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Carbon emission and export from Ket River, western Siberia

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Abstract

Despite recent progress in the understanding of the carbon (C) cycle of Siberian permafrost-affected rivers, spatial and seasonal dynamics of C export and emission from medium-size rivers remain poorly unknown. Here we studied one of the largest tributaries of the Ob River, the Ket River (watershed = 94,000 km²) which drains through virtually pristine dense taiga forest of the boreal zone in western Siberian Lowland (WSL). We combined continuous in-situ measurements of carbon dioxide (CO_2) concentration and flux (FCO_2), with methane (CH_4), organic and inorganic C (DOC and DIC, respectively), particulate organic C and total bacterial concentrations over a 834-km transect of the Ket River main stem and its 26 tributaries during spring flood and 12 tributaries during summer baseflow. The CO_2 concentration was lower and less variable in the main stem (2000 to 2500 µatm) compared to that in tributaries (2000 to 5000 µatm). The methane concentrations in the main stem and tributaries was a factor of 300 to 1900 (flood period) and 100 to 150 (baseflow period) lower than that of CO_2. The FCO_2 ranged from 0.4 to 2.4 g C m^{-2} d^{-1} in the main channel and from 0.5 to 5.0 g C m^{-2} d^{-1} in the tributaries, being the highest during August in tributaries and weakly dependent on season in the main channel. Only during summer baseflow, the DOM aromaticity, bacterial number, and needleleaf forest coverage of the watershed positively affected CO_2 concentrations and fluxes. We hypothesize that the relatively low variability in FCO_2 is due to flat homogeneous (bog and taiga forest) landscape that results in long water residence times and stable input of allochthonous DOM, which dominate the FCO_2. In summer baseflow, the DIC input from deeper flow paths might also contribute to CO_2 emission. The open water period (May to October) C emission from the Ket River basin was estimated to 127±11 Gg C y^{-1} which is lower than the lateral C export during the same period. Although this estimated C emissions contain uncertainties, stressing the need of better constrained FCO_2 and water coverage across seasons, we considered it conservative which emphasize the important role of WSL rivers for release of CO_2 to the atmosphere.

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Introduction

Assessment of greenhouse gas (GHG) emission from rivers is crucially important for understanding the C cycle under various climate change scenarios (Campeau and del Giorgio, 2014; Chadburn et al., 2017; Tranvik et al., 2018; Vonk et al., 2019; Vachon et al., 2020). Rivers receive terrestrial C and process and emit a significant share of this C during transit to the sea (Liu et al., 2022). Quantifications of riverine C emissions are sufficiently robust for relatively well studied regions of the world such as the European and N American boreal zone (Dawson et al., 2004; Dinsmore et al., 2013; Wallin et al., 2013; Leith et al., 2015), or Arctic and subarctic rivers of Alaska (Striegl et al., 2012; Crawford et al., 2013; Stackpoole et al., 2017). Despite significant progress in assessing riverine pCO_2 in previously under-represented or ignored regions such as lotic systems of Asia (Ran et al., 2015, 2017; Varol and Li, 2017) or South America (Almeida et al., 2017), these studies generally use a combination of pH and alkalinity (DIC) to calculate the pCO_2 instead of direct in-situ measurements, alike the studies of global emissions (Raymond et al., 2013; Lauerwald et al., 2015). In this regard, regional high spatial resolution measurements of CO_2 concentration and fluxes of under-represented regions are needed.

High latitude regions are important in this respect given their large C stocks, partly located in the permafrost, and the observed and projected warming (Turetsky et al., 2020). This is especially true for Siberia, hosting 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). There has been substantial progress in quantification of carbon (C) transport and emissions from Siberian permafrost-affected rivers (Lobbes et al., 2000; Raymond et al., 2007; Cooper et al., 2008; Semiletov et al., 2011; Feng et al., 2013; Griffin et al., 2018; Wild et al., 2019). However, spatial and seasonal features of C export and emission from tributaries of Siberian rivers are still remain poorly known. Existing data (Denfeld et al., 2013; Serikova et al., 2018; Karlsson et al., 2021; Vorobyev et al., 2021) suggest that C (predominantly as CO_2) emissions from Siberian rivers can vary largely over space and time. Such high variations do not allow reliable quantitative assessment of C emission and integrating these values into regional and global C models.

