



## Fluxes of methane and carbon dioxide from a small productive lake to the atmosphere

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**Abstract.** The fluxes of CH<sub>4</sub> and CO<sub>2</sub> to the atmosphere, and the relative contributions of ebullition and molecular diffusion, were determined for a small hypertrophic freshwater lake (Priest Pot, U.K.) over the period May to October 1997. The average total flux of CH<sub>4</sub> and CO<sub>2</sub> (estimated from 7 sites on the lake) was approximately 52 mmol m<sup>-2</sup> d<sup>-1</sup> and was apportioned 12 and 40 mmol m<sup>-2</sup> d<sup>-1</sup> to CH<sub>4</sub> and CO<sub>2</sub> respectively. Diffusion across the air-water interface accounted for the loss of 0.4 and 40 mmol m<sup>-2</sup> d<sup>-1</sup> of CH<sub>4</sub> and CO<sub>2</sub> respectively whilst the corresponding figures for ebullition losses were 12.0 (CH<sub>4</sub>) and 0.23 (CO<sub>2</sub>) mmol m<sup>-2</sup> d<sup>-1</sup>. Most CH<sub>4</sub> (96%) was lost by ebullition, and most CO<sub>2</sub> (99%) by diffusive processes. The ebullition of gas, measured at weekly intervals along a transect of the lake, showed high spatial and temporal variation. The CH<sub>4</sub> content of the trapped gas varied between 44 and 88% (by volume) and was highest at the deepest points. Pulses of gas ebullition were detected during periods of rapidly falling barometric pressure. The relevance of the measurements to global estimates of carbon emission from freshwaters are discussed.

### Introduction

Increasing atmospheric concentrations of the radiatively active gases CH<sub>4</sub> and CO<sub>2</sub> have stimulated research on their emission from terrestrial and aquatic environments (Conrad 1996; Segers 1998). On a global scale freshwater environments contribute more than 20% of the total CH<sub>4</sub> flux to the atmosphere (Khalil & Shearer 1993) and, because of their large area, wetlands are considered to be the most important source. However, estimates of the emission of CH<sub>4</sub> and CO<sub>2</sub> from freshwater lakes (Rudd & Hamilton 1978; Miller & Oremland 1988; Kling et al. 1992; Smith & Lewis 1992; Cole et al. 1994;

Michmerhuizen et al. 1996) suggest that the importance of lakes in the global emissions of CH<sub>4</sub> and CO<sub>2</sub> may have been underestimated (Ehhalt 1974).

In lakes, CH<sub>4</sub> and CO<sub>2</sub> have contrasting patterns of production, consumption and exchange with the atmosphere. Methane is only produced in anaerobic environments, usually within sediments but also in anoxic hypolimnia (Rudd & Taylor 1980; Kuivila et al. 1988; Casper 1992), while CO<sub>2</sub> is produced by respiration throughout lakes and lake sediments. Methane is consumed by highly efficient bacterial oxidation, particularly at oxic/anoxic boundaries where less than 10% of the CH<sub>4</sub> produced at depth may diffuse across the oxycline (Frenzel et al. 1990; Casper 1992; Sweerts et al. 1996). Carbon dioxide is consumed by photosynthesis (and to a lesser extent by chemosynthesis) and, because uptake depends on the availability of light, rates are highly variable vertically and temporally.

The main pathways of exchange between air and water are molecular diffusion across the air-water interface, ebullition from the sediment through the water column and, in littoral areas, transport through emergent macrophytes (Martens & Klump 1980; Sebach et al. 1985; Chanton et al. 1989). Pathways of atmospheric exchange for CH<sub>4</sub> and CO<sub>2</sub> will differ because of their different solubility, different concentrations in the epilimnion and, to a much lesser extent, their atmospheric partial pressures. Thus CH<sub>4</sub> is relatively insoluble (saturation in freshwater is about 1.6 mol m<sup>-3</sup> at 20 °C) and therefore high concentrations at depth lead to production of bubbles and loss to the atmosphere by ebullition. Surface waters are normally oxic so concentrations of CH<sub>4</sub>, and consequently rates of diffusive loss to the atmosphere, are typically low. In contrast, CO<sub>2</sub> is highly soluble (saturation is about 39 mol m<sup>-3</sup> at 20 °C) and therefore high concentrations can accumulate at depth. Although photosynthetic carbon depletion of CO<sub>2</sub> can occur in productive lakes leading to an influx of atmospheric CO<sub>2</sub> (Emerson 1975; Portielje & Lijklema 1995; Maberly 1996), many lakes are oversaturated with CO<sub>2</sub> (Cole et al. 1994) and so release CO<sub>2</sub> to the atmosphere, particularly in winter when productivity is low (Maberly 1996).

The main objective of this study was to quantify the rates of emission of CH<sub>4</sub> and CO<sub>2</sub> by molecular diffusion and ebullition from a small hypertrophic lake. A high resolution sampling regime was used to estimate the temporal and spatial variation of loss processes.

