Dear Dr Park,

Thank you for your careful reading and constructive suggestions. Below we reproduce all your comments (in black), followed by our point-by-point response and indication of the corresponding change in the revised (track-changed) manuscript. Line numbers refer to the tracked version that accompanies the resubmission.

Sincerely,

Truong An Nguyen (on behalf of all co-authors)

- L 16 (track-change version) "sign": Do you mean "direction?

Done.

- L 17: "poorly" constrained

Done.

- L 22 "in ca. 2005": around 2005

Done

- L 26 "aquatic metabolism": Does this refer to ER or NEP? Please specify it.

This refers to NEP.

L26: "the mean annual contribution of internal CO_2 production from net ecosystem respiration to total FCO_2 was 40%"

- L 36 "changing seasonal discharge control": Do you mean "reduced seasonal control by discharge"?

Yes.

L37: "The magnitude of this hysteresis diminished in the later macrophyte-dominated regime, indicating a reduced seasonal control by discharge on FCO_2"

- L 38: Please rephrase the beginning part of the sentence, like "This study demonstrates that river FCO_2 and its sources are dynamic…".

Done.

L38: This study demonstrates that river FCO_2 and its source are dynamic within and across years, driven by hydro-climatic variations and biological activity.

- L 40-42: Please clarify the two undefined terms "hydrogeological changes" and "ecological regime shifts". Do you mean hydro-climatic and groundwater influences by "hydrogeological"? It is not clear that, by the comprehensive term "ecological regime shifts", you meant ecological regime shifts "from phytoplanktonic-dominated to macrophyte-dominated communities", not metabolic regime shift.

L39-41: "Catchment-scale hydrogeological changes (including groundwater and surface water interactions) can be a more dominant driver of long-term riverine CO_2 evasion than in-stream ecological regime shifts (transitions from phytoplankton-dominated to macrophyte-dominated communities), controlling the balance between internal and external CO_2 production."

- L 51: Allochthonous inputs from upland sources can be delivered not only via groundwater but also (surface and subsurface) runoff.

L51: "Most CO_2 flux (FCO_2) is often assumed to come from "external" sources, delivered to streams via groundwater inputs, surface and subsurface runoff, and via temporary hydrologic connectivity with riparian wetlands"

- L 72: are "becoming" increasingly crucial

Done

- L 95: missed "by" FCO2 sampling campaigns

Done

- L 98: large rivers "across Europe (?)"

Yes.

L100: "The eutrophic state was common in large rivers across Europe throughout the 1980s and 1990s"

- L 114-125 "potential autotrophic activity": potential autotrophic dominance (?)

Yes, done.

- L125-127 "during the spring–summer growing season": during the growing season from spring to summer

Done.

- L 150: During "summer low flows" (without comma)

Done

- L 177-183: As the second reviewer commented, the brief description of the metabolism modeling is lacking in detail and thus still quite confusing. Please make it clear that you used an existing river metabolism model (Diamond et al., 2021), the principle of which could be briefly explained in the main text, for instance following the lines 177-178. Please also articulate how "these estimates are supported by the streamMetabolizer" and how "the K600 is constrained by daily river discharge and river depth with the formulations proposed by Raymond et al., 2012".

L173-195:

We estimated daily GPP, ER (g O2 m-2 d-1), and the gas transfer velocity coefficient (K600, d-1) by using a single-station, open-channel inverse modeling approach implemented with the streamMetabolizer R package (Appling et al., 2018). This Bayesian state-space modeling framework simultaneously estimates daily metabolism parameters (GPP, ER, and K600) by fitting modeled diel dissolved oxygen (DO) patterns to observed hourly DO concentrations based on inputs of hourly DO, solar radiation, and water temperature while explicitly accounting for both process and observation errors. To avoid unrealistic estimates and address the common issue of equifinality, where multiple combinations of ER and K600 can produce similar DO curves, the model constrains daily K600 estimates. The K600 is constrained by daily river discharge and river depth with the formulations proposed by Raymond et al., 2012. Model priors for K600 were derived from floating-dome and eddy-covariance measurements, and priors for GPP and ER were informed by previous metabolic studies in rivers (Diamond et al., 2021). The covariance between estimated ER and K600 was low (R^2 = 0.09), demonstrating reduced influence of equifinality problem (Appling et al., 2018). The detailed model setup for the Loire River was described by Diamond et al. (2021) and Diamond et al. (2025).

