Ecosystems (2012) 15: 1295–1307
DOI: 10.1007/s10021-012-9585-4

ECOSYSTEMS

Carbon Dioxide in Boreal Surface Waters: A Comparison of Lakes and Streams

Gesa A. Weyhenmeyer,[1,2]* Pirkko Kortelainen,[3] Sebastian Sobek,[1] Roger Müller,[1] and Miitta Rantakari[3,4]

[1]Department of Ecology and Genetics/Limnology, Uppsala University, Norbyvägen 18D, 752 36 Uppsala, Sweden; [2]Department of Aquatic Sciences and Assessment, Swedish University of Agriculture, Box 7050, 750 07 Uppsala, Sweden; [3]Finnish Environment Institute, Box 140, 00251 Helsinki, Finland; [4]Finnish Forest Research Institute, Box 18, 01301 Vantaa, Finland

ABSTRACT

The quantity of carbon dioxide (CO_2) emissions from inland waters into the atmosphere varies, depending on spatial and temporal variations in the partial pressure of CO_2 (pCO_2) in waters. Using 22,664 water samples from 851 boreal lakes and 64 boreal streams, taken from different water depths and during different months we found large spatial and temporal variations in pCO_2, ranging from below atmospheric equilibrium to values greater than 20,000 µatm with a median value of 1048 µatm for lakes ($n = 11,538$ samples) and 1176 µatm for streams ($n = 11,126$). During the spring water mixing period in April/May, distributions of pCO_2 were not significantly different between stream and lake ecosystems ($P > 0.05$), suggesting that pCO_2 in spring is determined by processes that are common to lakes and streams. During other seasons of the year, however, pCO_2 differed significantly between lake and stream ecosystems ($P < 0.0001$). The variable that best explained the differences in seasonal pCO_2 variations between lakes and streams was the temperature difference between bottom and surface waters. Even small temperature differences resulted in a decline of pCO_2 in lake surface waters. Minimum pCO_2 values in lake surface waters were reached in July. Towards autumn pCO_2 strongly increased again in lake surface waters reaching values close to the ones found in stream surface waters. Although pCO_2 strongly increased in the upper water column towards autumn, pCO_2 in lake bottom waters still exceeded the pCO_2 in surface waters of lakes and streams. We conclude that throughout the year CO_2 is concentrated in bottom waters of boreal lakes, although these lakes are typically shallow with short water retention times. Highly varying amounts of this CO_2 reaches surface waters and evades to the atmosphere. Our findings have important implications for up-scaling CO_2 fluxes from single lake and stream measurements to regional and global annual fluxes.

Key words: carbon; CO_2; climate; seasonality; boreal; lake; stream.

INTRODUCTION

Despite the small fraction of the surface of the Earth occupied by streams, rivers, ponds, lakes, and reservoirs a variety of studies show that inland waters play an important role in the global carbon cycle (Richey and others 2002; Cole and others

---

Received 8 February 2012; accepted 1 July 2012;

Author Contributions: G. W. designed the study, analyzed the data and wrote the paper; P. K. and M. R. provided Finnish data and S. S. and R. M. helped preparing Swedish data including calculations and GIS work. All authors substantially contributed to the method, result and discussion part of the paper.

*Corresponding author; e-mail: Gesa.Weyhenmeyer@ebc.uu.se

2007; Battin and others 2009; Tranvik and others 2009; Kosten and others 2010; Aufdenkampe and others 2011). These studies clearly demonstrate that inland waters are highly active sites for transport, transformation, and storage of considerable amounts of carbon received from the terrestrial environment. For example, Tranvik and others (2009) have shown that the estimated annual loss of 2 Gt is similar to the extent of annual total global net ecosystem production. Such global estimates include, however, large uncertainties.

One key uncertainty in the role of inland waters for global carbon budgets concerns seasonal and daily variations of carbon dioxide (CO_2) fluxes from inland waters. So far, global estimates are based upon daytime CO_2 emissions from inland waters with a clear bias towards summer values in the Northern Hemisphere north of 40°N (Cole and others 2007; Tranvik and others 2009). Daytime summer CO_2 values might overestimate CO_2 emissions from heterotrophic systems, typical for the large boreal region (Cole and others 1994), because photo- and microbial carbon transformations, known to drive CO_2 emissions in heterotrophic systems (Kaiser and Sulzberger 2004; McCallister and others 2005) have been shown to be enhanced by increased sunlight and increased water temperatures (Vähätalo and others 2003; Bergström and others 2010; Gudasz and others 2010), typically occurring at daytime during the summer.

Thus, the potential for CO_2 emissions from inland waters, here expressed as CO_2 partial pressure (pCO_2), might increase towards summer and decline again thereafter provided that increasing efficiency in photosynthesis does not counteract the increasing efficiency in photo- and microbial transformation in heterotrophic systems towards summer. Such increases in CO_2 emissions towards summer have, for example, been observed in a lake in Northern Sweden (Jonsson and others 2007b).

CO_2 emissions from inland waters might, however, also decrease towards summer along with decreasing hydrological inputs of CO_2 and dissolved organic carbon (DOC) from terrestrial ecosystems that have been found to be important drivers for pCO_2 variation in surface waters (Striegl and Michmerhuizen 1998; Sobek and others 2003; Humborg and others 2009; Stets and others 2009; Teodoru and others 2009). The influence of hydrological inputs of CO_2 and DOC on pCO_2 in lakes is supported by a variety of studies showing that precipitation is one of the best predictors for CO_2 concentrations both in boreal and tropical lakes (Rantakari and Kortelainen 2005; Marotta and others 2010).

Decreasing pCO_2 towards summer has also been observed by, for example, Kelly and others (2001), Kortelainen and others (2006) and Atilla and others (2011). In addition to hydrological controls, Kelly and others (2001) attributed summer pCO_2 declines to the influence of thermal stratification which reduces the ratio of epilimnetic area to the epilimnetic volume (Ae/Ve). Considering that epilimnetic sediments are an important site of degradation of organic carbon to CO_2, they suggested that a reduction in Ae/Ve resulted in a dilution of CO_2 in the epilimnion and thus in a pCO_2 decline towards summer. A stratification effect on pCO_2 has also been observed by Åberg and others (2010). They found that as soon as the epilimnion deepened, pCO_2 in the surface water of a relatively small (3.8 km^2) and deep (mean depth: 5 m, maximum depth 17 m) lake increased as a consequence of liberation of hypolimnion stored CO_2. Thus, according to previous studies, pCO_2 can either increase or decrease during summer.

We hypothesized that pCO_2 in small and shallow boreal lakes with short water retention times is controlled by processes that are similar to the ones occurring in streams with minimum pCO_2 values in lakes and streams during summer when hydrological inputs of CO_2 are low. To test this hypothesis, we used more than 850 boreal lake samples and more than 60 boreal stream samples from different water depths and different months as well as water discharge data. Data on rivers were not used for this study because most Swedish and Finnish rivers are either regulated or pass large agricultural regions, and are thus more heavily affected by human activity than streams and lakes.

METHODS

Data Material

The results of this study are based on four databases. The first database comprised inventory data from 756 small (median size of the 756 lakes: 0.2 km^2; 90 percentile: 2.3 km^2) and shallow (median depth of the 756 lakes: 4 m; 90 percentile: 6 m) boreal lakes (catchment covered by agriculture $<5\%$ and by forest and lake $\geq 80\%$) distributed over Sweden (Figure 1). The lakes were sampled at the water surface (0.5 m) above the deepest part of the lake during early autumn when the water column was mixed and water temperatures were around 4°C. Each of the 756 lakes was sampled in 1995, 2000, and 2005. Although the year 2000 was exceptionally wet, year-to-year variations remained smaller than spatial variations.

