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1 Where does the river end? Drivers of spatiotemporal variability in CO₂

- 2 concentration and flux in the inflow area of a large boreal lake
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31 Abstract

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River inflow affects the spatiotemporal variability of carbon dioxide (CO₂) in the water column of lakes and may locally influence CO₂ gas exchange with the atmosphere. However, spatiotemporal CO₂ variability at river inflow sites is often unknown leaving estimates of lake-wide CO₂ emission uncertain. Here, we investigated the CO₂ concentration and flux variability along a river-impacted bay and remote sampling locations of Lake Onego. During three years, we resolved spatial CO₂ gradients between river inflow and central lake and recorded the temporal course of CO₂ in the bay from the ice-covered period to early summer. We found that the river had a major influence on the spatial CO₂ variability during ice-cover periods and contributed ~35% to the total amount of CO₂ in the bay. The bay was a source of CO₂ to the atmosphere at ice-melt each year emitting 2-15 times the amount as an equally-sized area in the central lake. However, there was large interannual variability in the spring CO₂ emission from the bay related to differences in discharge and climate that affected the hydrodynamic development of the lake during spring. In early summer, the spatial CO₂ variability was unrelated to the river signal but correlated negatively with dissolved oxygen concentrations instead indicating a stronger biological control on CO₂. Our study reveals a large variability of CO₂ and its drivers at river inflow sites at the seasonal and at the interannual time scale. Understanding these dynamics is essential for predicting lake-wide CO₂ fluxes more accurately under a warming climate.

Introduction

Lakes and rivers are dynamics sites of carbon transport and processing and, at the global scale, a net source of carbon dioxide (CO₂) to the atmosphere (Cole et al. 2007, Tranvik et al. 2009; Aufdenkampe et al. 2011). Despite covering about five times less area on land than lakes and reservoirs, it is estimated that rivers and streams contribute up to 85% to the annual inland water CO₂ emission flux, indicating their disproportionally high influence for water-atmosphere CO₂ gas exchange (Cole et al. 2007, Raymond et al. 2013, Lauerwald et al. 2015). Global estimates of net aquatic CO₂ release range between 0.8 and 2.1 Pg C yr⁻¹, however, there are large uncertainties associated with these estimates (Cole et al. 2007, Raymond et al. 2013). While these are partly related to the challenge of accurately estimating global inland water area, there is furthermore a lack of information on spatial and temporal variability not only in CO₂ flux but also in its environmental drivers (Verpoorter et al. 2014; Hastie et al. 2017; Klaus et al. 2019). Large extends in this variability might be expected at the interface of lentic and lotic systems, i.e., at river inflow areas, which might add comparatively large uncertainty to whole-system CO₂ flux estimates. However, only limited information on CO₂ dynamics exist for these sites, although the hydrological contribution to CO₂ in lakes has been pointed out frequently (Schilder et al. 2013; Pacheco et al. 2015; Natchimuthu et al. 2017).

The reason why rivers and streams are on average more supersaturated in CO₂ than lakes, is their higher connection with the terrestrial environment along their margins (Raymond et al. 2013; Crawford et al. 2014). Fluvial export of dissolved organic carbon (DOC) from soils, which is partly mineralized to CO₂ during transport, as well as direct inputs of CO₂ from soil respiration both contribute to supersaturation and net emission of stream CO₂ into the atmosphere (Jones and Mulholland 1998; Worrall and Lancaster 2005; Öquist et al. 2009; Wallin et al. 2013; Crawford et al. 2014). In this context, it has been shown that fluvial export can also account for considerable fractions of excess CO₂ in lakes (Maberly et al. 2013; Chmiel et al. 2016), which indicates that the transition zone from rivers to lakes are probably important and highly dynamic hot spots for lake CO₂ emission. Since aquatic CO₂ concentrations are controlled by biological activity, water chemistry, and physical transport processes, their dynamics at inflow areas will be complex and vary with temporal changes in river discharge and lake hydrodynamics. In large systems with heterogeneous basin morphology and confined water circulation, substantial gradients in CO₂ might develop, such that a lack in information on spatial CO₂ variability might considerable bias whole-systems CO₂ flux assessments (Kelly et al. 2001; Paranaíba et al. 2018).

A lot of scientific effort has been dedicated to CO₂ flux dynamics in boreal aquatic ecosystems (Rantakari and Kortelainen 2005; Einola et al. 2011; Teodoru et al. 2011; Weyhenmeyer et al. 2012; Denfeld et al. 2015a). The boreal forest region is considered as one of the most important carbon (C) sinks on land; however, the high density of inland waters in this landscape counteracts this terrestrial C sink (Intergovernmental Panel on Climate Change (IPCC) 2013; Verpoorter et al. 2014; Lauerwald et al. 2015; Hastie et al. 2017). A large source of uncertainty in CO₂ emission from these systems arises from the period of ice-melt in spring and early summer. Boreal lakes typically experience ice-cover during substantial parts of the year; and it is anticipated that the sudden release of accumulated CO₂ at ice-melt accounts for a considerable proportion of the total annual CO₂ flux into the atmosphere (Weyhenmeyer et al. 2011; Karlsson et al. 2013; Jones et al. 2016). However, only a few studies have resolved temporal CO₂ trends under ice and quantified CO₂ emission flux at ice breakup based on direct *in-situ* measurements (Baehr and Degrandpre 2002, 2004; Denfeld et al. 2015a). These studies have demonstrated that the bio-physical environment under ice can be complex, such that large uncertainty remains about the extends and mechanisms of interannual CO₂ flux variability at ice-melt (Denfeld et al. 2018).

In this study, we investigated the impact of river inflow on the spatiotemporal variability in CO₂ concentration and flux in the second largest lake of Europe, Lake Onego (Republic of Karelia, Russia). During three successive years, we resolved vertical and horizontal gradients in, CO₂, DOC and dissolved inorganic carbon (DIC) concentrations and CO₂ fluxes between a river-impacted bay and the central lake area before and after the period of ice-melt. Furthermore, quantified the contribution of sediment and river CO₂ fluxes to under-ice CO₂ accumulation and monitored the partial pressure of CO₂ (pCO₂) in the bay to assess temporal trends of CO₂ from the ice-covered to the open water period and to quantify the CO₂ emission flux at ice-melt. We hypothesized that (1) spatial, seasonal and interannual CO₂ variability would be greater in the river-impacted bay than in the central lake (2) and that the bay would exhibit consistently higher CO₂ concentrations and fluxes to the atmosphere than the central lake due to the river inflow.

Methods

Study site

Lake Onego is located in western Russia and extends between 60.9-62.9°N and 34.3-36.5°E with a surface area of 9720 km². The lake has a mean and maximum depth of 30 and 127 m, respectively,

and its basin shape is defined by several elongated bays in its northern and a large central main basin in its southern part (Fig. 1). While Lake Onego is overall classified as an oligotrophic system, several of the bays exhibit meso- to eutrophic conditions related to human impacts in their watersheds (Sabylina et al. 2010; Efremova et al. 2019). The ice-cover season of Lake Onego typically lasts from December to mid-April (Filatov et al. 2019). River inflow into Lake Onego is provided through 52 large rivers (>10 km length) and more than 1150 smaller tributaries that deliver a total water volume of 13-28 km³ per year (Sabylina et al. 2010). The Shuya river is the second largest tributary that drains a 10'300 km² catchment of ~70 % boreal forest and ~30 % wetlands and lakes and delivers 23 % of the total annual discharge (Lozovik et al. 2007; Sabylina et al. 2010). The Shuya river water enters the lake through the lake's easternmost bay, the Bay of Petrozavodsk (PB), which has a surface area of 73 km² and a mean and maximum water depth of 16 and 27 m, respectively, and which is considered mesotrophic (Table 1; Sabylina et al. 2010; Efremova et al. 2019). Highest discharge is usually recorded from April to May during the spring melt season and lowest discharge from January to March, when the lake is ice-covered (Filatov et al. 2019).

Field campaigns

In 2015-2017, six sampling campaigns were carried out on Lake Onego with three campaigns taking place in March, when the lake was ice-covered and three campaigns taking place in early June, when the lake was ice-free. In addition, water samples were retrieved biweekly from the river mouth from February to May 2016 in order to resolve temporal changes in CO₂ concentration. The entire lake area enclosed in this study covered about 270 km2 in the western part of the lake including the PB area. Sampling points in the bay followed a transect from the Shuya river mouth towards the central lake, whereas, transects during the open water season in the central lake varied to some extend between years depending on the cruise of the research vessel. Maximum water depths over all sampling stations varied from 5 m at the river mouth to 84 m in the central lake (Fig.1).