In order to better understand and constrain the magnitude of C emission from Siberian rivers we studied the Ket River (watershed 94,000 km²), a typical tributary of the Ob River in western Siberia. The Ob

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river is the largest (in terms of watershed area) Siberian river and drains large pristine territories of taiga forest and bogs. The catchment of Ob includes extensive regions of permafrost but a major part of it (80 %) is situated in the permafrost-free zone of which very few data exist on riverine C emissions (Karlsson et al., 2021). The Ket river drains permafrost-free western Siberian forest and wetlands with almost no human activity, thus serving a representative system for understanding C cycling of permafrost-free rivers of an underrepresented region of the world. We followed, via a boat routing over the main stem and main tributaries of the river, the in-situ CO_2 concentrations combined with discrete regular sampling for dissolved CH_4, DOC, DIC, total bacterial number and particulate organic matter. These measurements were complemented with regular floating chamber measurements of CO_2 emission fluxes. We performed these observations during two main open water seasons of the year - the peak of the spring flood and the end of the summer baseflow. Our first objective was to quantify the difference in C concentration and emission during two seasons for the main steam and the tributaries and to relate these differences to main physico-chemical parameters of the water column and physio-geographical parameters (land cover) of the river watersheds. Our second objective was to obtain total C emission flux from the river watershed area and compare it to lateral export yield of dissolved and particulate carbon.

2. Study Site, Materials and Methods

2.1. Ket River and its tributaries

The Ket River main stem and its 26 tributaries sampled in this study include watersheds of distinct sizes (catchment area ranged from 94,000 at the Ket's mouth to 20 km² of smallest tributary), but rather similar lithology, climate and vegetation (**Fig. 1, Table S1**). This poorly accessible river basin is fully pristine (50 % forest, 40 % wetlands), and has almost no agricultural and forestry activity. The watershed of Ket has very low population density (0.27 person km^{-2}) and lacks road infrastructure due to absence of hydrocarbon exploration activity. In this regard, this river can serve as a model for medium size bog-forest rivers of the western Siberia Lowland and results obtained from this watershed can be extrapolated to much larger territory, comprising about 1 million km^2 of permafrost-free taiga forest and bog regions of the southern part of WSL.

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The mean annual air temperatures (MAAT) is -0.6..-0.9 °C and the mean annual precipitation is 520 mm y^{-1} in the central part of the basin. The lithology of this part of western Siberian lowland is dominated by Pleistocene silts and sands with carbonate concretions overlayed by quaternary deposits (loesses, fluvial, glacial and lacustrine deposits). The dominant soils are podzols in forest areas and histosols in peat bog regions.

The peak of annual discharge in 2019 occurred in the end of May; in August, the discharge was 3 to 5 times smaller (**Fig. 1**). From May 18 to May 28, 2019, and from August 30 to September 2, 2019, we started the boat trip in the middle course of the Ket River (Beliy Yar), and moved, first, 475 km upstream the Ket river till its most headwaters, and then moved 834 km downstream till the river mouth, with an average speed of 20 km h^{-1}. We stopped each 30-50 km along the Ket River and sampled for major hydrochemical parameters, GHG, river suspended matter and total bacterial number of the main stem. We also moved several km upstream of selected tributaries to record CO_2 concentrations for at least 1 h and to sample for river hydrochemistry. At several occasions during spring flood, we monitored CO_2 concentration and performed chamber measurements in the main stem and tributaries during both day and night time period.

2.2. CO_2 and CH_4 concentrations and CO_2 fluxes by floating chambers

Surface water CO_2 concentration was measured continuously, *in-situ* by deploying a portable infrared gas analyzer (IRGA, GMT222 CARBOCAP® probe, Vaisala®; accuracy ± 1.5%) of two ranges (2 000 and 10 000 ppm) as described in previous work of our group on the Lena River (Vorobyev et al., 2021). The probe was enclosed within a waterproof and gas-permeable membrane. For this, we used a protective expanded polytetrafluoroethylene (PTFE) tube or sleeve that is highly permeable to CO_2 but impermeable to water (Johnson et al., 2009). During the sampling, the sensor was left to equilibrate in the water for 10 minutes before measurements were recorded. The sensor was placed into a tube which was submerged 0.5 m below the water surface. A Campbell logger was connected to the system allowing continuous recording of the CO_2 concentration, water temperature and pressure every minute over 10 minute intervals yielding 732 individual pCO_2, water temperature and pressure values. The CO_2 concentrations in the Ket River tributaries included between 10 and 20 individual pCO_2 readings for each tributary (250 measurements in total). In addition to

