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

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10 **Abstract.** Lakes are hotspots of inland carbon cycling and are important sources of greenhouse gases (GHGs), such as carbon dioxide (CO_2). The significant role of CO_2 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 CO_2 fluxes from CO_2 measurements in both the water and the air,

not defined yet, I assume thin boundary layer. But note that this abbreviation is normally used a thermal boundary layer

and wind speed. However, one assumption for the TBL method is a homogeneous CO_2 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 CO_2 concentrations in 5 cm and 25 cm depth, CO_2 concentration in the air, wind speed, and water temperature profiles for one week in Bautzen Reservoir, Germany. While we found homogeneous CO_2 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 CO_2 concentration. Oxygen measurements support our hypothesis that respirational processes at the water surface cause a temporal CO_2 concentration gradient from the surface to the underlying water. Until now, the depth

25 of CO_2 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 CO_2 in the water strongly depend on depth and time of measurements.   I would go a bit further on the implications, what does mean of global carbon cycle?

1 Introduction

Lakes are hotspots of inland carbon cycling and are important sources of greenhouse gases (GHGs), such as carbon dioxide

30 (CO_2). The significant role of CO_2 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 CO_2 emissions from lakes is the basis for robust global CO_2 emission quantification (Raymond et al., 2013; Lauerwald et al., 2023).

As rule of thumb, it is recommended that each paragraph has 100-200 words and one single idea each.

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, CO_2 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

You mention before earth surface and atmosphere and you suddenly change to water atmosphere.
Also I think water-atmosphere, as we use air-sea

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

$$F = \Delta c_{CO_2} * k, \tag{1}$$

This method is much simpler than EC, because it only requires concentration measurements in both the water and

45 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 CO_2 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;

50 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

also the fact that most of these k-parametrization assume a zero-intercept

55 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

60 varying temperatures and solute concentrations, including CO_2 (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

65 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

check also Mustaffa et al., 2020 :)

gas exchange with the atmosphere by 32 % (Pereira et al., 2018). Under calm conditions, the SML thickens, becoming even

70 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

some reader might not know what that is

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

3

do not accurately reflect the conditions of the water-atmosphere interface. In a recent study, Rudberg et al. (2024) explored 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-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.

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.

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 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 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 Data and Statistics analysis

The platform data was prepared and exported from Python. For this study, the platform data, CO_2 probe data and oxygen

check how to cite that correctly, at least the version needs to be stated I think

data were compiled in R (R Core Team, 2023). All subsequent analyses, statistical computations, and visualizations were

140 performed in R. CO_2 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

How do you transform your 2-m wind to 10-m?

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

145 situ water and air p_{CO2} and *k* using equation 1.

Probably nice to know the "maths" behind the function for GPP and R, for example

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

150 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.

Out of curiosity (and also for paragraph consistency), do you have measurement of oxygen before the mixing,
when temperature was 30°C?

The result section needs a bit of re-estructure for clarity. For example, you talk about CO2 during the day in line 159 and again in line 17
I suggest to unify. Same get for other parameters.

6

add in M&M how this equilibrium is calculated. I guess is the CO2 from atmosphere (?). How did you get it?

consistency: in the main text you use Ta and Tw. Also, do you have the temperature at 5cm?

