RC2: 'Comment on egusphere-2022-485', Anonymous Referee #2, 30 Sep 2022 General comments

The manuscript entitled "Carbon emissions from Ket River, western Siberia" provides a meaningful contribution to the understanding of carbon export and emissions in the western Siberian Lowland. The title of the manuscript is sufficiently precise and the overall presentation is well structured and clear. Many findings presented in this study are relevant and bring new insights into the processes and controls of carbon processing in this environment. Since the system is influenced by multiple factors, some of the interpretations raised in the discussion are relatively vague or inconclusive. Still, all interpretations and conclusions seem to be well supported by the results. For this reason, I believe that the manuscript will be suitable for publication in "Biogeosciences" after a careful revision.

We thank the reviewer for positive evaluation of our work and we revised the text following all comments and better argued our interpretations.

I applaud the initiative of using floating chambers for direct measurements. Although they require more work, the study would provide completely different and much less accurate FCO2 estimations if they weren't employed. Maybe this finding could be emphasized in the abstract or in the final remarks.

We agree with this proposition and provided relevant information in the Abstract.

From a cost-effectiveness perspective, I do not see major problems in the approach you took for the final C emissions quantification (especially considering how difficult it is to perform multiple sampling cruises in these areas throughout the year). However, I think that the uncertainty calculation is too simplistic and most probably misleading. I urge the authors to follow best practices recommended at volume 1, chapter 3 of the "2006 IPCC Guidelines for National Greenhouse Gas Inventories" (IPCC, 2006). More specifically, Monte-Carlo approaches (based on probability density functions) have been successfully employed in other assessments. Also, the methods should show all the information required for reproducibility and traceability (e.g. by providing all the equations and later the full data set in online repositories). This does not seem to be the case in this manuscript.

Following this comment, we added necessary details and equations in section 2.2 as reproduced below:

For CH4 analyses, unfiltered water was sampled in 60-mL Serum bottles. For this, the bottles and caps were manually submerged at approx. 30 cm depth from the water surface. The bottles were closed without air bubbles using vinyl stoppers and aluminum caps and immediately poisoned by adding 0.2 mL of saturated HgCl<sub>2</sub> via a two-way needle system. In the laboratory, a headspace was created by displacing approximately 40% of water with N<sub>2</sub> (99.999%). Two 0.5-mL replicates of the equilibrated headspace were analyzed for their concentrations of CH<sub>4</sub>, using a Bruker GC-456 gas chromatograph (GC) equipped with flame ionization and thermal conductivity detectors (Serikova et al., 2019; Vorobyev et al., 2021). After every 10 samples, a calibration of the detectors was performed using Air Liquid gas standards (i.e. 145 ppmv). Duplicate injection of the samples showed that results were reproducible within  $\pm 5\%$ . The specific gas solubility for CH<sub>4</sub> (Yamamoto et al., 1976) were used in calculation of the CH<sub>4</sub> content in the water.

The CO<sub>2</sub> fluxes were measured by using two floating CO<sub>2</sub> chambers equipped with non-dispersive infrared SenseAir® CO2 loggers (Bastviken et al., 2015), at each of the 7 (spring flood) and 6 (summer baseflow) sampling location of the main stem and 26 tributaries following the procedures described elsewhere (Serikova et al., 2019; Krickov et al., 2021). The chambers were not anchored but slowly free-drifted together with the boat, because it is known that anchored chambers can artificially enhance fluxes due to turbulence thus providing erroneous estimates (Lorke et al., 2015). The CO2 accumulation rate inside each chamber was recorded continuously at 300 s interval. We used first 0.5-1 h of measurements for computing CO2 accumulation rate inside each chamber by linear regression. In addition to in-situ chamber measurements, CO<sub>2</sub> fluxes were calculated from wind speed and surface water gas concentrations using standard approaches (Guérin et al., 2007; Wanninkhof, 1992; Cole and Caraco, 1998). This technique is based on the two-layer model of Liss and Slater (1974), and widely used for GHG flux assessment (Repo et al. 2007; Laurion et al. 2010; Elder et al. 2018). The gas transfer coefficient was taken from Cole and Caraco (1998):

$$k_{600} = 2.07 + 0.215 \cdot U_{10}^{1.7} \tag{1}$$

where  $U_{10}$  is the wind speed taken at 10 m height. Average daily wind speed was retrieved from official data of the nearest weather station (Belyi Yar town) as published by Rosgidromet for the day of sampling. The gas transfer velocity was calculated in two ways - assuming zero wind speed and the actually measured wind speed at the site of sampling or at the Belyi Yar town, middle course of the Ket River.

