

Reply to reviewer 2

The work is within the scope of the journal as it addresses CO₂ and CH₄ pattern in some typical European river. The approach is sound, careful and the arguments are generally convincing

My first major issue – on the real usefulness of diel monitoring of CO₂ emissions in rivers.

The sentence in L 25 of the Abstract is questionable. It is unclear why continuous measurements of fCO₂ are really necessary given that day/night median values in water habitat (Table 2) which mostly contribute to C emissions (Table 1) are same, within +/- 20% (Table 2). This uncertainty is within the internal measurement uncertainty and hence can be neglected.

We think this argumentation is not valid. As can be seen in Figure 4 diurnal changes of the CO₂ flux were phase shifted compared to light. Thus both day and night periods see continuously changing CO₂ fluxes resulting in very similar means. It is true that just statistically comparing mean day and night values is not the best approach to analyse these diurnal pattern. If CO₂ would only be analyzed once per day, the error is anywhere in the range between 0 and 200 % - the result depends on the shape of the diurnal curve and the sampling time.

We acknowledge that automatic probe measurements are not essential to address this. Maybe sampling at dawn and in the afternoon and then reconstructing a diurnal curve can be sufficient. Thus, probes are very convenient but could be replaced by taking more than one manual measurement during a day. We will modify the discussion at this point.

The second issue is about potential importance of diurnal variations on the annual scale. Peak summer season and sunny weather may not have the same CO₂ pattern as cloudy and cooler weather during other period of the year in this part of Germany. At present, extrapolation to year-round time scale is not warranted

We completely agree. We explicitly address short term variability and do not calculate annual budgets. As we state in the manuscript we choose a situation in which we expected large variabilities. We agree to the reviewer that the situation is probably different in other parts of the year. We think, however, that our general conclusions are valid.

Some specific issues

L77-79 Please provide a justification for this hypothesis, based on available literature

We already have this point in the discussion. However, we agree that this needs to be introduced earlier. We will add a section to the introduction explaining why CH₄ (which depends on the sediment) is spatially variable.

L201 The rainfall during continuous monitoring is rather unfortunate and highly undesirable event, adding a new dimension (variable). Please explain how it was taken into account.

We do not consider this as unfortunate. Rain is naturally occurring and enabled us to look for the short term effect of rain. The reviewer is right that we did not discuss this point in the

manuscript. From our soil moisture probe data we do not see an effect of rain on soil moisture – most probable because there was so little rain. From another study (Koschorreck et al., 2022) we know that rain can reduce terrestrial CO₂ fluxes. However, in our case the rain event was obviously not strong enough to show a visible effect. We will add a sentence to the discussion. We will also add a figure with weather data including rainfall to the SI.

Rain is known to affect also water-atmosphere gas exchange (e.g. (Ho et al., 2000; Ho et al., 1997)). However, we cannot analyze this since our continuous aquatic measurements started after the rain in the first night.

Fig 3 is useful; however, the same plot for pCO₂ is needed. Please also consider presenting a plot for CO₂ fluxes of this kind to demonstrate spatial variability.

This point was also raised by reviewer 1. The greenhouse gas analyzer could also analyze CO₂, however the instrument has never been tested and calibrated for CO₂. Thus, no such figure could be provided. We will re-assess our raw data to figure out if CO₂ are reliable and can be used for a revision.

L310 Is this ‘small’ in GHG potential equivalent, or ‘small’ for the total C balance?

Its both. Given the fact that CO₂ fluxes are typically several orders of magnitude larger than CH₄ fluxes (in our case more than factor 1000) even multiplying with the GWP does not make a big difference. We will add “both in terms of the carbon balance and the global warming effect”.

L315-316 What is the reason of lower Kt at high pCO₂ – lower turbulence?

There is not a mechanistic direct link between k and pCO₂. What we mean is that in the middle of the river pCO₂ was higher but k was lower compared to the sides which resulted in similar flux at all sites.

L353-355 This statement is too general. See works on large tropical and temperate rivers (Mississippi, Congo) or subarctic rivers. On the latter (for instance, Taz, Ket, Lena, see <https://doi.org/10.5194/bg-19-1-2022>; <https://doi.org/10.5194/bg-18-4919-2021>; doi: 10.3389/fenvs.2022.98759), the diurnal dynamics of CO₂ emissions is not strongly pronounced.

The reviewer questions the general significance of diurnal changes of CO₂ emissions from larger rivers. As evidence he provided some references (of which not all seem to be the correct DOI). Vorobyev et al. (2021) indeed did not find pronounced diurnal variability in river Lena, which is not a surprise given the fact that there is little difference between day and night conditions in polar regions in June. There is contrasting evidence regarding the importance of diurnal variability in large tropical rivers (Haque et al., 2022; Ishaque, 1973). Thus we agree that our original statement was too general. We will change “is also relevant” to “can also be relevant”.

L368 In water, there is no constant CO₂ flux during the night (Fig 5a)

This is true and this is what we write. The sentence in L368 only refers to terrestrial sites.

L372-375 Justification of analogy with marine sediments is necessary

There are several studies on the physiology of benthic algae, mostly on in marine sediments. We see no reason to doubt the assumption that their underlying physiology should be the same for freshwater and marine benthic algae.

Refernces

- Haque, M.M., Begum, M.S., Nayna, O.K., Tareq, S.M. and Park, J.-H. 2022. Seasonal shifts in diurnal variations of pCO₂ and O₂ in the lower Ganges River. *Limnology and Oceanography Letters* 7(3), 191-201.
- Ho, D.T., Asher, W.E., Bliven, L.F., Schlosser, P. and Gordan, E.L. 2000. On mechanisms of rain-induced air-water gas exchange. *J Geophys Res-Oceans* 105(C10), 24045-24057.
- Ho, D.T., Bliven, L.F., Wanninkhof, R. and Schlosser, P. 1997. The effect of rain on air-water gas exchange. *Tellus Series B-Chemical and Physical Meteorology* 49(2), 149-158.
- Ishaque, M. 1973. Intermediates of denitrification in the chemoautotroph *Thiobacillus denitrificans*. *Arch.Microbiol.* 94, 269-282.
- Koschorreck, M., Knorr, K.H. and Teichert, L. 2022. Temporal patterns and drivers of CO₂ emission from dry sediments in agroynne field of a large river. *Biogeosciences* 19(22), 5221-5236.
- Vorobyev, S.N., Karlsson, J., Kolesnichenko, Y.Y., Korets, M.A. and Pokrovsky, O.S. 2021. Fluvial carbon dioxide emission from the Lena River basin during the spring flood. *Biogeosciences* 18(17), 4919-4936.