Review of 'Carbon emission and export from Ket River, western Siberia' by Lim et al.

General comment

Reviewer: In this work, Lim and colleagues reported the spatial and seasonal dynamics of C export and emissions from the Ket River mainstem and major tributaries by combining continuous in-situ measurements and discrete sampling. Although high latitude regions are an important component of the global carbon cycle due to their large carbon stocks, carbon emissions and export from permafrost-affected regions, especially those in Russia, are poorly studied due to logical constraints and inaccessibility. In view of the changing climate and thawing permafrost, this study is timely important in quantitatively assessing the spatial and seasonal patterns of dissolved carbon export and emissions in this permafrost-affected river basin and thus provides important insights into future riverine carbon cycling. This research work fits well with the scope of the journal Biogeosciences. But there are several major issues to be properly addressed during the revision stage.

Response: We are grateful to generally positive evaluation of our work and greatly revised the manuscript following the reviewer's comments.

Reviewer: My first major comment is on the observed stable behavior of CO2 in the Ket River basin. The authors have tried to explain the stable behavior of the CO2 dynamics (pCO2 and Fco2) by relating them to various physiochemical parameters. But it seems none of the physiochemical parameters is sufficiently strong to drive the pattern although they show pronounced spatial and seasonal variations, as shown in Table 1 and Figs 2 and 3. This is contrary to studies in other climates/regions. I am wondering whether these potential drivers are working in different (opposing) directions and have counteracted each other. The authors may need to think about this seriously, and re-examine the cause-effect relationships. Many of the current discussion statements are lack of evidence and speculative.

Response: We basically agree with this remark: none of the studied physico-chemical or landscape parameters is capable explaining the observed pattern. To test the possibility suggested by the reviewer – that potential drivers are working in different (opposing) directions and have counteracted each other – we performed a multi-parameter statistics of the full data set (Table S2 together with land cover parameters of the watershed) via PCA, but this did not allow identifying the main drivers and actually, the overall explanation capacity of two factors was below 26%. In addition to PCA, a Redundancy Analysis (RDA) was used to extract and summarize the variation in a set of response variables in C pattern that can be explained by a set of explanatory variables (environmental, climatic and hydrochemical factors). The RDA treatment did not provide additional insights into environmental control of C pattern across the rivers and seasons. After normalization, the main result was that the analyses are not statistically significant ($p > 0.05$).

However, we agree with the reviewer that the possibility of governing factors that counteract each other cannot be excluded, and we added pertinent sentences to the revised text of the Discussion (end of section 4.1). 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. However, further in-depth analysis of these interactions require much better seasonal resolution ideally over full period of the year, which was beyond the scope of the present study.

Note that a more likely explanation of remarkable stability in CO_2 concentrations and emissions and weak environmental control on dissolved and gaseous pattern in the Ket

River basin are (1) essentially homogeneous landscapes, lithology and quaternary deposits of the whole river basin (20-25 % bogs, 60-70% forest, 3-5 % riparian zone), and (2) strong dominance of allochthonous sources in both dissolved and particulate organic matter. The latter is consistent with the finding that the SUVA and bacterial number (TBC) positively correlated with both pCO_2 and FCO_2 during summer (Fig. 5 A, B), which may indicate non-negligible role of bacterial processing of allochthonous (aromatic) DOC delivered to the water column from wetlands and mires. Furthermore, the positive correlation between mean annual precipitation (MAP) and pCO_2 and FCO_2 during the baseflow could reflect the importance of water storage in the mires and wetlands (Fig. 5 D) during the summer time, and progressive release of CO_2 and DOC-rich waters from the wetlands to the streams.
To summarize our response, we did identify some possible drivers (allochthonous DOM, bacteria, mire coverage) but these factors operated essentially during the summer baseflow and could not explain the full spatial and seasonal pattern of C concentration and emission in the Ket River basin.

