

## Fluxes of CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O in hydroelectric reservoirs Lokka and Porttipahta in the northern boreal zone in Finland

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[1] Concentrations and fluxes of greenhouse gases methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), and nitrous oxide (N<sub>2</sub>O) were measured during open water conditions in two hydroelectric reservoirs, Lokka and Porttipahta, in the northern boreal zone in Finland. These reservoirs were located on peat and forest soils and were built in 1967 and 1970, respectively. Over 20 years after their flooding, the reservoirs were still largely supersaturated with dissolved CH<sub>4</sub> and CO<sub>2</sub>. Measured with floating static chambers, the stations in Lokka released more CH<sub>4</sub> (means of 5.3–119 mg m<sup>-2</sup> d<sup>-1</sup>) during the open water periods in 1994 and 1995 than the stations in Porttipahta (means of 2.5–4.8 mg m<sup>-2</sup> d<sup>-1</sup>), measured in 1995. The mean CO<sub>2</sub> emission rates in Lokka (21–133 mg m<sup>-2</sup> h<sup>-1</sup>) and Porttipahta (36–95 mg CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup>) were more similar. The chamber measurements could not detect episodic CH<sub>4</sub> ebullition in Lokka Reservoir, indicated by generally higher CH<sub>4</sub> fluxes (means of 2.6–660 mg m<sup>-2</sup> d<sup>-1</sup>) obtained with bubble gas collectors than with the chambers. The seasonal mean N<sub>2</sub>O fluxes were generally low, ranging from –89 to 270 μg m<sup>-2</sup> d<sup>-1</sup>. There was no clear association between the CH<sub>4</sub> emissions and the bottom type, including mineral soils and old peat deposits. The flooded vegetation, higher nutrient content, and primary production in the water column rather than old peat could account for the higher CH<sub>4</sub> emissions from the stations in Lokka. This conclusion is supported by the high content of modern carbon (C) in methane (percent modern C of 92–104%) that was extracted from the sediment of Lokka. The results suggested that if there is a good long-term availability of phosphorus and nitrogen, the intensive internal C cycle associated with the primary production could maintain high CH<sub>4</sub> and CO<sub>2</sub> production for decades, similar to the situation in eutrophied natural lakes. **INDEX TERMS:** 1615 Global Change: Biogeochemical processes (4805), 1845 Hydrology: Limnology, 1857 Hydrology: Reservoirs (surface); **KEYWORDS:** methane, carbon dioxide, nitrous oxide, reservoir, freshwater, boreal

### 1. Introduction

[2] Beaver ponds in temperate and boreal regions can emit large amounts of greenhouse gases, CH<sub>4</sub> and CO<sub>2</sub>, to the atmosphere because of the intense decomposition of flooded terrestrial organic matter [Ford and Naiman, 1988; Bubier et al., 1993; Yavitt and Fahey, 1994; Roulet et al., 1997]. These greenhouse gases are essential constituents in the C balance of ecosystems and contribute to the atmospheric CH<sub>4</sub> and CO<sub>2</sub> content. In addition to beavers, man has also changed the natural terrestrial C balance by flooding areas to construct different kinds of freshwater reservoirs. Rudd et al. [1993] stated that the reservoirs created for hydropower production in the boreal region

are significant but largely neglected sources of atmospheric CH<sub>4</sub> and CO<sub>2</sub>. This led to a discussion on the importance of the greenhouse gas emissions of reservoirs and hydropower and initiated studies to determine the actual amounts of the emissions [e.g., Gagnon and Chamberland, 1993; Svensson and Ericsson, 1993; Rosa and Schaeffer, 1994; Kelly et al., 1994, 1997; Duchemin et al., 1995, 1999; Fearnside, 1997; Gagnon, 1997; Rosenberg et al., 1997; Weissenberger et al., 1998; Galy-Lacaux et al., 1999; Scott et al., 1999].

[3] Natural northern lakes and wetlands have shown great variations in their CH<sub>4</sub> emissions [e.g., Harriss et al., 1993]. Similarly, variable greenhouse gas fluxes have been measured from reservoirs in the northern regions [Kelly et al., 1994, 1997; Duchemin et al., 1995, 1999; Scott et al., 1999] and tropics [Fearnside, 1997; Galy-Lacaux et al., 1999]. A flooding experiment in a wetland-rich boreal landscape showed that there can be major emissions of CH<sub>4</sub> and CO<sub>2</sub> during the first years following the flooding as a consequence of the decomposition of large amounts of fresh, easily degradable organic matter [Kelly et al., 1997; Scott et al., 1999]. The production of CH<sub>4</sub> may be further favored by anoxic conditions in the sediment [e.g., Hellsten and Väisänen, 1998]. The rate of gas production in a reservoir can be sufficient to float peat mats, especially during the first years after the flooding [Koskeniemi, 1987; Duchemin et al., 1995; Kelly et al., 1997; Scott et al., 1999]. This is considered to reduce over the course of time as the amounts of readily degradable organic matter

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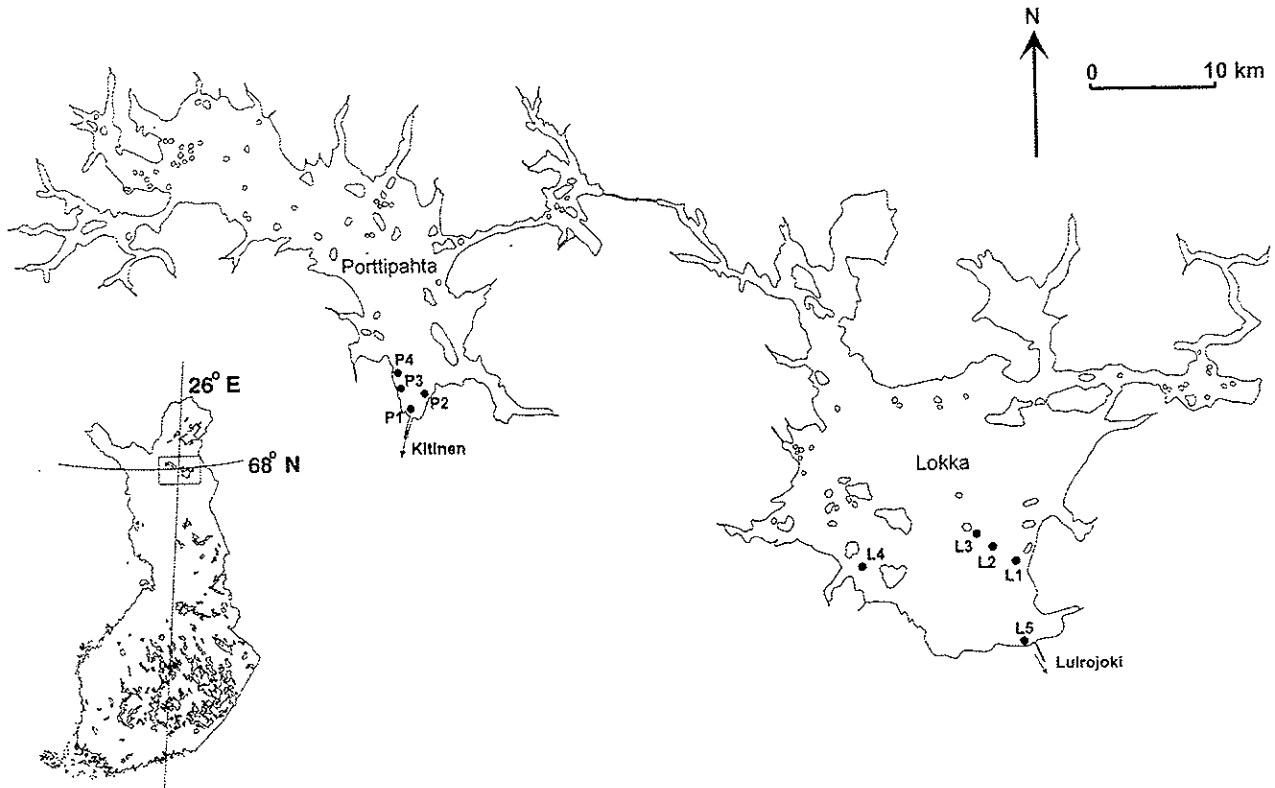
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**Figure 1.** Location of sampling stations in the hydroelectric reservoirs Lokka and Porttipahta in the northern boreal zone in Finland.

decreases. However, the release of  $\text{CH}_4$  and  $\text{CO}_2$  may remain high for some years, even for decades [Rudd *et al.*, 1993; Kelly *et al.*, 1994, 1997; Duchemin *et al.*, 1995, 1999; Weissenberger *et al.*, 1998]. The mechanisms that maintain high emissions are still poorly understood.

[4] We measured the fluxes of  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  in two different hydroelectric reservoirs, Lokka and Porttipahta, in the northern boreal zone in Finland and studied the associations of these fluxes to the physical, chemical, and biological characteristics of the study sites. The reservoirs were dammed for hydro-power over 20 years before our measurements, and they represent "old reservoirs" [e.g., Hellsten *et al.*, 1993].

## 2. Materials and Methods

### 2.1. Site Description

[5] The hydroelectric reservoirs, Lokka and Porttipahta, are located within the watercourse of the Kemijoki River in the northern boreal zone in Finland (Figure 1). In northern Finland the growing season lasts  $\sim 5$  months. Lokka has been flooded for hydropower production since 1967, and Porttipahta has been flooded since 1970. In addition to these reservoirs the Kemijoki River watercourse consists of two regulated natural lakes for a total of 17 hydropower stations whose energy production is  $\sim 4000$   $\text{GWh yr}^{-1}$ . Lokka ( $417 \text{ km}^2$ ) and Porttipahta ( $214 \text{ km}^2$ ) account for over 84% of the reservoir area in Finland and are the largest reservoirs in western Europe (Table 1).

[6] The land under Lokka was mainly peatlands, whereas mineral forest soils dominate the domains of Porttipahta (Tables 1 and 2). The reservoirs also differ in their morphology: Lokka is shallow and lake-like with a long residence time, whereas Portti-

pahta is deeper and more river-like with a short residence time (Table 1). On the basis of both total  $P$  concentration [Hellsten *et al.*, 1993] and primary production (this study), Lokka can be classified as eutrophic, whereas Porttipahta is mesotrophic [Lepistö, 1999]. Summertime sedimentation of organic matter, measured in August 1995, was slightly higher in Lokka ( $20 \text{ g m}^{-2} \text{ d}^{-1}$ ) than in Porttipahta ( $16 \text{ g m}^{-2} \text{ d}^{-1}$ ) [Hellsten and Väisänen, 1998].

[7] Five stations (L1-L5), each with dimensions of  $50 \text{ m} \times 50 \text{ m}$ , were selected in Lokka, and four stations (P1-P4) of the same size were selected in Porttipahta (Figure 1). The stations represented various flooded habitats (Table 2). The depths of the stations ranged from 5.7 to 9.0 m in Lokka and from 7.5 to 32.8 m in Porttipahta. The deepest stations (L2 and P1) were located close to the areas of maximum depth in the reservoirs. The thickness of peat on the bottom varied from 0 (original mineral soil) to 4 m, measured by ground penetration radar (E. Lappalainen, Geological Survey of Finland, unpublished data, 1994–1995).