and at 25 cm?
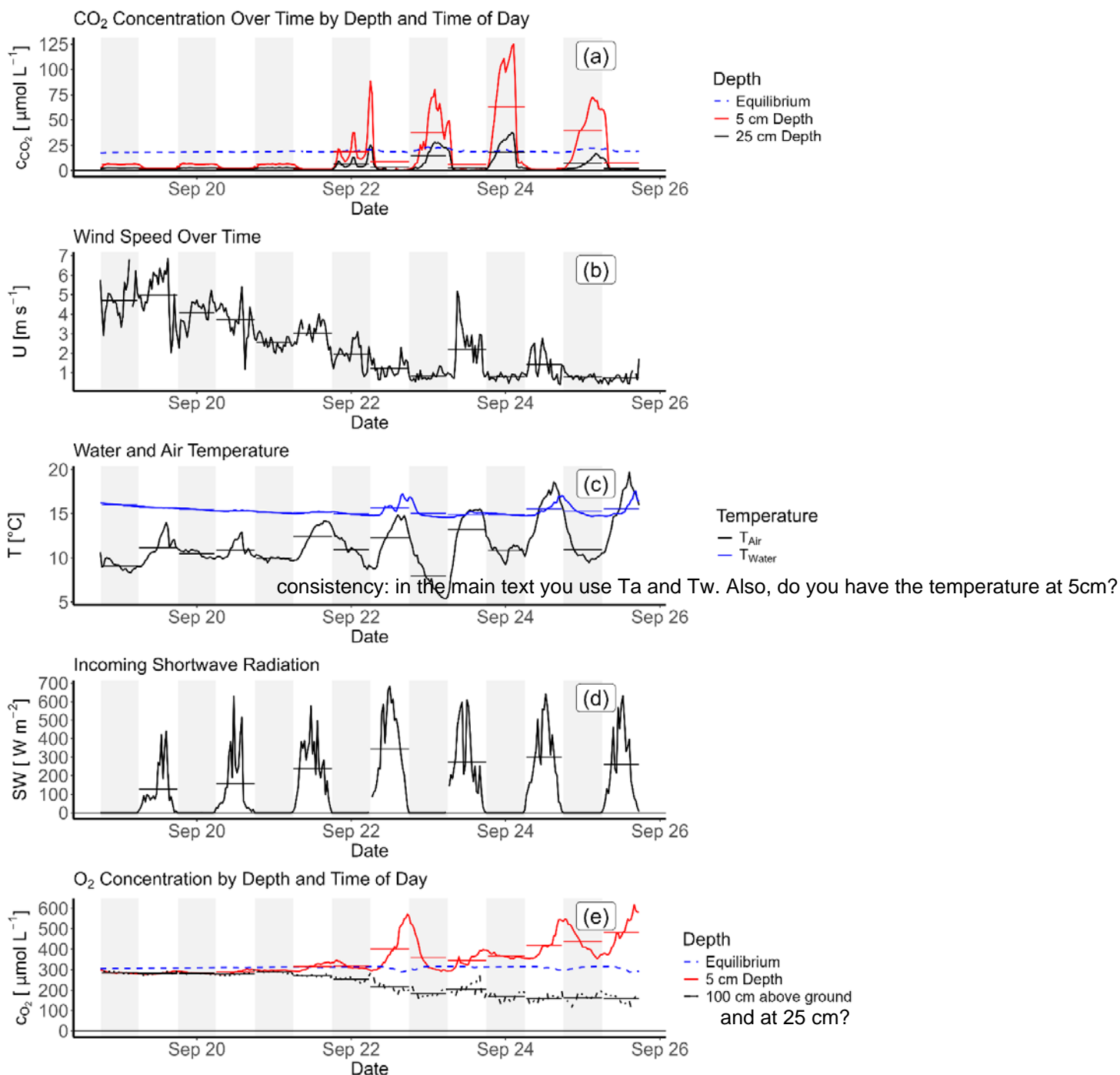
Figure 1: CO₂ concentrations measured in the two depths (a), Wind speed (b), Water temperature at 0.25 m depth + air temperature (c), incoming short-wave radiation (SW, d), and oxygen (e). Horizontal bars show mean values of days and nights. Grey highlights show night-time.

dissolved

the bars are a bit misliding, as sometimes there is a lot of variation. I was wondering if it could make more sense to add a box plot, where you will also show the mean and the range

7

The CO_2 concentration at the water surface showed a consistent diurnal pattern during the entire study period. At night, CO_2

160   concentration at 5 cm depth was generally higher than at 25 cm depth. Thus, every night of our study period a gradient of CO_2 concentration near the water surface developed. In contrast, no such gradient was observed during the. At both depths, CO_2 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

165   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 CO_2 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

U 10 m or U 2m? Also mentioned in the figure

170   weather conditions. The first period from September 19th to 21st was windy with U mostly above 3 m s^{-1}. However, during

Unify how you reference the figure, sometime a or A, sometimes space or not between number and letter

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 CO_2 concentrations near the water surface during the night showed a fundamentally different behaviour during those two periods (Figure 1 a). High CO_2 concentrations up to 125 µmol L^{-1} were observed during the

which is? needs to be stated in the M&M

calm period while during the windy period CO_2 was permanently undersaturated and at the detection limit of our probes.

175   Notably, nightly CO_2 concentrations in both depths were ten to twenty times higher during the calm period compared to the windy period. Starting on September 22nd, nightly CO_2 concentrations exceeded the equilibration concentration, leading to temporary supersaturation in calm nights. While the nightly mean CO_2 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. O_2 concentrations at both 5 cm depth and at

180   the bottom were slightly undersaturated during the windy period. When the water column started stratifying again (Figure 1 e), O_2 concentrations at the two depths started to diverge. While the O_2 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).