## Materials and methods

### *Study site*

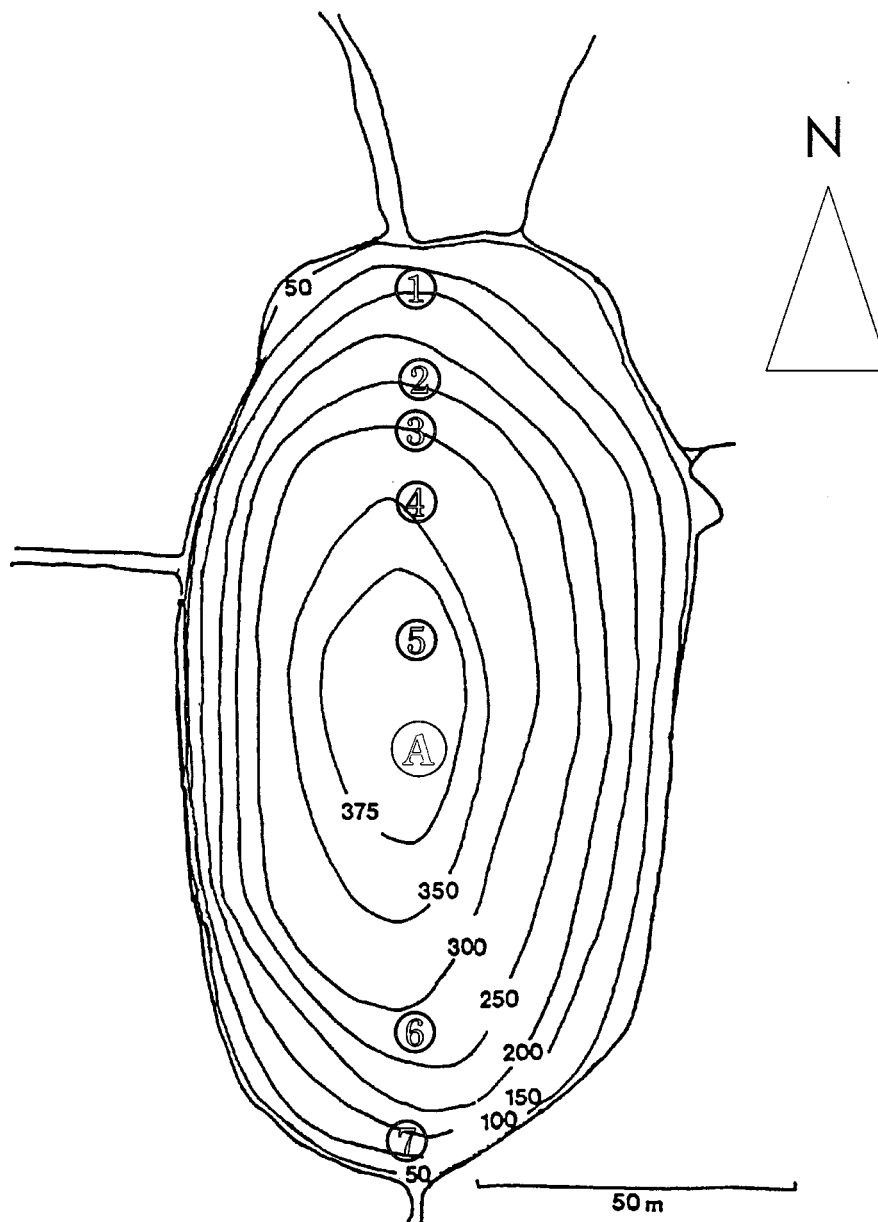
The study site was a small (1 ha) hypertrophic lake, Priest Pot, situated in fenland at the northern end of Esthwaite Water in the English Lake District, U.K. The small lake is fed by ground water, and by drainage ditches. The supply of nutrients from the cultivated catchment is sufficient to sustain high biological productivity. Like many other small water bodies, levels of essential nutrients in Priest Pot are typically high (e.g. total phosphorus  $600 \mu\text{g l}^{-1}$ ; chlorophyll a  $300 \mu\text{g l}^{-1}$ ). The maximum and mean depths were 3.9 and 2.3 m respectively but the sheltered location of the shallow lake allowed a stable thermal stratification of the water column. A benthic  $\text{O}_2$  consumption rate that exceeded the oxygen supply from the overlying water led to the establishment of an anoxic hypolimnion in summer. The organic carbon content is 22.5% of dry weight in the top six centimeter of the sediment (Goulder 1971). Samples were collected between May and October 1997. The basic limnology of Priest Pot is described by Davison and Finlay (1986) and a detailed account of the changes in the water column during stratification is provided by Finlay et al. (1997).

### *Gas sampling*

Duplicate gas traps were located at seven sites on a north-south transect of the lake (Figure 1) covering a depth range from 1.6 to 3.5 m. The traps consisted of inverted funnels (0.29 m internal diameter) sealed with rubber stoppers and suspended in wire frames for ease of handling. All traps were suspended 0.5 m above the sediment surface regardless of the depth of overlying water. On each occasion the traps were left *in situ* for 24 h and then the collected gas sub-sampled through the rubber stopper using syringes fitted with teflon “Mininert” push button valves (Supelco Inc.). The total volume of gas collected was estimated from an external scale on each funnel and checked with syringes. All samples were transported to the laboratory in a cool box and analysis of the gas composition commenced within 4 hours.

### *Water sampling*

All water samples were taken from the deepest point in the lake (Figure 1) where a mooring system allowed accurate positioning of the boat. The water column was sampled at 10 cm intervals using the multi-syringe sampler described by Heaney (1974). Upon retrieval, any gas bubbles were rapidly removed from the syringes which were then sealed with stoppered needles.



*Figure 1.* Bathymetric map of Priest Pot (depths in cm). The 7 sampling sites for ebullition are indicated with numbered circles, the main sampling point with a circled A.

Occasionally water samples were taken using a 0.5 litre bottle sampler, and sub-samples immediately removed into 20 ml syringes which were sealed as above.

## Gas analysis

### *Gas-trap samples*

The composition of the bubble gas was analysed using a Hewlett Packard 5701A gas chromatograph equipped with a 2 m 5A molecular sieve column for CH<sub>4</sub> and a 0.6 m carbosieve S (80/100 mesh) column for CO<sub>2</sub>. Each column was connected to a thermal conductivity detector. Flow rates were 1 ml s<sup>-1</sup> in both cases with oven temperatures of 70 °C (CH<sub>4</sub>) and 125 °C (CO<sub>2</sub>). O<sub>2</sub> and N<sub>2</sub> were also separated and detected in the CH<sub>4</sub> analysis. Samples of the bubble gas were injected via a gas sample valve fitted with a 0.5 ml sample loop. The loop was flushed with at least 4 times its volume of sample before injection. In all cases instrument calibration was performed using standard gas mixtures (10 and 50% CH<sub>4</sub> in N<sub>2</sub>; Phase Separation, U.K.).

