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Effects of temperature and oxygen availability on greenhouse gas and nutrient dynamics in sediment of a eutrophic mid-boreal lake

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Abstract. The effects of oxygen conditions and temperature on dynamics of greenhouse gases (CH_4, CO_2, N_2O) and nutrients (NH_4^+, NO_2^-+NO_3^-, tot-P) were studied in sediment of hyper-eutrophic Lake Kevätön, Finland. Undisturbed sediment cores were incubated at 6, 11, 16, and 23 °C in a laboratory microcosm using a continuous water flow technique with an oxic or anoxic water flow. The production of CO_2 increased with increasing temperature in both oxic (Q_{10} 3.2 ± 0.6) and anoxic (Q_{10} 2.3 ± 0.4) flows. The release of CH_4 increased with temperature in anoxic conditions (Q_{10} 2.3 ± 0.2), but was negligible with the oxic flow at all temperatures. The release of NH_4^+ increased with temperature with the oxic and anoxic flows (Q_{10} 2.4 ± 0.1). There was a net production of NO_2^-, NO_3^- and N_2O with the oxic flow at temperatures below 16 °C. The release of phosphorus was greater from the anoxic sediments and increased with temperature with both the anoxic (Q_{10} 2.9 ± 0.5) and oxic (Q_{10} 1.9 ± 0.1) flows. It is probable that the temperature of boreal lakes and the associated oxygen deficiency will increase as the climate becomes warmer. Our experiments showed that this change would increase the global warming potential of greenhouse gases released from sediments of eutrophic lakes predominately attributable to the increase in the CH_4 production. Furthermore, warming would also accelerate the eutrophication of lakes by increasing release of phosphorus and mineral nitrogen from sediments, which further enhance CH_4 production in sediments.

Introduction

Temperature and oxygen are among the most important factors regulating microbiological processes in sediments, processes which result in gas production and nutrient release (Klump and Martens 1989). The important greenhouse gases, methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O), are produced in aerobic and/or anaerobic microbial processes in sediment and water. In boreal regions, there is a large seasonal variation in sediment temperature as much as twenty Celsius degrees, and also the O_2 concentration in hypolimnia varies greatly. When evaluating the annual greenhouse gas and nutrient releases from sediments of boreal lakes, and the possible effects of global warming on the release rates, the gas and nutrient dynamics have to be studied at a variety of temperature and O_2 conditions.

Gas fluxes are closely related to the trophic state of lakes. Any increase in the availability of nutrients will enhance primary production, which then provides more substrates for heterotrophic microflora. Microbial decomposition of organic matter produces gases and mobilizes nutrients from organic matter (Søndergaard et al. 1990). Microbial oxygen consumption lowers the redox potential in sediments causing release of Fe-bound inorganic phosphorus (e.g. Holdren Jr and Armstrong (1980)). Release of nutrients from sediments will further accelerate eutrophication (internal nutrient loading) and gas production in sediments.

To our knowledge, there are no studies where the release of the major greenhouse gases, CO_2, CH_4 and N_2O, and nutrient dynamics have been simultaneously measured between sediment and water in a variety of temperature and oxygen conditions. In sediments, the mineralization rate of organic carbon is usually determined by the consumption of electron acceptors like O_2, NO_3^-, and SO_4^{2-} (see review by Capone and Kiene (1988)), only rarely have the production of gaseous end products of mineralization, CO_2 and CH_4, been measured (Jones and Simon 1980; den Heyer and Kalff 1998; Kelley et al. 1990; Kuivila and Murray 1984). The effect of temperature on methanogenesis in anaerobic sediment samples is well known (Kelly and Chynoweth 1981; Zeikus and Winfrey 1976). However, the net flux of CH_4 is the difference between its production and consumption. There are several studies on nitrogen cycling in freshwater sediments (see review by Seitzinger (1988)), but little is known about N_2O dynamics in sediments of boreal lakes under different temperatures and oxygen conditions.

Global warming can change not only the temperature but also the O_2 conditions in sediment and water of boreal lakes. The gas and nutrient dynamics would reflect these changes. We describe here the effects of changes in temperature and oxygen on gas and nutrient dynamics in sediments of a mid-boreal freshwater lake. We evaluate how the global warming potential of the major greenhouse gases, CO_2, CH_4 and N_2O, produced in sediments would change with an increase in temperature. The experiments were carried out with intact sediment cores in a laboratory microcosm allowing good control of the experimental conditions. Sediments were incubated under oxic and anoxic water flow in a temperature range relevant for freshwater sediments in the boreal environment.

Materials and methods

Study lake and sampling

Samples were taken from mid-boreal hyper-eutrophic Lake Kevätön (63°6′N, 27°37′E, Finland). This lake was initially eutrophied from sewage in 1930–1975, nowadays agriculture and internal loading are the most important sources of nutrients. Net primary production in Lake Kevätön was on average 590 mg C m^{-2} d^{-1} (in 1998, at the shallow profundal area with depth of 4 m), and the average gross sedimentation rates of phosphorus and nitrogen were 60 and 165 mg m^{-2} d^{-1}, respectively (in 1999). Like most of the lakes in Finland, Lake Kevätön is rather small (area of 4.07 km^2) and shallow (average depth 2.3 m, maximum depth 9 m). In 1997–1998, the temperature in the hypolimnion varied from 2 to 19 °C, and O_2 concentration from 0 to 10.8 mg O_2 l^{-1}.

Six undisturbed sediment cores were taken from a depth of 4 m in August 1998 during autumn overturn. At the sampling time, the temperature in the hypolimnion was 16 °C. Sediments were taken with a Limnos Sediment Sampler (Limnos Ltd, Turku, Finland) directly into the cores (acrylic tube, Ø 94 mm, core height 650 mm, sediment height 350–400 mm), which were incubated later in the laboratory microcosm.

