Atmospheric CO₂ Exchange of a Small Mountain Lake: Limitations of Eddy Covariance and Boundary Layer Modeling Methods in Complex Terrain

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Abstract  Lakes receive and transform significant amounts of terrestrial carbon and are often considered a source of atmospheric carbon dioxide (CO₂). Yet, continuous direct measurements of lake-atmosphere CO₂ exchange with high temporal resolution are sparse. In this study, we measured the CO₂ exchange of a mountain lake in the eastern Austrian Alps continuously for one year using the eddy covariance (EC) and the boundary layer model (BLM) approaches. Results from both the EC and the BLM methods indicated the lake to be a small source of atmospheric CO₂ with highest emissions in fall. EC flux measurements were affected by low-frequency contributions especially during low wind conditions. The CO₂ concentration gradient at the air-water interface decreased during night-time due to an increase in atmospheric CO₂ above the lake, likely caused by cold and CO₂-rich air draining from the surrounding land. Consequently, BLM fluxes were lower during night-time than during daytime. This diel pattern was lacking in the EC flux measurements because the EC instruments deployed at the shore of the lake did not capture low nocturnal lake CO₂ fluxes due to the local wind regime. Overall, this study illustrates the effect of the surrounding landscape on lake-atmosphere flux measurements. We conclude that estimating CO₂ evasion from lakes situated in complex topography needs to explicitly account for biases in EC flux measurements caused by low-frequency contributions and local wind regimes.

1. Introduction

The world’s streams, rivers, and lakes contribute substantially to the global carbon (C) cycle through the emission of carbon dioxide (CO₂) across the air-water interface. Current estimates quantified that 1–3.8 Pg C per year are released by inland waters to the atmosphere (Aufdenkampe et al., 2011; Battin et al., 2009; Cole et al., 2007; Drake et al., 2018; Raymond et al., 2013; Tranvik et al., 2009). These CO₂ emissions are on the same order of magnitude as terrestrial net ecosystem production and net CO₂ emissions related to anthropogenic land use changes (Ciais et al., 2013). Lakes and reservoirs account for ∼0.3–0.64 Pg C (Aufdenkampe et al., 2011; Cole et al., 2007; Holgerson & Raymond, 2016; Raymond et al., 2013; Tranvik et al., 2009) of the total inland water CO₂ emissions, making lakes important contributors to the C balance of the earth’s land surface.

Terrestrial CO₂ exchange is primarily driven by photosynthesis and respiration: atmospheric CO₂ is taken up by means of photosynthesis and stored in organic compounds in biomass. Part of this C is released back into the atmosphere through autotrophic and heterotrophic respiration and abiotic oxidation. Some terrestrial
C is also exported from the land into inland waters and potentially into the ocean (Ciais et al., 2013; Drake et al., 2018). Work from the past two decades has established that inland waters not only transport terrestrial C to the coastal oceans as "passive pipes" but also are able to process or transform C (Cole et al., 2007; Prairie & Cole, 2009). This research has concluded that only about one third to one half of the terrestrially derived C in headwaters eventually enters the ocean. The remainder is stored in sediments or outgassed to the atmosphere (Ciais et al., 2013; Mendonça et al., 2017; Raymond et al., 2013).

The diffusive CO₂ exchange across the air-water interface is driven by the CO₂ concentration difference (ΔCO₂) between water and air and the exchange coefficient (Liss & Slater, 1974). Methods to quantify CO₂ exchange at the air-water interface include (a) chamber methods, (b) concentration-gradient based methods including surface renewal or boundary layer models (BLM), and (c) micrometeorological approaches such as the eddy covariance (EC) method.

Although floating chambers provide a simple, cost efficient tool, this method is labor intensive, especially if non-automated systems are used, and covers only a small surface area (Duc et al., 2013). In addition, the chamber itself might influence gas exchange due to alterations of the gas concentration in the enclosure, self-heating, wind sheltering effects, and alterations of the flow field (Lorke et al., 2015; Matthews et al., 2003; Vingiani et al., 2020).

The BLM method is based on measurements of dissolved surface water and atmospheric gas concentrations and estimates of the gas transfer velocity (k). The advantages of the BLM method are that CO₂ concentrations (or data to infer CO₂ concentrations) are commonly measured in aquatic ecosystems (Cole et al., 1994; Hartmann et al., 2014) and that k can be estimated based on empirical relationships. Therefore, concentration-gradient approaches are widely used for CO₂ exchange estimates including, for example, recent estimates of global inland water CO₂ emissions (Cole et al., 2007; Raymond et al., 2013). However, lakes from different regions are not represented equally in existing data sets of aquatic CO₂ measurements (Cole et al., 2007; Hartmann et al., 2014; Raymond et al., 2013), and especially data from the Alpine region are sparse (Ejarque et al., 2021; Pighini et al., 2018). In addition, measurements are rarely done at time intervals and with adequate frequency to capture the temporal (seasonal, but also potentially diel) variability of air-water gas exchange (Zscheischler et al., 2017). Furthermore, the explicit determination of k is challenging and associated with large uncertainties. Values for k can be determined from trace gas experiments (Wanninkhof et al., 1985) or from flux measurements using for example, chamber or EC methods (e.g., Jonsson et al., 2008; Vachon et al., 2010). Those methods are labor intensive or have other drawbacks and effort was put into establishing empirical relationships from existing measurements of k. To date, several models exist (Klaus & Vachon, 2020). Gas transfer is dependent on surface water turbulence which in many lakes is predominantly regulated by wind speed (Jähne et al., 1987; Read et al., 2012; Xiao et al., 2017). Therefore, and because wind speed is quite simple to measure, wind speed is often used for the determination of k for lakes. Existing studies agree on that parametrizing k as a function of wind speed is reasonable, but also indicate that other factors like wind fetch, wave height, convection or buoyancy flux affect k (MacIntyre et al., 2010; Read et al., 2012; Vachon & Prairie, 2013) and that the wind-k-relationship might also, for example, depend on lake size and shape and therefore be lake specific (Klaus & Vachon, 2020).

