



Surface CO₂ Gradients Challenge Conventional CO₂ Emission Quantification in Lentic Water Bodies under Calm Conditions.

Patrick Aurich¹, Uwe Spank², Matthias Koschorreck¹

¹Department Lake Research, Helmholtz-Centre for Environmental Research – UFZ, Brückstraße 3a, 39114 Magdeburg, Germany

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²Chair of Meteorology, Institute of Hydrology and Meteorology, Faculty of Environmental Sciences, Technische Universität Dresden, Piener Straße 23, 01737 Tharandt, Germany

Correspondence to: Patrick Aurich (patrick.aurich@ufz.de)



10 **Abstract.** Lakes are hotspots of inland carbon cycling and are important sources of greenhouse gases (GHGs), such as
carbon dioxide (CO₂). The significant role of CO₂ in global carbon cycle makes quantifying its emission from various
ecosystems, including lakes and reservoirs, important for developing strategies to mitigate climate change. The thin
boundary layer method is a common approach to calculate CO₂ fluxes from CO₂ measurements in both the water and the air,
and wind speed. However, one assumption for the TBL method is a homogeneous CO₂ concentration between the
15 measurement depth and the water surface, where gas exchange takes place. This assumption might not be true under calm
conditions, when microstratification below the surface slows vertical exchange of gases. We used a floating outdoor
laboratory to monitor CO₂ concentrations in 5 cm and 25 cm depth, CO₂ concentration in the air, wind speed, and water
temperature profiles for one week in Bautzen Reservoir, Germany. While we found homogeneous CO₂ concentrations in the
two depths during wind speeds above 3 m s⁻¹, there was a vertical gradient observed during wind still nights. The
20 concentrations observed temporally ranged from undersaturation to supersaturation in 25 cm and 5 cm, respectively. Fluxes
calculated from the measured concentrations therefore would change from negative to positive, depending on the
measurement depth. Simultaneous Eddy Covariance measurements showed that even the measurements close to the surface
underestimated the actual CO₂ concentration. Oxygen measurements support our hypothesis that respirational processes at
the water surface cause a temporal CO₂ concentration gradient from the surface to the underlying water. Until now, the depth
25 of CO₂ measurements has not been questioned, as long as measurements were done in the upper mixed layer and close to the
surface. Our results provide evidence that representative measurements of CO₂ in the water strongly depend on depth and
time of measurements.

1 Introduction

Lakes are hotspots of inland carbon cycling and are important sources of greenhouse gases (GHGs), such as carbon dioxide
30 (CO₂). The significant role of CO₂ in global warming and climate dynamics makes quantifying its emission from various
ecosystems, including lakes and reservoirs, important for developing strategies to combat climate change. Proper
measurement of CO₂ emissions from lakes is the basis for robust global CO₂ emission quantification (Raymond et al., 2013;
Lauerwald et al., 2023).

The state-of-the-art method to quantify GHG fluxes between earth surface and atmosphere is Eddy Covariance (EC)
35 (Aubinet et al., 2012). Measurements by EC represent direct measurements covering large footprint areas at high temporal
resolution. However, EC systems are expensive and complex to run. Thus, there are only few EC sites on lakes worldwide.
In contrast to methane, which is often emitted by gas bubbles, CO₂ fluxes at the water surface are nearly exclusively driven
by diffusion. The by far most used approach to quantify diffusive aquatic GHG fluxes is the Thin Boundary Layer approach
(TBL, Lauerwald et al., 2023), also referred to as flux gradient method). The TBL approach, in contrast to EC, is an indirect
40 measurement to quantify diffusive gas exchange across the water atmosphere interface. The TBL flux is derived from the



concentration gradient between the water and the atmosphere (Δc_{CO_2}) multiplied by the gas exchange velocity (k , equation 1).

$$F = \Delta c_{CO_2} * k, \quad (1)$$

This method is much simpler than EC, because it only requires concentration measurements in both the water and atmosphere. The gas exchange velocity can be estimated from meteorological data, typically wind speed and eventually temperature or fetch, using empirical models (Cole and Caraco, 1998; McGillis et al., 2004; MacIntyre et al., 2010; Vachon and Prairie, 2013; MacIntyre et al., 2021). The temporal resolution can be comparable to the EC method when using submerged CO₂ probes. However, for both methods, uncertainties arise from situations involving very low wind speeds.

When there is no wind, EC systems cannot measure at all, because the method relies on air movements (Aubinet et al., 2012; Podgrajsek et al., 2014). But also, the TBL approach encounters difficulties under wind still conditions. While wind is the primary driver of gas transfer velocity and surface turbulence in large water bodies, its influence decreases under calm conditions, where factors such as surface cooling-induced convection (MacIntyre et al., 2010) and the lake's morphometry (Schilder et al., 2013) gain prominence in controlling gas exchange velocities. Consequently, predicting k based on wind speed alone introduces significant uncertainties. Thus, there is an urgent need to improve our ability to quantify aquatic GHG fluxes under low turbulence conditions.

While there are several attempts to improve the models that predict k (Cole et al., 2010; Crusius and Wanninkhof, 2003; MacIntyre et al., 2010; Vachon and Prairie, 2013), to our knowledge, the effect of uncertainty in $c_{CO_2,water}$ measurements on the TBL approach has hardly been investigated. In calm conditions, the absence of wind significantly reduces turbulence, leading to surface microstratification. This microstratification creates distinct layers within the mixed layer, each with varying temperatures and solute concentrations, including CO₂ (Åberg et al., 2010). Specifically, microstratification may result in dissolved gas gradients near the water's surface, suggesting that the actual layer engaging in atmospheric exchange becomes very thin. This challenges the assumption of the TBL approach that water just below the surface accurately represents the layer of gas exchange.

