RESEARCH ARTICLE

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Key Points:

- Large spatial variability in lake $p\text{CO}_{2\text{aq}}$ observed especially during the thermally stratified period
- Variability in $p\text{CO}_{2\text{aq}}$ influenced CO_2 flux more than k both spatially and temporally
- Measurements from ≥ 8 days scattered throughout the year at ≥ 5 points were required for representative fluxes

Supporting Information:

- Supporting Information S1

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Spatiotemporal variability of lake $p\text{CO}_2$ and CO_2 fluxes in a hemiboreal catchment

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Abstract Globally, lakes are frequently supersaturated with carbon dioxide (CO_2) and are major emitters of carbon to the atmosphere. Recent studies have generated awareness of the high variability in $p\text{CO}_{2\text{aq}}$ (the partial pressure corresponding to the concentration in water) and CO_2 fluxes to the atmosphere and the need for better accounting for this variability. However, studies simultaneously accounting for both spatial and temporal variability of $p\text{CO}_{2\text{aq}}$ and CO_2 fluxes in lakes are rare. We measured $p\text{CO}_{2\text{aq}}$ (by both manual sampling and mini loggers) and CO_2 fluxes, covering spatial variability in open water areas of three lakes of different character in a Swedish catchment for 2 years. Spatial $p\text{CO}_{2\text{aq}}$ variability within lakes was linked to distance from shore, proximity to stream inlets, and deepwater upwelling events. Temporally, $p\text{CO}_{2\text{aq}}$ variability was linked with variability in dissolved organic carbon, total nitrogen, and dissolved oxygen. While previous studies over short time periods (1 to 6 h) observed gas transfer velocity (k) to be more variable than $p\text{CO}_{2\text{aq}}$, our work shows that over longer time (days to weeks) $p\text{CO}_{2\text{aq}}$ variability was greater and affected CO_2 fluxes much more than k . We demonstrate that ≥ 8 measurement days distributed over multiple seasons in combination with sufficient spatial coverage (≥ 8 locations during stratification periods and 5 or less in spring and autumn) are a key for representative yearly whole lake flux estimates. This study illustrates the importance of considering spatiotemporal variability in $p\text{CO}_{2\text{aq}}$ and CO_2 fluxes to generate representative whole lake estimates.

1. Introduction

Inland waters such as lakes, rivers, and reservoirs actively process terrestrial carbon, and they are frequently supersaturated with CO_2 [Cole et al., 1994; Cole et al., 2007]. They are important sources of CO_2 to the global carbon budget [Aufdenkampe et al., 2011], and it was recently estimated that global inland waters emit 2.1 Pg C yr^{-1} in the form of CO_2 [Raymond et al., 2013]. Lakes are frequently net heterotrophic (respiration exceeds primary production), and the excess CO_2 is derived from the catchment through respiration of organic carbon in the water and as CO_2 from soil respiration [Battin et al., 2008; Cole et al., 1994; Duarte and Prairie, 2005].

The present knowledge about lake CO_2 emissions is largely based on estimates of gas transfer velocity (piston velocity, k) from, e.g., wind speed [Cole and Caraco, 1998; Crusius and Wanninkhof, 2003; Wanninkhof, 1992] along with measurements of surface water CO_2 concentrations (commonly expressed as the partial pressure in equilibrium with the surface water concentration, $p\text{CO}_{2\text{aq}}$) according to

$$F = k \times K_h (p\text{CO}_{2\text{aq}} - p\text{CO}_{2\text{atm}}) \quad (1)$$

where F is the flux ($\text{mmol m}^{-2} \text{ d}^{-1}$), k is the gas transfer velocity (m d^{-1}), K_h is the temperature-dependent Henry's constant (M atm^{-1}), and $p\text{CO}_{2\text{atm}}$ is the partial pressure of CO_2 in the atmosphere (μatm). Such measurements are typically only made a few times and at a few locations per studied system. In addition, $p\text{CO}_{2\text{aq}}$ is often estimated indirectly from measurements of alkalinity and pH, and issues with this approach have recently been highlighted as it can overestimate $p\text{CO}_{2\text{aq}}$ in waters rich in dissolved organic matter, being acidic or having low alkalinity [Abril et al., 2015]. Hence, the lack of direct measurements covering spatiotemporal variability makes it unclear how representative our current knowledge on lake CO_2 flux is.

Spatial variability in $p\text{CO}_{2\text{aq}}$ and CO_2 fluxes are now increasingly addressed, e.g., in tropical and boreal reservoirs [Pacheco et al., 2015; Roland et al., 2010; Teodoru et al., 2011] and Amazon floodplain lakes [Rudorff et al., 2011], and have been linked to river inputs, littoral zones, and photosynthesis. The variability of k with fetch or

distance to shore has been highlighted, and it has been found to affect CO_2 fluxes [Schilder et al., 2013; Vachon and Prairie, 2013]. However, the relative importance of k and $\text{pCO}_{2\text{aq}}$ in regulating CO_2 flux estimates on short (hours to days) and long (weeks to months) time scales is not known so far.

Multiple sources of temporal variability have been identified regarding CO_2 fluxes in lakes. It has been shown that rain events can increase CO_2 fluxes in lakes by enhancing respiration rates of new organic matter flushed to the lake and by direct CO_2 inputs through runoff [Ojala et al., 2011; Rantakari and Kortelainen, 2005; Vachon and del Giorgio, 2014]. Peaks in CO_2 fluxes have been observed during spring when the CO_2 accumulated under ice cover is released upon ice melt [Ducharme-Riel et al., 2015; Karlsson et al., 2013; López Bellido et al., 2009; Striegl and Michmerhuizen, 1998]. Lake mixing in autumn brings CO_2 -rich bottom water to the surface [Kelly et al., 2001; Ojala et al., 2011; Weyhenmeyer et al., 2012]. Some studies have also observed diel differences in $\text{pCO}_{2\text{aq}}$ due to the well-known balance between photosynthesis and respiration in lakes [Huotari et al., 2009; Sellers et al., 1995] or due to convective nighttime mixing bringing up deeper CO_2 -rich water in response to day-night differences in air temperature [Åberg et al., 2010; Eugster et al., 2003]. Other mechanisms through which CO_2 -rich bottom water reaches the surface include upwelling by internal seiches causing thermocline tilt induced by e.g., wind events [e.g., MacIntyre and Melack, 2009; Mortimer, 1952; Shintani et al., 2010] or thermocline erosion downward [Åberg et al., 2010; Jennings et al., 2012].

Altogether, the magnitude of spatial variability in $\text{pCO}_{2\text{aq}}$ and CO_2 fluxes, both within systems and between nearby systems in the same catchment, is poorly understood so far, and there is a lack of integrated analysis of both spatial and temporal variabilities. Accurate scaling to whole-lake fluxes requires representative data in which variability in space and time is appropriately accounted for in the measurements. Further, in order to account for the spatiotemporal variability in scaling and modeling, its extent, patterns, and interactions in space and time, have to be known and understood. As few studies have assessed the variability and the key drivers for $\text{pCO}_{2\text{aq}}$ and CO_2 fluxes from lakes integrating spatiotemporal variability, there is a great risk that present assessments are biased. For example, previous intensive $\text{pCO}_{2\text{aq}}$ measurements were typically designed to either cover large space under a short time (gas equilibrator screening or manual samples in several points [e.g., Borges et al., 2014; Pacheco et al., 2015; Roland et al., 2010]) or long time in specific locations (sensors collecting data or calculated $\text{pCO}_{2\text{aq}}$ from one or a few points over time [e.g., Åberg et al., 2010; Huotari et al., 2009; Pacheco et al., 2015]). Therefore, studies including both spatial and temporal variabilities are needed to better understand variability and to develop representative approaches for large-scale assessments of lake CO_2 fluxes.

To improve the understanding of spatiotemporal variability in small-lake CO_2 dynamics, and their implications for effectively upscaling lake fluxes to regional scales, we measured $\text{pCO}_{2\text{aq}}$ and CO_2 fluxes in the open water areas of three lakes in a catchment. The lakes included one whole lake, the open water parts of a downstream late successional lake (turning into a wetland), and the stream delta zone in the downstream catchment recipient lake. Measurements were made during ice-free periods of 2012 and 2013. Key questions addressed in this study were as follows:

1. How large was the spatiotemporal variability in $\text{pCO}_{2\text{aq}}$ and CO_2 flux?
2. What is the relative importance of $\text{pCO}_{2\text{aq}}$ and k for the variability in CO_2 flux?
3. How many chamber measurements in space and time were needed to representatively cover the observed spatiotemporal variability in CO_2 flux?

We also discuss potential explanations for the variability patterns observed.

2. Materials and Methods

2.1. Study Lakes

The lakes studied were Erssjön (58°22'16"N, 12°9'41"E), Följesjön (58°22'31"N, 12°9'13"E), and Skottenesjön (58°21'16"N, 12°7'53"E) located in the Skogaryd Research Catchment (SRC) in the Southwest of Sweden (Figure 1). SRC is a part of the "Swedish Infrastructure for Terrestrial Ecosystem Science" (SITES, www.field-sites.se). The mainstream in the catchment originates in a mire close to Erssjön and flows through Erssjön and Följesjön before draining into Skottenesjön (Figure 1). Erssjön is an ~62,000 m² lake with maximum depth fluctuating between 4.5 and 5 m in response to water level changes. Most of the lake was free of macrophytes. *Nuphar lutea* (L.) Sm., *Equisetum fluviatile* L., *Phragmites australis* (Cav.) Trin. ex Steud., and

Figure 1. The locations of the study lakes in the Skogaryd Research Catchment and of the floating chambers. The closed circles represent chambers where $p\text{CO}_{2\text{aq}}$ were sampled manually, and the open circles represent locations of the three chambers where CO_2 fluxes were monitored by using sensors. The cross hairs indicate positions where DIC profiles and O_2 measurements were made, the open triangles indicate the location of discharge monitoring stations, and the arrows denote the direction of streamflow in the catchment.

Carex spp. colonized the shores in low densities. Följesjön is a smaller, wind sheltered, late successional lake with an area of 37,500 m^2 . Most parts of the lake were covered with *Phragmites australis* and multiple *Carex* species (vegetated parts not included in this study). The measurements were made in the shallow open water areas (depths of 0.3–0.6 m) in the southern end—these open water areas being more representative of open water parts of wetlands than of deeper lakes. *Nuphar lutea* was present in parts of these areas, and this part of the lake was accessed by using a board walk constructed in 2011. Skottenesjön is a large 721,800 m^2 lake, and measurements were made in the western end of the lake in the delta area where the stream outlet from the Skogaryd Research Catchment entered the lake (Figure 1). This delta area was included as an attempt to study open waters of relevance for a full catchment under the assumption that the carbon emitted here, to a large extent, is derived from the upstream catchment. Because of the net flow of water from the studied area to the rest of the lake, and because Skottenesjön was too shallow (2.5 m) to have a large hypolimnion and extensive upwelling events, it is unlikely that CO_2 from other parts of the lake could reach the studied area. This part of the lake was moderately wind sheltered, with *Nuphar lutea* and *Nymphaea alba* L. along the shores and had a maximum depth of 1.2 m. The choice of study areas provided the opportunity to compare different types of nearby open water environments that were hydrologically connected. Erssjön, Följesjön, and Skottenesjön had open water areas of 90%, 30%, and 95%, respectively (for Skottenesjön this value represented the studied delta region only).