In contrast to the BLM approach, the EC method provides a tool to measure fluxes such as CO₂ exchange across a surface directly (Aubinet et al., 2012; Baldocchi et al., 1988). Although the EC method is well established for flux measurements in terrestrial environments, few long-term studies which measure gas exchange over aquatic ecosystems exist (Baldocchi, 2014; Pastorello et al., 2020). A drawback of this method is that the required instruments are rather expensive, while the advantages are that automated, near-continuous measurements are realized easily with little disturbance of the system and that the measured flux is representative of a comparatively large surface area. The upwind area contributing to the measured signal is called the footprint and usually extends several hundred meters. Because only the upwind area contributes to the EC signal, the source area depends on the wind direction. Therefore, wind patterns with typical diel variations often observed above complex terrain, like for example, land and lake breezes or valley wind systems, can lead to biased results.

The above-mentioned methods differ in temporal and spatial resolution. At the same time, lake-atmosphere CO₂ exchange often shows large spatial and temporal variability (e.g., Erkkilä et al., 2018; Spafford
Few studies directly compared two or more methods and the results showed different degrees of agreement (Baldocchi et al., 2020; Erkkilä et al., 2018; Jonsson et al., 2008; Podgrajsek et al., 2014). Therefore, more long-term research employing multiple methods simultaneously is needed to improve our understanding of the processes acting on different temporal or spatial scales (Baldocchi et al., 2020; Reed et al., 2018).

Here, both the BLM and the EC method were used to estimate the air-water CO$_2$ exchange of Lake Lunz, a small (0.68 km$^2$) lake situated in complex mountainous topography in the Austrian Alps. Measurements were conducted continuously for an entire year. The goal of this study was twofold: First, we aimed to compare the BLM and EC methods and to quantify and analyze differences between both methods. In the context of the measurement setting on a small lake in complex mountainous topography we hypothesized that EC measurements might be biased because lake fluxes cannot be captured during certain wind conditions. Second, we strived to quantify the CO$_2$ source or sink strength of Lake Lunz and the drivers of its temporal variability in order to improve our understanding of freshwater C cycling in mountain lakes of the Alps, an area which is experiencing rapid changes in climate and the hydrosphere (Blöschl et al., 2019; Gobiet et al., 2014). We captured the temporal variation of CO$_2$ fluxes and related them to temporal patterns of atmospheric and aquatic CO$_2$ concentrations, prevailing climatic conditions, and weather events. In addition, we measured wind speed and direction at two locations on opposing shores of the lake. This allowed us to observe the local wind regime and to assess its influence on the lake and the related CO$_2$ exchange.

2. Material and Methods

2.1. Site Description

This study was performed at Lake Lunz, a clear-water, oligotrophic mountain lake located in Lower Austria (47° 51’ N, 15° 03’ E), during a one year period (01.01.2017–31.12.2017). Lake bathymetry is steep with a mean and maximum depth of 20 and 34 m, respectively. The lake has an oval shaped surface area of about 0.68 km$^2$ with its longest distance of about 1.5 km roughly aligned from west to east (Figure 1).
The lake is situated in a steep and narrow valley at an elevation of 608 m. The ridge north of the lake reaches an elevation of about 900 m, while the slope south of the lake plateaus at about 1,500 m. The north and south slopes are densely forested with spruce (Picea abies) and larch (Larix decidua). On the east side, the main lake inlet (Oberer Seebach) enters the lake and the terrain is less steep and less densely vegetated. The lake discharges into one single outlet (Unterer Seebach) at the northwest end.

2.2. Eddy Covariance Measurements

During 2017, EC measurements were done at the east shore on a boardwalk extending about 15 m into the lake. Previously, fluxes were measured using the same EC instruments but installed on a floating platform (Ejarque et al., 2021). However, the floating platform was only operational during summer. Moreover, the movement of the platform may influence data quality and lead to higher data rejection during quality control. Therefore, a year-round operation of EC measurements on the shore was chosen and previous wind measurements suggested the highest data coverage on the east shore of the lake. The EC instruments included a 3-D sonic anemometer (R3, Gill Instruments, Lymington, UK) to measure sonic temperature and the three orthogonal wind components. CO₂ and H₂O mixing ratios were measured using an enclosed-path infrared gas analyzer (LI-7200, LI-COR Inc., Lincoln, NE, USA) with a heated intake tube of 0.71 m length. The gas analyzer was calibrated with standard CO₂ gas (400 ppm ± 2%; Messer Austria GmbH) and a dew point generator (LI-610, LI-COR Inc.) at the beginning of the campaign (18.01.2017). Calibration coefficients were checked again in May and varied by less than 2%. Instruments were installed at 3.9 m above the lake surface (about 1.2 m from water surface to boardwalk +2.7 m on boardwalk) and data were collected at 20 Hz. CO₂ fluxes (Fₚ) were calculated using the numerical ogive optimization (OgO) method (Sievers et al., 2015). The convention that negative fluxes are towards the surface (i.e., lake as sink) and positive away from the surface (i.e., lake as source) was adopted. Only data passing the quality criteria (see below) were considered. The EC method measures an upwind signal. Therefore, fluxes measured at the east shore were only representative of the lake when the wind was blowing from the west, that is, during times when a lake breeze or up-valley, westerly flows persisted (wind directions between 230° and 310°). Measurements affected by instrument malfunctioning and data measured directly during rain events were excluded. Overall, data coverage was about 15%.

2.2.1. Ogive Flux Analysis

Integrated on an annual time scale, lakes are estimated to be significant emitters of CO₂. Yet, fluxes on short time scales (e.g., half-hourly or hourly) are often small. Therefore, any interference from processes that lead to low-frequency contributions (e.g., advective flows) can be relatively large compared to the turbulent flux, and lake EC flux estimates have to follow stringent quality checks and sophisticated data processing. The OgO is an alternative approach to process EC data to estimate turbulent exchange while separating out low-frequency contributions and also accounting for high-frequency dampening or noise (Sievers et al., 2015). To estimate CO₂ fluxes, we followed the OgO method using the publicly available Matlab toolbox OOT version 1.1.0 (Sievers, 2019); calculations were done in Matlab version R2019b (The MathWorks Inc.). Examples of the OgO analysis and how it compares with standard EC processing is shown in the supplement (Text S1; Figures S1–S4).