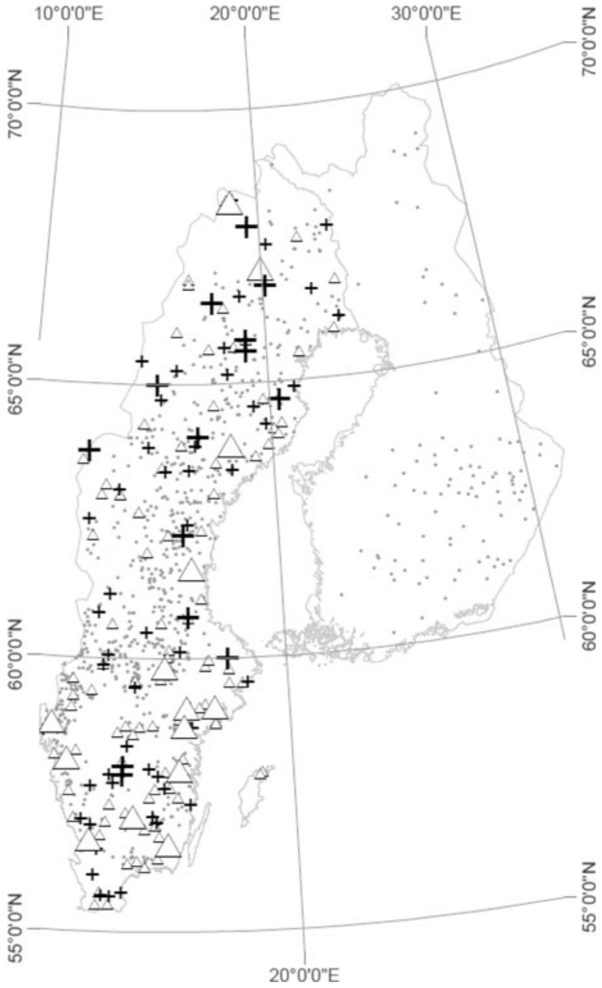

Figure 1. Map of Sweden and Finland, showing the locations of study lakes and streams. The biggest symbols represent the 14 lakes (*large triangles*) and 14 streams (*large crosses*) for which seasonal variations have been evaluated, the *small triangles* and *crosses* represent the 107 lakes and 64 streams, respectively, for which temporal data had been available and the *smallest dots* show all remaining lakes (>750) used in this study

For the evaluation of spatial variations we used median values of 1995, 2000 and 2005 for each lake which gave us representative lake-specific data for the autumn period. The sampling and analyzing procedure was performed by the certified water analyses laboratory at the Swedish University of Agricultural Sciences. Variables considered in this study were surface (0.5 m) water temperature (WT), pH, alkalinity (Alk), conductivity (Cond), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), chloride (Cl), sulfate (SO_4), nitrate-nitrogen (NO_3-N), total nitrogen (TN), total phosphorus (TP), absorbance at 420 nm of 0.45 µm filtered water in a 5-cm cuvette ($AbsF_{420}$), total organic carbon (TOC), and reactive silica (Si). The ratio $AbsF_{420}$/TOC was used as a proxy for the quality of TOC. TOC in Swedish boreal lakes usually contains 97% ± 5% DOC (von Wachenfeldt and Tranvik (2008)), thus TOC in this study can be seen as equivalent to DOC. All analyses were done according to standard limnological methods. The data are freely available and can be downloaded at http://www.slu.se/vatten-miljo. In addition to lake water measurements, we used GIS-derived data on lake morphometry and catchment characteristics, that is, mean lake depth (D_m), lake surface area (A), size of catchment area of the lake (ADA), elevation of lake (Alt), catchment-specific runoff (average 1961-1990; R), catchment-specific air temperature (average 1961-1990; AirT) and percentage of forest (% forest) and lake surface cover (% water) in the catchment area. The catchment-specific runoff was further used to calculate an average water residence time (WRT, in years) for lakes according to:

$$\mathrm{WRT} = \frac{V}{\mathrm{Area} \cdot R}, \tag{1}$$

where V is the lake volume, based on measured mean depth and lake surface area data (m^3), Area is the size of the lake catchment area excluding the lake area (m^2), and R is the modelled surface water runoff in the lake catchment, provided by the Swedish Meteorological and Hydrological Institute (SMHI, www.smhi.se) and available in GIS (in mm $year^{-1}$).

The second database comprised 107 boreal lakes and 64 boreal streams distributed over Sweden. The lakes were sampled between 4 and 107 times during 1983 and 2010 and the streams between 4 and 512 times during 1966 and 2010. Both lakes and streams were sampled at a water depth of 0.5 m. For all sampling occasions, data on WT, Alk, pH, NO_3-N, TN, TP, and TOC were available. All analyses were done according to standard limnological methods by the certified water analyses laboratory at the Swedish University of Agricultural Sciences. The data are freely available and can be downloaded at http://www.slu.se/vatten-miljo.

The third database was a sub-database from the second database and used for the evaluation of seasonal pCO_2 variations. Fourteen boreal lakes and 14 boreal streams had complete monthly data on WT, pH, Alk, Cond, Ca, Mg, Na, K, Cl, SO_4, NO_3-N, TN, TP, $AbsF_{420}$, TOC, and Si available from May to October during 1995–2010. The data were from surface waters (0.5 m). In the Swedish lakes we also had data on chlorophyll *a* (Chl*a*) concentrations in surface waters and on bottom water WT. In addition, we had for a variety of sampling occasions

Table 1. Physical and Water Chemical Characteristics of 14 Boreal Lakes (row 1–14) and 14 Streams (row 15–29)

Site	Median WT (°C)	CV WT (%)	Median Alk (mekv l^{-1})	CV Alk (%)	Median pH	CV pH (%)	Median TN (μg l^{-1})	CV TN (%)	Median TP (μg l^{-1})	CV TP (%)	Median TOC (mg l^{-1})	CV DOC (%)
Abiskojaure	9.20	39.08	0.18	26.43	7.11	2.36	198.00	41.52	4.00	58.71	1.45	90.01
Älgsjön	17.95	26.91	0.22	16.67	6.84	3.55	697.00	25.39	21.00	32.90	17.90	12.54
Allgjuttern	17.00	26.92	0.07	9.36	6.73	2.75	332.50	21.06	5.00	77.34	7.30	11.30
Brunnsjön	17.65	26.80	0.01	171.13	5.68	1.86	648.00	22.17	11.00	31.12	18.40	18.37
Fiolen	16.45	24.56	0.07	28.02	6.67	2.54	469.00	22.37	12.00	47.52	7.00	24.81
Fräcksjön	16.80	24.59	0.07	19.44	6.54	2.84	417.50	24.04	9.00	29.41	9.45	15.00
Jutsajaure	12.70	34.54	0.09	19.49	6.76	2.48	268.00	27.24	8.00	30.48	6.00	17.25
Övre Skärsjön	15.30	28.01	0.00	82.47	5.78	3.24	341.00	18.06	6.00	42.04	7.90	16.33
Remmarsjön	13.00	39.49	0.05	31.58	6.35	3.65	316.00	22.98	10.00	37.12	9.65	20.44
Rotehogstjärnen	16.85	25.08	0.01	128.98	5.66	4.71	411.50	21.81	14.00	27.55	12.05	18.06
Skärgölen	14.90	40.42	0.15	67.32	6.69	7.92	377.50	30.82	8.00	39.42	7.35	19.73
St Skärsjön	16.80	23.01	0.13	18.25	6.90	2.73	337.00	30.97	8.00	33.45	4.40	27.00
Stensjön	14.70	33.94	0.04	22.38	6.42	3.64	260.00	25.37	6.00	34.04	6.60	15.26
Stora Envättern	16.55	26.18	0.06	16.16	6.62	3.01	398.00	21.26	8.00	49.14	9.55	18.77
Akkarjåkkå	6.00	68.43	0.20	38.68	7.12	3.62	210.00	46.03	8.00	98.00	2.30	70.80
Bergmyrbäcken	6.25	65.11	0.08	73.86	6.65	5.88	263.00	39.86	7.00	67.49	7.00	43.74
Björnbackån	11.00	42.72	0.06	69.25	6.52	6.53	386.00	33.30	9.00	39.66	13.80	43.12
Bjurbäcken	8.00	66.76	0.07	84.37	6.46	7.38	526.00	28.89	17.00	39.88	18.70	25.39
Domneån	12.50	42.10	0.45	60.22	6.88	1.74	1108.00	26.80	33.50	29.83	12.60	44.40
Fiskonbäcken	3.50	108.17	0.05	48.42	6.65	3.93	209.00	39.93	5.00	82.94	2.90	64.99
Höjdabäcken	10.10	52.90	0.03	93.27	6.06	5.29	255.00	29.29	7.00	125.35	9.10	24.31
Laxtjärnsbäcken	10.00	69.34	0.10	36.45	6.83	3.67	240.00	40.73	5.00	65.82	4.90	28.20
Lilltjärnsbäcken	11.00	62.64	0.14	34.86	6.78	4.00	229.50	28.81	4.00	47.69	5.05	17.62
Muddusälven	8.20	69.99	0.12	59.24	6.95	3.70	343.00	29.76	8.00	43.39	6.50	20.68
Sävjaån Ingvasta	13.30	47.61	1.36	31.54	7.49	2.27	1144.50	29.68	52.00	45.83	23.25	26.80
Stormyrbäcken	10.50	59.57	0.17	60.03	6.61	4.27	343.00	34.91	10.00	44.99	9.30	35.96
Svedån Sved	11.25	43.61	0.20	30.01	7.03	3.50	334.00	49.98	10.00	69.54	6.85	55.81
Viepsajåkkå	9.00	60.29	0.14	39.52	6.99	4.16	226.00	43.17	6.00	99.64	3.20	48.38

