

## Methane fluxes at the sediment–water interface in some boreal lakes and reservoirs

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Methane (CH<sub>4</sub>) fluxes at the sediment–water interface were studied during summer in six lakes and two reservoirs in Finland. The oxygen penetration in the sediments of these boreal mesotrophic–hypereutrophic freshwater ecosystems varied from 0 to 8 mm, and the CH<sub>4</sub> concentrations within the uppermost 10 cm from 17 to 51 000 ppm(v). The diffusive methane fluxes to the overlying water column ranged from 0.44 to 105 mg m<sup>-2</sup> d<sup>-1</sup> and correlated negatively ( $R^2 = 0.68$ ) with the oxygen penetration in the sediment. This demonstrated that the CH<sub>4</sub> concentration and the diffusive CH<sub>4</sub> fluxes in the lake sediments are closely related to the O<sub>2</sub> conditions, which regulate both CH<sub>4</sub> production and CH<sub>4</sub> oxidation in the sediment. The comparison between the diffusive CH<sub>4</sub> fluxes at the sediment–water interface and CH<sub>4</sub> fluxes at the water–air interface previously measured *in situ* in one lake and two reservoirs showed that the sediment CH<sub>4</sub> fluxes poorly predict the CH<sub>4</sub> release from the water surface to the atmosphere. This indicates that the CH<sub>4</sub> oxidation in water column, advective transport of CH<sub>4</sub> and CH<sub>4</sub> ebullition have importance in the net CH<sub>4</sub> release to the atmosphere. The increased CH<sub>4</sub> concentration in water column close to the sediment is an indicator of serious oxygen depletion within sediment.

### Introduction

Methane (CH<sub>4</sub>) is an endproduct of anaerobic organic carbon decomposition in oxygen-depleted sediments (Kiene 1991). It is a greenhouse gas in the atmosphere (Khalil and Rasmussen 1983), and this knowledge has been the impetus to examine CH<sub>4</sub> emissions from various natural and disturbed ecosystems, including freshwater lakes (Michmerhuizen *et al.* 1996, Striegl and Michmerhuizen 1998, Casper *et al.* 2000, Huttunen *et al.* 2001a, 2001b, 2003, 2004, Joyce and Jewell

2003) and reservoirs (Duchemin *et al.* 1995, 2000, St. Louis *et al.* 2000, Huttunen *et al.* 2002, 2003, Joyce and Jewell 2003, Soumis *et al.* 2004).

Methane is produced in sediments by anaerobic methanogenic archaea. Their activity depends on many environmental factors, such as supply of organic matter, availability of electron acceptors and temperature (Kiene 1991). For example, Kelly and Chynoweth (1981) found that CH<sub>4</sub> production in the sediment increased with the increase in the input of organic matter to the

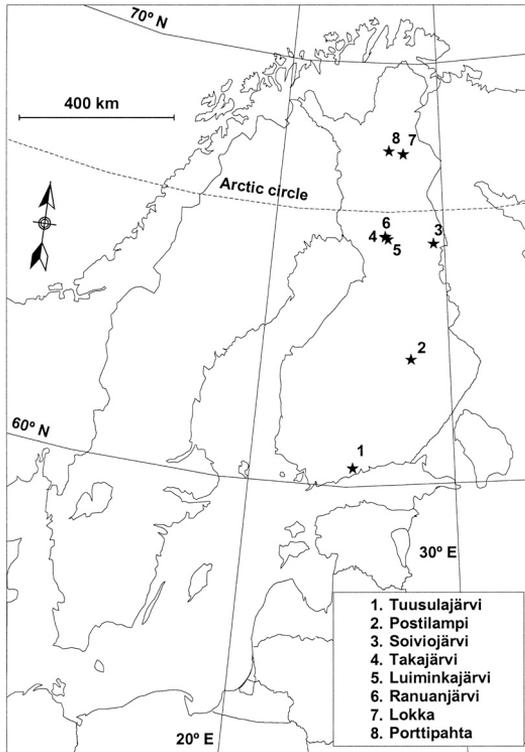


Fig. 1. Studied boreal lakes and reservoirs in Finland.

