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Potential springtime greenhouse gas emissions from a small southern boreal lake (Keihäsjärvi, Finland)

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Concentrations of dissolved greenhouse gases (GHGs) methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O) were investigated in a small southern boreal lake during the late winter ice-cover in 2000, 2001 and 2002. Potential emissions of these gases to the atmosphere at ice melt were estimated from their concentration profiles in the water column under ice during winter. The concentrations of CH_4, CO_2 and N_2O increased with the depth, but the year-to-year variations were low. Carbon dioxide contributed to 99% of the global warming potential (GWP) of the total springtime GHG emissions which ranged from 103 to 128 g CO_2-equivalents m^{-2}. The results indicated that these kinds of northern mesotrophic lakes are not important sources of CH_4 and N_2O, but are probably significant sources of CO_2.

Introduction

More complete knowledge of global carbon and nitrogen cycles has become essential, because increases in the concentrations of important atmospheric greenhouse gases (GHGs), like methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O), are changing the Earth's climate (Houghton *et al.* 2001). Northern terrestrial ecosystems play a crucial role in global GHG budgets due to their large areal coverage and susceptibility to climatic changes (e.g., Chapin *et al.* 2000). However, in northern landscapes, lakes are also abundant, thus the lake–atmosphere GHG fluxes and their environmental determinants need to be assessed for a better understanding of the regional GHG balances (e.g., Huttunen *et al.* 2003a).

The within-lake production and consumption of GHGs can largely reflect inputs of phosphorus (P), nitrogen (N) and carbon (C) from diffuse terrestrial sources in the catchments. This allochthonous loading depends on several factors, such as ecosystem types, land use practices and climate (e.g., Kortelainen & Saukkonen 1998, Mattsson *et al.* 2003). Lake CO_2 saturation and CO_2 emissions to the atmosphere increase with increasing inputs of allochthonous organic and/or inorganic carbon (Cole *et al.* 1994, Hope *et al.* 1996, Kortelainen *et al.* 2000, Striegl *et al.* 2001, Huttunen *et al.* 2003a, Sobek *et al.* 2003). Northern lakes are typically supersaturated with CO_2 with respect to atmospheric equilibrium, because respiration generally exceeds gross primary production in the lakes (Cole 1999). The nutrient-enrichment of lakes and associated oxygen depletion in the water column and sediment can promote lake-atmosphere CH_4 emissions (Michmerhuizen *et al.* 1996, Liikanen 2002, Huttunen *et al.* 2001, 2003a, 2003b). Organic, anoxic sediments favour anaerobic CH_4 production, whereas aerobic CH_4 oxidation can be limited in oxygen deficient conditions (Liikanen 2002). Nitrous oxide is produced in lakes during nitrification and denitrification processes and its saturation depends largely on eutrophication and availability of oxygen and nitrate (Liikanen 2002). Thus, changes in the water quality of lakes may be further reflected in the lake GHG balances.

Since there are still limited data on the winter GHG dynamics in northern lakes, this study was conducted to determine the springtime CO_2, CH_4 and N_2O concentration profiles in a small boreal lake. Determination of lake GHG contents in late winter integrates the GHG production and consumption in the lake over the whole ice-covered period because in winter the lake-atmosphere gas exchange is prevented by ice (e.g., Striegl *et al.* 2001). Thus, measurements of the GHG storages accumulated in the water column of the lake made it possible to estimate the potential GHG emissions from the lake at the spring ice melt. Water quality was also monitored allowing comparison with some previous studies on the spring GHG emissions from other northern lake ecosystems.

Material and methods

Study site

Measurements were conducted in Keihäsjärvi (61°54´N, 28°04´E), a lake in the southern boreal zone of Finland. Keihäsjärvi has a maximum depth of 10–11 m, a surface area of 0.23 km^2 and a catchment area of 2.56 km^2. Forests on mineral soils, forests on peat soils, surface waters and agricultural land cover 80.0%, 5.7%, 7.2% and 7.0% of the catchment area, respectively. A forest area of 13.5 ha close to the lake margin, dominated by *Picea abies* Karst., *Pinus sylvestris* L. and *Betula* spp., was logged in March 2000. An area of 9.5 ha was clear-cut and 4 ha harvested. The annual long-term (1971–2000) precipitation in the area is 613 mm and the mean annual temperature 3.4 °C (Finnish Meteorological Institute 2002).