Given are median values and the coefficient of variance (CV) based on monthly measurements from May to October from 1995 to 2010. For abbreviations of variables see ''Methods''.

lake bottom water oxygen (O_2) available as well as pH, Alk, Cond, Ca, Mg, Na, K, Cl, SO_4, NO_3-N, TN, TP, $AbsF_{420}$, TOC, and Si which we used to evaluate vertical differences in the variables over different seasons. From surface and bottom water WT, we determined WT differences as a measure of thermal stratification. We further assumed that lake waters are mixed when temperature differences between bottom and surface water are less than 2°C and larger than −2°C.

The lakes and streams were about evenly distributed over Sweden (Figure 1) and represented small, shallow, and oligotrophic waters (Table 1). The majority of the lakes had an average water retention time (equation 1) of less than 1 year, a mean lake water depth less than 5 m and a lake surface area less than 0.4 km^2. All streams had lakes upstream, and in most streams more than 60% of the water at the location of the measuring site had flowed through lakes. Thus, stream water characteristics reflect processes occurring in the terrestrial environment as well as in upstream lakes.

The fourth database comprised data from 99 Finnish lake sites, all of them located above the deepest parts of Finland's largest lakes, and sampled at different depths 1 to 34 times during the years 1998 and 1999. We used this database to evaluate vertical differences in $p\mathrm{CO}_2$ in large lakes over different seasons. The lakes are mainly situated in central and eastern Finland and were usually sampled three times a year, at the end of the winter stratification just before spring circulation, at the end of the summer stratification just before autumn circulation, and during autumn circulation. The water chemistry was analyzed from unfiltered samples in the accredited laboratories of the Regional Environment Centers in Finland. For this study we used data on WT, pH and dissolved inorganic carbon (DIC, measured as total inorganic carbon) that were available from different depths. For further information on methods and water quality and catchment characteristics of the lakes, see Rantakari and Kortelainen (2005).

Finally, we had modeled monthly mean water discharge values available from 176 streams and rivers distributed all over Sweden from 1995 to 2008. The water discharge values are based on a large variety of actual measurements of water discharge, air temperature and precipitation. The values are available from the SMHI, http://www.smhi.se.

Estimates of $p\mathrm{CO}_2$

Estimations of $p\mathrm{CO}_2$ differed between the Swedish and the Finnish waters because measurements of DIC were available for the Finnish lakes whereas they needed to be calculated for the Swedish waters with available Alk, pH and WT data. For the DIC calculation in the Swedish waters, we first adjusted equilibrium constants (K_1 and K_2) for in situ WT according to Stumm and Morgan (1996):

$$\log_{10} K_1 = -356.3094 - 0.06091964\mathrm{WT} + \frac{21834.37}{\mathrm{WT}} + 126.8339\log_{10}\mathrm{WT} - \frac{1684915}{\mathrm{WT}^2} \tag{2}$$

and

$$\log_{10} K_1 = -107.8871 - 0.03252849\,WT + \frac{5151.79}{\mathrm{WT}} + 38.92561\log_{10}\mathrm{WT} - \frac{563713.9}{\mathrm{WT}^2}, \tag{3}$$

where WT is the water temperature (in K).

As a next step, we calculated the concentrations of hydrogen [H^+] and hydroxide [OH^-] ions with measured pH values:

$$[H^+] = 10^{-\mathrm{pH}} \tag{4}$$

$$[\mathrm{OH}^-] = 10^{-(14-\mathrm{pH})} \tag{5}$$

With available [H^+], K_1, and K_2, we calculated the ionization fractions (α_1 and α_2) reported by Stumm and Morgan (1996):

$$\alpha_1 = \left(\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}\right)^{-1} \tag{6}$$

$$\alpha_2 = \left(\frac{[H^+]^2}{K_1 \cdot K_2} + \frac{[H^+]}{K_2} + 1\right)^{-1} \tag{7}$$

Finally, we calculated DIC (in μm):

$$\mathrm{DIC} = \frac{\mathrm{Alk} - [\mathrm{OH}]^- + [\mathrm{H}]^+}{\alpha_1 + 2\alpha_2} \cdot 1000, \tag{8}$$

where Alk is the alkalinity (in mEq l^{-1}).

The following steps were performed both for the Finnish and the Swedish data material. From DIC, we calculated the amount of carbon dioxide (CO_2; in μM):

$$\mathrm{CO}_2 = \frac{\mathrm{DIC}}{\frac{K_1}{[H^+]} + \frac{K_1 \cdot K_2}{[H^+]^2} + 1} \tag{9}$$

Finally, we determined $p\mathrm{CO}_2$ (in μatm):

$$p\mathrm{CO}_2 = \frac{\mathrm{CO}_2}{K_\mathrm{H} \cdot P \cdot 0.987} \tag{10}$$

where K_H is the WT-adjusted Henry's constant according to Stumm and Morgan (1996):

$$\log_{10} K_H = 108.3865 + 0.01985076\mathrm{WT} - \frac{6919.53}{\mathrm{WT}} - 40.45154 \log_{10} \mathrm{WT} - \frac{669365}{\mathrm{WT}^2} \tag{11}$$

and P is the air pressure (bar), adjusted for altitude (Alt; in meter above sea level)

$$P = (1013 - 0.1Alt) \cdot 0.001 \tag{12}$$

A variety of the Swedish samples had negative Alk values causing negative $p\mathrm{CO}_2$. These negative values were removed, reducing the database of 756 boreal lakes to a database of 709 lakes. No data had to be removed for the continuous time series of 14 boreal lakes and 14 boreal streams.

Statistical Methods

All statistical tests and calculations were carried out in JMP, version 9.0. Due to the non-normal distribution of many of our variables, tested by a Shapiro–Wilk test for normality, we restricted our statistical analyses to those that are robust against non-normal distributions, that is, non-parametric tests. To find important drivers for $p\mathrm{CO}_2$ on a spatial and temporal scale, we used partial least squares regressions (PLS). PLS analyses were chosen because of the method's insensitivity to X variable's interdependency and the insensitivity to deviations from normality (Wold and others 2001). PLS is commonly used to find fundamental relations between two matrices (X and Y), where the variance in X is taken to explain the variance in Y. In PLS, X-variables are ranked according to their relevance in explaining Y, commonly expressed as VIP values (Wold and others 2001). The higher the VIP values, the higher is the contribution of an X variable to the model performance. VIP values exceeding 1 are considered as important X variables. In our PLS analyses, pH always was the most important X variable explaining $p\mathrm{CO}_2$ variations both on a spatial and a temporal scale, but because pH, Alk, and WT have been used to calculate $p\mathrm{CO}_2$, we removed these three variables from all PLS analyses to avoid autocorrelation.

