estimate fluxes, yet not in a consistent manner (Phelps et al., 1998; Duchemin et al., 1999; Kankaala et al., 2006; Repo et al., 2007). Another part of our budget is based on the assumption that the difference between the before and after turnover storage terms is released to the atmosphere. However, part of the difference can be caused by CH_4 oxidation. Oxidation of CH_4 has often been larger in the fall than in the spring: in Lakes 227, Williams and Kevätön oxidation consumed only a small proportion of CH_4 in the water body during the spring overturn. In contrast, CH_4 consumption was larger in relatively shallow L. Kevätön, and 60–80% of the pre-overturn CH_4 storage was oxidized in deeper Lake 227 and meromictic Mekkojarvi in autumn (Rudd and Hamilton, 1978; Michmerhuizen et al., 1996; Liikanen et al., 2002; Kankaala et al., 2007). Thus the possible overestimation in the storage component would be larger in autumn, yet autumn contributed generally less than spring to the annual storage flux.

Samples in this study represent conditions prevailing at the deepest point of each lake. Those should quite well represent the diffusive flux of the open water period in large part of pelagic area, if the surface water is commonly horizontally well mixed (cf. Bastviken et al., 2004). Vegetated and very shallow littoral areas, in turn, fall outside

of this estimation. They most likely have much higher CH_4 emissions than predicted on the basis of CH_4 concentration in the pelagial (Smith and Lewis, 1992; Juutinen et al., 2003; Repo et al., 2007; Bastviken et al., 2008). The lake level storage flux may contain more uncertainty. The most extreme sample point CH_4 flux estimates, at both ends, were found in lakes that were quite deep at the sampling point (ca. 11 m). The lakes with the smallest fluxes were deep and larger than the average lake, while the greatest fluxes were found in deep small lakes. Since the sampling point storages only represent those at the deepest point, we calculated another estimate where the storages were estimated for the whole lake assuming horizontal mixing of each water layer, allowing more weight to the concentration of surface waters. The estimate probably represents the whole lake better, assuming a small or negligible horizontal variation in the CH_4 concentration, although sometimes the CH_4 concentrations can be higher in littoral/shallow water areas both close the surface and bottom (Schmidt and Conrad, 1993; Larmola et al., 2004; Murase et al., 2005; Repo et al., 2007).

The estimate of annual CH_4 release ranged from 2.4 to 3606 mmol m^{-2} a^{-1}, and from 1.6 to 727 mmol m^{-2} a^{-1} for the sampling point and averaged for the whole lake, respectively. Median sampling point CH_4 release from the 177 statistically selected lakes was 45 mmol m^{-2} a^{-1}, while median lake weighted estimate was only half of that (Fig. 5). The sampling point estimate is very similar to median CH_4 release estimate, 41 mmol m^{-2} a^{-1} for 8 Swedish lakes (Bastviken et al., 2004) (Fig. 6). CH_4 emission estimates including three components, ebullition, storage, and diffusion for 11 Wisconsin lakes (Bastviken et al., 2004), were comparable to highest release rates in our study, ranging from 42 to 1667 mmol m^{-2} a^{-1} with median of 580 mmol m^{-2} a^{-1}(Fig. 6). The difference between those lakes and our data is not fully explained by the missing ebullition estimate in our data, because diffusion and storage components alone resulted in a higher median estimate of 357 mmol m^{-2} a^{-1} for the Wisconsin lakes. The difference might be related different size ranges. Wisconsin lakes had similar total phosphorous values as the Swedish lakes, but their areas were very small (Fig. 6), smaller than smallest lake areas in our data.