- L 182: "an" R package

Done

- L 183: It looks like this study and Diamond et al. (2025) share the same data set and methodological approach. It would help readers assess the novelty of this study if you describe here or at the end of Introduction how two studies differ in specific approaches and aims.

L132-134: Besides, this study is complementary to a concurrent study by Diamond et al. (2025), which focuses on the river's internal biogeochemical mechanisms, including inorganic carbon uptake pathways and changes in the ecosystem quotient.

- L 212-213: using … based on Fick's law

Done

- L 215-216: Please provide relevant references or explain a little bit about this conversion from K600 to k600.

L226-228: We obtained kCO_2 (Eq. 2) using Schmidt number (Sc) at given water temperature (Eq. 3) scaling from the **gas transfer velocity k_{600}** (m d^{-1}) (Raymond et al., 2012). The k_{600} was calculated by multiplying river depth with **gas transfer velocity coefficient K_{600} (d^{-1}),** an output of *streamMetabolizer.*

- L 218: K600 or k600 or k600 estimated from K600?

Revised: "The k600 estimates, derived from K600 values output by the StreamMetabolizer model were selected for FCO_2 calculations"

- L 223-224: Please provide this definition at its first use (L 179), and also refer to the comment on L 215-216. These separate sentences can be combined to better explain K600 and its conversion to k600.

Done.

- L 229: Diamond et al. (2025) needs to be cited here, as the term was first used in this prior publication.

Done

- L 239-243: The two sentences can be revised or combined to enhance clarity and brevity, "…CO2 undersaturation relative to the atmosphere can occur temporarily. This state may reflect temporal lags likely due to prior autotrophic uptake that lowers CO2 levels within the carbonate system buffering capacity during the short transition between autotrophic and heterotrophic states."

L256-258: "The heterotrophic-sink, a temporary condition likely caused by temporal lags in the carbonate system's buffering capacity during the shift between autotrophic and heterotrophic states, indicates net conversion of biomass into water column CO_2 even CO_2 remains undersaturation relative to the atmosphere, likely due to prior autotrophic uptake"

- L 276: might lead to a "flattening", or a reduction in the magnitude…

Done

- L 303-304: "Notably, the Loire River was net autotrophic during 10 years from 1990 to 2000 (Figure 1b, 304 green bars)."

L326: "Notably, the Loire River experienced several years of net autotrophic state (Figure 1b, green bars), mainly in 1990-2000"

- L335-336: The joint occurrence of the heterotrophic-source state "each year" thus ranged from 47.3 ± 9.4% in 1990-2000 to 66.8 ± 11.3% in 2011-2021 (Table 1),

Done

- L 337: Fig. C2 is very useful in understanding environmental controls on the four trophlux states. Don't you think that this figure is worth a space in the main manuscript?

Thanks for the suggestion, but to maintain flow, we prefer keeping Table 1 in the main text which summarizes the key fluxes, occurrences, and hydroclimatic conditions in the main text. Figure C2 offers detailed statistical comparisons may better suited to the Appendix.

- L 340-341: The more important implication would be the long-term declining trend: "This implies that external CO2 sources, accounting for the remaining proportion in each periods, has declined…"

Done: "This implies that external CO_2 sources, accounting for the remaining proportion in each period, have declined over time."

- L 436-437: Don't you need to mention that the magnitude of -NEP did not change notably, but the spring-summer autotrophic state has significantly decreased in magnitude and duration over the recent decade (Fig. 1c), resulting in slight increases or persistent levels in the annual cumulative NEP.

L459-461: While the magnitude of -NEP did not change notably, the CO_2 consumption by autotrophic state has significantly decreased in magnitude and duration over the recent decade (Figure 3b), resulting in slight increases in annual cumulative NEP.

- L 453-455: I would invite you to contextualize your finding by comparing it with other studies. Here I introduce my own study, just as an example of studies that examined sink-source transitions depending on trophic conditions: https://doi.org/10.1016/j.watres.2021.117510.

We have revised the Discussion section accordingly. The text now compares the source-sink dynamics of the Loire with other large rivers, including the Seine River, France and the Han River, Korea study you kindly suggested.

