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Partial pressure of Carbon Dioxide in Boreal Surface Waters
– Similarities and Dissimilarities Between Lake and Stream
Ecosystems

Running title: $p\text{CO}_2$ variations in boreal lakes and streams

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ABSTRACT

The quantity of carbon dioxide (CO₂) emissions from inland waters into the atmosphere varies, depending on spatial and temporal variations in the partial pressure of CO₂ ($p\text{CO}_2$) in the waters. Using 22664 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 $p\text{CO}_2$, ranging from below atmospheric equilibrium to values $> 20,000 \mu\text{atm}$ with a median value of $1048 \mu\text{atm}$ for lakes ($n = 11538$ samples) and $1176 \mu\text{atm}$ for streams ($n = 11126$). During the spring water mixing period in April/May, variations in $p\text{CO}_2$ were not significantly different between stream and lake ecosystems ($P > 0.05$), suggesting that $p\text{CO}_2$ in spring is determined by processes that occur to a similar extent in both lakes and streams. During other seasons of the year, however, $p\text{CO}_2$ differed significantly between lake and stream ecosystems ($p < 0.0001$). The variable that best explained the differences in seasonal $p\text{CO}_2$ variations between boreal lakes and streams was the temperature difference between bottom and surface waters. Already small temperature differences resulted in a decline of $p\text{CO}_2$ in lake surface waters. Minimum $p\text{CO}_2$ values in lake surface waters were reached in July. Towards autumn $p\text{CO}_2$ strongly increased again in lake surface waters reaching values close to the ones found in stream surface waters. Although $p\text{CO}_2$ strongly increased in the upper water column towards autumn, $p\text{CO}_2$ in lake bottom waters still exceeded the $p\text{CO}_2$ in surface waters of lakes and streams. We conclude that throughout the year CO₂ is concentrated in bottom waters of boreal lakes, although these lakes are typically shallow with a short water retention time. Highly varying amounts of this CO₂ reaches surface waters and finally evades into the atmosphere. Our findings have important implications for up-scaling CO₂ fluxes from single lake and stream measurements to regional and global annual fluxes.

Keywords: carbon, CO₂, 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 2007; Battin and others 2009; Tranvik and others 2009; Kosten and others 2010; Aufdenkampe and others 2011). The 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. Tranvik and others (2009) have for example shown that the estimated annual loss of 2 Gt is similar to the annual total global net ecosystem production. Such global estimates include, however, large uncertainties. One large uncertainty concerns seasonal and daily variations of carbon dioxide (CO₂) fluxes from inland waters. So far, global estimates are based upon day-time CO₂ 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). Day-time summer CO₂ values might overestimate CO₂ emissions of heterotrophic systems, typical for the large boreal region (Cole and others 1994), since photo- and microbial carbon transformations, known to drive CO₂ 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; Gudas and others 2010), typically occurring during summer at day-time. Thus, CO₂ emissions from inland waters, here expressed as CO₂ partial pressure ($p\text{CO}_2$), 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 CO₂ emissions towards summer have, for example, been observed in a lake in Northern Sweden (Jonsson and others 2007b). CO₂ emissions from inland waters might, however, also decrease towards

66 summer along with decreasing hydrological inputs of CO₂ and dissolved organic carbon
67 (DOC) from terrestrial ecosystems that have been found to be important drivers for *p*CO₂
68 variations in surface waters (Striegl and Michmerhuizen 1998; Sobek et al. 2003; Humborg
69 and others 2009; Stets and others 2009; Teodoru and others 2009). The influence of
70 hydrological inputs of CO₂ and DOC on *p*CO₂ in lakes is supported by a variety of studies
71 showing that precipitation is one of the best predictors for CO₂ concentrations both in boreal
72 and tropical lakes (Rantakari and Kortelainen 2005; Marotta and others 2010). Decreasing
73 *p*CO₂ towards summer has also been observed by e.g. Kelly and others (2001), Kortelainen
74 and others (2006) and Atilla and others (2011). In addition to hydrological controls, Kelly and
75 others (2001) attributed the summer *p*CO₂ decline to the influence of thermal stratification
76 which reduces the ratio epilimnetic area to the epilimnetic volume (*A_e/V_e*). Considering that
77 epilimnetic sediments are an important site of degradation of organic carbon to CO₂, they
78 suggested that a reduction in *A_e/V_e* resulted in a dilution of CO₂ in the epilimnion and thus in
79 a *p*CO₂ decline towards summer. A stratification effect on *p*CO₂ has also been observed by
80 Åberg and others (2010). They found that as soon as the epilimnion deepened, *p*CO₂ in the
81 surface water of a relatively small (3.8 km²) and deep (mean depth: 5 m, maximum depth 17
82 m) lake increased as a consequence of liberation of hypolimnion stored CO₂. Thus, according
83 to previous studies, *p*CO₂ can either increase or decrease during summer. In order to get a
84 better understanding of seasonal *p*CO₂ variations and *p*CO₂ variations in general we
85 conducted this study in which we considered both lake and stream ecosystems of the boreal
86 region. We hypothesized that *p*CO₂ in small and shallow boreal lakes with a short water
87 retention time is determined by processes that are similar to the ones occurring in streams
88 with minimum *p*CO₂ values in lakes and streams during summer when hydrological inputs of
89 CO₂ are low. To test the hypothesis we used more than 850 boreal lake samples and more
90 than 60 boreal stream samples from different water depths and different months as well as