Incubations

The sediment cores were incubated in a laboratory microcosm using a continuous water flow (CWF) technique (Figure 1). The microcosm was placed in a dark, temperature controlled, room. Sediments were incubated at 6, 11, 16, and 23 °C, starting from 23 °C. The incubation time at each temperature was 7 days. Three sediment cores and one control core (core without sediment) were incubated with oxic water flow and three sediment cores and one control core with anoxic water flow.

The test water was bank filtrated and chemically [$Al_2(SO_4)_3$] coagulated lake water from the Kuopio waterworks (2.2 μg tot-P l^{-1}, 12 μg NH_4^+-N l^{-1}, 39 μg NO_2^-+NO_3^--N l^{-1}, 21 mg SO_4^{2-} l^{-1}, 70 μg Mn l^{-1}, < 1 mg Fe l^{-1}, 13 mg Ca l^{-1}, 3 mg org C l^{-1}, pH $\sim$ 6.7). The quality of water in Lake Kevätön varied with time (in 1998: 14–440 μg tot-P l^{-1}, 3–7100 μg NH_4^+-N l^{-1}, 2–310 μg NO_2^-+NO_3^--N l^{-1}, 0.6–7 mg SO_4^{2-} l^{-1}, 0.04–50 mg Fe l^{-1}, 7–17 mg org C l^{-1}, pH 6.6–8.2). Therefore, lake water was not used to omit errors in the experiments. Furthermore, lake water with plenty of algal biomass, should have been filtrated before usage. In the oxic water flow, the water in the reservoir (volume, 30 l) of the microcosm was saturated with air (oxic water, O_2 from 8.5 mg l^{-1} at 23 °C to 10 mg l^{-1} at 6 °C), whereas anoxic water was deoxygenated with N_2 (anoxic water, < 0.5 mg O_2 l^{-1}). Water was pumped from the reservoirs separately over each core (8 water lines, 6 to sediment and 2 to control cores) by a peristaltic pump (Ismatec, BVK-MS/CA8-6). The volume of overlying water in the cores was $\sim$550 ml, and the pumping rate was 50 ml h^{-1}. Overlying water was gently stirred with a rotating magnet to prevent stratification. The incubation core system consisted of a funnel system, which permitted differentiation between the diffusive and ebullited release rates of gases (Figure 1).

Measurements

Fluxes of dissolved methane (CH_4), carbon dioxide (CO_2), and nitrous oxide (N_2O) were measured at each temperature after a four days stabilization period when

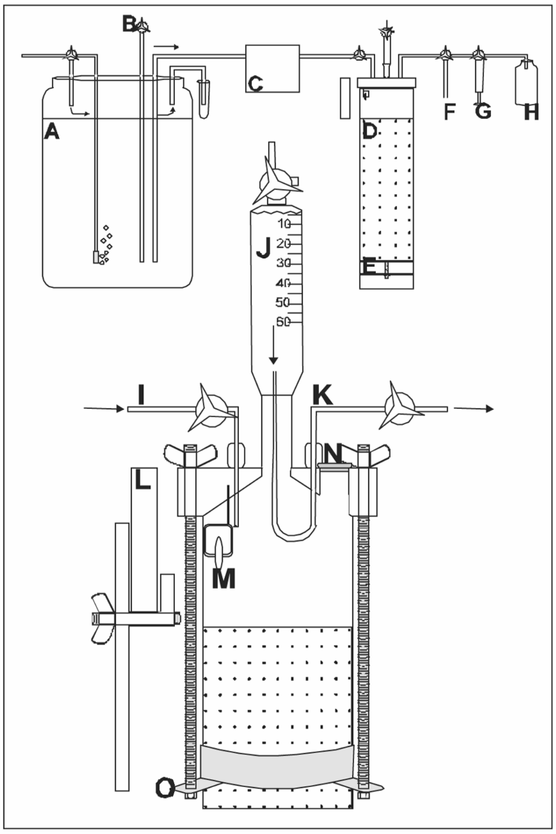

Figure 1. The continuous water flow system (A to H) with a gas and water tight lid (I to O). Components: reservoir (A), sampling outlet for reservoir water (B), peristaltic pump (C), sediment core (D), bottom cap (E), outflow to drain (F), water sampling with a syringe (G), water sampling with a flask (H), inflow (I), gas trap (J), outflow (K), magnetic stirrer (L), rotating magnet (M), port for electrodes (N), removable clamp (O).

steady state was reached. At each temperature, the gas fluxes were measured three times within a period of three days. Fluxes of ammonium (NH_4^+-N), phosphorus (tot-P), nitrite and nitrate ($NO_2^- + NO_3^-$-N), sulphate (SO_4^{2-}) and non-purgeable organic carbon (NPOC) at various temperatures were determined once at the end of the incubations. Water samples (20–30 ml) for dissolved gas analysis were taken by 50 ml syringes equipped with three-way stopcocks, and samples for nutrient analysis were collected in flasks from out-flowing water. The rates of the water flow from the cores were measured in each sampling. The fluxes of dissolved gases (mg or μg m^{-2} d^{-1}) were calculated from the differences in the gas fluxes between the control (no sediment) and sediment cores using flow rates and sediment surface area (69 cm^2). The control core was used to determine both gas concentrations in test water and the possible diffusion of gases through the microcosm materials. The fluxes of nutrients (mg m^{-2} d^{-1}) were calculated from the concentration differences in out-flowing water between the control (no sediment) and sediment cores using flow rates and sediment surface area.

Accumulated bubble gases were collected from the gas traps with syringes at the end of incubations. The volumes of bubbles and the concentrations of their gases were determined. To obtain average ebullited gas flux (mg or μg of m^{-2} d^{-1}) the amount of evolved gas was divided by the incubation time. Some gas from bubbles may re-dissolve (Chanton et al. 1989) increasing the dissolved gas flux and decreasing the ebullited gas flux. However, this does not affect the total gas fluxes.