RESULTS

General $p\mathrm{CO}_2$ Variations in Lakes and Streams and Co-varying Variables

Taking all available $p\mathrm{CO}_2$ values from lakes ($n = 11{,}538$) and streams ($n = 11{,}126$), we found significantly higher $p\mathrm{CO}_2$ values in streams than in lakes (Wilcoxon test: $P < 0.0001$). $p\mathrm{CO}_2$ in lakes ranged from below atmospheric equilibrium (less than 10% of the samples) to a maximum of 20,868 µatm with a median value of 1048 µatm. In streams, $p\mathrm{CO}_2$ had a higher median value with 1176 µatm and ranged from below atmospheric equilibrium (less than 10% of the samples) to a maximum of 26,891 µatm. Using PLS, we found that $p\mathrm{CO}_2$ variations during autumn water column mixing between the 709 boreal lakes, for which we had the most complete lake and catchment database available (17 water chemical and 9 catchment variables), were best explained by TOC concentrations (positive relation, VIP value = 1.60). Additional highly important X variables (VIP values > 1.3) were AbsF_{420} (positive relation), AirT (positive relation), and TN (positive relation). The variables Si, K, % forest, Ca, NO_3-N, D_m, % water, Mg, WRT, A, SO_4, and ADA were not important for $p\mathrm{CO}_2$ variations in our lakes during autumn (VIP values < 1). With the PLS-model, 36% of $p\mathrm{CO}_2$ spatial variations could be explained (excluding the variables pH, Alk, and WT).

We reached better model performance (up to 80% explanation of $p\mathrm{CO}_2$ variations) when we modelled temporal $p\mathrm{CO}_2$ variations in each of the 14 lakes for which we had monthly data available from 1995 to 2010. For the 14 lake-specific PLS models, we had in addition to the 17 water chemical variables that we used for the large-scale PLS model even Chl*a* and WT differences between surface and bottom waters as X variables available. We found that in all lakes, AbsF_{420} (positive relation), AbsF_{420}/TOC (positive relation), or WT differences (negative relation) were most important for $p\mathrm{CO}_2$ temporal variations (excluding the variables pH, Alk, and WT). Chl*a* was important for $p\mathrm{CO}_2$ variations in surface waters of only 5 out of 14 lakes (VIP > 1). In four of the five lakes Chl*a* was negatively related to $p\mathrm{CO}_2$, but in the lake where Chl*a* reached the highest VIP value, the relationship between Chl*a* and $p\mathrm{CO}_2$ was positive ($R^2 = 0.14$, $P < 0.001$; Figure 2). In this lake (Figure 2), as in most other lakes, $p\mathrm{CO}_2$ temporal variations showed a significant linear negative relationship to WT differences (R^2 up to 0.34, $P < 0.001$).

Modelling $p\mathrm{CO}_2$ temporal variations in each of the 14 streams with monthly data from 1995 to 2010 and using 17 water chemical variables as X variables showed different patterns from the lake PLS models. Unlike the lake models where either AbsF_{420}, AbsF_{420}/TOC, or WT difference came out as the most important variable for $p\mathrm{CO}_2$ variations, the stream models indicated highly deviating most important variables, that is, AbsF_{420}, TOC, Cl, Si,

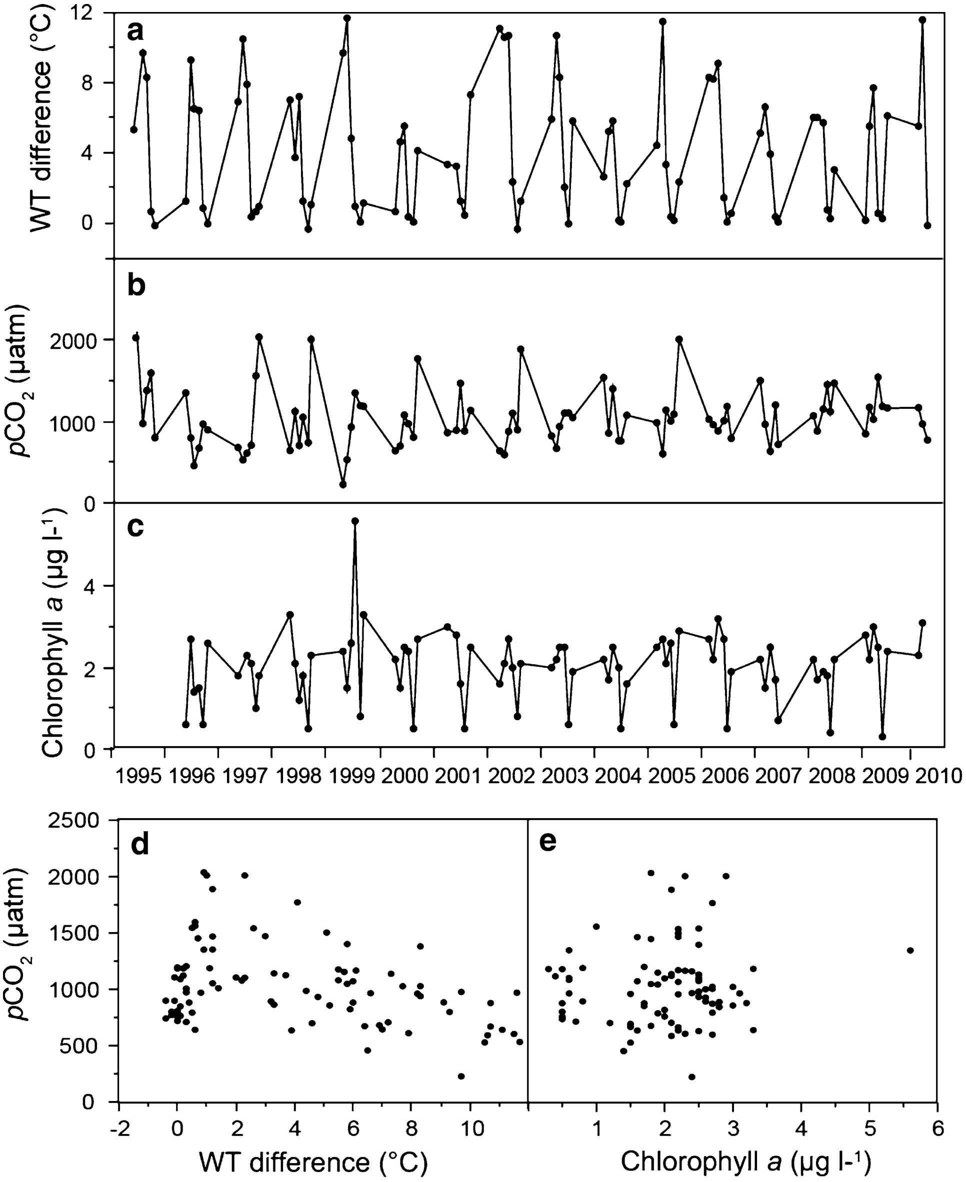

Figure 2. Monthly data on water temperature differences (WT difference) between surface and bottom waters (**a**), carbon dioxide supersaturation (pCO_2; **b**), and chlorophyll *a* concentrations (**c**) in Stensjön from 1995 to 2010. **d**, **e** Relations between pCO_2 and WT difference and chlorophyll *a*, respectively, in Stensjön. Stensjön was the lake where chlorophyll *a* concentrations reached the highest VIP value in a PLS model that has been used to predict pCO_2 temporal variations.

Na, Cond, Ca, Mg, or NO_3-N. In addition, *X* variables that were important for pCO_2 variations in some streams where unimportant in others. How much of the pCO_2 variations in the different streams could be explained was, like for lakes, highly varying, ranging from less than 22% to more than 86% (excluding the variables pH, Alk, and WT).