An ogive is an empirical cumulative distribution and here refers to the cumulative integral of the co-spectra of CO₂ concentration and vertical wind speed (w) from high to low frequencies, where the co-spectrum is the spectral decomposition of the flux estimate. Therefore, an ogive represents the cumulative contribution of different frequencies to the calculated flux. In theory, the ogive converges towards an asymptote with decreasing frequencies within an optimum averaging interval (Figure S1a). However, the inclusion of low frequency contributions may lead to a continuous increase (Figure S1b) or reversal (Figure S1c) of the ogive curve depending on the direction of the low frequency motions. In general, the low frequency contribution can be minimized in EC flux estimates by choosing the ideal averaging interval. Also, pre-treatment of the data with an appropriate detrending method can help to reduce any non-turbulent influence. However, in cases where the frequency range of turbulence and low-frequency contributions overlaps, the estimation of the ideal averaging time or detrending method is not straightforward and the OgO method addresses this issue. During the OgO an ogive density map is generated by calculating ogives for a multiplicity of data permutations based on different combinations of averaging intervals and detrending methods for a certain time.
window at any chosen point in time. Subsequently, a spectral distribution model is fitted to the obtained density map and the best fit is assumed to represent the pure turbulent flux (Figure S1).

Fluxes were calculated every 30 min. Averaging intervals were varied from 10 to 60 min around the query time. Basic quality control and preprocessing of raw data included de-spiking, gap detection, double rotation, and a time lag detection and removal (Aubinet et al., 2012; Vickers & Mahrt, 1997). Furthermore, only periods when the momentum flux in the energy containing frequency range was negative (i.e., directed towards the surface) were considered (Foken & Wichura, 1996; Sievers et al., 2015).

2.3. Additional Measurements of Weather, Radiation, and Lake Parameters

Meteorological conditions including air temperature (\(T_a\)) and relative humidity (RH), incoming and outgoing shortwave and longwave radiation (\(SW_{\text{in}}, SW_{\text{out}}, LW_{\text{in}},\) and \(LW_{\text{out}}\)) were measured at the boardwalk. Precipitation was recorded at a nearby weather station (TAWES Lunz am See). Wind speed and wind direction were (in addition to wind measurements at the EC station on the east shore) measured at the west shore of the lake using a 3-D sonic anemometer (CSAT3, Campbell Scientific). From May 12th to October 18th, 2017, water temperature (\(T_w\)) profiles were measured using 9 temperature probes (CS108 and CS109SS, Campbell Scientific) at 0.05, 0.2, 1, 2, 4, 7, 12, 17, and 22 m below the water surface fixed to a floating platform above the deepest point of the lake (Figure 1). Meteorological data and water temperature were measured at one-minute intervals and half-hourly mean values were stored on a data logger (CR10X, Campbell Scientific). Additionally, the lake water level was obtained from the Hydrographic Service of Lower Austria available at https://www.noel.gv.at/wasserstand/#/de/Messstellen.

2.4. Boundary Layer Model Approach

We measured atmospheric and surface water (~0.3 m depth) \(CO_2\) concentrations using a Greenhouse Gas (GHG) Sentinel™ (Axys Technologies Inc.) that was placed on a floating platform on the lake (Figure 1). The GHG Sentinel was equipped with a thermostatically controlled nondispersive infrared gas analyzer (LI-COR LI-820 \(CO_2\) analyzer), which measured the mole fraction of \(CO_2\) in the (equilibrated) air sample with a resolution of 1 ppm and an accuracy of \(\pm2.5\%\). The GHG Sentinel also measured temperature and pressure to allow for compensation of changes in gas density. The logged pressure and \(CO_2\) mole fraction were then used to compute the \(CO_2\) partial pressure (\(pCO_2\)) in the gas sample. Measurements were conducted from April 14th to October 29th at a three-hour interval (45 min equilibration time). Details on this method can be found elsewhere (Bastien et al., 2008).

We used \(CO_2\) fluxes from the OgO analysis (\(F_{C-Og}\)) and measurements of atmospheric and water \(CO_2\) concentrations to determine the gas transfer velocity \(k\) and to establish the lake-specific wind speed-\(k\) relationship. This relationship was then used to extrapolate \(k\) also to times when no measurements of \(F_{C-Og}\) were present. First, \(k\) was estimated as:

\[
k = \frac{F_{C-Og}}{C_w - C_a}
\]

(1)

where \(C_w\) is the \(CO_2\) concentration in the surface water and \(C_a\) is the theoretical concentration of \(CO_2\) in equilibrium with the atmosphere at the interface.

The dissolved \(CO_2\) concentrations \(C_w\) and \(C_a\) were calculated by multiplying p\(CO_2\) of the lake and the atmosphere, respectively, with the Henry’s solubility constant \(H_c\) (Equation 2 and 3):

\[
C_w = pCO_{2w} \ast H_c \quad \text{and} \quad C_a = pCO_{2a} \ast H_c;
\]

(2)

with

\[
\ln H_c = -58.0931 + 90.5069 \ast \frac{100}{T_w} + 22.294 \ast \ln \left( \frac{T_w}{100} \right),
\]

(3)

(Weiss, 1974); \(T_w\) in K, \(H_c\) in mol L\(^{-1}\) atm\(^{-1}\).
Using the Schmidt number (Sc) for CO$_2$ at the measured water temperature (Equation 5), $k$ was transformed to $k_{600}$ [cm h$^{-1}$], the standardized gas transfer velocity at 20°C (with Sc = 600):

$$k_{600} = k \times \left(\frac{600}{Sc}\right)^n$$

(4)

where $n = -2/3$ for $u < 2$ m s$^{-1}$ and $n = -1/2$ for higher wind speeds (Jähne et al., 1987) and

$$Sc = 1911.1 - 118.11 \times T_w + 3.4527 \times T_w^2 - 0.041320 \times T_w^3$$

(5)

(Wanninkhof, 1992); $T_w$ in °C.

To make our results comparable to existing wind-based models, $k_{600}$ was related to wind speed at 10 m height ($U_{10}$). To obtain $U_{10}$, sonic wind speed measured at height $z_m = 3.9$ m was extrapolated to 10 m height using the logarithmic wind law (Equation 6):

$$U_{10} = u \times \ln\left(\frac{10}{z_0}\right) + \ln\left(\frac{z_m}{z_0}\right)^{-1}$$

(6)

where $z_0$ represents the surface roughness length, which was set to 0.0001 m (Vihma & Savijärvi, 1991).