sediment, which agrees with the observation that the  $\text{CH}_4$  production capacity of sediment increases with increasing lake trophicity (Casper 1992). Although over 90% of the  $\text{CH}_4$  produced can be oxidized in the uppermost aerobic sediment layers and water column (Kiene 1991), high  $\text{CH}_4$  emissions have been detected from lakes and reservoirs which contain large amounts

of degradable organic matter in their sediments (Duchemin *et al.* 1995, Michmerhuizen *et al.* 1996, Striegl and Michmerhuizen 1998, Casper *et al.* 2000, Huttunen *et al.* 2001a, 2001b, 2002, 2003). The large number of lakes in northern regions have to be considered in the global  $\text{CH}_4$  budget. For example in Finland (Raatikainen and Kuusisto 1990) and Canada (Environment Canada 1998), the lakes occupy about 10% and 7.6% of the country's surface area, respectively.

We studied the distributions of  $\text{CH}_4$  and  $\text{O}_2$  in intact sediment cores taken from the sediments of some boreal lakes and reservoirs in Finland, and calculated the  $\text{CH}_4$  fluxes at the sediment–water interface by a diffusion model. Some of these fluxes were compared with those previously measured at the water–air interface *in situ*. The trophic state of these aquatic ecosystems varied, allowing us to study the effect of eutrophication-associated  $\text{O}_2$  depletion on the  $\text{CH}_4$  release from sediments.

## Material and methods

### Study sites

The study sites, six small freshwater lakes and two large hydroelectric reservoirs (Table 1), are located from the southern to the northern boreal zone in Finland (Fig. 1). The reservoirs were the largest in western Europe. The sites were shallow with mean depths ranging from 1.1 to 6.3 m (Table 1). The trophic states of the sites ranged

Table 1. Trophic state and morphometric properties of the studied lakes and reservoirs.

Lake/Reservoir <sup>a</sup>	Trophic state <sup>b</sup>	Volume (km <sup>3</sup> )	Area (km <sup>2</sup> )	Mean depth (m)	Max. depth (m)
Tuusulanjärvi	hypereutrophic	0.0192	5.95	3.2	10.0
Postilampi	hypereutrophic	0.00009	0.03	3.2	4.3
Soiviojärvi	eutrophic	0.0242	7.86	3.2	10.0
Takajärvi	eutrophic	0.0012	1.10	1.1	1.5
Luiminkajärvi	meso-eutrophic	0.0113	3.50	3.2	7.9
Ranuanjärvi	eutrophic	0.0196	4.80	4.1	8.5
Lokka	eutrophic	0.5–2.063	216–417	2.3–4.9	10.0
Porttipahta	mesotrophic	0.15–1.353	34–214	4.4–6.3	34.5

<sup>a</sup> Data for Tuusulanjärvi are from Pekkarinen (1990), Postilampi from Saarijärvi and Lappalainen (2001) and J.T. Huttunen (unpubl. data), Soiviojärvi from this study, Takajärvi, Luiminkajärvi and Ranuanjärvi from Puro *et al.* (1999), and reservoirs Lokka and Porttipahta from Hellsten *et al.* (1993) and Lepistö (1999).

<sup>b</sup> Classification is based on the average summer chlorophyll-*a* concentration in the epilimnion according to Forsberg and Ryding (1980).

from mesotrophic to hypereutrophic (Table 1), based on their average summer chlorophyll-*a* concentrations in the epilimnion (mesotrophic 3–7  $\mu\text{g l}^{-1}$ , eutrophic 7–40  $\mu\text{g l}^{-1}$ , and hypereutrophic > 40  $\mu\text{g l}^{-1}$ ; Forsberg and Ryding 1980). The sampling stations in reservoir Lokka and Takajärvi were situated at the sediment erosion/transportation zone, whereas the other sampling stations were situated at the sediment accumulation zone which generally represents the deepest profundal region of the lake (Table 2).