water discharge data. Data on rivers have not been used for this study since 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 of lake size: 0.2 km²; 90 percentile: 2.3 km²) and shallow (median of mean lake depth: 4 m; 90 percentile: 6 m) boreal lakes (catchment covered by agriculture < 5% and by forest and lake ≥ 80 %) distributed over Sweden (Fig. 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. 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 (SO₄), nitrate-nitrogen (NO₃-N), total nitrogen (TN), total phosphorus (TP), absorbance at 420 nm of 0.45 µm filtered water in a 5-cm cuvette (AbsF₄₂₀), total organic carbon (TOC) and reactive silica (Si). The ratio AbsF₄₂₀/TOC was used as a proxy for the quality of TOC. TOC in Swedish boreal lakes usually contains 97 ± 5 % dissolved organic carbon (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, i.e. 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 yrs) for lakes according to:

$$WRT = \frac{V}{Area \cdot R} \quad (\text{eq. 1})$$

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 $mm\ yr^{-1}$).

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 $p\text{CO}_2$ variations. 14 boreal lakes and 14 boreal streams had complete monthly data on WT, pH, Alk, Cond, Ca, Mg, Na, K, Cl, SO_4 , $\text{NO}_3\text{-N}$, TN, TP, AbsF_{420} , TOC and Si available from May to October during 1995 to 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 lake bottom water oxygen (O_2) available as well as pH, Alk, Cond, Ca, Mg, Na, K, Cl, SO_4 , $\text{NO}_3\text{-N}$, 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 temperatures 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 (Fig. 1) and represented small, shallow, and oligotrophic waters (Table 1). The majority of the lakes had an average water retention time (eq. 1) less than one 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 flown 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 $p\text{CO}_2$ 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 Swedish Meteorological and Hydrological Institute, <http://www.smhi.se>

Estimates of $p\text{CO}_2$

Estimations of $p\text{CO}_2$ differed between the Swedish and the Finnish waters since measurements of dissolved inorganic carbon (DIC) were available for the Finnish lakes while 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):

$$\log_{10}K_1 = -356.3094 - 0.06091964WT + \frac{21834.37}{WT} + 126.8339\log_{10}WT - \frac{1684915}{WT^2} \text{ (eq. 2)}$$

and

$$\log_{10}K_2 = -107.8871 - 0.03252849WT + \frac{5151.79}{WT} + 38.92561\log_{10}WT - \frac{563713.9}{WT^2} \text{ (eq. 3)}$$

where

WT is the water temperature (in K).

190

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

193 $[H^+] = 10^{-pH}$ (eq. 4)

194 $[OH^-] = 10^{-(14-pH)}$ (eq. 5)

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

197 $\alpha_1 = \left(\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]} \right)^{-1}$ (eq. 6)

198 $\alpha_2 = \left(\frac{[H^+]^2}{K_1 \cdot K_2} + \frac{[H^+]}{K_2} + 1 \right)^{-1}$ (eq. 7)

199 Finally, we calculated DIC (in μM):

200 $DIC = \frac{Alk - [OH^-] + [H^+]}{\alpha_1 + 2\alpha_2} \cdot 1000$ (eq. 8)

201 where Alk is the alkalinity (in mEq L^{-1})