2.2. Measurements of $p\text{CO}_{2\text{aq}}$

$p\text{CO}_{2\text{aq}}$ was measured both by manual sampling and by using CO_2 sensors (described below). The manual approach was based on plastic floating chambers deployed on the lakes and allowed to equilibrate the headspace CO_2 with the water for 24 h and subsequently being sampled manually (hereafter denoted as manual $p\text{CO}_{2\text{aq}}$ measurements [Bastviken et al., 2015; Panneer Selvam et al., 2014]). Chambers with an area of 0.08 m^2 and a volume of 7.5 L were used, and they were fitted with Styrofoam floats on their sides. They were covered with aluminum tape to minimize internal heating by sunlight. A piece of Styrofoam float was attached to the chamber with a 1 m line and plastic covered weights (sand filled plastic centrifugation tubes) serving as anchors were attached to this float with a longer line. This horizontal mooring of the chambers to the float

allowed chambers to move up and down with the waves. This type of chambers has been used frequently and was also shown not to bias the gas exchange measurements notably [Cole *et al.*, 2010; Gålfalk *et al.*, 2013; Lorke *et al.*, 2015]. As shown separately [see Bastviken *et al.*, 2015], 24 h was more than enough to reach equilibrium between the chamber headspace and the water, and the chamber headspace CO₂ levels were used to calculate pCO_{2aq}. As discussed in detail previously there may be a delayed response in pCO_{2aq} measured by the equilibrated chambers [Bastviken *et al.*, 2015]. It was found that the delay in capturing the real pCO_{2aq} by the chambers depended on the k . If the wind speeds were above 6 m s⁻¹, the response was within 1 h, whereas at lower wind speeds, the delay was 1 to 3 h. The maximum delay of 3 h was observed when the wind speeds were <1 m s⁻¹. The delay smoothened out some of the short-term temporal variability (over minutes-hours), and hence, diel pCO_{2aq} variability obtained from the equilibrated chambers can be seen as conservative.

Gas samples were collected from each chamber through a 25 cm long PVC tubing (inner and outer diameter of 3 and 5 mm, respectively) with an attached three-way luer-lock valve (Becton-Dickinson, USA). The samples were collected by using three 60 mL plastic syringes (Becton-Dickinson, USA) equipped with three-way valves for easy connection to the tube on the chamber. The gas inside the chamber was mixed by pumping 3 times with the first syringe before collecting 180 mL of gas (3 × 60 mL). This gas was then used to flush 20 mL vials (Agilent Technologies, USA) capped with natural pink rubber stoppers (Wheaton Industries Inc., USA) and Al caps (ApodanNordic, Denmark) by using an inflow needle and an outflow needle for the excess pressure to escape. Flushing with >7 vial volumes ensured that the gas in the vial corresponded to the gas in the chambers. After flushing with almost all the sample gas, the outflow needle was removed and 5 mL extra gas was added to ensure overpressure in the vial. The vials were prefilled with 0.7 mL of saturated NaCl solution prior to sampling, and they were kept upside down during storage, making the NaCl solution a gas barrier in addition to the stopper, to prevent any gas leakage. The sample integrity was confirmed when the overpressure in the vials was released prior to analysis (see below).

In Erssjön, the chambers were deployed in four depth categories (<0.5, 0.5–1, 1–2, and >2 m) along each of the five transects from the shore (Figure 1). Two chambers were also put in the center of the lake where the depth was >3.5 m. Hence, a total of 22 chambers were used in Erssjön. In Skottenesjön, 9–12 chambers were distributed in three depth categories (<0.5, 0.5–1, and 1–2 m) along three different transects in the delta area where a stream from the catchment flows into the lake (Figure 1). In Följesjön, 10 chambers were deployed along the boardwalk (Figure 1). Due to its shallow nature and fragmented macrophyte cover, no depth category separations could be made and no spatial analysis was done in Följesjön. Samples were collected from the chambers every 2 weeks between April and November in 2013. A total of 588 manual pCO_{2aq} measurements were made in the three lakes.

The pCO_{2aq} was also measured continuously by using chambers fitted with small inexpensive CO₂ sensors described in detail by Bastviken *et al.* [2015] (hereafter denoted as sensor pCO_{2aq}), by allowing them to measure for extended periods of time (after the CO₂ concentration in the chamber has reached equilibrium with the water concentration) with a logging interval of 1 h. The CO₂ sensors (CO₂ Engine® ELG, SenseAir AB, Sweden; measuring the range of 0–10,000 or in a few modified units of 0–15,000 ppm), driven by 9 V batteries, were used to log the CO₂ concentrations inside the chamber. The sensors were calibrated in N₂ (0 ppm CO₂) according to the manufacturer's guidelines (see Bastviken *et al.* [2015] for a detailed description of the sensors and installation in the chambers).

Five to 12 and two to four chambers with sensors were deployed on the surface of Erssjön, and along the boardwalk in Följesjön, respectively, in 2012 and 2013. In Skottenesjön, two to three chambers with sensors were deployed close to the delta area in 2013. The chambers were lifted up for maintenance and for changing batteries every 2–4 weeks. As explained previously in Bastviken *et al.* [2015], this maintenance interval was generally too long resulting in irregular data gaps in the later parts of the deployment periods (see Bastviken *et al.* [2015] for performance and uncertainty analysis of the sensors). Hence, the results from the periods without gaps were used to analyze temporal patterns, while spatial analyses were not made with sensor pCO_{2aq} data. The data from the sensors were filtered to remove data influenced by condensation by removing values which were greater than 10% of the median pCO_{2aq} 2 h before and after the measurements, similar to Bastviken *et al.* [2015]. When computing the time series of hourly mean pCO_{2aq} from all the chambers, an additional filter was applied to remove hourly means whose standard deviations were greater than

500 μatm (the standard deviation of mean $\text{pCO}_{2\text{aq}}$ from all the chambers on each manual $\text{pCO}_{2\text{aq}}$ measurement occasion was mostly below 500 μatm and hence chosen as a cutoff value), to minimize bias from outlier $\text{pCO}_{2\text{aq}}$ values.

In both methods (manual $\text{pCO}_{2\text{aq}}$ and sensor $\text{pCO}_{2\text{aq}}$), the $\text{pCO}_{2\text{aq}}$ (μatm) in the chamber after equilibration was proportional to the water concentration according to Henry's law and was calculated as

$$\text{pCO}_2 = P_{\text{total}} \times \frac{\text{ppm}_{\text{chamber}}}{10^6} \quad (2)$$

where P_{total} is the air pressure (μatm) and $\text{ppm}_{\text{chamber}}$ is the mixing ratio of CO_2 inside the chamber head-space measured by the sensor or in the manual samples (ppm).

2.3. Measurement of CO_2 Fluxes

2.3.1. Direct Measurements Using Chambers

CO_2 fluxes were measured by using floating chambers similar to those described above but slightly smaller (area 0.069 m^2 and volume 6.3 L) equipped with the CO_2 sensors. For the flux measurements, the sensors were programmed to log concentrations every 5 min for 30 min. Three of these chambers with sensors set for flux measurements were deployed in each lake, and they were positioned in each of three depth zones (0.5, 2.5, and 4 m in Erssjön and 0.5, 1, and 1.2 m in Skottenesjön; Figure 1). In Följesjön, three chambers were placed along the boardwalk. The rate of change in concentration, obtained by using a linear regression, was converted to moles using the ideal gas law and divided by area and time to obtain fluxes. Measurements where the R^2 values in the linear regression were less than 0.9 were discarded (<2% of the data removed). CO_2 fluxes were measured every 2 weeks from June to October in 2012 and from April to November in 2013. During every visit, fluxes were measured on two consecutive days. A total of 326 flux measurements were made in the three lakes.

2.3.2. CO_2 Fluxes From Modeled k

To analyze the spatial and temporal variabilities in CO_2 fluxes, we estimated CO_2 fluxes for the 22 chamber locations in Erssjön (where detailed whole lake $\text{pCO}_{2\text{aq}}$ measurements were made), using manual $\text{pCO}_{2\text{aq}}$ and k for each location. The k for each flux measurement in 2013 was estimated from the measured fluxes and manual $\text{pCO}_{2\text{aq}}$ measurements close to the flux chambers (surface water poured carefully into a 1025 mL bottle, shaken for 1 min with a 50 mL headspace and the headspace gas analyzed for CO_2 [Cole *et al.*, 1994]) according to equation (1). Taking advantage of the k determined near the CO_2 flux chambers and k for CH_4 measured by using a greater number of chambers in the lake from another study [see Natchimuthu *et al.*, 2016], location specific k for CO_2 was modeled. These k values were then used with the manual location specific $\text{pCO}_{2\text{aq}}$ to obtain CO_2 fluxes at the 22 locations of the lake.

2.4. Other Parameters

Weather data (air temperature, air pressure, wind speed, wind direction, and precipitation) were generally obtained from local weather stations situated between the lakes or close to the shore of Erssjön. In 2012, wind and precipitation data were obtained from mesoscale analysis by using the weather stations within 20 km by the Swedish Meteorological and Hydrological Institute, because of large gaps in weather data from the catchment. Cross calibration of data from different stations confirmed that all these data sources were comparable and could be used. Surface water temperature was measured with a thermometer (H-B Instrument Company, EASY-READ), and temperature profiles were made with a portable dissolved oxygen (O_2) probe (Hach, USA) with a range from 0 to 50 $^{\circ}\text{C}$ (accuracy $\pm 0.3^{\circ}\text{C}$). Mean and ranges of water chemistry variables in the three lakes are given in Table S1 in the supporting information.

In Erssjön, water samples for dissolved inorganic carbon (DIC) analysis were taken from the surface (6–10 cm depth) and every 0.35 m from the bottom 1.5 m of the water column at the center of the lake. DIC samples from the surface water (6–10 cm depth) in Följesjön and Skottenesjön were collected close to the board walk near the shore and close to the delta area, respectively. The concentration of DIC was determined by a head-space equilibration method [McAuliffe, 1971]. Forty milliliter of bubble free water was injected into 100 mL vials, preflushed with nitrogen and prefilled with 200 μL of H_3PO_4 . The vials were capped with 10 mm thick bromobutyl rubber stoppers and crimped with aluminum caps (ApodanNordic, Denmark) when prepared in the laboratory. Before injecting water into the vials, the excess pressure of nitrogen in the vials was released and equilibrated to the atmospheric pressure. Because the pH of the water was reduced to <2 in

the vials, all the DIC was converted to CO_2 , which partitioned into gaseous and dissolved phases according to Henry's law. The number of moles of CO_2 in the gas phase was determined by headspace gas analysis and the ideal gas law. The number of moles in the liquid phase was calculated by using Henry's law adjusted for temperature [Weiss, 1974]. The total number of moles in the two phases was divided by the water volume to get the concentration of DIC in water.