Both the regression analyses and lake type comparisons indicate increasing CH_4 emissions with decreasing depth, increasing total phosphorous concentration and decreasing lake area (Table 7, Fig. 5). The relationships between lake area and CH_4 emission were quite similar to those reported by Bastviken et al. (2004) in the same lake area range (Fig. 6). This suggests that lake size is a master variable that integrates those factors that actually determine the CH_4 fluxes. Lake area could thus be a useful scaling up tool (Fig. 6). Emissions estimates in this study represent the pelagic environment only, and use of these values for spatial extrapolation would likely result in an underestimate. Ebullitive flux of CH_4 and CH_4 evasion from the vegetated littoral zone are worth of recognition in small and shallow lakes, since both may contribute significantly to a lake scale CH_4 release. Sites of littoral vegetation and ebullition can contribute more than 50% of lake wide CH_4 release during the open water season in northern latitudes (Smith and Lewis, 1992; Huttunen et al., 2003; Juutinen et al., 2003; Bastviken et al., 2004; Walter et al., 2004). Ebullition may dominate CH_4 flux in many of the nutrient rich and shallow lakes in our study, and thus concentration data alone might give a biased indication of CH_4 emissions, causing some variation in observed data.

5 Conclusions

The current study focused on small northern lakes, where lake size tended to be a stronger predictor of methane concentrations than water chemistry itself. Lake size, i.e. depth or area, seems to integrate the combination of factors driving CH_4 concentration dynamics. Inversely, CH_4 concentration in bottom close water could serve as a measure of excess nutrients and occurrence of anoxia when doing environmental monitoring of lakes. In the absence of more accurate data, lake area from remote surveys could be used as an approximation for the CH_4 emissions in boreal and arctic landscapes with similar glacial history. Small lakes seem to have a disproportionate significance with respect to CH_4 release, even if large lakes dominate

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regional emission estimates in absolute numbers.

Acknowledgements. We thank R. Niinioja from Finnish Environment Centre (Joensuu) for the discussions and help with Finnish lake typology procedure. Study was funded by Finnish Academy.

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Table 1. Lake type definitions.

Lake Type	Abreviation	Definition	
Nutrient rich and calcareous	NRC	Alkalinity >0.4	winter turbidity >5 FTU
Clear, large	CL	Color <30 Pt mg L^{-1}	area > 40 km^2
Clear, small and middle size	CSm and M	Color <30 Pt mg L^{-1}	area <40 km^2
Clear, shallow	SSh	Color <30 Pt mg L^{-1}	mean depth <3 m
Humic, large	HL	Color 30–90 Pt mg L^{-1}	area >40 km^2
Humic, middle size	HM	Color 30–90 Pt mg L^{-1}	area 5–40 km^2
Humic, small	HSm	Color <30 Pt mg L^{-1}	area <5 km^2
Humic, shallow	HSh	Color 30–90 Pt mg L^{-1}	mean depth <3 m
Very humic	VH	Color >90 Pt mg L^{-1}	mean depth≥3 m
Very humic, shallow	VHSh	>Color 90 Pt mg L^{-1}	mean depth <3 m

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Table 2. Medians for alkalinity, turbidity, Ptot, Ntot, color and TOC of the surface water at fall, lake area (A), maximum depth (D) and proportional cover of agricultural land (Agr.), forests (For.), peat and water (Wat) in the catchments in the whole data and the different lake types. Mean annual temperature was measured in the nearest weather station (Finnish Meteorological Institute 1999 and 2000). Three lakes were not able to typify due to missing water chemistry data, and land cover distribution was analyzed only for 187 lakes. Type definitions from the Table 1.

