

## Temporal variations in surface water CO<sub>2</sub> concentration in a boreal humic lake based on high-frequency measurements

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We measured surface water CO<sub>2</sub> concentrations continuously at three different depths to reveal the seasonal, daily and diel CO<sub>2</sub> dynamics of a steeply stratified pristine, spring-meromictic, humic lake during April 2005–October 2006. The lake was supersaturated with CO<sub>2</sub> most of the time and was a net source of CO<sub>2</sub> to the atmosphere. The stability of stratification and the depth of water column mixing strongly controlled the surface water CO<sub>2</sub> concentrations. Surface water concentrations as high as 195 μmol l<sup>-1</sup> were measured when mixing extended to deep waters during spring ice breakup and autumn turnover. The concentrations were near the level of atmospheric equilibrium, about 15 μmol l<sup>-1</sup>, during periods of high stability. The yearly CO<sub>2</sub> fluxes to the atmosphere were 3.7 and 2.5 mol m<sup>-2</sup> in 2005 and 2006, respectively.

### Introduction

The idea that freshwater ecosystems are sites that mineralize allochthonous carbon compounds derived from the surrounding watershed, in addition to processing their own autochthonously produced organic carbon, is becoming widely accepted (e.g. Richey *et al.* 2002, Hanson *et al.* 2004, Salonen *et al.* 2005). Lacustrine ecosystems are thus supersaturated with CO<sub>2</sub> (Cole *et al.* 1994). Their role as ventilators of terrigenous carbon to the atmosphere are manifested in epilimnetic production:respiration (P:R) ratios or net ecosystem production (NEP) values that

in lakes are usually below 1 or 0, respectively (del Giorgio and Peters 1994). On a global scale P:R ratios and NEP define the roles played by lake ecosystems as sources or sinks of carbon and are thus useful tools during attempts to understand their roles as sources or sinks of atmospheric CO<sub>2</sub> (del Giorgio and Duarte 2002). The importance of lakes in global carbon cycling is emphasized by the recent finding that instead of the approx. 1.5% coverage as suggested previously, lakes, ponds and impoundments cover more than 3% of the earth's nonoceanic surface area (Downing *et al.* 2006). Thus, global material processing (e.g. carbon mineralization,

uptake of inorganic carbon in photosynthesis) by freshwater ecosystems is twice as important as previously believed.

Since global perspective studies of lacustrine carbon cycling are becoming more important, there is a need for detailed information on carbon dynamics. Intersystem differences as well as long-term changes in annual and general seasonal patterns in concentrations of carbon compounds have been studied for decades, but much less is known of the short-term variations (i.e. between weeks, days and times of the day) and details of seasonal changes. Lakes certainly are highly dynamic, since daily differences in temperature and irradiance are large enough to result in changes in photosynthesis as well as in respiration in systems where most of the photosynthetic microorganisms have generation times longer than one day (Reynolds 2006). Due to the shortcomings of the available measuring technology, scientists have until recently been forced to ignore the true dynamics but the situation is changing rapidly, since the new, reliable and affordable technologies facilitate continuous monitoring (Sellers *et al.* 1995, Kalff 2002, Hari *et al.* 2008).

In the boreal zone, where lakes are a characteristic feature of the postglacial landscape, the role of lacustrine ecosystems is further emphasized. In Finland there are about 190 000 lakes and ponds >0.05 ha in size and they cover on average of 10% (in some regions 20%) of the land-surface area (Raatikainen and Kuusisto 1990). Carbon-cycling studies in Finland have traditionally focused on seasonal and interannual variations, using extensive sampling protocols (e.g. Striegl *et al.* 2001, Rantakari and Kortelainen 2005). These intensive studies usually relied on a sampling interval of one week and thus the temporal resolution is fairly poor (Salonen *et al.* 2005; A. Ojala unpubl. data). In the present study we aimed at filling the apparent gap in knowledge of boreal lakes and investigated the dynamics of surface water CO<sub>2</sub> of one lake throughout two consecutive years, using continuous high-frequency measurements. The seasonal, weekly, daily and diel variations in CO<sub>2</sub> concentration studied are presumably under metabolic and physical control (cf. Hanson *et al.* 2006). We also present estimates of CO<sub>2</sub>

exchange between the lake and the atmosphere, calculated with the widely used gas exchange model of Cole and Caraco (1998). The study lake is a small pristine body of water that is the uppermost lake of a lake chain surrounded by an old-growth forest. Thus, it is a true reference lake under minimal anthropogenic influence and detailed information on the temporal dynamics of CO<sub>2</sub> can be utilized, e.g. in studies on the effects of climate change on boreal lacustrine ecosystems. By investigating a small lake, we also wanted to change the focus from large and medium-sized lakes to small lakes, which represent the bulk of the global freshwater area, but have so far been underemphasized in studies.

## Material and methods

### Study site

Our study lake, Lake Valkea-Kotinen, is situated in the Kotinen Nature Reserve area in Evo, southern Finland (61°14'N, 25°03'E). The lake surface area is 0.041 km<sup>2</sup> and its maximum and mean depths are 6.5 m and 2.5 m, respectively. The catchment area of the lake, which is 0.30 km<sup>2</sup>, consists of an old, pristine, mostly coniferous forest and a small area of peatland. As the uppermost lake in a lake chain, it has no inlet. For monitoring of long-range transboundary air pollution, Lake Valkea-Kotinen with its surrounding catchment area has belonged to the multidisciplinary International Cooperative Programme on Integrated Monitoring (ICP IM) since 1990 (Ruoho-Airola *et al.* 1998). Some results from the early years of monitoring of the lake are presented in Keskitalo *et al.* (1998). The lake is slightly acidic (yearly average in 2005–2006 for pH 5.2–5.3), has high levels of dissolved organic carbon (DOC) and water colour (DOC 13.3–13.7 mg l<sup>-1</sup>; colour 168–196 mg Pt l<sup>-1</sup>), and in terms of surface water (0–1 m) nutrients (total nitrogen (TN) 450–485 µg l<sup>-1</sup>; total phosphorus (TP) 14–15 µg l<sup>-1</sup>) it can be classified as oligotrophic or mesotrophic. Due to the occasionally high chlorophyll *a* concentrations (yearly average in 2005–2006 for chlorophyll *a* 14–15 µg l<sup>-1</sup>), however, the lake appears meso-eutrophic (Wetzel 2001).