On 12 March 2013, samples of DIC, water temperature, and $\text{pCO}_{2\text{aq}}$ were collected under ice cover. Water samples were collected from the above-mentioned positions from different depths (0.2, 1, 2, and 3 m in Erssjön; 0.2 m in Följesjön; and 0.2 and 0.6 m in Skottenesjön; the lakes were covered with ~30 cm of ice) by using a Ruttner sampler. For $\text{pCO}_{2\text{aq}}$, the sampled water was transferred carefully into a 1025 mL bottle. After creating a 50 mL air headspace, the bottle was shaken for 1 min and the headspace gas was analyzed for $\text{pCO}_{2\text{aq}}$.

2.5. Gas Analysis

The gas samples were analyzed for CO_2 by using a gas chromatograph (Agilent Technologies, USA, 7890A with a $1.8\text{ m} \times 3.175\text{ mm}$ Porapak Q 80/100 column from Supelco, a methanizer converting CO_2 to methane, and a flame ionization detector) either by manual injection or automatically with a 7697A headspace sampler (Agilent Technologies, USA) attached to the 7890A. Triplicates or replicates of serially diluted certified high concentration standard ($50,000 \pm 1000\text{ ppm}$), and an independent certified standard of $1985 \pm 40\text{ ppm}$ were used for calibration.

2.6. Data Analysis

The below sections describe the different analyses done on the $\text{pCO}_{2\text{aq}}$ and CO_2 fluxes to answer our research questions. Figure S1 in the supporting information gives an overview of the data, averaging, and methods used (spatial and temporal).

2.6.1. Spatial Analysis of $\text{pCO}_{2\text{aq}}$

For analysis of spatial patterns within the lakes, manual $\text{pCO}_{2\text{aq}}$ measurements were normalized to remove temporal variability from the data (by dividing each value with the mean value of the sampling day yielding relative spatial values) and analyzed for within lake differences by using the depth zone categories (in Erssjön and Skottenesjön only). An additional grouping in Erssjön, with measurements from transects close to the inlets in one category (chambers within 80 m from the inlets; see Figure 1) and all other measurements in another, was created to analyze the influence of stream inlets on $\text{pCO}_{2\text{aq}}$. Univariate general linear models (GLM) with Tukey's post-hoc test were used to compare differences among groups.

The $\text{pCO}_{2\text{aq}}$ data from the manual measurements in Erssjön were interpolated for mapping by Inverse Distance Weighted method (IDW). IDW utilizes the available measured data from surrounding locations to predict values for locations with no data, assuming that the predicted values are more similar to the measurements nearest to it than the ones further away [Environmental Systems Research Institute (ESRI), 2001].

2.6.2. Temporal Patterns of $\text{pCO}_{2\text{aq}}$

Stepwise multiple linear regressions of hourly sensor $\text{pCO}_{2\text{aq}}$ were performed with weather variables (mean air temperature, air pressure, precipitation, wind speed, and solar radiation) and discharge measurements (from the nearest monitoring station) during the time of measurement as predictors to check for factors affecting temporal patterns. To explore if weekly and seasonal temporal patterns could be linked to environmental variables, stepwise multiple linear regressions of mean $\text{pCO}_{2\text{aq}}$ of each measurement occasion from the manual $\text{pCO}_{2\text{aq}}$ measurements were made with weather variables, discharge measurements, and water chemistry variables (such as total P, total N, and dissolved organic carbon (DOC)) on the day of sampling as predictors. Residuals in all regression analysis were checked for normal distribution and randomness of errors, and the variables in some cases were $\log_{10}$ transformed to meet these criteria.

For diel analysis, hourly relative $\text{pCO}_{2\text{aq}}$ (sensor $\text{pCO}_{2\text{aq}}$ divided by the daily mean for each day) was divided into 4 h intervals (00:00–03:00, 04:00–07:00, 08:00–11:00, 12:00–15:00, 16:00–19:00, and 20:00–23:00) and a GLM of the relative $\text{pCO}_{2\text{aq}}$ with time categories and months as factors was analyzed.

2.6.3. Spatial and Temporal Analyses of CO_2 Fluxes in All Lakes

For spatial analysis, CO_2 fluxes were normalized to remove temporal variability from the data (relative spatial values) and analyzed for within-lake differences by using the depth zone categories (in Erssjön and

Skottenesjön only). GLM with Tukey's post-hoc test were used to compare differences among groups. For temporal trends and relationships with environmental variables, stepwise multiple linear regressions of biweekly mean CO₂ fluxes with weather variables, discharge measurements, and water chemistry variables from the day of sampling were performed. The CO₂ fluxes from the lakes were log₁₀ transformed for regression analysis if the residuals were nonnormal and if the errors were not random.

2.6.4. Relative Importance of pCO_{2aq} and *k* to CO₂ Fluxes

To analyze if *k* or pCO_{2aq} was more important for spatial variability in CO₂ fluxes, the manual pCO_{2aq}, modeled *k*, and the modeled CO₂ fluxes from Erssjön were normalized to obtain the relative spatial values (see above). To analyze the extent to which temporal variability in *k* or pCO_{2aq} influenced CO₂ fluxes, each value was instead divided by the mean value from that specific location (all sampling times considered) to remove spatial variability (relative temporal values). To analyze the strength of the relationships, stepwise multiple linear regressions of the relative spatial and relative temporal fluxes with relative values of pCO_{2aq} and *k* were made.

2.6.5. Representative Measurements of CO₂ Flux

The ability of various sampling efforts to generate representative whole-lake or annual mean CO₂ fluxes was studied by creating subsets of our measured data with an incremental number of chambers and sampling days, using a method similar to that of Wik *et al.* [2016]. The modeled CO₂ fluxes from *k* and manual pCO_{2aq} in Erssjön were used for this analysis. The data in spatial and temporal analyses were normalized to remove temporal variability (relative spatial fluxes) and spatial variability (relative temporal fluxes) from the analysis as described above. For spatial variability, the relative spatial fluxes were organized into several bins, each representing different scenarios based on an increasing number of chambers, and the mean flux was plotted against the number of chambers for each scenario [see Wik *et al.*, 2016]. As it was found that the spatial variability in pCO_{2aq} was higher during the stratified period, spatial analysis was made separately for each measurement occasion to find the number of chambers required in a worst-case scenario to generate representative fluxes. The first bin consisted of flux from each separate chamber, representing all possible single chamber fluxes. Bins 2, 3, 4, up to *n* consisted of means of each 100 random combinations of two, three, and four chambers up to *n* (where *n* = 21), in order to analyze the change in variability with the increase in the number of chambers. The number of chambers yielding 90% of the mean values within ±20% of the total spatial mean for all combinations was seen as representative for spatial variability. A similar analysis as above was done for temporal variability with the mean of relative temporal fluxes from each measurement occasion to check how many measurement days were needed to reproduce ±20% of the annual mean (*n* = 14). Increasing the number of random combinations of measurement locations or measurement days to more than 100 produced similar results in all cases. Additionally, to illustrate the bias when extrapolating fluxes at single locations or single days to the whole year, we compared our flux estimate from all chambers including all sampling times in Erssjön (using the modeled CO₂ fluxes from *k* and manual pCO_{2aq}) with (1) single time-single chamber measurements, (2) single time-multiple-chamber measurements, and (3) repeated-single chamber measurements to analyze the importance of representative CO₂ flux measurements.

All analyses were done in IBM SPSS Statistics 23 (IBM Corp., U.S.A) with a significance level of 0.05.

3. Results

3.1. Spatial Variability in pCO_{2aq} and CO₂ Fluxes

3.1.1. Between-Lake Variability

The mean pCO_{2aq} from the manual measurements were 1621 ± 561 μatm (mean ± 1 SD) (*n* = 321) in Erssjön, 7093 ± 2161 μatm (*n* = 130) in Följesjön, and 1345 ± 333 μatm (*n* = 137) in Skottenesjön (Figure 2; see Table 1 for ranges). The mean pCO_{2aq} measured by using the CO₂ sensors (covering longer time periods than the manual measurements) were 1629 ± 431 μatm (*n* = 3220) in Erssjön, 5697 ± 2517 μatm (*n* = 2424) in Följesjön, and 1422 ± 270 μatm (*n* = 1270) in Skottenesjön (Figure S2; see Table 1 for ranges). The overall median and mean from all lakes were 1571 and 2766 μatm for manual pCO_{2aq} and 1792 and 3017 μatm for sensor pCO_{2aq}, respectively. All CO₂ fluxes were positive (emission to the atmosphere), and no uptake of CO₂ was observed (Figure 2). The mean CO₂ fluxes measured were 46.8 ± 31.3 mmol m⁻² d⁻¹ (*n* = 129) in Erssjön, 64.9 ± 30.1 mmol m⁻² d⁻¹ (*n* = 108) in Följesjön, and 25.5 ± 13.5 mmol m⁻² d⁻¹ (*n* = 89) in Skottenesjön (Figure 2; see Table 1 for ranges). The overall median and mean CO₂ fluxes from all the three lakes were 40.5 and 47.0 mmol m⁻² d⁻¹, respectively.

Figure 2. CO₂ fluxes and manual pCO_{2aq} measurements using floating chambers in the three lakes. The CO₂ fluxes were measured during 2 years (2012 and 2013), whereas manual pCO_{2aq} was measured in 2013 only. Each box includes data from all spatial points, and the length of the boxes indicates the amount of spatial variability. The boxes show quartiles and the median, the whiskers denote data within 1.5 times of the interquartile range, and the black dots denote values outside the interquartile range. The *n* values in the panels denote the total number of observations in each lake.

The fluxes and pCO_{2aq} in the lakes were significantly different from each other (GLM, $p < 0.001$, $p < 0.001$), and Följesjön had the highest, followed by Erssjön and Skottenesjön (Figures 2 and 3). Mean flux and pCO_{2aq} in Följesjön were 1.4-fold and >2-fold higher, respectively, than the overall mean from all lakes.

3.1.2. Within-Lake Variability

The manual pCO_{2aq} measurements in Erssjön, which covered many parts of the lake, showed considerable variability over the lake (Figure 3). There was a significant interaction between depth and presence of inlet categories (GLM; $p < 0.001$), and the pCO_{2aq} was higher in the shallow depths only in the inlet zones, indicating strong influence of stream inlets on lake pCO_{2aq} (Figure 3). For example, measurements close to one major inlet in Erssjön had 1.4 to 2.0 times higher pCO_{2aq} than the rest of the lake in 9 out of 15 samplings.