### 2.2. Physical and Chemical Characteristics of Water

[8] Measurements in Lokka were conducted during the open water periods in 1994 and 1995. Porttipahta was visited only in 1995. Sampling in Porttipahta also included the period of the spring overturn. Some depth profiles of dissolved gases were also measured in Lokka during the ice cover in April 1994. All of the samples were taken during the daytime. Depth profiles for temperature, pH, conductivity, concentration of dissolved oxygen ( $\text{O}_2$ ), and redox potential were measured at 0.5–1 m depth intervals from the water column with an YSI/Grant 3800 water quality logger. The deepest station, P1, was sampled at 1–5 m depth intervals. Water samples for the determination of the concentrations of nitrate-nitrogen ( $\text{NO}_3^- \text{-N}$ ), ammonium-nitrogen ( $\text{NH}_4^+ \text{-N}$ ), and

**Table 1.** Characteristics of Hydroelectric Reservoirs Lokka and Porttipahta<sup>a</sup>

	Lokka	Porttipahta
Location	67°48'–68°02'N, 26°46'–27°01'E	67°57'–68°09'N, 26°05'–26°26'E
Flooding started	11 July 1967	17 Sept. 1970
Regulation range, m	5	11
Catchment area, km <sup>2</sup>	2280	2573
Annual mean runoff, m <sup>3</sup> s <sup>-1</sup>	26.5	28.0
Residence time, days	218–901 <sup>b</sup>	62–559 <sup>b</sup>
Area, km <sup>2</sup>	216–417 <sup>b</sup>	34–214 <sup>b</sup>
Mean depth, m	2.3–5.0 <sup>b</sup>	4.4–6.3 <sup>b</sup>
Maximum depth, m	10.0	34.5
Average period of ice cover	25 Oct. to 5 June	31 Oct. to 2 June
Bottom types		
Peatlands, %	75.7	44.7
Mineral forest soils, %	21.0	54.6
Water bodies, %	3.3	0.4

<sup>a</sup>Data from *Hellsten et al.* [1993] and *Virtanen et al.* [1993].

<sup>b</sup>Range from the minimum to the maximum.

phosphate-phosphorus (PO<sub>4</sub><sup>3-</sup>-P) and water color were obtained at the same depth intervals as above with a hand-driven pump device (Masterflex, model 75 18 – 22 Easy Load) through silicone tubing. The samples were analyzed within 24 hours of sampling. The concentrations of NO<sub>3</sub><sup>-</sup>-N and NH<sub>4</sub><sup>+</sup>-N were analyzed in Lapin Vesitutkimus Ltd. (Rovaniemi, Finland) according to the instructions for Decator AN 62/83 and Decator AN 50/84, and concentrations of PO<sub>4</sub><sup>3-</sup>-P were analyzed according to Finnish standard SFS 3026 (Finnish Standards Association SFS, Helsinki, Finland, see <http://www.sfs.fi/english.html>). Color of water was measured in the field with a comparator according to SFS 3023. Chlorophyll *a* was analyzed in Lapland Regional Environment Centre Laboratory (Rovaniemi, Finland) according to SFS 5772. Integrated samples (twofold Secchi depth) were filtered through Whatman GF/C glass fiber filters and extracted in 90% ethanol. The amount of chlorophyll *a* in the extract was measured spectrophotometrically (Hitachi, Model 100-30).

### 2.3. Gas Concentrations in the Water Column

[9] Water samples of 30 mL for the determination of the concentrations of dissolved CH<sub>4</sub>, total CO<sub>2</sub> (ΣCO<sub>2</sub> = CO<sub>2</sub> + HCO<sub>3</sub><sup>-</sup> + CO<sub>3</sub><sup>2-</sup>), and N<sub>2</sub>O were taken at 0.5–1 m intervals from the water column into polypropylene syringes (PD Plastipak, 60 mL, Becton Dickinson) equipped with three-way stopcocks (Connecta 3-way stopcock, Ohmeda GmbH + Co), using the hand-driven pump and silicone tubing. The deepest station, P1, was sampled at 1–5 m depth intervals. Samples were acidified in the field with sulfuric acid (1 mL H<sub>2</sub>SO<sub>4</sub>, 20%) for preservation and for the subsequent measurement of ΣCO<sub>2</sub>. The gas concentrations

were quantified within 24 hours in the laboratory using a headspace equilibration technique [*McAuliffe*, 1971], following the procedure presented by *Huttunen et al.* [2001a]. Nitrogen-filled syringes (30 mL water + 30 mL N<sub>2</sub>) were equilibrated by shaking vigorously for 3 min. The headspace gas concentrations were analyzed with two gas chromatographs (GC, Hewlett Packard 5890 Series II) equipped with a HayeSep Q (2 m × 1/8", 80/100 mesh) column, using flame ionization detector (FID) for CH<sub>4</sub>, thermal conductivity detector (TCD) for ΣCO<sub>2</sub>, and electron capture detector (ECD) for N<sub>2</sub>O (for details, see *Nykänen et al.* [1995]). The initial gas concentrations in the water were calculated from the measured headspace gas concentrations with Henry's law (R. Sander, Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry (version 3), 1999, available at <http://www.mpch-mainz.mpg.de/~sander/res/henry.html>), using the coefficients from *Lide and Fredrikse* [1995]. The CO<sub>2</sub> concentrations during sampling in situ were estimated from the measured ΣCO<sub>2</sub> concentrations based on the actual water pH and temperature [*Butler*, 1982]. The CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O concentrations were compared to their concentrations in water in equilibrium with the atmosphere. The equilibrium concentrations were calculated with Henry's law, assuming the atmospheric mixing ratios of 1.72 ppmv for CH<sub>4</sub> (from 1994 data), 358 ppmv for CO<sub>2</sub> (from 1994 data), and 312 ppbv for N<sub>2</sub>O (estimated from 1984–1994 data) and taking into account their annual increases of 0.01 ppmv yr<sup>-1</sup>, 1.5 ppmv yr<sup>-1</sup>, and 0.8 ppbv yr<sup>-1</sup>, respectively [*Intergovernmental Panel on Climate Change (IPCC)*, 1996].

### 2.4. Gas Fluxes

[10] Gas fluxes were measured using two techniques. First, the total fluxes of CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O were measured at the water-air interface with floating static chambers. The chambers (60 cm × 60 cm × 20 cm, volume 72,000 cm<sup>3</sup>, two to three replicates) were constructed of aluminum and equipped with floating pontoons. During the 30 min measuring period, four gas samples of 40 mL were taken from the chamber headspace through silicone tubing with similar polypropylene syringes as described above. Their gas concentrations were analyzed with the GC system described above. Gas flux rates were calculated from the linear changes in gas concentrations in the chambers during the measuring period. Chamber measurements were usually conducted simultaneously with the water sampling.

[11] Second, ebullition of gases was measured continuously with submerged funnel gas collectors. The collector [*Huttunen et al.*, 2001b] consisted of an inverted funnel (diameter of 20 cm) attached to the lower end of a PVC tube (length of 80 cm). The upper end of the tube contained a polypropylene syringe (piston

**Table 2.** Observed Depths and Flooded Soil Types of the Stations in Hydroelectric Reservoirs Lokka and Porttipahta

Station	Water Column Depth, m	Bottom type	Peat Thickness, m
<i>Lokka Reservoir</i>			
L1	7.0	open fen	1.3
L2	9.0	fine bog	<1
L3	5.7	mineral forest soil	0
L4	5.7	pine bog	2
L5	5.7	open fen	4
<i>Porttipahta Reservoir</i>			
P1	32.8	river	0
P2	8.6	mineral forest soil	0
P3	7.5	open fen	3
P4	7.9	mineral forest soil	0

removed), which trapped the bubbles, similar to that used in the gas samplings above. The collectors were floated at a depth of 1 m, and the rate of ebullition, i.e., the total volume of trapped bubbles, was detected in situ from the syringe. The syringe was equipped with a three-way stopcock, which allowed sampling for the analyses of bubble gas CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O contents by gas chromatography (GC). Five replicate gas collectors were anchored at each station.

[12] Gas samples for the measurement of radiocarbon (<sup>14</sup>C) content (percent modern carbon (PMC); modern is by definition 1950) and stable carbon isotopic ratio (<sup>13</sup>C/<sup>12</sup>C isotopic ratio, δ<sup>13</sup>C) of CH<sub>4</sub> in the bottom were collected at stations L1, L2, L3, and L5 in July 1994. The bubble gas samples were stirred from the bottom with a wooden rod into inverted 600 mL serum bottles. The bottles were capped under the water with rubber septa. CH<sub>4</sub> was separated from the samples, combusted to CO<sub>2</sub> over CuO<sub>2</sub> in sealed tubes and converted to graphite for accelerator mass spectrometry (AMS) measurements in the Dating Laboratory, University of Helsinki (Helsinki, Finland).

### 2.5. Primary Production and Bacterioplankton Production

[13] Phytoplankton primary production rates in the water column were measured using a <sup>14</sup>C method [Schindler *et al.*, 1972]. The samples were collected and incubated at every 1–2 m from the surface to the bottom (dark uptake at every 2 m). The incubation time varied from 3 to 24 hours (mainly 3 hours). The incubation was terminated by adding 0.5 mL of formalin (37%). Hydrochloric acid (100 μL 1 N HCl, pH of 1–2) was added to duplicate subsamples of 4 mL in order to drive off inorganic carbon, and open vials were kept at room temperature for 24 hours (no bubbling), after which 7 mL of Optiphase 3 (Wallac) scintillation solution were added. Radioactivity was counted with a Wallac 1410 scintillation counter. Primary and bacterial production rates were measured at every station of Lokka in 1994 (5–7 July, 26–28 July, and 16–17 August). In 1995, production measurements were made at stations L2, L4, and L5 (20–21 June and 16–17 August), at P1 (19 June, 10 July, and 15 August), and at P4 (14 August). Wintertime primary and bacterial production measurements were made at stations L2, L5, and P4 in 1995 (12–14 December). The daily production per square meter was estimated using the irradiation data from Sodankylä Observatory (Sodankylä, Finland).