### *Dissolved CH<sub>4</sub>*

The syringes were fitted with a teflon “Mininert” valve in the laboratory. The volume of water in the syringe samples was adjusted to 2 ml and a headspace of 8 ml helium was added and the valve closed. The samples were shaken for 0.5 minutes and then allowed to stand for 4 minutes before analysis of the headspace CH<sub>4</sub> concentration using a gas chromatograph equipped with FID (Perkin Elmer 8500) following the method described by Hall et al. (1996). Instrument calibration was performed using standard gas mixture (1% CH<sub>4</sub> in N<sub>2</sub>; Phase Separation, U.K.).

### *Dissolved inorganic carbon*

Water samples were kept at 4 °C in the dark for up to 2 hours before measurement. The total inorganic carbon (C<sub>T</sub>) concentration was measured by conversion to CO<sub>2</sub> (Maberly 1990). Between 20 and 50 µl were injected into 2 ml of 0.5 M phosphoric acid which was bubbled with nitrogen at 200 ml min<sup>-1</sup>. The sample was passed to an infra-red gas analyser (ADC Mk III), the output integrated over time and the concentration calculated by reference to a sodium bicarbonate standard.

## *pH*

A calibrated combination electrode (Radiometer, GK2401C) was used to measure pH. The temperature of the samples was rapidly adjusted to 20 °C whilst still enclosed in the syringe. A 10 ml aliquot was removed into a narrow necked vial and the pH measured with a slow rate of stirring. The *in situ* pH was calculated using a temperature coefficient of 0.01 pH unit decrease °C<sup>-1</sup> (Talling 1973). Concentrations of CO<sub>2</sub> were calculated from temperature, *in situ* pH, and the concentration of C<sub>T</sub> using the equations in Maberly (1996).

## *Air-water gaseous exchange*

Assuming that diffusion through the sub-surface boundary layer was the rate limiting step (House et al. 1984; Liss & Merlivat 1986) the flux of CH<sub>4</sub> and CO<sub>2</sub> across the air-water interface was calculated from the difference between the concentration just below the water surface (assumed to be at equilibrium with the air) and that measured in the bulk surface water (Sellers et al. 1995). The temperature-dependent equilibrium concentration of both CO<sub>2</sub> and CH<sub>4</sub> in the boundary layer was calculated using the equations of Rebsdorf et al. (1991) and Yamamoto et al. (1976) assuming an air concentration of 360 ppm for CO<sub>2</sub> and 1.7 ppm for CH<sub>4</sub>. The temperature-dependent diffusion coefficient was calculated following Maberly (1996) for CO<sub>2</sub> and Klump and Martens (1981) for CH<sub>4</sub>. Fick's first law was used to calculate the rate of flux across a boundary layer 200, 400 and 800 μm thick (the sheltered location of Priest Pot suggested that surface boundary layers were likely to be substantial). Chemical enhancement of CO<sub>2</sub> influx, as reported by Emerson (1975), was not taken into account as the pH of the immediate surface water was always less than 7.6.

Temperature and oxygen concentration were measured with a YSI Model 57 oxygen electrode and meter. Air pressure and wind velocity were measured by an automatic weather station located in 1 m height on a buoy in the centre of adjacent Esthwaite Water.

## **Results**

### *Dissolved CH<sub>4</sub> and CO<sub>2</sub>*

The pattern of stratification and oxygen depletion was similar in 1997 to previous years (Davison & Finlay 1986; Finlay et al. 1997). The water column was stratified from May until the end of September. Upon stratification, oxygen was rapidly depleted at depth and by the beginning of June oxygen could

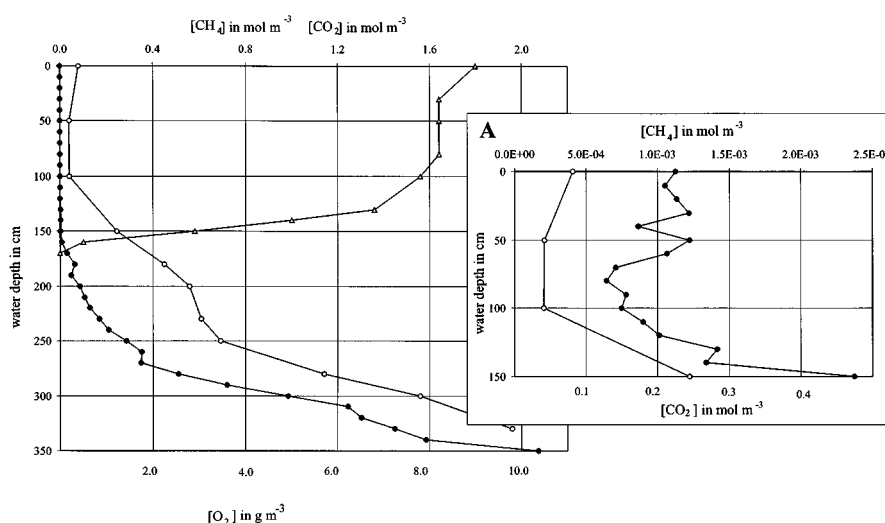


Figure 2. Example of high resolution depth profiles of  $\text{CH}_4$  – (closed circles) and  $\text{CO}_2$  – (open circles) and  $\text{O}_2$  – (triangles) concentrations, data collected on 27th ( $\text{CH}_4$ ) and 29th ( $\text{CO}_2$ ,  $\text{O}_2$ ) August 1997. The top 150 cm are expanded in A.

not be detected below 2.0 m. The depth of the oxycline varied slightly but at no time did it rise higher than 1.5 m from the water surface. An example depth-profile for the end of August shows oxygen depletion below 1.7 m, and high concentration of  $\text{CH}_4$  and  $\text{CO}_2$  in the hypolimnion (Figure 2).

