RC3: Anonymous Referee #3, 04 Oct 2022

1) GENERAL COMMENTS

Lim et al. report a high-quality data-set of CO2 and CH4 concentration measurements in the Ket River in Siberia obtained during high-water and low-water. This is a very useful contribution to on-going efforts to collect data to better evaluate the carbon emissions from inland waters because the studied river drains a remote and nearly undisturbed (pristine) watershed dominated by peat bog and taiga forest. Unfortunately, the analysis is (in my opinion) not well structured and the authors might want to spend some extra time on thinking through how to present and analyze the data, and profoundly re-structure the paper and streamline the present content.

For instance, the authors computed the fluxes of CO2 with a gas transfer velocity parameterization for lakes; this gave (unsurprisingly) very different results from the fluxes of CO2 measured with floating chambers. This was predictable and in my opinion not very useful, just distracting.

There is a misunderstanding concerning the origin of K_T = 4.46 m d^{-1}. This value was used for consistency with large Siberian rivers (Karlsson et al., 2021; Vorobyev et al., 2021), in agreement with world average for rivers of low velocity (Raymond et al., 2013). However, the fluxes obtained by the wind speed method are in more reasonable agreement with chamber measured fluxes (Table S2 of the Supplement): the calculated FCO_2 are generally 1.5 to 2 times higher than the measured values, but in 30% of cases the wind-speed calculated fluxes are similar to or lower than those measured by floating chambers.

Regarding formal aspects, the authors should spend some extra time producing high quality figures. Figure 2 is extremely confusing and does a very poor job at presenting this data-set that required a lot of effort to acquire. Figure 3 shows some nice patterns of pCO2 and CH4 concentration in terms of seasonal variations (high-water vs low-water) as well as in terms of stream size (main-stem vs tributaries). A more straightforward and attractive presentation and discussion could be built on these simple patterns. Instead, this nice and potentially interesting information is diluted in a lot of rather unnecessary elements such as computations of fluxes with inadequate gas transfer parameterizations and correlations with not very useful variables such as total bacterial counts (see comments below).

We removed all unnecessary information while adding the recommended citations and stream focusing the discussion of the results.

2) MAIN COMMENTS

L37 and L218: I'm unsure that the term "continuous" applies to measurements of CO2 to this study. My perception of "continuous measurements" is that water is continuously pumped through an equilibrator system connected to a CO2 detector (or equivalent setup) and then the data are logged at regular intervals (1 min or less) (Abril et al. 2014; Crawford et al. 2016b; 2017 Borges et al. 2019). This means that the measurement of CO2 is not interrupted for long periods (and runs for a few hours to a few days) while the boat is sailing. The authors made discrete samples with the boat stopped at a given spot. Albeit they made numerous measurements this should qualify as discrete sampling and not continuous. This is not just a semantic issue; the authors made 764 pCO2 measurements over the distance of the boat route (834 km) as stated L 218. This roughly corresponds to one measurement every 1 km. This is

still quite coarse to describe extremely dynamic river systems. As an example, Borges et al. (2019) showed very marked cross-channel gradients of CO2 in the mainstem Congo River, corresponding to a spatial scale of the order of 1 km (using what truly qualifies as "continuous").

We totally agree that the floating chamber measurements performed in the present study are discrete and not continuous. However, during the spring flood period, the CO_2 concentration was, indeed, measured continuously. As it is stated in the text, a Campbell logger was connected to the submerged CO_2 sensor system allowing continuous recording of the CO_2 concentration, water temperature and pressure every minute. We specified that these readings were averaged over 10 minute intervals yielding 732 individual pCO_2, water temperature and pressure values. At the same time, we admit that identifying and quantifying local-scale hot spots and hot moments of CO_2 release or uptake were not within the objectives of our study.

L150: The authors measured CO2 fluxes between water and air with floating chambers. Lorke et al. (2015) have shown that anchored chambers enhance turbulence under the chambers and artificially enhance fluxes, thus providing erroneous estimates. Please specify if the chambers used in the present study were anchored or free-drifting. If the chambers were anchored then the data should used with extreme caution, especially for the flood period when presumably the flow was higher. In my opinion, these chamber measurements are not necessary, and fluxes should be computed from gas transfer velocity using an adequate parametrizations applied to spatial data, please refer to Liu et al. (2022).