### Sediment sampling and the analyses of $\text{O}_2$ and $\text{CH}_4$ concentrations

Sediment samples were taken from the study lakes once in July or August from 1994 to 1997 (Table 2). The procedures of sampling and analyses of the  $\text{O}_2$  and  $\text{CH}_4$  concentrations are presented in Hellsten and Väisänen (1998). Briefly, 23–30-cm long sediment cores were taken with a Limnos gravity sediment corer (Limnos Ltd., Turku), containing a 50-cm acrylic core with an internal diameter of 10 cm. We did not measure the  $\text{O}_2$  and  $\text{CH}_4$  concentrations from the water above the sediment, because the overlying water can be mixed during sampling in this kind of an open-top corer. Penetration of  $\text{O}_2$  into the sediment was determined immediately after the sam-

plings at 1 mm intervals with Diamond General Microsensor II equipment and an  $\text{O}_2$  mini-electrode (Diamond General Development Corp., Ann Arbor, MI). The sediment cores were then sub-sampled at 1-cm depth intervals into 2-ml tubes. The tubes were immediately emptied into 60-ml polypropylene extraction syringes (pistons removed) (BD Plastipak, Becton Dickinson, Dublin) equipped with three-way stopcocks (Connecta, Ohmeda GmbH + Co, Erlangen). The pistons were reassembled to the extraction syringes filled with the sediment and ambient air. Half of the headspace gas in each extraction syringe was then injected into a separate sample syringe. From 5 to 15 ml of saturated NaCl solution (including 0.18 mol  $\text{l}^{-1}$  of  $\text{H}_2\text{SO}_4$ ) was then added into the extraction syringes for degassing all  $\text{CH}_4$  out from the sediment pore water and for preservation. The extraction syringe was shaken vigorously and the gas was injected into the sample syringe. The sample syringes were sent to the Laboratory of Environmental Microbiology, National Public Health Institute (Kuopio, Finland) where the  $\text{CH}_4$  analyses were carried out. The  $\text{CH}_4$  concentrations were determined within 24 h of sampling with a Hewlett-Packard 5890 Series II gas chromatograph (Palo Alto, CA) equipped with a flame ionization detector (FID) (for details see Huttunen *et al.* 2001a, 2002).

**Table 2.** Sampling time and characteristics of the sampling sites and sediments of the studied lakes and reservoirs.

Lake/Reservoir	Sampling time	Sampling depth (m)	Bottom type <sup>a</sup>	Sediment type <sup>b</sup>	Water content <sup>b</sup> (%)	Organic matter <sup>b</sup> (% D.W.) <sup>c</sup>	Porosity <sup>d</sup>
Tuusulanjärvi	August 1995	7.8	A	clay gyttja	89.0	11.7	0.90
Postilampi	August 1996	4.2	A	gyttja	88.3	42.7	0.97
Soiviojärvi	August 1994	9.8	A	silty gyttja	> 85 <sup>e</sup>	32.0	0.95
Takajärvi	July 1997	1.1	E	sandy gyttja	94.3	38.7	0.90
Luiminkajärvi	July 1997	6.2	A	silty gyttja	96.9	27.2	0.95
Ranuanjärvi	July 1997	7.1	A	gyttja	96.1	31.2	0.95
Lokka	August 1995	8.8	E/T	peaty gyttja	97.8	67.8	0.95
Porttipahta	August 1995	32.5	A	gyttja	95.1	45.5	0.92