## Measurements of surface water CO<sub>2</sub>

We used continuous measurements of CO<sub>2</sub> at the depths of 0.1, 0.5 and 1.5 m as described in Hari *et al.* (2008). In short, for each depth we used a measuring system in which a continuous airstream was circulated with a diaphragm pump (Rietschle Thomas (now Gardener Denver Thomas) SMG-4, Puchheim, Germany) in a closed loop consisting of gas-impermeable tubing (stainless steel and butyl rubber), a CO<sub>2</sub> analyser (CARBOCAP® GMP343; Vaisala Oyj, Vantaa, Finland), semipermeable silicone rubber tubing for gas collection and the pump. The pumps and CO<sub>2</sub> analysers were placed in a temperature-controlled box on a raft, also used for micrometeorological measurements (Vesala *et al.* 2006), whereas the semipermeable tubings were placed at the respective measuring depths. The gas collection tubings, CO<sub>2</sub> analyser and pump were connected with gas-impermeable tubings. The gas concentrations in the continuous airstream within the loop equilibrated with that in water around the semipermeable tubing and, thus, the CO<sub>2</sub> concentration of the water could be continuously measured in the gaseous phase. We cleaned the silicone rubber at 0.1 m and 0.5 m weekly or biweekly during the open-water period by gently scrubbing the surface and replaced them at all depths monthly or bimonthly depending on the time of year; the replacement of the tube at 1.5 m was considered adequate, since there were no changes in CO<sub>2</sub> readings before and after the operation. We used the analogue output option of the analysers with 0–2 V output signal and logged the readings with a Delta-T data logger (Delta-T Devices Ltd, Cambridge, UK) in 2005–2006. From March 2006 onwards we converted the analogue signal to digital readings with an analogue-to-digital (A/D) converter (Nokeval Oyj, Nokia, Finland) and logged them with a computer; simultaneously, temperature probes (Philips KTY81-110, Philips Semiconductors, Eindhoven, The Netherlands) were installed at each measuring depth. The sensor outputs in voltages were calibrated regularly, using standardized mixtures (400 ppm and 4000 ppm) of CO<sub>2</sub> (AGA Oy, Espoo, Finland) and the output signals were converted to ppm of CO<sub>2</sub>, using this two-point calibration

curve. The concentration of CO<sub>2</sub> in water ( $C$ ;  $\mu\text{mol l}^{-1}$ ) could then be determined, using the dependence of solubility of CO<sub>2</sub> as a function of temperature and an appropriate Henry's law constant ( $K_{\text{H}}$ ;  $\text{mol (l atm)}^{-1}$ ):

$$C = x_{\text{CO}_2} P K_{\text{H}}, \quad (1)$$

where  $x_{\text{CO}_2}$  is the CO<sub>2</sub> concentration (= probe output, ppm) and  $P$  the atmospheric pressure (atm). We used the humidity compensation of the probe to account for the water vapour effect on the CO<sub>2</sub> signals and assumed that the relative humidity (RH) = 100%. The logging interval was one minute and the data were further averaged for hourly and daily values. We began continuous CO<sub>2</sub> measurements on 9 April 2005 and continued until 6 March 2006. The measurements began again on 18 March 2006 with the new logging system and continued until 26 October 2006. Due to pump failure there was a break in the measurements from late May until late June in 2005. In July 2005 and August–September 2006 water leaked into the system and thus the data from 1.5 m were lost. Short data gaps due to calibration, system checkups, maintenance work and power failures were filled, using linear interpolation.

In addition to continuous measurements we used the CO<sub>2</sub> data from the ICP IM to verify the quality of our measurements. For this the lake was sampled weekly between 09:00 and 10:00 local time (GMT + 2 h) for surface water dissolved inorganic carbon (DIC) concentration and pH. The water for the samples (approx. 4 l) was taken from the lake surface with a polyethylene bucket equipped with a draining tube. The samples for DIC were drained into duplicate 25-ml glass-stoppered bottles so that the bottles were permitted to overflow at least three times their own volume to ensure that no air bubbles were left inside. The bottles were taken to the laboratory in a darkened icebox and DIC was measured within three hours by lowering the pH of the sample with strong acid and measuring the released CO<sub>2</sub> with an infrared (IR) gas analyser (URAS 3G; Hartmann & Braun AG, Frankfurt am Main, Germany). For pH measurements a 0.5-l bottle was filled and taken to the laboratory for analysis (Orion pH meter, model SA

720; Thermo Fisher Scientific, Inc., Waltham, MA, USA). The CO<sub>2</sub> concentration of the water was calculated from the DIC, pH and temperature according to Butler (1982). The temperature for the CO<sub>2</sub> calculation was measured on each sampling occasion with a temperature/dissolved oxygen meter (YSI 55; Yellow Springs Inc. Yellow Springs, OH, USA). The sampling for DIC and pH was conducted during the open-water periods from 27 April until 8 November in 2005 and from 8 May until 24 October in 2006. In addition one under-ice sampling was performed on 16 April 2006. The complete sampling protocol of the ICP IM lake studies can be found in Keskitalo and Salonen (1994).

### Additional measurements

We measured air temperature and pressure with DAVIS precision weather instruments (Davis Instruments Corp., Hayward, CA, USA) placed on the same raft as the continuous surface water CO<sub>2</sub> measurement equipment. The measurements at time intervals of 10 min with hourly and daily averaging for air pressure and temperature, respectively, began in both years in mid-April before ice breakup and ended in November–December after freeze-up. For precipitation we used the data of the Finnish Meteorological Institute collected at Lammi Biological Station, 20 km south from Lake Valkea-Kotinen.