The reviewer made a good point here. The chambers were not anchored but allowed to move together with the boat. We believe that chamber measurements are most valuable contribution of the present study, also noted by other reviewers. In the Supplementary Table S2, for interested reader, we provided results of flux calculations by different methods, assuming zero wind speed, actual wind speed and average K_T of 4.46 m d^{-1} for the WSL rivers. The latter value is reported merely for consistency with previous global estimations of CO_2 emissions from great Siberian rivers and their tributaries such as Ob (Karlsson et al., 2021) and Lena (Vorobyev et al., 2021). At the same time, all the interpretations and correlations presented in our discussion are based on actually measured chamber-based fluxes.

L154: The authors also computed the CO2 fluxes between water and air from CO2 concentrations and the gas transfer velocity. The cited references (Guérin, et al., 2007; Wanninkhof, 1992; Cole and Caraco, 1998) provide parameterizations for lakes that are inadequate for computing the gas transfer velocity in running waters. The authors provides these 3 references, although it was unclear to me which one was actually used in the computations. The gas transfer velocity in streams and rivers can be derived from stream flow and stream slope, that in turn can be derived from spatial data; please refer to Liu et al. (2022).

We agree that lake parameters are not always suitable for computing the gas transfer velocity in running waters. However, the Ket River and especially its tributaries exhibit quite low slope and velocity and the waters are often stagnant due to extremely flat terrain. For convenience, we calculated the fluxes for different wind speed and these fluxes were in reasonable agreement with those measured by floating chambers. Moreover, the range of K_T obtained in this study for the Ket River basin is consistent with that reported based on multiple measurements and calculations using stream flow and stream slope approach (1.2 – 1.5 m d^{-1}) by Serikova et al. (2018). Although the latter work did not encompass the Ket River main steam and tributaries, the permafrost-free

WSL rivers studied by Serikova et al. (2018) are highly similar to those of the Ket catchment.
Noteworthy that the k_T values calculated for western Siberia by Liu et al. (2022) based on reach-level slope and flow velocity (i.e., below or equaled to 2 m d^{-1}) are just in excellent agreement with those obtained in the present study with chamber measurements (Table 1 and Table S2). A likely explanation is relative low values of gas transfer velocity measured in the small streams of the Ket basin in this study (0.2 - 2.0 m d^{-1}, Table 1). These values are typical of lakes rather than rivers (i.e., Kokic et al., 2015) and stem from low flow rate, strongly forested and wind-protected river bed without distinct valley due to extremely flat orographic context of this part of the WSL (Serikova et al., 2018).

L 216: The authors state that there are no spatial variations in CO2. I suggest to mention here that CO2 in tributaries was higher than in the main stem. This corresponds to a "systematic" pattern of variation.
We totally agree and added this important information in the text. Note that, while CO_2 concentrations were different between tributaries and the main stem during both flood and baseflow, the CO_2 flux was not different between the main stem and tributaries regardless of season, as was assessed by Mann-Whitney U test (Table S4 B).

Also, I suggest that the authors extract the Strahler order of the sampled streams and rivers and analyze if there are differences by stream size. It is quite frequent that lower order streams show higher CO_2 values and higher order (Butman and Raymond 2011; Borges et al. 2019), although not always necessarily the case (Borges et al. 2018). Stream size could also be analyzed in terms of catchment area, in addition to Strahler order. Stream size can be used also for upscaling concentrations and fluxes, refer for example to Borges et al. (2019).
This is very valuable comment. We did examine the impact of stream size (catchment area) on CO_2 concentration and fluxes and found that CO_2 concentrations (but not fluxes) increased with a decrease of the river watershed area (Table 2). As such, it was not necessary to take into account the stream order for upscaling the C emissions from the Ket River basin.

<u>RESPONSES TO SPECIFIC COMMENTS of Reviewer No 3</u>

L 34 : I suggest to define « medium–size rivers »
50,000 to 300,000 km^2, added accordingly

L 34 : I suggest to remove « poorly » or replace by « largely » but « poorly unknown » is ackward.
Here we intended to say "poorly known"; corrected

L 40: I suggest to mention the months-years of sampling
May 2019 and end of August - beginning of September 2019

L40: I suggest to replace "CO2 concentration" by partial pressure of CO2.
Agree and corrected accordingly

L40-41: I suggest to mention the differences in pCO2 between base flow and flood period.
In the tributaries, the pCO_2 was 40% higher during baseflow compared to spring flood, whereas in the main stem, it did not vary significantly across the seasons

L41-43: I suggest to provide the range of the CH4 concentrations values rather than the ratio to CO2.
The CH_4 concentrations ranged from 0.05 to 2.0 µmol L^{-1}; added accordingly.

