1 Reviewer comments

- 2 Author responses
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4 <u>RC1</u>

MAJOR COMMENTS

Long-term patterns of CO2 levels and emissions in rivers have been reported by several
studies (Jones et al. 2003; Ran et al. 2015; 2021; Nydahl et al. 2017; Marescaux et al.
2018) (non-exhaustive list). Findings from these studies could be used to contextualize the
present study (Introduction) and to discuss differences or convergences by comparison
(Discussion).

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14 Reply:

15 Thank you for the references.

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In the introduction, we will include a paragraph reviewing the literature on long-term CO₂
emission patterns. In the discussion, we will draw on previous studies to compare with our
findings and examine time-dependent variations in region-specific attributes.

20

21 L 30: « water pollution » is extremely vague. This should be broken down into several human impacts on riverine systems that do not necessarily lead to the same change in 22 23 CO2 emissions. Eutrophication (increase of nutrient inputs) can potentially lead to 24 enhanced primary production and a CO2 sink in impounded large rivers such as the 25 Mississippi (Crawford et al. 2016). Conversely, croplands seem to also lead to enhanced organic carbon inputs from soils enhancing CO2 emissions compared to more natural land 26 27 cover such as forests (Borges et al. 2018; Mwanake et al. 2023) Wastewater inputs lead 28 to CO2 production in the river, although this impact seems very local, in the near vicinity of 29 the emissary (Marescaux et al. 2018).

- 30
- 31 Reply:

Thank you. We agree with you that "water pollution" is indeed a broad term, and it is important to consider its impacts on riverine CO₂ emissions from various perspectives.

34

Accordingly, we will expand our description to encompass different viewpoints, including the effects of organic carbon from agricultural runoff and domestic sewage (Borges et al., 2018; Marescaux et al., 2018; Mwanake et al., 2023), as well as the carbon sink impact attributable to eutrophication caused by increased nutrient levels (Crawford et al., 2016).

39

L 30 "this percentage continues to increase because the unprecedented anthropogenic stresses on riverine systems have led to many negative issues such as water pollution". I'm not sure this statement applies assertively to all climate zones (Crawford et al., 2016). According to Liu et al. (2022), tropical rivers are responsible for 57% of the riverine CO2 global emission, followed by temperate (30%) and Arctic regions (13%). The most direct anthropogenic impacts expected to affect riverine CO2 emissions should occur at
temperate latitudes (North America, Europe and parts of Asia) that account for less than a
third of total emissions. Note that this percentage was lower in earlier estimates for which
tropical rivers accounted for 80% of riverine CO2 emissions (Raymond et al. 2013;
Lauewarld et al. 2015).

50 51

1 Reply:

Thank you. We agree that the impacts of river pollution and restoration efforts on riverine
 CO₂ emissions, which result from human activities, should be concentrated in regions with
 high population density.

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56 We will revise the sentence to offer a more accurate depiction that incorporates the 57 suggestions you have provided.

58

L 34: Rivers do not have "ecosystem's natural carbon absorption and storage capabilities". Rivers do not store carbon in sediments and do not "absorb" carbon on contrary tend to emit CO2 to the atmosphere. High CO2 over-saturation in rivers occurs ubiquitously even in pristine (or near pristine) river basins such as the Amazon and Congo.

63

64 Reply:

Thank you very much for the correction. We agree that most rivers consistently serve as asource of carbon.

67

68 We will revise the text from this perspective.

69

L 37: It has been argued that CO2 emissions from lowland rivers in particular in the tropics are related to inputs from wetlands (Abril et al. 2014; Borges et al. 2015) that are conceptually different (Abril and Borges 2019) from "terrestrial organic carbon (OC)» (as stated).

74

75 Reply:

Thank you for the correction. We will add the reference and the information.

77

79

78 L38: Can you please clarify the role of «nutrient availability" in this context?

80 Reply:

81 We will delete the term "Nutrient availability" here, as it is misleading in this context.

82

L44-46: This argument is awkward. DOM produced by phytoplankton should indeed
sustain microbial respiration but phytoplankton also photosynthesized prior to DOM
release, so both effects should cancel each other in terms of net carbon fluxes.