Sampling and analyses

Sampling was conducted at the deepest point of the lake during the late winter ice cover, on 26 March 2000, 1 April 2001 and 15 April 2002. The samples were taken with a Ruttner-type Limnos water sampler (Limnos Ltd., Turku, Finland) through a hole drilled in the ice. The samples for water colour and the concentrations of total N (N_{TOT}), total P (P_{TOT}), ammonium N (NH_4-N) and nitrite and nitrate N [(NO_2+NO_3)-N] were taken from three depths: (i) 1 m below the water (and ice) surface, (ii) middle of the water column and (iii) 1 m above the bottom sediment. Samples for dissolved oxygen (O_2) and pH were obtained at 1–2-m depth intervals by overfilling glass sampling bottles without creating air bubbles in the water. Plastic bottles were used for other water quality analyses. Water quality characteristics were analysed in the laboratory of the North Savo Regional Environment Centre (Kuopio, Finland) using standard methods (the Finnish Standard Association SFS, Helsinki, Finland) given in Huttunen *et al.* (2001). Water temperature was measured in the field with a thermometer attached to the water sampler.

The sampling and analysis of dissolved GHGs in the water column followed the procedures described in Huttunen *et al.* (2001). Water samples for measurements of dissolved inorganic carbon (DIC, i.e. $\sum CO_2$ = free CO_2 + carbonate- and bicarbonate-CO_2), CH_4 and N_2O were collected at 1-m depth intervals from a depth of 1 m below the water surface down to a depth of 1 m above the sediment, as well as from a depth of 0.5 m above the sediment. In spring 2001, samples for the dissolved gases were taken in duplicate (two separate depth profiles). The samples were withdrawn from the Limnos-sampler into 50-ml polypropylene syringes (Terumo Europe, Belgium) equipped with three-way stopcocks (Codan Steritex, Denmark). The samples were acidified immediately in the field with sulphuric acid (1 ml H_2SO_4, 20% v/v) for preservation and for the measurement of DIC. The gas concentrations were quantified with a headspace equilibrium technique in the laboratory (University of Kuopio, Finland) within 24 h of sampling. Nitrogen-filled (30 ml of water + 30 ml of N_2) syringes were equilibrated by shaking for 3 minutes, after which the syringe headspace GHG concentrations were analysed by gas chromatography. The concentrations of dissolved GHGs in the samples were calculated from the measured headspace gas concentrations using Henry's law. The CO_2 concentrations *in situ* were calculated from the DIC based on actual water temperature and pH (for methods *see* Huttunen *et al.* 2001).

Calculation of potential GHG emissions at spring ice melt

The excess GHG storages accumulated in the water column under ice were calculated by subtracting the equilibrium GHG contents (calculated from the concentrations in water in equilibrium with the atmosphere) from the measured GHG contents at the different depths. The potential GHG emissions during the spring overturn after ice melt were calculated by summarizing the excess GHG storages at the different depths. Global warming potentials (GWP) were calculated for the spring GHG emissions in CO_2 equivalents (CO_2-e) by multiplying the emissions by their GWP values: 1 for CO_2, 23 for CH_4 and 296 for N_2O (100 yr time horizon) (Houghton *et al.* 2001).

Results and discussion

Water quality characteristics

The year-to-year variation in the water quality characteristics in Keihäsjärvi is shown in Table 1. The mean water colour and the mean concentrations of (NO_2 + NO_3)-N and N_{TOT} were highest in 2001, whereas P_{TOT} showed the highest mean value in 2002. According to the P_{TOT} and N_{TOT} concentrations Keihäsjärvi was mesotrophic. Most of the inorganic N in Keihäsjärvi was in the oxidised form, the (NO_2 + NO_3)-N concentration varied from 96 to 210 μg l^{-1}, whereas the NH_4-N was mostly below the detection limit (< 5 μg l^{-1}). The water pH varied only slightly during the study, from 6.2 to 6.8. The O_2 and water temperature profiles are described below.