The critical layer of diffusive gas exchange is the surface micro layer (SML). The SML is the interface between the water and the atmosphere and is characterized by high biological activity and physical processes that affect the interaction with the atmosphere (Gladyshev, 2002; Wurl et al., 2011). The SML is known for its enriched concentrations of algae, organic and inorganic solutes, and particles (Hardy, 1982). These components collectively distinguish the SML as a unique layer situated between the atmosphere and the underlying water. In the ocean, surfactants in the SML were found to reduce the diffusive gas exchange with the atmosphere by 32 % (Pereira et al., 2018). Under calm conditions, the SML thickens, becoming even more crucial for the diffusive exchange of gases (Rahlff et al., 2017). However, despite its importance, there remains a gap in our understanding of the interactions between the atmosphere, the SML, and the water beneath, particularly in fresh water environments. Dynamics in gas exchange between the epilimnion, the surface layer and the atmosphere could lead to systematic uncertainty in the quantification of the surface gas concentration, as samples might be collected from depths that



do not accurately reflect the conditions of the water-atmosphere interface. In a recent study, Rudberg et al. (2024) explored
75 how spatial and temporal differences affect the influence of k and c_{CO_2} on the variability of F_{CO_2} . By deploying a floating
chamber over several hours, the gas concentration in the chamber equilibrated with the gas concentration in the surface water
and enabled the quantification of the surface CO_2 concentration. With this approach they demonstrated that over long-term
periods, c_{CO_2} contributed more to F_{CO_2} variability than k . This finding emphasizes the need for precise c_{CO_2} measurements
when estimating fluxes using models. Similar research has been conducted in the ocean. Although CO_2 samples for gradient-
80 based flux models are usually collected a few meters below the water surface, Calleja et al. (2013) found significant
gradients between depths of 5-8 meters. Hari et al. (2008) found different CO_2 concentrations in 0.1 m and 0.5 m depth while
investigating a new method for CO_2 measurements. However, while these differences are attributed to varied biological
activities in the different depths, there is a lack of knowledge about the formation and characteristics of such gradients,
especially with regard to the SML and diffusive gas exchange with the atmosphere.
85 To better understand the importance of vertical CO_2 gradients at the water-atmosphere interface, we conducted an extensive
field experiment in a eutrophic reservoir. Our study is based on two key hypotheses: firstly, that temporal gradients of CO_2
concentrations are present close to the water surface, and secondly, that these gradients are influenced by meteorological
factors, such as wind. To assess the effect of an eventual surface CO_2 gradient on CO_2 fluxes we compared fluxes calculated
by the TBL approach with fluxes measured by EC during the same period.

90 **2 Materials and methods**

2.1 Study site

Measurements were made at Bautzen reservoir in Germany (51.218 °N, 14.466 °E). It is a dimictic reservoir, but high wind
exposure, a relatively large surface area (533 ha) as well as a circular shape, and the shallow depth (mean 7.4 m, maximum
13.5 m) result in a weak stratification during summer in some years (Benndorf, 1995; Spank et al., 2023). The eutrophic to
95 hypereutrophic reservoir (Kerimoglu and Rinke, 2013) serves for flow regulation of river Spree – the main river of Berlin. A
preceding study showed CO_2 uptake during the ice-free season of -9.8 and -71.0 g C m^{-2} during the ice-free season of 2018
and 2019, and CH_4 fluxes of 24.0 g C m^{-2} and 23.2 g C m^{-2} , respectively (Spank et al., 2023).

2.2 Meteorological field observatory

A floating outdoor laboratory (FOL) was operated to continuously observe the mass- and energy exchange between the
100 water surface and the atmosphere. A detailed description of FOL and its instrumentation of can be found in Spank et al.
(2020, 2023, 2024). The FOL provided reference data of the carbon dioxide flux (F_{CO_2}) between the water surface and the
atmosphere as well as data of wind speed (U), air temperature (T_a), relative air humidity (RH), air pressure (p_a), solar
radiation (R_g) and water temperature (T_w) in a temporal resolution of 30 minutes. In addition, the FOL served as a carrier for
the devices used during the measurement campaigns. The measurement height of meteorological sensors was 2 m above the



105 water surface in accordance with international standards. The thermistor chain used was configured to measure T_w at depths
of 0.25, 0.50, 0.75, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0, 6.0, 8.0, 10.0, 12.5, and 15.0 m. The eddy covariance measuring system,
which provides F_{CO_2} , was instrumented according to standards and guidelines given by Lee et al. (2004), Foken and Mauder
(2024), Aubinet et al. (2012) and Burba (2013). The EC data are representative for the pelagic zone of Bautzen reservoir. In
particular, carefully performed footprint analyses proved that effects and disturbances from surrounding terrestrial sites can
110 be almost completely ruled out (Spank et al. 2023). The EC post processing was based on the methodologies of Carbo
Europe (Aubinet et al., 1999) and ICOS (Sabbatini et al., 2018) and had been performed utilizing the software EddyPro 7.0.8
(LI-COR Biosciences 2023). However, the special measurement condition on a floating platform had to be taken into
accounted, which required an upstream correction of the sensor misalignment (Spank et al., 2020, 2023).

2.3 Dissolved Gases

115 To detect eventually occurring dissolved CO_2 concentration gradients at the water surface, we deployed two CO_2 probes
(Contros HydroC, -4H- JENA engineering, Germany) at different depth from September 18 to September 25 in 2022
(hereinafter referred to as *study period*). These probes, featuring diffusive membranes with a diameter of 8 cm, were
positioned so that the central points of their membranes were situated at depths of 0.05 m and 0.25 m, respectively. We used
a frame that consisted of two aluminium bars, which were connected by two cross bars in the middle. Aluminium extensions
120 on the cross bars were used to mount the CO_2 probes horizontally and allow adjustments of the measurement depths.
Buoyancy floats in the four corners were used to make the frame float below the surface (Figure S 1). The CO_2 probes were
powered by 24 VDC provided by the floating platform. To maintain the integrity of surface water stratification, we left the
membranes of the CO_2 probes uncovered. CO_2 measurements were logged internally by the probes every minute, with a
measurement cycle of 1400 minutes measuring, followed by 3 minutes zeroing and 37 minutes flushing. CO_2 probe
125 performance was validated before deployment by running both probes in a sink, using an infrared gas analyser (EGM-5, PP-
Systems, USA) coupled to a membrane contactor (MiniModule, Liqui-Cel, USA) as a reference system (as in Koschorreck et
al., 2021; Figure S 2). After deployment, internal data required post processing (as described in Fietzek et al., 2014) because
the measurements were out of the factory calibration range. In brief, the internal zero measurements using CO_2 absorbents
generate frequent calibration points for $pCO_2 = 0$. Daily zero measurements were used to calibrate signal outputs between
130 the last and the next zero measurement. Finally, a modified polynomial function was used to determine corrected CO_2
concentrations. During our sampling period, the reference signal was constant, indicating proper function of the sensor.
Oxygen concentrations were measured every 15 minutes by optical O_2 loggers. Surface O_2 concentration at 0.05 m depth
was measured with a miniDOT logger equipped with a miniWIPER (Precision Measurement Engineering, USA, wiping
frequency 12 hours) mounted at the same depth as the surface CO_2 probe. A D-Opto oxygen logger (ZebraTech, Nelson, NZ)
135 was installed in the bottom water at 1 m above the sediment using a separate mooring. Both oxygen sensors were calibrated
using a two-point calibration at 0 % and 100 % oxygen saturation and corrected for potential drift.