L 47 : I suggest to specify if this is this spatial or temporal "variability" ? or both ?
Both spatial and seasonal variability; added to the revised text
L 49 : The hypothesis of lower path soil-water CO2 inputs during summer is based on what ? During summer-time numerous processes contribute to increase CO2 in rivers compared winter such as higher temperature stimulating microbial metabolism, longer residence time and lower gas transfer velocity (lower river flow), in addition to changes in flow paths of soil-water flows (Borges et al. 2018).
The underground waters produced by dissolution of carbonate mineral-bearing rocks of the Ket catchment are better connected to the river during summer baseflow compared to spring flood. This is well established from former works on the WSL hydrochemistry across seasons (Pokrovsky et al., 2015, 2020). However, we totally agree with the reviewer that multiple processes acting in parallel can contribute to increased CO_2 in rivers in summer compared to early spring. To avoid speculations, we removed this sentence from the Abstract but discussed the works of Borges et al. (2018) in the revised section 4.1.

L51: "lateral" usually refers to exchange between river and riparian zones (e.g. floodplains). Term "downstream C export" might be more adequate. I suggest to specify if this downstream C export refers to inorganic, organic or total carbon and if dissolved or dissolved+particulate.
This is very pertinent remark. We consider the total downstream C export which includes DIC, DOC and POC. We stated this in the discussion section and revised the Abstract accordingly.

L67: define abbreviation pCO2
Partial CO_2 pressure; added to the text.

L69: This statement does not reflect current state of CO2 studies in rivers. There is a fast growing very large amount of studies reporting directly measured CO2 measurements either discretely (Alin et al. 2011; Borges et al. 2015; Amaral et al. 2018; 2022; Leng et al. 2022), continuously at fixed sites (Crawford et al. 2016a, Schneider et al. 2020; Gómez-Gener et al. 2021), and continuously underway (Abril et al. 2014; Crawford et al. 2016b; 2017; Borges et al. 2019). And this is also the case for studies in "under-represented or ignored regions" as stated, and for more than a decade (Alin et al. 2011).
We certainly agree with this remark. Moreover, the most recent study of Liu et al (2022) deals with directly measured CO_2 at the world wide scale. However, to the best of our knowledge, there is no information on measured CO_2 concentration in Siberian rivers other than of our group on the Lena and Ob Rivers (Vorobyev et al., 2021; Karlsson et al., 2021), limited data on the Kolyma River (Denfeld et al., 2013), and small WSL rivers across a permafrost gradient (Serikova et al., 2018). Therefore, by under-represented regions we meant all northern Eurasian territories between Scandinavia and Alaska. We modified the text for clarity and cited the useful papers noted by reviewer.

L 71-72: This is correct and there are some studies available (Abril et al. 2014; Crawford et al. 2016b; 2017 Borges et al. 2019). It could be useful to briefly mention if there is and what is

the added value to make continuous "regional high spatial resolution measurements" of CO2 compared to discrete measurements, based on past published papers.
We totally agree and cited the relevant papers in the revised text of the Introduction. We would like to underline that all available studies are limited to tropical and temperate zones of the world, and boreal regions of Western Europe and Northern America, and thus, further continuous and discrete measurements of CO_2 concentration and fluxes of under-represented regions such as Northern Eurasia are needed.

L73-74: Please clarify what do you mean by "High latitude regions are important". With respect to total CO2 emissions at global scale, rivers in high latitude regions are not important according to the study of Liu et al. (2022) who show that "tropical rivers are responsible for 57% of the global emission, more than temperate and Arctic regions combined (30 and 13%, respectively)".
Good point. Our argument here is not the current CO_2 emissions from high latitude regions, but future climate warming scenario, according to which boreal and permafrost-affected regions can release significant amount of soil C which is likely to be transformed into GHG in the aquatic systems.

L113: there's some sort of typo here " 0.6..-0.9 °C"
Thanks for pointing this out. The MAAT is -0.7 ± 0.1 °C.