The temporal variation in the concentrations of  $\text{CO}_2$  and  $\text{CH}_4$  in the surface water of Priest Pot is shown in Figure 3(A). The two gases showed essentially the same seasonal pattern but the concentration of  $\text{CO}_2$  was generally two orders of magnitude greater than that of  $\text{CH}_4$ . The concentration of  $\text{CO}_2$  varied from 27 to 326 (average 132)  $\text{mmol m}^{-3}$  and  $\text{CH}_4$  from 0.31 to 4.8 (average 1.3)  $\text{mmol m}^{-3}$ . These values are 2–20 and 120–1800 times greater than the air equilibrium concentrations of  $\text{CO}_2$  and  $\text{CH}_4$  respectively.

#### *Rates of diffusive flux*

Priest Pot was a source of both  $\text{CH}_4$  and  $\text{CO}_2$  to the atmosphere over the entire study period. Variation in the diffusive flux for both gases, based on a boundary layer thickness of 400  $\mu\text{m}$ , is shown in Figure 3(B). The flux for  $\text{CO}_2$  varied from 3.9 to 102, and for  $\text{CH}_4$  from 0.06 to 1.4  $\text{mmol m}^{-2} \text{d}^{-1}$  (Table 1). The diffusive loss of  $\text{CO}_2$  to the atmosphere was approximately two orders of magnitude larger than that for  $\text{CH}_4$ . The boundary layer thickness is typical for an average wind velocity of  $1.2 \text{ m s}^{-1}$  (Upstill-Goddard et al. 1990) which is appropriate for the sheltered location of Priest Pot. Wind

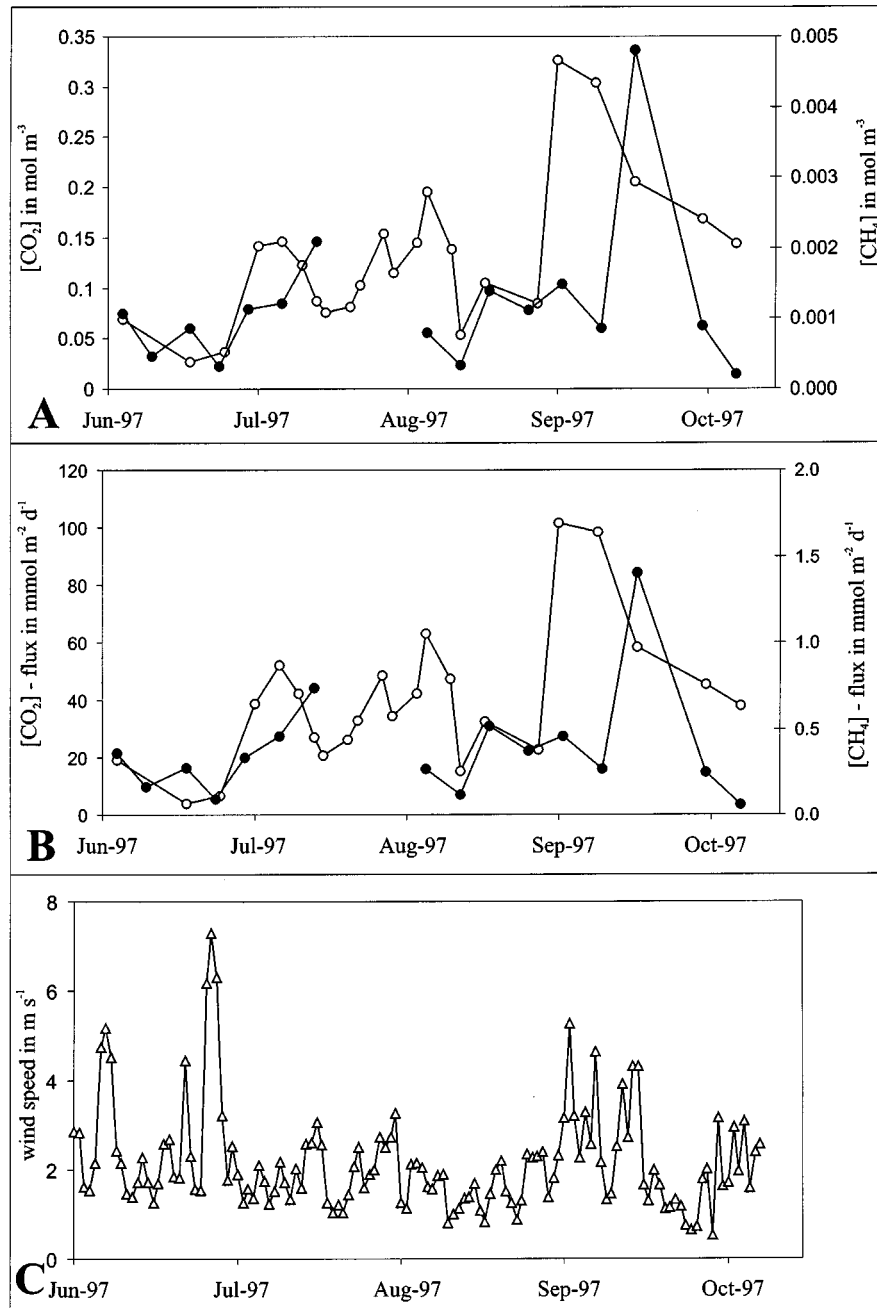


Figure 3. Seasonal variations for  $\text{CH}_4$  (closed circles) and  $\text{CO}_2$  (open circles) of (A) concentrations in the surface water, and (B) flux to the atmosphere for a boundary layer  $400 \mu\text{m}$  thick. Wind speed measured at the neighbouring Esthwaite Water is given as daily averages in (C).



*Table 1.* Diffusive fluxes of CH<sub>4</sub> and CO<sub>2</sub> measured at central point, all readings in mmol m<sup>-2</sup> d<sup>-1</sup>, surface-water temperature in °C.