86

87 Reply:

88 Thank you. The sentence will be deleted.

89 L 44: reference to "lakes and reservoirs » seems to be out of context here.

90 91 Reply: 92 Will be rephrased. 93 94 L49-50: statement "trophic status related to nutrient availability significantly impacts the levels of CO2 in rivers" is contradicted by the fact that CO2 emissions in rivers are in 95 96 majority related to lateral inputs of carbon from soils and ground-waters (Hotchkiss et al. 97 2015) or from wetlands (Abril and Borges 2019), and are not related to in-stream CO2 production from metabolism (Hotchkiss et al. 2015; Abril et al. 2014; Borges et al. 2019). 98 99 100 Reply: 101 In this study, Figures 3c and 3d demonstrate the significant and negative correlation 102 between RUE (the ratio of Chl-a to nutrient concentrations) and pCO₂. 103 The sentence will be rephrased deleting the terms 'trophic status related nutrient 104 105 availability' and replaced by 'nutrient concentration'. 106 L 51: reference to "biodiversity" seems out of context here. 107 108 109 Reply: Will be rephrased. 110 111 112 L 55: The authors should cite the "existing studies" they critique rather than stating this in 113 a vague way. 114 115 Reply: Thank you. Related studies will be cited (like Nydahl et al. (2017); Marescaux et al. (2018) 116 117 etc.) 118 L 55: Please clarify what is meant by "short term effects »? "effects" of what on what? Do 119 120 you mean short-term time-series? Some studies have reported relatively long time series 121 (Jones et al. 2003; Ran et al. 2015; 2021; Nydahl et al. 2017; Marescaux et al. 2018). It is 122 not necessary to downplay existing literature to put forward your own study. 123 124 Reply: 125 Thank you. In our study, "Short-term effects" is a relative term compared with continuous long term time series, refers to the analysis of F_{CO2} or CO₂ efflux below 10 years (decadal). 126 127 Will be clarified. 128 129 For the research you provided, While Ran et al. (2015) provided extensive data on long-130 term pCO₂, they did not conduct analyses related to F_{CO2}. After that, Ran et al. (2021) compared CO₂ efflux from the average of two periods (1980s to the 2010s) but did not offer 131

132 an exhaustive continuous time series analysis. Similarly, the work of Nydahl et al. (2017)

and Marescaux et al. (2018) was primarily directed towards understanding pCO_2 dynamics, with less emphasis on F_{CO2} . As a result, there is a research gap in continuous and longterm analyses of F_{CO2} and CO_2 efflux, which our research questions aim to address. Will be rephrased and related studies will be included.

137

L 55: What do you mean by «hydrological conditions»? CO2 emissions from rivers depend
 on CO2 concentration between water and air, and on the gas transfer velocity. Both are
 more or less indirectly linked to "hydrological conditions" but this should be clarified,
 especially when criticizing "existing studies".

142

143 Reply:

144 Thank you. In this research, we are using estimates of both the flow discharge and flow 145 velocity for the estimation of the gas transfer velocity and water surface area. The 146 parameters represent hydrological conditions.

147 This aspect will be clarified in the text.

148

L61: Please provide a reference to back this statement, and clarify compared to which other rivers was it the most polluted? At European level? Globally? It could be also useful to take into account size effects. A very small stream can be extremely impacted by wastewater from a small village, while very large rivers are unaffected by large cities because all inputs are diluted by high discharge.

154

155 Reply:

Thank you. Before 1990, the Elbe River was one of the most polluted rivers in Europeanscale. Related references will be added (ICPER, 2023; Kempe, 1982).

158

L 163: the equation relating river width and Q given by Raymond et al. (2012) was derived for small streams. Can you comment on its applicability to large rivers? Also this relation is probably affected by channelization and probably does not apply to highly engineered rivers such as the Elbe.

163

164 Reply:

165 Most of the Elbe River's flow, categorized with Strahler orders from 1 to 6, matches the

- 166 flow discharge range used to create the equation by Raymond et al. (2012) (Figure R1).
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Figure R1. Flow discharge distribution of tributaries of the Elbe River. Discharge data obtained and
resampled from GRADES (The Global Reach-scale A priori Discharge Estimates for SWOT) (Lin et al.,
2019; Yang et al., 2019).

For the larger segments of the river, classified as Strahler orders 7 and 8, primarily the mainstem, we compared our estimated river widths with the research of Mallast et al. (2020). Their measurements were derived from satellite imagery. The average river width we estimated showed good agreement with their findings (this research: 177 m for Strahler order 7&8 (Figure R2), versus Mallast et al. (2020): 183 m, with an area of 107 km² divided by a length of 594 km).

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182

180 Therefore, we believe the error introduced by our method in this research should be minor.181 An additional discussion of uncertainties will be added.