A map of interpolated manual pCO_{2aq} using the IDW method [ESRI, 2001] illustrates the spatial variability in pCO_{2aq} over time at Erssjön (Figure 3). The sampling periods can be divided into three categories—early mixing periods (Figures 3a, 3l, and 3m), later part of mixing periods (B, N, and O in Figure 3), and stratified periods (C to K in Figure 3). During the early mixing periods, pCO_{2aq} was generally high (CO₂-rich bottom water was mixed with surface water), with slightly higher pCO_{2aq} in central parts although the coefficient of variation (CV; ratio of the standard deviation to the mean expressed in %) was small, ranging from 5 to 8%. Later part of mixing periods in spring and autumn represents periods without stratification when the excess bottom water CO₂ had been vented to the atmosphere. Such periods had more or less similar pCO_{2aq} all across the lake surface, except for higher pCO_{2aq} near the stream inlet. The CV during this period ranged from 9 to 14%. The CO₂ concentrations in Erssjön began to increase steadily in the metalimnion and hypolimnion after stratification (Figure S3). During the stratified periods between 14 May and 4 September, the CV of pCO_{2aq} at specific sampling occasions ranged from 4 to as high as 39%, corresponding to pCO_{2aq} ranges of 1250–1450 µatm to 1100–3200 µatm, respectively. Some of our observations during this period indicated that upwelling from oscillating internal waves is important for spatial variability in pCO_{2aq}, when we compared average wind direction during the 24 h deployment period of the chambers to the pCO_{2aq} patterns. Figures 3c–3e (high pCO_{2aq} near the inlet to some extent masked the pattern in Figures 3d and 3e) and Figure 3h show higher pCO_{2aq} levels near the upwind end of the lake. In two occasions when the wind blew from many different directions (Figures 3f and 3g), surface waters showed variable pCO_{2aq}. On 7 and 21 August (Figures 3i and 3j), although the wind direction appeared to be constant, no upwelling was observed,

Table 1. Examples of Reported Directly Measured $p\text{CO}_{2\text{aq}}$ and Measured/Calculated CO_2 Fluxes From Freshwaters

Location	$p\text{CO}_{2\text{aq}}$ (μatm) ^a			CO_2 flux ($\text{mmol m}^{-2} \text{d}^{-1}$)			References
	Mean	Min	Max	Mean	Min	Max	
Tropical and temperate freshwaters	3707	36	23047				<i>Abril et al.</i> [2015]
Water bodies in South India	2927	400	11467	51.9	−28.2	262.4 ^b	<i>Panneer Selvam et al.</i> [2014]
Boreal lakes, Canada	631	340	2400				<i>Roehm et al.</i> [2009]
33 lakes, Sweden	1762						<i>Sobek et al.</i> [2003]
112 lakes, Norway	774	351	2512				<i>Larsen et al.</i> [2011]
Spring fluxes in Lake Pääjärvi, Finland				71.8 ^b	6.5 ^b	138.3 ^b	<i>López Bellido et al.</i> [2009]
Lake Gäddejärvi, Sweden	1809	1423	2332	33.0 ^c	25.0 ^c	67.0 ^c	<i>Kokic et al.</i> [2015]
Headwater lakes, Lake Gäddejärvi's catchment	2673	689	6458	50.0 ^c	7.0 ^c	125.0 ^c	<i>Kokic et al.</i> [2015]
Lakes, reservoirs and ponds, Finland				0.4–45 ^b	−1.8 ^b	73.0 ^b	<i>Huttunen et al.</i> [2003]
75 lakes, Norway and Sweden	1100			20.5 ^c	−10.8 ^c	82.0 ^c	<i>Yang et al.</i> [2015]
Erssjön, SRC, Sweden	1621 (1629) ^d	714 (602) ^d	3242 (3393) ^d	46.8 (56.6) ^e	5.0 (12.1) ^e	168.7 (147.4) ^e	This study
Följesjön, SRC, Sweden	7093 (5697) ^d	3394 (926) ^d	12961 (12432) ^d	64.9	19.2	165.3	This study
Skottenesjön, SRC, Sweden	1345 (1422) ^d	840 (740) ^d	3199 (2242) ^d	25.5	4.5	61	This study

^aAll $p\text{CO}_{2\text{aq}}$ in the studies reported here were measured directly by using a headspace equilibration method.

^b CO_2 fluxes were measured directly by using a floating chamber method.

^c CO_2 fluxes were estimated by using directly measured $p\text{CO}_{2\text{aq}}$ and modeled k from wind speed relationships.

^dManual $p\text{CO}_{2\text{aq}}$; numbers in brackets denote sensor $p\text{CO}_{2\text{aq}}$ for comparison.

^eNumbers in brackets denote modeled CO_2 fluxes in Erssjön by using manual $p\text{CO}_{2\text{aq}}$ and estimated k for CO_2 from *Natchimuthu et al.* [2016] (see section 2).

possibly due to the coincidence of this period with the oscillating phase of the internal waves. Because of the episodic nature of upwelling, it is likely that some of the upwelling events were captured by our sampling and some were not. Nevertheless, the observed spatial variability (up to 3-fold during the study period, with $p\text{CO}_{2\text{aq}}$ ranging from 1100 to 3200 μatm) illustrates the dynamic changes in surface water $p\text{CO}_{2\text{aq}}$ in Erssjön with higher variability during the stratified periods (Figure 3).

Due to the limited spatial coverage in Följesjön and Skottenesjön, the full extent of spatial variability could not be explored there. In Skottenesjön, the shallow depth zone (<0.5 m) which was also close to the stream inlet had significantly higher $p\text{CO}_{2\text{aq}}$ than the other depth zones (GLM; $p < 0.001$). The $p\text{CO}_{2\text{aq}}$ during the growing season ranged as much as 1500 to 3200 μatm in Skottenesjön and 6300 to 9950 μatm in Följesjön. The variation was generally lower during the other seasons (on an average 1100–1400 μatm and 6000–7600 μatm in Skottenesjön and Följesjön, respectively).

In Erssjön and Skottenesjön, the mean fluxes were 12 and 15% lower in the shallow depths (0.5 m) when compared to the overall mean flux (GLM; $p = 0.001$ and $p < 0.001$, respectively; Figures 4a and 4b). The fluxes in the other depths (2.5 and 4 m in Erssjön and 1 and 1.2 m in Skottenesjön) were similar (GLM; $p = 0.99$ and 0.23, respectively; Figures 4a and 4b).

3.2. Temporal Variability in $p\text{CO}_{2\text{aq}}$ and CO_2 Fluxes

3.2.1. Temporal $p\text{CO}_{2\text{aq}}$ Patterns

Measurements during winter (March 2013) showed that Erssjön accumulated $p\text{CO}_{2\text{aq}}$ in the water during ice cover, and levels increased from 4056 μatm just under the ice to 6131 μatm close to the sediments. After the ice melt, the highest mean $p\text{CO}_{2\text{aq}}$ was observed in this lake during the early mixing in April 2013 in both manual and sensor $p\text{CO}_{2\text{aq}}$ measurements (Figures 2 and S2). The second highest level was noted during the lake mixing period in mid-September (Figures 2 and S2). Otherwise, the $p\text{CO}_{2\text{aq}}$ levels varied over time although the higher levels were more frequent during the summer (Figure 2). High $p\text{CO}_{2\text{aq}}$ under the ice was also observed in the other two lakes. In Följesjön, $p\text{CO}_{2\text{aq}}$ values of 11,658 and 9749 μatm were measured in two different locations in the lake. $p\text{CO}_{2\text{aq}}$ in the water column of Skottenesjön ranged from 2334 to 2466 μatm . In these lakes, measurements were started only in May, and thus, the early spring peaks of $p\text{CO}_{2\text{aq}}$ were not captured in our data. There was a clear seasonality in Följesjön with $p\text{CO}_{2\text{aq}}$ levels rising from 4500 μatm in May to around 10,000 μatm in mid-September followed by a rapid decrease back to May levels (Figures 2 and S2). In Skottenesjön, the levels were more variable (Figure 2). During the ice-free periods, the variability over time in $p\text{CO}_{2\text{aq}}$ was up to 4.5, 3.3, and

Figure 3. (a–o) $p\text{CO}_{2\text{aq}}$ from manual measurements in Erssjön during 2013, interpolated by the inverse distance weighted method. The colored scale denotes the date-specific $p\text{CO}_{2\text{aq}}$, and the inset map denotes scale in relation to $p\text{CO}_{2\text{aq}}$ for the whole year for the purposes of comparison. The arrows at the top of the panels and the numbers above them show the average wind direction and speed (m s^{-1}) during the 24 h deployment period, and the cross arrows denote changing winds. The curved arrows at the bottom of Figures 3a, 3l, and 3m denote mixing periods. See Figure 1 for the locations in which these measurements were made.

Figure 4. Variability in CO_2 fluxes in the three depths in (a) Erssjön and (b) Skottenesjön measured with the floating chambers fitted with CO_2 sensors. The letters above the boxes represent the post-hoc test after GLM, and different letters mean significant difference at 0.05 level. The relative spatial fluxes were calculated by dividing the fluxes with mean flux of the sampling day to remove temporal variability.

3-fold in Erssjön, Följesjön, and Skottenesjön (corresponding to 700–3200, 3750–12250, and 1100–3200 μatm), respectively.

3.2.2. $\text{pCO}_{2\text{aq}}$ and Environmental Variables

Variability in the hourly sensor $\text{pCO}_{2\text{aq}}$ from the three lakes (Figure S2) could not be explained by any of the measured environmental variables. Instead, the whole-lake mean $\text{pCO}_{2\text{aq}}$ values from the manual measurements weakly increased with DOC in Erssjön ($R^2 = 0.36$, $p = 0.031$), total nitrogen concentration in Följesjön ($R^2 = 0.35$, $p = 0.041$), and strongly decreased with surface water dissolved O_2 concentration in Skottenesjön ($R^2 = 0.73$, $p < 0.001$; see Table 2). Strong relationships were found with air temperature (positive relationship) and wind speeds (negative relationship) in Följesjön when they were integrated over longer time periods (i.e., 5 days before sampling or more). When 5 day average air temperatures and wind speeds were used, they together explained 69% of the $\text{pCO}_{2\text{aq}}$ variability in this lake ($p = 0.001$; Table 2). This was not observed in the other two lakes.

3.2.3. Diel Changes Measured by Sensor $\text{pCO}_{2\text{aq}}$

Our continuous sensor data also showed a diel pattern in the three lakes (Figure 5). A GLM of the relative $\text{pCO}_{2\text{aq}}$ with time categories and months as factors showed that the diel changes were significantly different in all months ($p < 0.001$ in all cases; Figure 5). However, there was a significant interaction between time categories and months in all lakes ($p < 0.001$) and clear diel patterns were seen primarily during the summer, while the diel patterns were less clear during spring and/or autumn. The $\text{pCO}_{2\text{aq}}$ was normally higher between 08:00 and 11:00, than during midday or evening.

