Reviewer comments

Author responses

CC1

It is a very good idea to use long term monitoring data to investigate the effect of the socioeconomic changes in Germany after re-unification on GHG emissions from a large river. The paper contains a very nice dataset including both main river and tributary data which allows the investigation of both spatial and inter-annual pattern. However, in my eyes the manuscript does not fully exploit the potential of the dataset and has some serious issues which I would like to address in the following:

Reply:

Thank you for your thorough review and valuable additional input.

I cannot follow the argumentation that nutrient driven eutrophication should increase CO_2. Any CO_2 produced from decaying algae was fixed by those algae before. Thus, the cycle of primary production and algae mineralization cannot increase CO_2 emissions. In contrast it has the potential to reduce CO_2 emissions if algae are buried in the sediments – a scenario relevant for lakes but probably not for rivers.

Reply:

Thank you. It's true that eutrophication typically results in a decrease of CO_2 due to the uptake by photosynthetic phytoplankton. However, recent research suggests this impact could be reversed. For instance, Kim et al. (2021) found a V-shaped relationship between TN/TP and pCO_2, together with upshift relation between Chl-a and CO_2, indicating that beyond a certain threshold, eutrophication enhanced biomass could act as a source of CO_2 in the Han River, Korea. This is why we initially highlighted this potential. Ultimately, our results for the Elbe demonstrated a negative relationship between biomass and pCO_2 (Figures 3c and 3d), indicating effects of uptake rather than impact as a source in the Elbe River.

Will be rephrased.

I would hypothesize that correlation between N or P with CO_2 might be a pseudo correlation and not a direct mechanistic link. As written in the manuscript, wastewater contains both DOC and inorganic nutrients.

Reply:

In fact, in our view we believe that if the decrease in CO_2 were solely correlated with the amount of organic carbon, then a direct correlation between pCO_2 and DOC or TOC would be expected, which was not identified. The negative correlation between RUE and the pCO_2 suggests that biomass carbon uptake efficiency has the potential to contribute to the decrease in pCO_2.

In addition, before the unification, less wastewater treatment in Eastern Germany led to higher more labile carbon input to the river water.

In the manuscript a rather crude method is used to estimate river surface area. The resulting surface area of 735 km^2 (supplement) looks rather high. Divided by river length this means a river width of about 1 km – an unrealistic high value. In Mallast et al. (2020) we determined a surface area of 106 km^2 from satellite images.

Reply:

Thank you for providing this valuable reference information.

Mallast et al. (2020) utilized high-resolution satellite imagery to estimate the water area with great accuracy, which only included mainstem portion, refer to the 7-8 Strahler order river network considered for our estimation.

We also extracted this segment of the river network for comparison. Based on our estimation results for 2018, the river width results are quite similar, (this research: 177 m for Strahler order 7&8, versus Mallast et al. (2020): 183 m, with an area of 107 km^2 divided by a length of 594 km) (Figure R1).

Therefore, we believe that the error in our estimation is not significant, and the results are reliable. And we will add the comparation results for the uncertainties discussion.

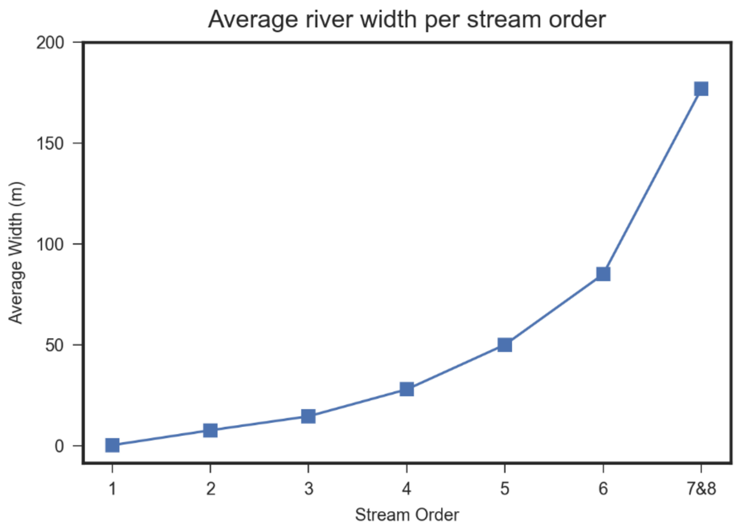

Figure R1: Estimated River width across different Strahler orders.

The gas transfer velocity was estimated from slope and flow velocity. However, there are also k600 data from River Elbe published (Matoušů et al., 2019). It should at least be checked how estimated k600 data compare to measured ones.

Reply:

We will compare the results with our calculations.

In Kamjunke et al. (2022) and Kamjunke et al. (2023) it was shown that there is a longitudinal gradient with plankton concentrations increasing downstream the river. It would be interesting to analyze the dataset in this paper with respect to this gradient. Was the transition zone between plankton poor and plankton rich water moving downstream after 1990?

Reply:
We are also interested in examining the longitudinal gradient in relation to plankton concentrations to identify the transition zone between areas of plankton-poor and plankton-rich waters downstream after 1990.