202

203 The following steps were performed both for the Finnish and the Swedish data material. From

204 DIC we calculated the amount of carbon dioxide (CO_2 ; in μM):

205 $CO_2 = \frac{DIC}{\frac{k_1}{[H^+]} + \frac{k_1 \cdot k_2}{[H^+]^2} + 1}$ (eq. 9)

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

207 $pCO_2 = \frac{CO_2}{K_H \cdot P \cdot 0.987}$ (eq. 10)

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

209 $\log_{10} K_H = 108.3865 + 0.01985076WT - \frac{6919.53}{WT} - 40.45154 \log_{10} WT - \frac{669365}{WT^2}$ (eq. 11)

210 and

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

212 $P = (1013 - 0.1Alt) \cdot 0.001$ (eq. 12)

A variety of the Swedish samples had negative Alk values causing negative $p\text{CO}_2$. 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 our 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, i.e. non-parametric tests. To find important drivers for $p\text{CO}_2$ 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 are 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 turned out as the most important X -variable explaining $p\text{CO}_2$ variations both on a spatial and a temporal scale, but since pH, Alk and WT have been used to calculate $p\text{CO}_2$ we removed these three variables from all PLS-analyses in order to avoid autocorrelation.

RESULTS

General $p\text{CO}_2$ variations in lakes and streams and co-varying variables

Taking all available $p\text{CO}_2$ values from lakes ($n = 11538$) and streams ($n = 11126$) we found significantly higher $p\text{CO}_2$ values in streams than in lakes (Wilcoxon-test: $P < 0.0001$). $p\text{CO}_2$ in lakes ranged from below atmospheric equilibrium (less than 10 % of the samples) to a maximum of $20,868 \mu\text{atm}$ with a median value of $1048 \mu\text{atm}$. In streams $p\text{CO}_2$ had a higher median value with $1176 \mu\text{atm}$ and ranged from below atmospheric equilibrium (less than 10 % of the samples) to a maximum of $26,891 \mu\text{atm}$. Using PLS, we found that $p\text{CO}_2$ 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 (VIP value = 1.60). Additional highly important X -variables (VIP values > 1.3) were AbsF_{420} , AirT and TN . The variables Si , K , % Forest, Ca , $\text{NO}_3\text{-N}$, D_m , % Water, Mg , WRT , A , SO_4 , and ADA were not important for $p\text{CO}_2$ variations in our lakes during autumn (VIP values < 1). With the PLS-model 36 % of $p\text{CO}_2$ spatial variations could be explained (excluding the variables pH , Alk and WT).

We reached better model performance (up to 80 % explanation of $p\text{CO}_2$ variations) when we modelled temporal $p\text{CO}_2$ 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 $\text{Chl}a$ and WT differences between surface and bottom waters as X -variables available. We found that in all lakes AbsF_{420} , $\text{AbsF}_{420}/\text{TOC}$ or WT differences were most important for $p\text{CO}_2$ temporal variations (excluding the variables pH , Alk and WT). $\text{Chl}a$ was important for $p\text{CO}_2$ variations in surface waters of only 5 out of 14 lakes (VIP > 1). In the lake where $\text{Chl}a$ reached the highest VIP value, temporal $\text{Chl}a$ variations were still weakly related to $p\text{CO}_2$ variations

while variations in WT difference showed good correspondence to $p\text{CO}_2$ temporal variations (Fig. 2).

Modelling $p\text{CO}_2$ 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} , $\text{AbsF}_{420}/\text{TOC}$ or WT difference came out as the most important variable for $p\text{CO}_2$ variations, the stream models indicated highly deviating most important variables, i.e. AbsF_{420} , TOC, Cl, Si, Na, Cond, Ca, Mg, or $\text{NO}_3\text{-N}$. In addition, X -variables that were important for $p\text{CO}_2$ variations in some streams were unimportant in others. How much of the $p\text{CO}_2$ 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 $p\text{CO}_2$ variations in lakes and streams

Dividing the data material of 22664 samples into four seasons, i.e. a winter season where some samples have been taken below an ice cover (January to March), a spring season where spring floods occur and the waters usually are highly turbulent (April, May), a summer season (June to September), and an autumn season where waters are turbulent again (October to December) we found highest $p\text{CO}_2$ values during the winter season, both in lakes and in streams. During winter time $p\text{CO}_2$ values were significantly higher in lakes than in streams (non-parametric Wilcoxon-test: $P < 0.0001$). During spring time $p\text{CO}_2$ showed lower values and there was no longer a significant difference in $p\text{CO}_2$ between lakes and streams (non-parametric Wilcoxon-test: $P > 0.05$). Lowest $p\text{CO}_2$ values were reached during summer in both lakes and streams but lakes had significantly lower $p\text{CO}_2$ values than streams (non-parametric Wilcoxon-test: $P < 0.0001$). Towards autumn $p\text{CO}_2$ increased again in both lakes

and streams with significantly higher $p\text{CO}_2$ in streams than in lakes (non-parametric Wilcoxon-test: $P < 0.0001$).