Reviewer: My second major comment is on the calculation of the annual flux of CO_2 emission and lateral C export. With very limited C sampling results covering a short period (Fig 1b), the annual flux estimates are prone to large errors. For example, CO_2 emissions during ice melting periods are exceptionally strong after a long period of CO_2 accumulation. But such emissions are not included or accounted for in the estimation.
Response: We understand and partially agree with this concern of the reviewer. However, our main argument that via performing both peak of the spring flood and summer baseflow sampling campaigns with unprecedented spatial resolution, we encompassed most important open-water period for the CO_2 and CH_4 evasion. In this regard, we believe that the spring flood (May-June) and summer baseflow (July-August-September) are largely sufficient to represent the majority of C evasion from the river waters. In fact, similar to previous study of rivers along a 2500 km transect of the WSL territory, the timing of the two sampling campaigns covered approximately 80% of the annual water discharge in the basins (Serikova et al., 2018). However, to better argument our response, in the figure below (Fig. R1) we presented unpublished data of our group on one site of the main stem and several small tributaries of the Ket River sampled in spring, summer and autumn (October before ice-on). It can be seen that the CO_2 concentration and emission flux during October are either equal or 1.5-2 times lower than that during summer (August). Because we postulated that the evasion during autumn is equal to that during summer baseflow, the assessment of overall C evasion from the Ket River basin used in the present study cannot sizably underestimate the real values.

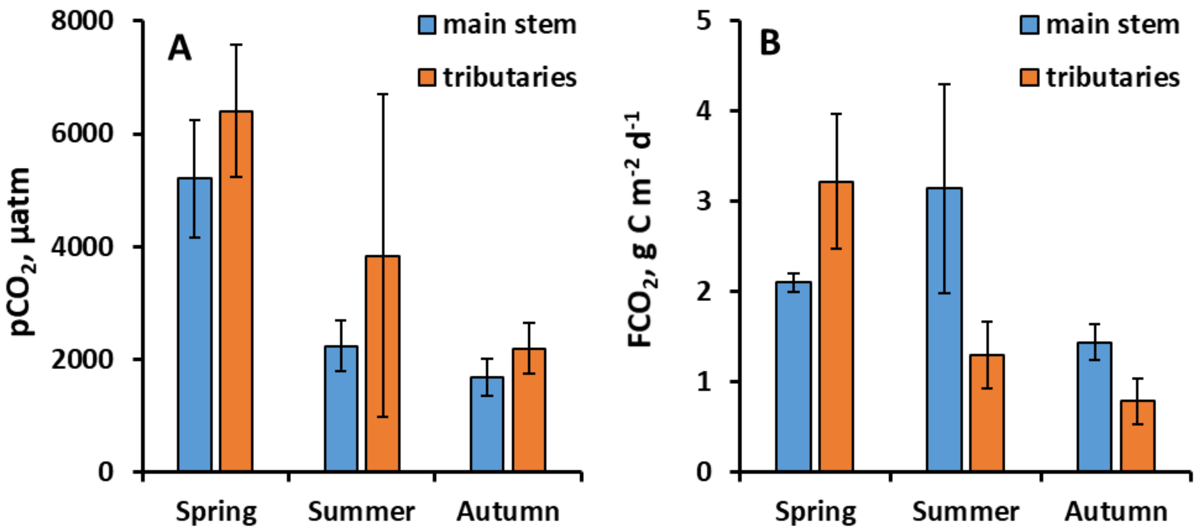

Fig. R1. A histogram of pCO_2 (A) and FCO_2 (B) in the Ket River main stem and several tributaries during three main open-water seasons. Unpublished data of our group.

Further, we explicitly stated that the study is focused on six months of open water period and we could not investigate the winter-time (under-ice) accumulation of GHG or a number of logistical reasons: one would not risk remaining on the river ice to capture the gas regime during ice cracking when the river physically 'explodes'. To the best of our knowledge, none of the Siberian river has been sampled for winter time C evasion so far, and this clearly requires a study in its own. Doing this on a small tributary could be an option, and this research is in progress by our group.

Reviewer: Likewise, the lateral fluxes based on monthly average discharge are likely with huge uncertainty. E.g., the strong DIC concentration differences between the flood and baseflow (Table 2) suggest significant dilution effect and changing flow paths.
Response: This is very pertinent remark. Our main argument on the validity of dissolved C (DOC and DIC) export fluxes used in the present study is a similarity of the total C yield for the Ket River (3.7 t C km^{-2}_{land} y^{-1}) and 1) values of the 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 2) the Ob River in its the middle course (3.6 t C km^{-2}_{land} y^{-1}, Vorobyev et al., 2019). These former studies of our group were performed with much better seasonal resolution, including both open water and glacial period of the year. For example, the latter study of the Ob River, which is very similar in the environmental context to the Ket River, actually included high frequency weekly sampling over several years of monitoring.

