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Spatial and seasonal variation in greenhouse gas and nutrient dynamics and their interactions in the sediments of a boreal eutrophic lake

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Abstract. Dynamics of greenhouse gases, CH_4, CO_2 and N_2O, and nutrients, $NO_2^- + NO_3^-$, NH_4^+ and P, were studied in the sediments of the eutrophic, boreal Lake Kevätön in Finland. Undisturbed sediment cores taken in the summer, autumn and winter from the deep and shallow profundal and from the littoral were incubated in laboratory microcosms under aerobic and anaerobic water flow conditions. An increase in the availability of oxygen in water overlying the sediments reduced the release of CH_4, NH_4^+ and P, increased the flux of N_2O and $NO_2^- + NO_3^-$, but did not affect CO_2 production. The littoral sediments produced CO_2 and CH_4 at high rates, but released only negligible amounts of nutrients. The deep profundal sediments, with highest carbon content, possessed the greatest release rates of CO_2, CH_4, NH_4^+ and P. The higher fluxes of these gases in summer and autumn than in winter were probably due to the supply of fresh organic matter from primary production. From the shallow profundal sediments fluxes of CH_4, NH_4^+ and P were low, but, in contrast, production of N_2O was the highest among the different sampling sites. Due to the large areal extension, the littoral and shallow profundal zones had the greatest importance in the overall gas and nutrient budgets in the lake. Methane emissions, especially the ebullition of CH_4 (up to 84% of the total flux), were closely related to the sediment P and NH_4^+ release. The high production and ebullition of CH_4, enhances the internal loading of nutrients, lake eutrophication status and the impact of boreal lakes to trophospheric gas budgets.

Introduction

Freshwaters are important sources of greenhouse gases, methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O) (Cicerone and Oremland 1988; Cole et al. 1994; Seitzinger and Kroeze 1998). Methane and CO_2 are produced through the mineralization of organic matter. From 7% to up to 75% of the sedimented carbon can be mineralized to CO_2 and CH_4 annually (Jones and Simon 1980; Adams and Fendinger 1985; Kelley et al. 1990). Shallow eutrophic freshwaters with high primary production and sedimentation form marked potential sources of CH_4. Nitrous oxide is mainly produced during denitrification as an intermediate by reduction of nitrate (NO_3^-) to molecular nitrogen (N_2). Some N_2O is also formed though nitrification by the oxidation of ammonium (NH_4^+) to nitrite (NO_2^-). High N_2O emissions have been measured from eutrophic, nitrogen loaded freshwaters (Seitzinger and Kroeze 1998).

In addition to the carbon gas production, mineralization of organic matter regenerates nutrients, nitrogen (N) and phophorus (P) from sediments back into the water column. Within two months 30–95% of P and N from algal cells can be mineralized to soluble inorganic nutrients and thus become available for primary production (De Pinto and Verhoff 1977). This internal nutrient loading can be an essential mechanism maintaining long-term eutrophication of lakes.

In the course of eutrophication, the increase in the amount of degradable organic matter increases mineralization, gas production (Jones and Simon 1980; Kelley et al. 1990) and the liberation of nutrients (e.g. Sinke et al. (1990)). Moreover, mineralization consumes oxygen, creating anaerobic conditions, which are favorable for release of CH_4, NH_4^+, and P (Sinke et al. 1990). Methane is of a particular importance in freshwaters. Oxidation of CH_4 contributes to anoxia, and the ebullition of CH_4 creates turbulence in the sediments enhancing the transportation of nutrients to the upper water column, where the nutrients can be used in primary production (e.g. Boström et al. (1988)). Even though it is known that there is a close association between gas and nutrient dynamics, only few studies have focused on the interactions between gas production and nutrient release in freshwater sediments (Sinke et al. 1990; Matinvesi 1996). The physical, chemical, and biological conditions differ greatly between littoral and profundal zones, which obviously influences the contribution of these zones to the total gas and nutrient fluxes within a lake.

We followed the spatial and seasonal variations and interactions of gas and nutrient dynamics in the littoral and profundal sediments of a eutrophic lake. The potential of sediments to produce the most important greenhouse gases, CH_4, CO_2 and N_2O, and nutrients, NH_4^+, P, NO_2^- and NO_3^-, were studied in a laboratory microcosm under aerobic and anaerobic conditions. The microcosm permitted the control of environmental parameters, allowing the comparison of the sediments taken from the various sites at different times of the year. We evaluated the relative importance of different zones in the gas and nutrient dynamics of the lake.

Materials and methods

Study site and sampling

Lake Kevätön is a mid-boreal, eutrophic lake (on average 73 μg tot-P L^{-1}, 1400 μg tot-N L^{-1}, 30 μg chlorophyll-a L^{-1} in 1998) in east-central Finland (63°6′ N,

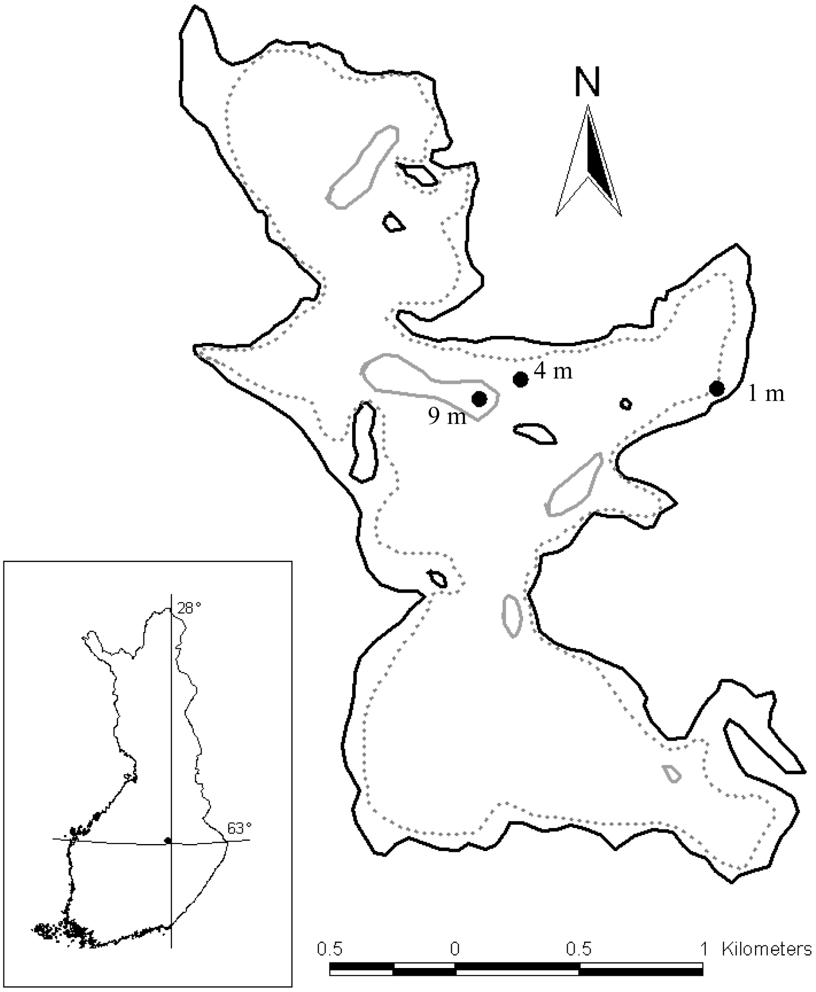

Figure 1. Study sites in littoral (1 m), shallow profundal (4 m), and deep profundal (9 m) of Lake Kevätön. Dotted gray contour line represents 1.5-m depth and solid gray contour line 6-m depth.