183 Figure R2: Estimated River width across different Strahler orders.

L 300: can you please provide a numerical comparison and a reference for the data for 184 the 1954-1977 period? 185 186 Reply: 187 188 The modeled pCO_2 and the corresponding data and plot will be added. 189 190 Can you please explain somewhere in text why the analysis was not extended back to 191 1954 and only started in 1984? 192 193 Reply: 194 Since our study conducted a temporal and spatial analysis. In this process, we integrated 195 a range of environmental indicators along with carbon. On the other hand, the data from 196 1954 was restricted to just one site (sample location of the local water works company Hamburg Wasser) and did not provide any environmental indicators (Kempe, 1982). 197 198 Consequently, we employed this data merely as a background reference value. A short 199 200 explanation will be added. 201 202 L341-344: This statement does not seem relevant. Indeed, it is conceivable that light 203 absorption by CDOM limits photosynthesis from aquatic primary producers, but in rivers CDOM mostly originates from soils. Also, DOM from phytoplankton is usually very labile 204 and is quickly consumed by micro-organisms. CDOM is usually related to highly 205 refractory substances, typically from soils. 206 207 208 Reply: 209 The sentence will be deleted. 210 211 L 370-373: Please clarify the text of the two hypothesis and also provide extra arguments and references to back them. 212 213 214 Reply: 215 The two main arguments are as follows: 216 217 Firstly, the treatment of municipal wastewater has resulted in a decrease in the amount of 218 labile organic carbon being directly introduced into the river, thereby reducing the potential 219 for its degradation into CO_2 (Lasaki et al., 2023). Secondly, the reduced discharge of heavy metals, along with reductions in nitrogen and phosphorus concentrations, has promoted a 220 healthier aquatic ecosystem (Qasem et al., 2021). Although photosynthesis and respiration 221 222 processes may balance each other, the net growth of aquatic plants contributes to the 223 overall reduction of CO₂ in the river if the rate of plant growth exceeds the rate of decomposition of plant residues (Demars et al., 2016). 224 225 226 Will be clarified with extra arguments and references. 227

6

What do you mean by "biomass amount » and why should it not increase in « restored 228 aquatic system"? 229

230

231 Reply:

232 The most important factor affecting biomass quantity is the toxicity from heavy metals, 233 which impedes biomass growth. As environmental conditions shift from polluted to non-234 polluted states, the quantity of biomass is expected to change, subsequently influencing 235 CO₂ levels. However, heavy metals primarily originate from industrial inputs, and the 236 closure of factories along with advanced wastewater treatment technologies has 237 significantly improved water quality (Amann et al., 2012). Since trace elements do not exceed the thresholds that limit phytoplankton growth, biomass remains relatively stable. 238

239

240 Will be rephrased. And a plot of temporal biomass amount variations will also be provided.

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242

What do you mean by "challenging through water quality treatments."

244 Reply:

245 The challenge could be that CO₂ emissions from sewage water discharge may be avoided at the cost of CO₂ emission of wastewater treatment plants through biological treatment 246 247 process and electricity consumption.

248

According to global estimates, the degradation of OC during wastewater treatment in 2010 249 250 contributed to approximately 770 Tq CO₂-equivalent GHG emissions, representing nearly 251 1.57% of the total global GHG emissions of 49,000 Tg CO₂ (Edenhofer, 2015).

252

253 On the other hand, the oxidized and anaerobic digestion of the organic carbon of 254 wastewater is converted mainly to CO₂ and CH₄ (Campos et al., 2016), thus offsetting the 255 reduction in CO₂ in wastewater treatment.

256

257 MINOR COMMENTS

Text contains numerous awkward phrasing or typos or redundancies. The senior co-258 259 authors should spend some time looking through the text and make the necessary 260 improvements; this is not the reviewer's job. Nevertheless, some are listed hereafter (not 261 an exhaustive list):

263 Reply:

264 We apologize for this oversight. We will do our utmost to significantly improve the language 265 quality of the text.