L476-485: "This capacity for CO2 uptake distinguishes the Loire from other comparable river systems that consistently report persistent emissions. For example, the highly urbanized Seine River (France) has remained a persistent CO2 source since the 1970s; even during periods of intense phytoplankton blooms, in-stream respiration and high loads of organic matter from wastewater treatment plants (WWTPs) overwhelmed any photosynthetic CO2 drawdown (Marescaux et al., 2018). Similarly, studies of the eutrophic Han River in South Korea show that while high phytoplankton biomass can reduce CO2 concentrations, the system remains a net source due to the rapid mineralization of both algal- and wastewater-derived organic matter (Kim et al., 2021). This high rate of mineralization can even be amplified by synergistic interactions, where mixing different organic matter pools leads to greater CO2 production than expected (Begum et al., 2019).

- L 536 "a decrease in NEP": Fig. 1 doesn't show any straightforward decrease in NEP, but the reduction in the duration and intensity of spring-summer autotrophy.

L569-570: Our data show that in the Loire, the long-term shift from phytoplankton to macrophyte-dominance in 2005 has resulted in a reduction in the duration and magnitude of seasonal autotrophy and greater annual net heterotrophy.

- L 539: Please italicize the species name "Corbicula fluminea".

Done

- L 549, 561-563: The current version of discussion focuses on groundwater inputs as the primary source of the long-term changes in lateral inputs. Again, lateral CO_2 transport from terrestrial sources occur not only via groundwater but also via runoff. Furthermore, don't you need to consider urban and agricultural wastewater as terrestrial sources, which might have served as important sources for eutrophication in earlier years? I would invite you to discuss how the long-term decreases in anthropogenic sources of both CO_2 and organic matter (such as WWTP effluents and urban/agricultural runoffs) potentially contributed to the observed decreases in lateral inputs. In the case of organic matter degradation, please also consider the potential priming or synergist effects of algal biomass on the biodegradation of rather recalcitrant terrestrial organic matter (refer to papers on priming effects: e.g., https://doi.org/10.1016/j.scitotenv.2019.04.123). The reduced autotrophy in recent years might have dampened algal priming effects on the biodegradation of allochthonous organic matter compared to the preceding trophlux phases.

Thanks for these sugggestion. The updated section now discusses how long-term decreases in anthropogenic sources, such as WWTP effluents and agricultural runoff, have contributed to the observed reduction in lateral inputs based on the studies of (Minaudo et al., 2015, 2016).

We have incorporated the concept of priming effects, using your reference, to explain how the decline in algal biomass likely dampened the biodegradation of terrestrial organic matter. During the Loire's earlier eutrophic, phytoplankton-dominated period, this effect was likely much stronger, boosting the absolute rate of internal CO_2 production. The subsequent decline in phytoplankton biomass and reduced autotrophy in recent years has likely dampened this synergistic effect.

L581-593: Contrary to our expectations, we observed a decreasing trend of FCO_2 attributable to an over 50% reduction in external CO_2 sources in the Loire River. This conclusion is supported by the key finding that, despite the overall decline in total FCO_2, the relative contribution of internal CO_2 production (−NEP/ FCO_2 ratio) notably increased from an average of 37 ± 27% to 57 ± 10% (Table 1). The Loire River has indeed experienced dramatic reductions in anthropogenic inputs from urban wastewater treatment plants and agricultural runoff since the early 1990s. Total phosphorus inputs decreased 4-fold between 1991-2019 (Minaudo et al., 2015), and total organic carbon fluxes declined more than three times from the early 1990s to 2012 (Minaudo et al., 2016). However, this decline in organic matter inputs cannot explain the observed decrease in FCO_2, as heterotrophic respiration did not significantly change over the study period (Figure 3b). Besides, a decrease in anthropogenic organic matter would theoretically lower internal CO_2 production, reducing the −NEP/ FCO_2 ratio. As our observations indicate the opposite trend, the significant reduction in total FCO2 must therefore be predominantly driven by declines in external inorganic carbon inputs from groundwater.

L480-485 about the OM respiration and priming effect: Similarly, studies of the eutrophic Han River in South Korea show that while high phytoplankton biomass can reduce CO2 concentrations, the system remains a net source due to the rapid mineralization of both algal- and wastewater-derived organic matter (Kim et al., 2021). This high rate of mineralization can even be amplified by synergistic interactions, where mixing different organic matter pools leads to greater CO2 production than expected (Begum et al., 2019).

- L 612: Please also consider the contribution of anthropogenic sources.

Agree. While our data points to a reduction in external (groundwater) sources as the primary mechanism for the decline in FCO2, the initial trigger for this change was indeed the long-term management of anthropogenic pressures within the catchment.