CO₂, DIC, and DOC sampling and analysis

To obtain the vertical and horizontal distribution of dissolved CO₂, dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) concentrations, water samples were taken at each station (Fig. 1) with a customized Ruttner sampler. At the river inflow, samples were retrieved from 0.5 m depth. Within the bay area, water samples for vertical profiles were obtained from up to five different locations with a depth resolution of 2-3 m starting at the lake surface. In the central lake, up to three different locations were sampled for vertical profiles and the depth resolution varied between 4 and

144 15 m, depending on the maximum water depth. In addition to the vertical profiles, water samples 145 were retrieved from the lake surface along two transects in June 2016 (TS, TB) and one transect (T0) 146 in June 2017, with a horizontal spacing of about 1-2 km between sampling points.

Samples for CO_2 were analysed as described by Sobek et al. (2003). Triplicates of each water sample were immediately transferred into 60 ml syringes, which were filled bubble-free, and adjusted to a volume of 30 ml. A headspace of 30 ml ambient air was added to each syringe and ambient air was collected in addition in separate syringes to correct for atmospheric CO_2 . The gas and water phase were then equilibrated by shaking the syringes for 2 min, and the pCO_2 in the headspace was measured with a portable infrared gas analyser (EGM-4, Environmental Gas Analyser). In addition to CO_2 , we also analysed the inorganic carbon (DIC) concentration, which followed the same procedure, except that a 20 ml water volume in the syringe was acidified with 100 μ L of diluted hydrochloric acid (HCl, 3.7%) and a headspace of 40 ml was added. Both CO_2 and DIC concentrations in the water were calculated via Henry's constant (Weiss 1974) after correction for the atmospheric pressure and the amount of CO_2 added to the headspace volume from the ambient air.

For analysing the dissolved organic carbon (DOC) concentration, water was filtered through prerinsed 0.45 µm cellulose membrane filter, acidified with HCl 3.7%, and kept at 4°C until analysis in the laboratory at EAWAG (Switzerland) using a Shimadzu TOC-L.

In-situ measurements of CO₂ and abiotic conditions

To measure the temporal course in CO_2 near the ice cover and near the lake bottom over the ice-melt period, two CO_2 sensors (ProOceanus Mini CO_2^{TM} , range: 0-5000 µatm, accuracy: \pm 100 µatm), were deployed at the bay centre in March 2015 and 2016 (Fig. 1, point IC). In 2015, the water depths corresponded to 3 m and 25 m, and in 2016 to 4.5 m and 26 m, respectively. The logger recorded pCO_2 at hourly intervals until retrieval in early June in each of the years. Sensors were calibrated before and after each campaign and data corrected for drift (0.5% per month).

In addition, temperature was recorded every 30 minutes on a separate mooring. In 2015, thermistors (RBRsolo) were installed at 5 and 25 m water depth about 50 m away from the CO₂ mooring. In 2016, temperature sensors (T-RBR and Vemco) were deployed on the CO₂ mooring, in equal

distances of 2 m between 4 and 26 m water depth. During sampling campaigns in June, temperature

and oxygen profiles were taken at each measurement site using CTD probes (Sea & Sun or

175 RBRconcerto).

Sediment CO₂ flux experiments

In March 2016, nine sediment cores were retrieved from three different sides of Lake Onego in order to quantify the flux of CO₂ from sediment into water via incubation experiments (Supplementary Information, Table S1). The upper five cm of sediment and the overlying ~20 cm of water were immediately transferred to incubation cores, without disturbing the sediment. To avoid mixing during transportation of the samples, the lid of each incubation core, which contains a tubing, was carefully pressed to the sediment surface, so that the overlying water could be removed and collected in bottles. All samples were stored dark and cold during transportation and upon experiment start at the laboratory at Uppsala University, where cores were carefully re-filled with the respective lake water sample, via the tubing in the lid, and without creating any visible disturbance of the sediment. The incubations followed the method described in (Gudasz et al. 2010), where the CO₂ flux is determined as the rate of change in DIC concentration in the water volume overlying the sediment (see Supplementary Information).

River discharge, climate data and ice-breakup dates

Discharge data of the Shuya River were provided by the All-Russian Scientific Institute of Hydrometeorological Information, and were available for the period 1955-2017 as monthly mean values. Air temperature, precipitation and wind speed data from the meteorological station in Petrozavodsk were obtained from the open database at http://rp5.ru and available as three-hour mean values for the period February 2005 to December 2017. The period of ice-breakup in PB for the years 2015-2017 was estimated from climate and in-situ monitoring data (see section In-situ measurements of CO₂ and abiotic conditions) and validated by satellite images from LANCE-MODIS Terra, which were available on a daily basis (Supplementary Information, Fig. S2). In addition, air temperature, wind speed, and wind direction during early summer campaigns were also recorded from the meteorological station mounted on top of the research vessel.

CO₂ flux calculations

The diffusive flux of CO₂ between lake and atmosphere was calculated using the boundary layer

model as described by *Liss & Slater* [1974]:

$$F_{CO2} = k_{CO2} \bullet M_{CO2} \bullet (C_w - C_{eq}) \tag{1}$$

where F_{CO_2} is the flux of CO₂ above the air-water interface in mmol m⁻² h⁻¹, k_{CO_2} the transfer velocity of CO₂ in m h⁻¹, M_{CO_2} the molar mass of CO₂, C_w the measured near-surface water molar concentration of CO₂, and C_{eq} the molar concentration of CO₂ in the surface water that is in equilibrium with the atmospheric concentration at surface water temperatures. The transfer velocity of CO₂ was estimated at standard conditions k_{600} (Schmidt number 600) using the equation of *Liss & Merlivat* [1986]:

$$k_{CO2} = k_{600} \cdot (Sc / 600)^n \tag{2}$$

where Sc is the Schmidt number (-) of CO_2 at water surface temperature (Wanninkhof 1992) and n is for wind speed $U_{10} \le 3.7$ m s⁻¹ and for $U_{10} > 3.7$ m s⁻¹. The gas transfer velocity k_{600} was calculated using the equation of Cole & Caraco [1998]:

$$k_{600} = 2.07 + 0.215 \cdot U_{10}^{1.7} \text{ cm h}^{-1}$$
 (3)

and additionally from the equations by *Crusius & Wanninkhof* [2003]:

216 for
$$U_{I0} < 3.7 \text{ m s}^{-1}$$
: $k_{600} = 0.72 \cdot U_{I0} \text{ cm h}^{-1}$

for
$$U_{10} > 3.7 \text{ m s}^{-1}$$
: $k_{600} = 4.33 \cdot U_{10} - 13.3 \text{ cm h}^{-1}$ (4)

- The C_{eq} of CO₂ was calculated according to *Wiesenburg & Guinasso* [1979], whereby the pCO₂ in the atmosphere was set to 397 µatm. For better comparability and to upscale CO₂ fluxes over the entire study area, we also calculated daily CO₂ fluxes (mmol m⁻² d⁻¹) using the median recorded U_{I0} (4 m s⁻¹) for all stations and dates. The deviation in flux values between the two k_{600} models was about 7% at this wind speed, and were reported as the mean value obtained from both of the two relationships.
- The same approach was applied to the CO₂ sensor data to obtain CO₂ emission fluxes at ice-melt and lake overturn in 2015 and in 2016. In 2016, however, the sensor at 4.5 m water depth had stopped measuring just before ice breakup occurred. Therefore, CO₂ fluxes could only be estimated from the

data recorded at 26 m water depth during a short a period of complete mixing conditions (see Supplementary Information).

Statistical analysis

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The sampling campaigns generated a spatial dataset of in total 349 CO₂ observations including 30 water column profiles and 71 surface water measurements obtained within 4-6 weeks before and after ice melt each year. In addition, the sensor measurements from ice-cover to open water periods revealed temporal records of in total 15 482 hourly *p*CO₂ measurements in the bay center.