[14] Bacterial production was estimated using the leucine incorporation method [Kirchman *et al.*, 1985]. Triplicate samples of 5 mL were incubated in combusted (450°C) 20 mL glass vials for 60 min with 125–149 nM of L-[<sup>14</sup>C]leucine (specific activity 311 mCi mmol<sup>-1</sup>, Amersham International). During the first field measurement the incubation was done in a polystyrene box at in situ temperature, and later it was done in situ at the depths similar to those used for primary production. The incubation was terminated by adding 100 μL of particle-free formalin (37%), and one formalin-terminated sample was used as a blank. Subsamples were extracted in 5% trichloroacetic acid (TCA, 5 mL) and filtered through 0.2 μm pore size cellulose nitrate filters (Sartorius). The filtration funnels were rinsed with 2 mL, and the filters were rinsed five times with 1 mL of 5% TCA. Both extraction and filtration were conducted in ice-cold conditions. The filters were dissolved in scintillation cocktail (Lumagel, Lumac), and the radioassay was performed within 1 week after the sampling using a liquid scintillation counter (Wallac 1410). The moles of leucine incorporated were converted into bacterial production with a factor of 7.71 × 10<sup>15</sup> μm<sup>3</sup> mol<sup>-1</sup> [Tulonen, 1993].

### 2.6. Statistical Analyses

[15] Correlation analyses (Pearson correlation coefficient *r*, SPSS for Windows, SPSS Inc.) were performed between the gas concentrations in the water column and water characteristics, using

1994 data from Lokka. The analyses were made separately for the depths of 1 m, middle of the water column, and 1 m above the bottom.

## 3. Results

### 3.1. Physical and Chemical Characteristics of Water

[16] The water column of shallow Lokka was effectively mixed by the wind during the open water periods in 1994 and 1995, and there were mostly minor differences in the physical and chemical characteristics of the water between the stations or between the sampling years (Tables 3 and 4). Owing to the lack of stratification, Lokka had always over 4.7 mg L<sup>-1</sup> of O<sub>2</sub> in the water column during the study seasons.

[17] At the deepest station, P1, in Porttipahta the water column was oxygen deficient both before and during the spring overturn in 1995. Nevertheless, after the overturn, all the stations in Porttipahta were well oxygenated (Table 5). Lokka showed higher concentrations of PO<sub>4</sub><sup>3-</sup>-P and NH<sub>4</sub><sup>+</sup>-N, but lower NO<sub>3</sub><sup>-</sup>-N concentrations than Porttipahta (station P1).

[18] Previously, it has been shown that the sediment of Lokka is anaerobic a few millimeters from the sediment surface during summer [Hellsten and Väisänen, 1998]. The sediment of Porttipahta also has only a thin aerobic surface layer.

### 3.2. Gas Concentrations in the Water Column

[19] Concentrations of CH<sub>4</sub> in Lokka ranged from 26 to 1670 nM during the two open water periods (Tables 3 and 4), being 9–532 times the concentration in equilibrium with the atmosphere. The CH<sub>4</sub> concentrations increased generally only slightly with increasing sampling depth. The seasonal mean CH<sub>4</sub> concentrations among the Lokka stations were generally higher in 1994 than in 1995.

[20] At the Porttipahta stations, CH<sub>4</sub> concentrations ranged generally from nondetectable (detection limit ~8 nM) to 268 nM after the spring overturn in 1995 (Table 5). The seasonal mean CH<sub>4</sub> concentrations there were almost the same as those in Lokka in 1995, except at P3, where one measurement showed a concentration of 31,800 nM.

[21] Concentrations of ΣCO<sub>2</sub> were 92–226 μM, and those of CO<sub>2</sub> were 8–130 μM at the Lokka stations in 1994 and 1995 (Tables 3 and 4), the CO<sub>2</sub> concentrations being 0.4–8.0 times the equilibrium level. The concentrations of ΣCO<sub>2</sub> and CO<sub>2</sub>, similar to the CH<sub>4</sub> concentrations above, showed only slight increases with depth in the water columns (not shown). The seasonal mean ΣCO<sub>2</sub> and CO<sub>2</sub> concentrations were somewhat lower in 1994 than in 1995 at most Lokka stations, but the variability within the reservoir was high.

[22] Porttipahta revealed ΣCO<sub>2</sub> concentrations of 128–606 μM and CO<sub>2</sub> concentrations of 40–443 μM after the spring overturn in 1995 (Table 5), the latter being 2.1–19 times the concentration in equilibrium with the atmosphere. The summertime mean ΣCO<sub>2</sub> and CO<sub>2</sub> concentrations in Porttipahta corresponded to those observed in Lokka.

[23] The reservoirs were mostly close to being in equilibrium with the atmosphere with respect of dissolved N<sub>2</sub>O during the open water periods. The N<sub>2</sub>O concentrations were 0.9–1.4 times the concentration in equilibrium with the atmosphere in Lokka (Tables 3 and 4) and 1.1–3.2 times the concentration in equilibrium with the atmosphere in Porttipahta (after the overturn, Table 5). The summer mean N<sub>2</sub>O concentrations ranged from 12 to 23 nM in the various stations.

### 3.3. CH<sub>4</sub> Fluxes

[24] The total CH<sub>4</sub> fluxes measured with the chambers ranged from uptake of atmospheric CH<sub>4</sub> (–6.2 mg m<sup>-2</sup> d<sup>-1</sup>) to emissions

Table 3. Concentrations of Gases and Physical and Chemical Characteristics of Water in Lokka in 1994<sup>a</sup>

	CH <sub>4</sub> , nM	ΣCO <sub>2</sub> , μM	CO <sub>2</sub> , μM	N <sub>2</sub> O, nM	Temperature, °C	O <sub>2</sub> , mg L <sup>-1</sup>	Redox, mV	pH	Conductivity, mS cm <sup>-1</sup>	Color, mg Pt L <sup>-1</sup>	PO <sub>4</sub> <sup>3-</sup> -P, μg L <sup>-1</sup>	NO <sub>3</sub> <sup>-</sup> -N, μg L <sup>-1</sup>	NH <sub>4</sub> <sup>+</sup> -N, μg L <sup>-1</sup>
	<i>Station L1, 21 June to 6 Sept. 1994</i>												
Mean	118	143	41	13	13.4	8.9	131	6.9	0.02	70	11	12	50
Min.	26	105	8	10	9.5	7.1	49	6.3	0.02	70	2	1	2
Max.	291	206	89	16	16.5	11.5	216	7.7	0.02	70	31	46	117
n	30	30	30	30	33	33	33	33	33	29	27	27	27
	<i>Station L2, 21 June to 6 Sept. 1994</i>												
Mean	199	161	58	13	13.0	8.8	144	6.7	0.02	70	10	14	87
Min.	59	124	10	11	9.1	6.6	14	6.3	0.02	60	3	1	6
Max.	1,670	226	121	15	15.9	11.9	212	7.6	0.02	70	39	38	240
n	41	41	41	41	50	50	50	50	50	48	38	38	38
	<i>Station L3, 21 June to 6 Sept. 1994</i>												
Mean	122	134	44	13	13.7	9.1	137	6.8	0.02	67	12	20	69
Min.	58	92	15	10	9.3	8.3	48	6.2	0.02	60	2	1	5
Max.	259	158	82	14	16.5	12.0	191	7.3	0.02	70	40	70	209
n	28	28	28	28	33	33	33	33	33	27	21	21	21
	<i>Station L4, 22 June to 6 Sept. 1994</i>												
Mean	226	136	52	12	13.1	8.5	126	6.7	0.02	72	7	24	60
Min.	125	111	23	10	10.4	8.0	69	6.1	0.02	70	2	1	5
Max.	460	166	90	15	15.6	9.6	172	7.1	0.02	80	9	66	163
n	26	26	26	26	27	27	27	27	27	20	17	17	17
	<i>Station L5, 5 June to 7 Sept. 1994</i>												
Mean	201	158	69	14	12.9	8.8	143	6.6	0.02	70	10	21	63
Min.	112	111	33	11	6.9	7.5	106	6.2	0.02	70	3	1	2
Max.	579	210	129	20	16.3	11.0	182	7.0	0.02	70	22	53	154
n	28	28	28	28	30	30	30	30	30	18	20	20	20

<sup>a</sup> Min, minimum; max., maximum; n, the number of samples.

Table 4. Concentrations of Gases and Physical and Chemical Characteristics of Water in Lokka in 1995<sup>a</sup>

	CH <sub>4</sub> , nM	ΣCO <sub>2</sub> , μM	CO <sub>2</sub> , μM	N <sub>2</sub> O, nM	Temperature, °C	O <sub>2</sub> , mg L <sup>-1</sup>	Redox, mV	pH	Conductivity, mS cm <sup>-1</sup>	Color, mg Pt L <sup>-1</sup>	PO <sub>4</sub> <sup>3-</sup> -P, μg L <sup>-1</sup>	NO <sub>3</sub> <sup>-</sup> -N, μg L <sup>-1</sup>	NH <sub>4</sub> <sup>+</sup> -N, μg L <sup>-1</sup>
Mean	73	184	130	16	11.5	10.0	171	6.3	0.02	NM	NM	NM	NM
Min.					11.5	9.8	161	6.1	0.02				
Max.					11.5	10.3	188	6.5	0.02				
n	1	1	1	1	5	5	5	5	5				
<i>Station L1, 21 June 1995</i>													
Mean	135	148	58	13	9.2	9.0	122	6.8	0.03	70	7	88	56
Min.	60	141	21	12	7.1	4.7	102	6.3	0.02	70	3	49	5
Max.	313	164	101	14	10.9	11.9	147	7.3	0.03	70	11	120	150
n	6	6	6	6	10	10	10	10	10	8	8	8	8
<i>Station L2, 16 Aug. 1995</i>													
Mean	56	151	93	14	9.6	10.7	131	6.4	0.03	NM	NM	NM	NM
Min.					8.7	9.1	126	6.3	0.02				
Max.					10.4	12.2	135	6.5	0.03				
n	1	1	1	1	5	5	5	5	5				
<i>Station L3, 17 Aug. 1995</i>													
Mean	84	147	69	14	11.8	8.8	105	6.8	0.02	NM	NM	NM	NM
Min.					10.9	7.5	87	6.5	0.02				
Max.					12.9	10.1	123	7.2	0.02				
n	1	1	1	1	6	6	6	6	6				
<i>Station L4, 21 June to 17 Aug. 1995<sup>b</sup></i>													
Mean	NM	NM	NM	NM	8.8	6.3	97	6.4	0.03	NM	NM	NM	NM
Min.					8.2	5.4	80	6.3	0.03				
Max.					9.9	7.3	109	6.5	0.03				
n					6	6	6	6	6				
<i>Station L5, 21 June 1995</i>													

<sup>a</sup> Min, minimum; max., maximum; n, number of samples; NM, not measured.<sup>b</sup> Greenhouse gas concentrations measured only on 17 August.