GHG concentrations and potential GHG emissions at spring ice melt

The depth profiles of dissolved GHGs and DIC in Keihäsjärvi varied only slightly between the samplings (Fig. 1a–d). The CH_4 concentration was up to 1390 nmol l^{-1} near the sediment and varied from undetectable (< 8 nmol l^{-1}) to 88 nmol l^{-1} in the upper water column (Fig. 1a). The concentrations of DIC, CO_2 and N_2O increased with increasing sampling depth (Fig. 1b–d), whereas the dissolved O_2 decreased with depth to as low as 0.8 mg l^{-1} near the sediment (Fig. 1e). Water temperatures were somewhat lower in spring 2001 than in 2000 and 2002 (Fig. 1f).

The total global warming potential (GWP) of springtime GHG emissions from Keihäsjärvi, representing maximum GHG emissions from the deepest point of the lake if the entire excess gas storage was released to the atmosphere at the ice melt, varied from 103 to 128 g CO_2-e m^{-2} (Table 2). Carbon dioxide contributed to the majority (99%) of the total GWP of the springtime emissions, whereas the GWPs of the CH_4 and N_2O emissions were negligible (Table 2). In contrast to the present study, large amounts of dissolved CH_4 are accumulated in some northern lakes during winter, suggesting high episodic CH_4 emissions to the atmosphere at the ice melt (Michmerhuizen *et al.* 1996, Kortelainen *et al.* 2000, Huttunen *et al.* 2001, 2003a, 2003b). For example, in the highly eutrophied Lake Kevätön in eastern Finland, CH_4 concentrations were as high as 587 000 nmol l^{-1} in the hypolimnion during late winter stratification (Huttunen *et al.* 2001), attributable to highly O_2 depleted conditions in the hypolimnion and sediment (Huttunen *et al.* 2001, 2003a, Liikanen 2002). The potential spring CH_4 emissions from the deepest point of Lake Kevätön were 15.7 and 22.2 g m^{-2} in 1997 and 1999, respectively (Huttunen *et al.* 2001). When the CH_4 storage in Lake Kevätön was integrated over the entire lake area, the emission was 0.26 g m^{-2} (in 1999) (Huttunen *et al.* 2003a), which also was higher than the CH_4 emissions in the present study (Table 2). In highly eutrophied

Lake Postilampi in eastern Finland, the springtime CH_4 emissions were estimated at 3.6–7.9 g m^{-2} (Huttunen *et al.* 2003b). In comparison, in 19 north-temperate lakes in Minnesota and Wisconsin, USA, the potential spring CH_4 efflux ranged from 0.006 to 2.97 g m^{-2}, depending on the presence of soft littoral sediments (Michmerhuizen *et al.* 1996). In mesotrophic Keihäsjärvi,

Table 1. Water quality characteristics in Keihäsjärvi. Water samples were taken in March/April in 2000, 2001 and 2002 at the deepest point of the lake at depths of 1 m below the water surface (surface), middle of the water column (middle) and 1 m above the sediment (bottom). ND = not defined.

Variable	Layer	2000	2001	2002	Mean 2000–2002	SD 2000–2002
Colour	surface	30	60	50	47	15
(mg l^{-1} Pt)	middle	35	60	50	48	13
	bottom	60	100	80	80	20
	Mean	42	73	60		
	SD	16	23	17		
pH	surface	6.8	6.5	6.4	6.6	0.2
	middle	6.4	6.3	6.4	6.4	0.1
	bottom	6.3	6.2	6.2	6.2	0.1
	Mean	6.5	6.3	6.3		
	SD	0.3	0.2	0.1		
NH_4-N	surface	< 5	< 5	< 5	< 5	ND
(µg l^{-1})	middle	< 5	< 5	< 5	< 5	ND
	bottom	8	< 5	8	ND	ND
	Mean	ND	ND	ND		
	SD	ND	ND	ND		
$(NO_2 + NO_3)$-N	surface	109	150	96	118	28
(µg l^{-1})	middle	116	150	110	125	22
	bottom	150	210	190	183	31
	Mean	125	170	132		
	SD	22	35	51		
N_{TOT}	surface	397	470	480	449	45
(µg l^{-1})	middle	435	470	440	448	19
	bottom	428	630	620	559	114
	Mean	420	523	513		
	SD	20	92	95		
P_{TOT}	surface	11	12	19	14	4
(µg l^{-1})	middle	12	13	14	13	1
	bottom	19	20	29	23	6
	Mean	14	15	21		
	SD	4	4	8		

Table 2. Potential GHG emissions at the spring ice melt from the deepest point of Keihäsjärvi and global warming potentials of the relevant emissions.