All the obtained data (full data set) are provided in Supplementary Table S2.

Specifically, we did use Monte-Carlo approach for assessing the CO<sub>2</sub> emissions and dissolved C export fluxes by other Siberian rivers (Serikova et al., 2018; Karlsson et al., 2021; Krickov et al., 2021). We actually did not find any significant (> 20-30%, comparable with inter-annual variability) difference in flux assessment via "classis" simplified approach and the Monte-Carlo (probability density functions). We believe that relative small number of observations (incompatible to recommendations of the IPCC guidelines on much large number of data on GHG inventories) prevent from efficient using of the Monte-Carlo approach in this relatively restricted data set of the Ket River

Estimations for lateral carbon fluxes and POC/DOC are not crucial for most of the conclusions in this paper and seem to be very simplistic and subject to large errors. I recommend authors to reconsider the importance given to the obtained values throughout the text and to improve methods section for a better traceability in this part. We agree that the lateral riverine export fluxes of DOC and POC do not constitute the central part of this work. However, the fluxes are important for assessing the C emission: export ratio, a fundamental parameter of carbon biogeochemical cycle, especially regarding the response of boreal ecosystems to on-going climate warming. We provided detailed description of the flux calculation in the newly added method section (2.4):

The C export flux (May to October) from the Ket basin was calculated based on monthly-averaged discharge at the river mouth in 2019 available from Russian

The C export flux (May to October) from the Ket basin was calculated based on monthly-averaged discharge at the river mouth in 2019 available from Russian Hydrological Survey and DOC, DIC and POC concentrations measured in the low reaches of the Ket River in this study (see hydrograph in Fig. 1). Annual

element fluxes should be usually estimated using a LOADEST method (Holmes et al., 2012) from calculated daily element loads. The latter typically obtained from a calibration regression, applied to daily discharge. This calibration regression can be constructed from time series of paired streamflow and measured element concentration data for sufficient period of the year. In our previous works in this and other similar boreal regions, we demonstrated that this method provides reasonable (within 10 to 30 %) agreement with monthly export fluxes calculated by multiplying mean monthly discharge by mean monthly concentration (Chupakov et al., 2020; Pokrovsky et al., 2022; Vorobyev et al., 2019), at least for the WSL territory. Given that the intrinsic uncertainties on mean monthly discharge are also between 20 and 30 % (see discussion in Pokrovsky et al., 2020), in this study, for open-water period export flux calculation, we used DOC, DIC and POC concentrations measured during spring flood (for May and June period) and baseflow (for August, September and October period). For the month of July, we used the mean concentrations of end of May and August-September which is in accord with seasonal discharge pattern of the Ket River. Note that the contribution of non-studied October month to total open water period water flux is < 10 % and thus cannot provide sizable uncertainties.

Our main argument on the validity of the validity of approach employed for lateral export flux assessment is that the lateral C loss (yield) for the Ket River (3.7 t C km $^{-2}$ land y $^{-1}$ ) is in agreement with regional C (DOC+DIC) yield by permafrost-free small and medium size rivers of the WSL (3 to 4 t C km $^{-2}$ land y $^{-1}$ , Pokrovsky et al., 2020) and with the Ob River in the permafrost-free zone (3.6 t C km $^{-2}$ land y $^{-1}$ , Vorobyev et al., 2019). Note that the latter study of the Ob River, which is very similar in the environmental context to the Ket River, included high frequency weekly sampling over several years of monitoring. Thus, the similarity of lateral export fluxes of the Ket and Ob Rivers support the validity of approaches for sampling and C yield calculation employed in the present study.