We received the same results when we used $p\text{CO}_2$ values from surface waters of our 14 lakes and 14 streams from which we had monthly values from May to October during 1995 to 2010 available: high $p\text{CO}_2$ values and no significant difference in $p\text{CO}_2$ between lakes and streams in May (non-parametric Wilcoxon-test: $P > 0.05$), high $p\text{CO}_2$ values in both lakes and streams in September and October, and low $p\text{CO}_2$ 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 $p\text{CO}_2$ in surface waters of lakes followed a clear sine function with high $p\text{CO}_2$ in spring and autumn and low $p\text{CO}_2$ during summer (Fig. 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 (Fig. 3c), WT, pH, AbsF₄₂₀, AbsF₄₂₀/TOC, NO₃-N, TN and Chl a . In streams we also found seasonal variations for the same variables with the exception of AbsF₄₂₀ and AbsF₄₂₀/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 (Fig. 3d). August was also the month when Chl a concentrations in lakes were highest and NO₃-N concentrations lowest. In contrast, $p\text{CO}_2$ started to increase again in August (Fig. 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), NO₃-N (higher in streams), AbsF₄₂₀ (higher in streams), AbsF₄₂₀/TOC (higher in streams) and *p*CO₂ (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 *p*CO₂ in streams than in lakes according to equations used for *p*CO₂ calculations (eqs. 2-11). Variables that might explain our observed significantly lower surface water *p*CO₂ values in lakes than in streams during summer were Chl*a*, AbsF₄₂₀, AbsF₄₂₀/TOC, Alk and the WT difference between bottom and surface waters. According to our PLS-models and the fact that seasonal variations in Chl*a* and Alk did not correspond to seasonal *p*CO₂ variations we regard the variables WT difference, AbsF₄₂₀ and AbsF₄₂₀/TOC as the most important variables for *p*CO₂ temporal variations in lake surface waters. Taking the monthly median *p*CO₂ of Swedish lake surface waters and relating them to the monthly median of the WT differences in the Swedish lakes we observed a 40 µatm decrease in *p*CO₂ in surface waters per 1°C increase in the WT difference between surface and bottom waters (Fig. 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 (Fig. 4a). The difference between *p*CO₂ in the surface waters of the large Finnish lakes and the small, shallow Swedish lakes coincide well with pH differences between the two lake types (Fig. 4b).

Vertical *p*CO₂ variations

In the 14 Swedish lakes *p*CO₂ was during all months significantly higher in bottom waters than in surface waters (non-parametric Wilcoxon-test: $P < 0.001$ for May, June, July, August, September and $P < 0.05$ for October). Also in the Finnish lakes *p*CO₂ in bottom waters significantly exceeded the one in surface waters (non-parametric Wilcoxon-test: $P < 0.001$ for

May, June, July and August) except during the months September and October when it was similar in bottom and surface waters (non-parametric Wilcoxon-test: $P > 0.05$). The occasions where $p\text{CO}_2$ in surface waters exceeded the ones in bottom waters were very rare and negligible in size, and they occurred during the mixing period (Fig. 5). During all months, including the months when the water column was mixed, $p\text{CO}_2$ in bottom waters of the 14 Swedish lakes were significantly higher than $p\text{CO}_2$ in streams (non-parametric Wilcoxon-test: $P < 0.001$). $p\text{CO}_2$ in bottom waters of lakes was significantly related to bottom water oxygen concentrations ($R^2 = 0.37$, $P < 0.0001$) but not to bottom water temperatures ($R^2 = 0.00$, $P > 0.05$).