L 148 : For a journal such as Biogeosciences I think it is insufficient to refer to other papers for basic methodological information. I suggest to provide details on the gas used for the headspace, on the calibration gases, on the detection limit, precision and accuracy. It could also be useful to mention the typical time interval between sampling and analysis.
This is important remark, also raised by other reviewers. For CH_4 analyses, unfiltered water was sampled in 60-mL Serum bottles. For this, the bottles and caps were submerged at approx. 30 cm depth from the water surface. The bottles closed without air bubbles using vinyl stoppers and aluminum caps and immediately poisoned by adding 0.2 mL of saturated $HgCl_2$ via a two-way needle system. The samples were stored approximately one week in the refrigerator before the analyses. In the laboratory, a headspace was created by displacing approximately 40% of water with N_2 (99.999%). Two 0.5-mL replicates of the equilibrated headspace were analyzed for their concentrations of CH_4, 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 ±5%. The specific gas solubility for CH_4 (Yamamoto et al., 1976) were used in calculation of the CH_4 content in the water.

L129-139: Similarly for CO_2 please provide information on precision. Is the stated accuracy given by the manufacturer or was this determined by the authors? Also specify how the Vaisala instrument was calibrated. Did you trust the factory calibration or did you carry out calibration in the lab? Was the probe checked for signal drift before and after the cruise against standards ? Did you measure atmospheric CO_2 with the Vaisala probe during the cruises as a check of good functioning ?

We agree that referring to previous publications for detailed description of analytical techniques is not appropriate. The calibration of the sensor was our priority during this study. Sensor preparation was conducted in the lab following the method described by Johnson et al. (2009). The measurement unit (MI70, Vaisala®; accuracy ±

0.2%) was connected to the sensor allowing instantaneous readings of pCO_2. The sensors were calibrated in the lab against standard gas mixtures (0, 800, 3 000, 8 000 ppm; linear regression with $R^2 > 0.99$) before and after the field campaign. The sensors' drift was 0.03-0.06% per day and overall error was 4-8% (relative standard deviation, RSD). Following calibration, post-measurement correction of the sensor output induced by changes in water temperature and barometric pressure was done by applying empirically derived coefficients following Johnson et al. (2009). These corrections never exceeded 5% of the measured values. During the cruise, we routinely measured atmospheric CO_2 with the probe ac a check for its good functioning. Furthermore, we tested two different sensors in several sites of the river transect: a main probe used for continuous measurements and another probe used as a control and never employed for continuous measurements. We did not find any sizable (>10%) difference in measured CO_2 concentration between these two probes.

L 144 : how was the water sampled and transferred to the serum vials ? With some sort of sampling bottle ? Niskin or equivalent ?
For CH_4 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.

L165: I suggest to define the "NIST" abbreviation
NIST is for National Institute of Standards and Technology.

L189-193: Please specify if the land cover data correspond to the whole catchment area upstream of the sampling point or if this corresponds to the riparian vegetation just adjacent to the sampling point.
The land cover data correspond to the whole catchment area upstream of the sampling point.

L 216 : I suggest to remove word « emission ». You cannot pre-suppose an emission, some rivers on some occasions can be sinks of CO_2 (Crawford et al. 2016b).
This is totally, true; we agree with this remark.

L 246: I'm not sure this "warning" is useful since the authors used a parameterization for lakes, and this was not a very good idea to start with.
We agree that this text is not at right place; this belongs to the Discussion. Results of the present study clearly demonstrate that high value of K_T (transfer velocity), pertinent to large Siberian rivers of the permafrost regions, can not be used for the Ket River and tributaries located in the boreal permafrost-free zone, due to slow flow rate and strong shading of the river bed by dense taiga forest, leading to quite short fetch. This has to be taken into account for Pan-Siberian upscale of emission fluxes. We reorganized this part in the revised version.

L 295 : It's quite unusual to look into the effect of catchment lithology on fluvial CO_2 and CH_4 concentrations. Lithology will affect the HCO3- content and DIC content, but with little direct impact on CO_2 levels and certainly not on CH_4. I suggest the authors restrict this analysis to DIC (or remove altogether this analysis that is just a distraction).
We totally agree that one cannot expect direct lithological control on CH_4 concentration in the river water (other than via pH buffering by carbonate rocks of the catchment). However, the carbonate rocks/concretions present in the mother rock can strongly affect

the CO_2 pattern, via notably underground discharge of DIC-rich waters during baseflow. This is consistent with absence of correlations during high flow (spring flood), when the rocks are essentially disconnected from the river. We would like to recall that first assessments of fluvial CO_2 emissions (Raymond et al., 2013) were largely based on pCO_2 values calculated from DIC+pH of the river waters. The latter parameters are directly controlled by the proportion of carbonate rocks on the catchment…
Following the recommendation of the reviewer, we greatly diminished the presentation of lithological aspects in the revised version.