Lakes	N	Alk. ($mmol\,l^{-}$)	Turb. (FTU)	Ptot ($\mu g\,l^{-1}$)	Ntot ($\mu g\,l^{-1}$)	Color ($Pt\,mg\,l^{-1}$)	TOC ($mg\,l^{-1}$)	A (km^2)	D (m)	T (°C)	pH	Agr. (%)	For. (%)	Peat (%)	Wat. (%)
Stat.	177	0.1	1.3	14	460	70	9	0.24	6.2	3.2	6.5	2.6	67	12	9
Eutr.	30	0.2	6.5	60	970	140	11	0.94	4.0	3.6	6.6	11.6	61	17	5
All	207	0.1	1.5	16	505	80	9	0.28	6.0	3.3	6.6	3.6	67	12	8
Types															
NRC	27	0.4	5.3	57	840	75	9	0.52	5.1	4.1	6.8	20.4	60	2	7
CL	1	0.2	1.1	15	280	15	5	44.26	26.5	3.1	7.2	4.2	72	6	17
CSm and M	17	0.1	0.6	6	270	15	4	1.35	13.4	3.2	6.7	2.3	68	6	19
CSh	21	0.1	0.7	6	300	20	5	0.14	6.2	1.5	6.8	0.0	69	5	13
HL	2	0.2	1.3	16	300	60	9	52.75	17.8	0.1	7.1	0.9	60	29	10
HM	4	0.2	0.9	11	510	35	8	20.17	15.6	3.6	7.0	3.8	58	18	17
HSm	19	0.1	1.0	11	360	50	8	1.03	14.0	2.2	6.5	3.0	71	9	11
HSh	45	0.1	1.3	14	485	65	9	0.19	4.0	2.8	6.5	4.2	70	11	10
VH	11	0.1	1.6	31	635	170	16	1.40	12.5	3.3	6.3	10.0	64	19	5
VHSh	57	0.1	2.0	24	635	160	17	0.10	3.8	3.4	6.3	1.5	63	22	5

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Table 3. Statistical distributions of CH_4 concentrations in 1 m below surface and 0.2 m above the sediment.

Depth	Sampling	Mean (μmol L^{-1})	Md (μmol L^{-1})	SD (μmol L^{-1})	min (μmol L^{-1})	max (μmol L^{-1})	N
Bottom	Winter	52.64	7.94	219.56	0.01	3013.76	202
Bottom	Spring	3.13	0.10	20.99	0	227.39	203
Bottom	Summer	20.60	0.27	104.16	0	1331.15	191
Bottom	Autumn	4.02	0.10	29.40	0	393.33	202
Surface	Winter	1.84	0.07	6.63	0	60.19	189
Surface	Spring	0.16	0.10	0.22	0.01	2.50	192
Surface	Summer	0.25	0.17	0.27	0.01	1.69	188
Surface	Autumn	0.22	0.08	0.59	0	5.12	187

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Table 4. Linear regression models for the CH_4 concentrations. Models for the whole lake group and for combined lake types were performed. Combined lake types were formed according the humic class (clear, humic or very hymic). Number following the data source information refers to the step of stepwise linear regression. All models are significant at level $p>0.01$, and all parameters are significant at level $p>0.05$. Dependent $\log_e$ transformed variable was dissolved CH_4 concentration (μmol L^{-1}), and independent $\log_e$ transformed variables were dissolved O_2 (mg L^{-1}), Ptot (μg L^{-1}), depth of sampling site (m), lake area (km^2), and TOC (mg L^{-1}). Three extreme cases ([CH_4] >1000 μmol L^{-1}) were excluded.