DISCUSSION

Our results show clear similarities but also clear dissimilarities in $p\text{CO}_2$ variations between small and shallow boreal lakes with a short water retention time and boreal streams. Similarities, supporting our hypothesis, were found in spring when $p\text{CO}_2$ in lake and stream ecosystems demonstrated comparable variations. In addition, overall seasonal patterns with highest $p\text{CO}_2$ in spring and autumn and lowest $p\text{CO}_2$ during summer following water discharge patterns were comparable between boreal lakes and streams. The seasonal $p\text{CO}_2$ variations were, however, much more pronounced in the lakes than in the streams.

As outlined in the introduction seasonal $p\text{CO}_2$ variations in surface waters, in particular in lakes, are not completely understood yet and have earlier revealed contrasting patterns with either maximum (e.g. Jonsson and others 2007a) or minimum $p\text{CO}_2$ values during summer (e.g. Kelly and others 2001; Kortelainen and others 2006; Atilla and others 2011). Seasonal variations in $p\text{CO}_2$ 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 $p\text{CO}_2$ primarily be driven by hydrological conditions. Accordingly, we found highest water discharges and highest $p\text{CO}_2$ values during spring and lowest ones 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 $p\text{CO}_2$ towards summer. An antagonistic effect of water discharge and photo- and microbial transformation on $p\text{CO}_2$ during summer might give an explanation why water discharge decreased faster towards summer than $p\text{CO}_2$ in streams (Fig. 3).

Hydrological conditions and catchment processes are likely to have an important impact not only on $p\text{CO}_2$ in streams but also on $p\text{CO}_2$ in small and shallow boreal lake waters with a short water retention time, as also suggested by Humborg and others (2009). Accordingly, we found high $p\text{CO}_2$ values in lake waters at high water discharges in spring and low $p\text{CO}_2$ values at low water discharges in summer (Fig. 3). The strong hydrological influence was probably the reason why we found comparable $p\text{CO}_2$ variations in lakes and streams during spring. We suggest that also autumn $p\text{CO}_2$ variations in lakes are mainly influenced by water discharge patterns, since we found TOC, which in Swedish waters is highly influenced by water discharge (Erlandsson and others 2008), being the most important variable for $p\text{CO}_2$ variations in lakes in autumn.

During summer, however, $p\text{CO}_2$ in streams and lakes seems to be affected by different processes, indicated by significantly lower $p\text{CO}_2$ values in surface waters of lakes than in streams. Most obvious differences between lakes and streams during summer are influences of thermal stratification and photosynthesis. Photosynthesis is expected to result in decreasing $p\text{CO}_2$ during day-time. We do not have data on photosynthesis in our lakes but based on

measurements on boreal lakes in general (e.g. Jonsson and others 2001, Einola and others 2011) and the fact that Chl*a* concentrations that can be regarded as a measure of photosynthesis was only important for $p\text{CO}_2$ variations in 5 out of 14 lakes in our PLS-models we assume that photosynthesis is only a minor process influencing $p\text{CO}_2$ in our heterotrophic boreal lakes. This statement is further strengthened by analyses of the seasonal development of $p\text{CO}_2$ and Chl*a* which show that these two variables are out of phase with highest Chl*a* concentrations in August and lowest $p\text{CO}_2$ values in July, resulting in a rather positive than negative relationship between Chl*a* and $p\text{CO}_2$ (Fig. 2).

The influence of thermal stratification on $p\text{CO}_2$ in lake surface waters was, however, clearly detectable, albeit our lakes were 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 a thermocline. Assuming that large parts of CO_2 are produced in the sediments or enter 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 relationship between $p\text{CO}_2$ 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). Since we also found a clear relationship between O_2 concentrations and bottom water $p\text{CO}_2$ we suggest that thermal stratification plays a decisive role for $p\text{CO}_2$ seasonal variation in lakes in addition to hydrological processes that in our case co-varied with the intensity of thermal stratification. We observed strongest thermal stratification and one of the lowest water discharges in July

(Fig. 3). Accordingly $p\text{CO}_2$ in lake surface waters reached its minimum in July (Fig. 3a). A strong relationship between intensity of thermal stratification and $p\text{CO}_2$ in the epilimnion was found both in Swedish and Finnish lakes but Finnish lakes had constantly lower $p\text{CO}_2$. The difference in $p\text{CO}_2$ between Swedish and Finnish lakes was reflected in pH differences (Fig. 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 $p\text{CO}_2$. It is, however, also possible that primary production is higher in the large lakes, resulting in a higher CO_2 consumption with consequent low $p\text{CO}_2$. In that case low $p\text{CO}_2$ would result in high pH. Independently on what the driver and the response is we found consistently higher $p\text{CO}_2$ values in the small Swedish lakes compared to the large Finnish lakes along the WT gradient (Fig. 4a). Further studies on the relative importance of processes determining $p\text{CO}_2$ in small and in large lakes are needed in order to fully understand $p\text{CO}_2$ variations over large scales.