I guess the answer is no but do you have measurements of CO2 in the bottom? If not, worth to considered for the next project :)

Carefull on using deltaCO2 for two different things: air-water (as in Equation 1) or 5-25 cm.
Find another abbreviation of metion all the time deltaCO2_(5-25cm)
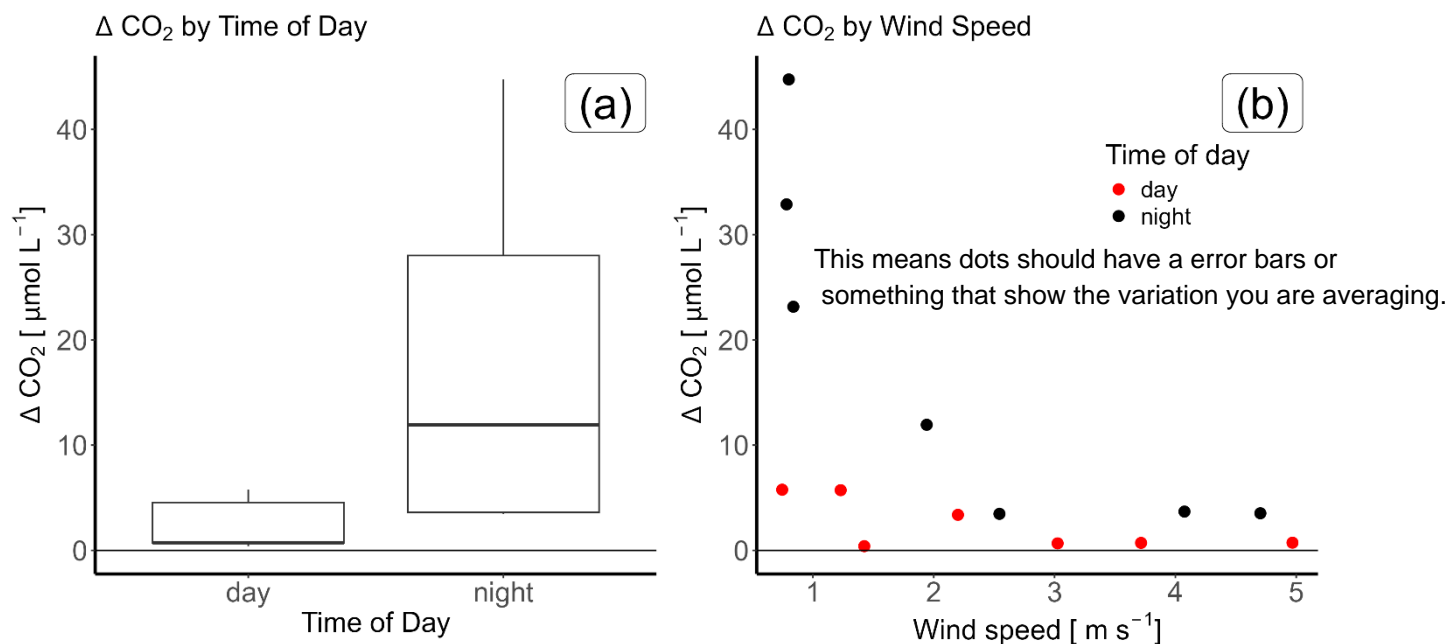
Figure 2: Dependence of CO2 difference between 5 cm and 25 cm depth on time of day (a) and wind speed (b). Both plots are based on mean values per time of day. See Stolle et al. (2020), figure 13. We presented k but could have also a relationship.

To gain a more detailed understanding of the CO_2 gradients at the surface, we calculated the difference in CO_2 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 CO_2 gradient was lower at high wind speeds for both day and night. However, while low wind speeds did not lead to higher CO_2 gradients during the day, the gradients in calm nights were 5 to almost 10-fold steeper (Figure 2 b). This diurnal development of a CO_2 gradient at the surface should have affected CO_2 emissions.