Finally, data were median-binned into 1 m s$^{-1}$ wind speed classes from 0 to 5 m s$^{-1}$ and one class for wind speeds above 5 m s$^{-1}$, and a linear model was fitted to median $k_{600}$ versus the median $U_{10}$ of each class (Jonsson et al., 2008). For low ratios of $C_w/C_a$ we observed large scatter in measured $k_{600}$ values because very small fluxes are difficult to measure. Therefore, data was only considered when $C_w/C_a > 1.2$ (Figure S5). The resulting linear model was then used to extrapolate $k$ values ($k_{600}$modeled) to times when no measurements of $F_{C-Og}$ were present. By applying Equation 4, $k_{600}$modeled was transformed to $i$modeled and the CO$_2$ flux $F_{C-BLM}$ was calculated based on Equation 1 as:

$$F_{C-BLM} = k_{modeled} \times (C_w - C_a)$$

(7)

Thus, and in contrast to our lake EC measurements, the calculated $F_{C-BLM}$ is independent of wind direction.

All analyses were done in Matlab version R2019b (The MathWorks Inc.).

3. Results

3.1. Environmental Conditions During the Study Period

The mean annual temperature for 2017 at the nearby weather station was slightly higher (7.7°C) than the long-term (last 20 years) mean of 7.3°C. The minimum and maximum air temperature were −20°C (January) and 35°C (beginning of August), respectively. The upper part of the water column (epilimnion) roughly followed the seasonal course of the air temperature with a maximum surface temperature of 24.4°C in mid-July. The sensors down to a depth of 12 m recorded a general increase in water temperature over the course of the summer, while the bottom temperature (17 m and below) stayed relatively constant around 5°C (Figure 2a). Lake Lunz is dimictic, yet complete mixing as indicated by a uniform temperature profile around 4°C occurred before and after our measurements started and ended in spring and fall, respectively.

Several temporary cooling periods were observed throughout the summer. The most pronounced events occurred at the end of July and in the beginning of September when surface temperatures dropped from 22.6 to 16°C and from 22.5 to 14.8°C (within 4 days), respectively. Both of those events were accompanied by large rain episodes with a cumulative precipitation of 85 and 108 mm leading to an increase of water level of 33 and 52 cm in July and September, respectively. Less pronounced cooling events were characterized by temperature drops of about 5°C and low precipitation (max. 40 mm) causing no marked increase in water level. Both the air and the surface water temperature increased again after the cooling event in July although the water temperature did not quite reach previous values. After the temperature drop at the beginning of September, surface water temperatures did not recover substantially but stayed at values around 15°C. At the same time, an increase in water temperature at 12 m depth was recorded, indicating an initial mixing of the water column to at least this depth (Figure 2a).
Annual precipitation amounted to 1,725 mm. January and June were the driest months with 74 and 82 mm, respectively. This was directly reflected in the lake water level, which stayed below the long-term mean throughout those months (Figure 2b). Heavy rain events caused sharp increases in water level (up to 50 cm within 2 or 3 days), most notably in winter and early spring (February and March) when they likely coincided with snowmelt (Ejarque et al., 2021); at the end of July after a long relatively dry period; and two heavy rain events in September. Rain episodes were generally associated with lower air temperature, which together with likely more groundwater inflow led to a temperature decrease in the epilimnion.

The lake was covered with ice from January 1st to February 22nd (Figure 2d, blue shaded area). Until the end of the year, no new ice cover was established.

### 3.2. Local Wind System

Daily average wind speed measured at the east shore ranged from 0.2 to 6 m s\(^{-1}\). At both measurement sites, typical diel variations in wind speed and direction were observed reflecting the thermo-/topographic setting of the lake (Figures 1 and 3). During night, westerly and easterly drainage flows converging to the lake were observed at the west and east shore, respectively (Figure 3; dark gray shaded area). After sunrise, a lake breeze (divergence at lake level) developed with onshore flows recorded at both sites (Figure 3; light blue area). On the west shore, the onshore, north-easterly wind persisted between 08:00 and 10:00h local time. Around noon, the up-valley, westerly flow was fully established, replacing the onshore breeze on the west shore and intensifying the westerly wind on the east shore (westerly mean wind speed: 2.3 m s\(^{-1}\); Figure 3; light gray area). After sunset, the nocturnal drainage flows with low wind speeds (mean wind speed of 0.6 m s\(^{-1}\)) re-established.
We also observed days when the lake breeze persisted throughout the day or when the westerly wind dominated the entire day and in some cases even throughout the night. The former cases were most frequent in August and characterized by very warm temperatures and low wind speeds (mean wind speed of 0.8 m s$^{-1}$), while the latter showed generally higher wind speeds than typical days, often during storms with precipitation. The mean wind speed of nocturnal westerly winds was 3.1 m s$^{-1}$.

### 3.3. Atmospheric and Near-Surface Water CO$_2$ Concentrations

The atmospheric CO$_2$ concentration generally showed a strong diel pattern with high values during the night and lower values during the day. During the summer months (June–August), $C_a$ was highest in the early morning with 18–19 µmol L$^{-1}$ (atmospheric CO$_2$ of 460 ppm) on average. After sunrise, the concentration decreased rapidly and stayed around 15 µmol L$^{-1}$ (400 ppm) throughout the day. After sunset and as soon as the nocturnal drainage flow established, the CO$_2$ concentration started to increase again. Interestingly, on days when no nocturnal drainage flow was observed and the westerly wind persisted, the CO$_2$ concentration stayed low also throughout the night. The daily course of atmospheric CO$_2$ on a typical day (doy 165; diel wind pattern) and on a day with persisting westerly winds (doy 168) is depicted in Figure S6.

Dissolved CO$_2$ in the epilimnion also showed a diel pattern, however, with a lower or even reversed amplitude compared to the atmospheric concentration (Figure 4, upper panels). Therefore, the difference in the CO$_2$ concentration at the air-water interface, $\Delta$CO$_2$, was low and sometimes negative at night and usually had its maximum around midday (Figure 4, lower panels). However, during times when the wind at the east shore was blowing from the lake (i.e., times when the air-water CO$_2$ exchange could be measured with the EC set-up), $\Delta$CO$_2$ showed no or a reverse diel pattern. During those times with onshore wind and valid EC lake flux measurements, the night-time mean $\Delta$CO$_2$ of 10.1 µmol L$^{-1}$ was higher than the overall night-time mean $\Delta$CO$_2$ of 3.2 µmol L$^{-1}$ considering all data (i.e., including also data during offshore wind conditions) (Figure 4, lower panels).