At the end of the incubations, the O_2 concentrations of overlying water (1 cm above the sediment surface) were measured with an oxygen electrode (Dissolved Oxygen Meter Oxi 330 with Dissolved Oxygen Probe CellOx 325, WTW). Sediment oxygen consumptions (SOC) were calculated during the oxic flow from the difference in the O_2 concentrations of water between the control and sediment cores using the flow rates. Redox potentials in the surface sediments (0.5 cm below the sediment surface), and pH in the overlying water (0.5 cm above the sediment surface) were measured with electrodes (Microprocessor pH meter pH320, WTW, with Hamilton pH electrode and with InLab®501 redox electrode).

Maximal penetration depth of O_2 and the gradient of dissolved O_2 in the sediment-water interface were measured at 6 °C at the end of the experiment using chemical microsensor equipment (product no. 1231, Diamond General Development Corp. USA) and a Clark type needle oxygen electrode (Ø = 0.9 mm, model 768-20R, Diamond General Development Corp. USA). The electrode was positioned with a minimanipulator which had a vertical resolution of 1 mm. The measurement interval was 1 mm starting from 2–4 mm above the sediment surface to the depth in the sediment where dissolved O_2 was depleted.

Analysis

Gas samples, concentrations of bubble gases and dissolved gases in water, were analysed within 24-h from the sampling. The gas concentrations in water were analysed using a headspace equilibration technique (McAuliffe 1971; Jones and Simon 1980). The water samples in syringes were preserved with sulphuric acid (1 ml H_2SO_4, 20% v/v) immediately after the sampling. Water was equilibrated in syringes with added nitrogen (N_2) 30–40 ml by shaking vigorously for 3 minutes. The CH_4, CO_2, and N_2O concentrations were determined with two gas chromatographs (HP 5890 Series II) equipped with a flame ionization (FI) detector for CH_4, a thermal conductivity (TC) detector for CO_2 and CH_4 (> 1000 ppm CH_4), and an electron capture (EC) 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 values from the Lide and Fredrikse (1995).

Nutrients in water were analysed from samples stored at −20 °C. Ammonium was determined photometrically according to the standard SFS 3032 (consistent with standards DS 224, NS 4746, SIS 02 81 34 (SFS Standardization 1976)). Total phosphorus was measured photometrically according to the standard SFS 3026 (consistent with standards DS 292, NS 4725, SS 02 81 27 (SFS Standardization 1986)). Combined nitrite and nitrate were analysed by flow analysis (FIA) and spectrometric detection based on the standard SFS-EN ISO 13395 (SFS Standardization 1997) applied with the Quikchem method 10-107-04-1-B for Lachat Instruments. Non purgeable organic carbon (dissolved C, excluding volatile C-compounds) was analysed with Shimadzu TOC-5000 Analyzer. Sulphate was measured by DIONEX 2010i ion chromatography equipped with a DIONEX Ion Pac® AS4A-SC 4 mm column.

Data processing

Q_{10} values for the fluxes of O_2, CO_2, CH_4, NH_4^+, and tot-P between sediment and water were calculated according to the Arrhenius equation. The Q_{10} values were determined for each sediment core and then the averages were calculated. Organic carbon mineralization rates were calculated as a sum of CO_2 and CH_4 produced (den Heyer and Kalff 1998). Respiratory quotients, the molar ratios of CO_2 production to O_2 consumption, were calculated for the sediments incubated with oxic water (Rich 1975). Global warming potentials (GWP, time horizon 100 yr) for CO_2, CH_4, and N_2O release from the sediments at each temperature were calculated as CO_2 mass equivalents using the coefficients of 21 for CH_4 and 310 for N_2O (IPPC 1996).

The SPSS statistical package was used in statistical analysis. The normal distribution of the gas and nutrient flux data was tested with Kolmogorov-Smirnov Test. Independent variable T-test and correlation analysis (Pearson correlation coefficients, two-tailed significances) were used for the fluxes and environmental variables. Linear regression models (stepwise method) were constructed for gas and nutrient fluxes with temperature, water O_2 concentration and/or redox potential as independent variables.

Results

Oxygen, redox potential and pH

The oxygen concentration and pH in the overlying water, the sediment oxygen consumption (SOC), and redox potential in the surface sediment in various experimental conditions are presented in Table 1. With the anoxic water flow, the O_2 concentration in overlying water was always < 0.1 mg O_2 l^{-1}. With the oxic water flow, the O_2 concentration in overlying water decreased with increasing temperature (Tables 1 and 3). With the oxic flow at 6 °C, O_2 penetrated to a depth of 9 mm. The SOC increased with temperature, with the Q_{10} being 1.5 ± 0.1 (Table 2). In the anoxic sediments, the redox potential did not correlate with temperature, but in the oxic sediments redox potential decreased with temperature (Tables 1 and 3). Redox potentials were positive with the oxic water flow at temperatures from 6 to

Table 1. Oxygen concentration and pH in overlying water, sediment oxygen consumption (SOC), and redox potential in the surface sediments with the oxic and anoxic water flows at different temperatures. Standard errors are presented in parentheses

Water flow	Temp (°C)	O_2 conc[a] (mg O_2 l^{-1})	SOC (mg O_2 m^{-2} d^{-1})	Redox Potential[b] (mV)	pH[c]
Anoxic	6	0 (0.02)**	nd	−120 (8)**	7.6 (0.03)***
	11	0 (0)*	nd	−120 (20)**	7.3 (0.03)***
	16	0 (0)*	nd	−110 (6)	6.8 (0.00)
	23	0 (0.03)*	nd	−130 (7)*	6.4 (0.15)
Oxic	6	6.6 (0.6)	510 (70)	71 (18)	6.8 (0.07)
	11	5.8 (0.6)	600 (80)	27 (8)	6.6 (0.03)
	16	3.9 (0.7)	830 (100)	−55 (23)	6.8 (0.03)
	23	2.0 (0.3)	930 (40)	−78 (9)	6.6 (0.03)

[a] O_2 concentration in overlying water 1 cm above the sediment surface, [b] 0.5 cm below sediment surface, [c] 0.5 cm above sediment surface. Asterisks denote significant differences between the oxic and anoxic flows (*** $p \leqslant 0.001$, ** $p \leqslant 0.001$, * $p \leqslant 0.05$), N = 3, nd = not determined.