Table 5. Concentrations of Gases and Physical and Chemical Characteristics of Water in Porttipahta in 1995<sup>a</sup>

	CH <sub>4</sub> , nM	ΣCO <sub>2</sub> , μM	CO <sub>2</sub> , μM	N <sub>2</sub> O, nM	Temperature, °C	O <sub>2</sub> , mg L <sup>-1</sup>	Redox, mV	pH	Conductivity, mS cm <sup>-1</sup>	Color, mg Pt L <sup>-1</sup>	PO <sub>4</sub> <sup>3-</sup> -P, μg L <sup>-1</sup>	NO <sub>3</sub> <sup>-</sup> -N, μg L <sup>-1</sup>	NH <sub>4</sub> <sup>+</sup> -N, μg L <sup>-1</sup>
	<i>Station P1, 8 June to 17 Aug. 1995</i>												
Mean	45	272	154	18	10.2	7.7	142	6.4	0.04	60	3.3	134	14
Min.	0	202	77	13	4.3	2.6	-93	6.0	0.03	20	1.0	110	5
Max.	268	606	443	47	14.4	9.9	207	7.2	0.06	100	8.0	170	67
<i>n</i>	22	22	22	22	31	31	31	31	31	24	15	15	15
	<i>Station P2, 11 July to 17 Aug. 1995<sup>b</sup></i>												
Mean	77	206	40	14	11.3	7.1	111	7.0	0.03	NM	NM	NM	NM
Min.	42	202		14	11.3	7.0	101	7.0	0.03				
Max.	111	209		15	11.3	7.6	119	7.1	0.03				
<i>n</i>	2	2	1	2	5	5	5	5	5				
	<i>Station P3, 14 Aug. 1995</i>												
Mean	31,800	128	84	23	13.3	9.2	175	6.3	0.03	NM	NM	NM	NM
Min.					13.3	8.9	162	6.2	0.03				
Max.					13.3	9.5	190	6.5	0.03				
<i>n</i>	1	1	1	1	5	5	5	5	5				
	<i>Station P4, 14 Aug. 1995</i>												
Mean	129	230	60	15	13.4	8.8	109	6.9	0.03	NM	NM	NM	NM
Min.					13.3	8.7	106	6.9	0.03				
Max.					13.5	8.8	111	6.9	0.03				
<i>n</i>	1	1	1	1	4	4	4	4	4				

<sup>a</sup>Min, minimum; max., maximum; *n*, number of samples; NM, not measured.

<sup>b</sup>Greenhouse gas concentrations measured only on July 11.

**Table 6.** Greenhouse Gas Fluxes Measured With Floating Chambers in Lokka and Porttipahta

Station	Measurement Period	CH <sub>4</sub> Flux, mg m <sup>-2</sup> d <sup>-1</sup>		CO <sub>2</sub> Flux, mg m <sup>-2</sup> h <sup>-1</sup>		N <sub>2</sub> O Flux, μg m <sup>-2</sup> d <sup>-1</sup>		n <sup>a</sup>
		Mean	Range	Mean	Range	Mean	Range	
<i>Lokka Reservoir 1994</i>								
L1	21 June to 6 Sept.	7.2	-0.4-16	21	-20-74	16	-179-97	5
L2	21 June to 6 Sept.	8.6	2.5-31	30	-32-62	-17	-123-100	4
L3	21 June to 6 Sept.	16	2.3-47	32	-30-155	22	-299-233	5
L4	22 June to 7 Sept.	19	2.6-48	72	-10-170	-7.1	-92-76	6
L5	5 June to 7 Sept.	11	5.6-26	68	12-114	44	-190-462	6
<i>Lokka Reservoir 1995</i>								
L1	21 June, 16 Aug.	20	6.9-34	90	87-93	210	-14-434	2
L2	16 Aug.	12		107		-89		1
L3	17 Aug.	5.3		44		-31		1
L4	21 June, 17 Aug.	10	4.9-16	37	-28-102	103	36-171	2
L5	21 June, 16 Aug.	119	-6.2-244	133	11-255	270	34-507	2
<i>Porttipahta Reservoir 1995</i>								
P1	18 June to 18 Aug.	4.8	-0.2-7.6	95	63-126	133	94-173	3
P2	18 June to 17 Aug.	2.5	-0.5-5.6	88	54-144	-22	-260-137	3
P3	14 Aug.	3.7		37		256		1
P4	14 Aug.	3.0		36		94		1

<sup>a</sup> The number of sampling days during the measuring period.

of up to 244 mg m<sup>-2</sup> d<sup>-1</sup> during the two summer periods at the Lokka stations (Table 6). In general, there were no clear seasonal patterns in the CH<sub>4</sub> flux measured by the chambers (Figure 2), and only minor differences were found in the fluxes between the stations. The mean chamber CH<sub>4</sub> fluxes were also rather similar between the summer periods in 1994 and 1995 (means of 12.4 and 33.3 mg m<sup>-2</sup> d<sup>-1</sup>, respectively); only station L5 showed unusually high CH<sub>4</sub> emission in 1995 (Table 6). The CH<sub>4</sub> fluxes obtained with the chambers in Lokka in 1994 showed a distribution tailing toward the higher values; 80% of the fluxes were below 20 mg m<sup>-2</sup> d<sup>-1</sup> (Figure 3). The chamber CH<sub>4</sub> fluxes in Porttipahta, measured during the summer 1995 after the spring overturn, ranged from -2.0 to 7.6 mg m<sup>-2</sup> d<sup>-1</sup> (mean of 3.5 mg m<sup>-2</sup> d<sup>-1</sup>) but generally were lower and less variable than those observed in Lokka (Table 6).

[25] Ebullitive CH<sub>4</sub> fluxes varied extensively during the bubble collection periods in Lokka (0-972 mg m<sup>-2</sup> d<sup>-1</sup>, means of 184 and 46.4 mg m<sup>-2</sup> d<sup>-1</sup> in 1994 and 1995, respectively), decreasing generally toward late summer (Figure 4 and Table 7). Four of the five stations of Lokka had higher mean time weighted ebullitive CH<sub>4</sub> fluxes in 1994 than in 1995 (Table 7). Similarly, bubble gas contained more CH<sub>4</sub> in 1994 (means for the stations 57-84%) than in 1995 (36-78%). The stations L3 and L5, which had the greatest CH<sub>4</sub> ebullition rates both in 1994 and 1995 (Figure 4 and Table 7), also showed the highest bubble gas CH<sub>4</sub> concentrations. The ebullitive CH<sub>4</sub> fluxes in 1994 and 1995 both had the distributions tailing toward the higher values (Figure 5). CH<sub>4</sub> ebullition was lower and less variable among the stations in Porttipahta (0-8.0 mg m<sup>-2</sup> d<sup>-1</sup>, mean of 0.8 mg m<sup>-2</sup> d<sup>-1</sup>) than in Lokka, and there the bubbles contained less CH<sub>4</sub> (25-35%). CH<sub>4</sub> in the bubbles stirred from the bottom of Lokka (Table 8) had high modern C contents (PMC = 92-104%). The δ<sup>13</sup>C values of CH<sub>4</sub> in the bubbles ranged from -60.1 to -67.0‰.

### 3.4. CO<sub>2</sub> Fluxes

[26] The total CO<sub>2</sub> fluxes measured with the chambers in Lokka ranged from -32 to 255 mg m<sup>-2</sup> h<sup>-1</sup> (Table 6), though there was no distinctive seasonal pattern (Figure 2). However, negative fluxes, i.e., uptake of atmospheric CO<sub>2</sub> as observed in 1994, occurred mostly during the first measurements in June. Most of the stations in Lokka presented lower mean CO<sub>2</sub> release rates in 1994 than in 1995 (means of 45 and 82 mg m<sup>-2</sup> h<sup>-1</sup>) (Table 6).

The chamber CO<sub>2</sub> emissions in Lokka in 1994 had a distribution tailing toward the higher values (Figure 3), similar to the chamber and ebullitive CH<sub>4</sub> fluxes.

[27] The chamber CO<sub>2</sub> fluxes varied from 36 to 144 mg m<sup>-2</sup> h<sup>-1</sup> after the spring overturn in 1995 at the stations of Porttipahta (mean of 64 mg m<sup>-2</sup> h<sup>-1</sup>), corresponding to the CO<sub>2</sub> emissions in Lokka (Table 6). The mean ebullitive CO<sub>2</sub> fluxes ranged from 0 to 2.6 mg m<sup>-2</sup> d<sup>-1</sup> among the stations in Lokka and Porttipahta; thus the ebullition had minor importance in the CO<sub>2</sub> release.

### 3.5. N<sub>2</sub>O Fluxes

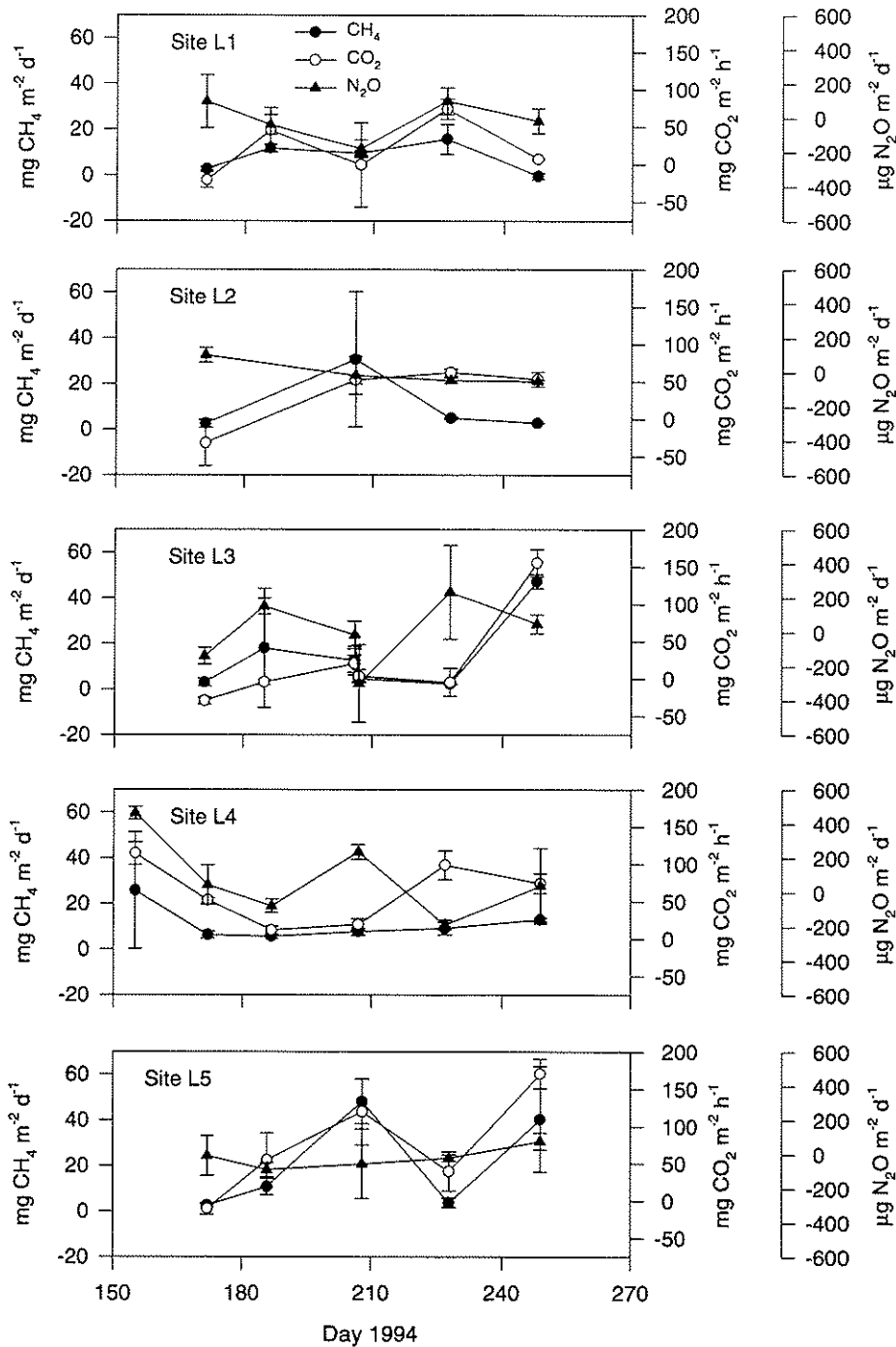
[28] The N<sub>2</sub>O fluxes were generally low in the reservoirs during the open water periods after the spring overturn, ranging from -299 to 507 μg m<sup>-2</sup> d<sup>-1</sup> (Table 6). There were no clear seasonal patterns in the N<sub>2</sub>O fluxes in Lokka in 1994 (Figure 2), and their frequency distribution was close to the zero (Figure 3). Mean ebullitive N<sub>2</sub>O fluxes were negligible, ranging at the stations from 0 to 0.7 μg m<sup>-2</sup> d<sup>-1</sup>; thus ebullition did not contribute significantly to the N<sub>2</sub>O exchange.