27°37′ E) (Figure 1). The lake was initially eutrophied by sewage in 1930–1975, while agriculture and internal loading are the most important present sources of nutrients. Lake Kevätön is dimictic with two stratification periods (from a few days to weeks in July 1998, and 5 months in November 1998 – April 1999) and is ice-covered from approximately November to April. The lake is shallow, with mean and maximum depths of 2.3 and 9 m, and with an area of 4.1 km^2. The littoral (depth 0–1.5 m), shallow profundal (depth 1.5–6 m), and deep profundal (depth 6–9 m) zones cover 30% (1.2 km^2), 67% (2.7 km^2), and 3% (0.14 km^2) of the lake surface area, respectively.

To study spatial and temporal variations in sediment gas and nutrient dynamics, triplicate sediment cores were taken in the summer (June 1998), autumn (August 1998) and winter (April 1999) from the littoral [1-m depth, middle infralittoral, growing *Phragmites australis* (Cav.) Trin. Ex Steud. and *Nuphar lutea* (L.) Sibth. & Sm.], shallow (4-m depth) and deep (9-m depth) profundal. Intact sediment cores were collected with a transparent acrylic tube, 9.4 cm in diameter and 65 cm in height, using a Limnos sediment sampler (Turku, Finland) from the profundal; a stainless steel piston corer, with a sharpened cutting edge, was required for sampling the littoral.

Laboratory incubations of sediments

The sediments were incubated in a laboratory microcosm using a continuous water flow technique (Liikanen et al. (2002c, 2002d)). The intact sediment cores and a control core (no sediment) were incubated with both aerobic water (9.3–10.5 mg O_2 L^{-1}, equilibrium with air) and with anaerobic water (0.1–1 mg O_2 L^{-1}, deoxygenated and controlled with N_2) to determine potential production of gases and nutrients with an overlying aerobic or anaerobic water column. The summer and autumn sediments were incubated first with aerobic and then with anaerobic water, and the winter sediments first with anaerobic and then with aerobic water according to the O_2 conditions in the hypolimnion of the lake at the time of sampling (Table 1). The total incubation time was one month. The study was conducted in a dark, temperature-controlled, room at 15 °C (close to the maximum summer temperature in the hypolimnion of the deep profundal). The test water was bank filtered, chemically [$Al_2(SO_4)_3$] coagulated, lake water from the Kuopio waterworks (Kuopio, Finland). Uniform test water (0.1 μM tot-P, 1 μM NH_4^+-N, 3 μM (NO_2^- + NO_3^-)-N, 230 μM SO_4^{2-}, < 20 μM Fe, and pH 6.7) was used in the experiments. The chemical composition of water in Lake Kevätön varied seasonally (hypolimnetic water at 9-m in 1998: 1–2.3 μM tot-P, 1–130 μM NH_4^+-N, 0–7 μM (NO_2^- + NO_3^-)-N, 0.6–67 μM SO_4^{2-}, and 6–146 μM Fe, and pH 6.8–7.5). Water was pumped from an 80-liter water reservoir over the cores by a peristaltic pump (Ismatec, BVK-MS/CA8-6, Switzerland) at a rate of 50 mL h^{-1}. Overlying water (volume, 500 mL) in the cores was gently stirred with a rotating magnet to prevent stratification. The incubation core system consisted of a funnel system allowing differentiation between the release rates of gases for both diffusion and ebullition.

Flux rates of gases and nutrients

The flux rates (μg or mg m^{-2} d^{-1}) of dissolved carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), nitrite and nitrate (NO_2^- + NO_3^-), ammonium (NH_4^+), phosphorus (P, total P), sulphate (SO_4^{2-}) and dissolved organic carbon (DOC) between sediment and water were determined from concentration differences in outflowing water between the sediment and control core using flow rates and sediment surface area (69 cm^2). The ebullient gas flux rates (μg or mg m^{-2} d^{-1}) of CO_2,

Table 1. Characteristics of the lake water and sediments of Lake Kevätön. Water temperature and O_2 concentrations in the hypolimnion (0.5–1 m above the sediment surface) and net primary production (NPP) in the epilimnion of Lake Kevätön. Content of carbon and nitrogen in the sediment, C/N-ratio in the 0–2 cm layer, and root biomass of the 0–10 cm littoral sediments (n = 3). Standard errors of the means are in parentheses. nd = not determined.

Site	lake water			sediment			
	temp. °C	O_2 conc. mg O_2 L^{-1}	NPP mg C m^{-2} d^{-1}	carbon mg C g^{-1}	nitrogen mg N g^{-1}	C/N	root biomass mg (DW) cm^{-3}
1-m depth (littoral zone)							
summer 98	20	nd	nd	nd	nd	nd	20 (7)
autumn 98	14	nd	nd	60	10	6	13 (0.6)
winter 99	0.7	nd	nd	70	12	5.8	5.2 (0.9)
4-m depth (shallow profundal zone)							
summer 98	15	10	880	55	11	5	–
autumn 98	9	nd	280	67	13	5.1	–
winter 99	3.3	1.7	nd	54	11	4.4	–
9-m (deep profundal zone)							
summer 98	13	9.6	950	87	16	5.4	–
autumn 98	9	9.7	510	86	17	5.1	–
winter 99	5.5	0.1	nd	88	17	5.2	–

CH_4 and N_2O from the sediments were calculated by dividing the amount of bubble gases produced with the incubation time and with the sediment surface area.

Water samples (20–30 mL) for analysis of dissolved CH_4, CO_2, and N_2O were taken 3–5 times a week from the out-flows by 50 mL syringes (Terumo Europe, Leuven, Belgium) equipped with three-way stopcocks (Codan Steritex, Hoejvangen, Denmark). Released bubbles were collected with the syringes from the gas traps when 3–10 mL of bubble gas had accumulated. The gas samples were analysed within 24 h. The dissolved gas concentrations in water were analysed using a headspace equilibration technique (Jones and Simon 1980). Water was equilibrated in the syringes with added nitrogen (see details in Liikanen et al. (2002c)) and headspace gas concentrations were determined with gas chromatography (Hewlett Packard, 5890 Series II equipped with a flame ionization detector for CH_4, a thermal conductivity detector for CO_2 and > 1000 ppm CH_4, and an electron capture detector for N_2O) (Nykänen et al. 1995). The dissolved gas concentrations in water were calculated from the headspace gas concentrations according to Henry's law, using the values after Lide and Fredrikse (1995).