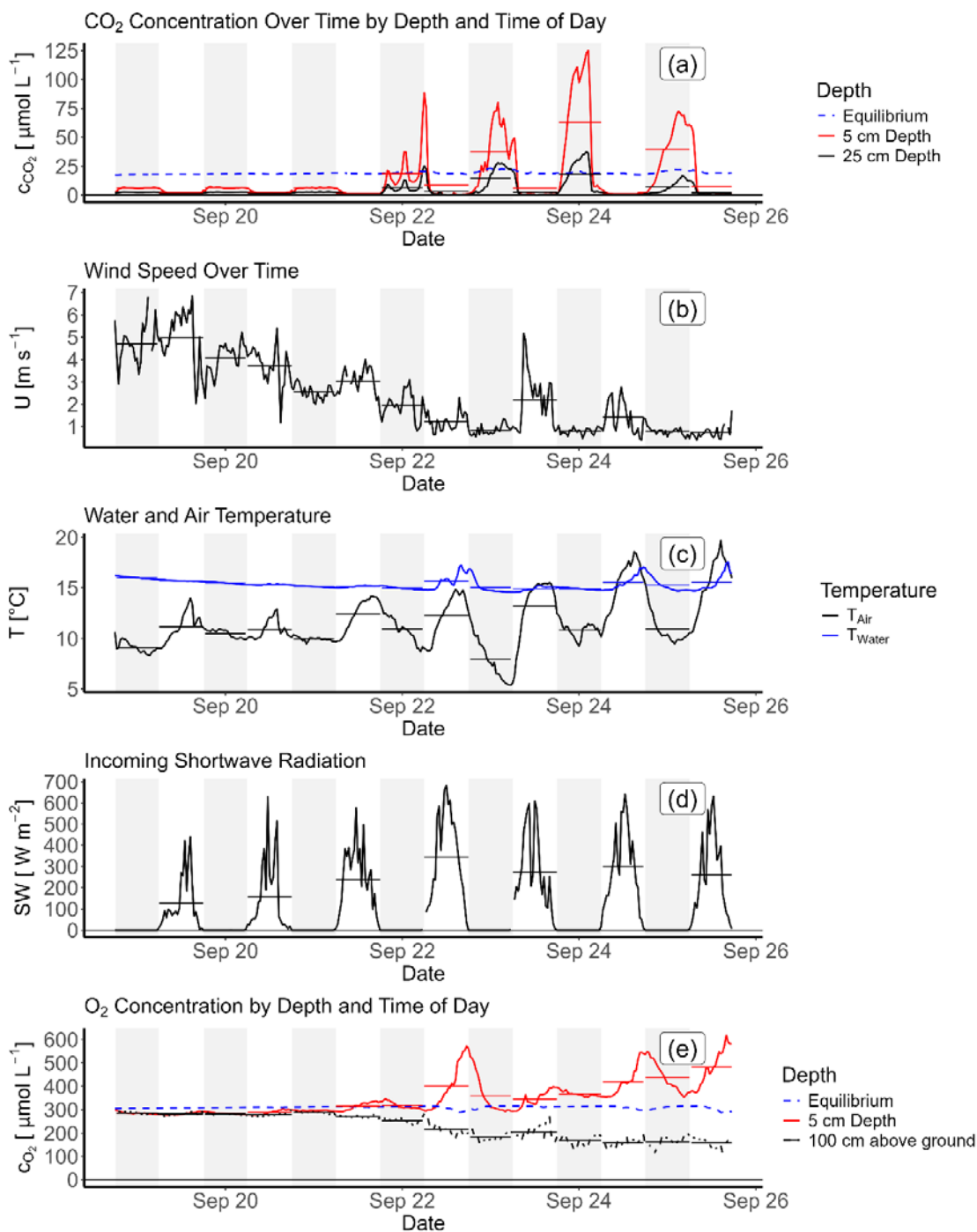


2.4 Data analysis and Statistics

The platform data was prepared and exported from Python. For this study, the platform data, CO₂ probe data and oxygen data were compiled in R (R Core Team, 2023). All subsequent analyses, statistical computations, and visualizations were performed in R. CO₂ and oxygen measurements were averaged over 30-minute periods. Day and night averages were calculated using sunrise and sunset times determined using the *is.day()* function. Gas transfer velocities were calculated from wind speeds at 10 meter height, using the *k.cole.base()* function, referring to the parametrization explained in Cole and Caraco (1998). Gross primary production (GPP) and respiration (R) were calculated using the *metab()* function. Those functions are part of the LakeMetabolizer package (version 1.5.5; Winslow et al., 2016). Gas fluxes were calculated from in situ water and air pCO₂ and *k* using equation 1.

3 Results

In 2022, Bautzen reservoir was thermally stratified from the beginning of May. During the stratification period (mean mixed layer depth = 4.4 m), the maximum temperature at the surface was 30 °C, while the temperature above the ground reached a maximum of 13 °C (Figure A 1). On September 9, 2022, a thunderstorm with strong winds hit the Bautzen region, leading to a shutdown and subsequent 5-day outage of the measurement platform. This storm also marked the end of the stratified season and started mixing of the reservoir. On September 18th, which marks the beginning of our extensive GHG measurements, T_w was 16 °C at both the surface and bottom. The oxygen C_{O₂} was 9.1 mg L⁻¹ at both the surface and the bottom.