				Parameters					
Set	$r^2_{adj.}$	Df_{res}	Variables	O_2	Ptot	Depth	Area	TOC	a
Winter, surface									
All 1	0.23	192	Depth			−0.553			1.513
All 2	0.32	191	Depth+O_2	−0.490		−0.415			2.285
All 3	0.36	190	Depth+O_2+Ptot	−0.390	0.243	−0.372			1.316
NRC	0.45	25	TOC					1.230	−2.294
Clear	0.50	35	O_2	−1.100					2.889
Humic 1	0.27	65	Depth			−0.564			1.454
Humic 2	0.40	64	Depth+Ptot		0.438	−0.457			0.138
Humic 3	0.47	63	Depth+Ptot+O_2	−0.435	0.383	−0.350			1.019
Very Humic 1	0.19	61	Depth			−0.610			1.627
Winter, bottom									
All 1	0.53	182	O_2	−1.817					3.776
All 2	0.59	181	O_2+Ptot	−1.500	0.464				1.923
All 3	0.61	180	O_2+Ptot+Area	−1.458	0.490				2.000
NRC 1	0.23	21	O_2	−1.247					3.897
NRC 2	0.47	20	O_2+Area	−1.411			−0.773		4.591
Clear 1	0.59	36	O_2	−2.004					3.793
Clear 2	0.63	35	O2+Ptot	−1.554	0.570				1.856
Humic 1	0.62	63	O_2	−2.017					3.912
Humic 2	0.66	62	O_2+Ptot	−1.719	0.560				1.900
Humic 3	0.71	61	O_2+Ptot+Depth	−1.563	0.666	−0.608			2.570
Very Humic 1	0.49	56	O_2	−1.577					3.582
Very Humic 2	0.52	55	O_2+Ptot	−1.367	0.422				1.775
Sumer, surface									
All 1	0.12	184	Depth			−0.074			0.338
All 2	0.16	183	Depth+Area			−0.054	−0.044		0.332
All 3	0.18	182	Depth+Area+O_2	−0.268		−0.051	−0.041		0.930
All 4	0.21	181	Depth+Area+O_2+TOC	−0.512		−0.075	−0.030	−0.093	1.733
NRC	ns								
Clear 1	0.28	36	Area	−0.065					0.211
Clear 2	0.37	35	Area+TOC	−0.051				−0.119	0.394
Humic 1	0.33	58	Depth			−0.164			0.542
Humic 2	0.59	57	Depth+O2	−1.528		−0.151			3.980
Very Humic 1	ns								
Summer, Bottom									
All 1	0.43	174	O_2	−1.092					2.695
All 2	0.47	173	O_2+Depth	−1.224		−0.406			3.634
All 3	0.48	172	O_2+Depth+Ptot	−1.120	0.187	−0.361			2.768
NRC	0.2	19	O_2	−0.983					2.875
Clear	0.45	31	O_2	−0.581					1.399
Humic 1	0.47	60	O_2	−1.174					2.831
Humic 2	0.56	59	O_2+Ptot	−0.954	0.565				0.714
Humic 3	0.59	58	O_2+Ptot+Depth	−1.163	0.500				1.912
Very Humic	0.44	57	O_2	−1.146					2.848

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Table 5. Bottom water CH_4 concentrations mean total phosphorus concentration in water column in the lakes classified according to occurrence of anoxia over a year in bottom water and. Results of different comparisons, i.e. good vs. poor status lakes, and three anoxia–Ptot level combinations in winter and summer, are separated by a row. Statistically significant differences in within a comparison are indicated with different letters.

		CH_4 (μmol L^{-1})			
	Set	Mean	Md	SD	N
Winter	Good status	6.263[a]	0.101	15.483	67
Winter	Poor status	185.045[b]	151.106	117.62	14
Winter	No anoxia	8.828[a]	0.325	17.703	95
Winter	Anoxia, Ptot<30	43.203[b]	29.079	56.621	57
Winter	Anoxia, Ptot>30	89.242[c]	57.05	100.249	47
Summer	Good status	2.037[a]	0.132	8.347	66
Summer	Poor status	58.558[b]	6.36	80.369	11
Summer	No anoxia	3.428[a]	0.159	13.009	93
Summer	Anoxia, Ptot<30	17.649[b]	1.25	42.409	55
Summer	Anoxia, Ptot>30	31.283[b]	0.779	69.6	42

Water was considered anoxic when O_2 saturation was below 5%.
Good status: Ptot below 30 μg L^{-1}, and bottom water never anoxic.
Poor status: Ptot over 50 μg L^{-1}, and bottom water was anoxic at two or more sampling times.
Cases with CH_4 concentration over 1000 μg L^{-1} were excluded.

Table 6. Proportional catchment land covers and total phosphorus concentration in water column in lakes classified according to occurrence of anoxia over a year in bottom water. Statistically significant differences in within a comparison are indicated with letters.