For comparing CO₂ concentrations, water column profile data were interpolated over depth to calculated mean values and the coefficient of variation (CV, %) for each profile. Mean CO₂ concentrations were non-normally distributed (Shapiro Wilk's test, p<0.01), therefore we used nonparametric Wilcoxon test to evaluate differences in mean CO₂ concentrations between bay and central lake as well as between seasons and between years. Furthermore, we tested whether CO₂ concentrations in the water column were correlated to DIC, DOC, and DO concentrations during the different seasons. Seasonal trends within the river CO₂ dataset of 2016 dataset and in-situ CO₂ measurements (non-normally distributed, p < 0.0001) were calculated by applying a Mann-Kendall test to the different periods (ice-covered, break-up/mixing, and stratified period), where significant increases and decreases in CO₂ concentration were calculated as the median slope (i.e., Theil-Sen estimator) of multiple regression lines through pairs of data points. In addition, synchrony (S) between surface and bottom water measurements was tested by pairwise cross-correlation of the time series within each year, where high synchrony is indicated by values near 1 and low synchrony by values near 0. Interannual variability in climate and discharge conditions in the PB area where assessed from the two long-term datasets. We calculated mean air temperatures and precipitation for the ice-melt periods and for the timespans between ice-breakup dates and the early June campaigns as well as the 95% confidence intervals for the same periods of the preceding decade. Furthermore, we tested for linear and non-linear relationships between discharge and precipitation data at the monthly, seasonal and annual timescale. All analyses were performed in R (R Development Core Team 2011) using the stats, mblm, Kendall, and synchrony packages.

254 Results

Variability in spring climate, discharge, ice breakup dates and lake stratification

- The years 2015, 2016, and 2017 were the wettest on the 13-year record and showed 83-172 % higher amounts of precipitation from January to May, than the mean of the preceding decade (Supplementary Information, Fig. S3). However, discharge and precipitation did not reveal any clear relationships at monthly, seasonal and interannual time scale (Filatov et al. 2019). Discharge from January to June followed the long-term pattern (Fig. S2) with lowest values in March (25-48 m³ s⁻¹) and highest values in May (223-335 m³ s⁻¹). The intensity of discharge from January to March differed however between years, with a $\sim 50\%$ lower average rate in 2015 (29 \pm 5 m³ s⁻¹) than in 2016 $(57 \pm 5 \text{ m}^3 \text{ s}^{-1})$ and in 2017 $(58 \pm 9 \text{ m}^3 \text{ s}^{-1})$. The average discharge from April to June, in contrast, reached a similar intensity in 2015 and 2016 (171 \pm 55 m³ s⁻¹, 161 \pm 36 m³ s⁻¹), but was about 30% higher in 2017 (212 \pm 72 m³ s⁻¹).
- Air temperatures differed considerably between the three years. In 2015 and 2016, mean air temperatures from March to mid-April were above the freezing point of 0 °C (1.3 and 0.2 °C), whereas spring in 2017 was considerably colder, with an average air temperature of -0.6 °C. This differences in spring air temperatures affected the timing of ice-breakup dates. In 2015 and 2016, the ice-started to crack in mid-April, however, while the total melt-process lasted only 3 days in 2015, it took about two weeks in 2016. In 2017, by contrast the complete ice-melt did not occur before the beginning of May (Figs. S2).

The timespan from the ice-breakup dates to the field campaigns in early June equaled 55, 40, and 30 days in 2015, 2016, and 2017, respectively; and air temperatures during these periods averaged 7.3 °C, 12.3 °C, and 5.0 °C. For comparison, the 95% CI air temperature range considering the same three periods over the preceding 10 years (2005-2014) were 6-8 °C, 8-9 °C, and 9-10 °C, which shows that the PB area experienced a relatively warm period after ice-break in 2016, and a relatively cold period in 2017 (Fig. S3). *In-situ* temperature records revealed a mixing period after ice-melt that lasted about 4 weeks in 2015, but only 8 days in 2016. By early June 2015 and 2016, the water column in the entire bay was thermally stratified, with surface water temperatures of 10-16 °C and 15-16 °C. Sampling points in the central lake revealed colder temperatures of 4 and 7 °C. The conditions in June 2017 differed considerably from the those of the two previous years, with surface water temperatures of 6-9 °C in the bay and 5-3 °C in the central lake. A thermal bar was observed 8 km outside the bay area, which separated the warmer water of the bay region from the still inversely

stratified open lake. This thermal 4 °C-front was observed between the bay and point C3 in 2017, while it was already ahead of point C2 in 2015 and 2016 (Fig. 2).

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Spatiotemporal variability in CO₂ concentrations

CO₂ concentrations at the river mouth varied between 45 and 168 μ mol L⁻¹. The lowest values (≤ 52 289 umol L⁻¹) were obtained in early June, whereas all other sampling dates of the ice-covered periods 290 and the spring melt season 2016 revealed CO_2 concentrations ≥ 105 µmol L⁻¹. The biweekly CO_2 291 dataset of the river mouth from 2016 indicated an overall decline in CO₂ concentrations from winter 292 293 to early summer (Mann-Kendall's $\tau = -0.4$, p < 0.05, n = 10, Supplementary Information, Fig. S6). CO₂ concentrations in the lake varied between 1 and 276 μmol L⁻¹ (pCO₂; 10-3892 μatm), with the 294 lowest values observed in surface waters in the central basin in early June, and the highest values in 295 296 bottom water layers of the bay during ice-covered periods. The bay showed overall a larger CO₂ concentration range (16-276 μ mol L⁻¹) and a higher vertical CO₂ variability (median CV = 17 %) than 297 the central basin (1-62 μ mol L⁻¹; median CV = 10%; Figs. 2,3,4). There were strong seasonal changes 298 299 in the spatial CO₂ variability of the bay. During ice-covered periods in 2016 and 2017, CO₂ maxima (> 100 μmol L⁻¹) were observed at intermediate water column depths and in bottom water layers near 300 the sediment (Figs. 3 and 4). Horizontally, CO₂ concentrations decreased from the river mouth (120-301 131 µmol L⁻¹) towards the central basin (31-40 µmol L⁻¹). These horizontal gradients were less 302 pronounced in early June, when CO₂ concentrations at the river mouth were 60% lower, and mean 303 water column CO_2 concentrations in the bay 7-38% lower than in March (p<0.001). Furthermore, we 304 305 found considerable interannual variability in CO₂ concentrations of the bay, where mean water column CO₂ concentration were significantly lower in 2015 than in 2016 and 2017. These differences were 306 307 not observed in the central lake (Table 2). The in-situ records at the bay center (Fig. 4) revealed an average (±SD) CO₂ concentration under ice 308 of $65 \pm 5 \mu mol L^{-1}$ at 3 m depth in 2015 (3 weeks of measurements) and of $98 \pm 11 \mu mol L^{-1}$ at 4.5 m 309 depth in 2016 (4 weeks of measurements). A positive trend of 1 µmol L⁻¹d⁻¹ was detected in 2015 310 (Mann-Kendall's τ =0.56, p<0.0001, n=431), however, no trend was detected for under-ice 311 measurements in 2016 at 4.5 m depth. The deep water sensor data, provided a highly different pattern. 312 313 In 2015, CO₂ concentrations at 25 m water depth, fluctuated strongly between 58-256 µmol L⁻¹ varying about 7 times stronger (CV=49%) than CO₂ at 3 m water depth (CV=7%). Similarly, CO₂ 314

- concentrations varied strongly at 26 m depth in 2016 (76-257 μ mol L⁻¹, CV = 23%), but revealed in
- addition a positive trend of 4 μ mol L⁻¹d⁻¹ (34 days, $\tau = 0.60$, p < 0.0001, n = 802).
- During the 4-week mixing period in 2015, the CO₂ concentrations at 3 m and 25 m water depth showed
- a high synchrony (S=0.94; mean pairwise correlation: 0.88 for n=600) with a decrease of 2 μ mol L⁻¹d⁻¹
- 319 1 ($\tau = -0.74$ and -0.58, p < 0.0001 and n = 360 each) over the first two weeks. Thereafter, CO₂
- 320 concentration remained rather stable but started to, fluctuated in a more asynchronous manner in the
- two depth layers during stratified conditions ($40 \pm 3 \mu mol L^{-1}$ and $49 \pm 6 \mu mol L^{-1}$ at 3 m and 25 m
- water depth).

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- 323 In 2016, when the ice started to break in mid-April, CO₂ at 4.5 m sensor stopped measuring. At 26 m
- water depth, CO₂ decreased for two weeks at a rate of -12 μ mol L⁻¹d⁻¹ ($\tau = 0.60$, p<0.0001, n=802)
- and remained stable at about $88 \pm 2 \mu mol L^{-1}$ for the 8-days mixing period. About one week after
- 326 stratification was established, later, CO₂ concentration at 26 m water depth started to increase at a rate
- of 2.2 μ mol L⁻¹d⁻¹ ($\tau = 0.77$, p < 0.0001, n = 481) over about one months.