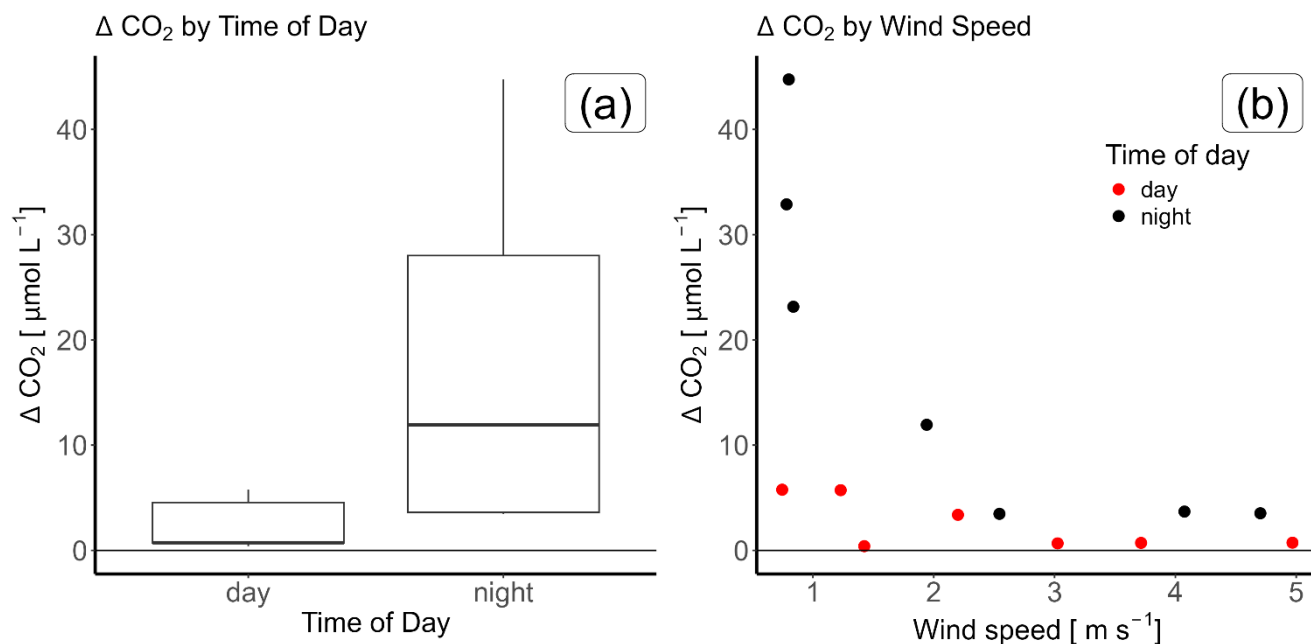


155 **Figure 1:** CO₂ concentrations measured in the two depths (a), Wind speed (b), Water temperature at 0.25 m depth + air temperature (c), incoming short-wave radiation (SW, d), and oxygen (e). Horizontal bars show mean values of days and nights. Grey highlights show night-time.



The CO₂ concentration at the water surface showed a consistent diurnal pattern during the entire study period. At night, CO₂ concentration at 5 cm depth was generally higher than at 25 cm depth. Thus, every night of our study period a gradient of CO₂ concentration near the water surface developed. In contrast, no such gradient was observed during the. At both depths, CO₂ concentrations increased with the disappearance of short-wave radiation at sunset and decreased with its increase at sunrise (Figure 2d). Mean air temperatures (T_a) ranged between 9 °C and 15 °C, with distinct diurnal patterns. The water temperature at 25 cm depth (T_{w25}) decreased slightly from 16 °C to 15 °C during the measurement period, except for September 23rd, 24th, and 25th, when water temperature increased by 1 °C during the day (Figure 1 C). During the days of September 23rd, 24th, and 25th, the air temperature was above the water temperature. On all other days and nights, the water temperature consistently remained higher than the air temperature.

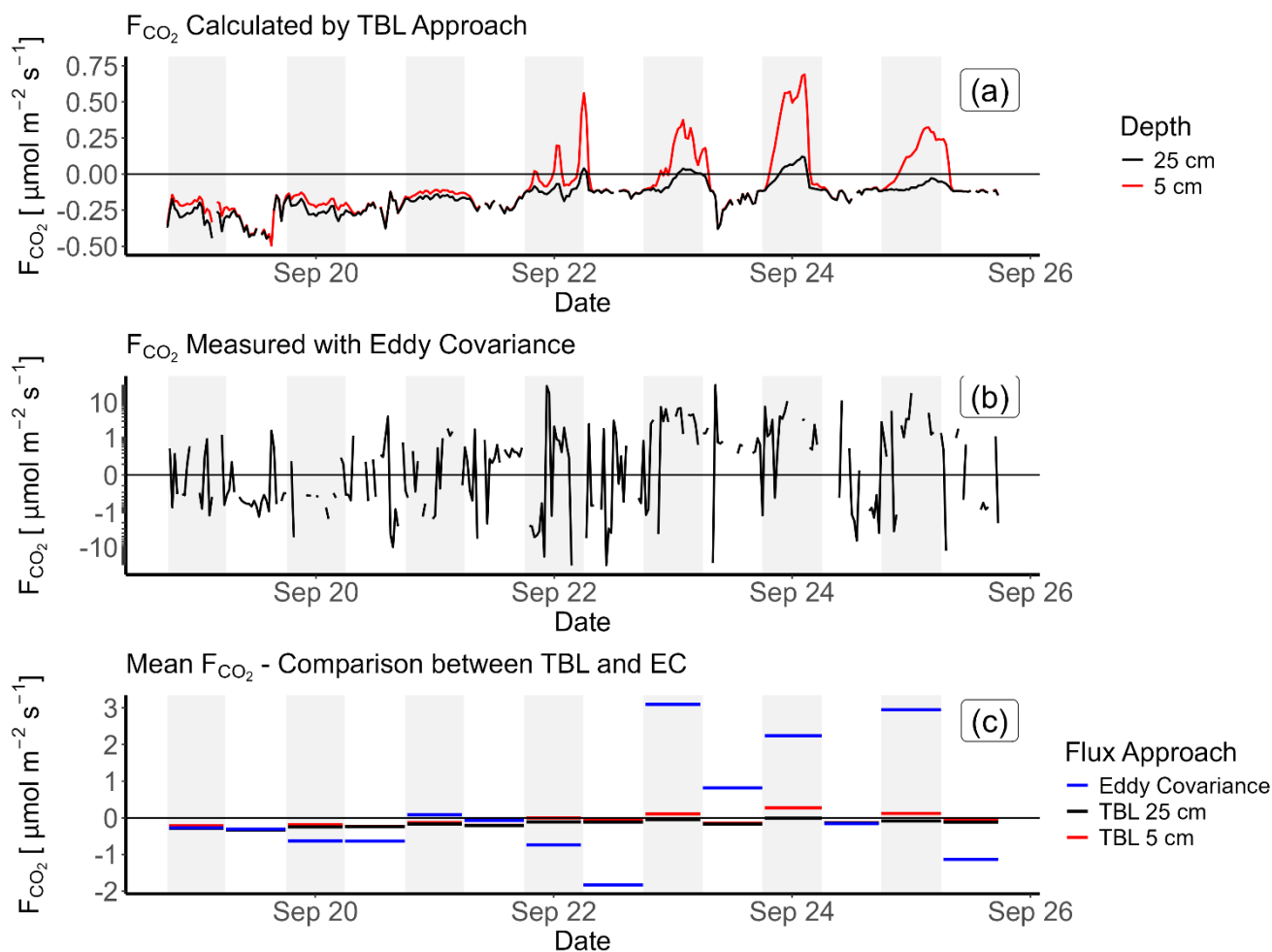
While the diurnal pattern of the CO₂ gradient at the water surface was consistent during our study period we observed large differences regarding the magnitude of this gradient. Our measurement period can be divided into two parts with differing weather conditions. The first period from September 19th to 21st was windy with U mostly above 3 m s⁻¹. However, during the second half of our sampling period, wind speeds were mostly below 3 m s⁻¹, with 63 % of those times even falling below 1 m s⁻¹ (Figure 1 b). The CO₂ concentrations near the water surface during the night showed a fundamentally different behaviour during those two periods (Figure 1 a). High CO₂ concentrations up to 125 μmol L⁻¹ were observed during the calm period while during the windy period CO₂ was permanently undersaturated and at the detection limit of our probes. Notably, nightly CO₂ concentrations in both depths were ten to twenty times higher during the calm period compared to the windy period. Starting on September 22nd, nightly CO₂ concentrations exceeded the equilibration concentration, leading to temporary supersaturation in calm nights. While the nightly mean CO₂ concentration at 5 cm depth exceeded the equilibration concentration in the nights of September 23rd to 26th, the mean concentration at 25 cm depth never surpassed equilibrium. The oxygen concentration was different between the two periods. O₂ concentrations at both 5 cm depth and at the bottom were slightly undersaturated during the windy period. When the water column started stratifying again (Figure 1 e), O₂ concentrations at the two depths started to diverge. While the O₂ concentration at the bottom continuously decreased over the rest of the sampling period, the concentration at 5 cm increased to supersaturation, showing clear diurnal patterns of oxygen production and consumption (Figure 1 e).