Set	Forest (%)	Peatland (%)	Water (%)	Agric. (%)	Settl. (%)
Good status	67.5^{a}	11.8^{a}	11.3^{a}	2.2^{a}	0.2^{a}
Poor status	70.5^{a}	2.4^{b}	4.4^{b}	9.9^{b}	0.5^{b}
No anoxia	65.2^{a}	15.8^{a}	9.8^{ab}	3.9^{a}	0.2^{a}
Anoxia, Ptot<30	70.3^{a}	10.1^{a}	8.9^{a}	1.2^{a}	0.1^{a}
Anoxia, Ptot>30	63.5^{a}	11.5^{a}	5.3^{b}	7.5^{b}	0.3^{b}

Water was considered anoxic when O_2 saturation was below 5%.
Good status: Ptot below 30 $\mu g\,L^{-1}$, and bottom water never anoxic.
Poor status: Ptot over 50 $\mu g\,L^{-1}$, and bottom water was anoxic at two or more sampling times.
Cases with CH_4 concentration over 1000 $\mu g\,L^{-1}$ were excluded.

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Table 7. Equation parameters for the estimated total annual CH_4 efflux ($mol\,m^{-2}\,a^{-1}$). Independent variables in the order they were entered to the stepwise linear regression analysis were maximum depth (m), lake area (km^2), and Ptot ($\mu g\,L^{-1}$). Model steps with cumulative regression coefficient ($R^2_{adj.}$) are indicated.

Model step	a	max depth	Ptot	Area	$R^2_{adj.}$	F	df
1	4.335	−0.617			0.24	64.30	197
2	4.006	−0.499	−0.151		0.30	42.40	196
3	2.663	−0.366	−0.195	0.366	0.36	38.30	195

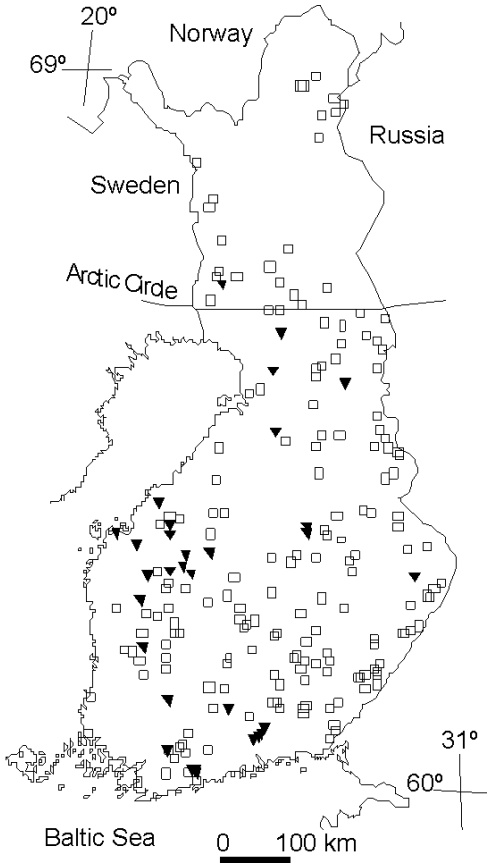

Fig. 1. Geographical distribution of the statistic sample of 177 lakes from Finnish Lake Survey data base (open symbols), and the additional sample of 30 lakes with the highest total phosphorous concentration (filled triangles).

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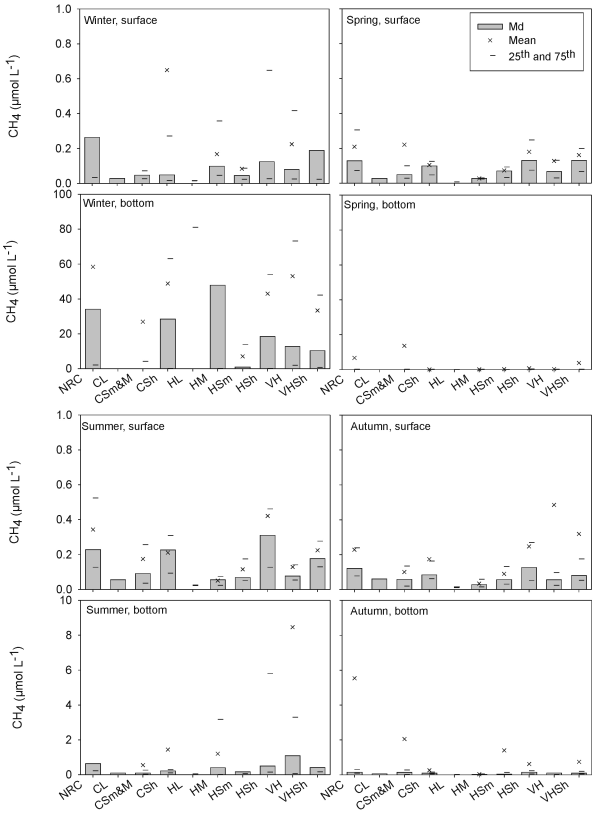