Relation of CO₂ with DOC and DIC and DO concentrations

- DOC and DIC concentrations varied between 0.47-1.58 mmol L⁻¹ and between 0.14-0.65 mmol L⁻¹,
- respectively (Table 2). Similar to CO₂, mean DOC concentrations in the bay were higher in 2016 and
- 332 2017 than in 2015, however, there was no difference in DOC concentrations between seasons. During
- ice-covered periods, CO₂ and DOC concentrations correlated positively; and the correlation was
- strongest when CO₂-rich bottom water layers were excluded from the relationship ($R^2 = 0.84$,
- 335 p < 0.0001, n = 59; Fig. S5). In early June, by contrast, DOC did not reveal any correlation with CO₂
- 336 (Supplementary Information, Fig. S8).
- 337 DIC concentrations did not differ between years, but exhibited seasonal differences. During ice-
- covered periods, DIC concentrations correlated negatively with CO₂ concentrations in the water
- column, excluding the bottom water layers ($R^2 = 0.38$, p < 0.0001, n = 83; Fig. S7). In bottom waters,
- 340 by contrast, CO₂ and DIC concentrations exhibited a strong positive correlation indicating a
- contribution of CO₂ from sediments into the lake water ($R^2 = 0.93$, p < 0.0001, n = 15; Fig. S7). In early
- June, DIC concentrations were weakly positively correlated with CO_2 concentrations ($R^2 = 0.24$,
- 343 p < 0.0001, n = 86; Fig. S5), however there was no discrepancy between water column and bottom
- water samples as it was observed in March samples. Overall, from March to June, mean DIC

- concentrations in the bay area had declined to similar extends as CO₂ concentrations with on average 54% lower values at the river mouth and 25-5% lower values along the central axis of the bay area, which indicates that -irrespective of the temporal variability - there was an overall reduction in water column inorganic carbon within the bay in early June as compared to in March.
- DO concentrations correlated negatively with CO₂ concentrations in early June. The strongest relationship ($R^2 = 0.77$, p < 0.001; n = 49) was found for data from June 2017, when maximum values in DO concentration (as well as saturation) coincided with minimum values in CO₂ concentrations near the location of the thermal bar (Fig. 2). During stratified conditions in June 2015 and 2016, CO₂ and DO concentrations correlated negatively but to different degrees in epilimnetic (< 5 m depth; $R^2 = 0.49$, p < 0.001; n = 36;) and in hypolimnetic waters of the bay ($R^2 = 0.41$, p < 0.001, n = 27).

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Spatiotemporal variability in CO₂ fluxes

- 358 CO₂ fluxes from water to the atmosphere ranged from -44 to 162 mmol m⁻² d⁻¹ at actual wind speeds
- and from -16 and 62 mmol m⁻² d⁻¹ when k_{CO2} was calculated using the median wind speed of 4 m s⁻¹
- 360 (Table 3). In the following, we refer for better comparability of the general patterns of CO₂ uptake
- and emission to the latter range of values.
- The CO₂ emission from the bay during the 4-week mixing period after ice-melt in 2015 averaged 11
- ± 4 (SD) mmol m⁻² d⁻¹, which amounts to a total CO₂ loss of ~260 t C when extrapolated to the entire
- bay area. The CO₂ measurements during the 8-days mixing period in 2016, returned an average flux
- of 30 ± 5 mmol m⁻² d⁻¹ (see supplement). For comparison; integrating over the same time span of the
- 366 first week of mixing after ice-melt in 2015 and 2016 the values from the two years return initial CO₂
- losses of ~100 t C and of (at least) 180 t C, respectively. For comparison, CO₂ flux estimates for the
- 368 central lake area were substantially lower with 2 to 7 mmol m⁻² d⁻¹ at ice breakup.
- To assess the contribution of different sources to the CO₂ stored in the bay under ice (~1800 t C in
- 370 mid-March 2016) and to the emission flux at ice-melt, we used the sediment and river datasets from
- 371 2016. Sediment incubation experiments returned CO_2 fluxes of 3.8 \pm 2.0 mmol m⁻² d⁻¹
- 372 (Supplementary Information, Table S1), which matches with the trend observed by the deep water
- sensors in 2016 (4 µmol L⁻¹ d⁻¹) as well as with values found in other studies addressing sediment
- 374 CO₂ fluxes at cold and oxic conditions (Gudasz et al. 2010; MacIntyre et al. 2018). There were no
- 375 significant differences between CO₂ fluxes in cores from the three sampling locations and we used

the average rate to estimate the magnitude of sediment CO₂ flux for the entire bay. This number equaled 3 t C d⁻¹ (2-4 t C d⁻¹, 95% CI). Since the freeze up of the bay in early January, the water volume provided by the river accounted for about one third of the bay water volume (disregarding mixing of water masses with the central lake), and the CO₂ influx averaged 8 t C d⁻¹ (7-10 t C d⁻¹) over this period. Together, these values indicate that the river and the sediments contributed 30-40% and 8-17%, respectively, to the total CO₂ content in the bay during the ice-covered period. However, the contribution of the river likely increased prior to ice-melt as the average river CO₂ influx increased to 22 t C d⁻¹ (19-25 t C d⁻¹) during the month of April.

In early June, CO₂ fluxes varied between 6-32 mmol m⁻² d⁻¹ in the bay. Only one measurement point at the outer edge of the bay (PB3) in June 2016 revealed CO₂ uptake by the lake (-1 mmol m² d⁻¹), which indicates that this area was overall an emitter of CO₂ to the atmosphere during the spring season of the three years. Measurement points in the central lake revealed both uptake and emission flux during early June (-16 to 25 mmol m⁻² d⁻¹). The two transects in June 2016 indicated a larger area of CO₂ uptake that extended from the shoreline northeast of the bay to the lake center (Fig. 5, -14 to 6 mmol m⁻² d⁻¹; median: -5 mmol m⁻² d⁻¹). In June 2017, in contrast, all measured locations in the central lake were emitting CO₂ (5-25 mmol m⁻² d⁻¹). The lowest values from this range were obtained for sampling points near the thermal bar, where maxima in dissolved oxygen as well as in chlorophyll-a concentrations were observed (Table 1, Fig 2).

Discussion

The impact of river inflow on spatiotemporal CO₂ variability

Rivers tend to be more saturated in CO₂ than lakes and account for a significantly higher share of the global inland water CO₂ emission (Raymond et al. 2013; Lauerwald et al. 2015). However, while the hydrological control of CO₂ in lakes has been emphasized in various studies (e.g., Einola et al. 2011; McDonald et al. 2013; Weyhenmeyer et al. 2015), only limited knowledge exists about the riverine influence on the spatiotemporal variability of CO₂ in lakes over seasons and years (Pacheco et al. 2015), and particularly not over the ice-covered periods.

In support of our first hypothesis, the spatial dataset of Lake Onego revealed a substantially larger CO₂ variability in the river-impacted bay than in the central lake, with the most profound changes at the seasonal (i.e., from ice-covered to open-water periods) time-scale. Water at the river mouth was

2-6 times more saturated in CO₂ than the atmosphere which is similar to the range of values observed in other large boreal rivers (Campeau and Del Giorgio 2014). Water in the central lake, in contrast, maintained CO₂ concentrations around atmospheric equilibrium concentrations, which is lower than median values (540-980 μatm) reported for 37 large boreal lakes in Finland during the winter, summer, and autumn season (Rantakari and Kortelainen 2005). The Shuya river was the main driver of the spatial configuration of CO₂, DOC, and DIC concentrations in the PB area, with the most apparent influence during the winter period. The vertical and horizontal concentration gradients, which developed during low discharge conditions from the river mouth towards the central lake, reflect the intrusion and gradual mixing of CO₂- and DOC-rich river water with the more diluted water of the lake. DIC concentration gradients showed an opposite pattern to those of CO₂ and DOC over most of the water column, due to the lower DIC content in the river than in the lake water (Fig. 2 and Fig. S3).