Seasonal pCO_2 Variations in Lakes and Streams

Dividing the data material of 22,664 samples into four seasons, that is, a winter season where some samples have been taken below an ice cover (from January to March), a spring season where spring floods occur and the waters usually are highly turbulent (April, May), a summer season (from June to September), and an autumn season where waters are turbulent again (from October to December), we found the highest pCO_2 values during the winter season, both in lakes and in streams. During winter time, pCO_2 values were significantly higher in lakes than in streams (non-parametric Wilcoxon test: $P < 0.0001$). During spring time, pCO_2 showed lower values and there was no longer a significant difference in pCO_2 between lakes and streams (non-parametric Wilcoxon test: $P > 0.05$). Lowest pCO_2 values were reached during summer in both lakes and streams but lakes had significantly lower pCO_2 values than streams (non-parametric Wilcoxon test: $P < 0.0001$). Towards autumn, pCO_2 increased again in both lakes and streams with significantly higher pCO_2 in streams than in lakes (non-parametric Wilcoxon test: $P < 0.0001$).

We obtained the same results when we used pCO_2 values from surface waters of our 14 lakes and 14 streams from which we had monthly values from May to October during 1995–2010: high pCO_2 values and no significant difference in pCO_2 between lakes and streams in May (non-parametric Wilcoxon test: $P > 0.05$), high pCO_2 values in both lakes and streams in September and October, and low pCO_2 values during June to August in both lakes and streams but with significantly higher values in streams than in lakes, in particular during July (non-parametric Wilcoxon-test: $P < 0.0001$). Thus, pCO_2 in surface waters of lakes followed a clear sine function with high pCO_2 in spring and autumn and low pCO_2 during summer (Figure 3a). Clear seasonal variations, here and previously defined as variations following a sine function (Weyhenmeyer 2009), were in lake surface waters also observed for WT differences (Figure 3c), WT, pH, $AbsF_{420}$, $AbsF_{420}$/TOC, NO_3-N, TN, and Chl*a*. In streams, we also found seasonal variations for the same variables with the exception of $AbsF_{420}$ and $AbsF_{420}$/TOC that did not show clear seasonal patterns in streams. Analyzing water discharge data that have been modeled for 176 streams and rivers distributed over Sweden showed maximum values during spring and minimum values during August (Figure 3d). August was also the month when Chl*a* concentrations in lakes were highest and NO_3-N concentrations lowest. In contrast, pCO_2 started to increase again in August (Figure 3a).

Although seasonal variations were observed in both lakes and streams, seasonality with clear minimum or maximum values during summer was generally more pronounced in lakes than in streams. As a consequence, we observed highly significant (non-parametric Wilcoxon test: $P < 0.0001$) differences between lake surface waters and streams in July for pH (higher in streams), Alk (higher in streams), WT (lower in streams), NO_3-N (higher in streams), $AbsF_{420}$ (higher in streams), $AbsF_{420}$/TOC (higher in streams), and pCO_2 (higher in streams). TP and TOC did not show significant differences between lake surface waters and streams in July (non-parametric Wilcoxon test: $P > 0.05$). Higher pH and lower WT in streams during summer are expected to result in lower pCO_2 in streams than in lakes, according to the equations used for pCO_2 calculations (equations 2–11). Variables that might explain our observed significantly lower surface water pCO_2 values in lakes than in streams during summer were Chl*a*, $AbsF_{420}$, $AbsF_{420}$/TOC, Alk, and the WT difference between bottom and surface waters. According to our PLS models, we regard WT difference, $AbsF_{420}$, and $AbsF_{420}$/TOC as the most important variables for pCO_2 temporal variations in lake surface waters. Taking the monthly median pCO_2 of Swedish lake surface waters and relating

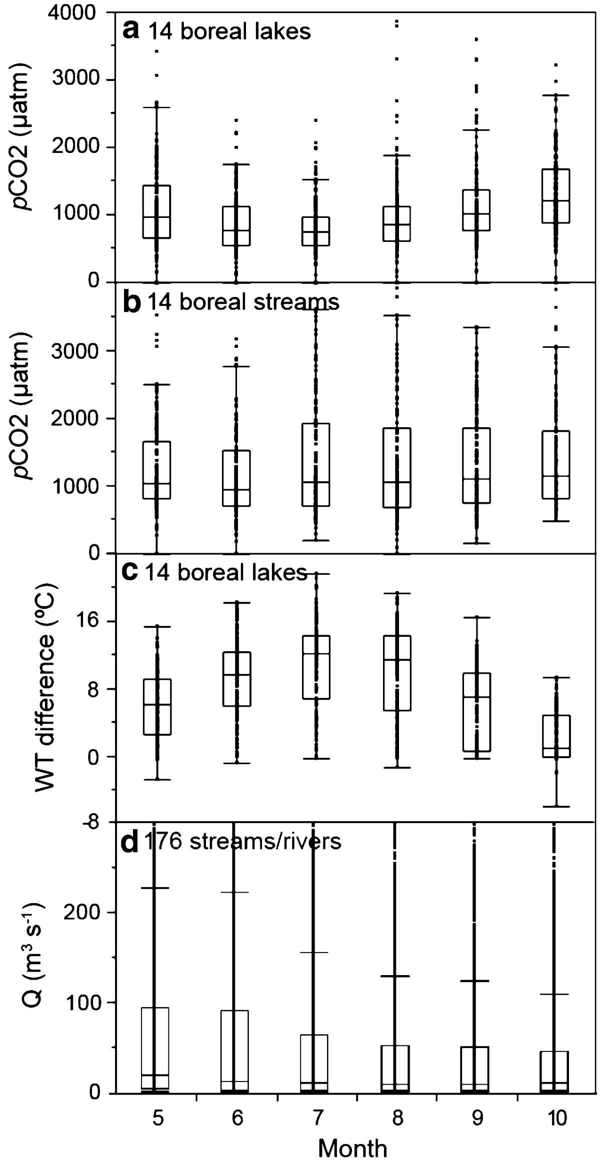

Figure 3. Quantile plots of monthly values on carbon dioxide supersaturation (pCO_2) in surface waters of 14 Swedish boreal lakes (**a**) and 14 Swedish boreal streams (**b**), on water temperature differences between bottom and surface waters (WT difference) in the same 14 Swedish boreal lakes from a (**c**) and on monthly mean water discharges from 176 stream/river sites (**d**). All data are based on complete time series from 1995 to 2010. pCO_2 and water difference in the lakes show similar clear seasonal variations.

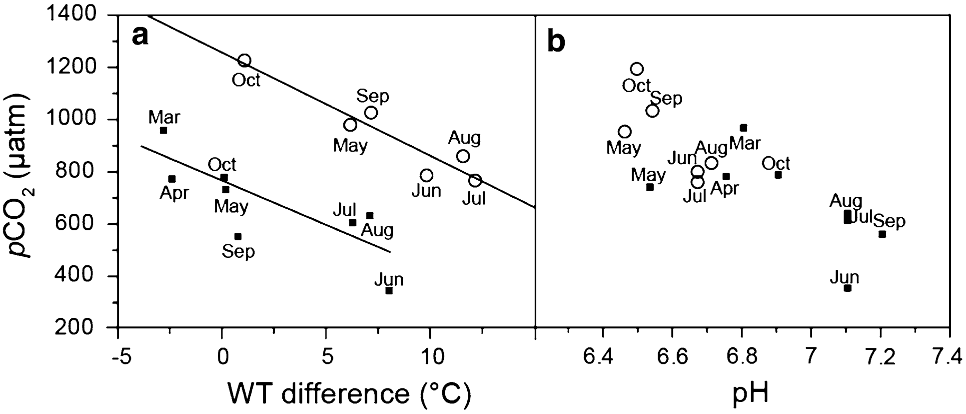

Figure 4. Monthly median values of available water temperature differences (WT difference) between bottom and surface waters (**a**) and monthly median values of pH (**b**) in relation to available monthly median values of carbon dioxide supersaturation (pCO_2) in surface waters of Swedish (14 lakes, data from 1995 to 2010; *open circles*) and Finnish (99 lakes, data from 1998 and 1999; *black squares*). For the Swedish lakes, the regression equation of panel a runs: $y = -40x + 1258$ ($R^s = 0.90$, $P < 0.01$, $n = 6$), and for the Finnish lakes: $y = -34x + 769$ ($R^2 = 0.64$, $P < 0.05$, $n = 8$).

them to the monthly median of the WT differences in the Swedish lakes, we observed a 40 µatm decrease in pCO_2 in surface waters per 1°C increase in the WT difference between surface and bottom waters (Figure 4a). The same pattern was observed in the Finnish lakes, but in these lakes, the intercept, which reflects lake water mixing conditions, was 489 µatm lower than in the Swedish lake surface waters (Figure 4a). The difference between pCO_2 in the surface waters of the large Finnish lakes and the small, shallow Swedish lakes corresponded well with pH differences between the two lake types (Figure 4b).