185 **Figure 2: Dependence of CO₂ difference between 5 cm and 25 cm depth on time of day (a) and wind speed (b). Both plots are based on mean values per time of day.**

To gain a more detailed understanding of the CO₂ gradients at the surface, we calculated the difference in CO₂ concentrations between 5 cm and 25 cm depths. Our measurements showed that the mean concentration gradient was significantly steeper during the night compared to during the day (t-test, $p < 0.05$, Figure 2 a). The magnitude of the gradient depended on wind speed (Figure 2 a). Generally, the mean CO₂ gradient was lower at high wind speeds for both day and night. However, while low wind speeds did not lead to higher CO₂ gradients during the day, the gradients in calm nights were 5 to almost 10-fold steeper (Figure 2 b). This diurnal development of a CO₂ gradient at the surface should have affected CO₂ emissions.

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195 **Figure 3: EC TBL comparison. Fluxes calculated from TBL approach (a) and measured by Eddy Covariance (b) with hourly resolution as well as averaged over every day and night periods (c). Grey highlights show night-time.**

We used our CO₂ concentration data to calculate CO₂ fluxes by the TBL approach and compared those fluxes with measurements done with Eddy Covariance (Figure 3). During the windy period, TBL fluxes were negative regardless of which CO₂ probe data we used and comparable to the fluxes measured by EC (Figure 3 a, b, and c). In calm nights, supersaturation of CO₂ led to positive TBL fluxes with data from both depths. Because at 25 cm depth oversaturation was only reached at the end of the night, mean night fluxes derived from 25 cm depth remained negative (Figure 3 c). EC fluxes during those nights were positive too, but significantly higher than TBL fluxes (Figure 3 b, c). In 5 out of 14 cases, the flux direction differed between the TBL approach and EC measurements, when using the measurements of the 25 cm probe for the TBL approach. In contrast, when using CO₂ measurements from the 5 cm probe, only 2 out of 14 instances show different flux directions. During our study period of 7 days, the total CO₂ emissions were -2.2 g m⁻² when calculated using the 5 cm data, -4.2 g m⁻² based on 25 cm data, and 4.6 g m⁻² as recorded by the eddy covariance system.



4 Discussion

Our data, showing the change from windy to calm weather conditions, and a mixed water column to formation of stratification, respectively, within a week, provided unique insights in the influence of microstratification on greenhouse gas exchange between lakes and the atmosphere. Our detailed CO₂ concentration measurements clearly showed the temporal development of a CO₂ gradient at the water surface. This observation is consistent with previous studies like Hari et al. (2008), whose results indicate CO₂ gradients within the upper 50 cm of the water layer.

During the windy period, CO₂ concentrations were as low as the detection limit of our probes at daytime, probably caused by photosynthetic CO₂ consumption by abundant phytoplankton. CO₂ undersaturation in high productive lakes is a common observation (Balmer and Downing, 2011; Zagarese et al., 2021). In that period, CO₂ concentrations were consistently lower than the atmospheric equilibrium concentration, turning the reservoir to a CO₂ sink during that time. The oxygen concentrations measured at the surface and above the bottom as well as the temperature profiles suggest that the entire water column was mixed in that period, likely leading to homogeneous CO₂ concentration across the whole water column, too. This observation is supported by the fact that no CO₂ gradient was measured during the day, while a slight gradient was detected at night. This occurs because CO₂ is consumed quickly during daylight hours, whereas at night, the uptake of CO₂ from the atmosphere leads to slightly higher concentrations at the water surface. This was reflected by our 5 cm probe measuring concentrations closer to atmospheric equilibrium than the 25 cm probe.

When the wind ceased at September 21st, the vertical distribution of gas concentrations changed. Starting on that day, oxygen concentrations at the surface and at the bottom began to increase and decrease, respectively. This observation indicates that the reservoir slowly underwent stratification again. While there was no difference in CO₂ gradients during calm daylight hours compared to windy days, we observed notably high CO₂ concentrations within the top 25 centimetres during calm nights. The high CO₂ concentrations during calm nights could be related to the effects of stratification. During windy periods, the mixed water layer depth was greater than during calm periods, resulting in a larger volume of water influenced by O₂ and CO₂ overturn in the photo-active layer. Phytoplankton may have decreased the CO₂ concentration in this large volume through photosynthesis over the days of strong winds. At night, respiration slightly increased the CO₂ concentration, but this was not enough to fully compensate for the daytime reduction. When windspeed decreased, the mixing depth and volume became smaller. During these calmer nights, respiration in the shallow mixed layer led to significant CO₂ accumulation at the surface. Additionally, microstratification within the top 25 cm of the water column could further restrict the volume available for CO₂ accumulation, potentially leading to even higher concentrations (Figure 4). Our findings are consistent with a study of Åberg et al. (2010), who found that short term CO₂ variations at the surface were best related to thermal dynamics within the upper mixed layer, whereas parameters like wind and radiation did not influence CO₂ concentrations. In our study we found negative effect of incoming solar radiation on CO₂ concentrations during the day, but a positive feedback during the night. Further, varying CO₂ concentrations haven been related to changes in lake metabolism after storms before (Vachon and del Giorgio, 2014).