The CO₂ concentration in bottom waters of the bay, in contrast, was controlled by CO₂ diffusing from the sediments as indicated by the high CO₂ concentration values and the positive correlation of CO₂ with DIC in these layers (Figs. 2,3,4, and Supplementary Information, Fig. S7). Our calculations from the 2016 dataset demonstrate that riverine CO₂ flux was about twice as important for the under-ice CO₂ budget of the bay as the sediment CO₂ flux. One hand, this ratio is likely to deviate between years with different discharge conditions, however, on the other hand the contribution of CO₂ by respiration in sediments may also be seen as an indirect influence of the river inflow. About 60% of the organic matter in PB originates from terrestrial sources and the bay area also acts as the primary deposition site for river particles (Sabylina et al. 2010). We therefore conclude that CO₂ dynamics under ice and the emission flux at ice-melt from this bay are largely driven by river inflow, and that similar condition could apply to several of the other bays in the north of PB. For instance, the 225 km² large bay of Kondopoga and the 80 km² large bay of Lizhma exhibit a similar mean depth as PB and receive water from two of the major tributaries of the lake (Podsechin et al. 2009; Sabylina et al. 2010). The spatial footprint of riverine CO₂, however, will vary with local morphometry and flow conditions, and it is therefore difficult to extrapolate from the PB area to other river inflow sites. However, regardless of the site-specific flow patterns, all tributaries together will deliver large quantities of CO₂ to the lake. It has been shown that fluvial organic matter inputs scale proportionally with discharge around the lake such that comparable conditions can be anticipated for CO₂ (Sabylina et al. 2010). Taking into account both spatial and temporal differences in CO₂ concentrations of the bay and the central lake at ice-melt in 2015 and 2016, indicates that the PB area emitted 8 (2-15, 95%) CI) times as much CO₂ as an equally-sized area in the central lake, which illustrates the need to integrate the various inflow regions when quantifying CO₂ emission from this large system.

The spatial variability of CO_2 in early June displayed a highly different pattern from the conditions found in March under ice. (Figs. 2, 3 and Supplementary Information, Fig. S7). After river discharge had peaked in April and May, both CO_2 and DIC concentrations at the river mouth showed a considerable decrease of ~50%, compared to the values obtained in March, which was probably related to a dilution effect during snowmelt and to decreased DIC export from soils (Kokic et al. 2015). DOC concentrations at the river mouth, in contrast, did not differ between seasons, which might be explained by the fact that DIC and DOC can be exported from different soil horizons during varying runoff conditions (Giesler et al. 2014; Nydahl et al. 2017). However, despite the difference in DOC and DIC changes, both their spatial gradients indicated the path of river intrusion up to 15 km past the bay area in early June. The spatial configuration of CO_2 , however, was disconnected from this pattern and CO_2 concentrations correlated with DO concentrations instead (Fig. 2). Together with observed maxima in chlorophyll-a concentrations in surface waters and at the thermal bar, these pattern demonstrate that biological processes (phytoplankton growth and organic matter breakdown) interfered the physically driven CO_2 signal from the river during this time of the year (Figs. 2, 3; Table 1).

Drivers of interannual CO₂ variability

The bay acted per m² as a consistently higher CO₂ source to the atmosphere than the central lake, which confirms our second hypothesis. However, there were also large interannual differences in the overall spring CO₂ emission from this region. First, our spatiotemporal CO₂ dataset from the ice-covered periods shows that mean water column CO₂ concentrations in the bay were 37-58% lower in March 2015 than in March 2016 and 2017. This lower CO₂ content could be explained by the 50% lower discharge rates during winter 2015 and these in turn to lower amounts of precipitation (Fig. S3). However, while precipitation was overall lower in 2015 than in the two following years (both at the seasonal and annual time scale; Fig. S3) we could not detect any clear relationship in the long-term discharge and precipitation dataset. Nevertheless, the precipitation data of the three study years reveal a considerably wetter spring in comparison to the previous decade; and several studies have shown that fluvial carbon export from soils and the CO₂ emission from rivers and lakes may correlate positively with annual precipitation (Kelly et al. 2001; Rantakari and Kortelainen 2005; Butman and

Raymond 2011; Öquist et al. 2014). It is therefore vital to capture such interannual differences in CO₂ dynamic and their controls at river-inflow sites.

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Second, the temporal courses of CO₂ measured *in-situ* in 2015 and 2016 supports the recent findings that CO₂ does not necessarily accumulate linearly and homogenously distributed under ice but that convective mixing patterns play an important role for CO₂ distribution and emission at ice-melt (Denfeld et al. 2015b, 2018; Pasche et al. 2019). This shows that the interplay of variation in discharge with hydrodynamic conditions under ice have a strong influence on CO₂ dynamics and drive the interannual variability in CO₂ emission flux at ice-melt. In this context, Pacheco et al. (2015) showed that variations in river intrusion depth can determine wether CO₂ is evaded directly into the atmophere during overflow, or dilutes within the water column during underflow conditions. This finding has important implications for assumptions made about CO₂ release at ice melt in large-scale CO₂ emission estimates (Cole et al. 2007; Raymond et al. 2013; Hastie et al. 2017). Although we could not calculate the emission flux for the entire ice-melt period in 2016, due to the CO₂ sensor failure at 4.5 m water depth, the comparison of flux values for the first week of mixing after ice-break in suggests that CO₂ emission was about twice as higher in 2016 than in 2015. There were no in-situ sensor CO₂ records available for the ice-melt and spring mixing period of 2017, however, CO₂ conditions in March 2017 were similar to those in March 2016, and the low water temperatures of the bay in June 2017 indicate that mixing period probably lasted longer than in 2016. Furthermore, CO₂ emission in early June were still considerably higher in 2017 (20 \pm 2 mmol m⁻² d⁻¹ 1) than in 2016 (12 \pm 3 mmol m⁻² d⁻¹). We therefore conclude that the CO₂ emission during spring mixing in 2017 exceeded the emission of the two previous years.

Third, we found large interannual differences in the CO₂ conditions in early June, which can be related to the variable climate of the three spring seasons (Fig S3). Air temperature data revealed an unusual warm and a comparatively cold period after ice-melt in 2016 and 2017, respectively, with consequences for the duration of the mixing period and the development of summer stratification in the lake. The more stable stratification in 2016 may have supported an earlier occurrence of phytoplankton spring blooms that decreased CO₂ values in surface waters during this year (Figs. 2 and S6). The cold and wet spring of 2017 on the contrary resulted in lower water temperatures and a closer proximity of the thermal bar to the bay area, which impacted spring bloom dynamics and subsequently the spatiotemporal CO₂ variability. The conditions during spring 2015 can be seen as an intermediate stage in comparison to the conditions of the other two years. The results reveal that the timing of sampling in relation to the varying spring conditions are crucial for estimating CO₂

fluxes during this time of the year. Continuous, long-term sampling is required to capture such temporal variations, especially during the critical period of ice melt.

Climate warming has implications for the hydrological connectivity between aquatic ecosystems on multiple levels. With shorter ice-cover seasons, earlier onsets of summer stratification, and changing precipitation patterns in northern latitudes, it is vital to understand the mechanisms and their interplay that control CO₂ dynamics in these systems (De Stasio et al. 1996; Lopez et al. 2019). The PB area has lost 20 days of lake-ice cover on average over the past 60 years (Filatov et al. 2019). If this trend persists the ice-covered period might decrease from 5 to less than 3 month by the end of the 21st centur. Furthermore, long-term data of the Shuya river indicate that discharge has been increasing since 1991 during winter months (Filatov et al. 2019). Resolving CO₂ variability in river inflow areas is vital to assess linkages and bottlenecks between systems. Further studies also at other river-inflow areas and over the entire annual cycle are needed in order to capture the whole range of CO₂ variability at these sites and to predict their role in whole-lake CO₂ fluxes under global change.

518 Conclusions

The ice-melt period is a critical time window for CO₂ emission from lakes, however, large-scale estimates presently do not resolve temporal variability and spatial gradients in CO₂ for such systems at all. Our CO₂ dataset for Lake Onego, the second largest lake in Europe, demonstrates large seasonal and interannual differences in CO₂ concentration in a river-impacted bay region and indicates conditions under which substantial parts of the lake can be turned from a CO₂ sink into a CO₂ source at ice-melt. We conclude that the boundaries between aquatic sub-systems (e.g., between river, bay and open lake areas) are highly dynamic in space and time and that resolving these dynamics is crucial to quantify and predict CO₂ emission from large lakes more accurately. Such efforts, however, can only be achieved by integral measurements or modelling of spatial, seasonal, and interannual variability of CO₂ concentrations and fluxes. For future research on large-scale CO₂ flux dynamics, we recommend to better integrate near-shore areas of large lakes because these may add comparatively more uncertainty to whole-lake CO₂ emission estimates than more remote locations.