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continuous *in-situ* CO_2 measurements, we estimated pCO_2 via measured pH and DIC values, using the set of constants typically applied for riverine pCO_2 estimation in organic-rich waters (Cai and Wang, 1998; DelDuco and Xu, 2017). The U-test (Mann-Whitney) demonstrated a lack of significant difference in CO_2 concentrations measured by Vaissala and calculated from the pH and DIC of the river water.

For CH_4 analyses, unfiltered water was sampled in 60-mL Serum 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. Headspace was created in the laboratory and CH_4 concentrations were analyzed using a Bruker GC-456 gas chromatograph (GC) equipped with flame ionization and thermal conductivity detectors. Further details of CH_4 analyses are described elsewhere (Serikova et al., 2019; Vorobyev et al., 2021).

The CO_2 fluxes were measured by using two floating CO_2 chambers equipped with non-dispersive infrared SenseAir® CO_2 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). In addition to *in-situ* chamber measurements, the CO_2 flux was calculated from measured CO_2 concentration using standard approaches (Guérin et al., 2007; Wanninkhof, 1992; Cole and Caraco, 1998). The value of K_T (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 nearest meteo-station located in the Belyi Yar town, middle course of the Ket River. For comparison with previous estimates, we also used a gas transfer velocity of 4.46 m d^{-1} measured in the 4 largest rivers of Western Siberia Lowalnd (WSL) in June 2015 (Ob', Pur, Pyakupur and Taz rivers, Karlsson et al., 2021) which is representative for large lowland rivers (Alin et al., 2011; Beaulieu et al., 2012).

2.3. Chemical analyses of the river water

The dissolved oxygen (CellOx 325; accuracy of ±5%), specific conductivity (TetraCon 325; ±1.5%), and water temperature (±0.2 °C) were measured in-situ at 20 cm depth using a WTW 3320 Multimeter. The pH was measured using portable Hanna instrument via combined Schott glass electrode calibrated with NIST buffer solutions (4.01, 6.86 and 9.18 at 25°C), with an uncertainty of 0.01 pH units. The temperature of buffer

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solutions was within ± 2°C of that of the river water. The water was sampled in pre-cleaned polypropylene bottle from 20-30 cm depth in the middle of the river and immediately filtered through disposable single-use sterile Sartorius filter units (0.45 µm pore size). The first 50 mL of filtrate was discarded. The DOC and Dissolved Inorganic Carbon (DIC) were determined by a Shimadzu TOC-VSCN Analyzer (Kyoto, Japan) with an uncertainty of 3% and a detection limit of 0.1 mg/L. Blanks of MilliQ water passed through the filters demonstrated negligible release of DOC from the filter material. The SUVA was measured via ultraviolet absorbance at 254 nm using a 10-mm quartz cuvette on a Bruker CARY-50 UV-VIS spectrophotometer.

The concentration of C and N in suspended material (Particulate Organic Carbon and Nitrogen (POC and PON, respectively)) was determined via filtration of 1 to 2 L of freshly collected river water (at the river bank or in the boat) with pre-weighted GFF filters (47 mm, 0.45 µm) and Nalgene 250-mL polystyrene filtration units using a Mityvac® manual vacuum pump. Particulate C and N were measured using catalytic combustion with Cu-O at 900°C with an uncertainty of ≤ 0.5% using Thermo Flash 2000 CN Analyzer at EcoLab, Toulouse. The samples were analyzed before and after 1:1 HCl treatment to distinguish between total and inorganic C; however the ratio of $C_{organic}$: $C_{carbonate}$ in the river suspended matter (RSM) was always above 20 and the contribution of carbonate C to total C in the RSM was equal in average 0.3±0.3% (2 s.d., n = 30).