Dissolved NO_2^- + NO_3^-, NH_4^+, P, SO_4^{2-} and DOC were measured at the end of the incubation periods from water samples collected in flasks from the outflows, and were stored at −20 °C. Combined NO_2^-+NO_3^- were determined by the FIA (flow injection analysis) method according to the standard SFS-EN ISO 13395 (SFS Standardization 1995) and the instructions of the manufacturer (Lachat Quick Chem 8000, Milwaukee, WI). Ammonium was determined photometrically according to the standard SFS 3032 (SFS Standardization 1976). Total phosphorus was measured photometrically according to the standard SFS 3026 (SFS Standardization 1986). Sulphate was measured by a DIONEX 2010i ion chromatography equipped with a DIONEX Ion Pac® AS4A-SC 4 mm column (Dionex Corp., USA). Dissolved organic carbon (DOC) was analysed with a Shimadzu TOC-5000 Analyzer (Shimadzu Corp., Japan).

Oxygen, redox and pH conditions in the microcosms

At the end of the incubation periods, sediment redox potentials, pH and O_2 concentrations in the overlying water were determined with electrodes (Microprocessor pH meter pH320, WTW, Germany, with Hamilton pH electrode, Switzerland, and with InLab®501 redox electrode, Mettler Toledo, Switzerland; Dissolved Oxygen Meter Oxi 330 with Dissolved Oxygen Probe CellOx 325, WTW, Germany). Sediment O_2 consumption (SOC, mg m^{-2} d^{-1}) was calculated from the differences in overlying water O_2 concentrations between the sediment and control cores with the aerobic flow using flow rate and sediment surface area.

Profiles of dissolved O_2 concentration and redox potential at the sediment-water interface were measured with miniature electrodes at the end of the incubations. Dissolved O_2 concentrations and sediment O_2 penetration (SOP) were measured after the aerobic and once after the anaerobic incubation (from the autumn sediments) with a Clark type needle oxygen electrode (o.d., 0.9 mm, model 768-20R, Diamond General Development Corp. USA) using a chemical microsensor (product no. 1231, Diamond General Development Corp. USA). Dissolved O_2 concentrations were measured at 1-mm intervals from 2–4 mm above the sediment surface to the depth where dissolved O_2 was depleted. Redox potentials were determined from the autumn and winter sediments with a combination redox-potential needle electrode (o.d 1.3 mm, Diamond General Development Corp. USA) connected to a pH/mV meter (MP 120 pH meter, Mettler Toledo, Switzerland) at 2–5 mm intervals from 2–6 mm above the sediment surface to a depth of −40 or −50 mm. The electrodes were positioned with a minimanipulator, which permitted 1-mm vertical resolution.

Carbon mineralization and respiratory quotient

Carbon mineralization rates were calculated as the sum of the CO_2–C and CH_4–C produced (den Hayer and Kalff 1998). Respiratory quotients (RQ–value), the molar ratio of CO_2 production to O_2 consumption, were calculated for the sediments incubated with the aerobic water flow (Rich 1978).

Lake and sediment characteristics

Temperature and dissolved O_2 concentration in the hypolimnion of Lake Kevätön were measured 0.5–1 m above the sediment surface during the years 1998 and 1999. Dissolved O_2 was determined with an iodometric Winkler procedure according to standard SFS-EN 25813 (SFS Standardization 1995). *In situ* net primary production (NPP) of phytoplankton was measured using a ^{14}C technique over a 24-h period (Keskitalo and Salonen 1994). NPP was determined every second week from June to September 1998 in the epilimnion of the deep (0–4 m) and shallow profundal (0–2 m).

Root biomasses of the littoral microcosm sediments were determined from the sediment layer of the 0–10 cm section at the end of the experiments. Carbon (C) and nitrogen (N) contents of the sediments in the 0–2 cm layer were determined with a LECO CHN-600 element analyzer from the sediment samples stored at −20 °C.

Statistical analysis

Statistical analyses were performed using the SPSS statistical package (SPSS Inc. USA). The normal distribution of the flux rates and environmental variables were tested with the Kolmogorov-Smirnov Test. Correlation analysis (Pearson correlation coefficients, two-tailed significances) and non-parametrical tests with Mann-Whitney U and Kruskal-Wallis Post Hoc tests, were done to compare the flux rates and environmental variables between the different sediments. All the sites were studied simultaneously for seasonal variation and correspondingly all seasons for spatial variation. The sediments collected from all the sites and during all seasons were compared regarding the effect of anaerobic and aerobic conditions.

Results

Lake and sediment characteristics

In June 1998, the sampling took place in the beginning of the summer stratification, in August 1998 during autumn overturn, and in April 1999 at the end of winter stratification. The hypolimnion of Lake Kevätön was aerobic in the summer and autumn, but in the winter sampling the profundal sediments had been anaerobic for over three months (Table 1). Net primary production of phytoplankton (NPP) was higher in summer than in autumn (Table 1). From June to September 1998, the average NPP in the deep profundal and shallow profundals were 670 and 590 mg C m^{-2} d^{-1}, respectively. The root biomasses of the littoral sediments were highest in summer and lowest in winter (Table 1). The C and N contents were highest in the deep profundal sediments and were equal in the shallow profundal and littoral sediments (Table 1).

Conditions in the microcosms

In all sediments, sediment O_2 consumption (SOC) was lower in winter than in autumn and summer ($P = 0.001$) (Table 2). With the aerobic flow, sediment O_2 con-

Table 2. Conditions in the microcosms. Overlying water O_2 concentration (1 cm above the sediment surface), sediment oxygen penetration (SOP) and consumption (SOC), molar ratio of CO_2 production to O_2 consumption (RQ), sediment redox potential (0.5 cm below the sediment surface) and volumetric ebullition rate in the sediments. Averages ($n = 3$) and standard errors of the means in parentheses.

sediment		O_2 dynamics					
treatment	sampling time	O_2 conc (mg O_2 L^{-1})	SOP (mm)	SOC (mg O_2 m^{-2} d^{-1})	RQ	redox (mV)	ebullition (mL m^{-2} d^{-1})
1-m (littoral zone)							
anaerobic	summer 98	0.4 (0.2)	nd	nd	nd	−62 (17)	170 (71)
	autumn 98	0.2 (0)	1.8 (0.3)	nd	nd	−52 (34)	56 (37)
	winter 99	0.3 (0)	nd	nd	nd	−100 (19)	51 (9)
aerobic	summer 98	4.6 (0.9)	3.7 (0.2)	530 (150)	1.5 (0.1)	130 (11)	110 (30)
	autumn 98	5.3 (1.7)	7.5 (1.7)	690 (290)	1.2 (0.1)	160 (6)	42 (19)
	winter 99	6.9 (0.4)	6.2 (0.6)	170 (57)	3.2 (0.9)	88 (32)	62 (7.7)
4-m (shallow profundal zone)							
anaerobic	summer 98	0.1 (0.1)	nd	nd	nd	−100 (2)	16 (16)
	autumn 98	0.2 (0)	2.5 (0.5)	nd	nd	−160 (3)	35 (14)
	winter 99	0.3 (0)	nd	nd	nd	−200 (13)	63 (35)
aerobic	summer 98	4.9 (0.1)	1.5 (0.3)	490 (27)	1.3 (0.3)	37 (5)	15 (15)
	autumn 98	3.8 (0.4)	2.8 (0.4)	970 (58)	1 (0.2)	56 (11)	17 (8.5)
	winter 99	7.0 (0)	4.5 (0.5)	180 (13)	2.5 (0.3)	−25 (6)	75 (15)
9-m (deep profundal zone)							
anaerobic	summer 98	0.0 (0)	nd	nd	nd	−140 (7)	140 (8)
	autumn 98	0.3 (0)	1 (0)	nd	nd	−120 (4)	120 (6.4)
	winter 99	0.3 (0)	nd	nd	nd	−160 (8)	59 (18)
aerobic	summer 98	2.5 (0.3)	2.3 (0.4)	890 (39)	1.3 (0.2)	−43 (6)	80 (40)
	autumn 98	6.3 (0)	2.8 (0.2)	500 (11)	1.9 (0.2)	15 (11)	48 (9.8)
	winter 99	6.0 (0.2)	3.2 (0.8)	400 (34)	1.7 (0.1)	−26 (25)	93 (26)