We used a chain of Vemco temperature-logging probes (Vemco, Halifax, NS, Canada) placed at the depths of 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.5 m to continuously record water temperature. The logging interval was at maximum one hour and the readings were further averaged for daily values. The values for depths greater than 4.5 m were linearly extrapolated. The mixing depth — defined as the depth where the temperature decrease exceeded 1 °C m<sup>-1</sup> — was calculated from the daily temperature values from 0.5 m downwards. When this decrease was found at more than one depth, only the uppermost was considered. Since the lake was strongly stratified in summer, the calculations of mixing depth using the vertical interval of 0.5 m appeared crude. Thus we wanted further estimation for interannual differences in density stratification

patterns and calculated Brunt-Väisälä stability frequencies ( $N_s$ ) (s<sup>-1</sup>) from the density gradient ( $\partial\rho_w/\partial z$ ) across 0.5–1.5 m, using the equation:

$$N_s = \sqrt{\frac{g}{\rho_w} \frac{\partial\rho_w}{\partial z}}, \quad (2)$$

where  $g$  (m s<sup>-2</sup>) is acceleration due to gravity,  $\rho_w$  (kg m<sup>-3</sup>) the water density and  $z$  (m) the depth.

We measured wind speed and CO<sub>2</sub> concentration in the air 1.5 m above the lake surface with a Metek ultrasonic anemometer (USA-1; Metek GmbH, Elmshorn, Germany) and an IR gas analyser (LI-7000; Li-Cor Inc., Lincoln, NE, USA), respectively (Vesala *et al.* 2006). The air CO<sub>2</sub> concentration was used to calculate the equilibrium concentration of surface water CO<sub>2</sub> ( $C_{eq}$ ) with the temperature-adjusted Henry's law constant.

### CO<sub>2</sub> flux calculations

For estimates of the CO<sub>2</sub> fluxes we used the daily means from the actual measurements of surface water (0.1 m) CO<sub>2</sub> concentration ( $C_{sur}$ ),  $C_{eq}$ , surface water temperature and wind speed ( $U$ ). The gap in continuous  $C_{sur}$  data in May–June 2005 was filled with discrete sampling data and linear interpolation. The CO<sub>2</sub> flux (mmol m<sup>-2</sup> d<sup>-1</sup>) was calculated using the following equation:

$$F = \alpha k(C_{sur} - C_{eq}), \quad (3)$$

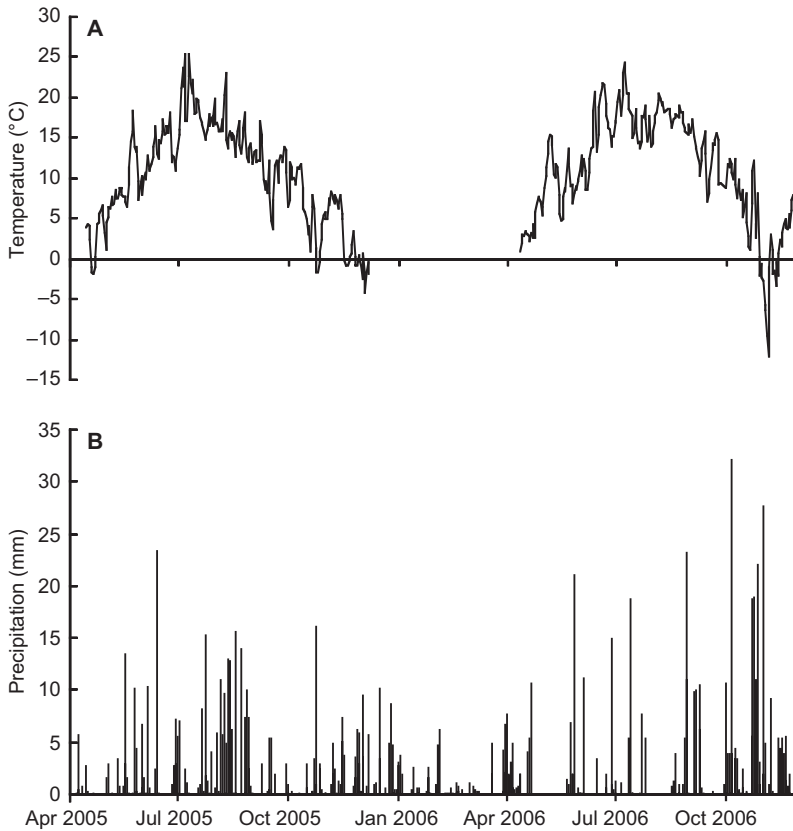
where  $\alpha$  is a chemical enhancement factor that was assumed to be one and  $k$  is a piston velocity that was calculated from the equation:

$$k/k_{600} = (Sc/Sc_{600})^{-2/3}, \quad (4)$$

where  $Sc$  is the Schmidt number that was taken from Jähne *et al.* (1987) and  $Sc_{600}$  is the Schmidt number 600 at the temperature of 20 °C. The factor  $k_{600}$  is the corresponding value for  $Sc_{600}$  and was calculated using the equation empirically determined for low-wind speed conditions by Cole and Caraco (1998):

$$k_{600} = 2.07 + 0.215U_{10}^{1.7}, \quad (5)$$

where  $U_{10}$  refers to the wind speed at the 10-m



**Fig. 1.** Daily averages of (A) air temperature (°C) and (B) precipitation (mm).

height. For conversion of our wind speed values to wind speed at 10 m we used the following equation (*see* Crucius and Wanninkhof 2003):

$$U_{10} = 1.22U \quad (6)$$

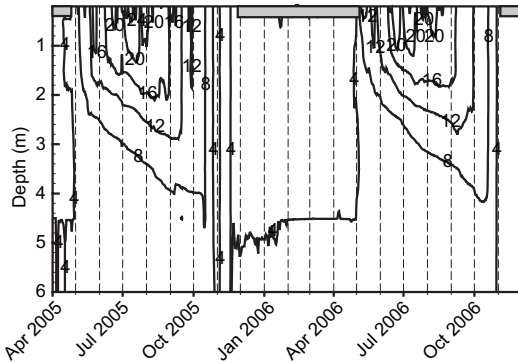
## Results

### Air temperature and precipitation

During the measuring periods, the daily air temperature showed typical seasonal patterns (Fig. 1A). In 2006, the beginning of May and mid-June were very warm, and when the daily temperatures in general were considered, the measuring period in 2006 was 0.7 °C warmer than in 2005. Based on the monthly averages (not shown), June and August in 2006 were > 2 °C warmer than in 2005, and only July and November were slightly warmer in 2005 than in 2006.