Date	Water temperature at surface	CH <sub>4</sub>	Date	CO <sub>2</sub>
10 Jun	19.5	0.16		
18 Jun	16.8	0.28	16 Jun	3.89
24 Jun	15.2	0.09	25 Jun	6.69
30 Jun	14.7	0.34	02 Jul	38.65
07 Jul	22.0	0.46	07 Jul	52.35
14 Jul	19.9	0.74	14 Jul	27.00
06 Aug	17.9	0.27	06 Aug	63.20
13 Aug	21.0	0.12	13 Aug	15.44
27 Aug	17.8	0.37	29 Aug	22.78
03 Sep	15.8	0.46	02 Sep	101.56
11 Sep	16.0	0.27	10 Sep	98.51
18 Sep	14.0	1.40	18 Sep	58.52
02 Oct	13.0	0.25	02 Oct	45.48
09 Oct	13.0	0.06	09 Oct	37.99

speed measured at the nearby Esthwaite Water, which is much larger and not so sheltered as Priest Pot, was on average 2.1 m s<sup>-1</sup> over the study period (Figure 3(C)). Increasing the thickness of the boundary layer would decrease the flux proportionately.

#### *Spatial variation in gas ebullition and composition*

The rate of gas ebullition varied with water depth (Figure 4). At the four sites where water depth was less than 3 m the seasonal average rates were very similar at about 162 ml m<sup>-2</sup> d<sup>-1</sup>. This increased to between 236 and 380 ml m<sup>-2</sup> d<sup>-1</sup> for the three deepest sites. Averaged over all the sites and study period, CH<sub>4</sub> was the dominant constituent of the gas bubbles (66%) although nitrogen (36%), CO<sub>2</sub> (3%) and traces of oxygen were also found (Figures 4 and 5). As most of the traps were suspended in anoxic water for the duration of the study oxygen probably entered the gas phase during the sub-sampling procedure when the traps were suspended in aerobic water for several minutes. The proportional content of CH<sub>4</sub> increased monotonically with depth from 43.7% at 1.6 m to 88.1% at 3.5 m (Figure 4). The average volume and composition of the trapped gases from the 7 sites on the transect

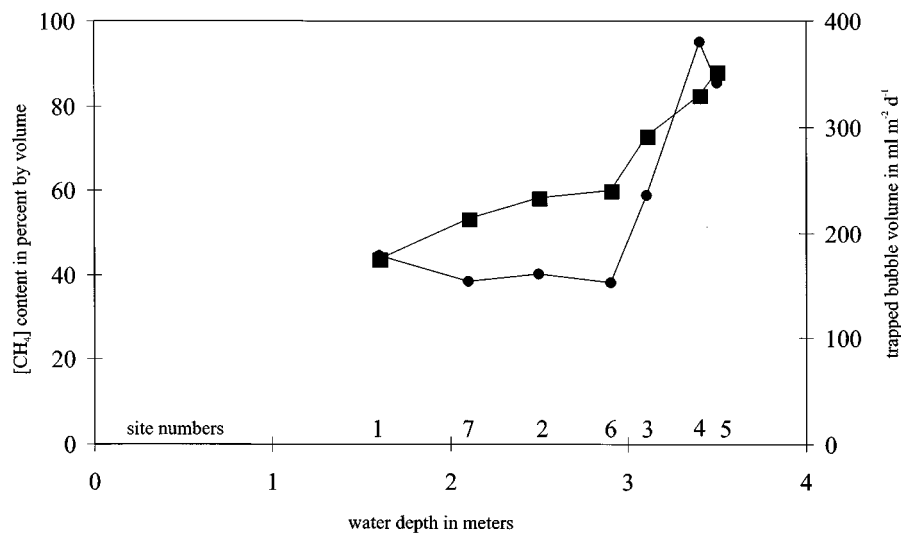


Figure 4. Average total gas ebullition (black dots) and CH<sub>4</sub> content (black boxes) for the seven sites over the study period as a function of water depth.

of the lake were used to calculate the total loss of CH<sub>4</sub> and CO<sub>2</sub> from the lake by ebullition. The different composition and smaller volume of gas from the shallower sampling sites resulted in a higher contribution of deeper sediments to the loss of CH<sub>4</sub> and CO<sub>2</sub> than from the shallower.

#### *Temporal variation in gas ebullition and composition*

The release of gas from a deep site (trap site 4) and a shallow site (trap site 7) is compared in Figure 5. There was a general trend for rates of gas release to increase over the study period with sharp peaks of release in August and October (see also Table 2). These peaks corresponded with rapidly falling barometric pressure (Figure 6). When the water column mixed around the end of September to beginning of October, the surface sediments became oxidised and the methane content of the ebullient gas decreased to 30%.

## **Discussion**

### *Pathways of emission*

Lakes are directly linked to the atmospheric carbon pool by two gases, CH<sub>4</sub> and CO<sub>2</sub>, both of which are radiatively active and contribute to global climate change. Methane is primarily produced by decomposition in anaerobic environments. The persistence of such conditions in sediments means that lakes