sumption regulated the dissolved O_2 concentration in the overlying water, O_2 concentrations varied from 2.5 to 7 mg L^{-1}. With the anaerobic flow, the overlying water O_2 concentration was < 0.4 mg L^{-1}. The overlying water O_2 concentration correlated positively with sediment O_2 penetration (SOP) ($r = 0.54$, $P = 0.003$). Oxygen penetrated deeper in the littoral than in the profundal sediments ($P = 0.044$, Table 2).

There was a strong positive correlation between the overlying water O_2 concentration and sediment redox potential (Table 3). Aerobic overlying water increased sediment redox potentials down to the deepest measured depth of 5 cm (Figure 2A–2D). The sediment redox potential changed from positive to negative approximately at the depth where dissolved O_2 in sediments become depleted, but with the anaerobic flow the sediment redox potentials were always negative (Table 2, Figure 2A–2D). With the aerobic flow, the sediment redox profiles were variable and differed between the sediments, whereas with the anaerobic flow, all the sediments

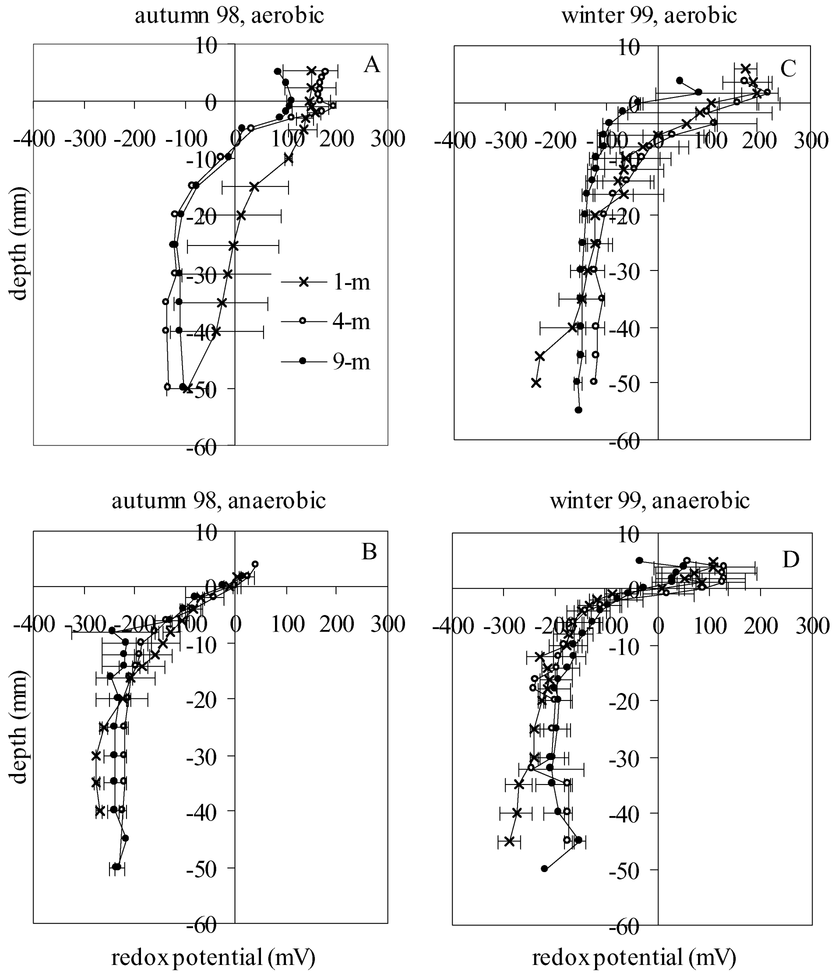

Figure 2. Redox potential profiles in the sediments in the autumn (A.-B.) and the winter (C.-D.) sediments with microcosm aerobic and anaerobic flows. Error bars represent standard error of the means.

showed similar redox profiles (Figure 2A–2D). The redox potentials were higher in the littoral than in the deep profundal sediments ($P = 0.014$) (Table 2). Overlying water pH of 6.1–6.6 with the aerobic flow was lower than pH of 6.6–8.2 with the anaerobic flow ($P < 0.001$).

Flux rates of gases

Release of CH_4 was highest with the anaerobic flow ($P < 0.001$) (Figure 3A–3C). The CH_4 fluxes correlated negatively with the overlying water O_2 concentrations and the sediment redox potentials (Table 3). The release of CH_4 was greatest from

Table 3. Pearson correlation coefficients (*r*) showing the significant correlations between the environmental variables and the flux rates of gases and nutrients in the microcosm sediments. The number of samples (*n*) is 16 in the littoral, 35–36 in the profundal, and 51–52 in whole lake.

	littoral			profundal				whole lake		
variable	O_2 conc.	redox	CO_2 plus CH_4	O_2 conc.	redox	CO_2 plus CH4	ebullition	CO_2 conc.	redox	CO_2 plus CH4
redox	0.81***		–	0.81***		–	–	0.76***		–
CO_2	–	–	0.94***	–	0.33**	0.95***	–	–	–	0.95***
CH_4	–	–	0.78***	–0.58***	–0.44*	0.69***	0.62***	–0.53***	–0.36**	0.71***
N_2O	–	–	–	0.50**	0.60***	–	–	0.32*	–	–
NO_2^-+NO_3^-	0.79***	0.83***	–	0.87***	0.81***	–	–	0.79***	0.62***	–
NH_4^+	–	–0.56*	–	–0.54***	–0.34*	0.79***	0.52***	–0.44***	–0.46***	0.61***
tot-P	–	–	0.56*	–0.52**	–0.45**	0.49**	0.38*	–0.42**	–0.49*	0.45***

(* = $P \leqslant 0.05$; ** = $P \leqslant 0.01$; *** = $P \leqslant 0.001$).

the deep profundal and littoral sediments ($P = 0.009$). The CH_4 fluxes were lower in winter than in summer or autumn ($P = 0.004$).

Production of CO_2 in the sediments was similar with the aerobic and anaerobic flows (Figure 3D–3F). The highest CO_2 flux rates were measured from the deep profundal sediments with the highest carbon content ($P = 0.001$). The CO_2 production was lower in winter than in summer and autumn ($P < 0.001$).