9
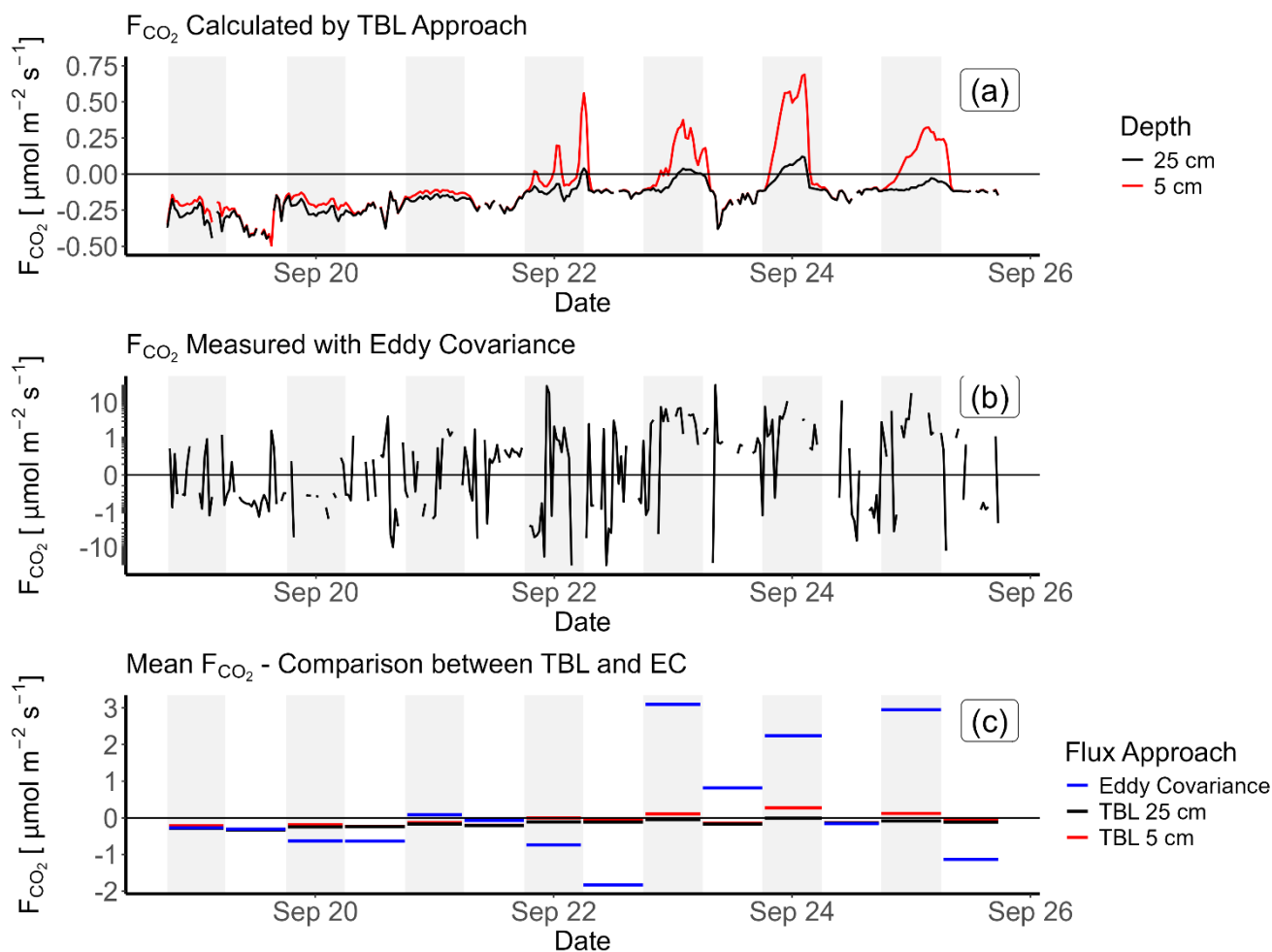
Figure 3: EC TBL comparison. Fluxes calculated from TBL approach (a) and measured by Eddy Covariance (b) with hourly resolution as well as averaged over every day and night periods (c). Grey highlights show night-time.

It is always nicer when you can understand the caption and figure without the need to read the paper. Please explain all more precise

We used our CO_2 concentration data to calculate CO_2 fluxes by the TBL approach and compared those fluxes with careful with the wording, 5 ms-1 is not particularly windy :)

measurements done with Eddy Covariance (Figure 3). During the windy period, TBL fluxes were negative regardless of

which CO_2 probe data we used and comparable to the fluxes measured by EC (Figure 3 a, b, and c). In calm nights,

supersaturation of CO_2 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 CO_2 measurements from the 5 cm probe, only 2 out of 14 instances show

emission through your study period? We need a time so you can get rid of your time unit.

different flux directions. During our study period of 7 days, the total CO_2 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.

How relieable are the EC-flux without wind/very low wind speed? You mentioned before they have problems.

10

The discussion is again very interesting but difficult to read. I suggest to find the main finding of each figure, explaining in the result section and then discussed her
If the journal allow, adding headers sections to the discussion will also help the reader

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

210 exchange between lakes and the atmosphere. Our detailed CO_2 concentration measurements clearly showed the temporal development of a CO_2 gradient at the water surface. This observation is consistent with previous studies like Hari et al. (2008), whose results indicate CO_2 gradients within the upper 50 cm of the water layer.

in the ocean I measure very low CO2 concentrations but never 0. Is this actually possible/documented? Is like CO2 anoxia?
During the windy period, CO_2 concentrations were as low as the detection limit of our probes at daytime, probably caused by photosynthetic CO_2 consumption by abundant phytoplankton. CO_2 undersaturation in high productive lakes is a common

215 observation (Balmer and Downing, 2011; Zagarese et al., 2021). In that period, CO_2 concentrations were consistently lower than the atmospheric equilibrium concentration, turning the reservoir to a CO_2 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 CO_2 concentration across the whole water column, too. This observation is supported by the fact that no CO_2 gradient was measured during the day, while a slight gradient was