Table 2. The Q_{10} values for the gas and nutrient flux rates between sediment and water according to the Arrhenius equation for the temperature range from 6 to 23 °C. Standard errors are presented in parentheses

Fluxes	Q_{10}		p[a]
	oxic	anoxic	
SOC	1.5 (0.1)	nd	–
CO_2	3.2 (0.6)	2.3 (0.4)	0.312
CH_4	nd	2.3 (0.2)	–
(CH_4+CO_2)-C	2.3 (0.4)	3.0 (0.4)	0.318
NH_4^+	nd	2.4 (0.1)	–
Tot-P	1.9 (0.1)	2.9 (0.5)	0.219

[a] probability of the significance in the T-test comparing the Q_{10} values with the oxic and anoxic flows, n = 3.

11 °C. Overlying water pH was generally from 6.4 to 6.8, only the anoxic cores at 6–11 °C were out of this range (Table 1). The slightly higher pH in these anoxic cores could be explained by the higher pH of the test water they received.

Gas fluxes

The CO_2 production correlated positively with temperature and negatively with pH and redox potential (Figure 2a, Table 3). Temperature and sediment redox potentials explained 75% of the variation in the CO_2 fluxes (Table 4). CO_2 was released mainly by diffusion, ebullition was not the source of CO_2. The Q_{10} for the CO_2 production was higher with the oxic flow than with the anoxic flow, but the difference was not significant (Table 2). The respiratory quotients, molar ratios of CO_2

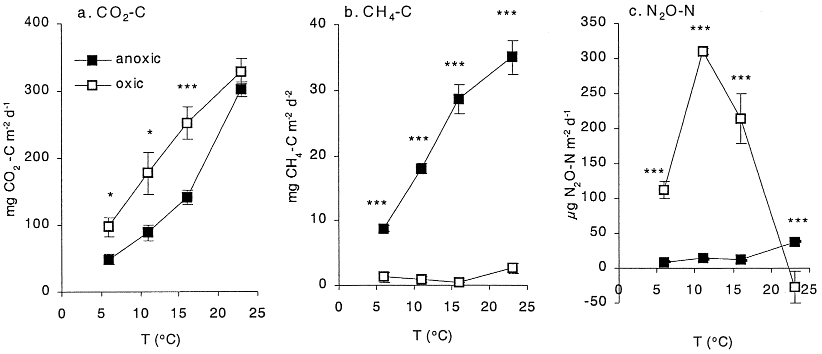

Figure 2. Means and standard error of means (n = 9) of diffusive a) CO_2, b) CH_4, and c) N_2O fluxes from the sediments with the oxic and anoxic water flows at different temperatures. Asterisks denote significant differences between the oxic and anoxic flows (*** $p \leqslant 0.001$, ** $p \leqslant 0.01$, * $p \leqslant 0.05$).

production to O_2 consumption, were 0.5, 0.8, 0.8 and 0.9 at 6, 11, 16 and 23 °C, respectively.

The CH_4 fluxes increased with temperature with the anoxic water flow (Figure 2b, Table 3), Q_{10} being 2.3 ± 0.2 (Table 2). With the oxic flow, CH_4 fluxes were minor; 15, 5, 2 and 7% of those measured with the anoxic flow at 6, 11, 16, 23 °C, respectively. Some CH_4 was released in bubbles at 23 °C from two anoxic (2.4 and 11 mg CH_4 m^{-2} d^{-1}) and from one oxic (5.7 mg CH_4 m^{-2} d^{-1}) replicates. These occasional ebullition fluxes were not included into the average CH_4 fluxes presented in Figure 2b. The dissolved CH_4 in overlying water was not in equilibrium with the CH_4 concentrations in bubbles (Henry's Law). This was shown by the fact that the bubble formation did not increase the concentration of dissolved CH_4. Evidently the rather short retention time (11 h) of water in the cores and the narrow gas traps with water column of 10 cm prevented the increase in the dissolved CH_4 concentration. The dissolved CH_4 flux correlated negatively with the overlying water O_2 concentration and the sediment redox potential (Table 3). The water O_2 concentration explained 46% of the variation in the CH_4 fluxes (Table 4). The CH_4 fluxes showed a negative correlation with the fluxes of NO_2^-+NO_3^- ($r = -0.73$, $p < 0.001$), and positive correlation with the fluxes of organic carbon ($r = 0.71$, $p < 0.001$).

The highest N_2O release occurred from the oxic sediments at 6–16 °C, at 23 °C the sediment did not release N_2O with the oxic flow (Figure 2c). With the anoxic water flow, the N_2O production was low at each temperature. The N_2O production correlated positively with the overlying water O_2 concentration and the sediment redox potential (Table 3), redox and O_2 explained 63% of the variation in the N_2O fluxes (Table 4). The N_2O release correlated also positively with the fluxes of NO_2^-+NO_3^- ($r = 0.73$, $p < 0.001$) and negatively with the NH_4^+ release ($r = -0.58$, $p < 0.01$). Ebullition was not the source of N_2O.

Both with the oxic and anoxic flows, the total gaseous carbon fluxes [(CO_2+CH_4)-C] increased with temperature (Figure 3a). Up to 16 °C, the carbon gas fluxes were slightly greater from the oxic sediments than from the anoxic ones.