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References

- Aufdenkampe, A. K., E. Mayorga, P. a Raymond, J. M. Melack, S. C. Doney, S. R. Alin, R. E. Aalto,
- and K. Yoo. 2011. Riverine coupling of biogeochemical cycles between land, oceans, and
- 546 atmosphere. Front. Ecol. Environ. 9: 53–60. doi:10.1890/100014
- Baehr, M. M., and M. D. Degrandpre. 2002. Under-ice CO 2 and O 2 variability in a freshwater lake.
- Biogeochemistry **61**: 95–113.
- Baehr, M. M., and M. D. Degrandpre. 2004. In situ pCO2 and O2 measurements in a lake during
- turnover and stratification: Observations and modeling. Limnol. Oceanogr. **49**: 330–340.
- Butman, D., and P. A. Raymond. 2011. Significant efflux of carbon dioxide from streams and rivers
- in the United States. Nat. Geosci. 4: 839–842. doi:10.1038/ngeo1294
- Campeau, A., and P. A. Del Giorgio. 2014. Patterns in CH4 and CO2 concentrations across boreal
- rivers: Major drivers and implications for fluvial greenhouse emissions under climate change
- scenarios. Glob. Chang. Biol. **20**: 1075–1088. doi:10.1111/gcb.12479
- 556 Chmiel, H. E., J. Kokic, B. A. Denfeld, and others. 2016. The role of sediments in the carbon budget
- of a small boreal lake. Limnol. Oceanogr. **61**: 1814–1825. doi:10.1002/lno.10336
- Cole, J. J., and N. F. Caraco. 1998. Atmospheric exchange of carbon dioxide in a low-wind
- oligotrophic lake measured by the addition of SF6. Limnol. Oceanogr. **43**: 647–656.
- doi:10.4319/lo.1998.43.4.0647
- 561 Cole, J. J., Y. T. Prairie, N. F. Caraco, and others. 2007. Plumbing the Global Carbon Cycle:
- Integrating Inland Waters into the Terrestrial Carbon Budget. Ecosystems 10: 172–185.
- 563 doi:10.1007/s10021-006-9013-8
- Crawford, J. T., N. R. Lottig, E. H. Stanley, J. F. Walker, P. C. Hanson, J. C. Finlay, and R. G.
- 565 Striegl. 2014. CO2 and CH4 emissions from streams in a lake-rich landscape: Patterns, control,
- and regional significance. Global Biogeochem. Cycles **28**: 1–14.
- 567 doi:10.1002/2013GB004661.Received
- 568 Crusius, J., and R. Wanninkhof. 2003. Gas transfer velocities measured at low wind speed over a lake.
- Limnol. Oceanogr. **48**: 1010–1017. doi:10.4319/lo.2003.48.3.1010
- Denfeld, B. A., H. M. Baulch, P. A. del Giorgio, S. E. Hampton, and J. Karlsson. 2018. A synthesis of

- carbon dioxide and methane dynamics during the ice-covered period of northern lakes. Limnol.
- 572 Oceanogr. Lett. doi:10.1002/lol2.10079
- 573 Denfeld, B. A., M. B. Wallin, E. Sahlée, S. Sobek, J. Kokic, H. E. Chmiel, and G. A. Weyhenmeyer.
- 574 2015a. Temporal and spatial carbon dioxide concentration patterns in a small boreal lake in
- relation to ice cover dynamics. Boreal Environ. Res. **20**: 679–692.
- 576 Denfeld, B. A., M. B. Wallin, E. Sahlée, S. Sobek, J. Kokic, H. E. Chmiel, and G. A. Weyhenmeyer.
- 577 2015b. Temporal and spatial carbon dioxide concentration patterns in a small boreal lake in
- relation to ice cover dynamics. Boreal Environ. Res. **20**: 1–14.
- 579 Efremova, T. A., A. V Sabylina, P. A. Lozovik, V. I. Slaveykova, M. V Zobkova, and N. Pasche.
- 580 2019. Seasonal and spatial variation in hydrochemical parameters for Lake Onego (Russia):
- Insights from 2016 field monitoring. Inl. Waters accepted.
- Einola, E., M. Rantakari, P. Kankaala, P. Kortelainen, A. Ojala, H. Pajunen, S. Mäkelä, and L.
- Arvola. 2011. Carbon pools and fluxes in a chain of five boreal lakes: A dry and wet year
- 584 comparison. J. Geophys. Res. Biogeosciences 116: 1–13. doi:10.1029/2010JG001636
- Filatov, N. N., V. Baklagin, T. Efremova, L. Nazarova, and N. Palshin. 2019. Climate change impacts
- on the watersheds of Lakes Onego and Ladoga from remote sensing and in situ data. Inl. Waters
- 587 Accepted.
- Giesler, R., S. W. Lyon, C. M. Mörth, J. Karlsson, E. M. Karlsson, E. J. Jantze, G. Destouni, and C.
- Humborg. 2014. Catchment-scale dissolved carbon concentrations and export estimates across
- six subarctic streams in northern Sweden. Biogeosciences 11: 525–537. doi:10.5194/bg-11-525-
- 591 2014
- 592 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**: 478–481.
- 594 doi:10.1038/nature09383
- Hastie, A., R. Lauerwald, G. Weyhenmeyer, S. Sobek, C. Verpoorter, and P. Regnier. 2017. CO2
- evasion from boreal lakes: Revised estimate, drivers of spatial variability, and future projections.
- 597 Glob. Chang. Biol. 2: 1–18. doi:10.1111/gcb.13902
- 598 Intergovernmental Panel on Climate Change (IPCC). 2013. Climate Change 2013: The Physical
- Science Basis. Working Group I Contribution to the Fifth Assessment Report of the
- Intergovernmental Panel on Climate Change Rep, Cambridge Univ. Press.
- Jones, J. B. J., and P. J. Mulholland. 1998. Carbon Dioxide Variation in a Hardwood Forest Stream:
- An Integrative Measure of Whole Catchment Soil Respiration. Ecosystems 1: 183–196.
- Jones, J. R., D. V. Obrecht, J. L. Graham, M. B. Balmer, C. T. Filstrup, and J. A. Downing. 2016.
- Seasonal patterns in carbon dioxide in 15 mid-continent (USA) reservoirs. Inl. Waters 6: 265–
- 605 272. doi:10.5268/IW-6.2.982
- 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.
- 610 2001. Natural variability of carbon dioxide and net epilimnetic production in the surface waters
- of boreal lakes of different sizes. Limnol. Oceanogr. **46**: 1054–1064.
- doi:10.4319/lo.2001.46.5.1054
- Klaus, M., D. A. Seekell, W. Lidberg, and J. Karlsson. 2019. Evaluations of climate and land
- management effects on lake carbon cycling need to account for temporal variability in CO₂
- concentrations. Global Biogeochem. Cycles. doi:10.1029/2018GB005979
- 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. Biogeosciences **120**: 13–28. doi:10.1002/2014JG002706
- Lauerwald, R., G. G. Laruelle, J. Hartmann, P. Ciais, and P. A. G. Regnier. 2015. Spatial patterns in
- 620 CO2 evasion from the global river network. Global Biogeochem. Cycles 29: 534–554.
- doi:10.1002/2014GB004941.
- 622 Liss, P. S., and L. Merlivat. 1986. Air-Sea Gas Exchange Rates: Introduction and Synthesis, *In* In:
- Buat-Ménard P. (eds) The Role of Air-Sea Exchange in Geochemical Cycling. NATO ASI
- Series (Series C: Mathematical and Physical Sciences), vol 185. Springer, Dordrecht.
- Liss, P. S., and P. G. Slater. 1974. Flux of gases across the Air-Sea interface. Nature 247: 181–184.
- doi:10.1038/247181a0
- 627 Lopez, L. S., B. A. Hewitt, and S. Sharma. 2019. Reaching a breaking point: How is climate change
- influencing the timing of ice breakup in lakes across the northern hemisphere? Limnol.
- 629 Oceanogr. 1–11. doi:10.1002/lno.11239
- 630 Lozovik, P. A., A. K. Morozov, M. B. Zobkov, T. A. Dukhovicheva, and L. A. Osipova. 2007.
- Allochthonous and autochthonous organic matter in surface waters in Karelia. Water Resour. 34:
- 632 204–216. doi:10.1134/S009780780702011X
- Maberly, S. C., P. A. Barker, A. W. Stott, and M. M. De Ville. 2013. Catchment productivity controls
- 634 CO2 emissions from lakes. Nat. Clim. Chang. 3: 391–394. doi:10.1038/nclimate1748
- MacIntyre, S., A. Cortés, and S. Sadro. 2018. Sediment respiration drives circulation and production
- of CO 2 in ice-covered Alaskan arctic lakes . Limnol. Oceanogr. Lett. 3: 302–310.
- doi:10.1002/lol2.10083
- 638 McDonald, C. P., E. G. Stets, R. G. Striegl, and D. Butman. 2013. Inorganic carbon loading as a
- primary driver of dissolved carbon dioxide concentrations in the lakes and reservoirs of the
- contiguous United States. Global Biogeochem. Cycles 27: 285–295. doi:10.1002/gbc.20032
- Natchimuthu, S., I. Sundgren, M. Gålfalk, L. Klemedtsson, and D. Bastviken. 2017. Spatiotemporal
- variability of lake pCO2 and CO2 fluxes in a hemiboreal catchment Sivakiruthika. J. Geophys.
- Res. Biogeosciences **122**: 30–49. doi:10.1002/2016JG003449.
- Nydahl, A. C., M. B. Wallin, and G. A. Weyhenmeyer. 2017. No long-term trends in pCO2 despite