On average, the lake was supersaturated with CO$_2$ during all months except for August with the monthly mean $C_w$ ranging from 13.6 µmol L$^{-1}$ (August) to 36.2 µmol L$^{-1}$ (October). In May (20.8 µmol L$^{-1}$) and July (16.3 µmol L$^{-1}$), $C_w$ was very close to the equilibrium concentration $C_e$ of 20.8 and 16.1 µmol L$^{-1}$ in May and July, respectively, and several periods of undersaturation were observed (Figure 2c). The rain/cooling events in July generally led to a short-term decrease in surface water CO$_2$ concentration. In the beginning of August, the CO$_2$ concentration increased before dropping below atmospheric equilibrium for the rest of the month. The mixing of
the water column induced by the heavy rain in the beginning of September (Figures 2a and 2b) eventually led to a strong increase in surface water CO$_2$ concentration and despite some fluctuations it continuously stayed above atmospheric concentrations afterwards (Figure 2c). By the end of the measurements at the end of October, the water concentration exceeded atmospheric concentrations by more than 30 µmol L$^{-1}$ (500 ppm) (Figure 2c).

### 3.4. Directly Measured CO$_2$ fluxes

CO$_2$ fluxes estimated with the EC method using standard EC data processing showed generally small fluxes with high short-term temporal variation. An analysis of the respective co-spectra and ogives revealed that often large and variable contributions in the low-frequency range were causing this high variability. No clear spectral gap could be determined making it difficult to exclude low-frequency contributions based on a fixed averaging time. Processing the EC data by applying the OgO method (Text S1; Figure S1) helped to reduce scatter and reveal flux patterns (Figure S2 and S3). Comparing both results (i.e., results from the conventional EC processing and results using the OgO method) showed that largest discrepancies occurred during lake-breeze and low wind conditions (Figure S4).

In the following, direct flux estimates based on the OgO method are presented. Overall, the lake acted as a net source of CO$_2$ with an overall mean (±1 std) emission rate of 0.25 (±0.36) µmol m$^{-2}$ s$^{-1}$. For the direct flux measurements, no clear diel variation was observed while fluxes showed seasonal variability with a generally increasing trend towards fall (Figures 2d and 5). The highest monthly mean fluxes were observed in October which then decreased slightly towards the end of the year. During the ice free period, April, May, and July showed on average the lowest fluxes. During those months, several periods of C uptake could be observed (Figure 2d), which coincided with cooling of the surface water temperature and rain events on the same or previous days.

### 3.5. Gas Transfer Velocity and BLM CO$_2$ fluxes

We obtained a linear model for our measured $k_{600}$ values across different wind speeds ($U_{10}$). The best fit model (±SE) to the data was (Equation 8):

$$k_{600}^{\text{modeled}} = 2.35 (\pm 0.47) \times U_{10} + 3.29 (\pm 1.77);$$

$R^2 = 0.86$ (Figure 6).

We compared our measured $k_{600}$ values and the results of $k_{600}^{\text{modeled}}$ with values obtained by three commonly used wind speed based models present in the literature: Cole and Caraco (1998; $k_{600}^{\text{C&C}}$), Crusius and Wanninkhof (2003; $k_{600}^{\text{C&W}}$), and Jonsson et al. (2008; $k_{600}^{\text{J}}$). In the wind range from 0 to $\sim 6$ m s$^{-1}$, we observed an overall underestimation of $k_{600}^{\text{C&C}}$ and $k_{600}^{\text{C&W}}$, although being within the confidence inter-
vals for very low wind speeds. Despite still being lower than our linear model, the k600J-model was closer and within our confidence intervals. Also, the median binned data confirmed the overall underestimation especially of the k600C&C-model at the given wind speed for this mountain lake system. This detailed comparison is depicted in Figure 6.

CO2 fluxes $F_{C-BLM}$ resulting from the gas transfer model showed a diel trend especially during summer (June, July) and fall (September, October) with higher fluxes during daytime (Figure 5).

Overall, the average (±1 std) flux from the BLM method with our $k_{600}$ estimate was 0.06 (±0.15) µmol m$^{-2}$ s$^{-1}$, which is substantially lower than the average directly measured flux $F_{C-Og}$. Average fluxes using established $k_{600}$ models were 0.02 (±0.06), 0.02 (±0.1), 0.04 (±0.11) µmol m$^{-2}$ s$^{-1}$ for the k600C&C-, k600C&W-, and k600J-model, respectively. It should be noted, however, that the CO2 flux from the lake can only be measured directly with the EC method when the wind is blowing from the lake. When we averaged only fluxes during times when the wind was blowing from the lake and valid EC flux data existed, the value for $F_{C-BLM}$ increased to 0.13 (±0.24) µmol m$^{-2}$ s$^{-1}$. Average $F_{C-Og}$ during the exact same period was significantly higher with 0.22 (±0.41) µmol m$^{-2}$ s$^{-1}$ (statistical significance tested with Wilcoxon signed rank test; $p << 0.05$).

Monthly mean fluxes calculated with the BLM method further showed that the lake acted as a source of atmospheric CO2 during most months. This monthly CO2 evasion estimate was always lower than monthly mean $F_{C-Og}$ and even negative in May and August (Figure 7). Highest fluxes were observed in October independent of the chosen calculation method.

Monthly mean $F_{C-Og}$ and $F_{C-BLM}$ applying different $k_{600}$ models and averaged only over time periods when both valid EC and pCO2 data existed are shown in Figure S7.

4. Discussion

Wind speed and direction, atmospheric and surface water CO2 concentrations, and air-water CO2 exchange were measured at a small mountain lake situated in a narrow, steep valley of the eastern European Alps. Si-
multaneous wind measurements on opposing shores of the lake revealed the existence of a local wind regime that also affected local atmospheric CO$_2$ concentrations. This, together with seasonal variations of CO$_2$ concentrations in the lake water column, predominantly controlled the variation in lake-atmosphere CO$_2$ exchange.