Fig. 2. CH_4 concentrations of surface and bottom close water in the different lake types (see Table 1). Right and left panels show the difference in the CH_4 concentrations before and after turn-over periods, respectively. Mean (x), median (bar), and 25th and 75th percentile (–) are indicated. Note the different scales and that some mean and upper quartiles are outside of the scales.

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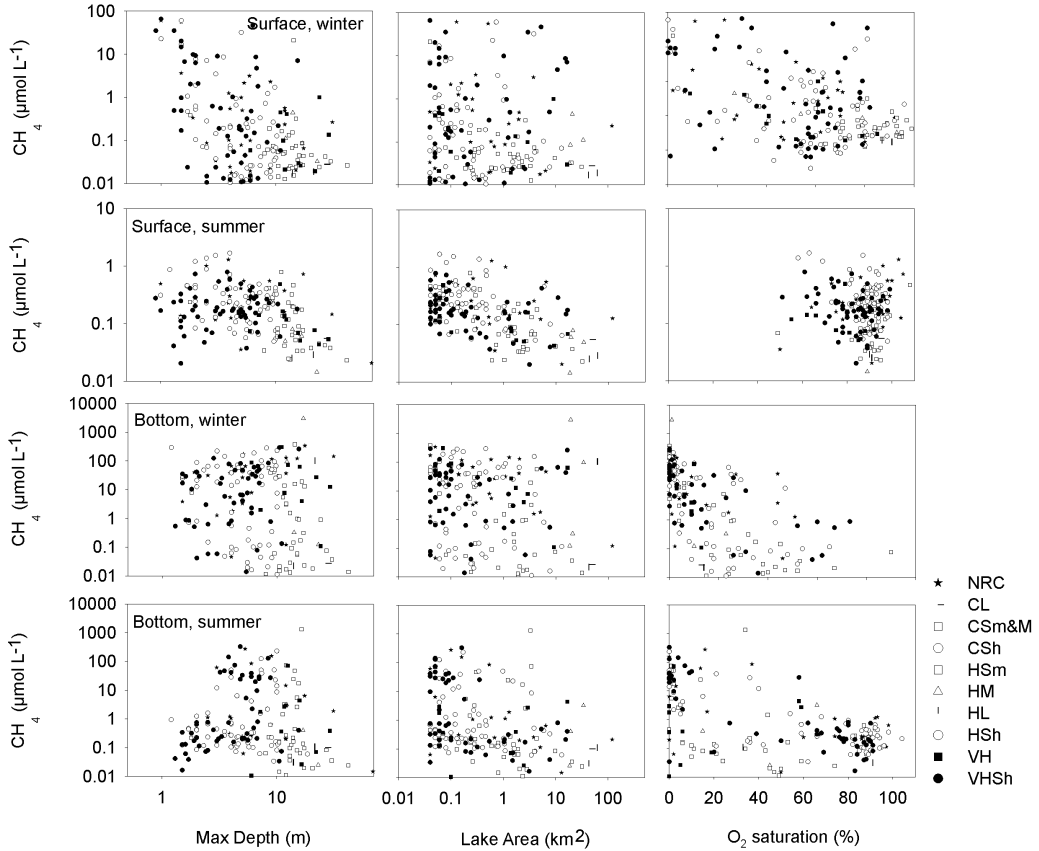

Fig. 3. Surface and bottom water CH_4 concentrations before the over-turn periods during late winter and late summer in relation to maximum depth (left), lake area (middle), and oxygen saturation (right).