Table 3. Pearson correlation coefficients (two tailed significance) between gas and nutrient fluxes and environmental variables

	Oxic flow					Anoxic flow[a]		Both flows			
	Temp	O_2 conc	SOC	redox	CO_2	Temp	CO_2	Temp	O_2 conc	redox	CO_2
O_2 conc	−0.91 ***		−0.97 ***	0.73 **	−0.94 ***	–	–	–		0.89 ***	–
SOC	0.82 ***	−0.97 ***		−0.66 *	0.96 ***	nd	nd	0.82 ***	−0.97 ***	−0.66 *	0.96 ***
redox	−0.90 ***	0.73 **	−0.66 *		−0.60 *	–	–	−0.40 *	0.89 ***		–
pH	–	–	–	–	−0.61 *	−0.97 ***	−0.88 ***	−0.68 ***	–	–	−0.71 ***
Flux											
CO_2	0.78 **	−0.94 ***	0.96 ***	−0.60 *		0.93 ***		0.81 ***	–	–	
CH_4	–	–	–	–	–	0.84 ***	0.85 ***	–	−0.68 ***	−0.60 **	–
N_2O	–	0.62 *	–	–	–	0.85 ***	0.92 ***	–	0.73 ***	0.50 *	–
NH_4^+	0.80 **	−0.94 ***	0.91 ***	–	0.94 ***	0.95 ***	0.97 ***	0.83 ***	−0.55 **	−0.43 *	0.83 ***
Tot-P	–	−0.66 *	0.72 **	–	0.78 **	0.85 ***	0.80 **	0.56 **	−0.56 **	−0.46 *	0.42 *
NO_2^-+NO_3^-	–	0.64 *	−0.63 *	–	−0.69 *	−0.65 *	−0.80 **	–	0.90 ***	0.74 ***	–
NPOC	–	–	–	–	–	–	–	–	−0.65 ***	−0.62 **	–

[a] = O_2 concentration and redox potential do not have significant correlations with gas and nutrient fluxes with the anoxic flow. n = 12 with the oxic and anoxic flows, n = 24 with both flows, except for SOC n = 12, – = no significant correlation, *** $p \leqslant 0.001$, ** $p \leqslant 0.01$, * $p \leqslant 0.05$, nd = not determined.

At 23 °C, both flows showed equal gaseous carbon release. The Q_{10} for the gaseous carbon flux was slightly higher with the anoxic flow than with the oxic flow (Table 2). Global warming potential (GWP) of released gases increased with temperature and was greater with the anoxic sediments than with the oxic sediments at the two highest temperatures studied (Figure 3b).

Nutrient fluxes

The NH_4^+ fluxes from the sediments increased with temperature (Figure 4a). The Q_{10} for the NH_4^+ production in the anoxic sediments was 2.4 ± 0.1 (Table 2). With the oxic flow, NH_4^+ was sometimes consumed at 6 and 11 °C, therefore the Q_{10} value was not determined. From the oxic sediments, the release of NH_4^+ was 31, 37, 37 and 100% of those measured from the anoxic sediments at 6, 11, 16 and 23

Table 4. Linear regression models for predicting gas and nutrient fluxes between sediment and water. Data is from the experiments with both oxic and anoxic flows. Standard errors are presented in parentheses

Flux	Independent variable	Coefficient	Constant	r^2
CO_2–C[a]	temperature[c] redox[d]	16 (2.1) 0.48 (0.18)	−16 (29)	0.75
CH_4–C[a]	O_2 conc[e]	−3.5 (0.81)	20 (2.8)	0.46
N_2O-N[b]	O_2 conc[e] redox[d]	65 (14) −1.2 (0.5)	−140 (65)	0.63
NH_4^+-N[a]	temperature[c] O_2 conc[e] redox[d]	2 190 (230) −5 970 (1110) 170 (41)	13 200 (5680)	0.88
$(NO_2^-+NO_3^-)$-N[a]	O_2 conc[e]	1 760 (180)	−5 080 (640)	0.81
Tot-P[a]	temperature[c] O_2 conc[e]	100 (41) −240 (97)	640 (720)	0.47
NPOC[a]	O_2 conc[e]	−15 (3.9)	34 (13)	0.43

Units: [a] (mg m^{-2} d^{-1}), [b] (μg m^{-2} d^{-1}), [c] (°C), [d] (mV), [e] (mg O_2 l^{-1}).

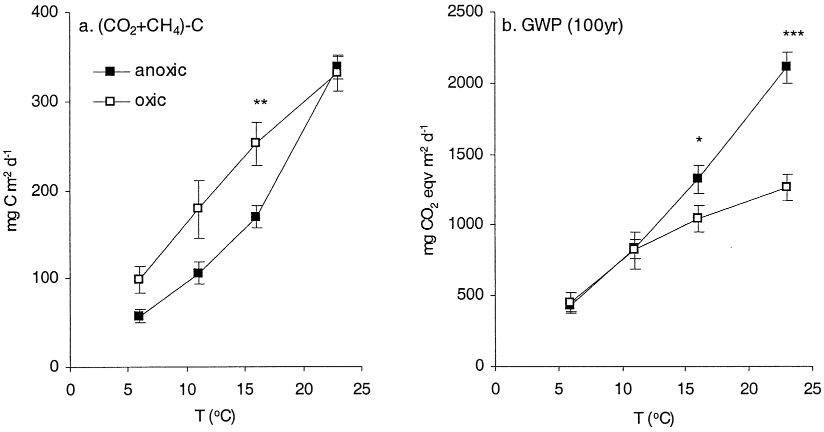

Figure 3. Means and standard error of means (n = 9) of a) gaseous carbon fluxes, and b) GWP of CO_2, CH_4 and N_2O fluxes in CO_2 equivalents (time horizon 100 yr, (IPPC 1996)) from the sediments with the oxic and anoxic water flows at different temperatures. Asterisks denote significant differences between the oxic and anoxic flows (***$p \leqslant 0.001$, ** $p \leqslant 0.01$, * $p \leqslant 0.05$).