### 3.6. Water Characteristics and Concentrations and Fluxes of Gases in Spring

[29] Measurements were started before the spring overturn on 8 June in 1995 at station P1 in Porttipahta (see Figure 6). Then the water column had anoxic hypolimnion, (O<sub>2</sub> concentration down to 0.2 mg L<sup>-1</sup>), with negative redox potentials (down to -173 mV). The O<sub>2</sub> deficiency in the bottom waters lasted until 12 June (day 162), whereas the upper water column had at least a moderate O<sub>2</sub> content during the entire open water period (Table 5). The O<sub>2</sub> concentration in the lower water column increased during the overturn, reaching 2.6 mg L<sup>-1</sup> on 19 June (day 169) and 6.4 mg L<sup>-1</sup> after the overturn on 11 July (day 191).

[30] As a result of accumulation of gases during winter under the ice, the gas concentrations at P1 were much higher before and during the spring overturn (up to 71,800 nM CH<sub>4</sub>, 673 μM CO<sub>2</sub>, and 139 nM N<sub>2</sub>O) than after the water column started to circulate (Figure 6). Before the overturn, the gas concentrations in the water column generally showed a clear increase with depth. The CO<sub>2</sub> concentration, however, increased from the surface down to a depth of 17 m and then decreased toward the bottom. The N<sub>2</sub>O concentration increased down to a depth of 21 m, with a much lower concentration deeper in the water column. The gradients in



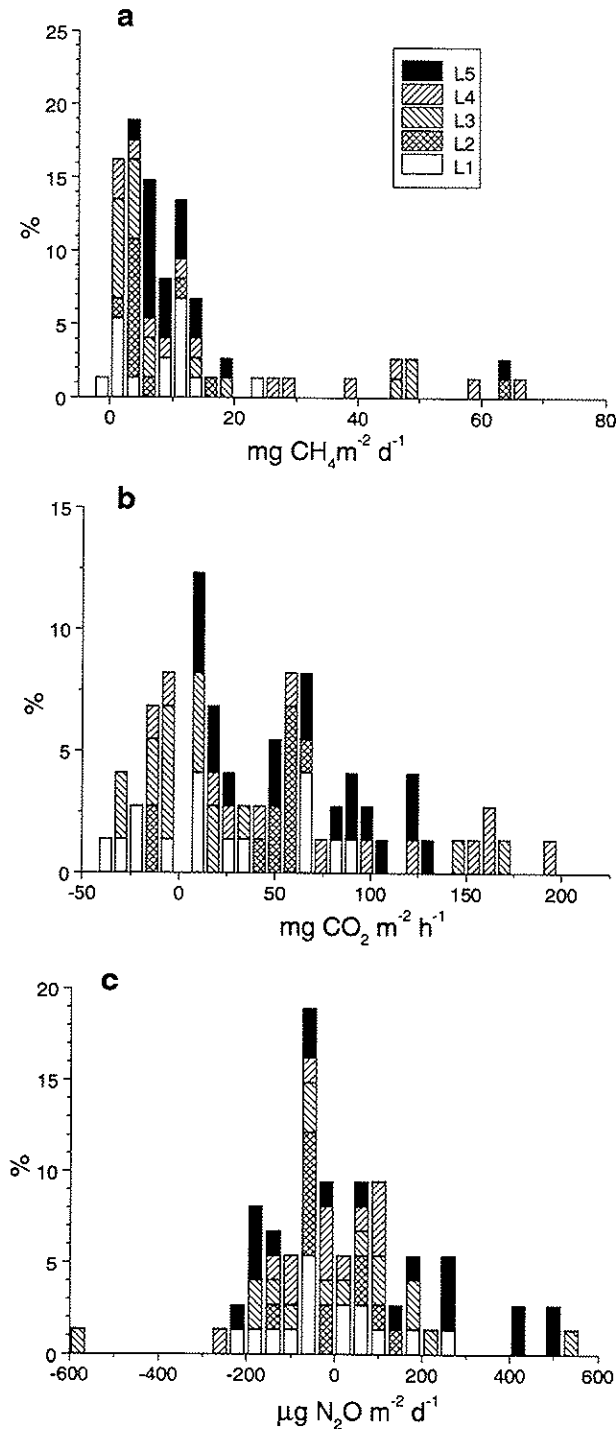


**Figure 2.** Seasonal patterns in the CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub>O fluxes (daily means and their standard deviations as error bars) measured with floating chambers at the stations in reservoir Lokka during the open water period in 1994.

the gas concentrations became less steep during the overturn, when the hypolimnion was mixed with the epilimnion. Gases were conducted, in part, to the atmosphere, as shown by the high gas emissions at the water surface during the overturn (up to 335 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>, 878 mg CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup>, and 3009 µg N<sub>2</sub>O m<sup>-2</sup> d<sup>-1</sup>, Figure 6). The changes in the water column greenhouse gas stores between 8 and 19 June at station P1 indicated CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O losses of 5.9, 230, and 0.02 g m<sup>-2</sup>, respectively. The corresponding

CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O emissions measured with the chambers during this overturn period were 1.7, 135, and 0.02 g m<sup>-2</sup>, respectively.

[31] In April 1994, steep vertical gas concentration gradients were also found below the ice at stations L1 and L2 in Lokka. In these stations the concentrations showed rather similar depth-related trends as seen at the station P1 in Porttipahta before the spring overturn. A large amount of gas rich in CH<sub>4</sub> was stored below the ice at station L5. However, our methods did not permit



**Figure 3.** Frequency distribution of the chamber  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  fluxes measured in reservoir Lokka during the open water period in 1994.

quantifying this gas store, but they did prove that there was bubble formation also during the winter.

### 3.7. Relationships between Gas Fluxes, Gas Concentrations, and Water and Station Characteristics

[32] The gas concentrations and fluxes varied within the reservoirs and were not clearly associated with the depth or bottom

type. Station L5 in Lokka, with the highest  $\text{CH}_4$  emission, was located in an area with the thickest inundated peat cover ( $\sim 4$  m at L5; other stations in Lokka had 0–2 m of peat, Table 2). This station was also more exposed to winds than the other stations. The correlations between the gas concentrations and water characteristics were generally weak, except between the bottom water  $\text{N}_2\text{O}$  concentration and water temperature ( $r = -0.76$ ,  $P < 0.001$ , and  $n = 26$ ) and the bottom water  $\text{N}_2\text{O}$  and  $\text{O}_2$  concentrations ( $r = 0.67$ ,  $P < 0.001$ , and  $n = 23$ ).

### 3.8. Primary Production, Bacterial Production, and Total Gas Fluxes

[33] Mean primary production rates varied among the stations of Lokka from  $620$  to  $1640$   $\text{mg C m}^{-2} \text{d}^{-1}$  in 1994 and from  $345$  to  $507$   $\text{mg C m}^{-2} \text{d}^{-1}$  in 1995 (Figure 7). The bacterial production rates were  $69$ – $199$   $\text{mg C m}^{-2} \text{d}^{-1}$  in 1994 and  $61$ – $135$   $\text{mg C m}^{-2} \text{d}^{-1}$  in 1995, being 10–26% of the primary production rates. Porttipahta (station P1) showed lower primary and bacterial production rates (means of  $272$  and  $46$   $\text{mg C m}^{-2} \text{d}^{-1}$ , respectively) than Lokka.