220 detected at night. This occurs because CO_2 is consumed quickly during daylight hours, whereas at night, the uptake of CO_2 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

225 indicates that the reservoir slowly underwent stratification again. While there was no difference in CO_2 gradients during calm daylight hours compared to windy days, we observed notably high CO_2 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
I think it is not defined: is like the mixed layer detph in oceanography?
influenced by O2 and CO2 overturn in the photo-active layer. Phytoplankton may have decreased the CO_2 concentration in

230 this large volume through photosynthesis over the days of strong winds. At night, respiration slightly increased the CO_2 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 CO_2 accumulation at the surface. Additionally, microstratification within the top 25 cm of the water column could further restrict the volume available for CO_2 accumulation, potentially leading to even higher concentrations (Figure 4). Our

235 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).

11

this paper could be of interest for the neuston discussion: https://doi.org/10.3389/fmars.2019.00011

240   Interestingly, the 5 cm probe, despite being closer to the surface, recorded higher CO_2 concentrations than the underlying water. This requires a CO_2 producing process in the surface layer, likely biological respiration. There are various groups of organisms that could increase CO_2 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 CO_2. 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 CO_2 concentration at night. Mean gross primary production and

confusing in the same paragraph, nutrients will help for photosynthesis

250   respiration in the calm period were 10.4 mg O_2 L^{-1} d^{-1} and -9.0 mg O_2 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 CO_2 production and accumulation even more.

Could we relate that to the slick formation and the effect of CO2 (slow gas-transfer)?
If it is what we call a bloom, it should also decrease CO2 via very high photosynthesis.

255   Moreover, the effect of convective mixing within the top water layer plays an important role in the distribution of CO_2 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 CO_2 in the water column. While we did not find signs of thermal microstratification at the surface during nights with strong CO_2 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 CO_2 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 CO_2 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 CO_2 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 CO_2 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 CO_2 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 CO_2 gradient which probably continued towards the water-atmosphere interface. Our uppermost probe measured the mean CO_2 concentration between 1 and 10 cm depth and it

here you will need SML sampling o microsensors (possible to use in lakes (?)) :).
Also nice work from Alexia D. Saint-Macary

is plausible that the concentration at the water surface was even higher than measured by that probe. To measure the "real"

275   concentration at the surface CO_2 measurements would need to be conducted even closer to the SML. Floating chambers have

been used to measure CO_2 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 CO_2 concentration on short time scales and with high vertical resolution. only if the concentration of air and water are very similar