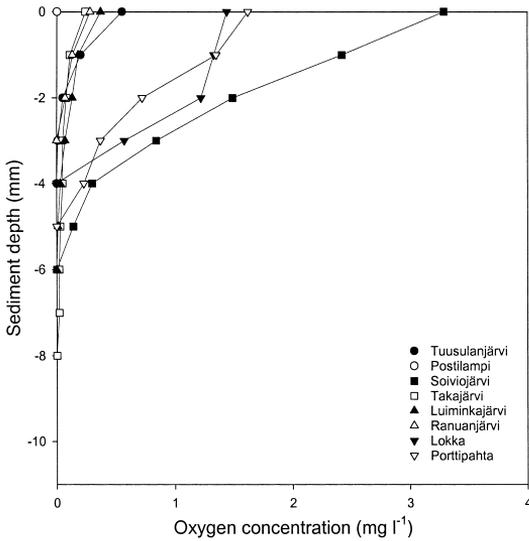
<sup>a</sup> According to Håkanson and Jansson (1983), A = accumulation, T = transportation, E = erosion.

<sup>b</sup> Data for Tuusulanjärvi are from Pekkarinen (1990), Postilampi from Saarijärvi and Lappalainen (2001) and this study, Soiviojärvi from this study, Takajärvi, Luiminkajärvi and Ranuanjärvi from Puro *et al.* (1999), and Lokka and Porttipahta from Hellsten *et al.* (1993).

<sup>c</sup> D.W. is dry weight.

<sup>d</sup> Estimated from the data presented by Sweerts (1990).

<sup>e</sup> Based on the penetrometer measurement, described in Håkanson and Jansson (1983).



**Fig. 2.** Oxygen concentrations in the surficial sediment in the studied lakes and reservoirs.

### Calculation of CH<sub>4</sub> fluxes at the sediment–water interface

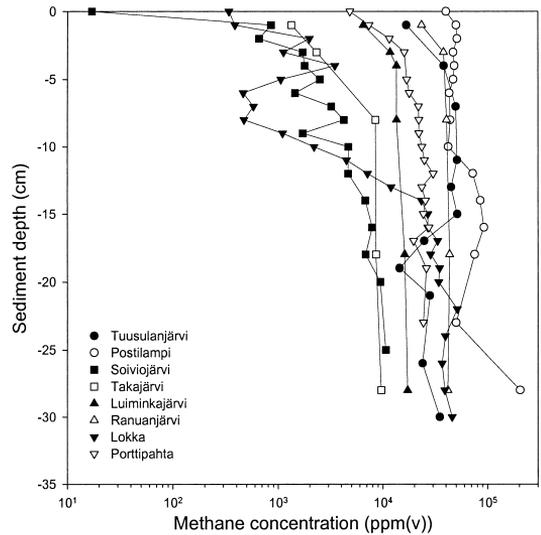
The diffusive CH<sub>4</sub> fluxes from the sediments were calculated using Fick's first law of diffusion according to Berner (1980) (Eq. 1):

$$J_s = -\phi(D_0\theta^{-2})\left(\frac{dc}{dz}\right) \quad (1)$$

where  $J_s$  is the diffusive CH<sub>4</sub> flux at the sediment–water interface (Sweerts 1990),  $\phi$  the porosity of the sediment (values 0.90–0.97 were estimated for from data presented by Sweerts (1990), based on the sediment type and the amount of organic matter in the sediments in our study; Table 2),  $D_0$  the diffusion coefficient for CH<sub>4</sub> in water ( $1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ; Broecker and Peng 1974),  $\theta$  the tor-

**Table 3.** Methane fluxes at the sediment–water interface in the studied lakes and reservoirs.

Lake/Reservoir	Methane flux (mg m <sup>-2</sup> d <sup>-1</sup> )
Tuusulanjärvi	72
Postilampi	105
Soiviojärvi	8.6
Takajärvi	4.8
Luiminkajärvi	27
Ranuanjärvi	76
Lokka	0.44
Porttipahta	25



**Fig. 3.** Methane concentrations (ppm(v)) in the sediments of the studied lakes and reservoirs.

tuosity (value 1.2 was approximated for the tortuosity squared from Sweerts (1990)), and  $dc/dz$  the measured vertical 2–3 cm CH<sub>4</sub> concentration gradient within the first 4 cm of the surface sediment. Positive fluxes indicate here a loss of CH<sub>4</sub> out from the sediment.