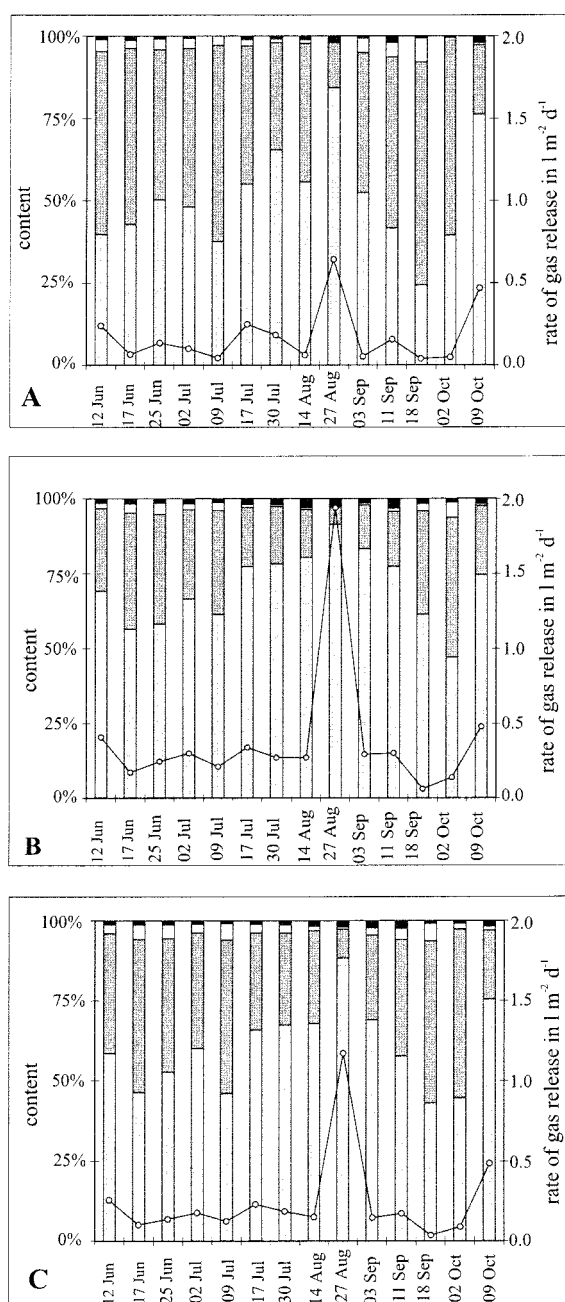


Figure 5. Seasonal variations in composition and rate of gas released, (A) at shallow site (trap site 7), (B) at deep site (trap site 4) and (C) average over all trap sites. Bars indicate % content of  $\text{CH}_4$  (light grey);  $\text{CO}_2$  (black);  $\text{N}_2$  (dark grey); and  $\text{O}_2$  (white); total gas release rate is shown by the line.

Table 2. Ebullition fluxes of CH<sub>4</sub> and CO<sub>2</sub> from all sites, all readings in mmol m<sup>-2</sup> d<sup>-1</sup>.

Date	Trap site 1		Trap site 2		Trap site 3		Trap site 4		Trap site 5		Trap site 6		Trap site 7	
	CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>
12 Jun	8.09	0.10	8.51	0.19	6.30	0.16	13.72	0.30	10.87	0.25	1.90	0.08	4.24	0.12
17 Jun	0.22	n.d.	0.56	n.d.	1.98	0.05	4.71	0.14	9.33	0.16	1.60	0.02	1.28	0.05
25 Jun	0.41	n.d.	1.93	n.d.	7.27	0.17	7.03	0.18	6.72	0.16	1.43	n.d.	3.24	0.06
02 Jul	2.21	0.01	6.98	0.08	3.70	0.06	9.17	0.23	11.13	0.27	2.11	0.05	2.56	0.04
09 Jul	2.24	0.01	0.56	n.d.	3.14	0.09	6.01	0.14	6.70	0.19	2.03	0.07	0.71	0.00
17 Jul	4.50	0.03	8.84	0.08	6.15	0.19	15.27	0.36	14.30	0.24	4.68	0.09	5.11	0.05
30 Jul	1.09	0.00	5.20	0.06	6.42	0.15	12.05	0.28	15.02	0.35	5.80	0.14	6.43	0.09
14 Aug	1.73	0.03	2.91	0.03	6.66	0.18	11.92	0.45	10.98	0.31	4.24	0.15	1.53	0.04
27 Aug	92.92	1.30	52.89	0.82	58.23	1.67	108.37	2.92	66.79	1.91	31.05	0.89	29.26	0.56
03 Sep	0.00	0.00	0.57	n.d.	8.96	0.76	13.65	0.24	13.94	0.19	5.87	0.12	1.59	0.03
11 Sep	0.00	0.00	0.06	n.d.	6.26	0.13	10.32	0.44	13.25	0.47	4.04	0.15	2.43	0.12
18 Sep	0.00	0.00	0.00	0.00	0.75	0.00	1.49	0.04	2.68	0.06	0.12	n.d.	0.35	0.01
02 Oct	0.37	0.02	0.75	0.01	2.25	0.05	2.35	0.07	4.20	0.09	0.89	0.02	0.79	0.01
09 Oct	13.56	0.36	18.60	0.36	11.79	0.31	14.09	0.31	13.49	0.28	14.65	0.34	14.24	0.39

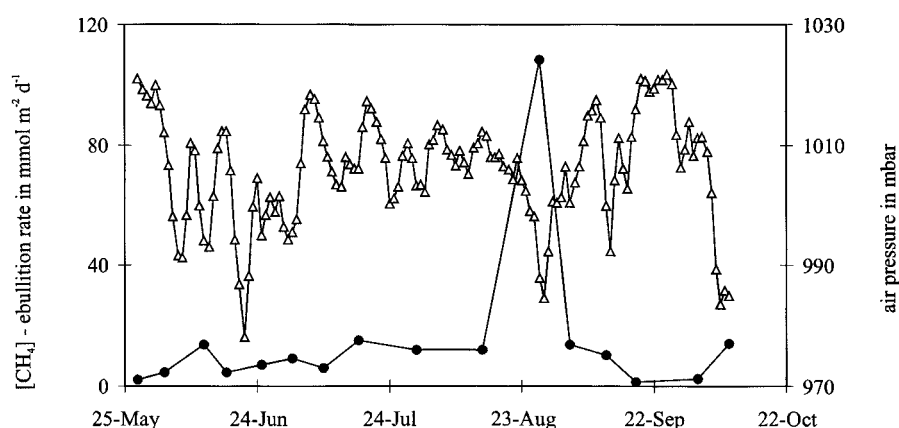


Figure 6. Means of methane ebullition rate (black dots) and daily means of atmospheric pressure (open triangles) over study period.