4.1. The Local Wind Regime and Its Consequences for Lake CO$_2$ Flux Measurements

We observed a land breeze during night-time and the development of a lake breeze in the morning. During night, lakes often are warmer than the surrounding land promoting the rise of air masses above the lake and drawing in cooler air from the surrounding land. Especially in mountainous regions, lakes—as in our case—are often surrounded by steep hills and therefore represent a relative low point within the landscape. In sloping terrain, nocturnal down-slope drainage flows are common (Aubinet et al., 2005; Pypker et al., 2007) which enhance the effect of the land breeze. Drainage of cold air is also associated with drainage of CO$_2$ from terrestrial ecosystem respiration (Aubinet et al., 2005; Kang et al., 2017). This pattern can also be observed in our data set, where a significant increase of atmospheric CO$_2$ occurred as soon as the wind turned from onshore to offshore. Because the diffusive air-water CO$_2$ exchange depends on the lake-atmosphere CO$_2$ concentration difference, a sudden increase of atmospheric CO$_2$ concentration can transiently suppress or even reverse CO$_2$ emissions from the lake. Continuous measurements of pCO$_2$ in the air and in the surface water allowed calculating the fluxes based on modeled gas transfer velocities. Those results confirmed a diel trend of CO$_2$ exchange with higher fluxes during the day and lower fluxes during the night. Direct EC measurements of CO$_2$ fluxes, on the other hand, did not reveal a diel pattern of lake-atmosphere CO$_2$ exchange. Instead, night-time fluxes were the same order of magnitude and occasionally even higher than during daytime and barely showed night-time CO$_2$ uptake. EC measurements, however, are dependent on wind direction. Because our EC set-up was located on the east shore of the lake, fluxes from the lake could only be measured when westerly winds persisted. Due to the given thermo-topographic conditions this was the case primarily during daytime, although occasionally the wind was blowing from the lake also during night. Nocturnal onshore wind was characterized by comparatively high wind speeds. During those conditions, the nocturnal increase in atmospheric CO$_2$ concentration and the resulting decrease of ΔCO$_2$ were not observed, likely due to the absence of drainage flows and better atmospheric mixing during strong westerly winds. Consequently, a decrease in lake-atmosphere CO$_2$ fluxes is not expected during those nights and, in our case, lake EC flux measurements are therefore biased towards higher fluxes.

This is crucial to consider when measuring lake-atmosphere CO$_2$ exchange using the EC method in lakes and is especially critical if the measurements are performed from the shore of the lake. Considering flux estimates based on modeled $k$, our study demonstrates the importance of local atmospheric CO$_2$ concentration and its temporal variability. In non EC-studies, fluxes are often calculated by assuming a constant average atmospheric pCO$_2$. However, especially when surface water concentrations are close to equilibrium, small temporal and local differences in atmospheric CO$_2$ can determine the lake being a source or sink for CO$_2$. 

4.2. Comparison of Flux Results Based on the EC and the BLM Method

Although both $F_{C-Og}$ and $F_{C-BLM}$ indicated that the lake on average was a small source of CO$_2$, discrepancies between the two methods remained. $F_{C-BLM}$ was consistently lower than $F_{C-Og}$ which previously was observed in other studies (Erkkilä et al., 2018; Huotari et al., 2011; Mammarella et al., 2015) and primarily attributed to uncertainties in the estimation of $k$. In our case, part of the discrepancies was probably caused by a diel bias in EC measurements. However, even when comparing measurements taken during the exact same time periods, differences remained and were most pronounced in August when a negative ΔCO$_2$
implied CO\textsubscript{2} uptake, while \( F_{\text{C-Og}} \) suggested CO\textsubscript{2} release. This discrepancy could be caused by spatial variability of CO\textsubscript{2} fluxes because the two methods generally differ in spatial resolution, and in our case the two methods also covered different parts of the lake. The EC set-up was on the shore, therefore \( F_{\text{C-Og}} \) represents fluxes from relatively shallow waters. On the other hand, \( C_w \) which was used to calculate \( F_{\text{C-BLM}} \) was measured near the center, at the deepest point of the lake. Other studies have also observed within lake spatial variability of \( F_c \) and \( C_w \) (Kelly et al., 2001; Loken et al., 2019; Xiao et al., 2020) and often reported higher values for shallow water. For example, EC measurements at a Finnish lake showed higher fluxes when the footprint was above shallower water (Erkkilä et al., 2018). Spafford and Risk (2018) used floating chambers to measure \( F_c \) along a transect in the littoral zone and found higher and more variable fluxes closest to the shore. Shallow water might be warmer and therefore increase microbial respiration and the resulting emission of CO\textsubscript{2}. Moreover, sediments are closer to the water surface and the mixing layer can extend all the way to the lake bottom more easily (Holgerson, 2015). Close to the shore, organic material from the surrounding land can accumulate and directly provide decomposable substrate for microbial respiration (Xiao et al., 2020). In addition, surface water and hyporheic CO\textsubscript{2} inflows (Peter et al., 2014) will also have a higher effect on lake water CO\textsubscript{2} closer to the shore.

Although the applied OgO method provides a tool to reduce low-frequency impact on direct flux measurements, non-turbulent contributions to the estimated fluxes cannot be completely precluded. This, as well as uncertainty in the estimation of \( k \), can be an additional cause for the observed discrepancies between the methods.

We found better agreement between \( F_{\text{C-Og}} \) and \( F_{\text{C-BLM}} \) in fall, indicating that lake mixing led to a homogeneous increase in \( C_w \) across the entire lake surface. This is in contrast to the study by Baldocchi et al. (2020), who found good agreement between the EC and BLM method during the stratified period but diverging results during the fall turnover period at Lake Mendota. However, Lake Mendota is much larger than Lake Lunz. Therefore, it is likely that lake mixing at Lake Mendota was less homogeneous and thus increased the spatial heterogeneity of lake CO\textsubscript{2} fluxes.