The maximum daily temperatures were measured in both years in July and were 25.4 °C and 24.3 °C in 2005 and 2006, respectively.

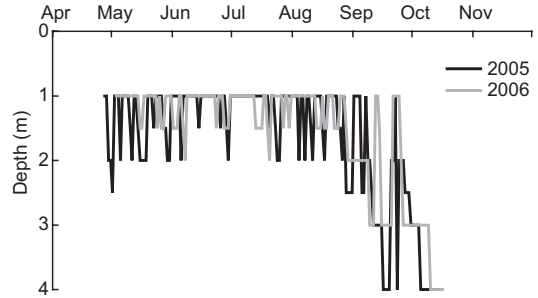
Although the total precipitation was similar during the open-water periods studied, i.e. 382 mm and 386 mm in 2005 and 2006, respectively, the timing of rain events was different. In 2006, there were long rain-free and sunny periods from late April until mid-August, whereas in 2005 the rains were more regular. Late summer in 2005 was especially rainy, as indicated by August precipitation that was 2.7 times higher than in 2006 and comprised 34% of the total during the open-water period. In 2006, most of the rain fell in autumn and October contributed 45% to the total precipitation (Fig. 1B). There were more days when it rained (precipitation > 0.1 mm) in 2005, when they comprised 47% of all open-water period days, whereas the respective value was only 39% in 2006.



**Fig. 2.** Contour plot drawn from daily averages of water temperature ( $^{\circ}\text{C}$ ) vs. time and depth (m). Gray horizontal bars represent ice-covered periods.

### Water temperature and ice-cover dynamics

The open-water periods lasted from 26 April until 27 November in 2005 and from 2 May until 3 November in 2006 (Fig. 2), i.e. the period was 30 days longer in 2005. The ice covered intervals preceding the open-water periods were 161 and 156 days, respectively. Due to rapid warming of the surface water, there was no complete spring turnover and the lake was thus spring-meromictic in both years. In contrast to spring the autumn turnover, which started when the water temperature dropped to  $7^{\circ}\text{C}$ , was complete in 2005 as well as in 2006. However, in 2005 it lasted for app. one month, but only a week in 2006, and was terminated when the lake froze. In summer the water column was strongly stratified. In 2006 when the spring and early summer were warm,



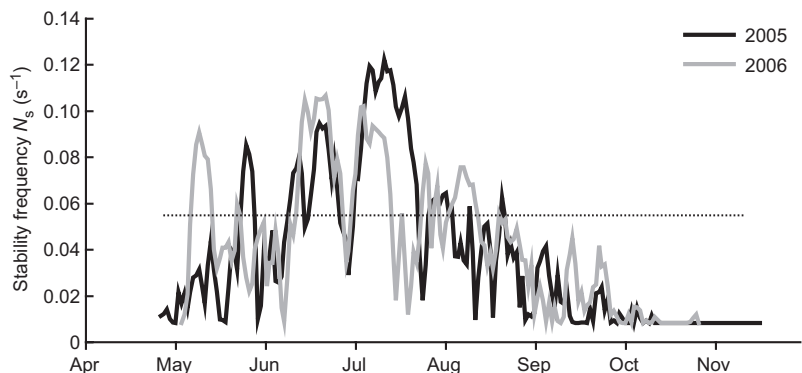
**Fig. 3.** Daily variation in mixing depth (m) in 2005 and 2006.

the surface water warmed up faster than in 2005. Stratification was also stronger, i.e. the mixing depth varied less and was usually between 1 and 1.5 m, whereas in 2005 the water was regularly mixed down to two metres (Fig. 3).

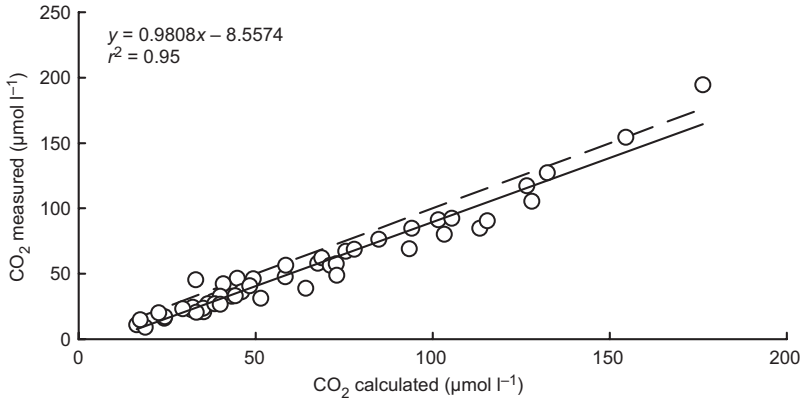
Stability frequencies closely followed the air temperatures and the stable conditions (see below) coincided with the warm periods in May, June and July (Fig. 4). Sudden decreases in air temperatures and also intensive rains resulted in concomitant increase in instability, as seen when the stable summer periods ended. The rapid onset of stability in 2006 immediately after ice breakup was remarkable. The stability was strongest in July 2005, i.e.  $0.122\text{ s}^{-1}$ , although in general the water column was slightly more stable in 2006 than in 2005.

### Surface water CO<sub>2</sub> concentration

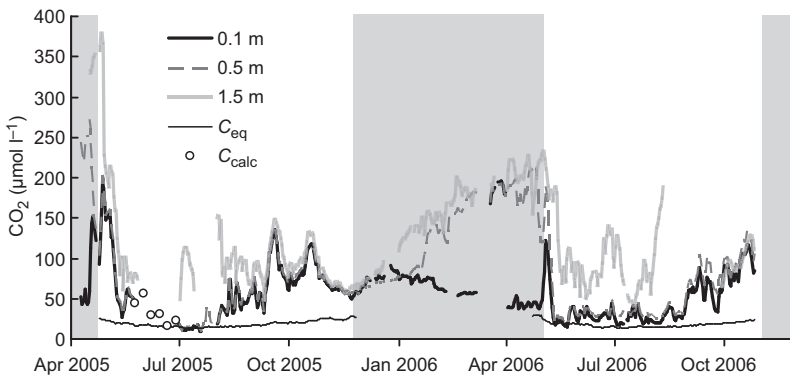
To verify our CO<sub>2</sub> concentration data we plotted the concentrations calculated from the discrete



**Fig. 4.** Daily variation in stability frequencies ( $\text{s}^{-1}$ ) in 2005 and 2006. Above the horizontal dashed line ( $0.055\text{ s}^{-1}$ ) the stratification was stable.