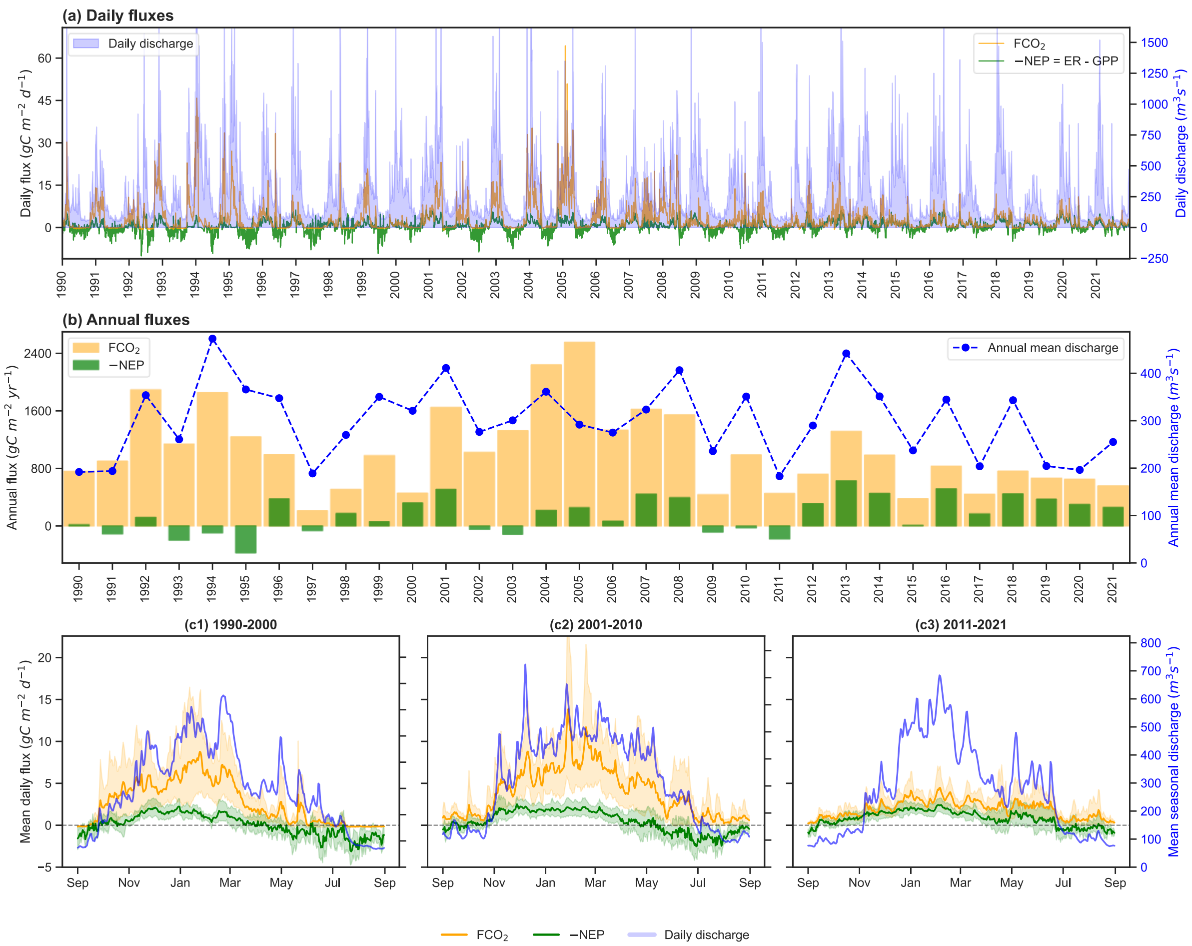
L650-655: We report a strong long-term decrease in CO2 fluxes (-62% over the 32 years) and an increase in the contribution of heterotrophy (–NEP) to this CO2 outgassing flux. The Loire River's transformation from severe eutrophication to oligotrophic conditions involved dramatic reductions in anthropogenic inputs, including reductions from nutrients and organic matter in urban and agricultural runoff. However, these anthropogenic changes primarily influenced internal CO2 production through altered organic matter processing within the river, while the observed external CO2 source reduction appears driven by groundwater biogeochemical changes that cascaded from surface ecological shifts.