Total microbial cell concentration was measured after sample fixation in glutaraldehyde, by a flow cytometry (Guava® EasyCyteTM systems, Merck). Cells were stained using 1 µL of a 10 times diluted SYBR GREEN solution (10000x, Merck), added to 250 µL of each sample before analysis. Particles were identified as cells based on green fluorescence and forward scatter (Marie et al., 2001).

2.5. Landscape parameters and water surface area of the Ket River basin

The physio-geographical characteristics of the 26 Ket tributaries and the 7 points of the Ket main stem (**Table S1, Fig. S1**) were determined by applying available digital elevation model (DEM GMTED2010), soil, vegetation and lithological maps. The landscape parameters were typified using TerraNorte Database of Land Cover of Russia (Bartalev et al., 2020; http://terranorte.iki.rssi.ru). This included various type of forest (evergreen, deciduous, needleleaf/broadleaf), grassland, tundra, wetlands, water bodies and riparian zones.

The climate parameters the watershed were obtained from CRU grids data (1950-2016) (Harris et al., 2014) and NCSCD data (Hugelius et al., 2013; doi:10.5879/ecds/00000001), respectively, whereas the biomass and soil OC content were obtained from BIOMASAR2 (Santoro et al., 2010) and NCSCD databases. The lithology layer was taken from GIS version of Geological map of the Russian Federation (scale 1 : 5 000 000, http://www.geolkarta.ru/). We quantified river water surface area using the global SDG database with 30 m² resolution (Pekel et al., 2016) including both seasonal and permanent water for the open water period of 2019 and for the multiannual average (reference period 2000-2004). We also used a more recent GRWL Mask Database which incorporates first order wetted streams (Allen and Pavelsky, 2018).

2.6. Data analysis

Carbon concentrations and fluxes for all dataset were tested for normality using a Shapiro-Wilk test. In case of the data were not normally distributed, we used non-parametric statistics. Comparisons of GHG parameters in the main stem and tributaries during two sampling seasons were conducted using a non-parametric Mann Whitney test at a significance level of 0.05. For comparison of unpaired data, a non-parametric H-criterion Kruskal-Wallis test was used to reveal the differences between different study sites. The Pearson rank order correlation coefficient ($p < 0.05$) was used to determine the relationship between CO_2 concentrations and emission fluxes and main landscape parameters of the Ket River tributaries, as well as other potential drivers such as pH, O_2, water temperature, specific conductivity, DOC, DIC, particulate carbon and nitrogen, and total bacterial number.

3. Results

3.1. Greenhouse gases and dissolved and particulate C

The main hydrochemical parameters and greenhouse gases concentration and emission fluxes of the Ket River and its tributaries are listed in **Table 1** and primary data are provided in **Table S2** of the Supplement. Continuous pCO_2 measurements in the main stem during the spring (764 individual data points over the full distance of the boat route (834 km), demonstrated a lack of systematic change in CO_2 concentration from headwaters to the mouth. There were strong but non-systematic variations in CO_2

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concentrations in the tributaries during the summer (**Fig. 2 A, B**). The CH_4 concentration (**Table 1 and Fig. S2 A, B**) was low in the Ket River (around 0.17 and 0.86 µmol L^{-1} in May and August, respectively) and in the tributaries (range 0.09 to 2.57 µmol L^{-1}, 2 to 3 times higher values during the baseflow). These values are consistent with the range of CH_4 concentration in other Siberian Rivers such as Lena (0.03 to 0.199 µmol L^{-1}, Bussman, 2013; Vorobyev et al., 2021). In the Ket River main stem and tributaries, the CH_4 concentrations are 280-1900 and 100-154 times lower than those of CO_2 during spring and summer, respectively. Consequently, diffuse CH_4 emissions (**Table 1, Fig. S2 C, D)** constituted 0.1 to 0.5% of total C emissions and are not discussed in further detail.

During spring flood, CO_2 fluxes ranged from 0.26 to 3.2 g C m^{-2} d^{-1} in the main stem and tributaries (**Table 1; Fig. 2 A**). During baseflow, the flux in the tributaries varied from 0.37 to 7.4 g C m^{-2} d^{-1} and was a factor of 2 to 3 higher than that in the main stem (**Fig. 2 B, C, Table 1**). Note that peaks of CO_2 and CH_4 concentration at the main stem were not linked to conflux with tributaries. The CO_2 concentration in the river water and gas transfer velocity assessed from discrete measurements by floating chambers (K_T = 0.08-1.83 m d^{-1} in the main stem; 0.2-1.86 m d^{-1} in the tributaries, **Table 1**) allowed for calculation of the continuous CO_2 fluxes (**Fig. 2 A**). For this, we used an average value of k 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.