Vertical pCO_2 Variations

In the 14 Swedish lakes, pCO_2 was significantly higher in bottom waters than in surface waters for all months (non-parametric Wilcoxon test: $P < 0.001$ for May, June, July, August, September, and $P < 0.05$ for October). Also in the Finnish lakes, pCO_2 in bottom waters significantly exceeded pCO_2 in surface waters (non-parametric Wilcoxon test: $P < 0.001$ for May, June, July, and August) except during the months of September and October when it was similar in bottom and surface waters (non-parametric Wilcoxon test: $P > 0.05$). The occasions where pCO_2 in surface waters exceeded that in bottom waters were rare and negligible in size, and they occurred during the mixing period (Figure 5). During all months, including the months when the water column was mixed, pCO_2 in bottom waters of the 14 Swedish lakes was significantly higher than pCO_2 in streams (non-parametric Wilcoxon test: $P < 0.001$). pCO_2 in bottom waters of lakes was significantly negatively related to bottom water oxygen concentrations ($R^2 = 0.37$, $P < 0.0001$) but not related at all to bottom water temperatures ($R^2 = 0.00$, $P > 0.05$).

DISCUSSION

Our results show clear differences and similarities in pCO_2 variations between boreal lakes and streams. In spring, prior to thermal stratification in lakes, pCO_2 measurements were similar in lakes and streams. In addition, overall seasonal patterns characterized by the highest pCO_2 in spring and autumn and lowest pCO_2 during summer following water discharge were comparable between boreal lakes and streams. The seasonal pCO_2 variations were, however, much more pronounced in lakes than in streams.

As outlined in the introduction, seasonal pCO_2 variations in surface waters, particularly in lakes, are not completely understood yet and have revealed contrasting patterns with either maximum (for example, Jonsson and others 2007a) or minimum pCO_2 values during summer (for example, Kelly and others 2001; Kortelainen and others 2006; Atilla and others 2011). Seasonal variations in pCO_2 are a result of CO_2 and bicarbonate inputs from the terrestrial environment, photosynthesis, photo- and microbial mineralization and water column mixing. In streams we expect pCO_2 to be primarily driven by hydrological conditions. Accordingly, we found the highest water discharges and highest pCO_2 values during spring and the

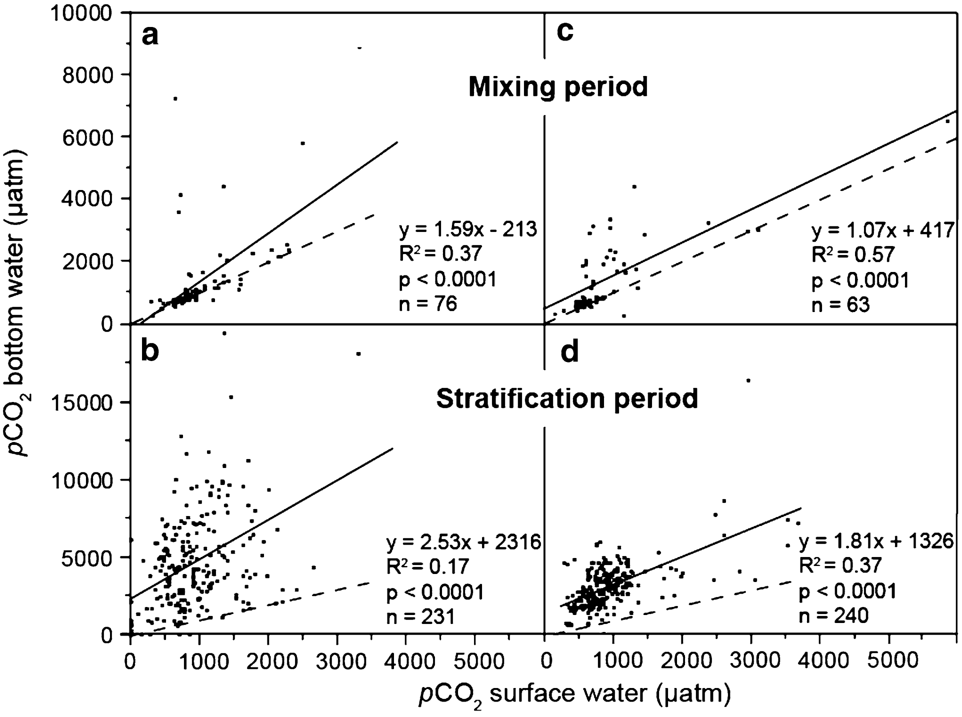

Figure 5. Relationships between surface water carbon dioxide supersaturation (pCO_2) and bottom water pCO_2 in Swedish (**a**, **b**) and Finnish (**c**, **d**) lakes during the mixing and stratification period. The Swedish dataset comprises 14 boreal lakes with monthly data from May to October during 1995 to 2010 (due to missing bottom water data, the data series are not complete), and the Finnish datasets includes available data from 99 lakes samples during March and October in 1998 and 1999. The *dashed lines* represent the 1:1 relationship.

lowest during summer. Hydrological conditions and catchment processes probably counteracted the influence of photo- and microbial transformations in streams which we expected to result in increased pCO_2 towards summer. An antagonistic effect of water discharge and photo- and microbial transformation on pCO_2 during summer might give an explanation why water discharge decreased faster towards summer than pCO_2 in streams (Figure 3).

Hydrological conditions and catchment processes are likely to have an important effect not only on pCO_2 in streams but also on pCO_2 in small and shallow boreal lake waters with short water retention times, as suggested by Humborg and others (2009). Accordingly, we found high pCO_2 values in lake waters at high water discharges in spring and low pCO_2 values at low water discharges in summer (Figure 3). The strong hydrological influence was probably why we found comparable pCO_2 variations in lakes and streams during spring. We suggest that also autumn pCO_2 variations in lakes are mainly influenced by water discharge patterns, because we found TOC, which in Swedish waters is highly influenced by water discharge (Erlandsson and others 2008), to be the most important variable for pCO_2 variations in lakes in autumn.

During summer, however, pCO_2 in streams and lakes seems to be affected by different processes, indicated by significantly lower pCO_2 values in surface waters of lakes than in streams. Most obvious differences between lakes and streams during summer are the effects of thermal stratification and photosynthesis. Photosynthesis is expected to result in decreasing pCO_2 in summer during the daytime. We do not have data on photosynthesis in our lakes but based on measurements on boreal lakes in general (for example, Jonsson and others 2001; Einola and others 2011) and the fact that Chl*a* concentration that can be regarded as a measure of photosynthesis was only important for pCO_2 variations in 5 out of 14 lakes in our PLS models, we assume that photosynthesis is only a minor process influencing pCO_2 in our heterotrophic boreal lakes. This statement is further strengthened by the fact that the lake where Chl*a* received the highest VIP value in the PLS model for pCO_2 variations showed a positive and not a negative relationship between Chl*a* and pCO_2. We attribute the positive relationship to deviating seasonality patterns of Chl*a* and pCO_2 in this particular lake. In Stensjön pCO_2 and Chl*a* are out of phase with the highest Chl*a* concentrations in August and lowest pCO_2 values in July (Figure 2). Such deviating seasonality patterns reflect that photosynthesis is not the dominant process determining pCO_2 variations in our boreal waters.