## Results

The O<sub>2</sub> concentrations decreased with increasing depth in the sediments, except in lake Postilampi where even the uppermost sediment was anoxic (Fig. 2). Soiviojärvi had the highest O<sub>2</sub> concentrations in its sediment. Reservoirs Lokka and Porttipahta had rather similar O<sub>2</sub> profiles, and the O<sub>2</sub> concentrations in their sediments were greater than those in Takajärvi, Ranuanjärvi, Luiminkajärvi and Tuusulanjärvi, which all had similar O<sub>2</sub> profiles in their sediments. The oxygen penetration into the sediment varied from 0 mm in lake Postilampi to 8 mm in Takajärvi (Fig. 2).

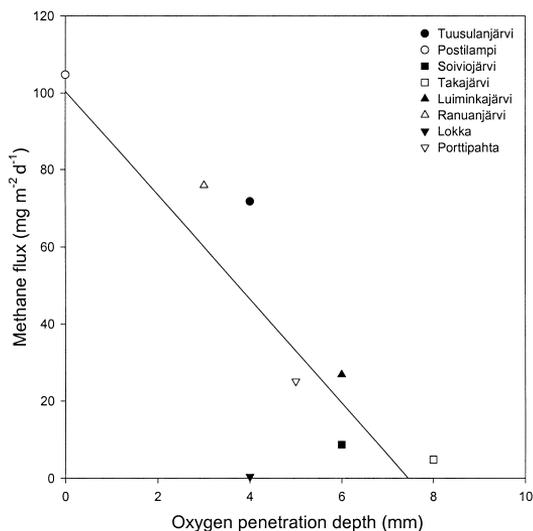
The CH<sub>4</sub> concentrations generally increased with increasing sediment depth, with the highest vertical gradient found in reservoir Lokka (Fig. 3). Among all the sediments, the CH<sub>4</sub> concentrations ranged from 17 to 51 000 ppm(v) (parts per million by volume, i.e.  $\mu\text{l l}^{-1}$ ) within the uppermost 10 cm, the maximum being as high as 200 000 ppm(v) at the depth of 28 cm. The sedi-

ment  $\text{CH}_4$  concentrations were highest in lake Postilampi and lowest in Soiviojärvi (Fig. 3), the situation opposite to the sediment  $\text{O}_2$  concentrations (Fig. 2).

The diffusive  $\text{CH}_4$  fluxes at the sediment–water interface were higher in Postilampi, Ranuanjärvi and Tuusulanjärvi than in Luiminkajärvi, Soiviojärvi and Takajärvi (Table 3). Reservoir Lokka had the lowest  $\text{CH}_4$  flux whereas Reservoir Porttipahta had an intermediate flux compared with the  $\text{CH}_4$  fluxes of the lakes. The diffusive  $\text{CH}_4$  flux at the sediment–water interface correlated negatively ( $R^2 = 0.68$ ,  $n = 8$ ,  $p < 0.05$ ) with the oxygen penetration depth in the sediments (Fig. 4).