Reviewer: Overall, this manuscript was well written, but the structure could be further improved by moving the discussion statements from the Results section to the Discussion section.
Response: We followed the recommendations of the reviewer and revised the manuscript accordingly.

A further language editing is also needed before its resubmission.
Response: We carefully check for spelling and grammar errors and improved the style of many sentences in the revised version. Note that the APC of accepted manuscripts include full English proofread of the text.

Specific comments (with line number):
L42-43: 100 to 150 times?
Response: Yes, revised accordingly

L64: even for these regions, the estimates are still with great uncertainty.
We agree and alerted the reader about uncertainty on these estimates

L80: delete 'remain'
Response: Revised accordingly

L95: essentially speaking, the two sampling campaigns represent the two extremes (highest flow and lowest flow, respectively). A question then is whether it is reasonable to use these extremes for annual flux estimation (emission and downstream export)?
Response: Please note that a combination of natural factors such as low runoff, lack of relief and highly homogenous landscape coverage of the permafrost-free zone of western Siberia in general and of the Ket River basin in particular provides quite smooth hydrographs of the rivers. In this regard, the spring flood period is extended over 2 month, from the beginning of May to middle of July, whereas summer baseflow includes second half of July, August and September. We added this information in the revised text (section 2.1).

L108: what is hydrocarbon exploration? I don't understand this.
Response: This means that there is no oil and gas development and production activity in the Ket watershed area, revised the text.

L113: delete '.' after -0.6. also, references are needed to this paragraph describing the background information.
Response: Revised accordingly and added some references (Frey and Smith, 2007; Pokrovsky et al., 2015) as requested.

L119: Have the authors finished the cruise (1300 km in total) and sampling within 3 days? Sounds an impossible task.
Response: There were two boat trips in this study. The spring time cruise took 11 days on the river for 1309 km overall trip length. During summer baseflow, the 4-days trip was shortened by 200 km due to too low water level in the headwaters and some tributaries. We added this missing information in the revised text. Note that we did not perform day/night monitoring in August which allowed greatly shortening the overall cruise time.

L125-126: what's the sampling frequency for the day/night circle?
Response: The FCO_2 measurement frequency was one per hour and CO_2 concentration was recorded continuously and averaged for 5 minute interval. Added to revised text.

L152: change 'location' to 'locations'. **– Fixed.**

Reviewer: Also, it would be helpful to briefly describe the measurement procedures, instead of referring readers to published papers for details. These papers might not be accessible to some of the journal readers.
Response: We agree and added the following information in the revised text of the section 2.2: CO_2 fluxes were measured with two floating chambers equipped with nondispersive infrared CO_2 logger (ELG, SenseAir). The CO_2 accumulation rate inside each chamber was recorded continuously at 300 s interval. We used first 0.5–1 h of measurements for computing CO_2 accumulation rate inside each chamber by linear regression.

L154: what are the standard approaches? Please clarify and provide details.
Response: CO_2 fluxes were calculated from wind speed and surface water gas concentrations. 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; Juutinen et al. 2009; Laurion et al. 2010; Elder et al. 2018). The gas transfer coefficient was taken from Cole and Caraco (1998):

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

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.
We added this missing information, together with details of CH4 measurements in the revised text of section 2.2.

L156: For flowing streams and rivers, the major driver of the gas transfer velocity is flow velocity, not wind speed.
Response: This is certainly true for other boreal rivers with high runoff, high flow velocity and pronounced turbulence. The rivers of western Siberian Lowland exhibit slow flow rate, and calculation of the C evasion using river slope (velocity) as performed by Serikova et al. (2018) does not improve the accuracy of K_T calculation because all of the water surfaces of the sampled rivers were considered flat and had a laminar flow. In fact, the water flow was calm and lacked turbulence throughout the river course, even at peak discharge, due to the overall flat terrain of the WSL.

L181: The DIC concentrations in base flow is even higher than the DOC concentrations (table 1). But here the contribution of carbonate C to total C is only 0.3%. this looks problematic. please double check.
Response: This is a misunderstanding. The DIC dominated dissolved (< 0.45 µm) load of the rivers during baseflow. However, due to the dominance of peat and clay soils of the river watersheds and lack of carbonate minerals in the river suspended matter (RSM), the concentration of inorganic carbon in the suspended (> 0.45 µm) fraction of the river load was negligibly small compared to that of organic carbon. This observation is fully consistent with previous studies of suspended (Krickov et al., 2019) and dissolved (Pokrovsky et al., 2020) load of other WSL rivers.