Spring	Potential emission (g m^{-2})			GWP[a] (g CO_2-equivalents m^{-2})			
	CH_4	CO_2	N_2O	CH_4	CO_2	N_2O	Total
2000	0.004	114	0.004	0.081	114	1.050	115
2001	0.004	102	0.003	0.087	102	0.913	103
2002	0.025	127	0.003	0.579	127	0.978	128

[a] GWP = Global warming potential (100 yr time horizon) (Houghton *et al.* 2001).

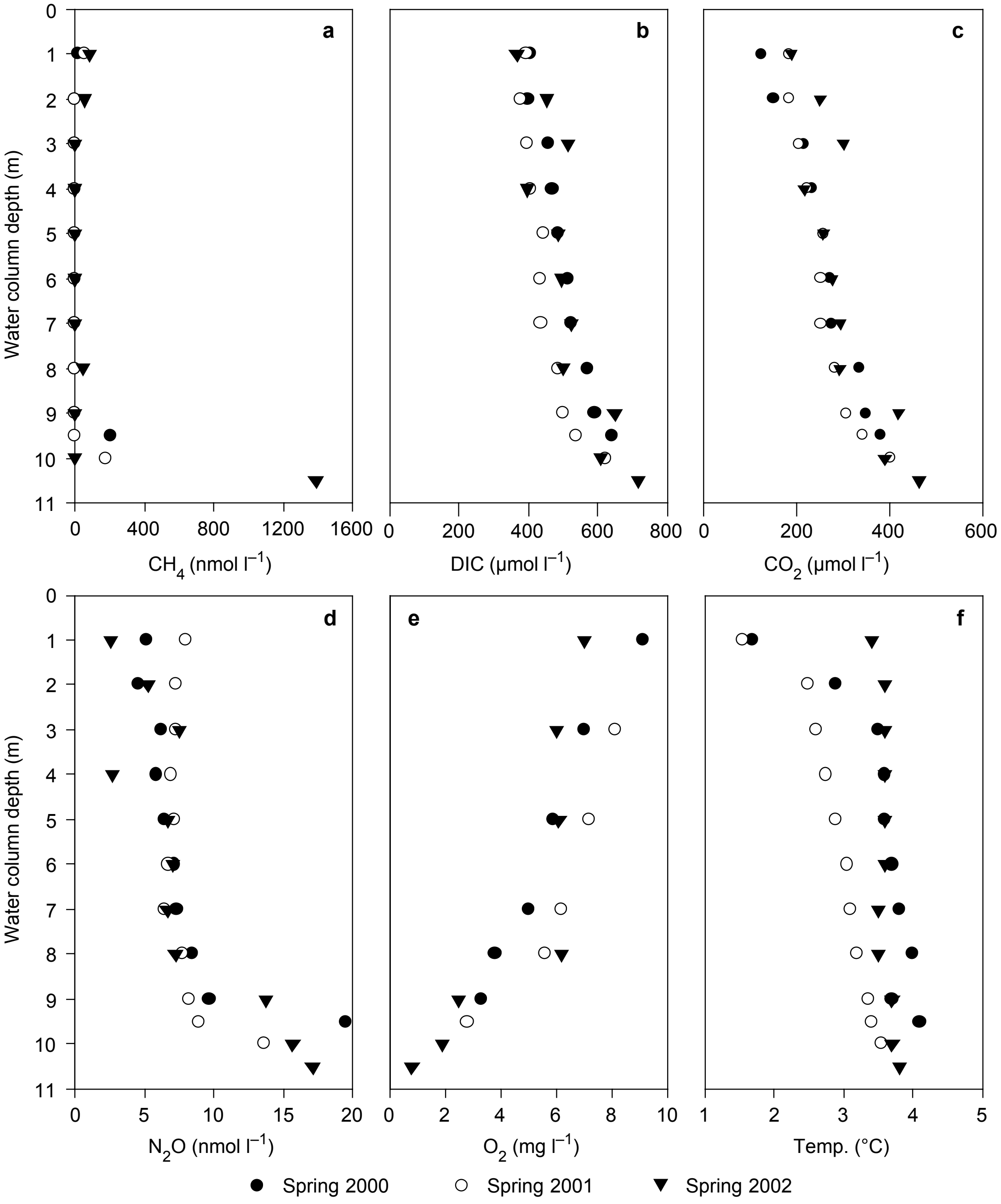

Fig. 1. Concentrations of dissolved (**a**) methane, (**b**) inorganic carbon, (**c**) carbon dioxide, (**d**) nitrous oxide and (**e**) oxygen, and (**f**) temperature in the water column of boreal Keihäsjärvi during the late ice-covered period in March/April 2000, 2001 and 2002.

O_2 was present throughout the water column (Fig. 1e), which could limit the anaerobic CH_4 production in the sediment and/or increase the aerobic CH_4 oxidation in the water column and sediment (e.g., Liikanen 2002). In oligotrophic Mäkijärvi and humic Vehmasjärvi, lakes in eastern Finland, potential springtime CH_4 emissions were 0.011 and 0.026 g m^{-2} in 1999, respectively (Huttunen *et al.* 2003a), corresponding to the emissions in the present study (Table 2). Since the high springtime CH_4 emissions are often associated with highly O_2 depleted conditions typical of shallow eutrophied lakes with soft organic sediments (*see* Huttunen *et al.* 2003b), a major increase in the trophic state and a drop in the hypolimnic oxygenation should precede major increases in the CH_4 emissions from oligotrophic-mesotrophic lakes as Keihäsjärvi here.

The CO_2 concentrations in Keihäsjärvi (Fig. 1c) were similar to mean excess CO_2 concentrations reported for non-oxygenated (250–310 μmol l^{-1}) and artificially oxygenated (280–470 μmol l^{-1}) sites in highly eutrophied lakes Kevätön and Pöljänjärvi, eastern Finland (Huttunen *et al.* 2001). The potential springtime CO_2 emissions at these sites ranged from 112 to 187 g m^{-2} (Huttunen *et al.