## Discussion

There was a large variation in the sediment  $\text{CH}_4$  concentration profiles between the study sites. This variation is a result of the complex interactions between factors such as microbial processes, amount and quality of organic matter, availability of electron acceptors, nutrient supply, temperature, pH and physical mixing of the water column/sediment surface (Kiene 1991). Furthermore, up to over 90% of the  $\text{CH}_4$  produced in anoxic sediments can be oxidized by  $\text{CH}_4$ -oxidizing bacteria at the oxic sediment–water interface and in the water column (Kuivila *et al.* 1988, Frenzel *et al.* 1990, Kiene 1991, Liikanen *et al.* 2002). The relatively strong negative correlation between the  $\text{CH}_4$  fluxes and the  $\text{O}_2$  penetration in the surface sediments of the study sites highlighted the crucial role of  $\text{O}_2$  in the regulation of diffusive  $\text{CH}_4$  fluxes from the boreal freshwater sediments. The results demonstrated that the release of  $\text{CH}_4$  from lakes to the atmosphere can be increased by increasing eutrophication, which causes  $\text{O}_2$  depletion of the water column and sediment (*see also* Huttunen *et al.* 2003). Huttunen *et al.* (2001a) showed that wintertime accumulation of  $\text{CH}_4$  in eutrophied boreal lakes could be decreased by artificial oxygenation of the hypolimnion, which supports this conclusion. Natural oligotrophic-mesotrophic lakes in Finland have also shown lower  $\text{CH}_4$  emissions to the atmosphere throughout the year than eutrophied, seasonally oxygen depleted



**Fig. 4.** A linear regression between  $\text{CH}_4$  flux at the sediment–water interface and oxygen penetration depth in the sediment of the studied lakes and reservoirs ( $R^2 = 0.68$ ,  $n = 8$ ,  $p < 0.05$ ).

lakes (Huttunen *et al.* 2003, 2004). However, it should be stressed that our results represent the warm period only and do not include seasonal variation (e.g., Striegl and Michmerhuizen 1998, Huttunen *et al.* 2003).

The data of the present study did not show any major difference in the  $\text{CH}_4$  fluxes between the study lakes and the 25–27 years old reservoirs. The  $\text{CH}_4$  emissions from reservoirs have generally been proposed to exceed those of natural lakes partially due to decomposition of flooded organic matter (St. Louis *et al.* 2000). However, it should be noted that most of the lakes in our study were relatively eutrophic, while the reservoirs were more oligotrophic than most of the lakes and situated at higher latitudes (Fig. 1 and Table 1). The  $\text{CH}_4$  fluxes at the sediment–water interface in the profundal zone of our boreal lakes and reservoirs, 0.44–105  $\text{mg m}^{-2} \text{d}^{-1}$ , correspond to the fluxes measured from the sediments of various temperate lakes; e.g., 3.1–119  $\text{mg m}^{-2} \text{d}^{-1}$  in four basins (average 27  $\text{mg m}^{-2} \text{d}^{-1}$ ) of acidic alpine Lake Orta, Italy (Adams and Baudo 2001), 1.7  $\text{mg m}^{-2} \text{d}^{-1}$  in the profundal zone of eutrophic Müggelsee (Rolletschek 1997) and 37–111  $\text{mg m}^{-2} \text{d}^{-1}$  (average 66  $\text{mg m}^{-2} \text{d}^{-1}$ ) in eutrophic Plußsee (Adams and Naguib 1999), Germany. For comparison, the

CH<sub>4</sub> fluxes from the sediments of tropical Rapel and La Paloma reservoirs in Chile have ranged from 20.9 to 401 mg m<sup>-2</sup> d<sup>-1</sup> during the summer season (Adams *et al.* 2000).