L297-298: This is also quite unusual. I would envisage seasonal variations precipitation to explain seasonal variations of CO2, but not spatial variations during a given period, in this case base flow. Correlation does not necessary imply causation, some correlations are spurious or indirect. There's a possibility that this is relate to stream size, as precipitation at catchment scale, also captures catchment surface area in an area of relatively homogeneous precipitation. I suggest to remove altogether this analysis that is just a distraction.
We agree that correlation does not necessary imply causation, and we alerted the reader in the revised version. Note that we also attempted Principal Component Analysis (PCA) which, however, did not allow any better identification of possible driving factors. Therefore, we cannot exclude that these potential physico-chemical, microbiological and landscape drivers are working in different (opposing) directions and have counteracted each other.
Our tentative explanation for positive correlations between mean annual precipitation (MAP) and pCO_2 and FCO_2 during the baseflow is that they could reflect the importance of water storage in the mires and wetlands during the summer time, and progressive release of CO_2 and DOC-rich waters from the wetlands to the streams. Note that there is a positive relationship between pCO_2 and river catchment area, which is in line with proposition of the reviewer.

L 346: The paper of Gómez-Gener et al. (2021) gives a reasonably good account of diel variations of pCO_2 in temperate rivers but reports measurement in an extremely limited number of sites in tropical rivers. So this study does not allow to make generalizations on "tropical rivers". There are other studies in tropical rivers that have shown that diel variations of CO_2 are undetectable such as the Congo (Borges et al. 2019) because aquatic pelagic primary production is low (Descy et al. 2018) due to strong light attenuation the water column by DOM.
This is an excellent comment, which helps a lot to explain the lack of variation in the case of the Ket River which also has high aromatic DOC content. Note that many streams considered in Gómez-Gener et al. (2021) work are low in DOC, or this DOC is essentially autochthonous. We thank the reviewer for pointing out these important papers on tropical rivers and we carefully revised the text and better argued our explanations.

L363-367: This is a reasonable explanation. However, "homogeneous landscape" and "strong allochthonous sources of organic carbon" can still lead to variations of CO_2 per stream size, with small systems showing higher values than large systems as predicted conceptually (Hotchkiss et al. 2015) and verified at basin-scale (e.g. Borges et al. 2019).
We totally agree with this remark. Indeed, 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. Consistent with this, we

observed systematically higher CO_2 concentration and flux in small tributaries [which were fed by mire waters with 'non-processed' OM] compared to the main stem (Table 2).

L 381: I suggest to remove the word "interesting". This is self-evaluation, let the readers decide what's interesting. Same applies to word "notable" L 361.
We agree with these remarks.

L 477-515: Section "Concluding remarks" provides a summary of the paper and thus duplicates the content of abstract. This section could be removed or streamlined.
We agree and greatly revised this section via shortening it and focusing on most important findings and perspectives.

In Figure 2, I suggest to show the « continuous » pCO_2 measurements data points as a discrete symbols (dots) rather than a line.
With spatial resolution of this figure, dots representing continuous pCO2 reading would be shown as a line. We improved the spatial resolution of this figure following the recommendation of the reviewer.

Figure 2 is incredibly confusing and in my opinion undermines the large sampling effort. I suggest to make separate figures for pCO2 and FCO2 and not try to show all of the data together in single plot. Please provide a graphical representation of the pCO2 during the flood period. If I understand correctly the symbols, the blue diamonds in plot A) are for the FCO2 and not pCO2 in the tributaries. But Table 1 shows that pCO2 was measured in the tributaries during the flood period. I also suggest to remove the "continuous FCO2". The term is misleading since it's FCO2 computed from "continuous" pCO2. Also since the figure mixes FCO2 measured with the chambers and computed with a gas transfer velocity and that the values are very different, the impression given by the figure is very confusing.
We thank the reviewer for noted inconsistences in this figure: these were now corrected. We basically agree with this remark; we removed the fluxes computed with fixed gas transfer velocity. We believe that calculated 'continuous' fluxes are useful. In the revised version, these fluxes were calculated based on directly measured pCO_2 and K_T values calculated as an average of two adjacent chambers, instead of fixed or wind-based K_T value.
We strongly revised this figure as following:

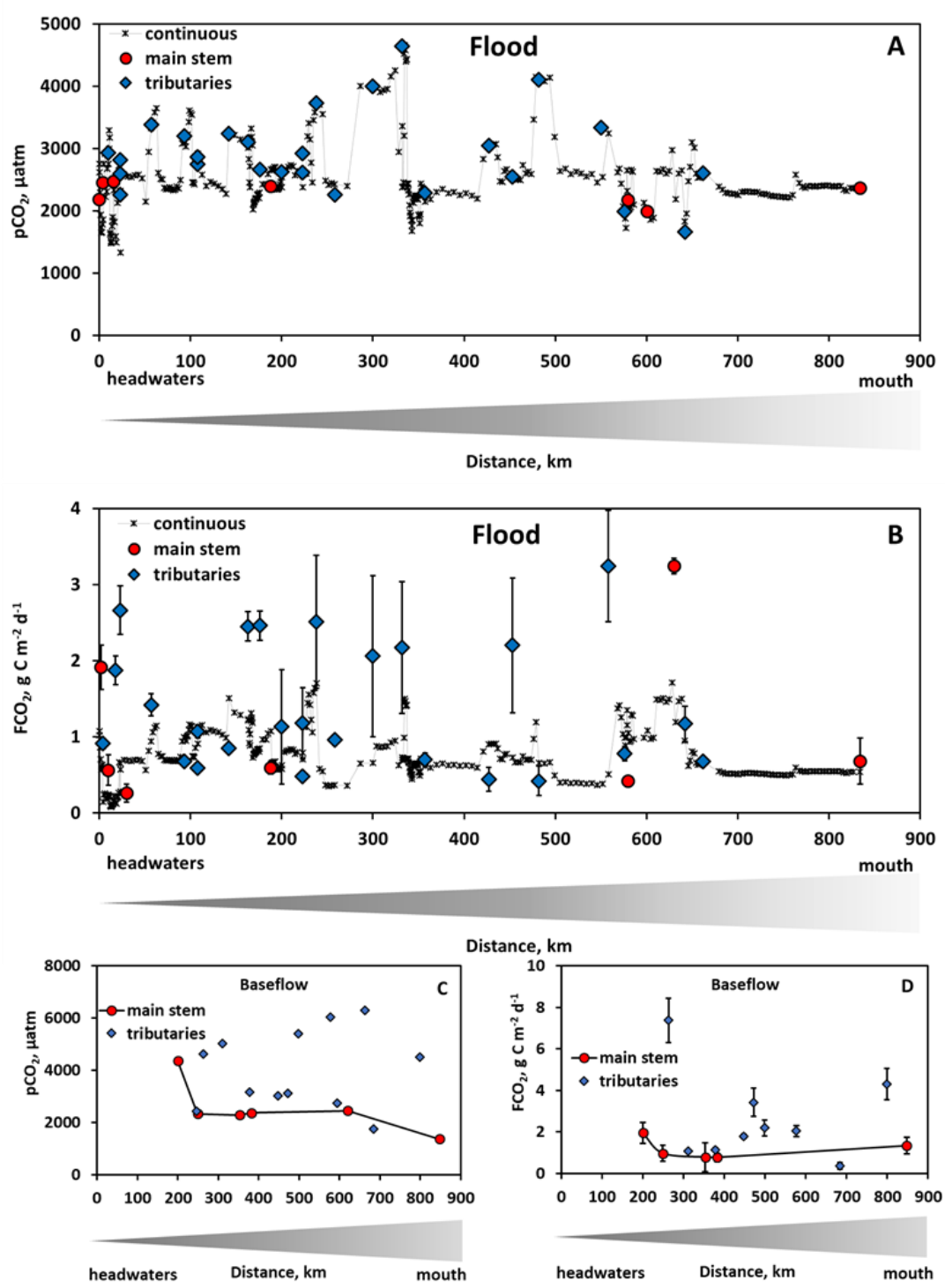

Figure R1. The measured pCO_2 (**A, C**) and CO_2 fluxes (**B, D**) during spring flood (**A, B**) and summer baseflow (**C, D**) of the Ket River main stem and tributaries (over the 830 km distance, from the headwaters to the mouth (left to right). The symbols represent discrete in situ pCO_2 (Vaissala) and FCO_2 (floating chambers) measurements of the main stem (red circles) and tributaries (blue diamonds). Continuous in-situ pCO_2 measurements and calculated FCO_2 are available only for the main stem in spring (black crosses). For the latter, we used an average value of gas transfer velocity (k_T) between two chamber sites (separated by a distance of 50 to 100 km) to calculate the FCO_2 from in-situ measured pCO_2 in the river section between these two sites. Note that during summer baseflow, the water level did not allow reaching the headwaters of the Ket River (first 0-200 km on the river course).