°C, respectively. The NH_4^+ flux correlated negatively with the overlying water O_2 concentration and the sediment redox potential, and positively with temperature and

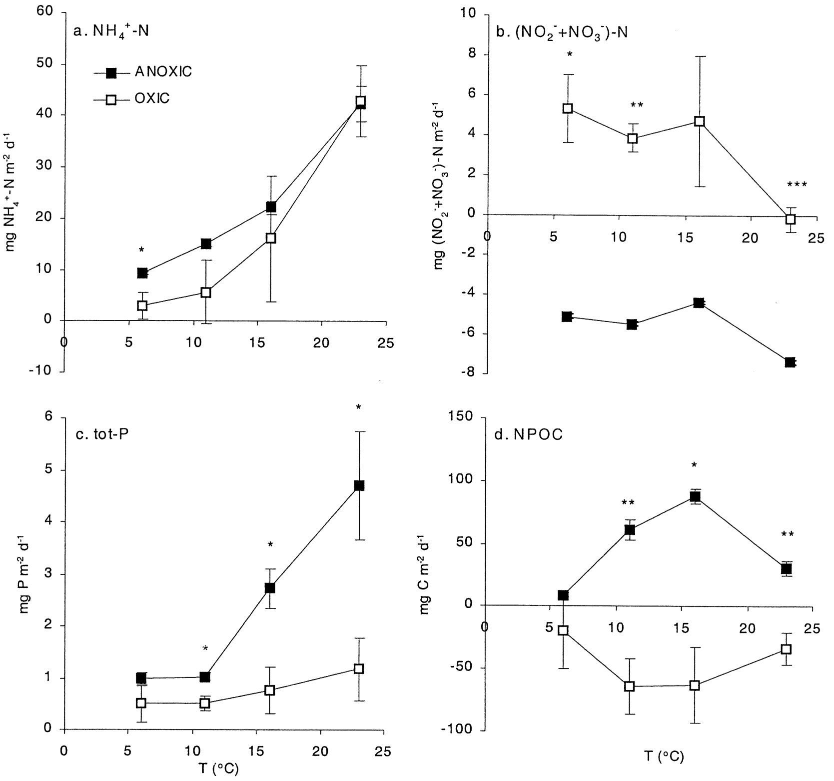

Figure 4. Means and standard error of means (n = 3) of a) NH_4^+, b) NO_2^-+NO_3^-, c) tot-P, d) NPOC fluxes from the sediments with the oxic and anoxic water flows at different temperatures. Asterisks denote significant differences between the oxic and anoxic flows (*** $p \leqslant 0.001$, ** $p \leqslant 0.01$, * $p \leqslant 0.05$).

CO_2 production (Table 3). Temperature, water O_2 concentration and sediment redox potential explained 88% of the variation in the NH_4^+ fluxes (Table 4).

With the oxic water, the sediments were sources of NO_2^-+NO_3^- at 6–16 °C, but at 23 °C the NO_2^-+NO_3^- flux between sediment and water was negligible. The sediments consumed nitrogen oxides during the anoxic flow (Figure 4b). The NO_2^-+NO_3^- flux correlated positively with the overlying water O_2 concentration and with the sediment redox potential (Table 3). The water O_2 concentration explained 81% of the variation in the NO_2^-+NO_3^- fluxes (Table 4). The NO_2^-+NO_3^- flux correlated negatively also with the NH_4^+ release ($r = -0.53$, $p < 0.01$).

Tot-P fluxes correlated positively with temperature and CO_2 production, and negatively with the overlying water O_2 concentration (Figure 4c, Table 3). Temperature and O_2 explained 47% of the variation in the P fluxes (Table 4). Temperature had more extreme effects on the tot-P fluxes in the anoxic conditions (Table 2).

Organic carbon (NPOC) was released from the sediments under the anoxic water flow but was consumed with the oxic flow (Figure 4d). The organic carbon flux correlated negatively with the overlying water O_2 concentration and with the sediment redox potential (Table 3). The water O_2 concentration explained 43% of the variation in the NPOC fluxes (Table 4).

The difference in the SO_4^{2-} concentrations between in- and out-flowing water was minor and the SO_4^{2-} fluxes were not calculated.

Discussion

Microbial activity and carbon dynamics

The measured oxic CO_2 fluxes in this study, 98 mg CO_2-C m^{-2} d^{-1} at 6 °C and 330 mg CO_2-C m^{-2} d^{-1} at 23 °C, are similar to the fluxes of 100 mg CO_2-C m^{-2} d^{-1} at 3.5 °C and 420 mg CO_2-C m^{-2} d^{-1} at 23 °C measured by Kelley et al. (1990) from the vegetated river sediments in North Carolina, USA. In this study, the availability of O_2 was an important factor affecting the degradation pathways. Enhanced O_2 consumption at high temperatures leads to O_2 deficiency in sediments restricting aerobic mineralization. Therefore this kind of experiment with intact sediments and oxic overlying water allows the determination of 'apparent' Q_{10} value for CO_2 production because the effect of O_2 availability is included within the temperature response. The apparent Q_{10} values for CO_2 production shown in Table 3 are the averages calculated for temperature range from 6 to 23 °C. In fact, there was an anomaly in the Q_{10} values calculated for different the temperature ranges in the experiments with the oxic water flow. Calculated Q_{10} values for the CO_2 production at temperature ranges of 6–11, 11–16, and 16–23 °C showed the maximum Q_{10} of 4.2 ± 1.1 at temperatures occurring at 6 to 11 °C, at this temperature range the O_2 concentration in overlying water was at its highest. The Q_{10} was lowest, 2.1 ± 0.3, in temperature range from 16 to 23 °C. At 23 °C, the CO_2 production was almost equal in sediments with oxic and anoxic water flows as a result of the high O_2 consumption creating anaerobiosis in the whole sediment profile, also in the uppermost sediment. The CO_2 release is the difference between those microbial processes producing and those processes consuming CO_2. With the oxic water flow, CO_2 can be produced in sediments by both aerobic and anaerobic carbon mineralization processes, but in totally anoxic sediments CO_2 is produced only in anaerobic processes. The CO_2 can be consumed in oxic conditions in chemolithothrophic processes like in nitrification (Rich 1975) and in anoxic conditions CO_2 can be reduced to CH_4 in methanogenesis and to acetate in homoacetogenesis (e.g. Schulz and Conrad (1996)). The apparent Q_{10} values of 3.2 and 2.3 in the oxic and anoxic sediments determined in this study are close to the Q_{10} values of 2 to 2.9 for CO_2 production in boreal peat soils (Silvola et al. 1996).