3.2.4. Temporal Patterns in CO_2 Flux

Large temporal variability in CO_2 fluxes was noted during the study period in all three lakes. The fluxes were generally higher and more variable during the summer and was most evident in the shallower lakes. We did not find any significant relationship between CO_2 fluxes and solar radiation, and our fluxes were not negative (no CO_2 uptake by the lake) at any time during the study. CO_2 fluxes increased with increasing wind speed in all the three lakes ($R^2 = 0.35$, 0.13, and 0.31 for Erssjön, Följesjön, and Skottenesjön respectively; $p < 0.05$, see Table 2 for equations). The relationship with wind speed was weaker in the wind sheltered Följesjön; however, when air temperature was added to the regression model, the relationship improved (adjusted $R^2 = 0.30$, $p = 0.001$; Table 2). CO_2 fluxes closely followed $\text{pCO}_{2\text{aq}}$ in the three lakes, and the concentrations had better explanatory power than wind speed, and the R^2 values were 0.46 and 0.67 in Följesjön and Skottenesjön ($p = 0.010$ and 0.001, respectively; Table 2). In Erssjön, adding wind speed to the model along with manual $\text{pCO}_{2\text{aq}}$ improved the R^2 to 0.57 ($p = 0.002$; Table 2).

Table 2. Linear Regressions With Weather and Water Chemistry Variables and Mean $p\text{CO}_{2\text{aq}}$ From Manual Measurements and CO_2 Fluxes in the Three Lakes

Lake	Regression Equation ^a	<i>n</i>	R^2 or adjusted R^{2b}	<i>p</i>
Mean CO_2 Flux				
ERS	$\text{Log}_{10} \text{ flux} = 1.362 + 0.574 \text{ log}_{10} \text{ wind}$	49	0.35	<0.001
ERS ^c	$\text{Flux} = -30.203 + 0.028 p\text{CO}_{2\text{aq}} + 11.583 \text{ wind}$	15	0.57	0.002
FJS	$\text{Log}_{10} \text{ flux} = 1.315 + 0.276 \text{ log}_{10} \text{ temp} + 0.319 \text{ log}_{10} \text{ wind}$	42	0.30	0.001
FJS ^c	$\text{Flux} = 7.881 + 0.009 p\text{CO}_{2\text{aq}}$	13	0.46	0.010
SKS	$\text{Log}_{10} \text{ flux} = 1.068 + 0.639 \text{ log}_{10} \text{ wind}$	36	0.31	<0.001
SKS ^c	$\text{Flux} = -27.503 + 0.040 p\text{CO}_{2\text{aq}}$	12	0.67	0.001
Mean $p\text{CO}_{2\text{aq}}$				
ERS	$\text{Log}_{10} p\text{CO}_{2\text{aq}} = 0.460 + 2.020 \text{ log}_{10} \text{ DOC}$	13	0.36	0.031
FJS	$\text{Log}_{10} p\text{CO}_{2\text{aq}} = 3.678 + 1.075 \text{ log}_{10} \text{ total N}$	12	0.35	0.041
FJS ^d	$\text{Log}_{10} p\text{CO}_{2\text{aq}} = 3.467 + 0.459 \text{ log}_{10} \text{ temp} - 0.485 \text{ log}_{10} \text{ wind}$	12	0.69	0.001
SKS	$\text{Log}_{10} p\text{CO}_{2\text{aq}} = 4.816 - 1.758 \text{ log}_{10} \text{ O}_2$	12	0.73	<0.001

^aRelationships of fluxes ($\text{mmol m}^{-2} \text{ d}^{-1}$) and $p\text{CO}_{2\text{aq}}$ (μatm) with wind speed (wind; m s^{-1}), air temperature (temp; $^{\circ}\text{C}$), dissolved organic carbon (DOC; mg L^{-1}), total nitrogen (total N; mg L^{-1}) and dissolved O_2 (O_2 ; mg L^{-1}). The $p\text{CO}_{2\text{aq}}$ and CO_2 fluxes were averaged across space in all cases.

^b R^2 and adjusted R^2 values are reported for regression models with single predictor and more than one predictors, respectively.

^cData from 2013 only, where $p\text{CO}_{2\text{aq}}$ is available from manual measurements.

^dFive-day average weather data.

3.3. k and $p\text{CO}_{2\text{aq}}$ as Drivers of CO_2 Flux Variability

Plots of the normalized CO_2 fluxes versus normalized $p\text{CO}_{2\text{aq}}$ and k values showed a stronger relationship with $p\text{CO}_{2\text{aq}}$ for both time ($R^2 = 0.91$, $p < 0.001$; Figure 6a) and space ($R^2 = 0.89$, $p < 0.001$; Figure 6b) normalized values (using manual $p\text{CO}_{2\text{aq}}$, modeled k , and modeled fluxes in Erssjön described in section 2.3.2). Hence, the variability in $p\text{CO}_{2\text{aq}}$ was larger and affected the fluxes more than k , spatially and temporally (Figures 6c and 6d). Additionally, the temporal variability in the modeled CO_2 flux was twice the spatial variability (up to 10 and 4.5-fold corresponding to ranges of 15–146 and 26–118 $\text{mmol m}^{-2} \text{ d}^{-1}$), respectively).

3.4. How to Make Representative Measurements?

Our analysis of modeled CO_2 flux from Erssjön, based on data from varying number of chambers and sampling days, demonstrated that single-time, single-point sampling does not represent the results based on many points during the whole year (Figures 7 and 8 and Table S2). A greater number of chambers were required to capture within $\pm 20\%$ of the mean CO_2 flux based on all chambers during the stratified periods when compared to spring and autumn (8–11 chambers versus 1–5, respectively; Figure 7). This reflects higher variability in $p\text{CO}_{2\text{aq}}$ during summer stratification, presumably due to upwelling events (Figure 3). However, in general, measurements on relatively few locations (less than 5) were needed to produce yearly estimates within $\pm 20\%$ of the grand mean using all our data (Figure 7). Measurements on many occasions in time was much more important due to greater variability in time among chambers (Table S2). Our analysis shows that temporally, samples from at least 8 days, distributed over a year, were required to reach an annual mean of within $\pm 20\%$ of the mean based on all samplings in Erssjön (Figure 8 and Table S2).

4. Discussion

4.1. How Large was the Spatial Variability in $p\text{CO}_{2\text{aq}}$ and CO_2 Fluxes?

4.1.1. Between-Lake Variability

The $p\text{CO}_{2\text{aq}}$ and CO_2 fluxes measured in this study were within the ranges reported in other freshwater studies (Table 1). Följesjön had higher $p\text{CO}_{2\text{aq}}$ and CO_2 fluxes than the other two lakes in the catchment. Följesjön is a small, shallow lake with abundant macrophytes and low O_2 concentration in the water column. It has been suggested that small shallow lakes can emit significantly more CO_2 and can have higher $p\text{CO}_{2\text{aq}}$ than larger lakes because of a greater sediment-to-lake volume ratio, and increase in DOC and relative sediment respiration as lake water volume decreases [Holgersson and Raymond, 2016; Kelly et al., 2001; Kortelainen et al., 2006; Roehm et al., 2009]. Skottenesjön's low CO_2 fluxes could be explained by a combination of high O_2 concentration in the water (possibly an indication of high primary productivity; see section 3.2.2) and also

Figure 5. Sensor $p\text{CO}_{2\text{aq}}$ in the three lakes in 2012 and 2013 (data for both years and all depths combined) showing the magnitude of diel variability during different months. The y axis denotes the relative change in $p\text{CO}_{2\text{aq}}$ with respect to the daily mean $p\text{CO}_{2\text{aq}}$ (i.e., each $p\text{CO}_{2\text{aq}}$ value divided by the daily mean $p\text{CO}_{2\text{aq}}$) to show the magnitude of diel change. The relative $p\text{CO}_{2\text{aq}}$ values were divided into six time categories of 00:00–03:00, 04:00–07:00, 08:00–11:00, 12:00–15:00, 16:00–19:00, and 20:00–23:00. The letters above the boxes represent Tukey's post-hoc test from a GLM with the time categories, and if the letters are different, the groups are significantly different at a significance level of 0.01.

likely due to the position of the lake further downstream in the catchment (Figure 1) and disconnected from the high $p\text{CO}_{2\text{aq}}$ in the headwaters. Just before entering Skottenesjön (about 100 m from the delta), much of the CO_2 in the stream was observed to be vented to the atmosphere in a waterfall (mean stream $p\text{CO}_{2\text{aq}}$ of $1500 \mu\text{atm}$ after the waterfall; $n = 3495$, measurements during 2013–2014 [Natchimuthu *et al.*, 2017]). Thus, the part of Skottenesjön that was sampled received lower $p\text{CO}_{2\text{aq}}$ stream water from the catchment than Erssjön, potentially explaining the low $p\text{CO}_{2\text{aq}}$ in the lake. In contrast, Erssjön, which is close to the upper parts of the stream network, has a stream inlet providing water originating in a mire and having high $p\text{CO}_{2\text{aq}}$ levels (mean stream $p\text{CO}_{2\text{aq}}$ of $3700 \mu\text{atm}$; $n = 587$; measurements during 2013–2014 [Natchimuthu *et al.*, 2017]).

4.1.2. Within-Lake Variability

Comparison of the $p\text{CO}_{2\text{aq}}$ patterns with average wind direction indicated that the within-lake spatial variability is partly due to upwelling in combination with oscillating internal waves (Figure 3). In stratified lakes, periods with unidirectional winds could force epilimnetic water to the downwind end, compress the thermocline causing it to tilt, and result in an upwelling of cool metalimnetic or hypolimnetic water at the upwind

Figure 6. Comparison of estimated normalized fluxes with (a and b) normalized $p\text{CO}_{2\text{aq}}$ (dark grey) and k (light grey) in Erssjön during 2013 showing a stronger dependence of fluxes, both spatially and temporally, on the variability in $p\text{CO}_{2\text{aq}}$ than on the k (R^2 of 0.89 and 0.91 ($p < 0.001$) for space and time, respectively). The relative spatial and temporal values were normalized to remove temporal and spatial variabilities, respectively (see text for details). Original values are plotted against (c and d) CO_2 fluxes for comparison.

end of the lake [e.g., Coman and Wells, 2012; MacIntyre and Melack, 2009; Mortimer, 1952; Naithani et al., 2002; Shintani et al., 2010]. Upon relaxation of wind, the tilted thermocline then oscillates due to gravitational forces until disturbed by another wind event [Mortimer, 1952]. Many studies have shown that availability of nutrients and primary productivity can vary spatially in a lake because of upwelling events induced by wind which brings nutrient-rich hypolimnetic water to the surface [e.g., Corman et al., 2010; MacIntyre et al., 1999; MacIntyre and Jellison, 2001]. Thus, it is not surprising that CO_2 concentrations can also be variable in the surface water during the upwelling episodes, although not widely reported previously. It has to be noted that the spatial variability was small during the later part of the mixing periods in spring and autumn (except for the high $p\text{CO}_{2\text{aq}}$ near the inlets; Figure 3). During these periods, it may be sufficient to sample only a few locations to represent the lake-wide $p\text{CO}_{2\text{aq}}$. The findings of high $p\text{CO}_{2\text{aq}}$ near stream inlets in Erssjön and Skottenesjön were similar to the previous observations of high $p\text{CO}_{2\text{aq}}$ in river inflow regions in a study by Roland et al. [2010] in five Brazilian reservoirs and in a floodplain lake in lower Amazon [Rudorff et al., 2011].