We will add data concerning the longitudinal gradient to the plankton concentrations from a series of monitoring stations in case they show meaningful results.

The dataset also should allow the comparison of different tributaries. Statistical relations between CO_2 and other parameters could be checked for each tributary separately. This can be used to investigate the drivers of CO_2 in the different sub-catchments. The effect of the tributaries on the main stream, however, is probably difficult to detect. In Bussmann et al. (2022) for example we showed that the high dilution effect at the confluence did not allow the detection of CH_4 import from the tributaries into the main river.

Reply:
Thank you for your valuable suggestion to utilize the dataset for comparing various tributaries and examining the statistical relationships between CO_2 and other parameters for each tributary individually. We will attempt to conduct separate statistical analyses for each tributary where water chemistry data are available.

Recent literature shows that CO_2 concentrations in rivers fluctuate diurnally (Gómez-Gener et al., 2021). Thus, scaling up CO_2 emissions from single datapoints means accepting a systematic uncertainty. Our own measurements show that diurnal fluctuation of CO_2 is an issue in River Elbe (manuscript in preparation). This could be relevant in long term time series, if the time of day when samples were taken changed during the time series.

Reply:
Thank you. The long-term effect is also important since respiration obviously dominates photosynthesis during the night (Gómez-Gener et al., 2021). However, according to the datasets of FGG, the time distribution listed below (Figure R2), most of the sampling happened during daytime, therefore, it is not available to analysis the impact in this event.

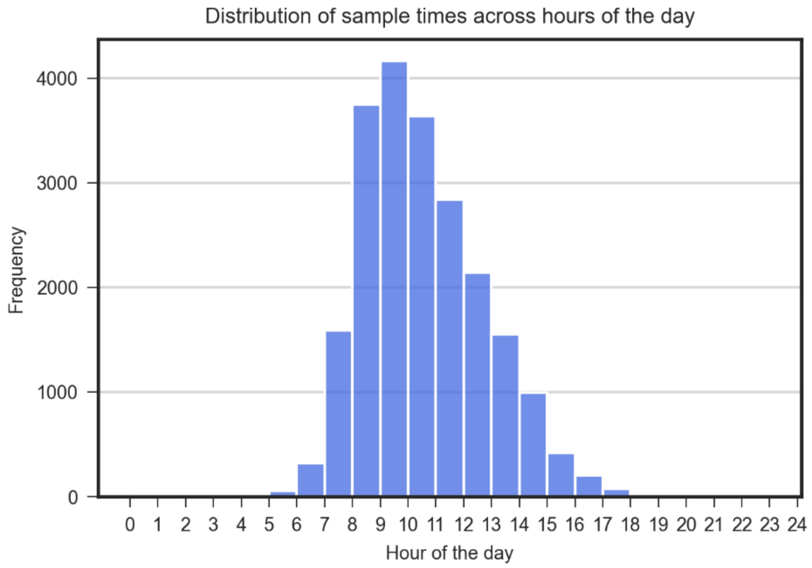

Figure R2. Distribution of manual sampling times in the Elbe River

If CO_2 emissions are primarily driven by DOC mineralization the dataset should allow a quantitative comparison between the two. Was DOC decreasing downstream and how does that downstream decrease of DOC compare quantitatively to CO_2 emissions? Such a question could be investigated by looking at monitoring data from longer reaches without major tributaries.

Reply:
Indeed, decreasing trends for both DOC fluxes and CO_2 emissions have been observed in our research. Conducting a quantitative analysis to determine whether the decrease in DOC is the primary driver of the reduction in CO_2 emissions in the Elbe River is an excellent suggestion.

We will add a section on quantitative analysis to address this.

An analysis of long-term changes of water quality in river Elbe was recently published by (Wachholz et al., 2022)

Reply:
The recent publication highlights the decrease in nutrient concentrations and underscores the importance of water quality management, providing new resources for our research.

We will add it as a reference.

References

Gómez-Gener, L., Rocher-Ros, G., Battin, T., Cohen, M. J., Dalmagro, H. J., Dinsmore, K. J., Drake, T. W., Duvert, C., Enrich-Prast, A., Horgby, Å., Johnson, M. S., Kirk, L., Machado-Silva, F., Marzolf, N. S., McDowell, M. J., McDowell, W. H., Miettinen, H., Ojala, A. K., Peter, H., . . . Sponseller, R. A. (2021). Global carbon dioxide efflux from rivers enhanced by high nocturnal emissions. *Nature Geoscience*, *14*(5), 289-294. https://doi.org/10.1038/s41561-021-00722-3

Kim, D., Lim, J. H., Chun, Y., Nayna, O. K., Begum, M. S., & Park, J. H. (2021). Phytoplankton nutrient use and CO(2) dynamics responding to long-term changes in riverine N and P availability. *Water Res*, *203*, 117510. https://doi.org/10.1016/j.watres.2021.117510

Mallast, U., Staniek, M., & Koschorreck, M. (2020). Spatial upscaling of CO2 emissions from exposed river sediments of the Elbe River during an extreme drought. *Ecohydrology*, *13*(6). https://doi.org/10.1002/eco.2216