Similarly to the Q_{10} of CO_2 production, the Q_{10} for O_2 consumption is also an 'apparent' value. At high temperatures, the solubility of O_2 in water is low and microbial activity is high leading to O_2 deficiency in overlying water. Therefore, in our experiment the O_2 concentration in overlying water was not constant at various temperatures and the measured SOCs do not represent the maximal SOCs expressed usually as sediment O_2 demand (SOD). The maximal Q_{10} value of 2.8 ± 0.14 for SOC was calculated at 11–16 °C and the minimum of 1.6 ± 0.1 at 16–23 °C. The apparent mean Q_{10} 1.5 (± 0.1) for the whole temperature range of 6–23 °C is probably an underestimate, being lower than the SOD of 1.65–2.75 (at 0–21 °C) determined by Jensen and Andersen (1992) for the undisturbed sediments of shallow eutrophic lakes in Denmark.

At 23 °C, molar CO_2 production and O_2 consumption were equal, which implies that aerobic respiration was the main sink for O_2. At lower temperatures ($\leqslant$ 16 °C), more O_2 was consumed than CO_2 was produced. This indicates that in addition to aerobic organic carbon mineralization, O_2 was also consumed in chemolithothrophic microbial processes e.g. in nitrification (shown as a formation of NO_2^- and NO_3^- $\leqslant$ 16 °C), where CO_2 is consumed (Rich 1975). Another explanation for the low (<1) ratio of CO_2 production to O_2 consumption is that O_2 was used in CH_4 oxidation, where 1.6 moles of O_2 is consumed in the production of 1 mole of CO_2 (Joergensen and Degn 1983). The CO_2 could also have been consumed in homoacetogenesis. Schulz and Conrad (1996) found that at low sediment temperatures (4 °C) homoacetogenesis dominated over the methanogenesis from H_2/CO_2.

The optimum temperature for the CH_4 production in aquatic sediments has reported to be between 35 and 42 °C (Zeikus and Winfrey 1976), which is considerably higher than *in situ* temperatures in boreal lakes. We determined the Q_{10} values for the CH_4 production using intact anoxic sediment cores, whereas the published Q_{10} values for sediments have been carried out with sediment slurry incubations. Our Q_{10} value, 2.3 (± 0.2), for the rate of the CH_4 production in anoxic intact sediments is similar to the average Q_{10} of 2.4 found by Kelly and Chynoweth (1981) for the profundal sediments of Michigan lakes, and slightly lower than the Q_{10} of 2.8 reported by Thebrath et al. (1993) for littoral sediments from Lake Constance. However, much more severe effects of temperature on CH_4 production have been reported in temperate and subarctic peat soils, where the Q_{10} of the CH_4 production varied from 5.3 to 16 in slurry incubation (Dunfield et al. 1993). These results indicate that the CH_4 production in profundal sediments is affected less by changes in temperature than the CH_4 production in northern peat soils.

With the oxic flow, the dissolved CH_4 fluxes were negligible. This is because methanogenesis in the uppermost oxygenated sediments is inhibited by O_2 and part of the CH_4 diffused from the deeper anoxic sediment layers is oxidized in sediment surface (e.g. Frenzel et al. (1990); Sweerts et al. (1991)). In our sediments, aerobic microbial processes did exists in the uppermost 9 mm sediment layer (O_2 penetration depth at 6 °C). Also the greatest CH_4 oxidation potentials were found in the top 0–1 cm sediment layer (unpublished data). Apparently, the redox potential had to be below −100 mV in the uppermost sediment to allow extensive CH_4 release (see Figure 1a and Table 1).

An increase in the temperature increased carbon mineralization in the sediments, i.e. the sum of produced CH_4 and CO_2. Organic carbon mineralization rates from 57 to 340 mg (CH_4+CO_2)-C m^{-2} d^{-1} at 6 and 23 °C were similar to the rates of 90 and 290 mg (CH_4+CO_2)-C m^{-2} d^{-1} at 6 and 23 °C found by den Heyer and Kalff (1998) for littoral and profundal sediments of nine Quebec lakes. Up to temperatures of 16 °C, the oxic flow showed a somewhat higher carbon degradation rate than the anoxic flow, at 16 °C the difference was statistically significant. At 23 °C, the decomposition rates with the oxic and anoxic flows were equal indicative of O_2 depletion also in the sediment profile with the oxic flow. This was also shown by the disappearance of NO_2^-+NO_3^- from the oxic water. Our results agree with the conclusion of Wellsbury et al. (1996) on the importance of anaerobic organic carbon mineralization in freshwater sediments. Most of the carbon was released also from anoxic sediments as CO_2-C, the CH_4-C production was a maximum of 17% of the total gaseous carbon flux. Several fermentation processes as well as sulphate reduction can produce CO_2. According to Lovley and Klug (1986) sulphate reduction has importance in organic matter degradation, when the SO_4^{2-} concentration exceeds 5.8 mg SO_4^{2-} l^{-1} (60 μM). In our experiments, we used SO_4^{2-} concentration of 20 mg SO_4^{2-} l^{-1}, a concentration commonly found in freshwater lakes. However, the experimental concentrations did not allow us to reveal the possible role of sulphate reduction in the CO_2 production. The difference of < 1 mg SO_4^{2-} l^{-1} in SO_4^{2-} concentrations in out-flowing water between the control and sediment cores was negligible compared to the overlying water SO_4^{2-} concentration of 20 mg SO_4^{2-} l^{-1}. The reduction of 1 mg l^{-1} in SO_4^{2-} with these experimental conditions corresponded to the sulphate reduction rate of 170 mg SO_4^{2-} m^{-2} d^{-1}, which would yield 130 mg CO_2-C mg m^{-2} d^{-1}.