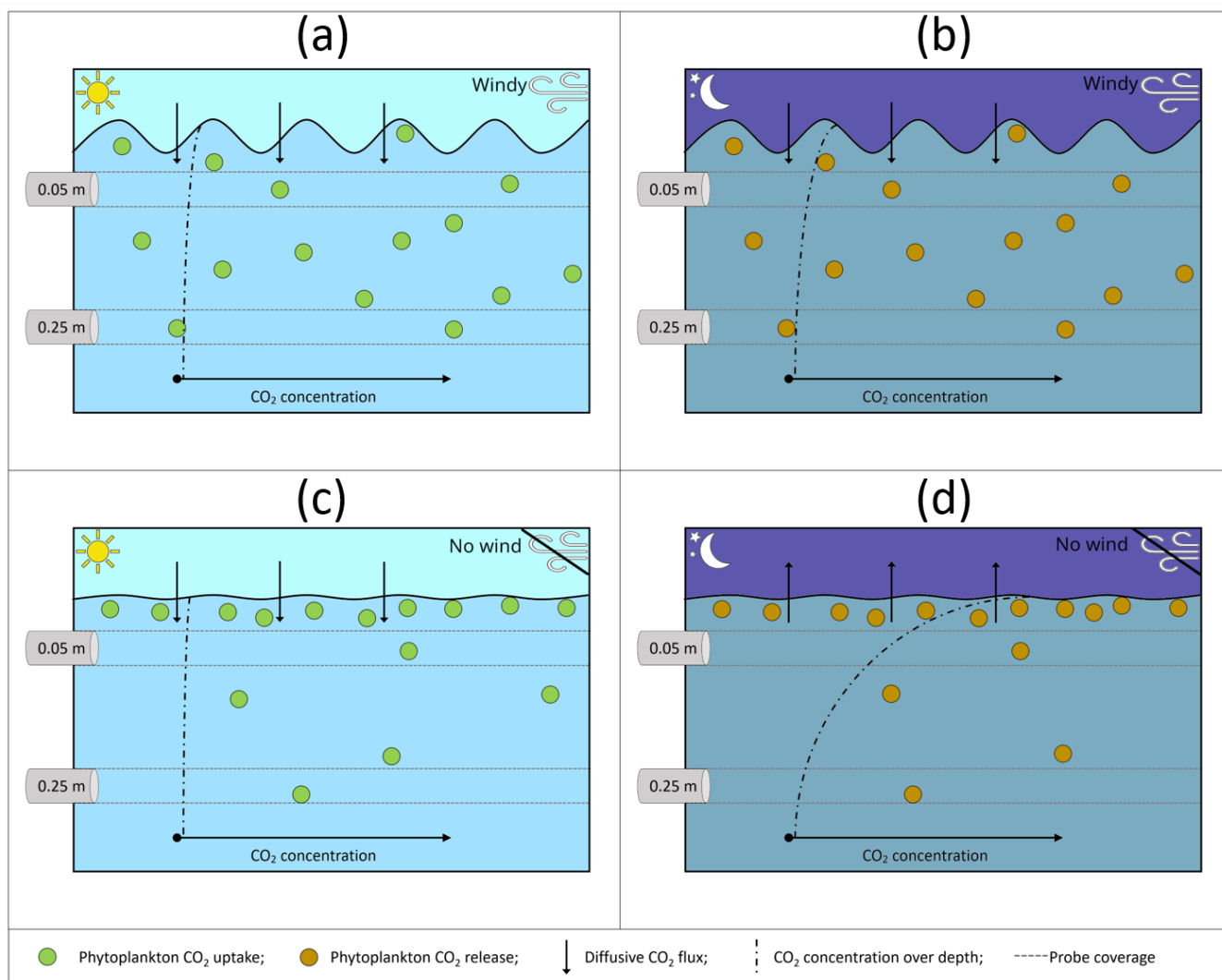
240 Interestingly, the 5 cm probe, despite being closer to the surface, recorded higher CO₂ concentrations than the underlying
water. This requires a CO₂ producing process in the surface layer, likely biological respiration. There are various groups of
organisms that could increase CO₂ in the 5 cm layer, such as neuston, which comprises organisms living at or even within
the surface micro layer. Phytoplankton was found to float at the water surface at wind speeds lower than 3 m s⁻¹ (Zhang et al.,
2021). Further, some species migrate from the lower boundary of the epilimnion to the surface during night. This behaviour
245 is called diel vertical migration and is used to access food while avoiding predators that need light for hunting (Ringelberg,
1999). Both neuston and migrating species are respiring during the night, thereby producing CO₂. Furthermore, the vertical
mixing during windy periods likely increased nutrient availability for phytoplankton, potentially triggering growth and
accumulation of algae at the water surface (Nürnberg et al., 2003). These phytoplankton switch from net photosynthesis
during the day to respiration at night, thereby increasing CO₂ concentration at night. Mean gross primary production and
250 respiration in the calm period were 10.4 mg O₂ L⁻¹ d⁻¹ and -9.0 mg O₂ L⁻¹ d⁻¹, respectively, which is comparable to other
hyper-eutrophic lakes, especially after storm events (Williamson et al., 2021). During algal blooms, the water surface is often
covered by a mat of floating algae. Although we lack chlorophyll data, satellite images taken before and after our
measurement period suggest rapid algal growth following the storm events that occurred just before our study (Figure B 1).
Such mats can become very dense, possibly increasing CO₂ production and accumulation even more.

255 Moreover, the effect of convective mixing within the top water layer plays an important role in the distribution of CO₂
concentrations. Convective mixing, driven by water density differences due to cooling at the water surface, can enhance the
vertical movement of water, thereby influencing the distribution of CO₂ in the water column. While we did not find signs of
thermal microstratification at the surface during nights with strong CO₂ gradients, we contrastingly observed conditions
favoring convection (Figure 1 c). Further, meteorological parameters such as atmospheric stability, emitted long wave
260 radiation, or sensible heat flux, indicate unstable conditions in the air above the water. From this, we infer that the biomass
accumulated at the water surface could either produce CO₂ at rates that exceed its transport in the upper water layer, or the
algal mats acted as a physical barrier between the water and air, leading to increased stability of the water beneath the mats
by preventing atmospheric instability from influencing the water below.

The CO₂ gradient measured during calm nights was fundamentally influencing the fluxes calculated with the TBL method.
265 While it is generally acknowledged that daytime measurements do not reflect the concentrations at night (Erkkilä et al.,
2018), the depth of CO₂ measurements has not been questioned so far, as long as measurements were done in the upper
mixed layer and close to the surface. Our measurements provide evidence that representative measurements of the CO₂
concentration in the water strongly depend on depth and time of measurements. In our results, the depth of measurement
even determined whether the TBL method would result in efflux or influx (Figure 3bn). This was especially visible at night
270 when the flux calculated from the CO₂ concentration measured at 25 cm depth was negative, while both EC measurements
and TBL based on the measurements in 5 cm showed significant positive fluxes. The fact that the EC fluxes were higher than
the TBL fluxes based on the 5 cm probe could be explained by the CO₂ gradient which probably continued towards the
water-atmosphere interface. Our uppermost probe measured the mean CO₂ concentration between 1 and 10 cm depth and it



275 is plausible that the concentration at the water surface was even higher than measured by that probe. To measure the “real” concentration at the surface CO₂ measurements would need to be conducted even closer to the SML. Floating chambers have been used to measure CO₂ in the surface by deploying them as closed systems, therefore equilibrating the chamber volume with the surface water (Rudberg et al., 2021). However, equilibration for that method is slow and introduces a time delay for measured concentrations, which means that the temporal resolution is weak. Therefore, the method is not suited to directly measure CO₂ concentration on short time scales and with high vertical resolution.