**Fig. 5.** Calculated surface water CO<sub>2</sub> concentrations (µmol l<sup>-1</sup>) vs. corresponding daily averages from continuous measurements. Dashed line = 1:1 line, solid line = fit of the regression.



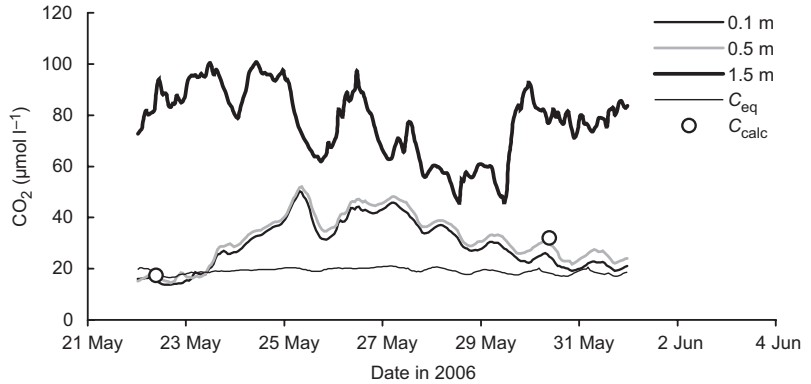
**Fig. 6.** Daily averages of surface water CO<sub>2</sub> concentrations (µmol l<sup>-1</sup>) at different depths, CO<sub>2</sub> concentrations calculated from DIC and pH ( $C_{\text{calc}}$ ) and atmospheric equilibrium concentration ( $C_{\text{eq}}$ ). Shaded blocks represent ice-covered periods.

DIC and pH samples against the corresponding daily CO<sub>2</sub> values from the continuous measurements (Fig. 5). The verification confirmed that the continuous measurements agreed well with the discrete samples ( $r^2 = 0.95$ ,  $P < 0.0001$ ,  $N = 50$ ), but the CO<sub>2</sub> concentration estimates calculated from the DIC and pH were in general slightly higher than the corresponding daily means of our direct measurements ( $x$ -intercept of the regression line  $8.72 \mu\text{mol l}^{-1}$  and slope 0.98).

In both study periods, the CO<sub>2</sub> concentrations in the surface water showed a seasonal mixing and stratification pattern similar to that found for temperature (Fig. 6). In contrast to temperature, the highest values of surface water CO<sub>2</sub> concentrations (195 and  $122 \mu\text{mol l}^{-1}$  in 2005 and 2006, respectively) were observed just after ice breakup when partial mixing brought CO<sub>2</sub>-rich water from deeper waters to the surface. However, the CO<sub>2</sub> gradient between the surface and 1.5 m did not disappear in spring of either 2005 or 2006 but remained throughout the summer and was finally lost in the autumn turnover. The

spring peak in CO<sub>2</sub> concentration was followed by a period in May when the surface water CO<sub>2</sub> concentration rapidly declined to near the atmospheric equilibrium. The rate of this decline — integrated as an areal value for the one-metre surface layer and calculated for the period from the day after ice breakup to the day the concentrations began to increase again — was  $10.7$  and  $19.0 \text{ mmol m}^{-2} \text{ d}^{-1}$  for 2005 and 2006, respectively, i.e. it was clearly faster in 2006. During these spring periods the average ( $\pm$  SD) surface-water CO<sub>2</sub> concentrations were  $84.5 \pm 52.1$  and  $37.1 \pm 28.5 \mu\text{mol l}^{-1}$  in 2005 and 2006, respectively. The concentrations remained low during the summer stratification periods ( $20.3 \pm 9.9$  and  $28.0 \pm 6.6 \mu\text{mol l}^{-1}$  in 2005 and 2006, respectively) and occasionally even dropped below atmospheric equilibrium during the day. Due to the deepening of the mixing depth (i.e. the increase in  $z_m/z_{\text{eu}}$ ) and the following immediate pulses of the CO<sub>2</sub>-rich water to the surface, the CO<sub>2</sub> concentrations in the surface water began to increase again in August. In 2005, the heavy

**Fig. 7.** Example of surface water CO<sub>2</sub> concentrations ( $\mu\text{mol l}^{-1}$ ) from hourly averaged continuous measurements at different depths, CO<sub>2</sub> concentrations calculated from DIC and pH ( $C_{\text{calc}}$ ) and atmospheric equilibrium concentration ( $C_{\text{eq}}$ ).



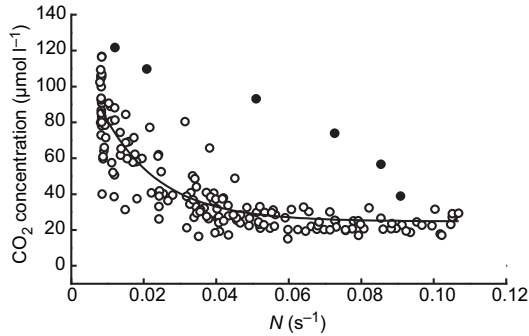
rains already triggered the event in early August whereas in 2006 thermocline deepening began in late August. The daily average CO<sub>2</sub> concentrations during the autumn turnover periods were  $70.6 \pm 22.7$  and  $80.6 \pm 25.2 \mu\text{mol l}^{-1}$  in 2005 and 2006, respectively. In winter the CO<sub>2</sub> concentrations under the ice cover gradually increased to a maximum of  $232 \mu\text{mol l}^{-1}$  observed at 1.5 m immediately before ice breakup on 2 May 2006. The CO<sub>2</sub> concentration gradient between 0.1 m and 0.5 m disappeared several days before ice breakup, indicating that small-scale mixing occurred under the ice cover. At the very surface the apparent concentrations decreased from late December onwards when the silicone rubber tube was eventually enclosed in the ice. It was freed from the ice sheet in March and thus, the low surface water concentrations in April before ice breakup represented the CO<sub>2</sub> concentrations of the surface water.