* 2001), also being similar to the potential CO_2 emissions in Keihäsjärvi (Table 2). When the CO_2 storages were integrated over the surface areas of lakes Kevätön, Vehmasjärvi and Mäkijärvi mentioned above, their springtime CO_2 emissions were 20–37 g m^{-2} (Huttunen *et al.* 2003a), which are lower than the emissions at the deepest points of Keihäsjärvi (Table 2) and Lake Kevätön (*see* above). The CO_2 supersaturation typical of northern lakes has been largely regulated by the inputs of allochthonous carbon from the catchments (e.g., Striegl *et al.* 2001), and a positive relation between lake CO_2 and DOC concentrations is also well documented (Hope *et al.* 1996, Kortelainen *et al.* 2000, Sobek *et al.* 2003). The relatively small variation in the water colour in Keihäsjärvi (Table 1) suggested low variation in the lake DOC, because DOC and colour vary synchronously in northern lake ecosystems (Pace and Cole 2002).

The potential spring N_2O emissions from Keihäsjärvi were low (Table 2) as previously reported for summer N_2O fluxes in temperate and boreal lakes (Mengis *et al.* 1997, Huttunen *et al.* 2003a). Thus, it is unlikely that northern mesotrophic lakes would be significant sources of N_2O at spring ice melt. In conclusion, the potential CH_4 and N_2O emissions were negligible from mesotrophic Keihäsjärvi, which suggests that these gases may have a minor importance in the total springtime GHG emissions from small boreal lakes with low to moderate trophic states. The CO_2 emissions accounted for 99% of the total GWP of the potential spring GHG emissions and were similar to those measured previously from eutrophied lakes. Thus, the wintertime accumulation of CO_2 under ice and its potential release to the atmosphere at spring ice melt should be taken into account when estimating the annual CO_2 balances for northern lakes with different trophic states.

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