L195: what is the spatial resolution of the biomass and soil OC content datasets?
Response: The biomass and soil OC content were obtained from BIOMASAR2 dataset in raster format with spatial resolution of 1 x 1 km (Santoro et al., 2010).

The soil OC content was taken from the Northern Circumpolar Soil Carbon Database (NCSCD). The original NCSCD dataset produced in GIS vector format corresponding to 1:1000000 scale of topographic map. It could be rasterized to 1 x 1 km pixel resolution [http://www.bbcc.su.se/data/ncscd/ and http://su.diva-portal.org/smash/record.jsf?pid=diva2%3A637770&dswid=1526)]
Added to revised text accordingly.

L219: a lack of systematic change? Note the pCO2 changed by a factor of 2 when tributaries with high CO2 concentrations join the mainstem.
Response: This is a very good point. We agree that the original sentence was poorly formulated; we intended to state that there was no systematic change in CO_2 concentration between the headwaters and the low reaches of the Ket River. The impact of CO_2-rich tributaries is indeed clearly seen and we revised the text as necessary.

L241-247: these are not results, move them to the discussion section.
Response: We totally agree and shifted this paragraph to the Discussion (section 4.1).

L297-298: would the precipitation quickly infiltrate into soil and become groundwater?
Response: Yes, this is certainly possible, notably in the permafrost-free zone of the WSL, as also discussed in L 398-406 of the original manuscript. However the majority of river feeding in the region occurs from bogs/mire at the tributaries, that quickly release the atmospheric water to the hydrological network. This is demonstrated by water isotope study in the WSL (Ala-aho et al., 2018a, b), and discussed in details in section 4.1 (L 373-376).

L306: as the measurements were performed at the flood peak, this may have caused overestimation.
Response: We agree that estimations of total C emissions extrapolated to the full period of spring flood should be considered with caution. However we do not expect sizable overestimation of the fluxes; see our detailed response to major comment No 2. It can be seen in Fig. 2 B that May and June exhibit the highest runoff which corresponds to the highest water coverage of the floodplain, as also confirmed by our recent study od the Ob River middle course and its floodplain zone (Krickov et al., 2021).

L316: how were these %s determined?
Response: This range reflects both the uncertainty of the water coverage of the territory as analyzed in details by Krickov et al. (2021) based on high temporal and spatial resolution study of C emissions in the floodplain of the river, together with limitations on the seasonal and spatial variations of CO_2 emission in the Ket basin assessed in the present study.

L338-340: why the co2 flux pattern is different from the pco2 pattern?
Response: Both parameters are directly measured in the field, and strictly speaking, independent of each other. This represents the main added value of the present study compared to previous works where FCO_2 was calculated based on hydrochemical measurements in the rivers (Raymond et al., 2013 for example). Enhanced or decreased CO_2 evasion measured by floating chambers relative to calculated fluxes can be caused by water turbulence, wind speed and CO_2 variations in the air at the river surface. Furthermore, the CO_2 concentration measurements encompass quite short period of

exposure (typically 5-10 min) compared to fluxes measured by floating chambers; the latter are deployed for 30-60 min period.
Note that the difference of the pattern between continuous pCO_2 and calculated CO_2 flux (green dashed line in Fig. 2A) may stem from the fact that this FCO_2 was calculated with K_T = 4.46 m d^{-1}, from in-situ measured pCO_2 values which were averaged over 10-km distance.

L357-358: Another possible reason is because the measurements were actually not performed in the true headwater streams. All the sites, include the tributary ones, are located along the mainstem and not in the headwater region as shown in Fig. 1.
Response: We thank the reviewer for pointing out this possibility. We cannot provide a straightforward response to whether the pCO_2 increases in the most headwaters compared to the middle course of the tributaries. Note that we typically moved several km upstream of selected tributaries as far as the small boat could go (see Fig. R2 below). Further moving became impossible due to too shallow depths or abundant tree trunks. No need to say that walking in these pristine forest was not feasible. As such we believe that we did our best to tackle still accessible parts of the headwaters, but we acknowledge that further studies are needed to fully address this issue.