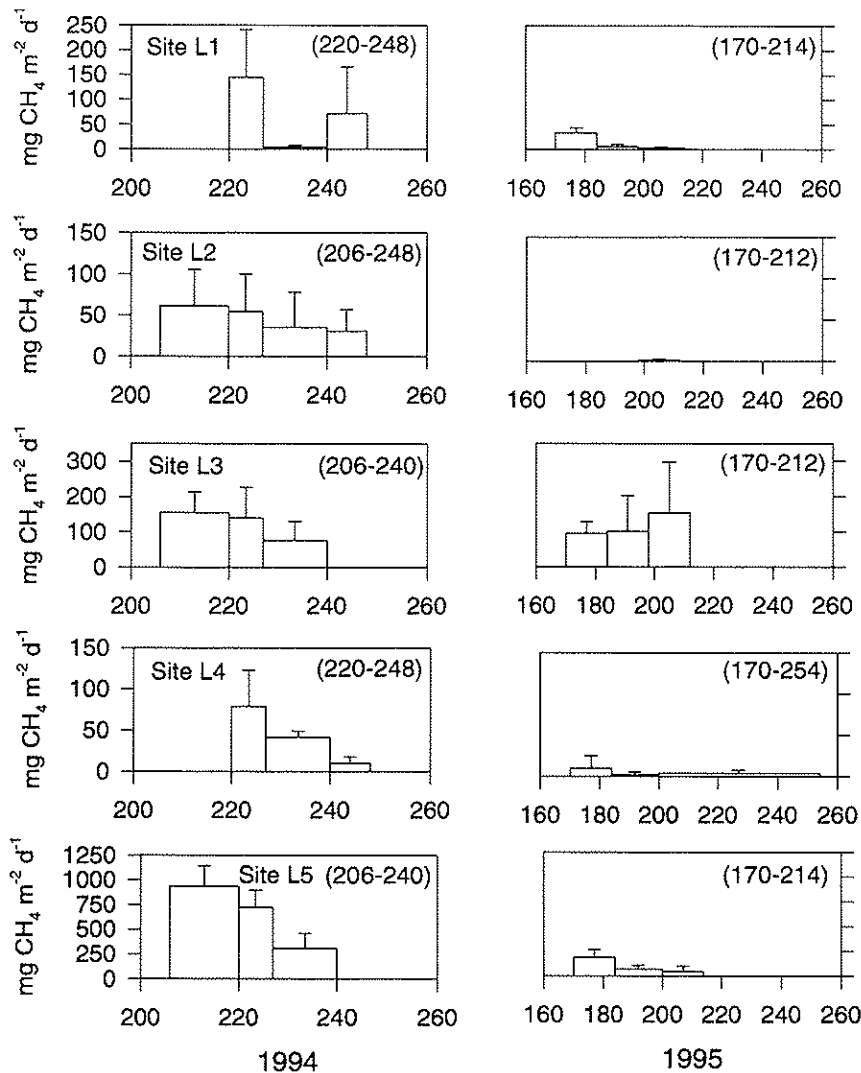
[34] At the Lokka stations the mean chamber  $\text{CH}_4$ -C fluxes were  $9.3$  and  $25$   $\text{mg m}^{-2} \text{d}^{-1}$  in 1994 and 1995, respectively, and were greater than the mean chamber  $\text{CH}_4$ -C emission in Porttipahta (mean of  $2.6$   $\text{mg m}^{-2} \text{d}^{-1}$ ) (Figure 7). The mean ebullitive  $\text{CH}_4$ -C emissions were  $138$  and  $35$   $\text{mg m}^{-2} \text{d}^{-1}$  at the Lokka stations in 1994 and 1995, respectively, and  $0.6$   $\text{mg m}^{-2} \text{d}^{-1}$  in Porttipahta (Figure 7). The mean  $\text{CO}_2$ -C emissions from Lokka ranged from  $138$  to  $472$   $\text{mg m}^{-2} \text{d}^{-1}$  in 1994 and from  $242$  to  $871$   $\text{mg m}^{-2} \text{d}^{-1}$  in 1995 (means of  $292$  and  $538$   $\text{mg m}^{-2} \text{d}^{-1}$ ) (Figure 7). The mean  $\text{CO}_2$ -C emissions from the Porttipahta stations were from  $242$  to  $622$   $\text{mg m}^{-2} \text{d}^{-1}$  (mean of  $419$   $\text{mg m}^{-2} \text{d}^{-1}$ ) in 1995. Generally,  $\text{CO}_2$  accounted for most of the C release from the reservoirs to the atmosphere. The C gas emissions at the stations were mostly lower than the primary production rates (Figure 7).

[35] During the open water period (142 days assumed) the mean chamber (total)  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  emissions from Lokka were  $1.8$ ,  $152$ , and  $0.002$   $\text{g m}^{-2}$  in 1994 and  $4.7$ ,  $280$ , and  $0.01$   $\text{g m}^{-2}$  in 1995, respectively. In Porttipahta the mean chamber  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  emissions were  $0.53$ ,  $232$ , and  $0.02$   $\text{g m}^{-2}$  during the open water period (151 days assumed) in 1995. The mean ebullitive  $\text{CH}_4$  emissions in Lokka were  $26$  and  $6.6$   $\text{g m}^{-2}$  in 1994 and 1995, respectively, and in Porttipahta they were  $0.11$   $\text{g m}^{-2}$  in 1995.

## 4. Discussion

### 4.1. Release and Regulation of Greenhouse Gases

[36] During the open water periods, Lokka and Porttipahta were mostly supersaturated with  $\text{CH}_4$  and  $\text{CO}_2$ , a feature common to many natural temperate/boreal ponds and lakes [Hamilton *et al.*, 1994; Striegl and Michmerhuizen, 1998; Huttunen *et al.*, 1999, 2001c; Riera *et al.*, 1999] and reservoirs [Kelly *et al.*, 1994, 1997; Duchemin *et al.*, 1995, 1999; Scott *et al.*, 1999]. Although the waters of Lokka and Porttipahta had rather similar  $\text{CH}_4$  and  $\text{CO}_2$  concentrations, Lokka showed higher  $\text{CH}_4$  emissions, especially by ebullition, these being among the highest emissions measured from northern aquatic and terrestrial wetland ecosystems (Table 9). The  $\text{CH}_4$  emissions in Porttipahta were comparable to the lowest levels. Nevertheless, the  $\text{CO}_2$  emissions from Lokka and Porttipahta were almost the same and similar to values for  $\text{CO}_2$  emissions presented for northern ponds, lakes, and reservoirs ( $0.7$ – $229$   $\text{mg CO}_2 \text{ m}^{-2} \text{ h}^{-1}$ ) [Duchemin *et al.*, 1995; Kelly *et al.*, 1997; Riera *et al.*, 1999; Huttunen *et al.*, 2001c], although perhaps below those described for shallow wetland ponds and beaver ponds ( $132$ – $458$   $\text{mg CO}_2 \text{ m}^{-2} \text{ h}^{-1}$ ) [Yavitt and Fahey, 1994; Hamilton *et al.*, 1994; Roulet *et al.*, 1997].



**Figure 4.** Seasonal patterns in the ebullitive  $\text{CH}_4$  flux in reservoir Lokka during the open water periods in 1994 and 1995. The actual measuring periods are shown in parenthesis in each part. Error bars are the standard deviations of fluxes measured with five replicate gas collectors.

[37] The higher  $\text{CH}_4$  emissions in Lokka highlight the importance of sediment bubble formation in  $\text{CH}_4$  release. Bubble formation occurs in the sediment when the partial pressures of dissolved sediment gases exceed the apparent hydrostatic pressure [Chanton and Whiting, 1995]. Therefore the higher  $\text{CH}_4$  ebullition rates in Lokka, compared to those in Porttipahta, suggested that there was a greater  $\text{CH}_4$  production rate in Lokka. The higher  $\text{CH}_4$  concentrations in bubble gas from Lokka also indicated higher ebullition of  $\text{CH}_4$  because the  $\text{CH}_4$  content in bubbles increases with increasing ebullition rate [Chanton and Whiting, 1995]. Because of high solubility of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  in water their concentrations in the bubbles were low, as were their ebullitive fluxes. Furthermore, during the open water period the overall production of  $\text{N}_2\text{O}$  was probably small.

[38] C gas emissions in Lokka and Porttipahta showed a poor association with the characteristics of the flooded ecosystem type. The high  $\text{CH}_4$  fluxes from the peaty station L5 in Lokka could be attributed more to the wind expose rather than the occurrence of peat. In a recently flooded reservoir, fluxes of  $\text{CH}_4$  and  $\text{CO}_2$  have

been reported to increase following the impounding owing to the decomposition of fresh plant biomass, rather than the degradation of peat [Kelly *et al.*, 1997]. Nevertheless, floating peat mats in this reservoir seemed to release more  $\text{CH}_4$  than the adjacent water areas without floating peat [Scott *et al.*, 1999]. However, Lokka is an old reservoir, where the area of floating peat has drastically decreased with time [Ruuhijärvi *et al.*, 1976]; obviously, the trend has been similar in the  $\text{CH}_4$  emissions.

[39] Duchemin *et al.* [1995] measured  $\text{CH}_4$  and  $\text{CO}_2$  emissions from hydroelectric reservoirs with varying age (1–13 years after the flooding) in northern Quebec. They concluded that processes taking place in the water column, such as oxidation and vertical advection of gases, had a great importance in the C gas emissions to the atmosphere and that the emissions were not related to the type of the flooded ecosystem. They classified exceptionally high  $\text{CH}_4$  and  $\text{CO}_2$  emissions as “above-average emissions,” attributing them to unusual sampling conditions, including strong winds, floating peat mats, and water column depths <1 m. Keller and Stallard [1994] and Galy-Lacaux *et al.* [1999] have also reported

**Table 7.** Ebullitive CH<sub>4</sub> Fluxes in Lokka and Porttipahta

Station	Measuring Period	Ebullitive Flux, mg CH <sub>4</sub> m <sup>-2</sup> d <sup>-1</sup>		
		Mean <sup>a</sup>	Range	N <sup>b</sup>
<i>Lokka Reservoir 1994</i>				
L1	9 Aug. to 6 Sept.	58	3.5–145	3
L2	26 July to 6 Sept.	47	31–61	4
L3	26 July to 6 Sept.	101	0.5–154	4
L4	9 Aug. to 6 Sept.	55	9.6–79	3
L5	26 July to 6 Sept.	660	310–972	4
<i>Lokka Reservoir 1995</i>				
L1	20 June to 12 Sept.	16	2.4–34	5
L2	20 June to 12 Sept.	2.6	0–7.8	5
L3	23 June to 12 Sept.	120	94–178	5
L4	20 June to 12 Sept.	4.4	2.0–9.9	3
L5	20 June to 12 Sept.	89	38–186	5
<i>Porttipahta Reservoir 1995</i>				
P1	19 June to 14 Aug.	0	0	3
P2	19 June to 14 Aug.	0.7	0–1.4	3
P3	19 June to 14 Aug.	2.1	0.1–8.0	3
P4	19 June to 14 Aug.	0.2	0.1–0.2	3

<sup>a</sup> The time weighted average flux.

<sup>b</sup> The number of gas collections during the measuring periods.

that CH<sub>4</sub> ebullition from sediments may increase with decreasing water column depth. Since the CH<sub>4</sub> ebullition rates at the 5.7–9 m deep stations in Lokka varied rather randomly, showing no dependence on the depth, we propose that the variation in water column depth was not responsible for the spatial variation in CH<sub>4</sub> ebullition. The different CH<sub>4</sub> ebullition rates between the reservoirs could not be explained by the depth either because the depths of the stations P2–P4 in Porttipahta corresponded to those of the stations in Lokka (Table 2). Recent studies in a eutrophied Lake Kevätön (maximum depth ~10 m) in Finland have shown that the rate of ebullition can even increase toward the deepest point of the lake, probably because of an increase in the amount of anaerobically decomposing, fresh organic matter within the sediment [Huttunen *et al.*, 1999; A. Liikanen, University of Kuopio, unpublished data, 1998–2000]. In that lake (area of 4.07 km<sup>2</sup>) the wind action may be less important for the gas exchange than in the large reservoirs in this study, especially in Lokka [cf. MacIntyre *et al.*, 1995].