It should be noted that in our case estimates of \( F_{\text{C-Og}} \) and \( F_{\text{C-BLM}} \) are not completely independent, because we used \( F_{\text{C-Og}} \) to determine \( k \). Estimating \( k \) independently using the \( k_{600,C\&W}^{-} \), \( k_{600,C\&C}^{-} \), or \( k_{600} \)-model always resulted in less agreement between \( F_{\text{C-BLM}} \) and \( F_{\text{C-Og}} \). Therefore, the lake specific estimate of \( k \) seems to better account for lake characteristics affecting the wind-\( k \)-relationship. On the other hand, spatial variability in CO\textsubscript{2} fluxes might be masked to some extent by our approach, because the measurements of pCO\textsubscript{2} and \( F_{\text{C-Og}} \) to estimate \( k \) were taken at different locations. Other studies also observed discrepancies between wind-based BLM CO\textsubscript{2} fluxes and EC measurements and related them to enhanced gas transfer due to convective mixing (e.g., Eugster et al., 2003; Mammarella et al., 2015; Podgrajsek et al., 2015). When estimating \( k \) from flux measurements, enhanced \( F_{\text{C-Og}} \) will be directly mapped into \( k \), which may explain the differences between our \( k \)-model and the other models. However, we did not explicitly account for convective mixing in our \( k \)-model as suggested by MacIntyre et al. (2010) or Erkkilä et al. (2018). Although this could possibly explain the remaining differences between \( F_{\text{C-Og}} \) and \( F_{\text{C-BLM}} \), the effect is likely rather small in our case: convective mixing caused by surface cooling will mostly occur during night when the surface water is warmer than the air above. During those times, we observed the lowest values of \( \Delta \text{CO}_2 \) and therefore also an enhanced gas transfer would still result in rather small fluxes.

### 4.3. Temporal Variability and Potential Drivers of CO\textsubscript{2} Fluxes

Overall, our results generally showed a similar seasonal pattern in \( F_{\text{C-BLM}} \) and \( F_{\text{C-Og}} \). Fluxes were low in spring and in contrast to other studies no bursts of CO\textsubscript{2} were observed during ice out (Ducharme-Riel et al., 2015; Huotari et al., 2011; Karlsson et al., 2013), although, on average, fluxes were higher in March than in January and February. On average, the lake acted as a net source of CO\textsubscript{2} also during the summer. Nevertheless, several periods of CO\textsubscript{2} uptake were observed especially in July and overall the variability of CO\textsubscript{2} fluxes was high. Frequent undersaturation and CO\textsubscript{2} uptake has been observed in other studies as well, especially for eutrophic lakes (Baldocchi et al., 2020; Balmer & Downing, 2011). In our study, periods of CO\textsubscript{2} uptake were rather associated with temporal cooling of air and surface water temperature and, most of the time, light rainfall and low incident sunlight. Therefore, increased biological activity of primary producers in relation to photosynthetic active radiation is unlikely to explain the observed CO\textsubscript{2} uptake. Nevertheless,
given that primary production in lakes often is limited by nutrients (Prairie & Cole, 2009), we hypothesize that the light rainfall may also have enhanced productivity by increasing nutrient availability through enhanced fluvial inflow or partial mixing of the lake water column, while the colder temperatures temporarily decreased respiration. Generally, \( C_w \) was rather low and the cooling of the water may have led to a considerable increase in CO\(_2\) solubility. In addition, direct input of rainwater could have caused an additional dilution effect at the surface. In contrast, heavy rain events, as indicated by a marked increase of lake water level, were generally followed by an increase in \( C_w \) and also \( F_w \) most pronounced at the beginning of August and at the beginning of September. In those cases, runoff from the catchment probably led to an increased organic and inorganic C load (Ejarque et al., 2021). In the beginning of September, the heavy precipitation event likely also caused upwelling of CO\(_2\) rich water. Afterwards, \( C_w \) stayed high and highest fluxes were eventually observed in October due to several storm events with very high wind speeds. This implies that physical, rather than biological, factors drive CO\(_2\) emissions at this small mountain lake.

Likewise, high pCO\(_2\) and higher CO\(_2\) emissions induced by lake mixing were observed at other small, temperate lakes (Huotari et al., 2011; Mammarella et al., 2015). At Lake Erie, on the other hand, large CO\(_2\) uptake was observed during lake turnover, where the mixing of the water column provided nutrients and ideal growing conditions for increased algal growth (Ouyang et al., 2017). In general, in large eutrophic lakes, temporal variation in pCO\(_2\) or CO\(_2\) fluxes can be largely driven by biological activity (Ouyang et al., 2017; Reed et al., 2018; Xiao et al., 2020).

Direct EC CO\(_2\) flux measurements indicated that Lake Lunz, on average, emitted 0.25 \( \mu \)mol m\(^{-2}\) s\(^{-1}\) equivalent to 259 mg C m\(^{-2}\) d\(^{-1}\). This is likely an overestimation, as an average flux of 0.06 \( \mu \)mol m\(^{-2}\) s\(^{-1}\) or 62 mg C m\(^{-2}\) d\(^{-1}\) was estimated using the BLM method.

### 4.4. Relating CO\(_2\) Fluxes of Lake Lunz to Other Lake EC Flux Measurements

Our results are within the range of reported results from EC measurements at lakes in different regions (Table 1). Also, low data coverage (15% in our case) appears to be a common problem of lake EC flux measurements (Erkkilä et al., 2018; Huotari et al., 2011; Jonsson et al., 2008), although surpassing data coverage which can generally be achieved by manual measurements. To the authors’ knowledge no comparable continuous direct measurements from Alpine lakes exist. Also, direct comparison of the measured fluxes to other lakes is difficult due to different time frames, instrumentation, and flux processing (detailed information on instrumentation and data processing as reported in the respective papers is given in Table S1 in the supporting information). Most of the conducted studies were short-term measurements focusing on spring or fall turnover. Multi-year investigations are predominantly from northern boreal regions and usually include only the ice-free periods. Overall, this demonstrates that continuous, long-term, direct flux measurements at lake ecosystems and a coherent flux processing strategy for those systems are still lacking.