The fluxes of CH<sub>4</sub> have also been measured at the water–air interface at the sampling locations of this study in lake Postilampi and reservoirs Lokka and Porttipahta. The CH<sub>4</sub> flux we observed at the sediment–water interface in lake Postilampi (105 mg m<sup>-2</sup> d<sup>-1</sup>) was higher than the mean water–atmosphere CH<sub>4</sub> emissions of 57–78 mg m<sup>-2</sup> d<sup>-1</sup>, measured from the lake during the open water seasons in 1996–1998 with floating chambers (Huttunen *et al.* 2003). The lower flux to the atmosphere could result from the CH<sub>4</sub> oxidation at the oxycline (e.g., Kiene 1991). In contrast, the diffusive sediment–water CH<sub>4</sub> flux in reservoir Lokka (0.44 mg m<sup>-2</sup> d<sup>-1</sup>) was lower than the mean CH<sub>4</sub> emissions of 8.6 and 12 mg m<sup>-2</sup> d<sup>-1</sup> to the atmosphere during the open water seasons in 1994 and 1995 (Huttunen *et al.* 2002). This suggests that CH<sub>4</sub> in reservoir Lokka was transported from the sediment mainly by ebullition. The CH<sub>4</sub>-rich bubbles released from the sediment can largely bypass oxidation processes in the surface sediment and water column (Kiene 1991, Chanton and Whiting 1995). The CH<sub>4</sub> concentrations in the surface sediment were lower in reservoir Lokka than generally in the lakes of this study, but in the deeper sediments of Lokka, the CH<sub>4</sub> concentrations were obviously high enough to support bubble formation (Fig. 3). A physical disturbance of the bottom sediment may trigger episodic ebullition in this kind of a shallow and open reservoir (Duchemin *et al.* 2000, Joyce and Jewell 2003). In Lokka, the ebullitive fluxes of CH<sub>4</sub> measured with submerged bubble traps have mostly exceeded the CH<sub>4</sub> fluxes at the water–air interface measured with floating chambers (Huttunen *et al.* 2002). In our sediment sampling and sub-sampling some bubbles could be lost from the sediment, leading to an underestimation of the sediment CH<sub>4</sub> concentrations. The sampling stations in reservoir Lokka and Takajärvi with the lowest CH<sub>4</sub> fluxes (Table 2) were situated in the sediment erosion/transportation zones. There the physical mixing of the hypolimnion and sediment surface could also affect the sediment CH<sub>4</sub> concentration profiles, thus the actual CH<sub>4</sub> fluxes from these sediments were probably not controlled by the diffusion and ebullition only.

The CH<sub>4</sub> ebullition also had a large contribution to the CH<sub>4</sub> emission from Postilampi; the release of CH<sub>4</sub> in the bubbles had been 36–46 mg m<sup>-2</sup> d<sup>-1</sup> during the summer 1996 (Huttunen *et al.* 2001b). In reservoir Porttipahta, the diffusive sediment–water CH<sub>4</sub> flux (25 mg m<sup>-2</sup> d<sup>-1</sup>) was higher than the mean CH<sub>4</sub> emission measured with floating chambers, 4.8 mg m<sup>-2</sup> d<sup>-1</sup> (Huttunen *et al.* 2002), emphasizing importance of CH<sub>4</sub> oxidation in the water column in the regulation of CH<sub>4</sub> emissions to the atmosphere. The CH<sub>4</sub> ebullition from reservoir Porttipahta was low compared with the CH<sub>4</sub> emissions measured with the chambers (Huttunen *et al.* 2002).

Although our measurement of the diffusive CH<sub>4</sub> fluxes at the sediment–water interface predicted the increase in CH<sub>4</sub> release from the sediments with increasing O<sub>2</sub> depletion, the method failed to predict the actual CH<sub>4</sub> emissions from lakes to the atmosphere. This is because the net CH<sub>4</sub> production and CH<sub>4</sub> fluxes to the atmosphere are controlled by both the production and oxidation of CH<sub>4</sub> and by the physical mechanisms that transport CH<sub>4</sub> from the sediment through the water column to the atmosphere. The close association between the CH<sub>4</sub> flux and O<sub>2</sub> conditions in the surface sediments indicated that increased CH<sub>4</sub> concentrations near the sediments of boreal lakes could be regarded as a sign of a serious oxygen depletion of the sediment. The sediment oxygen depletion, which can be partially attributed to CH<sub>4</sub> oxidation, and the associated CH<sub>4</sub> ebullition can cause further eutrophication by increasing the internal nutrient loading in the lakes (Saarijärvi and Lappalainen 2001, Liikanen *et al.* 2003).

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