The N_2O was produced in the shallow profundal sediments with the aerobic flow. From the other sediments (littoral and deep profundal), N_2O fluxes were negligible (Figure 3G–3I). The N_2O fluxes correlated positively with the overlying water O_2 concentration (Table 3) and with the flux of $NO_2^- + NO_3^-$ ($r = 0.54$, $P < 0.001$), and negatively with the flux of NH_4^+ ($r = -0.32$, $P = 0.022$).

Ebullition of gases was greatest from the littoral and deep profundal sediments ($P = 0.002$) (Table 2) and was highest in the summer. In these sediments, ebullition was an important pathway for CH_4 transport, accounting for up to 84% of the total CH_4 flux. The content of CH_4 in the bubble gases varied greatly, from zero up to 97, 53, and 18% in the deep profundal, in the littoral and in the shallow profundal sediments, respectively. In the summer, autumn and winter, up to 97, 51, and 19% of bubble gases consisted of CH_4, respectively. Ebullition was not an important flux pathway for CO_2 and N_2O; their concentrations in the bubble gas were below 1% and 5 ppm, respectively.

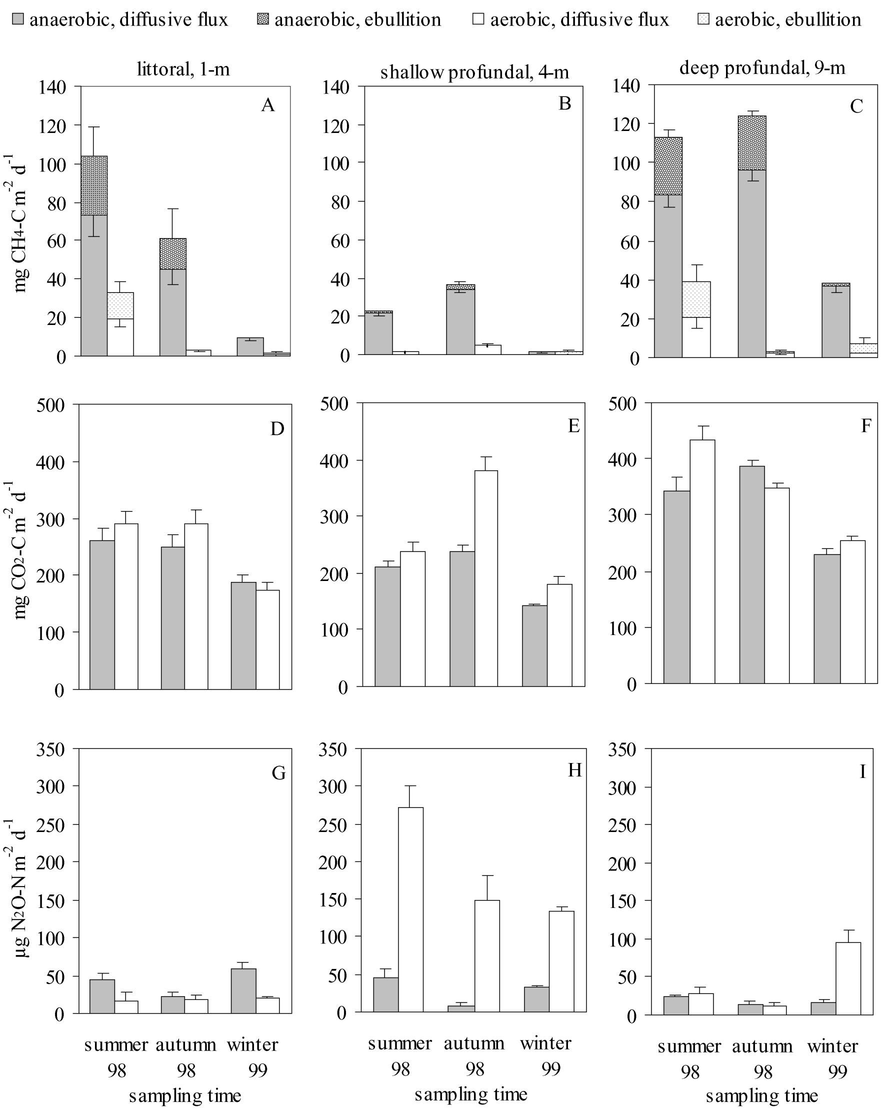

Figure 3. The dissolved and ebullitive fluxes of methane (A.-C.), carbon dioxide (D.-E.) and nitrous oxide (G.-H.) from the littoral, shallow, and deep profundal sediments with microcosm aerobic and anaerobic flows. Error bars represent standard error of the means.

Carbon mineralization and respiratory quotient

Carbon mineralization, the sum of CO_2-C and CH_4–C, was greatest in the deep profundal sediments where the C content was highest ($P = 0.001$). Mineralization was lower in the winter than in the summer and autumn ($P < 0.001$) (Figure 4A–

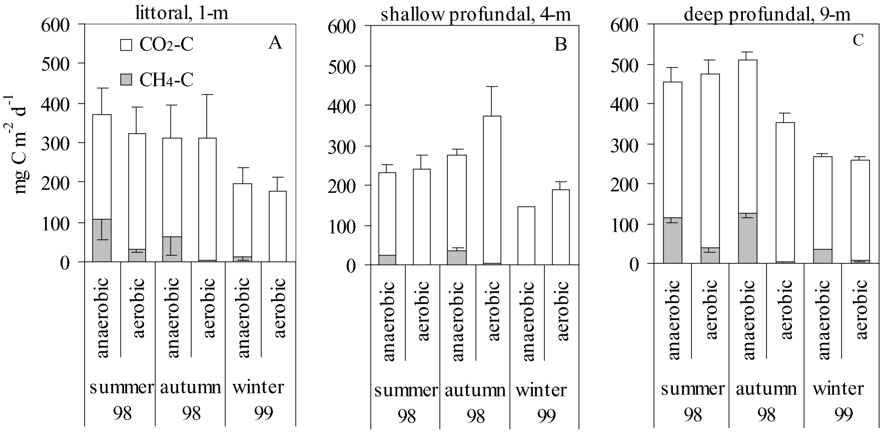

Figure 4. A.-C. Carbon mineralization rate in the littoral, shallow, and deep profundal sediments with microcosm aerobic and anaerobic flows. Error bars represent standard error of the means.

4C). Mineralization rates were similar with the aerobic and anaerobic flows. Methane accounted for 1–34% of the carbon mineralization with the anaerobic flow and for 0–15% with the aerobic flow. The respiratory quotient (RQ), molar ratio of CO_2 production to O_2 consumption, was always greater than unity (Table 2). The highest RQ–values were measured in the littoral and shallow profundal sediments in the winter.

Flux rates of NO_2^- + NO_3^-, NH_4^+, tot-P, SO_4^{2-} and DOC

The microcosm sediments acted as either a source (during aerobic flow) or a sink (always during anaerobic flow and sometimes with the aerobic flow) of $NO_2^- + NO_3^-$ (Figure 5A–5C). The flux rates of $NO_2^- + NO_3^-$ correlated positively with the overlying water O_2 concentration and the sediment redox potential (Table 3), and negatively with the flux of NH_4^+ ($r = -0.37$, $P = 0.008$).