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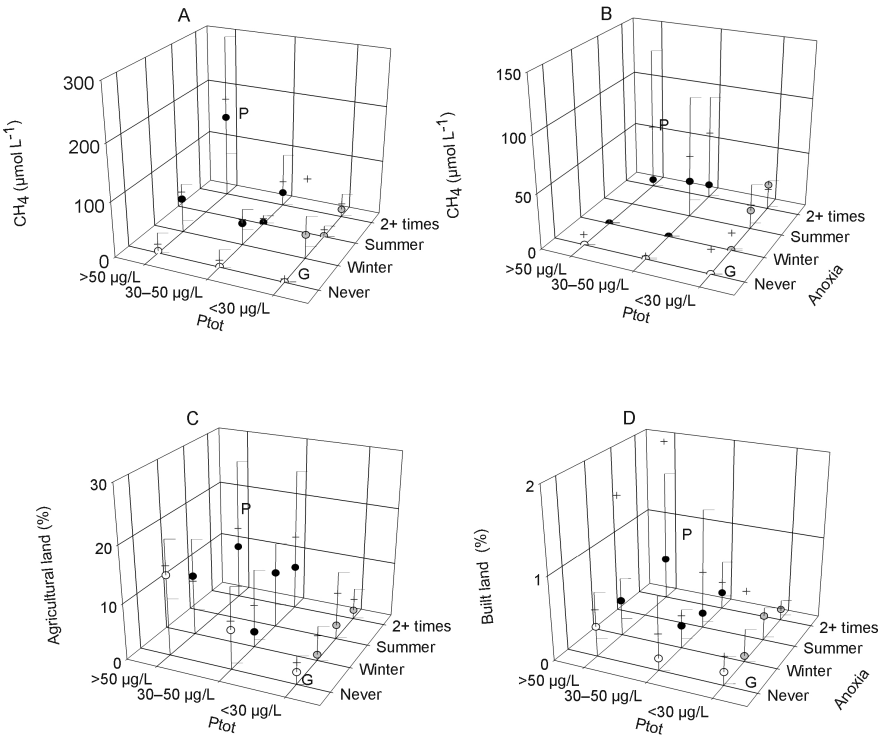

Fig. 4. CH_4 concentrations of the bottom close water in the winter **(A)** and the summer **(B)**, and proportional catchment cover of agricultural land **(C)** and settlements **(D)** in the lakes categorized by frequency of anoxia and total phosphorus (Ptot). All data is included in the graphs, but comparison of means were calculated excluding CH_4 values >1000 $\mu g\,L^{-1}$. Lake groups "poor" and "good or excellent" are indicated by letters G and P. Never anoxic, and at least sometimes anoxic low Ptot lakes are indicated by open and grey symbols, respectively.