In Erssjön and Skottenesjön, the mean CO_2 fluxes were lower at the shallow depths than the deeper depth zones (Figure 4). Similar pattern of lower CO_2 fluxes closer to the shore than in the center was observed in a study by Schilder et al. [2013], due to the lower k in the near shore areas, because of wind sheltering effects. Thus, spatial variability in k may have contributed to the spatial CO_2 flux patterns in both Erssjön and Skottenesjön.

4.2. How Large was the Temporal Variability in $p\text{CO}_2$ and CO_2 Fluxes?

4.2.1. Temporal Patterns in $p\text{CO}_{2\text{aq}}$

In stratified lakes, peaks in CO_2 emissions have been observed in spring and autumn [Karlsson et al., 2013; Striegl and Michmerhuizen, 1998], agreeing with the observations of higher $p\text{CO}_{2\text{aq}}$ in Erssjön during the early parts of lake-mixing periods. Positive relationships of $p\text{CO}_{2\text{aq}}$ with DOC have been observed previously [e.g.,

Figure 7. Analysis of number of chambers required (denoted by vertical dashed lines) to capture the uncertainties in CO_2 fluxes in Erssjön within $\pm 20\%$ of the mean flux from all chambers (denoted by horizontal dashed lines) during the different sampling occasions of the year 2013. The fluxes were normalized to remove temporal variability (see section 2 for details), and all the panels are plotted to the same scale for comparison. The grey areas denote values within 5th and 95th percentiles in each bin.

Figure 8. Number of sampling days required (denoted by vertical dashed line) to reach an uncertainty of within $\pm 20\%$ of the mean fluxes (denoted by horizontal dashed lines) from all measurements in Erssjön in the year 2013. The fluxes were normalized to remove spatial variability (see section 2 for details). The grey areas denote values within 5th and 95th percentiles in each bin.

Jonsson *et al.*, 2007; Kelly *et al.*, 2001; Larsen *et al.*, 2011; Roehm *et al.*, 2009; Sobek *et al.*, 2003], and they have been associated with the increase in respiration in response to the increased supply of DOC. It could also indicate simultaneous transport of DOC and CO_2 from soils to the lake. Thus, external inputs appear to have influenced the $\text{pCO}_{2\text{aq}}$ in Erssjön.

Nutrient supply can decrease the CO_2 levels by stimulating primary production [Cole *et al.*, 2000; Gu *et al.*, 2011]; however, in some cases nutrients like N and P could enhance CO_2 production through bacterial mineralization [Larsen *et al.*, 2011], possibly explaining the positive correlation of $\text{pCO}_{2\text{aq}}$ and total nitrogen in Följesjön. Another potential explanation is the simultaneous transport of nitrogen and CO_2 from the root zones and soils of the surrounding areas, or simply simultaneous release of dissolved nitrogen and CO_2 from organic matter degradation. The strong negative relationship between O_2 and $\text{pCO}_{2\text{aq}}$ in Skottenesjön indicates the influence of photosynthesis and respiration on $\text{pCO}_{2\text{aq}}$ and such correlations have also been shown in other studies [e.g., Kortelainen *et al.*, 2006; Roehm *et al.*, 2009]. Therefore, $\text{pCO}_{2\text{aq}}$ in Skottenesjön may have been more affected by internal lake processes than in the other lakes.

Studies in boreal and tropical regions have shown that increase in temperature increases organic carbon mineralization rates in sediments [Gudas *et al.*, 2010; Marotta *et al.*, 2014]. Similarly, an increase in $\text{pCO}_{2\text{aq}}$ was related to increase in water temperature in the mixed layer in a humic lake in northern Sweden [Åberg *et al.*, 2010]. Thus, in Följesjön the higher concentration of CO_2 in the summer months was likely due to the more efficient warming of the shallow water column and the higher respiration rates supported by the warmer water. The relationship of $\text{pCO}_{2\text{aq}}$ in Följesjön with temperature and wind, when integrated over 5 days before sampling (Table 2), indicated that $\text{pCO}_{2\text{aq}}$ can depend on the balance between CO_2 input to the water from in situ degradation or hydrological transport, and CO_2 loss to the atmosphere. Altogether, the best explanatory variables for $\text{pCO}_{2\text{aq}}$ differed between the different lakes (Table 2), indicating that there may be no single variable that can serve as strong predictor for many lakes. Instead multivariate analyses based on extensive data sets may be a more promising way to model $\text{pCO}_{2\text{aq}}$ across systems.

4.2.2. Diel Variability in $\text{pCO}_{2\text{aq}}$

Diel variability in $\text{pCO}_{2\text{aq}}$ was measured in all three study lakes. Previous studies have also observed diel changes in $\text{pCO}_{2\text{aq}}$ with higher $\text{pCO}_{2\text{aq}}$ during the dark period when compared to the daytime [e.g., Åberg *et al.*, 2010; Hamilton *et al.*, 1994; Huotari *et al.*, 2009; Natchimuthu *et al.*, 2014; Sellers *et al.*, 1995], due to the balance between photosynthesis and respiration in the lake. Indeed, the diel patterns in the lakes were more pronounced during warm growing seasons than during other seasons having lower temperatures

and lower productivity, as also noted by Huotari *et al.* [2009] (Figure 5). In our data, there was a delay in capturing the peak $p\text{CO}_{2\text{aq}}$ because of the chamber design and the dependence on turbulence in the surface water to equilibrate the gas in the chamber (see section 2.2). Hence, because of the slow equilibration times, the peak $p\text{CO}_{2\text{aq}}$ during the period of 08:00–11:00 represented the situation a few hours earlier in the morning [see Bastviken *et al.*, 2015].

4.2.3. Temporal Variability in CO_2 Flux

Increased fluxes with higher variability during the warm growing seasons in the lakes were similar to the observations by Huotari *et al.* [2011] and Åberg *et al.* [2010]. A few other studies have shown that primary production during the growing season can sometimes result in an uptake by the system [Huotari *et al.*, 2011; Karlsson *et al.*, 2013; Natchimuthu *et al.*, 2014], although there can be emissions during other seasons, but this could not be seen in our study.

The relationships of flux with wind speed (Table 2) are likely linked to greater turbulence in the water surface increasing gas fluxes, as has been found in many studies [Cole and Caraco, 1998; Jonsson *et al.*, 2008; Wanninkhof, 1992]. Increased turbulence is probably also coupled with higher renewal rates of CO_2 from the bottom waters of the lake (patterns indicative of upwelling found on multiple occasions; Figure 3).

4.3. The Importance of k Versus $p\text{CO}_{2\text{aq}}$ for the CO_2 Flux

In a study of spatial variability in diffusive fluxes in 22 European lakes [Schilder *et al.*, 2013], it was shown that k_{600} varied to a much higher degree than CO_2 concentrations. This study was based on snapshot measurements over a few hours once in each system. The spatial variability in $p\text{CO}_{2\text{aq}}$ was quite small during short measurement periods in our study as well. The variability in k , responding over time frames of minutes to physical forcing by, e.g., wind, is more dynamic over short periods (within days) than $p\text{CO}_{2\text{aq}}$, and thereby more important for flux variability over short periods. However, on a longer time scale and when more heterogeneity in $p\text{CO}_{2\text{aq}}$ from the whole lake is included, $p\text{CO}_{2\text{aq}}$ was more important than k in regulating CO_2 fluxes (Figure 6). Accordingly, the strong relationship of CO_2 fluxes with $p\text{CO}_{2\text{aq}}$ in both space and time (Figure 6) shows that the variability in $p\text{CO}_{2\text{aq}}$ is a key for assessing CO_2 fluxes. Hence, the variability in k (from wind speed, fetch, convection, etc.) appeared to be lower than the variability in $p\text{CO}_{2\text{aq}}$ (from balance between respiration and primary production, hydrological transport, and upwelling). The influence of hydrological input may be reduced with prolonged residence time of the system so there may be differences in the relative importance of $p\text{CO}_{2\text{aq}}$ and k among lakes depending on lake size/volume and regional climate.

4.4. Improved Measurements Needed for Representative Fluxes

In our study lake Erssjön, samples from ≥ 8 chambers during stratification periods and 5 or less in spring and autumn distributed in space, and from ≥ 8 days scattered in time throughout the year, were necessary to capture an annual mean of within $\pm 20\%$ of the measured mean fluxes (Figures 7 and 8). It has to be noted that this is based on our analysis of measurements in Erssjön only. In other lakes, the presence of, e.g., stream inlets, groundwater input zones, macrophytes, and basin shape could play a role in deciding the number of sampling points. Also, the spatial variability can change dramatically over time and a single sampling point in this study could not provide representative estimates during all time periods. Temporally, data from lake circulation periods and stratified periods are very likely to be important for annual CO_2 estimates. Therefore, we emphasize that spatial and temporal heterogeneity should be considered in as many studies as possible to get a robust estimate of whole lake CO_2 fluxes and to improve the landscape greenhouse gas budgets. To illustrate the amount of underestimates or overestimates in whole lake annual fluxes, we made an analysis of modeled fluxes from Erssjön (yearly flux per m^2 , 268 ice free days in 2013; Table S2) and compared our flux estimate of $15.2 \text{ mol m}^{-2} \text{ yr}^{-1}$ from all of our data (from all chambers including all sampling times) with other less intensive sampling approaches. The comparison shows the following:

1. Single-time, single-chamber measurements produce very uncertain estimates of the annual lake CO_2 flux estimate ranging from 3.3 to $39.5 \text{ mol m}^{-2} \text{ yr}^{-1}$ depending on the sampling time and the location.
2. Single-time, multiple-chamber measurements can be equally problematic (estimate ranges from 5.6 to $34.3 \text{ mol m}^{-2} \text{ yr}^{-1}$ depending on the sampling date; Table S2).
3. Repeated-single-chamber measurements cancel out some of the heterogeneity in the fluxes (Table S2), as the temporal variability was greater than the spatial variability in this lake (estimate ranges from 11.9 to $17.8 \text{ mol m}^{-2} \text{ yr}^{-1}$ depending on the sampling location). However, this is true only if sampling covers

all seasons of the full year, as the spatial heterogeneity was observed to be higher during the growing seasons. If the sampling misses key periods of high-flux variability or overrepresents them, it is very likely that the repeated-single-chamber measurements underestimate or overestimate the whole lake annual fluxes. Altogether, one option is to make frequent measurements covering the whole year using fewer number of chambers. If this is not possible due to logistical constraints, measurements on at least 8 days are required in ≥ 8 locations during stratification periods and ≤ 5 in spring and autumn in Erssjön to obtain representative flux estimates.

Moreover, the variability estimate (1 SD) of $8.7 \text{ mol m}^{-2} \text{ yr}^{-1}$ when including all chambers and all sampling times was similar to the variability estimate in time ($8.1 \text{ mol m}^{-2} \text{ yr}^{-1}$), and higher than the variability estimate in space ($1.5 \text{ mol m}^{-2} \text{ yr}^{-1}$). This further emphasizes the importance of including temporal variability in flux measurements and confirms the results shown in Figures 7 and 8. Hence, large-scale assessments based on measurements from single or a few locations in lakes and collected at a few points in time [e.g., Kortelainen et al., 2006; Roehm et al., 2009] may be substantially biased. The bias will depend on how well the data represented episodic events, such as emissions associated with lake circulation periods or upwelling, diel and seasonal variability, and high flux areas near stream inlets. Hence, in the choice of how to allocate sampling resources, it may be more desirable to make improved measurements covering temporal variability in fewer systems yielding robust and representative data rather than sampling a large number of systems once at one or few sampling locations.

