Dear Dr Gwenaël Abril

The second revision of our manuscript received very constructive critics, and we carefully addressed each comment of the reviewer in the newly revised version.

You stated that "Wind speed parametrization of gas transfer velocities for lakes cannot be applied in a river, even with low slope and low current velocities and without any justification." We totally agree with this comment; in our work we did not use for presentation of Results and Discussion the wind speed calculated gas transfer velocities, neither the fixed K_T used previously for large Siberian rivers. Results of alternative methods of flux calculation were presented only in the Supplement, and this was done for consistency with other works in this field (including the most complete one of Castro-Morales et al. (2022)). Now we removed all mentioning of wind speed parametrization and relevant numbers from the revised manuscript and the Supplement.

Following your recommendation, we calculated gas transfer coefficients for sampled rivers taking into account hydraulic variables and compared them with those obtained in the field with drifting chambers. The relevant discussion has been added to L 423-443 of the section 4.1. Again, we would like to underline that all the interpretation of the data were based on chamber-measured fluxes.

Responses to Reviewer No 3

The authors have made some improvements on the paper, but I think they could still make an extra effort to bring this work to the standards of Biogeoscience and that the paper does justice to the enormous effort in acquiring these data.

We further revised our manuscript and performed necessary calculations of transfer coefficients.

I still think it is useless and unjustified to use the parameterization of Cole and Caraco (1998) developed for lakes to compute fluxes in a river. This just adds to confusion and distraction to the paper. On the other hand it would be extremely useful to compute the gas transfer velocity from slope and flow using parameterization for rivers as used by Liu et al. (2022). This approach is applicable to all rivers (large and small) even those with low flow and low slope as Ket river. Liu et al. (2022) explain in detail how to make the computations, this can be achieved without too much effort with some GIS modelling. The authors could then use the gas transfer velocity from the chamber measurements to validate the modelled values.

We agree with this remark and removed all the parametrization of Cole and Caraco (1998), developed for lakes, from the revised manuscript. The only reason of presenting Cole and Caraco (1998) method was for the consistency with other works on Siberian rivers, in particular, the Ambolikha River (Castro-Morales et al., 2022). In the newly revised version, we performed the K_T calculations following the work of Liu et al. (2022) as requested by the reviewer as described in L 433-441 of the revised Discussion. Specifically, gas transfer velocity (k) was estimated from channel slope (S) and flow velocity (V) using either equation (4) of Raymond et al. (2012)

or equation (5) of Raymond et al. (2012):

k₆₀₀ = 2841 SV + 2.02

Both equations have been shown to predict reasonable k over large spatial scales in various regions as reviewed by Liu et al. (2022).

Raymond, P. A., Zappa, C.J., Butman, D., Bott, T.L., Potter, J., Mulholland, P., Laursen, A. E., McDowell, W. H., and Newbold, D.: Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers. *Limnology and Oceanography: Fluids and Environments*, *2*(1), 41-53. <u>https://doi.org/10.1215/21573689-1597669</u>, 2012.

The table R1 below lists the obtained values, in comparison to chamber-measured transfer coefficients, as median and IQR for all rivers of the Ket basin (main stem and tributaries):

Table R1. Chamber-measured and calculated transfer coefficients for all studied rivers of the Ket basin.

К _т , m d ⁻¹	median	IQR	Q1	Q₃
Measured by chambers	0.69	0.76	0.47	1.23
Raymond et al., 2012, eq. 4	1.02	1.25	0.27	1.52
Raymond et al., 2012, eq. 5	1.81	0.51	1.69	2.19

For convenience, we illustrated results of these comparison in Fig. R1 below:



Fig. R1. Comparison of gas transfer coefficients for all rivers and streams of the Ket basin, measured by floating chamber and calculated using average channel slope and flow velocity, using two different equations of Raymond et al. (2012). Note a very good agreement between measured and calculated (Eqn. 4 of Raymond et al., 2012) transfer coefficients for the rivers of the Ket basin.

The use of multiple gas transfer velocity values is confusing, and this is worsened by the fact that the legend of figures and Table that are not explicit. Table 1 and Figure 3 report FCO2 and FCH4 and because the legend is very short it is not possible to know just by reading the table/figure what these values correspond to. Are these the chamber measurements (for FCO2) or the computed values ? If these are the computed values how were the computations made ? With the constant Kt of 4.46 m d-1 "representative for large lowland rivers" (L207), the gas transfer velocity computed from wind with Cole and Caraco, or using an average K derived from chambers ?