very good and explicative diagrams
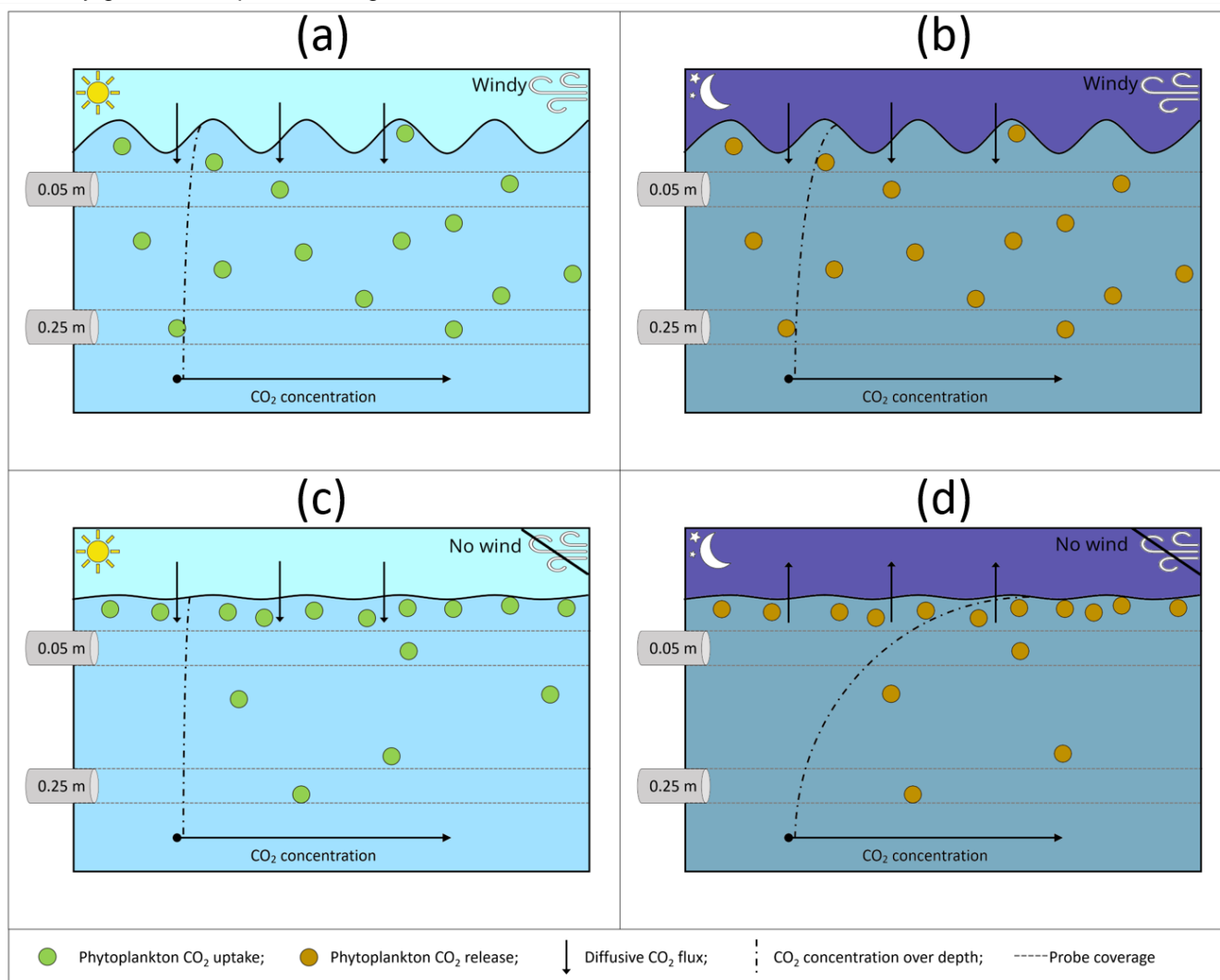
Figure 4: Schematic of CO_2 accumulation in the surface water, with CO_2 probes located in 5 cm and 25 cm depth. (a): wind-induced turbulence causes homogeneous distribution of phytoplankton, resulting in CO_2 decrease in both measuring depths during the day. (b): wind induced turbulence causes homogeneous distribution of phytoplankton. CO_2 is produced by respiration, but the CO_2 concentration across the whole water column is low, thus respiration is compensating strong undersaturation. CO_2
285   uptake from the atmosphere causes slightly increased concentration in 5 cm. (c): CO_2 concentration is low in the whole mixed

During day, there is also a phytoplankton CO2 release, just that problably the uptake is bigger.
Also just noticing, sometimes you talk about phytoplankton and sometime algae. In oceanography we use phytoplankton

You are missing here the following explanation, to be consistent like in (d) **layer, but calm conditions cause phytoplankton to accumulate at the surface. (d): Calm conditions cause phytoplankton to accumulate at the water surface. Respiration causes CO_2 increase in this layer, which is causing CO_2 emissions during calm nights.**

Conclusions

Our results show that the surface CO_2 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 CO_2 concentrations can develop. That effect can turn a CO_2 under-saturated lake to a temporary CO_2 source. very short conclusion section. Here you should emphasize what is your study implication