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262

L40 + L 337: Labile instead of "liable"? 267

268

269 Reply:

Will be replaced. 270

271

272	L 55: context instead of « contest" ?
273	
274	Reply:
275	Will be replaced.
276	
277	L42: "phytoplankton behaviors » is awkward, please rephrase.
278	
279	Reply:
280	Will be rephrased.
281	
282	L61: most instead of "highest"
283	
284	Reply:
285	Will be replaced.
286	
287	L66: "FCO2 efflux » is redundant sinc "F" of "FCO2" abbreviates the word flux.
288	
289	Reply:
290	Will be replaced.
291	
292	L68: "high-resolution" is self-evaluation, please simply state instead the actual time step of
293	the data.
294	
295	Reply:
296	Extra descriptions will be added.
297	
298	L 368: "CO2 drawdown ratio by water quality management" is awkward, please rephrase.
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300	Reply:
301	Will be rephrased.
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316 References

317 Amann, T., Weiss, A., & Hartmann, J. (2012). Carbon dynamics in the freshwater part of the Elbe 318 estuary, Germany: Implications of improving water quality. Estuarine, Coastal and Shelf 319 Science, 107, 112-121. https://doi.org/10.1016/j.ecss.2012.05.012 320 Borges, A. V., Darchambeau, F., Lambert, T., Bouillon, S., Morana, C., Brouyere, S., Hakoun, V., 321 Jurado, A., Tseng, H. C., Descy, J. P., & Roland, F. A. E. (2018). Effects of agricultural land 322 use on fluvial carbon dioxide, methane and nitrous oxide concentrations in a large 323 European river, the Meuse (Belgium). Sci Total Environ, 610-611, 342-355. 324 https://doi.org/10.1016/j.scitotenv.2017.08.047 325 Campos, J. L., Valenzuela-Heredia, D., Pedrouso, A., Val del Río, A., Belmonte, M., & Mosquera-326 Corral, A. (2016). Greenhouse gases emissions from wastewater treatment plants: 327 minimization, treatment, and prevention. Journal of Chemistry, 2016. 328 Crawford, J. T., Loken, L. C., Stanley, E. H., Stets, E. G., Dornblaser, M. M., & Striegl, R. G. (2016). 329 Basin scale controls on CO2 and CH4 emissions from the Upper Mississippi River. 330 Geophysical Research Letters, 43(5), 1973-1979. https://doi.org/10.1002/2015gl067599 331 Demars, B. O. L., Gíslason, G. M., Ólafsson, J. S., Manson, J. R., Friberg, N., Hood, J. M., Thompson, 332 J. J. D., & Freitag, T. E. (2016). Impact of warming on CO2 emissions from streams 333 countered by aquatic photosynthesis. Nature Geoscience, 9(10), 758-761. 334 https://doi.org/10.1038/ngeo2807 335 Edenhofer, O. (2015). Climate change 2014: mitigation of climate change, . Cambridge University 336 Press. 337 ICPER. (2023). International Commission for the Protection of the Elbe River · ICPER. 338 (https://www.ikse-mkol.org/ last access on 2023-12-04). 339 Kempe, S. (1982). Long-term records of CO2 pressure fluctuations in fresh waters. SCOPE/UNEP 340 Sonderband, 52, 91-332. 341 Lasaki, B. A., Maurer, P., Schönberger, H., & Alvarez, E. P. (2023). Empowering municipal 342 wastewater treatment: Enhancing particulate organic carbon removal via chemical 343 advanced primary treatment. Environmental Technology & Innovation, 32. 344 https://doi.org/10.1016/j.eti.2023.103436 345 Lin, P., Pan, M., Beck, H. E., Yang, Y., Yamazaki, D., Frasson, R., David, C. H., Durand, M., Pavelsky, 346 T. M., Allen, G. H., Gleason, C. J., & Wood, E. F. (2019). Global Reconstruction of 347 Naturalized River Flows at 2.94 Million Reaches. Water Resour Res, 55(8), 6499-6516. 348 https://doi.org/10.1029/2019WR025287 349 Mallast, U., Staniek, M., & Koschorreck, M. (2020). Spatial upscaling of CO2 emissions from 350 exposed river sediments of the Elbe River during an extreme drought. *Ecohydrology*, 351 13(6). https://doi.org/10.1002/eco.2216 352 Marescaux, A., Thieu, V., Borges, A. V., & Garnier, J. (2018). Seasonal and spatial variability of the 353 partial pressure of carbon dioxide in the human-impacted Seine River in France. Sci Rep, *8*(1), 13961. <u>https://doi.org/10.1038/s41598-018-3</u>2332-2 354 355 Mwanake, R. M., Gettel, G. M., Wangari, E. G., Glaser, C., Houska, T., Breuer, L., Butterbach-Bahl, 356 K., & Kiese, R. (2023). Anthropogenic activities significantly increase annual greenhouse 357 gas (GHG) fluxes from temperate headwater streams in Germany. Biogeosciences, 358 20(16), 3395-3422. https://doi.org/10.5194/bg-20-3395-2023

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