loose methane to the atmosphere throughout the year (Fallon et al. 1980; Miller & Oremland 1988; Whalen & Reeburgh 1990; Smith & Lewis 1992; Michmerhuizen et al. 1996). In contrast, production as well as decomposition mediate changes in the concentration of  $\text{CO}_2$ . While some lakes tend to act as sources of  $\text{CO}_2$  to the atmosphere (Rebsdorf et al. 1991; Cole et al. 1994), in others the concentration of  $\text{CO}_2$  in surface waters is very dynamic and the lake can switch rapidly between uptake and release (Emerson 1975; Talling 1976; Portielje & Lijklema 1995; Maberly 1996). Priest Pot was a net source of both  $\text{CH}_4$  and  $\text{CO}_2$  to the atmosphere from June to October 1997, despite supporting high concentrations of photosynthetic organisms in the metalimnion and hypolimnion in this (data not shown), as in previous years (Finlay et al. 1997). Striegl and Michmerhuizen (1999) described also two lakes in Minnesota as sources of  $\text{CH}_4$  and  $\text{CO}_2$  to the atmosphere during open-water period.

In Priest Pot, the two gases were lost to the atmosphere by different pathways. Ninety-six per cent of the  $\text{CH}_4$  was lost by ebullition while 99% of the  $\text{CO}_2$  was lost by diffusion across the air-water interface. These estimates were based on an assumed boundary layer thickness of  $400 \mu\text{m}$ , but the pattern of release is robust when calculated at  $200$  and  $800 \mu\text{m}$ : ( $\text{CH}_4$  92 to 98% release by ebullition,  $\text{CO}_2$  98.8 to 99.7% release by diffusion). The contrasting pathways of loss for the two gases result from chemical and biological factors. The ebullient gas bubbles released were composed primarily of  $\text{CH}_4$  rather than  $\text{CO}_2$ , despite rather similar concentrations of each, at least in the anoxic hypolimnion (e.g. Figure 2), because of the much lower solubility of  $\text{CH}_4$ . The high rate of diffusive loss of  $\text{CO}_2$  at the air-water interface results

from its concentration in the surface water which was, on average, 110 times greater than the concentration of  $\text{CH}_4$ , producing a concentration difference with the air-equilibrium concentration of nearly 100-fold. Given the similar concentrations of  $\text{CO}_2$  and  $\text{CH}_4$  in the hypolimnion (Figure 2), the lower concentrations of  $\text{CH}_4$  in the surface water are a consequence of the rate of oxidation at the oxic/anoxic boundary exceeding the net rate of uptake of  $\text{CO}_2$  via photosynthesis. Furthermore, methane oxidation leads to  $\text{CO}_2$  production and so will increase the concentration of  $\text{CO}_2$  in surface waters.

Ebullition appears to be the major route of  $\text{CH}_4$  emission to the atmosphere in some but not all lakes (Miller & Oremland 1988; Smith & Lewis 1992). In five high latitude lakes diffusion was the primary pathway for  $\text{CH}_4$  loss and the authors explained 40% of the variability in emissions by changes in concentration of  $\text{CH}_4$  in the surface water (Smith & Lewis 1992).

#### *Temporal changes in $\text{CH}_4$ ebullition*

At all the trap sites there was an increase in rate of ebullition from June to August, to about  $12 \text{ mmol m}^{-2} \text{ d}^{-1}$  (Table 2, Figure 5). This is presumably a result of increasing supersaturation of  $\text{CH}_4$  in the interstitial water of the sediment and possibly increasing rates of decomposition as water temperature increased at depth.

Superimposed on this general trend were periods of greater release when the volume of ebullient gas could be more than 10 times the average over the study period. These episodes (see 27 August and 9 October, Figures 5, 6) corresponded to low barometric pressures (988 and 985 mbar) and a 2% decrease in air pressure triggered a 10-fold increase (27 August) in the volume of gas released from the sediment (Figure 6). Increased rates of  $\text{CH}_4$  ebullition have been observed during decreased hydrostatic pressure in tidal systems (Chanton & Martens 1988; Martens & Chanton 1989) or caused by falling water levels e.g. in the Amazon Basin (Bartlett et al. 1988). Mattson and Likens (1990, 1993) were the first to report a correlation between low air pressure (a decrease of 1 to 3%) and increased rates of  $\text{CH}_4$  release (18%) in a freshwater lake. In Mirror Lake the events leading to stimulated rates of  $\text{CH}_4$  release were associated with heavy rain and passage of a hurricane and so were also linked to physical disturbance (Mattson & Likens 1993). In the present study, the two release maxima occurred when wind speed and air pressure were both low (Figures 3(C), 6), and disturbance of the sediment would be very unlikely. Enhanced rates of gas release, triggered by low barometric pressure can only occur if the concentration of  $\text{CH}_4$  within the sediment is high. Thus, in August the  $\text{CH}_4$  concentration was already over-saturated within the hypolimnion ( $1.59 \text{ mol m}^{-3}$  at 3.4 m) and low pressure elicited a large release of gas. In contrast, in June  $\text{CH}_4$  concentrations in the

hypolimnion were only  $0.70 \text{ mol m}^{-3}$  and the amount of  $\text{CH}_4$  in the sediment interstitial water is likely to have been much lower on this occasion. Similarly in October, the low pressure only resulted in a small increase in rate of gas release. At this time Priest Pot had destratified and  $\text{CH}_4$  concentration near ( $0.24 \text{ mol m}^{-3}$  at 3.4 m) and in the surface of the sediment will also have been low.