In addition to the seasonal variations, the daily variations in surface water CO<sub>2</sub> concentrations were large and sometimes we observed a two-fold difference between two successive days. The variations were observed in spring as well as in late summer at the time when stratification was breaking down, but they were especially clear during the stratification period at 1.5 m (Fig. 6). The rainy periods resulted in increases of surface water CO<sub>2</sub> concentrations; e.g. from 1 until 12 August 2005 surface water CO<sub>2</sub> increased from 18 to  $74 \mu\text{mol l}^{-1}$ , whereas the concentrations tended to decrease during dry, sunny periods. For example, from 19 until 25 September 2006 the surface water CO<sub>2</sub> decreased from 71 to  $33 \mu\text{mol l}^{-1}$  (Figs. 1 and 6).

There was also a clear weather-driven dynamics in diel CO<sub>2</sub> concentrations; e.g. in May 2006 the CO<sub>2</sub> concentration dropped below the atmospheric equilibrium, i.e.  $\sim 18 \mu\text{mol l}^{-1}$ , presumably due to primary production (Fig. 7). Later, during the rainy and cloudy days on 23, 24 and 26 May, the concentration increased to  $50 \mu\text{mol l}^{-1}$ . The diel dynamics in surface-water CO<sub>2</sub> concentration was visible almost throughout the growing season, slowly fading towards the freeze-up together with decreasing irradiance (data not shown). The diel variations in surface-water CO<sub>2</sub> concentration were most clear during sunny days when the minimum was observed late in the evening and maximum before noon, reflecting the metabolism of the lacustrine ecosystem (Fig. 7).

Since the weather-driven changes in the mixing depth and the surface water CO<sub>2</sub> concentration were closely associated, we plotted  $N_s$  against the surface water CO<sub>2</sub> (Fig. 8). The relationship followed best the first-order exponential decay function with a plateau at concentration  $24.74 \mu\text{mol l}^{-1}$  ( $C_{\text{sur}} = 106.07 \exp(-N_s/0.0157) + 24.74$ ;  $r^2 = 0.71$ ,  $N = 177$ ). When stratification was stable ( $N_s > 0.055 \text{ s}^{-1}$ ), the supply of hypolimnetic CO<sub>2</sub> was cut off and the escape to the atmosphere and biological uptake of CO<sub>2</sub> could lower the concentration to near the level of atmospheric equilibrium. When the stability was low the injections of hypolimnetic CO<sub>2</sub> increased the surface water concentration. However, in 2006 immediately after ice breakup, the surface water warming occurred so rapidly that the CO<sub>2</sub> decline could not keep pace with the stability formation.





**Fig. 8.** Stability frequency ( $s^{-1}$ ) vs. surface water  $CO_2$  concentration in 2006. The curve follows the first-order exponential decay function  $CO_2 = 106.07\exp(-N_s/0.0157) + 24.74$ . Filled circles represent six consecutive days during the spring period of rapid  $CO_2$  concentration decline and stability formation (see text).

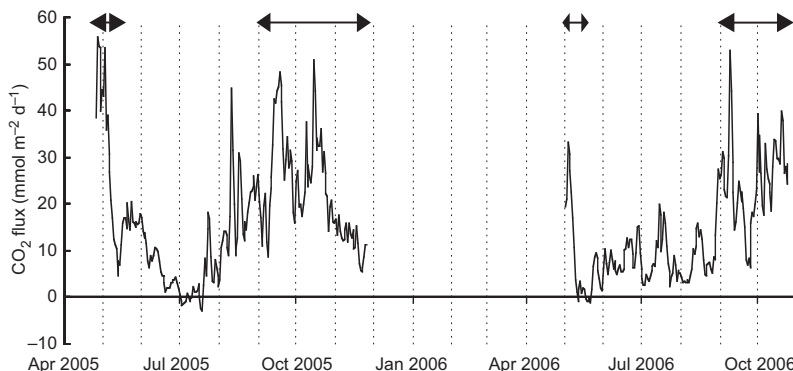
## $CO_2$ flux

Since our flux calculations were based on  $CO_2$  concentration differences between the surface water and the atmosphere, the daily  $CO_2$  flux estimates closely followed the surface water  $CO_2$  concentration. The highest efflux —  $55.6 \text{ mmol m}^{-2} \text{ d}^{-1}$  — during the study period occurred in 2005 immediately after ice breakup. In 2006, the highest efflux with a maximum value of  $52.7 \text{ mmol m}^{-2} \text{ d}^{-1}$  was observed on 9 September during the autumn turnover (Fig. 9). Due to surface-water  $CO_2$  concentrations below the atmospheric equilibrium, short periods of influx were observed in July 2005 and May 2006. Since the period of autumn turnover was longer in 2005, the  $CO_2$  accumulated in the water column was effectively vented out and thus the flux just before freeze-up was low, i.e. below  $10 \text{ mmol m}^{-2} \text{ d}^{-1}$ . In

2006, when the autumn was short, the  $CO_2$  flux was much higher (about  $20\text{--}30 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) by the time of freeze-up and presumably a higher  $CO_2$  storage remained over winter. In assuming a zero  $CO_2$  flux during the ice-covered period (J. Huotari unpubl. data), we ended with the annual  $CO_2$  flux estimates of  $3.7 \text{ mol m}^{-2}$  and  $2.5 \text{ mol m}^{-2}$  for 2005 and 2006, respectively, i.e. the flux of the warm year with a dry sunny summer was 32% lower than that of the year with a more rainy and cloudy summer. The fluxes during the autumn turnover periods — calculated from early September when the stratification began to break down until freeze-up — comprised 50% and 61% of the total fluxes during the open-water periods of 2005 and 2006, respectively. The corresponding proportions for spring peaks were 16% and 7%, respectively, reflecting the very rapid formation of stable stratification in 2006. In 2005 the period of heavy rains in August resulted in a high summertime flux with a contribution of 15% to the total flux (Fig. 9).