The fluxes of NH_4^+ were highest from the deep profundal sediments with the highest mineralization rate ($P < 0.001$) (Figure 5D–5F). With the aerobic flow, the release of NH_4^+ was lowest ($P = 0.001$), and the winter sediments even consumed NH_4^+ from the overlying water. The flux of NH_4^+ correlated negatively with the overlying water O_2 concentration and the sediment redox potential, and positively with the carbon mineralization rate (Table 3) and the sediment O_2 consumption ($r = 0.54$, $P = 0.005$). In the profundal cores, NH_4^+ fluxes correlated positively with the ebullition rate (Table 3).

The release of P was lower in the littoral than in the profundal sediments ($P = 0.001$) and was reduced with the aerobic flow ($P = 0.04$) (Figure 5G–5I). The flux of tot-P correlated negatively with the overlying water O_2 concentration and the sediment redox potential, and positively with the carbon mineralization rate (Table 3) and the sediment O_2 consumption ($r = 0.51$, $P = 0.009$). In the profundal sediments, P fluxes correlated positively with the ebullition rate (Table 3).

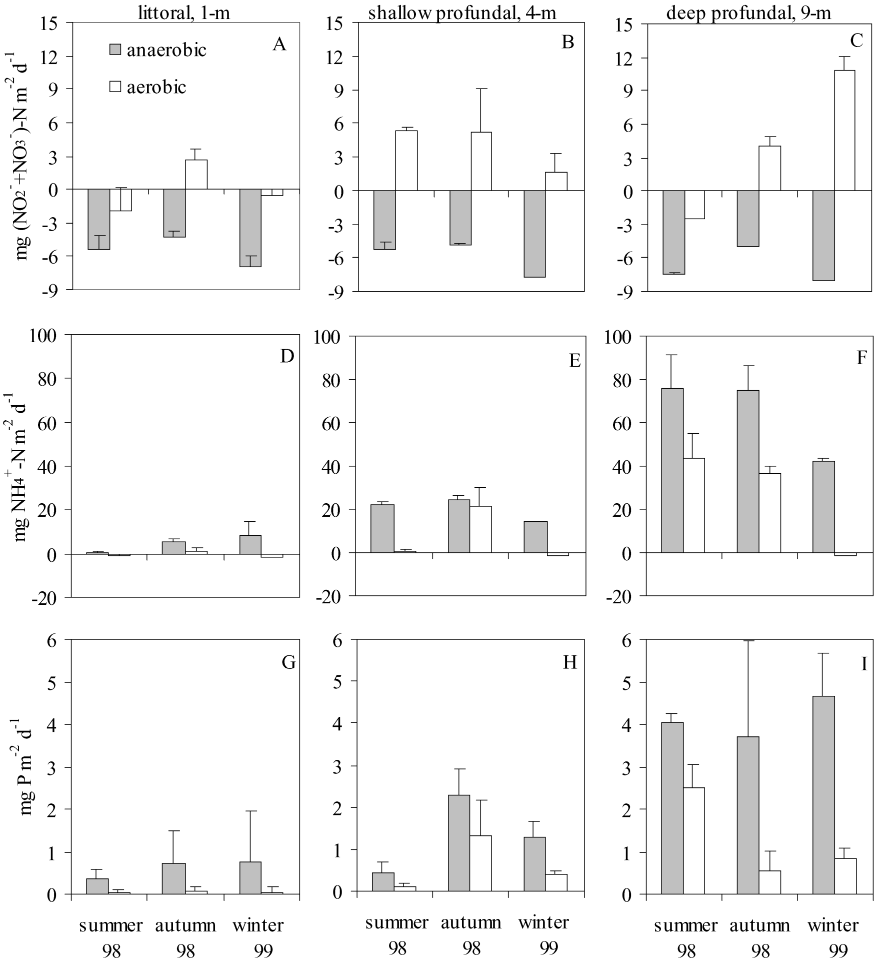

Figure 5. Fluxes of nitrite and nitrate (A.-C.), ammonium (D.-F.) and phosphorus (G.-I.) from the littoral, shallow, and deep profundal sediments with microcosm aerobic and anaerobic flows. Error bars represent standard error of the means.

The flux of SO_4^{2-} from sediment to water varied from −320 to 66 mg SO_4^{2-} m^{-2} d^{-1}, with SO_4^{2-} usually being consumed in the sediments. The dissolved organic carbon (DOC) flux varied from −150 to 390 mg C m^{-2} d^{-1}.

Gas and nutrient dynamics in Lake Kevätön

The shallow profundal area, which covers 67% of the Lake Kevätön surface area, was the most important contributor to the gas and nutrient release (Figure 6). On average, 80% of the N_2O, mineral N [sum of NH_4^+-N and (NO_2^- + NO_3^-)-N] and P, 65% of the CO_2 and 40% of the CH_4 release was estimated to occur from the shal-

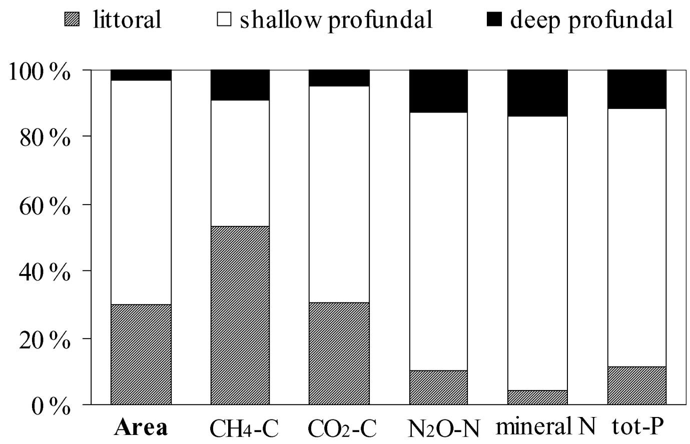

Figure 6. Contribution of the littoral (0–1.5 m), shallow (1.5–6 m) and deep profundal (6–9 m) areas to whole lake gas and nutrient dynamics. The bars show percentages of areas and average areal fluxes determined with the sediment cores taken in summer, autumn, and winter and run with microcosm aerobic and anaerobic flow.

low profundal area. The littoral, accounting for 30% of the surface area, contributed over 50% to the CH_4 budget. The deep profundal region, comprising only 3% of the lake area, contributed less than 14% to the total gas and nutrient release, although it had the highest fluxes (Figures 3 and 5).

Discussion

Carbon mineralization and production of CO_2 and CH_4

The production of both CO_2 and CH_4 is a good measure of both aerobic and anaerobic organic carbon mineralization in freshwater sediments. When mineralization is measured only as a consumption of various oxidants, the contribution of methanogenesis is neglected. The carbon mineralization rates (sum of CO_2 and CH_4) in the sediments of Lake Kevätön, 110–570 mg C m^{-2} d^{-1}, are within the range from −600 to 1340 mg C m^{-2} d^{-1} reported for Quebec lake sediments (den Hayer and Kalff 1998). With the aerobic flow, almost all of the carbon mineralized was released as CO_2, but with the anaerobic flow CH_4 accounted for up to 34% of the carbon mineralization. In previous studies, the proportion of CH_4, from the sum of CO_2 and CH_4, varied from 20 to 42% (Kelly et al. 1988; Kelley et al. 1990; den Hayer and Kalff 1998).