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Figure 4: Schematic of CO₂ accumulation in the surface water, with CO₂ probes located in 5 cm and 25 cm depth. (a): wind-induced turbulence causes homogeneous distribution of phytoplankton, resulting in CO₂ decrease in both measuring depths during the day. (b): wind induced turbulence causes homogeneous distribution of phytoplankton. CO₂ is produced by respiration, but the CO₂ concentration across the whole water column is low, thus respiration is compensating strong undersaturation. CO₂ uptake from the atmosphere causes slightly increased concentration in 5 cm. (c): CO₂ concentration is low in the whole mixed



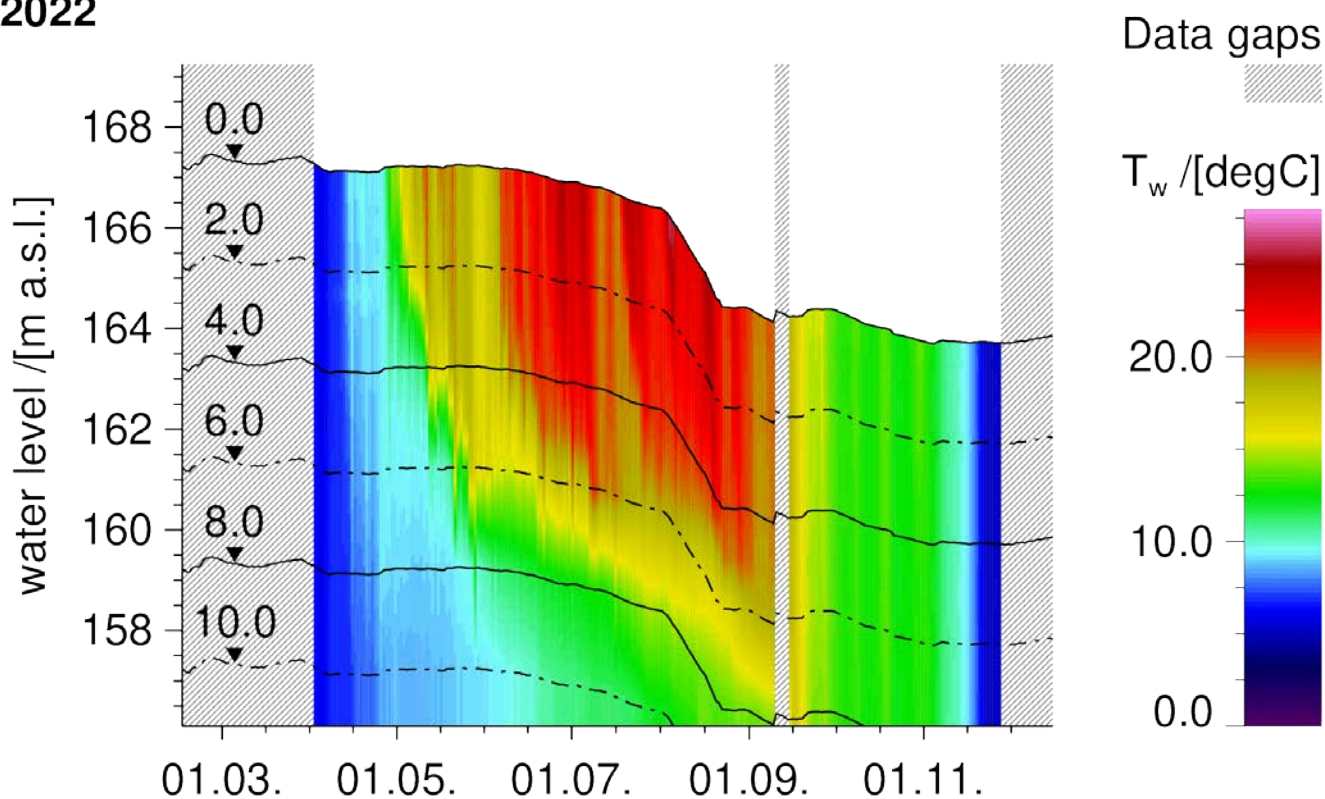
layer, but calm conditions cause phytoplankton to accumulate at the surface. (d): Calm conditions cause phytoplankton to accumulate at the water surface. Respiration causes CO₂ increase in this layer, which is causing CO₂ emissions during calm nights.