## Discussion

With the  $CO_2$  probe data and gap filling we were able to create a continuous, verified dataset on the seasonal dynamics of surface water  $CO_2$  in a boreal pristine lake that serves as a reference for future studies on sites under more intensive anthropogenic influence. The small but consistent discrepancy between our direct continuous  $CO_2$  measurements and discrete  $CO_2$  estimates calculated from DIC and pH can be explained by the fact that the samples for DIC and pH were always taken in the morning when the sur-



**Fig. 9.** Daily averages of  $CO_2$  flux ( $\text{mmol m}^{-2} \text{ d}^{-1}$ ) over the open-water periods of 2005 and 2006. Double arrows refer to the periods discussed in the text.

face water CO<sub>2</sub> concentrations were near their daily maximum due to nighttime respiration and convective mixing. However, there must also be other explanations, since when the values from the corresponding sampling times (data not shown) were compared the calculated estimates were still higher than the readings given by the direct probe measurements ( $x$ -intercept of the regression line  $6.92 \mu\text{mol l}^{-1}$  and slope  $1.01$ ,  $r^2 = 0.96$ ,  $P < 0.0001$ ,  $N = 50$ ). The same small discrepancy between direct measurements and calculations was reported by Cole *et al.* (1994), Cole and Caraco (1998) and Baehr and DeGrandpre (2002). Despite the good agreement between the two methods, we want to emphasize the importance of continuous measurements, since the diel and daily variations of surface water CO<sub>2</sub> concentration can sometimes be very high, as seen in Lake Valkea-Kotinen in early summer, and these variations are easily missed with discrete sampling protocols. This was also pointed out by Sellers *et al.* (1995) who tested continuous measurements of surface water CO<sub>2</sub> for estimation of CO<sub>2</sub> flux between a shallow pond and the atmosphere.

We could detect the same seasonal pattern of surface water CO<sub>2</sub> in the humic Lake Valkea-Kotinen as compiled by Riera *et al.* (1999 and references therein) for dimictic clear-water lakes in the north temperate zone, i.e. (i) accumulation of CO<sub>2</sub> under the ice, (ii) high concentrations and a rapid decline after ice breakup, (iii) lower concentrations during stratification, and (iv) high concentrations during autumn turnover. The surface water CO<sub>2</sub> concentrations in Lake Valkea-Kotinen were similar to those found by Riera *et al.* (1999) and Striegl and Michmerhuizen (1998) in Crystal Bog, Wisconsin, USA, and Shingobee Lake, Minnesota, USA, respectively, but in these lakes the annual fluxes were  $6.7$  and  $8.0 \text{ mol m}^{-2}$ , i.e. substantially higher than in Lake Valkea-Kotinen where the flux estimates were only  $2.5$  and  $3.7 \text{ mol m}^{-2}$ . However, in Mirror Lake, New Hampshire, USA, direct measurements of  $p\text{CO}_2$  resulted in concentrations comparable to ours and the annual flux estimate of about  $2.5 \text{ mol m}^{-2}$  was similar to that in Lake Valkea-Kotinen (Cole and Caraco 1998). CO<sub>2</sub> flux measurements conducted with the eddy covariance technique in Lake Valkea-Kotinen over

the open-water period in 2003 also gave a daily average flux of  $0.22 \mu\text{mol m}^{-2} \text{ s}^{-1}$  (Vesala *et al.* 2006), which agrees well with our estimates, if converted to the same units, of  $0.16$  and  $0.20 \mu\text{mol m}^{-2} \text{ s}^{-1}$ . Kortelainen *et al.* (2006) estimated in their survey on lakes in Finland that the average annual escape of CO<sub>2</sub> from lakes  $< 0.1 \text{ km}^2$  in size is  $8.5 \text{ mol m}^{-2}$ , i.e. 2–3-fold larger than our estimate from Lake Valkea-Kotinen. Due to the sheltered position of our lake, the mean of the daily wind speeds used in flux calculations was half that used by Kortelainen *et al.* (2006) and two thirds of that used by Riera *et al.* (1999), which partly explains the difference. However, by doubling the factor  $U_{10}$  in our calculations we end up with the annual fluxes of  $5.2$  and  $3.5 \text{ mol m}^{-2}$  in 2005 and 2006, respectively, which are still clearly lower than those reported in Kortelainen *et al.* (2006). Kortelainen *et al.* (2006) did not reveal the range of flux estimates but they found that CO<sub>2</sub> supersaturation was associated with land-use cover on the lake catchment. Thus, the small CO<sub>2</sub> flux from Lake Valkea-Kotinen probably reflects its pristine state in the middle of old-growth forest and position in the lake chain.

We detected low concentrations of CO<sub>2</sub> immediately underneath the ice cover before ice breakup which is somewhat surprising and in contrast to the general pattern of under-ice accumulation, but refers to consumption of CO<sub>2</sub> and thus the under-ice primary production as reported e.g. by Baehr and DeGrandpre (2004). The CO<sub>2</sub> concentration calculated from DIC and pH samples taken two weeks before ice breakup confirmed that surface water CO<sub>2</sub> was already near the atmospheric equilibrium, i.e.  $33 \mu\text{mol l}^{-1}$ . The dissolved oxygen concentration was  $19.1 \text{ mg l}^{-1}$  (136% of saturation) immediately beneath the ice, which also implies that photosynthetic activity had drawn down the CO<sub>2</sub>. We could also detect a diel variation in surface water CO<sub>2</sub> concentration under the late winter ice, which may have been light-driven but the results were somewhat blurred by small-scale convective mixing (data not shown). Moreover, the ICP IM data from 1991 to 1996 showed that 2–3 weeks before ice breakup the rate of primary production in Lake Valkea-Kotinen was  $1.5\text{--}8.1 \text{ mmol m}^{-2} \text{ d}^{-1}$ , which is 16%–86% of the

long-term summertime average (ICP IM unpubl. data).