Dissolved organic carbon (NPOC) release rates of 7–88 mg C m^{-2} d^{-1} with the anoxic flow were much lower than the gaseous carbon production. Thus carbon was released from these sediments mainly as gaseous compounds. With the oxic flow, dissolved organic carbon was consumed from the overlying water probably as a result of oxidation in the uppermost sediments.

Nitrogen dynamics

The Q_{10} value of 2.4 (± 0.2) for the NH_4^+ production in the anoxic sediments was similar to the average values of 2.1–2.4 found by van Luijn et al. (1999) for anoxic muddy and sandy sediments in a eutrophic lake in the Netherlands. The NH_4^+ produced will be oxidized via nitrification to NO_2^- and NO_3^- if O_2 is available. Nitrification would be a reason for the lower NH_4^+ fluxes with the oxic flow. The nitrogen oxides, NO_2^-+NO_3^-, were produced in the oxic sediments at temperatures below 16 °C. At low temperatures, the higher O_2 concentration in the overlying water allowed O_2 to penetrate deeper into the sediments. Thus nitrification could have taken place deeper in the sediments producing there more NO_2^- and NO_3^-. At high temperatures, the lack of O_2 in sediments limited oxidation of NH_4^+ to NO_2^- and NO_3^-. If one assumes that the difference in the NH_4^+ and CH_4 fluxes between the anoxic and oxic flows is mainly due to oxidation (van Luijn et al. 1999), then between 0–69% of NH_4^+ and 85–98% of CH_4 was oxidized. These results show that methane oxidising bacteria can compete successfully with nitrifying bacteria for O_2, as described by Sweerts et al. (1991); van Luijn et al. (1999).

In anoxic conditions, NO_2^- and NO_3^- are reduced in denitrification to N_2O and N_2. If NO_3^- and NO_2^- are reduced effectively to N_2, then the formation of N_2O remains insignificant. Here N_2O was released from the sediments only with the oxic flow at the temperatures showing production of NO_2^- and NO_3^-, i.e. from 6 to 16 °C. This shows that in anaerobic conditions, N_2O production was limited by the lack of nitrification and availability of NO_3^- needed in denitrification. N_2O is produced both in nitrification and denitrification processes (e.g., Seitzinger (1988)). The differentiation between these two processes cannot be done here.

Phosphorus dynamics

In our sediments, phosphorus (P) release from the sediments increased with increasing CO_2 production. It has been proposed that temperature-dependent release of P is clearly associated with the microbial activity in the sediments (Holdren Jr and Armstrong 1980; Søndergaard et al. 1990). Søndergaard et al. (1990) emphasised that microbial activity would release P from decomposing organic matter. Gärcher and Meyer (1993) demonstrated that sediment bacteria can act as a source or sink for phosphate due to hydrolysation or formation of polyphosphates depending on redox conditions in sediments. According to Holdren Jr and Armstrong (1980), the increase in microbial activity with increasing temperature results in O_2 depletion and lower redox potentials, following reduction of Fe (III) to Fe (II) and release of P from iron(hydr)oxyphosphate precipitate. Here the oxic conditions lead to considerable reduction in the release of P from the sediments at all temperatures.

The Q_{10} value of 1.9 for the phosphorus release during the oxic flow was much lower than the value of 2.9 when there was anoxic flow. Both of these values are lower than the values of 3.5 to 6.8 found by Jensen and Andersen (1992) for aerobic surface sediment in shallow eutrophic lakes in Denmark. In the oxic sediment, temperature did not correlate with the P fluxes. It is likely that with the oxic flow oxidation reactions in the uppermost sediment layer, especially the amount of Fe (III) predominantly regulated the phosphorus release. However, in the anoxic sediments when Fe (III) was reduced to Fe (II) and could not bind P, the rate of P release was more dependent on organic matter mineralization regulated by temperature. The regression model stressed the importance of both O_2 and temperature in P dynamics.

Global warming potential (GWP) of gases released from the sediments

Our results show that in freshwater sediments of eutrophic lakes CH_4 has importance in the global warming potential of gases released from sediments. Due to the high CH_4 production during the anoxic flow, the GWP of gases was higher than that of the gases released from the sediments with the oxic flow. Since the GWP of CH_4 is 21 times the GWP of CO_2, the changes in CH_4 fluxes are of major importance in any assessment of GWP of these gases. The N_2O production was low compared to the production rates of CH_4 and CO_2, and did not have any major contribution to the total GWP.

Global warming and lake sediments

Climatic warming would increase the water temperature and cause a longer duration of summer stratification periods and longer ice-free seasons in the boreal lakes (Schindler et al. 1990). Longer stratification and anoxic conditions during summer months would enhance oxygen deficiency and release of CH_4, NH_4^+, and P from sediments. In contrast to the summer stratification, winter stratification would become shorter causing better oxygen status in the hypolimnia during winter (Fang and Stefan 2000). In the boreal region, air temperature has been modelled as increasing by 1–3 °C from year 1860 up to 2050 (Mitchell et al. 1995). The same increase in temperature of hypolimnia would increase sediment O_2 consumption by 5–15%, CO_2 production by 13–66%, and CH_4 production in anoxic sediments by 13–39%. This elevated carbon gas production can probably be maintained, since primary production, on average 590 mg C m^{-2} d^{-1} in the shallow profundal of Lake Kevätön, can provide enough organic carbon for mineralization (340 mg C m^{-2} d^{-1} at 23 °C). Warming of 1–3 °C would increase the release of NH_4^+ by 14–42% from anoxic sediments, and the release of tot-P by 9–57%. The high sedimentation of nutrients, 60 mg P m^{-2} d^{-1} and 165 mg N m^{-2} d^{-1}, in Lake Kevätön can fuel the increased nutrient release rates at higher temperatures. As a result of the increase in nutrient release from the sediments and the associated increase in primary production and oxygen deficiency, the CH_4 emissions would increase more than predicted by the temperature increase alone.

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