Responses to specific comments: Lines 34-35 = Poorly known? **Yes, corrected accordingly.** 

Lines 42-43 = Please consider also including the pCH4 ranges. **0.05 to 2.0 µmol L<sup>-1</sup>: added accordingly** 

Lines 50-54 = Please consider revisiting these last sentences after a careful revision of the methods employed in the uncertainty calculations. I think it is important to be very clear on what are the limitations of these estimations right in the abstract to avoid poor usage of the emission values. For example, you mention in lines 50-51 that "C emission from the Ker River basin was estimated to 127+-11 Gg C y-1", however, you've discarded important hot moments/spots, soil emissions/uptake, etc. I guess you should use another term instead of "River basin" here.

This is very pertinent remark. By this sentence we intended to say "C emissions from the fluvial network (main stem and tributaries) of the Ket River". We also added a sentence on the uncertainties of our conservative estimations and indicated a need for better spatial and temporal resolution

Lines 73-83 = please consider including some of the values instead of presenting this information in a more qualitative way.

Abrupt permafrost thaw may release 80 Pg C and gradual thaw may release up to 200 Pg C by 2300 (Turetsky et al., 2020); added accordingly.

Line 113 = I am not sure if "-0.6..-0.9°C" is a proper way of presenting the temperature range.

We checked the climate data and stated that the MAAT is -0.7  $\pm$ 0.1 °C.

Line 201 = I am not a native English speaker, but "wetted streams" doesn't seem right. Here we intended to state "wetted" in contrast to "active"; more precise term is "temporary non-active streams"

Line 226 = Please consider including the pCH4 ranges. The range of CH4 concentration is from 0.05 to 2.0  $\mu$ mol L<sup>-1</sup>

Line 244 = This may be a bit far-fetched, but what about emissions linked to vegetation or other hot spots that helps gas leakages? I know this is a completely different context, but something like seen in floodplain trees (e.g. Pangala et al., 2017), maybe? Also, some pictures of the river and streams in the supplementary material would help readers to have a better idea of the environment.

This is very pertinent remark. This part of the text was moved to the Discussion and we added the possibility of emissions from flooded trees, not investigated in this study.

In the revised Fig. S4, we also presented typical environments of the main stem and tributaries during the spring flood: flooded birch forest (A), abundant grassland (B), and tree-sheltered main stem (C) as illustrated below:



Fig. R1. Typical landscapes of the Ket River and tributaries during spring flood (May 2019)

Lines 376-380 = To me it seems that you have raised a hypothesis (fluxes comes from bog water), tested it (calculate the bog area) and the results "falsified" your hypothesis. Shouldn't you then present an alternative hypothesis here?

This is true. We could not find any other single 'alternative' factor capable of describing the emission pattern. We added the following text in the revised Discussion:

The main unexpected result of this study is that none of the physiochemical parameters of the water column and the landcover factor is sufficiently strong to drive the CO<sub>2</sub> and CH<sub>4</sub> patterns, although they show pronounced spatial and seasonal variations. A likely explanation is that simultaneous operation of multiple aquatic processes that include carbon, oxygen, nutrient, and plankton and peryphyton dynamics as well as sediment respiration control the CO<sub>2</sub> and CH<sub>4</sub> exchanges with the atmosphere, as it is known for boreal lakes and floodplain zones of the boreal rivers (i.e., Bayer et al., 2019; Zabelina et al., 2021; Krickov et al., 2019). Given that even a multiparametric statistics (PCA) did no demonstrate sizable explanation capacity of the data set, we cannot exclude that these potential physico-chemical, microbiological and landscape drivers are working in different (opposing) directions and have counteracted each other.

Lines 381-386 = Does it has any relationship with increased primary productivity per area inland? Any estimates?

Good point. Unfortunately, we do not have primary productivity data with sufficient spatial resolution to test this hypothesis, because the size of the Ket River tributaries is quite small. Currently, this work is in progress at the scale of much large Siberian watersheds. Note that the total vegetation biomass of the catchment positively (but not significantly at p < 0.05) correlated with  $CO_2$  concentration and fluxes in other western Siberian watersheds (Krickov et al., 2022, submitted to Sci. Total Environ).

Line 456 = Also mentioned "Ket basin", I guess this is inaccurate.

Thank you pointing this out. Yes, here we meant fluvial network of the Ket River; corrected accordingly.

We thank Reviewer # 2 for his/her very pertinent and useful comments.