EC measurements at lakes pose several challenges. First, the choice for the site of instrument set-up is crucial. Several studies were conducted from floating platforms being advantageous in terms of land influence and acceptable wind directions. However, the movement of the platform might influence not only the wind measurements (Eugster et al., 2003) but also gas analyzers (Eugster et al., 2020) and other instruments might be sensitive to motion and this has to be considered in data processing. Set up on shore provides easier handling and maintenance but, as shown in our case, might be prone to biased data collection because only certain wind directions can be accepted. By choosing a site, also downwind conditions have to be considered as sharp surface transitions (e.g., lake to forest) can influence the wind field (Kenny et al., 2017). A basic requirement to acquire defensible flux measurements is that the terrain within the footprint is reasonably flat and homogenous—a condition seemingly well fulfilled for a lake surface. Nevertheless, high scatter and unrealistic flux values are commonly observed in aquatic EC measurements independent of the chosen instruments or measurement location (e.g., Czikowsky et al., 2018; Eugster et al., 2003; Liu et al., 2016) indicating that the sharp contrast between a water surface and its surrounding land can impair the measurements. For example, different magnitudes and even direction of CO\(_2\) fluxes on land versus water can lead to local concentration differences enhancing the potential for advective fluxes leading to non-turbulent/low-frequency contributions to the measured flux (Sun et al., 1998). Differences in surface characteristics (albedo, heat capacity, moisture) can lead to differential heating which in turn also drives air movement and can lead to advective airflow and the development of typical wind systems (Bischoff-Gauß...
et al., 2006) as also observed in our study. For terrestrial ecosystems, stable, low wind conditions are known to be challenging, concerning especially night-time flux quantification (Aubinet, 2008). For lakes, large influence from non-local processes has also been observed for high wind speeds (Esters et al., 2020). Yet overall, we could not determine any generalized condition under which the unrealistic flux values occurred.

In the past, this issue has been addressed with different solutions, for example, by shorter averaging times (Eugster et al., 2003; Vesala et al., 2006), more stringent thresholds for quality criteria (Czikowsky et al., 2018; Huotari et al., 2011), or rigorous outlier removal (Franz et al., 2016). Our data also showed unrealistic large fluxes and variability. Although an extensive (raw) data analysis naturally showed that low

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Table 1
Overview of EC CO₂ Flux Measurements at Lakes

| Reference | Lake/location | Time frame | Flux (mg C m⁻² d⁻¹) |
|-----------|---------------|------------|---------------------|
| Our study | Lake Lunz, Austria | 1 year (2017) | 259 |
| Anderson et al. (1999) | Williams Lake, MN, USA | 5 × 1 week (spring/summer/fall) | -186–2800 |
| Armani et al. (2020) | Itaipu Lake, Brazil | January–November 2013 | 301 |
| (non-continuous) |
| Czikowsky et al. (2018) | Lake Pleasant, NY, USA | September 16–October 11, 2010 | 348 |
| Du et al. (2018) | Erhai Lake, China | 2012–2015 | 322–443 |
| Erkkilä et al. (2018) | Lake Kuivajärvi, Finland | Fall 2014 (16 days) | 363–1,130 |
| Eugster et al. (2003) | Toolik Lake, AK, USA | Short term | 114 |
| (2–4 days in July) |
| Eugster et al. (2003) | Soppensee, Switzerland | Short term | 289 |
| (3 days in September) |
| Eugster et al. (2020) | Toolik Lake, AK, USA | Ice free periods | 200 |
| 2010–2015 |
| Franz et al. (2016) | Polder Zarnekov, Germany | May 2013–May 2014 | 118 |
| Han et al. (2020) | Ngoring Lake, Tibet | Ice free periods | -830–130 |
| 2011–2013 |
| Huotari et al. (2011), see also Vesala et al. (2006) | Lake Valkea-Kotinen, Finland | Ice free periods | 210 (186–266) |
| 2003–2007 |
| Jammet et al. (2017) | Villasjön, Sweden | June 2012–December 2014 | 228 |
| Jonsson et al. (2008) | Lake Merasjärvi, Sweden | June–October 2005 | 221 |
| Kim et al. (2016) | Eastmain-1 reservoir, Canada | Ice free periods | 1,140 |
| 2006–2009 |
| Liu et al. (2015) | Erhai Lake, China | 1 year (2012) | 466–1,284 |
| Liu et al. (2016) | Ross Barnett Reservoir, MS, USA | 1 year (2008) | 321 |
| Lohila et al. (2015) | Pallasjärvi, Finland | July–October 2013 | 210 |
| Mammarella et al. (2015); see also Heiskanen et al. (2014) | Lake Kuivajärvi, Finland | June–October 2010 & 2011 | 726 |
| Morin et al. (2018) | Douglas Lake, MI, USA | June–September/October 2013 & 2014 | 726 |
| Podgrajsek et al. (2015) | Lake Tämnnen, Sweden | September 2010–September 2012 | 187 |
| Polsenaere et al. (2013) | Floodplain lake, Brazil | November 19–22, 2011 | 612 |
| Potes et al. (2017) | Alqueva reservoir, Portugal | June 2–October 2, 2014 | -38 |
| Reed et al. (2018) see also Baldocchi et al. (2020) | Lake Mendota, WI, USA | 2012–2017 | -151−—636 |
| Shao et al. (2015) see also Ouyang et al. (2017) | Lake Erie, USA | October 2011–September 2013 | 173 |
| Sollberger et al. (2017) | Lake Klöntal, Switzerland | March–June 2012 | 15.5 |

Abbreviations: CO₂, carbon dioxide; EC, eddy covariance.
5. Conclusion

Direct measurements of CO₂ exchange between a small lake and the atmosphere were conducted and related to the temporal variability of atmospheric and surface water CO₂ concentrations and meteorological conditions. The lake acted as a small source of CO₂, showing distinct seasonal and diel patterns of CO₂ fluxes. Spring and summer fluxes were low and highest fluxes were observed in October after partial lake mixing. Several CO₂ uptake periods were observed, usually during cold and rainy weather and likely driven by physical rather than biological factors. Fluxes calculated using the BLM method showed a diel pattern with lower fluxes during the night. Drainage flows from the surrounding land and low wind speeds during night led to increased atmospheric CO₂ and in consequence decreased ΔCO₂ resulting in reduced CO₂ emissions or even CO₂ uptake by the lake. This pattern was lacking in the results of the EC flux measurements due to the instrument deployment on the shore of the lake which allowed lake flux measurements only during certain wind conditions. In general, we propose that the influence of the surrounding landscape needs to be considered when measuring lake-atmosphere fluxes, especially when fluxes are small and when dealing with lakes situated in complex topography: for EC the location of instruments and possible biases in flux measurements need to be addressed while for BLM, besides pCO₂ in the water, also atmospheric pCO₂ should be measured locally and with high temporal resolution.

Conflict of Interest

The authors declare that they have no conflict of interest.

Data Availability Statement

Data presented and analyzed in this work is available online at https://doi.org/10.5281/zenodo.4519167.

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