[40] During the first years following the flooding the total P concentration was higher in Porttipahta than in Lokka but decreased later below the level of Lokka [Hellsten *et al.*, 1993]. It seems likely that the sediments of Lokka with their greater peat deposits have a long-term capacity to release nutrients (P and N), thus supporting higher primary production. The measured primary production and heterotrophic bacterial production rates were higher both in Lokka and Porttipahta than are generally found in natural lakes in northern Finland [Arvola *et al.*, 1993, 1994]. The primary production values obtained in this study were also higher than those measured earlier, ~20 years ago, in Lokka [Heinonen and Airaksinen, 1974; Jones and Ilmavirta, 1983]. Since the early phases of this reservoir's history, the color of the water has decreased by ~50%, which explains the increase in primary production. Nonetheless, the primary production was limited by humic water (color of 60–72 mg Pt L<sup>-1</sup> in 1994–1995). At a depth of 2 m the rate of primary production was 13% of that at the surface, decreasing at greater depths to <2% of the surface values. According to ratios of mineral nutrients, both P and N limit the primary production in Lokka, but Porttipahta is mostly P limited. The annual primary production was estimated to be 65 g C m<sup>-2</sup> in Lokka and 23 g C m<sup>-2</sup> in Porttipahta. Bacterial production was 19% of the annual primary production in Lokka and 28% in

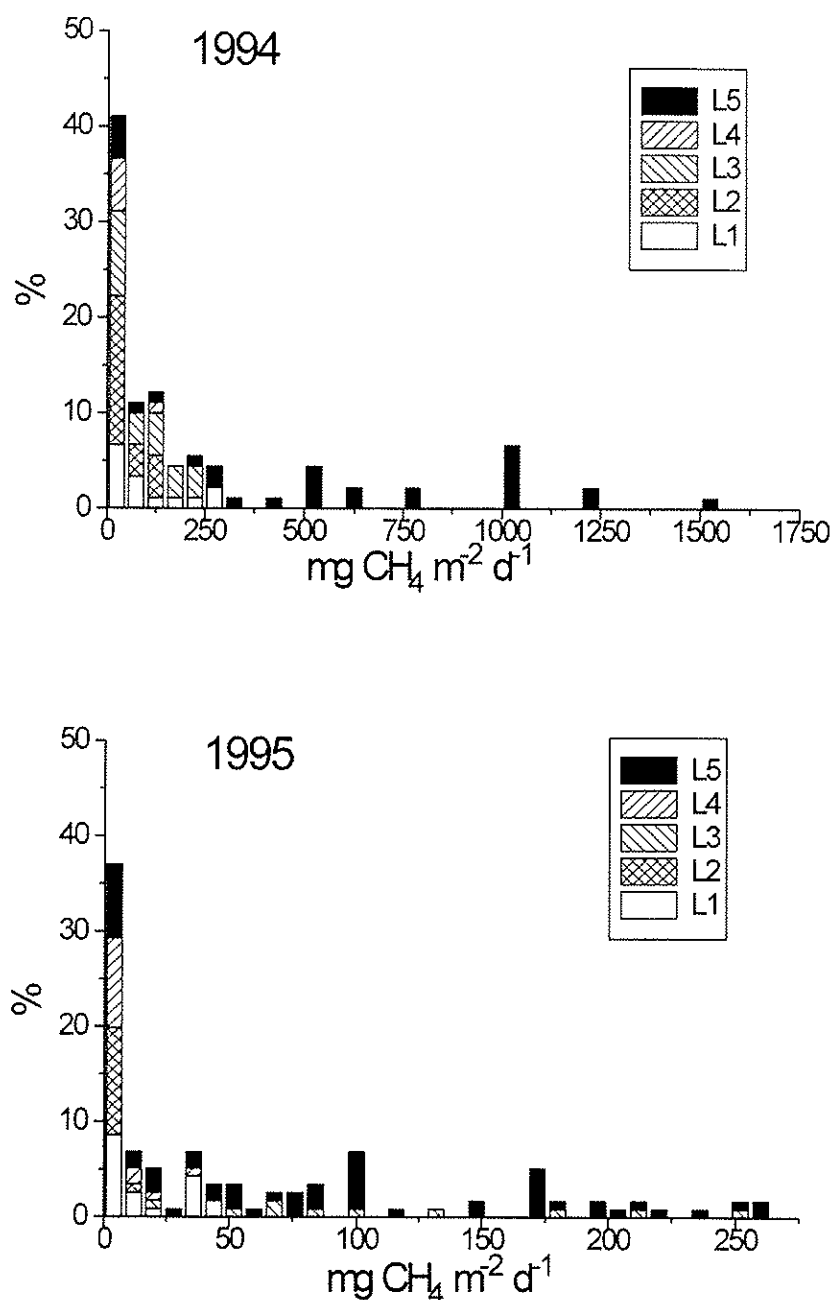
Porttipahta. In winter, bacterial production (1–3 mg C m<sup>-3</sup> d<sup>-1</sup>) exceeded primary production (0.2–0.7 mg C m<sup>-3</sup> d<sup>-1</sup>).

#### 4.2. Origin of the Gas Fluxes

[41] Production of CH<sub>4</sub> in lakes is suggested to increase with increasing organic matter input [Kelly and Chynoweth, 1981; Schmidt and Conrad, 1993]. There is strong evidence that the flooded previous biomass and fresh organic C derived from primary production rather than old peat deposits have great importance in the CH<sub>4</sub> and CO<sub>2</sub> production in Lokka and Porttipahta. This conclusion was further supported by the high modern C content in CH<sub>4</sub> in the bubbles extracted from the sediment of Lokka. In contrast, the wintertime CH<sub>4</sub> production in north Siberian lakes was fueled by old Pleistocene-aged C (PMC ranging from 0.2 to 35.3%) [Zimov *et al.*, 1997]. In some humus-rich natural lakes the fluxes of C gases are more closely related to the allochthonous C [Striegl and Michmerhuizen, 1998; Riera *et al.*, 1999; Huttunen *et al.*, 2001c] than we suspected to be in Lokka and Porttipahta. Allochthonous C is suggested to have importance in the gas production in some Canadian reservoirs [Weissenberger *et al.*, 1998]. It can well be that primary production is an important C source for methanogenesis, especially in shallow, highly productive reservoirs, such as the eutrophic reservoir Lokka, where the CH<sub>4</sub> emissions were similar to those measured from natural eutrophied lakes in Finland (Table 9) [Huttunen *et al.*, 1999; J. T. Huttunen, University of Kuopio, unpublished data, 1997–1999]. For example, in the pelagic region of eutrophied Lake Kevätön with the summertime primary production of ~600–700 mg C m<sup>-2</sup> d<sup>-1</sup>, the mean CH<sub>4</sub> emissions have been 18.3–190 mg m<sup>-2</sup> d<sup>-1</sup> during the open water period. Planktonic primary production has special importance in the production of modern C in Lokka and Porttipahta because erosion by ice and waves prevents the development of littoral vegetation. In natural lakes, littoral vegetation provides substrates for methanogenesis and can have high CH<sub>4</sub> emissions [Alm *et al.*, 1996; Hyvönen *et al.*, 1998].

[42] Oxidation can decrease the release of CH<sub>4</sub> from natural lakes [Chanton and Whiting, 1995; King and Blackburn, 1996] and reservoirs [Duchemin *et al.*, 1995; Kelly *et al.*, 1997]. The aerobic CH<sub>4</sub> oxidation in the sediment is restricted to the first millimeters of the uppermost sediment [King and Blackburn, 1996], where over 90% of the CH<sub>4</sub> produced can be oxidized [Frenzel *et al.*, 1990]. In the sediments of Lokka and Porttipahta the CH<sub>4</sub> oxidation is possible down to the depth of 3–5 mm, the maximum depth of oxygen penetration in these sediments [Hellsten and Väisänen, 1998]. In Lokka, ebullition had high contribution to the total CH<sub>4</sub> release. There the relative importance of CH<sub>4</sub> oxidation was probably lower than in Porttipahta, where ebullition was low. Oxidation affects mainly the diffusive CH<sub>4</sub> flux because CH<sub>4</sub> in the bubbles can bypass the CH<sub>4</sub> oxidation in the sediment and water column [Chanton and Whiting, 1995]. CH<sub>4</sub> in the bubbles from Lokka sediment had low δ<sup>13</sup>C, indicating that this CH<sub>4</sub> was not oxidized because CH<sub>4</sub> oxidation increases δ<sup>13</sup>C in the residual CH<sub>4</sub> [see Whiticar, 1996].

[43] The decomposition of organic matter in the water column could have a higher capacity to produce CO<sub>2</sub> in Lokka than in Porttipahta, as seen in the higher bacterial production rates in Lokka. However, because primary production was higher in Lokka, i.e., the consumption of CO<sub>2</sub> in the water column was greater, it is not surprising that the reservoirs had rather similar CO<sub>2</sub> emissions. The chamber technique measures the exchange rates of gases between the atmosphere and the uppermost water column, which are regulated by factors such as wind speed, temperature and gas concentrations at the water-air interface [MacIntyre *et al.*, 1995]. If photosynthesis is blocked by the opaque chambers, the CO<sub>2</sub> concentration gradient can be eventually disturbed, causing an error in the CO<sub>2</sub> exchange estimate. On the basis of the CO<sub>2</sub> flux measurements using both trans-



**Figure 5.** Frequency distribution of the ebullitive  $\text{CH}_4$  fluxes in reservoir Lokka during the open water periods in 1994 and 1995.

parent and opaque chambers in Finnish lakes with varying trophicity, opaque chambers give as an average 35% higher  $\text{CO}_2$  emission than the transparent chambers (J. T. Huttunen, University of Kuopio, unpublished data, 1997–1999). On the other hand, *Kling et al.* [1992] concluded that the  $\text{CO}_2$  release measured during daytime might underestimate the daily  $\text{CO}_2$  release. These could cause some inaccuracy to our estimates of the reservoir  $\text{CO}_2$  fluxes but allow comparisons between the different sampling stations.