There was noticeable vertical mixing of the surface water several days before ice breakup which equalized the CO<sub>2</sub> concentrations at 0.1 and 0.5 m but did not reach 1.5 m. The mixing was probably due to enhanced light penetration through the snow-free thin ice which caused convection by heating up the water below the ice (Mathews and Heaney 1987). Springtime mixing under the ice was also reported by Baehr and DeGrandpre (2004) who observed in an 11-m-deep flow-through lake a complete spring turnover that lasted for 11 days. However, in Lake Valkea-Kotinen mixing was restricted to the very surface, since the humic coloured water was already stratified under the ice. The CO<sub>2</sub> concentration at 1.5 m did not attain the surface water concentration until the autumn turnover, which confirms the spring meromixis of the lake.

During the rapid decline in CO<sub>2</sub> concentration after ice breakup (Fig. 6), the daily mean escape of CO<sub>2</sub> was  $30.9 \pm 16.7$  and  $13.9 \pm 12.2$  mmol m<sup>-2</sup> d<sup>-1</sup> in 2005 and 2006, respectively, suggesting that in 2005 supplemental CO<sub>2</sub> from the deeper water layers must have entered the surface, whereas in 2006 biological uptake was significant for the surface water CO<sub>2</sub> decline. The ICP IM primary production measurements in Lake Valkea-Kotinen, conducted weekly with 24-h bottle incubations and using the <sup>14</sup>C technique, gave net production rates, i.e. CO<sub>2</sub> consumptions that were 31% of the surface water CO<sub>2</sub> loss rates for both 10 May 2005 and 8 May 2006 (ICP IM unpubl. data). The role of biological uptake in spring CO<sub>2</sub> loss has often been regarded as negligible (e.g. Striegl and Michmerhuizen 1998, Anderson *et al.* 1999, Striegl *et al.* 2001), but Baehr and DeGrandpre (2004) estimated that in Placid Lake, Montana, USA, net community production immediately after ice breakup accounted for about 75% of the decrease in surface water pCO<sub>2</sub>. Our results suggest that in 2005 in Lake Valkea-Kotinen 23.5 mmol m<sup>-2</sup> d<sup>-1</sup> of CO<sub>2</sub> were transported from the deeper water layers to the surface layer via partial mixing of the water column and only about 10% of the decline in surface water CO<sub>2</sub> was due to biological uptake. In 2006, the importance of biological CO<sub>2</sub> uptake increased to 30%, whereas 70% of

the concentration decline was due to escape. Furthermore, the community respiration was 16% higher in 2006 than in 2005 and was almost 20-fold higher than the supplemental CO<sub>2</sub> from the deeper waters, whereas in 2005 the supplemental CO<sub>2</sub> was twice as high as the surface water community respiration (unpubl. ICP IM data). The temperature data confirmed these findings and showed that the mixing depth was greater in spring 2005 than in 2006 (Fig. 3). The stability frequency was also about three times higher in 2006 than in 2005 (Fig. 4) which also indicates that in 2005, when the CO<sub>2</sub> efflux was higher, the partial mixing after ice breakup extended deeper than in 2006 when the surface water was more effectively sealed off from the bottom waters. However, we had no feasible ways to measure lateral CO<sub>2</sub> fluxes, i.e. CO<sub>2</sub> transported to the lake in groundwater, and this may have caused some errors in our calculations.

Photochemical mineralization of dissolved organic matter to CO<sub>2</sub> plays a significant role in DIC production in some surface waters (e.g. Granéli *et al.* 1996). In Lake Valkea-Kotinen most of the mineralization occurs in the top 10 cm of the water column and the summertime mean for photochemical production of CO<sub>2</sub> is 0.99 mmol m<sup>-2</sup> d<sup>-1</sup> (Vähätalo *et al.* 2000). This is only about 10% of the long-term summer time average (June–August) of epilimnetic (0–1 m) community respiration (10.0 mmol m<sup>-2</sup>) (ICP IM unpubl. data).

Lake Valkea-Kotinen appeared to be net heterotrophic, since it was mostly supersaturated with CO<sub>2</sub> and acted as a net source of atmospheric CO<sub>2</sub>. However, the periods of subatmospheric CO<sub>2</sub> concentrations suggest that there were occasions when net autotrophy prevailed. These moments coincided with the shallowest mixing depths in July 2005 and in May and July 2006. When the mixing depth increases, the light climate of primary producers deteriorates and the conditions favour respiration at the expense of primary production (cf. Staehr and Sand-Jensen 2007). Simultaneously, CO<sub>2</sub>-rich water is intruded into the surface layers. Both mechanisms increase the surface water CO<sub>2</sub> concentration but it is difficult to discriminate between them (Hanson *et al.* 2006). We did not analyse in detail the reasons for deepening of the mixing depth but the physi-

cal control of surface water CO<sub>2</sub> concentration is clear (Fig. 8). Air temperature and wind speed changes as well as precipitation are known to alter lake thermal structure and mixing dynamics (e.g. MacIntyre *et al.* 2006). The effect of precipitation on the mixing depth as well as on fluxes was seen in August 2005 when the rainy period increased the surface water CO<sub>2</sub> and resulted in abnormally high summer efflux. This differs from the results of Kelly *et al.* (2001) who found no link between precipitation and pCO<sub>2</sub>. However, high summer effluxes due to heavy rains were also measured from a larger, nearby humic lake where doubling in summertime precipitation caused a flux peak in July–August that comprised 46% of the annual flux (A. Ojala unpubl. data). There, most of the CO<sub>2</sub> originated directly from the catchment and not from the mineralization of allochthonous DOC. Due to climate change extreme precipitation events in northern Europe have been predicted to increase both in magnitude and frequency (IPCC 2007). This will most probably increase the carbon load from catchments to lakes and result in higher lacustrine efflux of CO<sub>2</sub> to the atmosphere.

Autumn mixing allows the CO<sub>2</sub> accumulated in the hypolimnion during summer to be released to the atmosphere. In spring-meromictic lakes such as Lake Valkea-Kotinen also part of the CO<sub>2</sub> accumulated during the preceding winter is not released until next autumn. Hence the role of autumn turnover in annual flux is emphasized in this type of small, sheltered boreal lake. Warm autumns that presumably would prolong the autumn turnover were predicted to increase in frequency due to climate warming (IPCC 2007). Piao *et al.* (2008) already showed that warm autumns cause a net CO<sub>2</sub> release from forested ecosystems. We can assume that the same also holds in lake ecosystems and that the source effect is further emphasized.

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