The influence of thermal stratification on pCO_2 in lake surface waters was, however, clearly detectable, despite our lakes being rather small and shallow. The influence of thermal stratification on biogeochemical cycling in lakes is well known (Keller 2007). Thermal stratification can result in nutrient depletion in the epilimnion, and oxygen depletion in the hypolimnion as element exchanges between epi- and hypolimnion are hindered by thermal stratification. Assuming that a large fraction of CO_2 is produced in the sediments or enters the hypolimnion via groundwater, a strong thermocline will result in CO_2 accumulation in the hypolimnion. The CO_2 accumulation in the hypolimnion occurs at the same time as O_2 is consumed, indicated by our observed negative relationship between pCO_2 and O_2. Consequently, O_2 concentrations have earlier been shown to be well related to CO_2 concentrations. In 177 randomly selected Finnish lakes, for example, as much as 79% of the variation in CO_2 could be explained by O_2 concentration only (Kortelainen and others 2006). Because we also found a clear negative relationship between O_2 concentrations and bottom water pCO_2 we suggest that thermal stratification plays a critical role for the distribution of pCO_2 in the water column of lakes.

A strong negative relationship between intensity of thermal stratification and pCO_2 in the epilimnion was not only found in Swedish lakes but also in Finnish lakes. Finnish lakes had, however, constantly lower pCO_2. The difference in pCO_2 between Swedish and Finnish lakes was reflected in pH differences (Figure 4b). We are, however, not able to differentiate between pH being a cause or a response variable. It is possible that pH in the large Finnish lakes is higher due to a larger lake volume giving the lakes a better buffering capacity and due to a higher relative importance of agriculture in the catchment area (Rantakari and Kortelainen 2005). In that case, high pH would result in low pCO_2. It is, however, also possible that primary production is higher in the large lakes, resulting in a higher CO_2 consumption with consequent low pCO_2. In that case, low pCO_2 would result in high pH. Independently of what the driver and the response is we found consistently higher pCO_2 values in the small Swedish lakes compared to the large Finnish lakes along the WT gradient (Figure 4a). Further studies on the relative importance of processes determining pCO_2 in small and in large lakes are needed to fully understand pCO_2 variations over large scales.

Once WT differences between surface and bottom waters become negligible towards autumn and the water column starts to mix, pCO_2 in surface waters of lakes reaches values that are close to the ones found in streams (Figure 3a, b). These results correspond to the findings of Bellido and others (2009), Huotari and others (2009), and Laurion and others (2010) who all found maximum gas losses during water mixing periods. Highest pCO_2 values, however, are observed below ice cover, as seen in this study and earlier reported by Kortelainen and others (2006). How far the accumulated CO_2 below an ice cover evades into the atmosphere at ice-off remains still unclear. We have indications from our results that CO_2 is accumulated in bottom waters throughout the year despite spring and autumn circulation. Such an accumulation of pCO_2 in bottom waters of lakes that exceeds pCO_2 in streams is likely a result of many processes: incomplete water column mixing, CO_2 input from groundwater into deeper parts of a lake and/or higher CO_2 production in the lower water column by remineralization of organic matter that has settled out from the epilimnion.

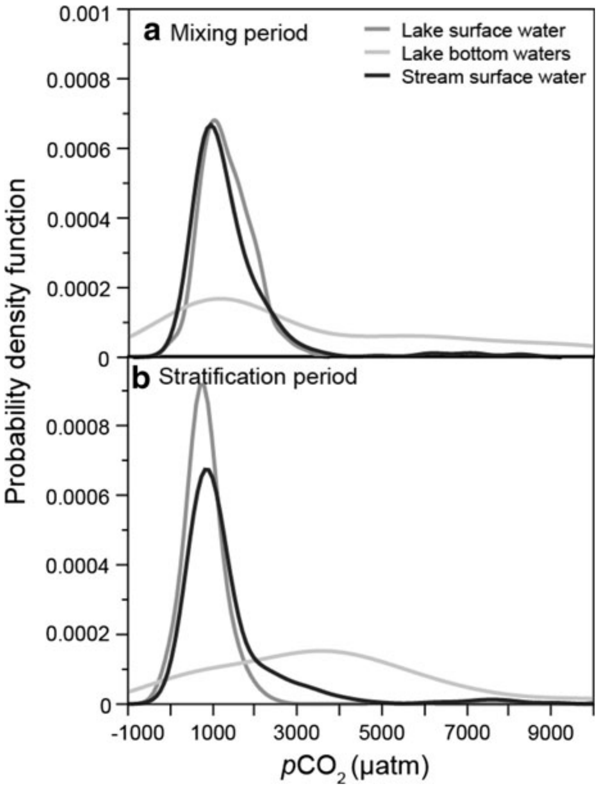

Figure 6. Probability density functions of carbon dioxide supersaturation (pCO_2) in lake surface waters (*dark grey*), lake bottom waters (*light grey*) and stream surface waters (*black*) during the water column mixing period in October (**a**) and during summer stratification in July (**b**). The figure is based upon monthly data from 14 boreal lakes and 14 boreal streams during 1995–2010.

Although CO_2 in our small and shallow lakes might primarily be produced in the catchment or in the sediments, we have indications for epilimnetic CO_2 production because we found decreasing $AbsF_{420}/TOC$ ratios in surface water of lakes towards summer. Decreasing $AbsF_{420}/TOC$ ratios correspond to a preferential degradation of colored organic matter which has been observed for waters that have been exposed to solar radiation, suggesting a strong influence of photomineralization (Moran and others 2000; Vähätalo and others 2000. Seasonal variations in AbsF$_{420}$/TOC were not detectable for streams, probably because of other processes overriding the effect of photomineralization in typically shaded boreal streams.

From our results, we conclude that seasonal $p\mathrm{CO}_2$ variation in boreal lakes and streams follows water discharge patterns, but that lakes during summer are additionally affected by WT differences between surface and bottom waters, causing pronounced differences in $p\mathrm{CO}_2$ variations between lakes and streams and also between lake surface and bottom waters (Figure 6). According to our results, $p\mathrm{CO}_2$ reaches minimum values in surface waters during summer. If such minimum $p\mathrm{CO}_2$ values are the basis for annual flux estimates on a global scale, CO_2 fluxes from inland waters to the atmosphere will be underestimated. More research on seasonal and also on daily $p\mathrm{CO}_2$ variation is needed to reduce uncertainties in global estimates of CO_2 released from surface waters to the atmosphere.

ACKNOWLEDGEMENTS

G.A.W. is a research fellow of the Royal Swedish Academy of Sciences supported by a grant from the Knut and Alice Wallenberg Foundation. Funding for this study was also received by the Nordic Centre of Excellence ''CRAICC - Cryosphere-atmosphere interactions in a changing arctic climate'' supported by NordForsk, the Swedish Research Council (621-2009-2711) and the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (214-2009-272 and the Strong Research Environment ''CoW - Color of Water''). Many thanks go to the Swedish Environmental Protection Agency and the IVM laboratory for financing, sampling, and analyzing thousands of water samples. We are also grateful to the very constructive comments of two reviewers.

REFERENCES

Åberg J, Jansson M, Jonsson A. 2010. Importance of water temperature and thermal stratification dynamics for temporal variation of surface water CO_2 in a boreal lake. J Geophys Res Biogeosci 115:10. doi:10.1029/2009jg001085.

Atilla N, McKinley GA, Bennington V, Baehr M, Urban N, DeGrandpre M, Desai AR, Wu C. 2011. Observed variability of Lake Superior pCO_2. Limnol Oceanogr 56:775–86.

Aufdenkampe AK, Mayorga E, Raymond PA, Melack JM, Doney SC, Alin SR, Aalto RE, Yoo K. 2011. Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. Front Ecol Environ 9:53–60.