- L 741: Please distinguish K600 from k600 to be consistent with the main text.

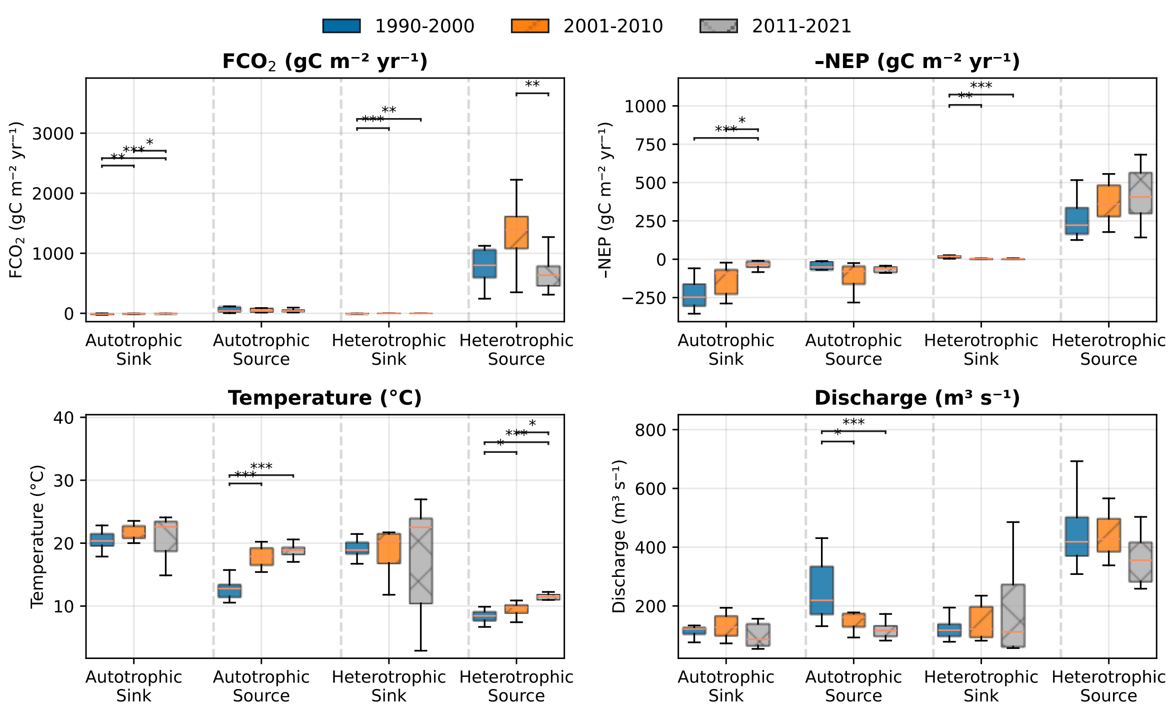
L779-780: The k600 values in this study which were derived from K600 output of StreamMetabolizer model were compared with the seven k600 values calculated from seven fitted equations proposed by Raymond et al. (2012)

- Figures: Please check whether the green color, displayed against a grey one, would conform to the journal guidelines on color schemes ("it is important that the colour schemes used in your maps and charts allow readers with colour vision deficiencies to correctly interpret your findings. Please check your figures using the Coblis – Color Blindness Simulator and revise the colour schemes accordingly.")

- Fig. 1a: Please revise the legend so that the minus sign (not hyphen) in front of NEP can be clearly identified.
Thanks. We change the grey color into orange for Figure 1 and correct -NEP into −NEP.



(a) Daily fluxes
Daily discharge
FCO2
−NEP = ER - GPP
Daily flux (gC m−2 d−1)
Daily discharge (m3s−1)
(b) Annual fluxes
FCO2
−NEP
Annual mean discharge
Annual flux (gC m−2 yr−1)
Annual mean discharge (m3s−1)
(c1) 1990-2000
(c2) 2001-2010
(c3) 2011-2021
Mean daily flux (gC m−2 d−1)
Mean seasonal discharge (m3s−1)
Sep
Nov
Jan
Mar
May
Jul
Sep
FCO2
−NEP
Daily discharge



1990-2000
2001-2010
2011-2021
FCO2 (gC m−2 yr−1)
-NEP (gC m−2 yr−1)
Temperature (°C)
Discharge (m3 s−1)
Autotrophic Sink
Autotrophic Source
Heterotrophic Sink
Heterotrophic Source