Oxygen availability did not affect the carbon mineralization rate, but the increased O_2 content reduced the release of CH_4 from the sediments. Huttunen et al. (2001) observed that hypolimnetic CO_2 concentrations *in situ* in Lake Kevätön were similar for either anaerobic or aerobic conditions in the hypolimnion. Aerobic surface sediments inhibit methanogenesis and part of the CH_4 diffusing from the deeper anaerobic sediment layers becomes oxidized (e.g. Sweerts et al. (1991)). The diffusive release of CH_4 was most effectively inhibited by the influx of O_2 in the autumn in the deep profundal sediments, when the sediments were well oxygenated. This was the only time when positive redox potentials were measured in the deep profundal sediments. Winfrey and Zeikus (1979) observed that during autumn overturn, methanogenesis was able to proceed in sediments only below a depth of 5 cm. However, even when there was an abundance of O_2 at the sediment-water interface, sediments of a eutrophic lake can still be major sources of CH_4. In the summer, when primary production provided fresh organic material, the littoral and deep profundal sediment showed release of CH_4 even with the aerobic flow. The thin aerobic layer in the sediments was not able to oxidize all of the CH_4 produced in the deeper anaerobic sediment layers. In addition, CH_4 was released in bubbles from anaerobic sediments, thus bypassing the aerobic sediment-water interface.

More CO_2 was produced than O_2 was consumed in the sediments, highlighting the importance of anaerobic processes in organic carbon degradation (Rich 1978). In the case of aerobic degradation, the molar ratio of CO_2 production to O_2 consumption (RQ–value) is reported to be less than unity, 0.85 being the most commonly quoted value (Wetzel 1975). With O_2 deficiency, some bacteria can utilize electron acceptors other than O_2 in degrading organic matter. Rich (1978) found hypolimnion RQ–values that varied from 0.4 in early summer up to 10.8 during winter stratification. In our study, the highest RQ–values, from 1.7 to 3.2 (Table 2), were also determined from the winter sediments, which had been in anaerobic conditions for over three months. The high RQ–values and low O_2 consumption in the winter sediments imply that microbial communities had adapted to the anaerobic conditions. Aerobic respiration was low and anaerobes made the greatest contribution to the sediment CO_2 production.

The spatial variation in the mineralization and carbon gas production was associated with the sediment carbon content. Carbon mineralization and the production and ebullition rates of CH_4 were greatest in the deep profundal sediments with the highest sediment carbon content. Since the average primary production in the deep and shallow profundal sites was similar, organic matter from other parts of the lake drove mineralization in the deep profundal sediments. The sediments did not contain allochthonous organic material since the C/N-ratio in the sediments was from 5 to 6, similar to the planktonic C/N-ratio of 5.6 determined in eutrophic waters dominated by plankton (Håkanson and Jansson 1983). Greater CH_4 flux rates were measured in previous studies on profundal sediments in eutrophic Lake Blelham Tarn (Jones and Simon 1981) and in eutrophic Lake Dagow (Casper 1996). However, in oligotrophic Lake Stechlin (Casper 1996), in oligotrophic Lake Constance (Thebrath et al. 1993) and in oligo- and meso-oligotrophic Quebec lakes (den Hayer and Kalff 1998), littoral sediments had higher CH_4 production and carbon mineralization. The evaluation of littoral mineralization and CH_4 dynamics is difficult. The littoral consists of various zones (Wetzel 1975); mineralization and CH_4 dynamics can vary greatly between zones (den Hayer and Kalff 1998; Juutinen et al. 2001). In the present work only one of the littoral zones was examined, i.e. the middle infralittoral segment without macrophytes. Thus it is difficult to estimate littoral mineralization and CH_4 dynamics precisely. Since the plants are important for the ventilation of CH_4 from sediments to the atmosphere, and the upperlittoral zones growing macrophytes have in previous studies shown higher fluxes (Juutinen et al. 2001) than the infralittoral sediments studied here, our measurements from the middle infralittoral might underestimate the littoral CH_4 production in Lake Kevätön. Methanogenesis in the shallow profundal sediments might also have been underestimated, even though it is still lower than that of the deep profundal sediments. According to our previous studies (Liikanen et al. 2002a), a sulphate (SO_4^{2-}) concentration of 200 μM, which was used in this study, reduces the flux of CH_4 from the shallow profundal sediments with low organic carbon content, but does not inhibit methanogenesis in the organic deep profundal sediments (the effects of SO_4^{2-} were not studied in the littoral sediments). However, 200 μM SO_4^{2-} concentration did not enhance the total carbon mineralization in either of the profundal sediments (Liikanen et al. 2002a). Sulphate concentration in the hypolimnion of Lake Kevätön in 1998 varied form 0.6 to 67 μM.

The temporal variation in the carbon mineralization was regulated by the availability of fresh carbon. In the winter, when primary production had ceased, the carbon mineralization potential in the sediments was at its lowest. At constant temperatures, the flux of CH_4 from the sediments was reported to be regulated by the rate of organic influx (e.g., Kelly and Chynoweth (1981)). Although the effect of temperature on carbon mineralization was not studied here, according to our previous studies temperature significantly regulated the carbon mineralization rate, where the Q_{10} for (CO_2+CH_4)-C production was from 2.3 to 3.0 in the shallow profundal sediments (Liikanen et al. 2002d).

Release of phosphorus and nitrogen from the sediments

The deep profundal sediments with the highest carbon content and mineralization rate also showed the greatest release of P and NH_4^+, emphasising the importance of these sediments as a nutrient reservoir. Mineralization liberated P and N from organic matter into the sediment pore water. In addition, low O_2 content and redox potential created conditions favorable to the release of P and NH_4^+ to overlying water.

Significant P fluxes were measured from the deep profundal during all seasons and from the shallow profundal sediments in the autumn, which showed high mineralization rates. The aerobic surface sediments generally blocked the release of P from the sediments, but in summer P was also released from the aerobic sediments at the deep profundal. The mineralization of P was probably high, and it is likely that this nutrient was transported from deeper anaerobic sediment layers by gas convection (as discussed below). Phosphorus release was regulated by the sediment redox potential. Phosphorus is normally liberated from the iron(hydr)oxyphosphate precipitate when Fe (III) is reduced to Fe (II) (e.g. Boström et al. (1988)), when the reduction of Fe (III) occurs at redox potentials below 100 mV (Jones 1982).