5. Conclusions

The studied lakes were supersaturated in $\text{pCO}_{2\text{aq}}$ at all times and had widely varying $\text{pCO}_{2\text{aq}}$ and CO_2 fluxes linked to lake morphology, stream inlets, and stratification dynamics. Repeated CO_2 measurements at many locations in lakes and under extended periods in time yielded new insights in the variability of CO_2 in space and time. The $\text{pCO}_{2\text{aq}}$ measurements showed that spatial variability in lakes can be significant, especially during stratification periods when $\text{pCO}_{2\text{aq}}$ can be affected by upwelling events by wind-driven thermocline oscillations. The patterns clearly show that the common single-point and single-time measurements are not representative and may have a >2 -fold bias also in the quite small lakes studied. Further, the importance of k versus pCO_2 as drivers for the flux variability could be compared. Unlike previous studies, the integrated assessment of both spatial and temporal variabilities in this study showed that $\text{pCO}_{2\text{aq}}$, rather than k , affects the CO_2 fluxes the most, and improved sampling strategies are needed to get representative lake CO_2 fluxes. In addition, we were able to identify and suggest the number of flux chamber measurements needed to properly represent CO_2 fluxes in space and time in lakes of a very important size class ($>90\%$ of the global lakes are smaller than 0.1 km^2 [Verpoorter et al., 2014]). These results provide ways toward substantially improved future measurement efforts. Such improved measurements can now be more efficiently realized by using recently developed tools. When affordable, flux towers can be used [e.g., Eugster et al., 2003; Heiskanen et al., 2014]. Manual or automated flux chambers [Duc et al., 2013] combined with low-cost CO_2 sensors [Bastviken et al., 2015] can also provide powerful tools for a greater number of systems.

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References

- Åberg, J., M. Jansson, and A. Jonsson (2010), Importance of water temperature and thermal stratification dynamics for temporal variation of surface water CO_2 in a boreal lake, *J. Geophys. Res.*, *115*, G02024, doi:10.1029/2009JG001085.
- Abril, G., et al. (2015), Technical Note: Large overestimation of pCO_2 calculated from pH and alkalinity in acidic, organic-rich freshwaters, *Biogeosciences*, *12*(1), 67–78, doi:10.5194/bg-12-67-2015.
- Aufdenkampe, A., E. Mayorga, P. Raymond, J. Melack, S. Doney, S. Alin, R. Aalto, and K. Yoo (2011), Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere, *Front. Ecol. Environ.*, *9*(1), 53–60, doi:10.1890/100014.
- Bastviken, D., I. Sundgren, S. Natchimuthu, H. Reyier, and M. Gålfalk (2015), Technical note: Cost-efficient approaches to measure carbon dioxide (CO_2) fluxes and concentrations in terrestrial and aquatic environments using mini loggers, *Biogeosciences*, *12*(12), 3849–3859, doi:10.5194/bg-12-3849-2015.
- Battin, T. J., L. A. Kaplan, S. Findlay, C. S. Hopkinson, E. Marti, A. I. Packman, J. D. Newbold, and F. Sabater (2008), Biophysical controls on organic carbon fluxes in fluvial networks, *Nat. Geosci.*, *1*(2), 95–100, doi:10.1038/ngeo101.
- Borges, A. V., C. Morana, S. Bouillon, P. Servais, J.-P. Descy, and F. Darchambeau (2014), Carbon cycling of Lake Kivu (East Africa): Net autotrophy in the epilimnion and emission of CO_2 to the atmosphere sustained by geogenic inputs, *PLoS One*, *9*(10), e109500, doi:10.1371/journal.pone.0109500.
- Cole, J. J., and N. F. Caraco (1998), Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF_6 , *Limnol. Oceanogr.*, *43*(4), 647–656, doi:10.4319/lo.1998.43.4.0647.

- Cole, J. J., N. F. Caraco, G. W. Kling, and T. K. Kratz (1994), Carbon dioxide supersaturation in the surface waters of lakes, *Science*, 265(5178), 1568–1570, doi:10.1126/science.265.5178.1568.
- Cole, J. J., M. L. Pace, S. R. Carpenter, and J. F. Kitchell (2000), Persistence of net heterotrophy in lakes during nutrient addition and food web manipulations, *Limnol. Oceanogr.*, 45(8), 1718–1730, doi:10.4319/lo.2000.45.8.1718.
- Cole, J. J., et al. (2007), Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget, *Ecosystems*, 10(1), 172–185, doi:10.1007/s10021-006-9013-8.
- Cole, J. J., D. L. Bade, D. Bastviken, M. L. Pace, and M. Van de Bogert (2010), Multiple approaches to estimating air–water gas exchange in small lakes, *Limnol. Oceanogr. Methods*, 8(6), 285–293, doi:10.4319/lom.2010.8.285.
- Coman, M. A., and M. G. Wells (2012), Temperature variability in the nearshore benthic boundary layer of Lake Opeongo is due to wind-driven upwelling events, *Can. J. Fish. Aquat. Sci.*, 69(2), 282–296, doi:10.1139/f2011-167.
- Corman, J. R., P. B. McIntyre, B. Kuboja, W. Mbemba, D. Fink, C. W. Wheeler, C. Gans, E. Michel, and A. S. Flecker (2010), Upwelling couples chemical and biological dynamics across the littoral and pelagic zones of Lake Tanganyika, East Africa, *Limnol. Oceanogr.*, 55(1), 214–224, doi:10.4319/lo.2010.55.1.0214.
- Crusius, J., and R. Wanninkhof (2003), Gas transfer velocities measured at low wind speed over a lake, *Limnol. Oceanogr.*, 48(3), 1010–1017, doi:10.4319/lo.2003.48.3.1010.
- Duarte, C. M., and Y. T. Prairie (2005), Prevalence of heterotrophy and atmospheric CO₂ emissions from aquatic ecosystems, *Ecosystems*, 8(7), 862–870, doi:10.1007/s10021-005-0177-4.
- Duc, N. T., S. Silverstein, L. Lundmark, H. Reyier, P. Crill, and D. Bastviken (2013), Automated flux chamber for investigating gas flux at water–air interfaces, *Environ. Sci. Technol.*, 47(2), 968–975, doi:10.1021/es303848x.
- Ducharme-Riel, V., D. Vachon, P. del Giorgio, and Y. Prairie (2015), The relative contribution of winter under-ice and summer hypolimnetic CO₂ accumulation to the annual CO₂ emissions from northern lakes, *Ecosystems*, 18(4), 547–559, doi:10.1007/s10021-015-9846-0.
- ESRI (2001), *Using ArcGIS™ Geostatistical Analyst*, Environmental Systems Research Institute, Redlands, Calif.
- Eugster, W., G. Kling, T. Jonas, J. P. McFadden, A. Wüest, S. MacIntyre, and F. S. Chapin (2003), CO₂ exchange between air and water in an Arctic Alaskan and midlatitude Swiss lake: Importance of convective mixing, *J. Geophys. Res.*, 108(D12), 4362, doi:10.1029/2002JD002653.
- Gälfalk, M., D. Bastviken, S. Fredriksson, and L. Arneborg (2013), Determination of the piston velocity for water–air interfaces using flux chambers, acoustic Doppler velocimetry, and IR imaging of the water surface, *J. Geophys. Res. Biogeosci.*, 118, 770–782, doi:10.1002/jgrg.20064.
- Gu, B. H., C. L. Schelske, and M. F. Coveney (2011), Low carbon dioxide partial pressure in a productive subtropical lake, *Aquat. Sci.*, 73(3), 317–330, doi:10.1007/s00027-010-0179-y.
- Gudasz, C., D. Bastviken, K. Steger, K. Premke, S. Sobek, and L. J. Tranvik (2010), Temperature-controlled organic carbon mineralization in lake sediments, *Nature*, 466(7305), 478–481, doi:10.1038/nature09186.
- Hamilton, J. D., C. A. Kelly, J. W. M. Rudd, R. H. Hesslein, and N. T. Roulet (1994), Flux to the atmosphere of CH₄ and CO₂ from wetland ponds on the Hudson Bay lowlands (HBLs), *J. Geophys. Res.*, 99(D1), 1495–1510, doi:10.1029/93JD03020.
- Heiskanen, J. J., I. Mammarella, S. Haapanala, J. Pumpanen, T. Vesala, S. MacIntyre, and A. Ojala (2014), Effects of cooling and internal wave motions on gas transfer coefficients in a boreal lake, *Tellus, Ser. B*, 66, 22827, doi:10.3402/tellusb.v66.22827.
- Holgerson, M. A., and P. A. Raymond (2016), Large contribution to inland water CO₂ and CH₄ emissions from very small ponds, *Nat. Geosci.*, 9, 222–226, doi:10.1038/ngeo2654.
- Huotari, J., A. Ojala, E. Peltomaa, J. Pumpanen, P. Hari, and T. Vesala (2009), Temporal variations in surface water CO₂ concentration in a boreal humic lake based on high-frequency measurements, *Boreal Environ. Res.*, 14(A), 48–60.
- Huotari, J., A. Ojala, E. Peltomaa, A. Nordbo, S. Launiainen, J. Pumpanen, T. Rasilo, P. Hari, and T. Vesala (2011), Long-term direct CO₂ flux measurements over a boreal lake: Five years of eddy covariance data, *Geophys. Res. Lett.*, 38, L18401, doi:10.1029/2011GL048753.
- Huttunen, J. T., J. Alm, A. Liikanen, S. Juutinen, T. Larmola, T. Hammar, J. Silvola, and P. J. Martikainen (2003), Fluxes of methane, carbon dioxide and nitrous oxide in boreal lakes and potential anthropogenic effects on the aquatic greenhouse gas emissions, *Chemosphere*, 52(3), 609–621, doi:10.1016/S0045-6535(03)00243-1.
- Jennings, E., S. E. Jones, L. Arvola, P. A. Staehr, E. Gaiser, I. D. Jones, K. C. Weathers, G. A. Weyhenmeyer, C. Y. Chiu, and E. De Eyto (2012), Effects of weather-related episodic events in lakes: An analysis based on high-frequency data, *Freshwater Biol.*, 57(3), 589–601, doi:10.1111/j.1365-2427.2011.02729.x.
- Jonsson, A., J. Åberg, and M. Jansson (2007), Variations in pCO₂ during summer in the surface water of an unproductive lake in northern Sweden, *Tellus, Ser. B*, 59(5), 797–803, doi:10.1111/j.1600-0889.2007.00307.x.
- Jonsson, A., J. Åberg, A. Lindroth, and M. Jansson (2008), Gas transfer rate and CO₂ flux between an unproductive lake and the atmosphere in northern Sweden, *J. Geophys. Res.*, 113, G04006, doi:10.1029/2008JG000688.
- Karlsson, J., R. Giesler, J. Persson, and E. Lundin (2013), High emission of carbon dioxide and methane during ice thaw in high latitude lakes, *Geophys. Res. Lett.*, 40, 1123–1127, doi:10.1002/grl.50152.
- Kelly, C. A., E. Fee, P. S. Ramlal, J. W. M. Rudd, R. H. Hesslein, C. Anema, and E. U. Schindler (2001), Natural variability of carbon dioxide and net epilimnetic production in the surface waters of boreal lakes of different sizes, *Limnol. Oceanogr.*, 46(5), 1054–1064, doi:10.4319/lo.2001.46.5.1054.
- Kokic, J., M. B. Wallin, H. E. Chmiel, B. A. Denfeld, and S. Sobek (2015), Carbon dioxide evasion from headwater systems strongly contributes to the total export of carbon from a small boreal lake catchment, *J. Geophys. Res. Biogeosci.*, 120, 13–28, doi:10.1002/2014JG002706.
- Kortelainen, P., M. Rantakari, J. T. Huttunen, T. Mattsson, J. Alm, S. Juutinen, T. Larmola, J. Silvola, and P. J. Martikainen (2006), Sediment respiration and lake trophic state are important predictors of large CO₂ evasion from small boreal lakes, *Global Change Biol.*, 12(8), 1554–1567, doi:10.1111/j.1365-2486.2006.01167.x.
- Larsen, S., T. Andersen, and D. O. Hessen (2011), The pCO₂ in boreal lakes: Organic carbon as a universal predictor?, *Global Biogeochem. Cycles*, 25, GB2012, doi:10.1029/2010GB003864.
- López Bellido, J., T. Tulonen, P. Kankaala, and A. Ojala (2009), CO₂ and CH₄ fluxes during spring and autumn mixing periods in a boreal lake (Pääjärvi, southern Finland), *J. Geophys. Res.*, 114, G04007, doi:10.1029/2009JG000923.
- Lorke, A., et al. (2015), Technical note: Drifting versus anchored flux chambers for measuring greenhouse gas emissions from running waters, *Biogeosciences*, 12(23), 7013–7024, doi:10.5194/bg-12-7013-2015.
- MacIntyre, S., and J. M. Melack (2009), Mixing dynamics in lakes across climatic zones, in *Encyclopedia of Inland Waters*, edited by G. E. Likens, pp. 603–612, Academic Press, Oxford.
- MacIntyre, S., and R. Jellison (2001), Nutrient fluxes from upwelling and enhanced turbulence at the top of the pycnocline in Mono Lake, California, *Hydrobiologia*, 466(1), 13–29, doi:10.1023/a:1014563914112.
- MacIntyre, S., K. M. Flynn, R. Jellison, and J. R. Romero (1999), Boundary mixing and nutrient fluxes in Mono Lake, California, *Limnol. Oceanogr.*, 44(3), 512–529, doi:10.4319/lo.1999.44.3.0512.