Conclusions

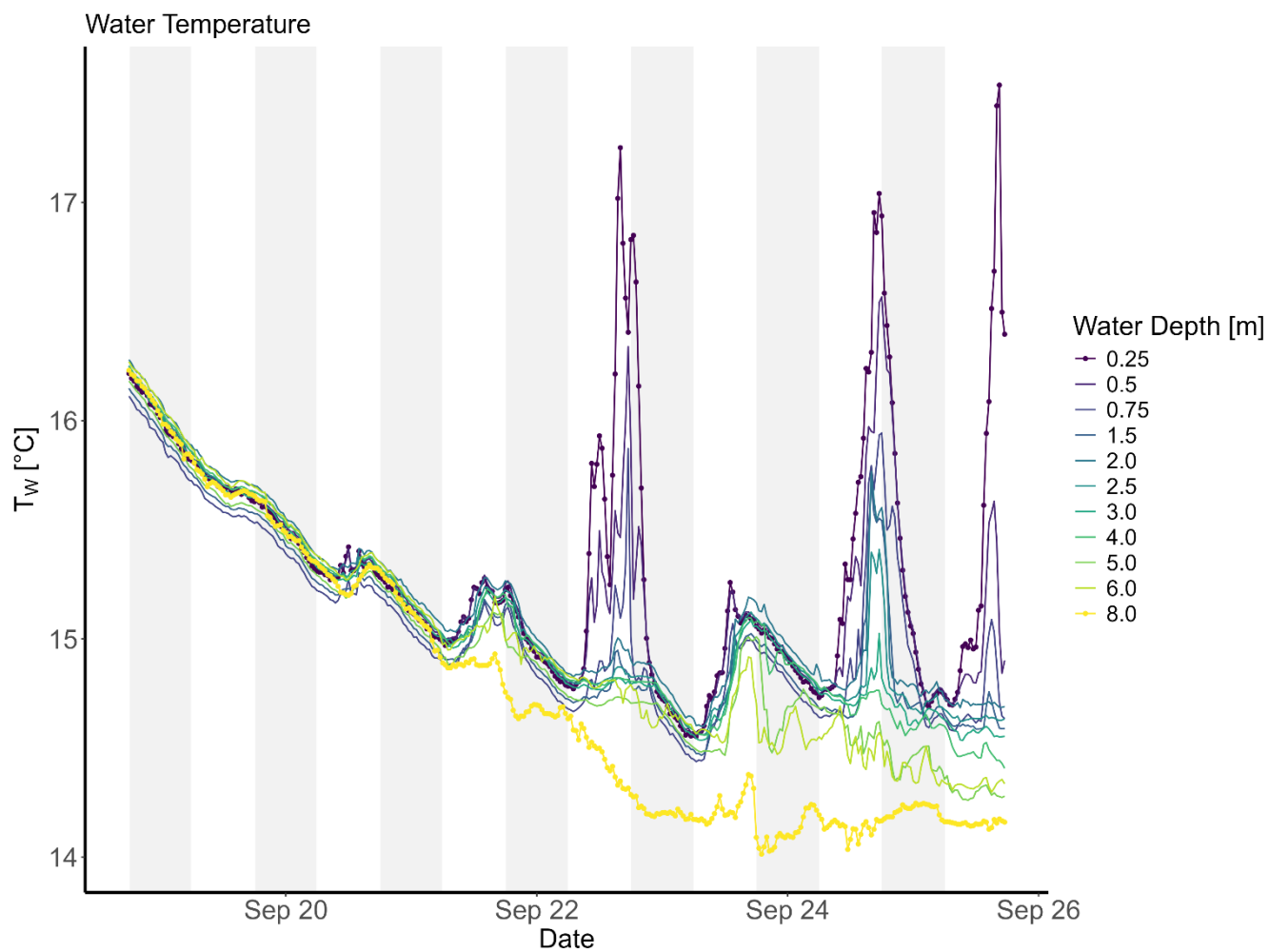
Our results show that the surface CO₂ gradient is regulated by an interplay of physical and biological processes (Figure 4).
290 Only when limited mixing of the surface layer comes together with high accumulation of biomass in the surface water a thin surface layer with high CO₂ concentrations can develop. That effect can turn a CO₂ under-saturated lake to a temporary CO₂ source.

Appendix A: Detailed water temperature graphs

2022



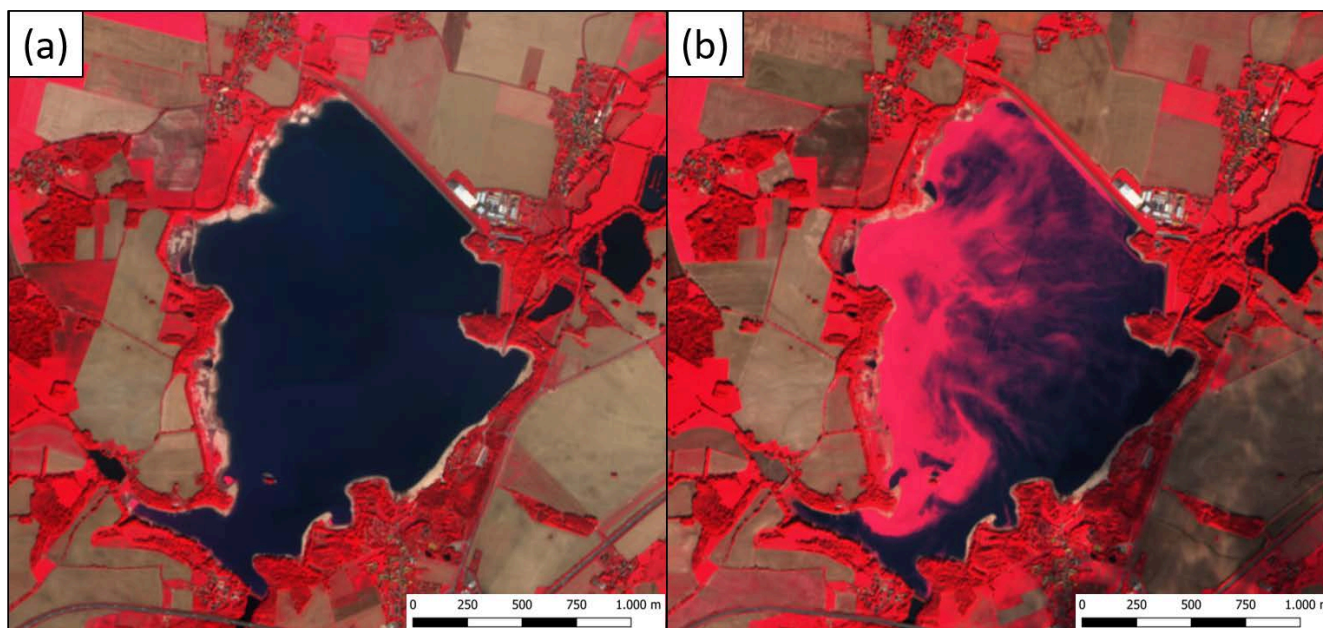
295 Figure A 1: Water level (meters above sea level) and water temperature profile from April 1st to November 28th in 2022 at Bautzen reservoir. Solid and dot-dashed black lines indicate water depths of 2 m, 4 m, 6 m, 8 m, and 10 m. Grey bars highlight missing data.



300 **Figure A 2: Detailed water temperatures across the water column during the extensive sampling period. Dotted lines highlight surface and bottom temperatures. Grey highlights show night-time.**



Appendix B: Satellite images of the reservoir



305 **Figure B 1: False colour images from Sentinel-2 L2A taken on September 5th (a) and 25th (b), 2022, provided by the European Space Agency (ESA) and accessed via the EO Browser (<https://apps.sentinel-hub.com/eo-browser/>, Sinergise Solutions d.o.o., a Planet Labs company). September 5th was selected because it was the last day without cloud coverage before the sampling period. The images show the state of the reservoir during the algal bloom described in this manuscript. The false colour images, which are typically used to highlight specific features like vegetation or water, do not show the water surface properly on September 25th, due to algal coverage. This clearly highlights the intensity of the algal bloom, which was likely covering the water surface.**

310 **Code availability**

Code is available upon request to the corresponding author.

Data availability

Data are available upon request to the corresponding author.

Author contribution

315 All authors contributed to the study's conception and design. Field measurements were carried out by PA and US. Meteorological data were processed by US, while limnological data were processed by PA. PA performed the data analysis. PA wrote the first draft of the manuscript, and all authors contributed to the final version. All authors read and approved the final manuscript.



Competing interests

320 The authors declare that they have no conflict of interest.

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