In the microcosm experiments, the highest N fluxes were measured from the deep profundal sediments with the highest mineralization rates. The average net release of mineral N [sum of NH_4^+-N and (NO_2^- + NO_3^-)-N] from the profundal sediments of 36 mg N m^{-2} d^{-1} with the anaerobic flow was slightly higher than the average release of 22 mg N m^{-2} d^{-1} with the aerobic flow. Nitrogen was released mainly as NH_4^+, especially with the anaerobic flow. When O_2 was available, NH_4^+ was oxidized to NO_2^- and NO_3^- (nitrification). The produced NO_2^- and NO_3^- were further reduced deeper in the anaerobic sediments to N_2O and N_2, resulting in lower (NO_2^- + NO_3^-)-N release than NH_4^+-N. Thus, there was an overall lower mineral N fluxes with the aerobic flow. The production of N_2O was dependent on the production of NO_2^- and NO_3^-, which implies a close coupling between nitrification and denitrification. The N_2O was produced with the aerobic flow only in those sediments which showed low CH_4 fluxes with the anaerobic flow. In those sediments, CH_4 oxidation (methanotrophy) did not consume all of the O_2, leaving a portion of the O_2 for NH_4^+ oxidation. This indicates that those sediments which produce N_2O have different characteristics than those sediments most favorable for the production of CH_4.

The ebullition of gases increased the release of NH_4^+ and P from the profundal sediments. Ebullition causes turbulence in sediments and results in the resuspension of sediment particles and pore water rich in nutrients. It has been speculated that ebullition might be an important mechanism in transferring nutrients from sediments to the water column (Boström et al. 1988; Matinvesi 1996). Significant correlations (Table 3) between the ebullition rate and the release rate of NH_4^+ and P in the profundal sediments were observed in the microcosm experiments. Therefore, the production and ebullition of CH_4 as bubbles plays an important role in the internal loading pathway for nutrients.

The microcosm experiments revealed differences in nutrient dynamics between the littoral and profundal sediments. Even though, carbon was mineralized and released to the water column at similar rates for both the littoral and profundal zones, hardly any P or N was released from the littoral sediments. The littoral sediment did not serve as storage reservoir for nutrients in the same way as the profundal sediments. Perhaps the littoral plants had been responsible for taking up any excess nutrients from the pore waters.

Greenhouse gas dynamics

The amount of CH_4 released from the sediments to the overlying water column was similar to the CH_4 flux from *in situ* surface waters to the atmosphere (Huttunen et al. (1999), S Juutinen, personal communication) when the sediment CH_4 flux rates were measured at *in situ* O_2 conditions in the microcosms (Figure 7). With aerobic overlying water, most of the CH_4 produced in anaerobic sediments was oxidized at the sediment-water interface, observed as negligible CH_4 emissions both in laboratory and *in situ*. We have also determined significant CH_4 oxidation in the water column of Lake Kevätön in 2000 (Liikanen et al. 2002b). This water column CH_4 oxidation during summer stratification would have been efficient to consume all CH_4 released from the summer sediments studied here. However, during summer stratification with anaerobic hypolimnion, the sediment-water CH_4

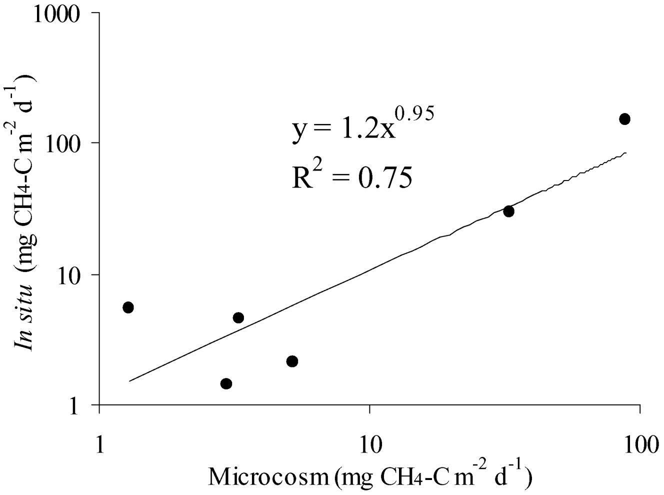

Figure 7. The CH_4 flux between the sediment and water measured in laboratory vs. the CH_4 flux at the *in situ* air-water interface (Huttunen et al. (1999): S Juutinen, personal communication) The laboratory fluxes are the statistical means with aerobic or anaerobic flows in the microcosm depending on the *in situ* O_2 condition in the hypolimnion during the measurements. The laboratory CH_4 fluxes measured at 15 °C with the anaerobic flow were calculated at corresponding *in situ* temperatures using a Q_{10}-value of 2.3 (Liikanen et al. 2002d).

fluxes were similar to the *in situ* fluxes at the air-water interface. Probably, most of the CH_4 from sediments is released *in situ* in bubbles directly to the atmosphere without meeting significant CH_4 oxidation. It is important that the potential CH_4 production in the sediments, measured in laboratory microcosm, can be used to compare the actual *in situ* CH_4 emissions at various zones of lake. Also, the N_2O fluxes in the microcosm experiments reflected the negligible *in situ* fluxes of N_2O at the air-water interface (J Huttunen, personal communication). The sediment CO_2 flux was not closely associated with air-water CO_2 fluxes, since primary production and decomposition (respiration) in the water column are major controllers of lake CO_2 dynamics.

Methane was the most important of the sedimentary greenhouse gases released to the atmosphere. The relative importance of a greenhouse gas can be evaluated from its global warming potential (GWP), which is a measure of a radiative force of a gas expressed as grams of CO_2 equivalents (IPCC 1996). We calculated that CH_4 accounted for 3–70%, CO_2 for 24–93% and N_2O < 12% of the total GWP of the sedimentary gases (100 yr time horizon, IPCC 1996). The GWP can be applied only for gases released to the atmosphere. Thus, the importance of sedimentary CO_2 release in the GWP cannot be determined, since the CO_2 dynamics in the water column play a significant role in lake CO_2 emissions. However, most of the sedimentary CH_4 and N_2O was expected to be released to the atmosphere, as discussed above. Under anaerobic conditions sediments can contribute significantly to the atmospheric CH_4 load. We measured that up to 84% of the total CH_4 emissions can be transported via ebullition, CH_4 being released directly to the atmosphere contributing the thropospheric gas content. Even though N_2O is a strong greenhouse gas, radiatively 310 times more efficient than CO_2 and 15 times more efficient than CH_4 (100 yr time horizon, IPCC 1996), its contribution to the GWP is low due to its negligible production in this lake environment.

Extrapolation of microcosm results to the whole lake

In spite of the fact that the shallow profundal area had the lowest flux rates, its coverage is 67% of the lake area, and therefore has a major impact on gas and nutrient dynamics in Lake Kevätön. The littoral area which comprises 30% of the lake surface, had high CH_4 production and is probably the most important source of CH_4. The importance of the littoral in CH_4 production has to be a crude estimate since only one littoral zone, the middle infralittoral zone, was studied. Although the sediment-to-water flux rates of CO_2, CH_4, NH_4^+, and P were greatest in the deep profundal sediments, the small area (3%) of the deep profundal had minor importance in the total gas and nutrient dynamics for Lake Kevätön. Lake monitoring programs focus generally on the deepest sites of lakes. According to the present results, studies conducted only in the deep profundal do not allow upscaling of gas and nutrient fluxes for the whole lake and are, therefore, not useful for large scale freshwater biome budget calculations, at least for shallow boreal lakes.

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