Appendix A: Detailed water temperature graphs
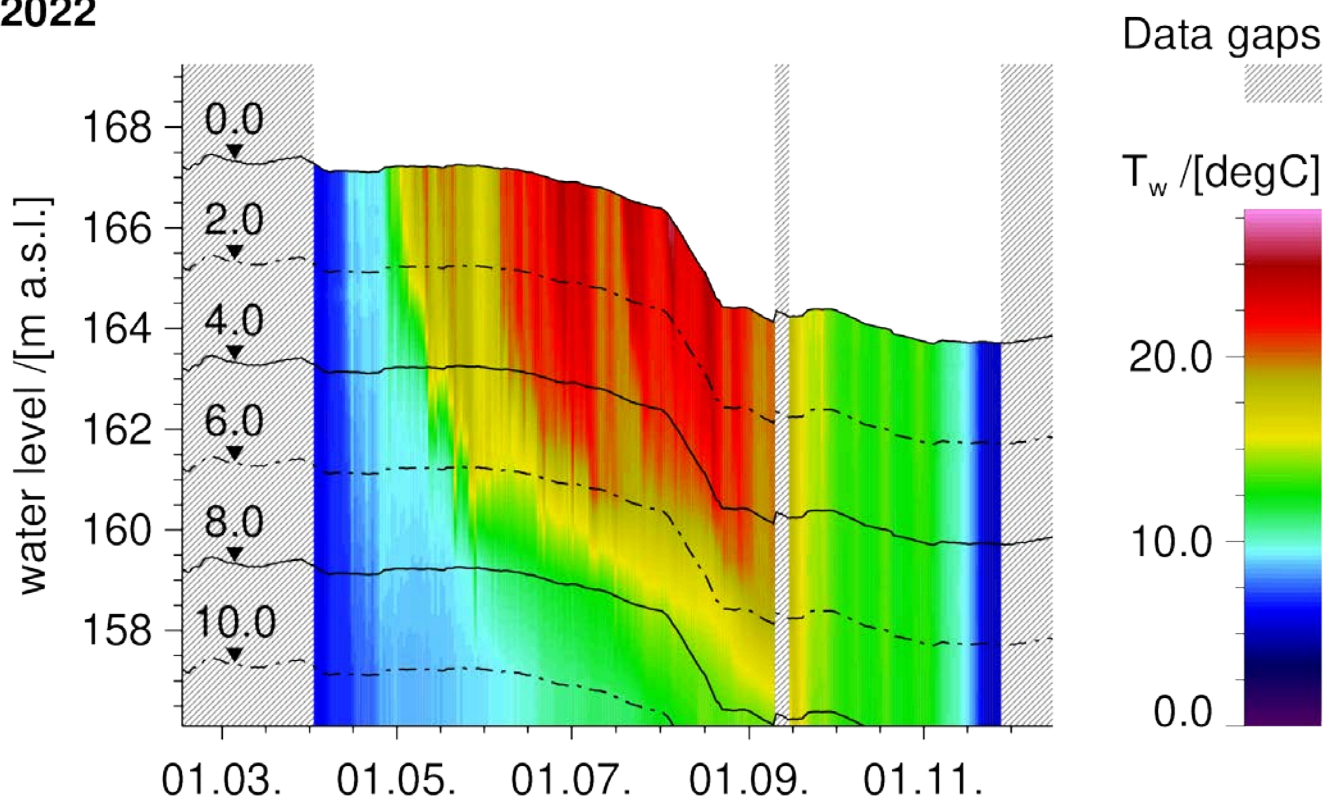
295 **Figure A 1: Water level (meters above sea level) and water temperature profile from April 1st to November 28th in 2022 at Bautzen reservoir. Solid and dot-dashed black lines indicate water depths of 2 m, 4 m, 6 m, 8 m, and 10 m. Grey bars highlight missing data.**
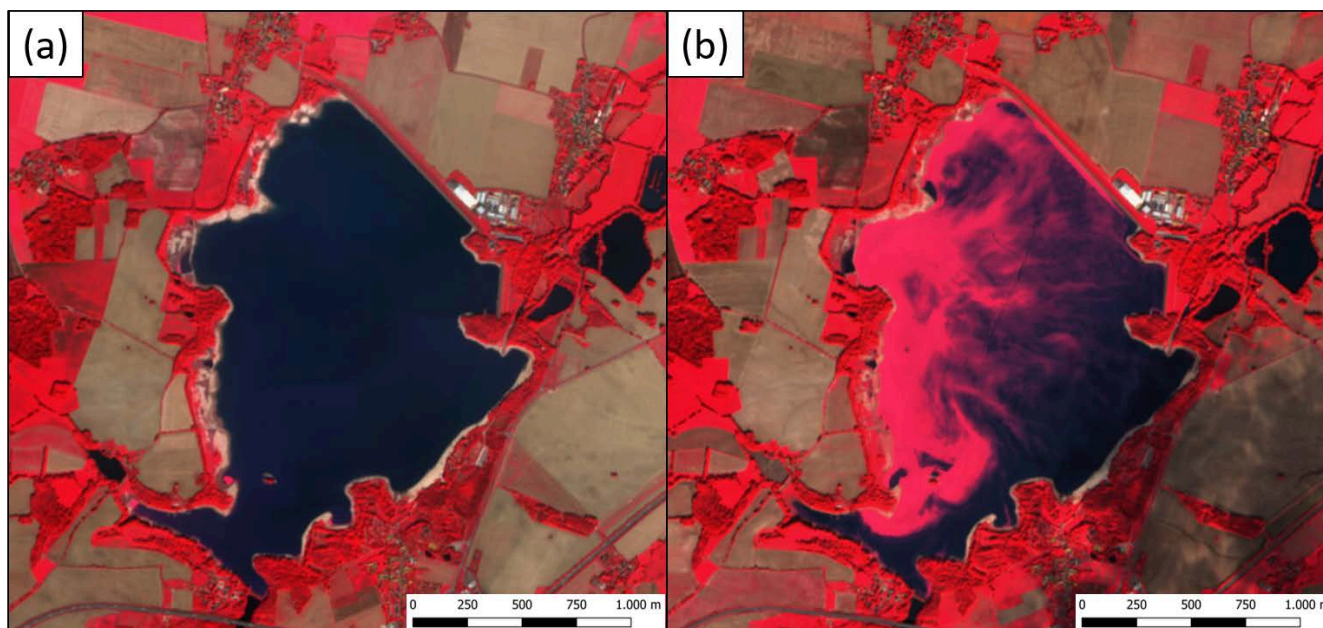
14
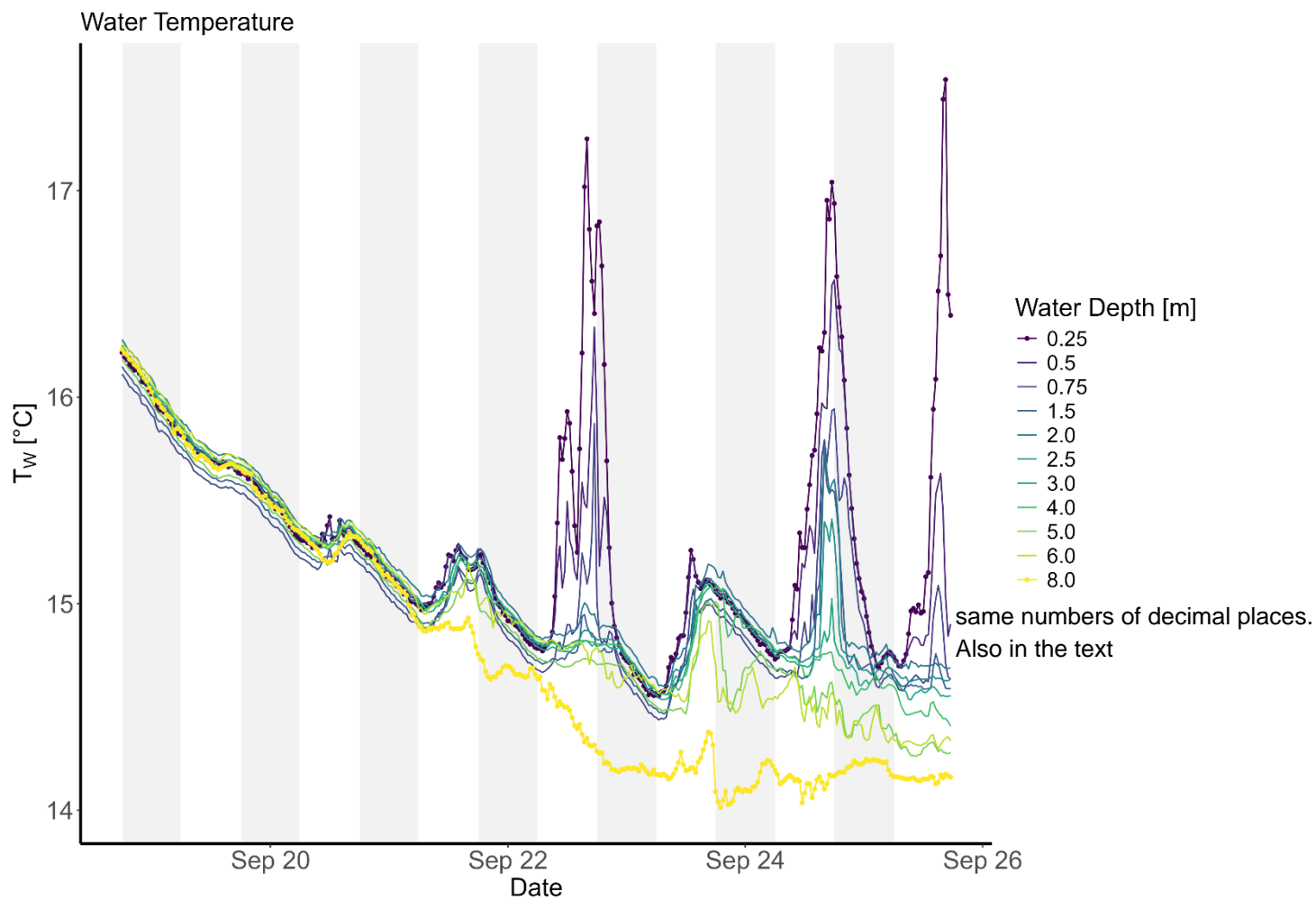
Figure A 2: Detailed water temperatures across the water column during the extensive sampling period. Dotted lines highlight surface and bottom temperatures. Grey highlights show night-time.

It is not surface, it is 25 cm :)

Appendix B: Satellite images of the reservoir

I would say here what the false colour shows. We need to read quite a lot to find it out.

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.

If you get a phytoplankton bloom, it could probably also be affecting temperature in the SML.
See Wurl et al. 2018 (doi.org/10.1029/2018GL077946)

Code availability

Code is available upon request to the corresponding author.

Data availability

Data are available upon request to the corresponding author.

Is this allowed by the journal and DFG? I will strongly recommend/suggest to submit to PANGAEA or similar repository.

Author contribution

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.

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Competing interests0

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

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