Jones and Simon (1980) found pulses of  $\text{CH}_4$  release from nearby eutrophic Blelham Tarn in Cumbria, U.K. which they explained as resulting from pulses of labile organic carbon into the sediments. An additional, and not necessarily mutually exclusive explanation, is that low pressure was also involved. Combining the data of Jones and Simon (1980) with contemporary archive barometric readings from a local weather station indicated that high rates of ebullition did coincide with low air pressure (data not shown).

#### *Contribution of lakes to atmospheric $\text{CH}_4$ and $\text{CO}_2$*

The emission rates determined for  $\text{CH}_4$  and  $\text{CO}_2$  correspond to a C-loss of  $52 \text{ mmol m}^{-2} \text{ d}^{-1}$  or  $6.2 \text{ kg}$  per day from this one-hectare lake. Diffusive loss of  $\text{CO}_2$  was the primary route of carbon release to the atmosphere. Methane contributed 24% of the total carbon loss.

The average rate of methane emission from Priest Pot between July and October 1997 was about  $9.7 \text{ mmol m}^{-2} \text{ d}^{-1}$ . This is greater than the average rate calculated by Smith and Lewis (1992) from a literature survey of more than 20 lakes covering a range of latitudes which gave a mean of  $2.6$  and a standard deviation of  $0.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ . However, it falls within the range found for productive temperate lakes (Table 3). The present data for Priest Pot do not include estimates of loss through emergent macrophytes. Priest Pot is fringed by *Phragmites australis* (Cav.) Trin. ex Steudel, *Typha latifolia* (4% of lake area), and *Nuphar lutea* (L.) Sm. (18% of lake area). The range of efflux rates reported for these plants, of between  $0.4$  and  $27 \text{ mmol m}^{-2} \text{ d}^{-1}$  for *Phragmites* (Brix et al. 1996),  $9$  to  $16 \text{ mmol m}^{-2} \text{ d}^{-1}$  for *Typha* sp. (Chanton et al. 1993; Sebachner et al. 1985), and  $22 \text{ mmol m}^{-2} \text{ d}^{-1}$  for water lilies (Dacey & Klug 1979), are equivalent to, or slightly exceed the average rate we estimated, reducing the error introduced by ignoring this pathway.

Annual rates of carbon release from Priest Pot were calculated from the average emission rates during the stratified period between May and September and from the October measurements for the remainder of the year. The  $\text{CO}_2$ -flux for the period of destratification was probably slightly overestimated as the  $\text{CO}_2$  concentration in October was higher than in May. Since Priest Pot is seldom covered by ice, accumulation and subsequent pulses of emission (e.g. Kling et al. 1992; Michmerhuizen et al. 1996) are unlikely. The

Table 3. Methane fluxes from different aquatic systems (all readings calculated to  $\text{mmol m}^{-2} \text{d}^{-1}$ ).

Rate	Object	Notes	Reference
0.034–0.73	Searsville L. (freshwater reservoir)	diffusion	Miller & Oremland 1988
0.034–69.6	Searsville L. (freshwater reservoir)	diffusion + ebullition	Miller & Oremland 1989
0.019–0.074	Big Soda L. (meromictic)	diffusion + ebullition	Miller & Oremland 1990
0.06–0.20	Soap L. (meromictic)	diffusion + ebullition	Miller & Oremland 1991
0.001–4.8	Mono L. (meromictic)	diffusion + ebullition	Miller & Oremland 1992
0.5–24	Lake Wingra (eutrophic)	ebullition	Barber & Ensign 1979
0–60	Can Shield lakes	evasion	Rudd & Hamilton 1978
0.34	Priest Pot (hypertrophic)	diffusion	this study
12.4	Priest Pot (hypertrophic)	ebullition	this study
0.05–4.26	Mirror lake (softwater)	ebullition	Mattson & Likens 1990, 1993
2.0–2.5	beaver pond	diffusion + ebullition	Naiman et al. 1991
2.4	L. Mendota	diffusion	Fallon et al. 1980
1.6	high altitude lakes		Smith & Lewis 1992
0.05–0.55	Can Shield lakes (oligotrophic)	diffusion	Rudd et al. 1993
0.67–1.32	Canadian reservoirs	diffusion	Rudd et al. 1993
0.08–1.02	N Alaska lakes	diffusion	Kling et al. 1992

annual rates of emission for Priest Pot were  $1.81 \text{ mol CH}_4 \text{ m}^{-2}$  and  $14.2 \text{ mol CO}_2 \text{ m}^{-2}$ .

The conservative assumption by Ehalt (1974) that only 10% of a lake surface can emit methane is probably an underestimate. The data presented here for Priest Pot showed high spatial variability, but methane emission from all depths.



If we assume that 30–50% of the surface of a lake can emit methane, the average annual rates of  $1\text{--}25 \times 10^{12}$  g CH<sub>4</sub> (Cicerone & Oremland 1988) are increased to  $36\text{--}51 \times 10^{12}$  g CH<sub>4</sub>. This is similar to  $55 \times 10^{12}$  g CH<sub>4</sub> a<sup>-1</sup> calculated by Smith and Lewis (1992) based on a literature survey of arctic, temperate, and tropical lakes as well as open water and macrophyte regions, assuming CH<sub>4</sub> release from 50% of a lake surface. Using the data for Priest Pot the annual loss to the atmosphere from freshwaters could be as great as  $72 \times 10^{12}$  g CH<sub>4</sub> and  $156 \times 10^{12}$  g CO<sub>2</sub> based on a surface area for lakes and other inland waters of  $2.5 \times 10^6$  km<sup>2</sup> (Wetzel 1983).

These high values for Priest Pot may be realistic and may reflect the large amount of organic matter available for decomposition at this site. This uncertainty highlights the need to obtain more accurate estimates on a greater variety of lakes, taking spatial and temporal heterogeneity into account, in order to improve global estimates of methane release. In particular, the triggering of large bursts of CH<sub>4</sub> release by low atmospheric pressure, suggest that even weekly sampling may not be sufficient to estimate rates of accurately.

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