#### 4.3. Greenhouse Gas Fluxes at Ice Out

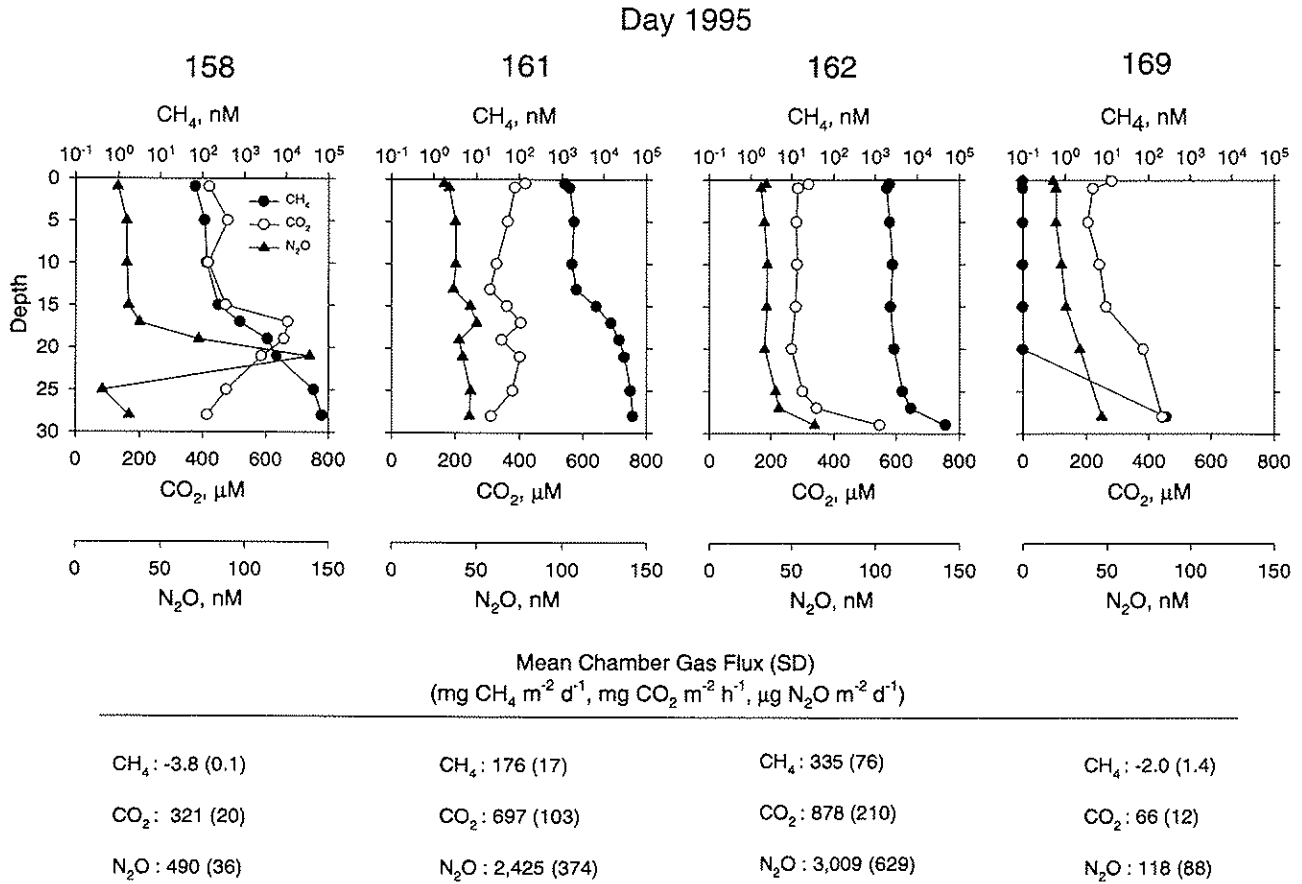
[44] The respective maximum daily  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  emissions from Porttipahta (station P1) during the spring over-

turn were up to 70, 9, and 23 times the emissions calculated for the open water period. The springtime  $\text{CH}_4$  emission,

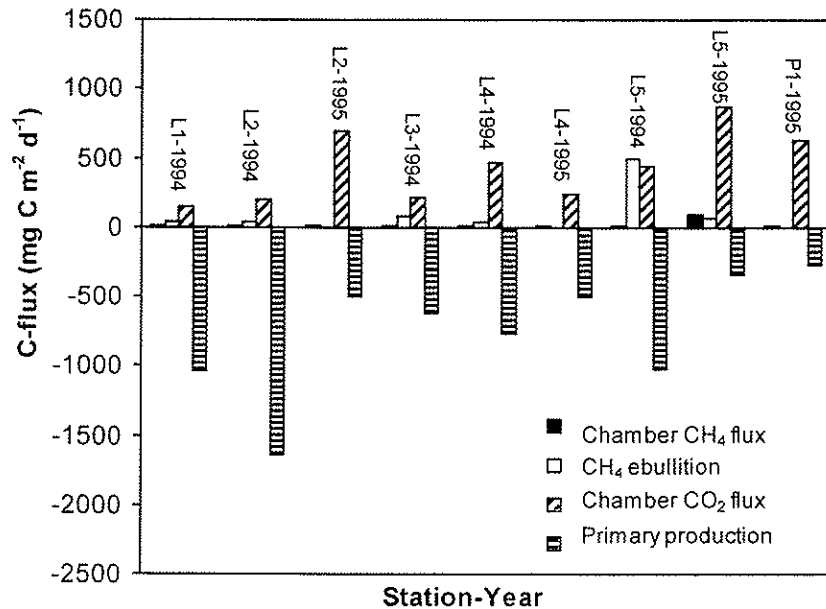
**Table 8.** Modern Carbon Content (PMC) and  $^{13}\text{C}/^{12}\text{C}$  ratio of  $\text{CH}_4$  in the Bubble Gas Samples Taken in July 1995 from the Bottom of Lokka<sup>a</sup>

Station	PMC, %	$\delta^{13}\text{C}$ , ‰
L1	98	-63.8
L2	104	-63.7
L3	92	-67.0
L5	101	-60.1

<sup>a</sup>Data represent mean values for duplicate samples.



**Figure 6.** CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O concentrations in the water column and the greenhouse gas fluxes at the water-air interface at the deepest station P1 in Porttipahta before, during, and after the spring overturn in 1995.



**Figure 7.** Mean chamber (total) fluxes of CH<sub>4</sub>-C and CO<sub>2</sub>-C, ebullition rates of CH<sub>4</sub>-C, and photosynthetic primary production at some stations in reservoirs Lokka and Porttipahta during the open water periods in 1994 and 1995.

**Table 9.** Examples of Seasonal Mean CH<sub>4</sub> Emissions From Different Temperate/Boreal Habitats, Including Reservoirs, Lakes, Ponds, Beaver Ponds, and Wetlands/Peatlands in North America and Finland

Location	Latitude, °N	Habitat(s)	CH <sub>4</sub> , mg m <sup>-2</sup> d <sup>-1</sup>	Reference (Method) <sup>a</sup>
Quebec	53°–54°	two boreal reservoirs: regular fluxes above-average fluxes	shallow/deep stations 8.0/2.6 57/30	1 (c)
Ontario	49°	boreal lake experimental boreal reservoir: <sup>b</sup> preflooding fluxes postflooding fluxes	0.0, 0.2 peat area/pond area –0.06–176/17 48/88	1 (c, g) 2 (c, g)
Ontario	49°	five floating peat mats in an experimental boreal reservoir	244–644	3 (c)
Minnesota	47°	two temperate lakes	101–140	4 (c)
Wisconsin	46°	four temperate lakes	1.9–27.4	5 (g)
Ontario	51°	three groups of ponds in boreal/ subarctic wetlands	110–180	6 (g)
Quebec	50°	two boreal beaver ponds	14.0–16.2	7 (c)
Manitoba	55°	boreal beaver pond	109	8 (m)
Ontario	47°–50°	four boreal beaver ponds 12 boreal peatlands	139–919 0.4–67.5	9 (c)
Finland	63°	three boreal lakes <sup>b</sup>	1.1–190	10 (c)
Finland	61°	<i>Equisetum fluviatile</i> stands in a boreal lake	286	11 (c)
Finland	67°–68°	two boreal ponds	3.5–7.6	12 (c)
Finland	61°–62°	six minerogenous boreal peatlands 10 ombrogenous boreal peatlands	22.6–345.1 5.2–152.6	13 (c)
Finland	67°–68°	boreal reservoir Lokka <sup>b</sup> boreal reservoir Porttipahta <sup>b</sup>	5.3–119 (2.6–660) <sup>c</sup> 2.5–4.8 (0–2.1) <sup>c</sup>	14 (c)

<sup>a</sup>References are as follows: 1, *Duchemin et al.* [1995, 1999]; 2, *Kelly et al.* [1997]; 3, *Scott et al.* [1999] (see also *Kelly et al.* [1997]); 4, *Striegl and Michmerhuizen* [1998] and R. G. Striegl (U.S. Geological Survey, Denver, personal communication, 2000); 5, *Riera et al.* [1999]; 6, *Hamilton et al.* [1994]; 7, *Ford and Naiman* [1988]; 8, *Roulet et al.* [1997]; 9, *Bubier et al.* [1993]; 10, *Huttunen et al.* [1999] and J. T. Huttunen (University of Kuopio, unpublished data, 1997–1999); 11, *Hyvönen et al.* [1998]; 12, *Huttunen et al.* [2001c]; 13, *Nykänen et al.* [1998]; 14, this paper. Results obtained by the following methods: c, chamber techniques; g, models using the CH<sub>4</sub> concentration gradient at the water-air interface; m, micrometeorological techniques.

<sup>b</sup>Results represent seasonal mean emissions for individual study sites within habitat(s), otherwise seasonal mean emissions for habitat(s).

<sup>c</sup>Ebullition of CH<sub>4</sub> given in parenthesis.

measured with the chambers and from the changes in the water column gas store during the 11 day overturn period, was higher than the CH<sub>4</sub> emission during the rest of the open water period, and the spring CO<sub>2</sub> and N<sub>2</sub>O emissions were similar to the emissions occurring during the rest of the season. The corresponding high spring CH<sub>4</sub> and CO<sub>2</sub> emissions are typical of northern lakes in general [e.g., *Michmerhuizen et al.*, 1996; *Striegl and Michmerhuizen*, 1998; *Riera et al.*, 1999]; thus the wintertime gas production should be considered when determining the magnitude of the annual greenhouse gas emissions of northern reservoirs. For example, according to *Michmerhuizen et al.* [1996], the episodic springtime emission can account for as much as 40% of the annual CH<sub>4</sub> release in small lakes. The N<sub>2</sub>O concentrations in Lokka and Porttipahta were close to the atmospheric equilibrium level during the summer, as is the case generally in natural northern ponds and lakes [*Knowles et al.*, 1981; *Huttunen et al.*, 2001c]. However, during the period of ice cover, N<sub>2</sub>O also accumulated in the reservoirs, resulting to the high spring N<sub>2</sub>O emissions as reported for artificially oxygenated eutrophic lakes [*Huttunen et al.*, 2001a; *Kortelainen et al.*, 2000]. Our results show that N<sub>2</sub>O can be produced in reservoirs at low temperature. Although the total denitrification, i.e., the sum of produced N<sub>2</sub>O and N<sub>2</sub>, would decrease with decreasing temperature, the ratio of N<sub>2</sub>O to N<sub>2</sub> produced in denitrification is known to increase with decrease in temperature, thus enhancing the N<sub>2</sub>O production [*Melin and Nommik*, 1983].

## 5. Conclusions

[45] The CH<sub>4</sub> emissions in Lokka were among the highest emissions measured from northern aquatic and terrestrial ecosystems, while those in Porttipahta were comparable to the lowest flux rates reported. This illustrates the high variability in the CH<sub>4</sub> emissions from northern hydroelectric reservoirs. Lokka and Porttipahta, like many other natural and artificial lake ecosystems, also released CO<sub>2</sub> during the summer, in contrast to natural boreal peatlands and forests, which sequester CO<sub>2</sub> from the atmosphere.

[46] Our results indicate that the flooded biomass and trophic state, i.e., the amount of nutrients and associated primary production rates, rather than old peat deposits, could be the key factors regulating the CH<sub>4</sub> and CO<sub>2</sub> production in northern reservoirs. Therefore the prediction of the long-term greenhouse gas fluxes from reservoirs requires knowledge on the flooded ecosystems and also the postflooding trophic conditions in the reservoirs. The wintertime greenhouse gas production and consequent springtime emissions also should be considered when estimating the annual greenhouse gas emissions from northern reservoirs.

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