Once WT differences between surface and bottom waters become negligible towards autumn and the water column starts to mix $p\text{CO}_2$ in surface waters of lakes reaches values that are close to the ones found in streams (Fig. 3a and 3b). 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 $p\text{CO}_2$ values, however, are observed below ice cover, as seen in this study and earlier reported by Kortelainen and others (2006). In 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 $p\text{CO}_2$ in bottom waters of lakes that exceeds $p\text{CO}_2$ in streams can be 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.

Although CO_2 in our small and shallow lakes might primarily be produced already in the catchment or in the sediments we have indications for epilimnetic CO_2 production since we found decreasing $\text{AbsF}_{420}/\text{TOC}$ ratios in surface water of lakes towards summer. Decreasing $\text{AbsF}_{420}/\text{TOC}$ ratios correspond to a preferential degradation of coloured 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 $\text{AbsF}_{420}/\text{TOC}$ 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 $p\text{CO}_2$ variations in boreal lakes and streams follow water discharge patterns, but that lakes during summer are additionally strongly affected by WT differences between surface and bottom waters, causing pronounced differences in $p\text{CO}_2$ variations between lakes and streams and also between lake surface and bottom waters during summer (Fig. 6). According to our results $p\text{CO}_2$ reaches minimum values in surface waters during summer. If such minimum $p\text{CO}_2$ values are the basis for annual flux estimates on a global scale, CO_2 fluxes from inland waters into the atmosphere will probably slightly be underestimated. More research on seasonal and also on daily $p\text{CO}_2$ variations is needed to decrease uncertainties in global estimates.

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Table 1. Physical and water chemical characteristics of 14 boreal lakes (row 1-14) and 14 streams (row 15 to 29). 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.

Site	Median	CV	Median	CV	Median	CV	Median	CV	Median	CV	Median	CV
	WT (°C)	WT (%)	Alk (mekv L ⁻¹)	Alk (%)	pH	pH (%)	TN (µg L ⁻¹)	TN (%)	TP (µg L ⁻¹)	TP (%)	DOC (mg L ⁻¹)	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
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Figure legends

Fig. 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.

Fig. 2. Monthly data on water temperature differences (WT difference) between surface and bottom waters (panel a), carbon dioxide supersaturation ($p\text{CO}_2$; panel b), and chlorophyll *a* concentrations (panel c) in Stensjön from 1995 to 2010. Panels d and e show the relations between $p\text{CO}_2$ 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 $p\text{CO}_2$ temporal variations.

Fig. 3. Quantile plots of monthly values on carbon dioxide supersaturation ($p\text{CO}_2$) in surface waters of 14 Swedish boreal lakes (panel a) and 14 Swedish boreal streams (panel b), on water temperature differences between bottom and surface waters (WT difference) in the same 14 Swedish boreal lakes from panel a (panel c) and on monthly mean water discharges from 176 stream/river sites (panel d). All data are based on complete time series from 1995 to 2010. $p\text{CO}_2$ and water difference in the lakes show similar clear seasonal variations.

Fig. 4. Monthly median values of available water temperature differences (WT difference) between bottom and surface waters (panel a) and monthly median values of pH (panel b) in relation to available monthly median values of carbon dioxide supersaturation ($p\text{CO}_2$) 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: $y = -40x + 1258$ ($R^2 = 0.90$, $P < 0.01$, $n = 6$), and for the Finnish lakes: $y = -34x + 769$ ($R^2 = 0.64$, $P < 0.05$, $n = 8$).

Fig. 5. Relationships between surface water carbon dioxide supersaturation ($p\text{CO}_2$) and bottom water $p\text{CO}_2$ in Swedish (panels a and b) and Finnish (panels c and 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.

Fig. 6. Probability density functions of carbon dioxide supersaturation ($p\text{CO}_2$) in lake surface waters (dark grey), lake bottom waters (light grey) and stream surface waters during the water column mixing period in October (panel a) and during summer stratification in July (panel b). The figure is based upon monthly data from 14 boreal lakes and 14 boreal streams during 1995 to 2010.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6