- increasing organic carbon concentrations in boreal lakes, streams, and rivers. Global
- Biogeochem. Cycles **31**: 985–995. doi:10.1002/2016GB005539
- Öquist, M. G., K. Bishop, A. Grelle, L. Klemedtsson, H. Laudon, A. Lindroth, M. B. Wallin, and M.
- B. Nilsson. 2014. The Full Annual Carbon Balance of Boreal Forests Is Highly Sensitive to
- Precipitation. Environ. Sci. Technol.
- Öquist, M. G., M. Wallin, J. Seibert, K. Bishop, and H. Laudon. 2009. Dissolved inorganic carbon
- export across the soil/stream interface and its fate in a boreal headwater stream. Environ. Sci.
- Technol. **43**: 7364–7369. doi:10.1021/es900416h
- Pacheco, F. S., M. C. S. Soares, A. T. Assireu, M. P. Curtarelli, 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**: 147–162. doi:10.5194/bg-12-147-2015
- Paranaíba, J. R., N. Barros, R. Mendonça, A. Linkhorst, A. Isidorova, F. Roland, R. M. Almeida, and
- S. Sobek. 2018. Spatially Resolved Measurements of CO2 and CH4 Concentration and Gas-
- Exchange Velocity Highly Influence Carbon-Emission Estimates of Reservoirs. Environ. Sci.
- Technol. **52**: 607–615. doi:10.1021/acs.est.7b05138
- Pasche, N., H. Hofmann, D. Bouffard, C. J. Schubert, P. A. Lozovik, and S. Sobek. 2019.
- Implications of river intrusion and convective mixing on the spatial and temporal variability of
- under-ice CO2. Inl. Waters **Accepted**.
- Podsechin, V., H. Kaipainen, N. Filatov, T. Frisk, A. Paananen, A. Terzhevik, and H. Vuoristo. 2009.
- Development of Water Protection of Lake Onega. Finnish Environ. **36**: 0–39.
- Rantakari, M., and P. Kortelainen. 2005. Interannual variation and climatic regulation of the CO2
- 667 emission from large boreal lakes. Glob. Chang. Biol. 11: 1368–1380. doi:10.1111/j.1365-
- 668 2486.2005.00982.x
- Raymond, P. a, J. Hartmann, R. Lauerwald, and others. 2013. Global carbon dioxide emissions from
- inland waters. Nature **503**: 355–9. doi:10.1038/nature12760
- Sabylina, A. V., P. a. Lozovik, and M. B. Zobkov. 2010. Water chemistry in Onega Lake and its
- tributaries. Water Resour. **37**: 842–853. doi:10.1134/S0097807810060102
- 673 Schilder, J., D. Bastviken, M. van Hardenbroek, P. Kankaala, P. Rinta, T. Stötter, 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
- 676 Sobek, S., G. Algesten, A. K. Bergström, M. Jansson, and L. J. Tranvik. 2003. The catchment and
- climate regulation of pCO2 in boreal lakes. Glob. Chang. Biol. 9: 630–641. doi:10.1046/j.1365-
- 678 2486.2003.00619.x
- 679 De Stasio, B. T., D. K. Hill, J. M. Kleinhans, N. P. Nibbelink, and J. J. Magnuson. 1996. Potential
- effects of global climate change on small north-temperate lakes: Physics, fish, and plankton.
- Limnol. Oceanogr. **41**: 1136–1149. doi:10.4319/lo.1996.41.5.1136

682 Teodoru, C. R., Y. T. Prairie, and P. A. del Giorgio. 2011. Spatial Heterogeneity of Surface CO2 683 Fluxes in a Newly Created Eastmain-1 Reservoir in Northern Quebec, Canada. Ecosystems 14: 684 28-46. doi:10.1007/s10021-010-9393-7 685 Tranvik, L. J., J. A. Downing, J. B. Cotner, and others. 2009. Lakes and reservoirs as regulators of 686 carbon cycling and climate. Limnol. Oceanogr. 54: 2298–2314. 687 doi:10.4319/lo.2009.54.6 part 2.2298 Verpoorter, C., T. Kutser, D. a. Seekell, and L. J. Tranvik. 2014. A Global Inventory of Lakes Based 688 689 on High-Resolution Satellite Imagery. Geophys. Res. Lett. 41: 6396–6402. 690 doi:10.1002/2014GL060641 691 Wallin, M. B., T. Grabs, I. Buffam, H. Laudon, A. Ågren, M. G. Öquist, and K. Bishop. 2013. 692 Evasion of CO2 from streams - The dominant component of the carbon export through the 693 aquatic conduit in a boreal landscape. Glob. Chang. Biol. 19: 785-797. doi:10.1111/gcb.12083 694 Wanninkhof, R. H. 1992. Relationship between wind speed and gas exchange. J. Geophys. Res. 97: 695 7373-7382. doi:10.1029/92JC00188 696 Weiss, R. F. 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Mar. 697 Chem. 2: 203–215. 698 Weyhenmeyer, G. a., P. Kortelainen, S. Sobek, R. Müller, and M. Rantakari. 2012. Carbon Dioxide in 699 Boreal Surface Waters: A Comparison of Lakes and Streams. Ecosystems 15: 1295–1307. 700 doi:10.1007/s10021-012-9585-4 701 Weyhenmeyer, G. A., S. Kosten, M. B. Wallin, L. J. Tranvik, E. Jeppesen, and F. Roland. 2015. 702 Significant fraction of CO2 emissions from boreal lakes derived from hydrologic inorganic 703 carbon inputs. Nat. Geosci. 8: 933–936. doi:10.1038/NGEO2582 704 Weyhenmeyer, G. A., D. M. Livingstone, M. Meili, O. Jensen, B. Benson, and J. J. Magnuson. 2011. 705 Large geographical differences in the sensitivity of ice-covered lakes and rivers in the Northern 706 Hemisphere to temperature changes. Glob. Chang. Biol. 17: 268–275. doi:10.1111/j.1365-707 2486.2010.02249.x 708 Wiesenburg, D. A., and N. L. Guinasso. 1979. Equilibrium Solubilities of Methane, Carbon 709 Monoxide, and Hydrogen in Water and Sea Water. J. Chem. Eng. Data 24: 356–360. 710 doi:10.1021/je60083a006 711 Worrall, F., and A. Lancaster. 2005. The Release of CO2 from Riverwaters – the Contribution of 712 Excess CO2 from Groundwater. Biogeochemistry 76: 299-317. doi:10.1007/s10533-005-6449-4 713 714 715 716