Fig. R2. The headwaters of typical small tributaries of the Ket River: Okunevka River (A) and Malaya Anga River (B, C). We could move only several km upstream of tributaries until the tree logs or shallow (30-50 cm) and narrow (1-2 m) channel prevented further progress. Photo credit by Artem Lim.

L366-367: If allochthonous C inputs are the dominant source, pCO2 should have a clear relationship with distance to terrestrial C inputs, i.e., there should be higher pCO2 in tributaries than in the mainstem.
Response: The reviewer is totally right, and we indeed observed systematically higher CO_2 concentration and flux in small tributaries [fed by mire waters with non-processed OM] compared to the main stem; added to revised version. Unfortunately, we could not map in necessary details the tributaries and the main stem watershed to determine the exact distance between the sampling point and potential source of terrestrial C input (specific bog or a floodplain lake). To quantify such a relationship, specially designed study with high spatial resolution (meter to 10 meter pixel size) is needed (such as, for instance, Krickov et al., 2021: https://doi.org/10.1016/j.ecolind.2021.108164) which was beyond the scope of the present work.

L402: change 'at' to 'in'. **– Fixed.**

L427-452: For these comparisons (similarity and differences), it is quite difficult to follow. Putting them into a table may help. Also, the authors need to make a critical and comprehensive discussion, rather than a general sentence on the possible reasons. This is quite speculative.
Response: These comparisons are a bit outside of the mainstream of the section (C emission vs export) so that we preferred to strongly shorten this paragraph and remove some irrelevant comparisons. Note that we discuss possible reasons for the observed differences between the Ket River and other boreal rivers in L450-452 of the original version of the manuscript. At the same time, a detailed analysis of environmental physico-chemical, microbiological and landscape factors controlling C pattern in rivers of boreal zone based on other available studies is beyond the scope of the present research (not a review) paper. These literature studies often lack necessary quantitative information on landscape parameters and full hydrochemistry of the water column for each specific watershed. As such, a quantitative comparison with results of the present study is not possible.

L456: This ignorance may have caused great errors to the annual estimates. Emissions of CO2 during ice melting is exceptionally strong and make a disproportionate contribution to the annual flux estimate
Response: We agree with this remark; however, in this work we dealt only with open water period. Extensive response to this and second major comment of the reviewer is provided above.

L460: unclear description of the Ob River.
Response: Simplified to "The Ob River in the permafrost-free zone"

L467: change 'thus' to 'this' **– Fixed.**

L502-503: any evidence to support this argument?
Response: Good point. Here we hypothesized that microbial processing and photodegradation of particulate organic carbon in the water column can be among the main drivers of CO_2 supersaturation of the river waters as it is known from field observations and incubation experiments (Attermeyer et al., 2018). These authors demonstrated that riverine POC is 14 times more biodegradable than DOC, and the

POC concentration in the Ket River basin increased 4-fold between spring and summer (Table 1, this study). As another support of this argument, we note a local maximum of POC concentration in WSL rivers located at the permafrost thaw boundary (Krickov et al., 2018). This maximum was used to tentatively explain elevated CO_2 emissions observed in this part of the WSL, discontinuous to sporadic permafrost zone (Serikova et al., 2018).

Fig 2: for b&c, change the x-axis to 0-900 for consistency and easy understanding. **- Fixed**

Fig 4e: much higher pco2 during the daytime than the nighttime? Why?
Response : The reviewer made a good point here, and we thank him/her for pointing this out. After careful analysis of our field work books, we noted that there was quite heavy rainfall, almost full day when the CO_2 peak was observed at 7 pm. As such, CO_2 mobilization of DOM-rich mire waters from the watershed of the relatively small river Segondenka ($S_{watershed}$ = 472 km^2) could explain such a local maximum at the end of the day. Note that the impact of photodegradation of DOM in the water column is unlikely given that end of the day maximum were not observed in other rivers such as Sochur (Fig. 4 A).

Fig 5d: very low r2, what is the p-value?
Response: This panel is provided to illustrate a lack of statistically significant (at $p < 0.05$) correlation between pCO_2 and wetland coverage of the river watershed, in order to support the statements in L 370-376 of the original text. The p-value here is below 0.5.

We thank the Reviewer # 1 for his/her very pertinent remarks and corrections.