We are sorry for not being sufficiently explicit about data presentation. Throughout the main text, tables and figures, we always used only chamber-measured fluxes and measured gas transfer coefficients. Figure 3 and Table 2 present chamber-measured CO₂ fluxes; we added this information in the figure legend and table caption.

There is (in my opinion) very little gain in computing fluxes with all these different methods. On the contrary this is just a distraction and source of confusion for the readers.

We totally agree and removed all mentioning of different methods of flux calculation. In the newly revised version, we present only chamber-measured CO₂ fluxes.

I still think it would be useful to extract Strahler order and plot the data as function of Strahler order rather than bundling all of the data into "tributaries". This is quite useful approach, check figure 2 of Butman & Raymond (2011, https://www.nature.com/articles/ngeo1294). Given the enormous amount of work to acquire the data, the authors might want to spend a couple of hours extracting Strahler order that can be computed with DEM data and GIS tools such as Quantum GIS (freeware).

The Strahler order of studied rivers ranges from 2 to 9; added to the text (L 113-114) and revised Table S1. Following the reviewer's suggestion, we plotted the pCO_2 and chamber-measured FCO_2 and K_T as a function of stream order (Fig. S5 of revised manuscript), presented for convenience in Fig. R2 below:



Fig. R2. Distribution of CO₂ concentration (**A**), chamber-measured flux (**B**) and chamber-based gas transfer velocity (**C**) across stream orders in the Ket River basin during spring flood (green squares) and summer baseflow (red circles).

As expected at such low slopes and extremely flat terrain, there is no impact of stream order on CO₂ emissions regardless of season.

I still think it is superfluous to present in table 2 the correlations of fluvial CO2 and CH4 with lithology. There is no established link between lithology and CH4. Lithology affects HCO3- content but not CO2. The fluvial CO2 content depends mainly on respiration not lithology. The respiration that leads to CO2 in streams occurs in soils and/or in-stream. This is why Lauerwald et al. (2015, doi:10.1002/ 2014GB004941) modelled CO2 in rivers using catchment net primary production and not lithology. This is why CO2 in rivers correlates with DOM rather than Ca2+.

We agree and removed lithology aspect from the revised version of Table 2.

L 76 : The authors have not scrutinized the literature sufficiently. There have been direct measurements of CO2 in "Northern Eurasia". Please refer to the work of Castro-Morales et al. (2022) in the Ambolikha River in northeast Siberia, published in December 2021. It is not the job of reviewers to make the literature overview for the authors. This paper should be relevant for the discussion as it also reports diurnal variations.

We would like to point out that the work of Castro-Morales et al has been cited in both the initial submission and revised version of our manuscript.

We made sure that we cited all works relevant to CO₂ emissions in Siberian river waters in the newly revised version, and added a few more references. We strongly reorganized the text in the Introduction (L 79-85). Note that we did not analyze in details the vast literature on Scandinavian fluvial systems; this would require a review paper in its own.

L81 : I still do not understand what you mean by "high latitude regions are important". This statement is so vague it could mean anything.

We removed this rather vague sentence from the Introduction.

L83: So, what ? In which form will this carbon be released? Will this carbon release impact atmospheric CO_2 or CH_4 ? If the organic carbon is released in extremely refractory form and is not converted (or converted super slowly) by microbial activity into CH_4 or CO_2 , then this will have no impact on atmospheric carbon content.

We removed these lines from the revised text; discussion this issue goes above the objectives of this work. We simply stated that "The on-going interest to Siberia comes from the fact that this region hosts large C stocks in soils and wetlands intersected by extensive river networks that deliver majority of water and C to the Arctic Ocean (Feng et al., 2013)."

I suggest that the authors make their data-set publically available on publication either as a supplement or an entry in a data-repository (zenodo or equivalent).

Most of the data are presented in the Supplement (Table S2). However, following this important remark, we uploaded all primary data on continuous pCO₂ in the Ket River to the Mendeley database, where we publish all other similar data on Siberian Rivers:

Pokrovsky, O., Lim, A., Krickov, I., Korets, M., Vorobyev, S.: "Ket River hydrochemistry, CO₂ concentration and landscape parameters", Mendeley Data, V1, doi: 10.17632/snwbkvg6tc.1, 2022. We added necessary 'Data availability' statement in the revised manuscript.

We thank the reviewer for very pertinent remarks that allowed significant improvement of the manuscript.

Oleg S. Pokrovsky