Figure captions

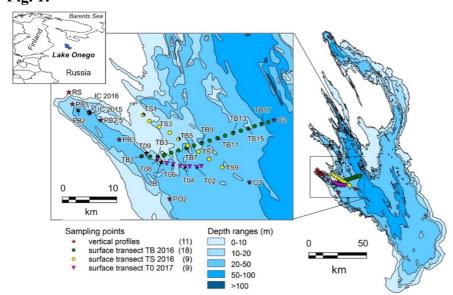
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- Fig. 1: Geographic location and bathymetric map of Lake Onego including sampling stations (red stars) and surface measurements along transect during ice-free conditions in June 2016 (TS, yellow dots; TB, orange dots) and in June 2017 (T0, purple dots).
- Fig. 2: Transects of water temperature (°C), dissolved oxygen saturation (%), CO₂ concentrations (μmol L⁻¹), DIC and DOC concentrations (mmol L⁻¹) between the entry of the Shuya river and the central basin of Lake Onego, measured in June 2015 (left panel), 2016 (center panel), and 2017 (right panel). Dashed black lines indicate the transition from the Bay of Petrozavodsk to the central main basin. The dashed white lines mark the location of the thermal bar in June 2017.
- Fig. 3: CO₂ concentration (μmol L⁻¹), DIC and DOC concentration (mmol L⁻¹) along the sampling stations between the entry of the Shuya River (RS) and the transition of Petrozavodsk Bay to the central basin of Lake Onego (PB3), measured during ice-cover periods in March 2016 (left panel) and 2017 (right panel).
- Fig. 4: Temporal course of CO₂ concentrations (μmol L⁻¹) at 3/4.5 m (surface, black line) and at 25/26 m (near-bottom, grey line) water depth in 2015 (a) and 2016 (b). The periods of ice cover are indicated by darker shaded areas and the ice break-up period by lighter shaded areas. The vertical dashed lines show the beginning of the stratified period. Note the log scale on the y-axis.
- Fig. 5: Lateral variability in CO₂ flux to the atmosphere (mmol m⁻² d⁻¹) in the Bay of Petrozavodsk and the central basin of Lake Onego on 3rd-7th June 2016. Fluxes were calculated using the median wind speed (4 m s⁻¹) over the area. Sampling stations are marked as open circles.

739 Figures

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740 Fig. 1:



742 Fig. 2:

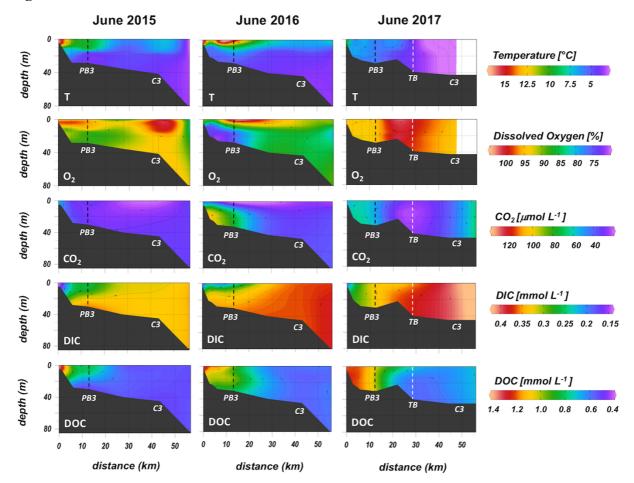


Fig. 3:

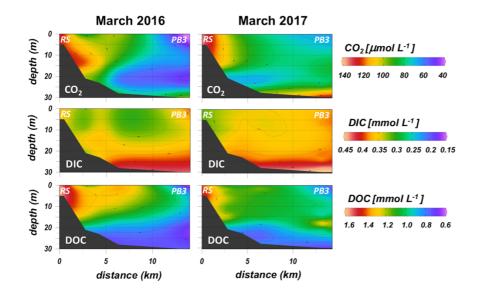
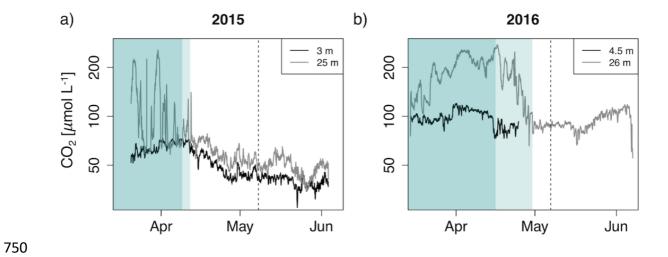
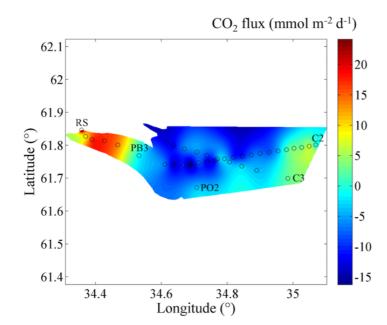


Fig. 4:749



751 Fig. 5:



Tables

Table 1: Nutrient and chlorophyll-a contents at the Shuya River mouth and in Lake Onego.
Nutrient values are given as mean water column concentrations and chlorophyll-a as the total
concentration range obtained during winter and spring sampling campaigns from 2015-2017
(Efremova et al. 2019, Suarez et al. 2019).

Site	\mathbf{Z}_{\max}	TN	TP	chlorophyll-a
	[m]	$[mg L^{-1}]$	$[\mu g \ L^{\text{-}1}]$	[µg L ⁻¹]
Shuya River mouth	5	0.52-1.04	35-37	-
Bay of Petrozavodsk	27	0.44-0.51	20-23	0.5-6.1
Central lake basin	127	0.37-0.40	6-8	0.5-1.5*
Thermal bar (2017)	21	-	-	4.4-8.9*

770 *June data only

Table 2: Water column CO₂, DIC, and DOC concentrations for several stations in Lake Onego, obtained from vertical profiles in March and June 2015, 2016, and 2017. Values denote mean and standard deviation of linearly interpolated profile data.

Location	CO ₂ [µmol L ⁻¹]		DIC [m	mol L ⁻¹]	DOC [mmol L-1]	
Year	March	June	March	June	March	June
River Shuya						
2015	120	52	0.33	0.14	1.18	1.33
2016	129	45	0.29	0.17	1.54	1.34
2017	131	52	0.31	0.15	1.58	1.50
<i>PB-1</i>						
2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2016	104 ± 17	86 ± 19	0.21 ± 0.02	0.31 ± 0.03	1.24 ± 0.13	1.04 ± 0.06
2017	97 ± 14	62 ± 1	0.35 ± 0.02	0.27 ± 0.00	1.11 ± 0.09	1.23 ± 0.03
C (bay centre)						
2015	52 ± 23	34 ± 3	0.37 ± 0.04	0.28 ± 0.03	0.67 ± 0.03	0.79 ± 0.10
2016	82 ± 18	81 ± 21	0.22 ± 0.02	0.30 ± 0.06	1.07 ± 0.02	1.02 ± 0.15
2017	79 ± 7	62 ± 1	0.37 ± 0.02	0.28 ± 0.00	0.97 ± 0.12	1.20 ± 0.02
<i>PB-3</i>						
2015	n.d.	30 ± 1	n.d.	0.30 ± 0.04	n.d.	0.73 ± 0.11
2016	66 ± 29	62 ± 23	0.36 ± 0.02	0.31 ± 0.04	0.83 ± 0.13	0.99 ± 0.07
2017	85 ± 23	52 ± 1	0.39 ± 0.04	0.32 ± 0.00	0.98 ± 0.12	0.96 ± 0.13
C3 (open lake)						
2015	35 ± 3	27 ± 4	0.36 ± 0.01	0.33 ± 0.00	n.d.	0.80 ± 0.07
2016	35 ± 4	34 ± 3	0.21 ± 0.01	0.36 ± 0.00	0.73 ± 0.02	0.58 ± 0.02
2017	n.d.	39 ± 0	n.d.	0.40 ± 0.00	n.d.	0.36 ± 0.02

Table 3: Range in surface water CO₂ concentration, CO₂ flux, and water temperature in Lake Onego during June 2015, 2016, and 2017

Location	CO ₂ [µmol L ⁻¹]	CO ₂	T [°C]		
Year		C&C 1998	C&W 2003	Mean at 4 m s ⁻¹	
Petrozavodsk Bay					
2015	29-52 (<i>n</i> =3)	8-71	13-161	6-32	9.3-16.2
2016	31-45 (<i>n</i> =5)	-1-26	0-24	-1-25	10.9-16.1
2017	51-63 (<i>n</i> =4)	19-69	11-162	17-26	5.9-9.2
Central lake basin					
2015	20-33 (<i>n</i> =3)	-1-4	-2-4	-1-4	3.6-6.9
2016	1-30 (<i>n</i> =32)	-21-9	-44-21	-16-6	7.1-16.7
2017	33-62 (<i>n</i> =11)	5-42	9-96	5-25	2.5-6.0