- Marotta, H., L. Pinho, C. Gudas, D. Bastviken, L. J. Tranvik, and A. Enrich-Prast (2014), Greenhouse gas production in low-latitude lake sediments responds strongly to warming, *Nat. Clim. Change*, 4(6), 467–470, doi:10.1038/nclimate2222.
- McAuliffe, C. (1971), GC determination of solutes by multiple phase equilibration, *Chem. Tech.*, 1(1), 46–51.
- Mortimer, C. H. (1952), Water movements in lakes during summer stratification: Evidence from the distribution of temperature in Windermere, *Philos. Trans. R. Soc., B*, 236(635), 355–398, doi:10.1098/rstb.1952.0005.
- Naithani, J., E. Deleersnijder, and P. D. Plisnier (2002), Origin of intraseasonal variability in Lake Tanganyika, *Geophys. Res. Lett.*, 29(23), 2093, doi:10.1029/2002GL015843.
- Natchimuthu, S., B. Panneer Selvam, and D. Bastviken (2014), Influence of weather variables on methane and carbon dioxide flux from a shallow pond, *Biogeochemistry*, 119(1), 403–413, doi:10.1007/s10533-014-9976-z.
- Natchimuthu, S., I. Sundgren, M. Gålfalk, L. Klemetsson, P. Crill, Å. Danielsson, and D. Bastviken (2016), Spatio-temporal variability of lake CH₄ fluxes and its influence on annual whole lake emission estimates, *Limnol. Oceanogr.*, 61(S1), S13–S26, doi:10.1002/lno.10222.
- Natchimuthu, S., M. B. Wallin, L. Klemetsson, and D. Bastviken (2017), Spatio-temporal patterns of stream methane and carbon dioxide emissions in a hemiboreal catchment in Southwest Sweden, *Sci. Rep.*, in press.
- Ojala, A., J. López Bellido, T. Tulonen, P. Kankaala, and J. Huotari (2011), Carbon gas fluxes from a brown-water and a clear-water lake in the boreal zone during a summer with extreme rain events, *Limnol. Oceanogr.*, 56(1), 61–76, doi:10.4319/lno.2011.56.1.0061.
- Pacheco, F. S., M. C. S. Soares, A. T. Assireu, M. P. Curtarelli, F. Roland, G. Abril, J. L. Stech, P. C. Alvalá, and J. P. Ometto (2015), The effects of river inflow and retention time on the spatial heterogeneity of chlorophyll and water–air CO₂ fluxes in a tropical hydropower reservoir, *Biogeosciences*, 12(1), 147–162, doi:10.5194/bg-12-147-2015.
- Panneer Selvam, B., S. Natchimuthu, L. Arunachalam, and D. Bastviken (2014), Methane and carbon dioxide emissions from inland waters in India—Implications for large scale greenhouse gas balances, *Global Change Biol.*, 20(11), 3397–3407, doi:10.1111/gcb.12575.
- Rantakari, M., and P. Kortelainen (2005), Interannual variation and climatic regulation of the CO₂ emission from large boreal lakes, *Global Change Biol.*, 11(8), 1368–1380, doi:10.1111/j.1365-2486.2005.00982.x.
- Raymond, P. A., et al. (2013), Global carbon dioxide emissions from inland waters, *Nature*, 503(7476), 355–359, doi:10.1038/nature12760.
- Roehm, C. L., Y. T. Prairie, and P. A. del Giorgio (2009), The pCO₂ dynamics in lakes in the boreal region of northern Québec, Canada, *Global Biogeochem. Cycles*, 23, GB3013, doi:10.1029/2008GB003297.
- Roland, F., L. O. Vidal, F. S. Pacheco, N. O. Barros, A. Assireu, J. P. H. B. Ometto, A. C. P. Cimleris, and J. J. Cole (2010), Variability of carbon dioxide flux from tropical (Cerrado) hydroelectric reservoirs, *Aquat. Sci.*, 72(3), 283–293, doi:10.1007/s00027-010-0140-0.
- Rudorff, C. M., J. M. Melack, S. MacIntyre, C. C. F. Barbosa, and E. Novo (2011), Seasonal and spatial variability of CO₂ emission from a large floodplain lake in the lower Amazon, *J. Geophys. Res.*, 116, G04007, doi:10.1029/2011JG001699.
- Schilder, J., D. Bastviken, M. van Hardenbroek, P. Kankaala, P. Rinta, T. Stotter, and O. Heiri (2013), Spatial heterogeneity and lake morphology affect diffusive greenhouse gas emission estimates of lakes, *Geophys. Res. Lett.*, 40, 5752–5756, doi:10.1002/2013GL057669.
- Sellers, P., R. H. Hesslein, and C. A. Kelly (1995), Continuous measurement of CO₂ for estimation of air–water fluxes in lakes: An in situ technique, *Limnol. Oceanogr.*, 40(3), 575–581, doi:10.4319/lno.1995.40.3.0575.
- Shintani, T., A. de la Fuente, Y. Nino, and J. Imberger (2010), Generalizations of the Wedderburn number: Parameterizing upwelling in stratified lakes, *Limnol. Oceanogr.*, 55(3), 1377–1389, doi:10.4319/lno.2010.55.3.1377.
- Sobek, S., G. Algesten, A.-K. Bergström, M. Jansson, and L. J. Tranvik (2003), The catchment and climate regulation of pCO₂ in boreal lakes, *Global Change Biol.*, 9(4), 630–641, doi:10.1046/j.1365-2486.2003.00619.x.
- Striegl, R. G., and C. M. Michmerhuizen (1998), Hydrologic influence on methane and carbon dioxide dynamics at two north-central Minnesota lakes, *Limnol. Oceanogr.*, 43(7), 1519–1529, doi:10.4319/lno.1998.43.7.1519.
- Teodoru, C. R., Y. T. Prairie, and P. A. del Giorgio (2011), Spatial heterogeneity of surface CO₂ fluxes in a newly created Eastmain-1 reservoir in northern Quebec, Canada, *Ecosystems*, 14(1), 28–46, doi:10.1007/s10021-010-9393-7.
- Vachon, D., and P. del Giorgio (2014), Whole-lake CO₂ dynamics in response to storm events in two morphologically different lakes, *Ecosystems*, 17(8), 1338–1353, doi:10.1007/s10021-014-9799-8.
- Vachon, D., and Y. T. Prairie (2013), The ecosystem size and shape dependence of gas transfer velocity versus wind speed relationships in lakes, *Can. J. Fish. Aquat. Sci.*, 70(12), 1757–1764, doi:10.1139/cjfas-2013-0241.
- Verpoorter, C., T. Kutser, D. A. Seekell, and L. J. Tranvik (2014), A global inventory of lakes based on high-resolution satellite imagery, *Geophys. Res. Lett.*, 41, 6396–6402, doi:10.1002/2014GL060641.
- Wanninkhof, R. (1992), Relationship between wind-speed and gas-exchange over the ocean, *J. Geophys. Res.*, 97(C5), 7373–7382, doi:10.1029/92JC00188.
- Weiss, R. F. (1974), Carbon dioxide in water and seawater: The solubility of a non-ideal gas, *Mar. Chem.*, 2(3), 203–215, doi:10.1016/0304-4203(74)90015-2.
- Weyhenmeyer, G., P. Kortelainen, S. Sobek, R. Müller, and M. Rantakari (2012), Carbon dioxide in boreal surface waters: A comparison of lakes and streams, *Ecosystems*, 15(8), 1295–1307, doi:10.1007/s10021-012-9585-4.
- Wik, M., B. F. Thornton, D. Bastviken, J. Uhlbäck, and P. M. Crill (2016), Biased sampling of methane release from northern lakes: A problem for extrapolation, *Geophys. Res. Lett.*, 43, 1256–1262, doi:10.1002/2015GL066501.
- Yang, H., T. Andersen, P. Dörsch, K. Tominaga, J.-E. Thrane, and D. Hessen (2015), Greenhouse gas metabolism in Nordic boreal lakes, *Biogeochemistry*, 126(1), 211–225, doi:10.1007/s10533-015-0154-8.