Figure 5 : pCO2 should be in the Y-axis and the potential predictors/descriptors (SUVA, land cover) in the X-axis.
The correlation of pCO2 and TBC in Fig. 5B is weak and not very informative. The TBC only informs on the presence of microbes and not their activity. Also, if CO2 comes from soil-water as suggested by the authors then it is not produced in-stream and we should not expect a correlation with TBC. This cannot go both ways.

We agree with these remarks and strongly reorganized this figure as following, via presenting only most significant (p < 0.05) correlations:

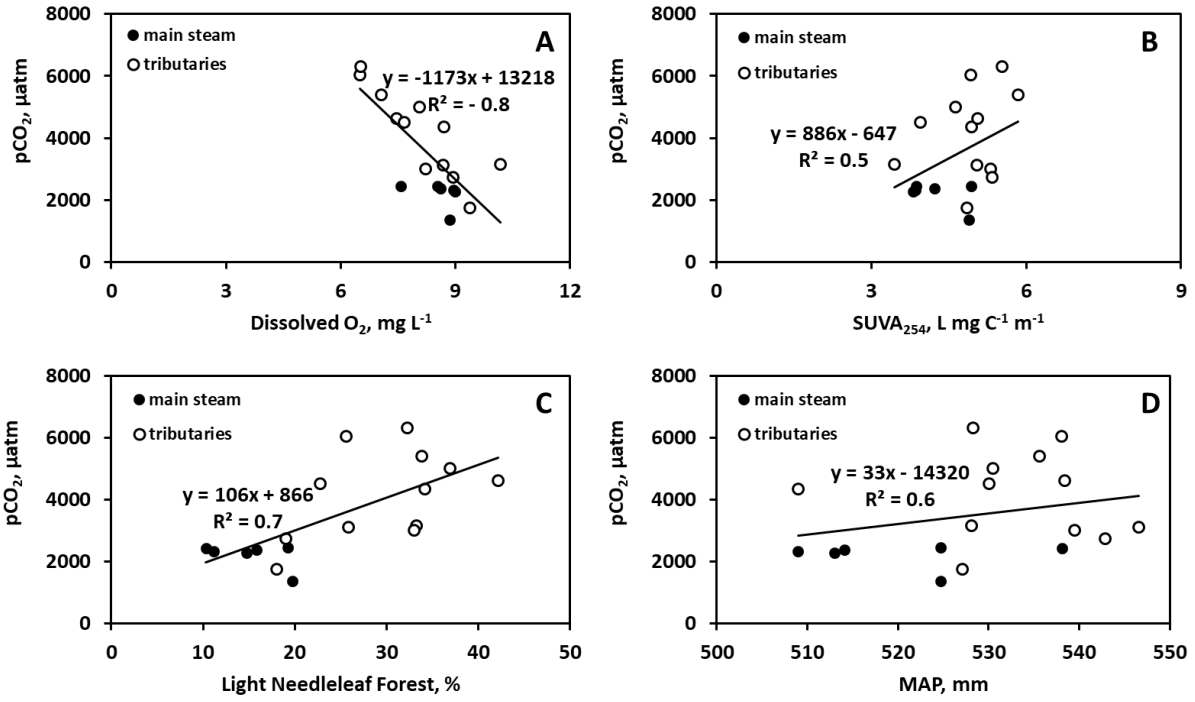

Figure R2. Significant (p < 0.05) control of dissolved oxygen (A), $SUVA_{254}$ (B), light needleleaf forest (C), and mean annual precipitation (D) on CO2 concentration in the Ket River and tributaries during summer baseflow.

We thank Reviewer # 3 for his/her very pertinent and useful comments.