Battin TJ, Luyssaert S, Kaplan LA, Aufdenkampe AK, Richter A, Tranvik LJ. 2009. The boundless carbon cycle. Nat Geosci 2:598–600.

Bellido JL, Tulonen T, Kankaala P, Ojala A. 2009. CO(2) and CH(4) fluxes during spring and autumn mixing periods in a boreal lake (Paajarvi, southern Finland). J Geophys Res 114:G04007.

Bergström I, Kortelainen P, Sarvala J, Salonen K. 2010. Effects of temperature and sediment properties on benthic CO(2) production in an oligotrophic boreal lake. Freshw Biol 55:1747–57.

Cole JJ, Caraco NF, Kling GW, Kratz TK. 1994. Carbon-dioxide supersaturation in the surface waters of lakes. Science 265: 1568–70.

Cole JJ, Prairie YT, Caraco NF, McDowell WH, Tranvik LJ, Striegl RG, Duarte CM, Kortelainen P, Downing JA, Middelburg JJ, Melack J. 2007. Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. Ecosystems 10:171–84.

Einola E, Rantakari M, Kankaala P, Kortelainen P, Ojala A, Pajunen H, Makela S, Arvola L. 2011. Carbon pools and fluxes in a chain of five boreal lakes: a dry and wet year comparison. J Geophys Res 116:G03009. doi:10.1029/2010jg001636.

Erlandsson M, Buffam I, Fölster J, Laudon H, Temnerud J, Weyhenmeyer GA, Bishop K. 2008. Thirty-five years of synchrony in the organic matter concentrations of Swedish rivers explained by variation in flow and sulphate. Glob Change Biol 14:1191–8.

Gudasz C, Bastviken D, Steger K, Premke K, Sobek S, Tranvik LJ. 2010. Temperature-controlled organic carbon mineralization in lake sediments. Nature 466:478–81.

Humborg C, Mörth CM, Sundbom M, Borg H, Blenckner T, Giesler R, Ittekkot V. 2009. CO(2) supersaturation along the aquatic conduit in Swedish watersheds as constrained by terrestrial respiration, aquatic respiration and weathering. Glob Change Biol 16:1966–78.

Huotari J, Ojala A, Peltomaa E, Pumpanen J, Hari P, Vesala T. 2009. Temporal variations in surface water CO_2 concentration in a boreal humic lake based on high-frequency measurements. Boreal Environ Res 14:48–60.

Jonsson A, Meili M, Bergström AK et al. 2001. Whole-lake mineralization of allochthonous organic carbon in a large humic lake (Örträsket, N. Sweden). Limnol Oceanogr 46: 1691–700.

Jonsson A, Aberg J, Jansson M. 2007a. Variations in pCO(2) during summer in the surface water of an unproductive lake in northern Sweden. Tellus Ser B 59:797–803.

Jonsson A, Algesten G, Bergstrom AK, Bishop K, Sobek S, Tranvik LJ, Jansson M. 2007b. Integrating aquatic carbon fluxes in a boreal catchment carbon budget. J Hydrol 334: 141–50.

Kaiser E, Sulzberger B. 2004. Phototransformation of riverine dissolved organic matter (DOM) in the presence of abundant iron: effect on DOM bioavailability. Limnol Oceanogr 49:540–54.

Keller W. 2007. Implications of climate warming for boreal shield lakes: a review and synthesis. Environ Rev 15:99–112.

Kelly CA, Fee E, Ramlal PS, Rudd JWM, Hesslein RH, Anema C, Schindler EU. 2001. Natural variability of carbon dioxide and net epilimnetic production in the surface waters of boreal lakes of different sizes. Limnol Oceanogr 46:1054–64.

Kortelainen P, Rantakari M, Huttunen JT, Mattsson T, Alm J, Juutinen S, Larmola T, Silvola J, Martikainen PJ. 2006. Sediment respiration and lake trophic state are important predictors of large CO_2 evasion from small boreal lakes. Glob Change Biol 12:1554–67.

Kosten S, Roland F, Marques D, Van Nes EH, Mazzeo N, Sternberg LDL, Scheffer M, Cole JJ. 2010. Climate-dependent CO_2 emissions from lakes. Global Biogeochem Cycles 24:7. doi:10.1029/2009gb003618.

Laurion I, Vincent WF, MacIntyre S, Retamal L, Dupont C, Francus P, Pienitz R. 2010. Variability in greenhouse gas emissions from permafrost thaw ponds. Limnol Oceanogr 55:115–33.

Marotta H, Duarte CM, Meirelles-Pereira F, Bento L, Esteves FA, Enrich-Prast A. 2010. Long-term CO_2 variability in two shallow tropical lakes experiencing episodic eutrophication and acidification events. Ecosystems 13:382–92.

McCallister SL, Bauer JE, Kelly J, Ducklow HW. 2005. Effects of sunlight on decomposition of estuarine dissolved organic C, N and P and bacterial metabolism. Aquat Microb Ecol 40:25–35.

Moran MA, Sheldon WM, Zepp RG. 2000. Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter. Limnol Oceanogr 45:1254–64.

Rantakari M, Kortelainen P. 2005. Interannual variation and climatic regulation of the CO_2 emission from large boreal lakes. Glob Change Biol 11:1368–80.

Richey JE, Melack JM, Aufdenkampe AK, Ballester VM, Hess LL. 2002. Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO_2. Nature 416:617–20.

Sobek S, Algesten G, Bergstrom AK, Jansson M, Tranvik LJ. 2003. The catchment and climate regulation of pCO(2) in boreal lakes. Glob Change Biol 9:630–41.

Stets EG, Striegl RG, Aiken GR, Rosenberry DO, Winter TC. 2009. Hydrologic support of carbon dioxide flux revealed by whole-lake carbon budgets. J Geophys Res 114:G01008. doi:10.1029/2008jg000783.

Striegl RG, Michmerhuizen CM. 1998. Hydrologic influence on methane and carbon dioxide dynamics at two north-central Minnesota lakes. Limnol Oceanogr 43:1519–29.

Stumm W, Morgan JJ. 1996. Aquatic chemistry: chemical equilibria and rates in natural waters. New York: Wiley-Interscience.

Teodoru CR, Del Giorgio PA, Prairie YT, Camire M. 2009. Patterns in pCO(2) in boreal streams and rivers of northern Quebec, Canada. Global Biogeochem Cycles 23:11. doi:10.1029/2008gb003404.

Tranvik LJ, Downing JA, Cotner JB, Loiselle SA, Striegl RG, Ballatore TJ, Dillon P, Finlay K, Fortino K, Knoll LB, Kortelainen PL, Kutser T, Larsen S, Laurion I, Leech DM, McCallister SL, McKnight DM, Melack JM, Overholt E, Porter JA, Prairie Y, Renwick WH, Roland F, Sherman BS, Schindler DW, Sobek S, Tremblay A, Vanni MJ, Verschoor AM, von Wachenfeldt E, Weyhenmeyer GA. 2009. Lakes and reservoirs as regulators of carbon cycling and climate. Limnol Oceanogr 54:2298–314.

Vähätalo AV, Salkinoja-Salonen M, Taalas P, Salonen K. 2000. Spectrum of the quantum yield for photochemical mineralization of dissolved organic carbon in a humic lake. Limnol Oceanogr 45:664–76.

Vähätalo AV, Salonen K, Munster U, Järvinen M, Wetzel RG. 2003. Photochemical transformation of allochthonous organic matter provides bioavailable nutrients in a humic lake. Archiv für Hydrobiologie 156:287–314.

von Wachenfeldt E, Tranvik LJ. 2008. Sedimentation in boreal lakes—the role of flocculation of allochthonous dissolved organic matter in the water column. Ecosystems 11:803–14.

Weyhenmeyer GA. 2009. Increasing dissimilarity of water chemical compositions in a warmer climate. Global Biogeochemical Cycles 23:GB2004. doi:10.1029/2008gb003318.

Wold S, Sjöström M, Eriksson L. 2001. PLS-regression: a basic tool of chemometrics. Chemom Intell Lab Syst 58:109–30.