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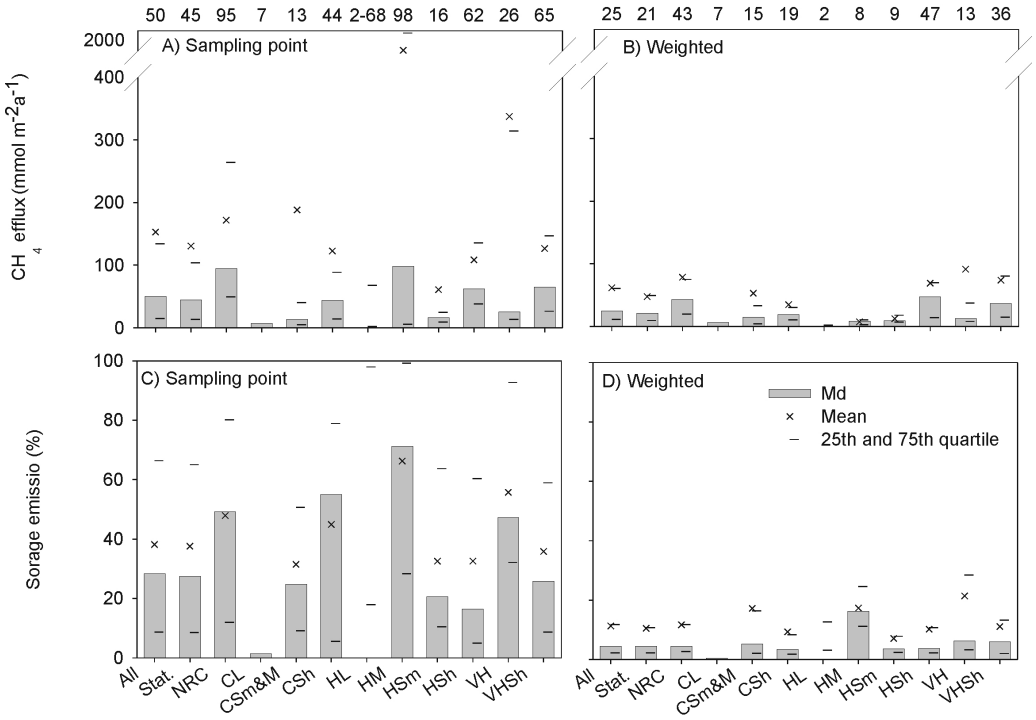

Fig. 5. Methane flux estimates (mmol m^{-2} a^{-1}) for the sampling point **(A)** and for a unit area of the whole pelagic **(B)**, and corresponding proportional storage fluxes from the lakes (**C** and **D**). Type medians of CH_4 fluxes are shown in the top. All: 207 lakes, Stat: statistic lake sample (n=177), NRC: nutrient rich and calcareous, CL: clear large, CSm and M: clear small and middle size, CSh: clear shallow, HL: humic large, HM: humic middle size, HSm: humic small, HSh: humic shallow, VH: very humic, and VHSh: very humic shallow.

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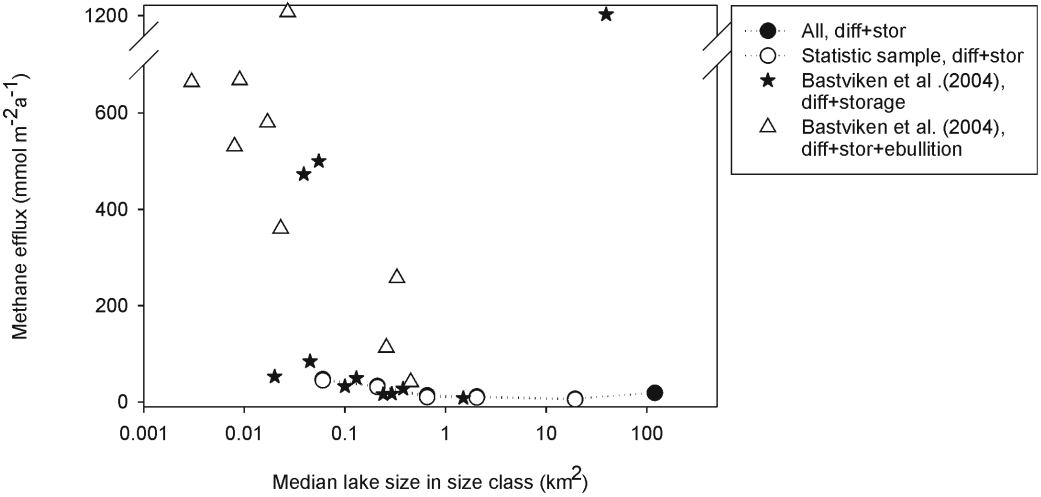

Fig. 6. Median annual CH_4 emissions from the size classified lakes relative to the lake size (circles). Estimates of CH_4 release from some Swedish and Wisconsin lakes (Bastviken et al., 2004) are plotted for a comparison. Lakes where only diffusion and storage fluxes were included to the estimate (stars) and lakes where also ebullition was included to the estimate (triangles).

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