The wind calculated flux was 1.2 to 2 times higher than that measured by chambers, whereas the calculation with K_T = 4.46 m d^{-1} overestimated the flux by a factor of 3.7 to 6.0. In both cases, the overestimation of calculated flux relative to chamber-measured flux was most pronounced in the tributaries rather than in the main stem. Overall, due to small size and short fetch of the Ket River and its tributaries, we believe that lower values of K_T are more pertinent to the studied river basin. Given that the area is highly flooded, this is consistent with observations in other flooded regions, where a canopy of vegetation protects the water-air interface from wind stress thus rendering the gas transfer velocity lower compared to open water such as large river (i.e., Foster-Martinez and Variano, 2016; Ho et al., 2018; Abril and Borges, 2019). We therefore warn against the use of high value of transfer velocity, suitable for large rivers of the boreal zone, for assessing the emissions in medium and small size, sheltered streams with extensive riparian vegetation.

The DIC concentration increased 5 to 10 times between the spring (2.4 to 2.8 mg L^{-1}) and summer baseflow (18 to 20 mg L^{-1}) and the pH increased by 0.5-0.7 units between spring freshet and summer baseflow (**Fig. 3** and **Fig. S3 A, B** of the Supplement). The DOC concentration ranged from 18 to 25 mg L^{-1} during flood and from 15 to 18 mg L^{-1} during baseflow (**Fig. 3**). There was no systematic variations in DOC concentration over the 834 km of the main stem (20.7 ± 3.6 and 15.0 ± 1.4 mg L^{-1} in May and August, respectively); however, it was slightly higher and more variable in the tributaries (22.0± 4.0 and 16.5 ± 7.4 mg L^{-1}, **Fig. S3 C, D**). The $SUVA_{254}$ remained highly stable throughout the seasons for both the tributaries and the main stem (range from 4.2 to 4.9 L mg C^{-1} m^{-1}, **Table 1**). The POC was 3 times higher during baseflow compared to spring and ranged from 2 to 10 mg L^{-1} (**Fig. 3** and **Fig. S3 E, F**). The total bacterial number ranged from 5.0×10^5 to 8.7×10^5 cells mL^{-1} for the main stem and tributaries without significant ($p > 0.05$) seasonal variation (**Fig. 3** and **S3 G, H**).

3.2. Diurnal and spatial variation in CO_2 concentration and flux

The diel (day/night) measurements of CO_2 concentrations have been performed on six tributaries of the Ket River during the spring flood period (**Fig. 4**). In two of them (Sochur ad Lopatka) we measured both CO_2 concentration and CO_2 fluxes via floating chambers. Continuous CO_2 concentrations exhibited a variation between 5 and 25% of the average value. Only in the case of a small tributary Segondenka (**Fig. 4 E**), when we measured CO_2 over 38 h, there was a local maximum in concentration between 6 and 7 pm during the first and second day of monitoring, without any significant link to the water temperature. The deviation of FCO_2 from the average value over the period of observation in two tributaries (**Fig. 4 A, B**) did not exceed 20%, without any detectable difference between day and night period.

The spatial variation in pCO_2 and FCO_2 were tested during spring time in the flood zone of the Ket River middle course, where the flood zone was connected to the main channel. Regardless of the distance from the main stem and the size of the water body, the variation in pCO_2 and chamber-based fluxes were within 30% of the values measured in the main stem. This suggests that the main stem parameters can be used for upscaling the C emissions to the overall flood plain during May, provided that the water bodies are connected to the rivers. Further test of spatial variation were performed on selected small tributaries, when

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we moved 8 to 16 km upstream towards the headwaters and monitored the CO_2 concentration in the river water. There was no sizable trend in CO_2 concentration over several km length of the tributary, consistent with small fluctuations over the hundred km-scale of the main stem (**Fig. S4**). Altogether, rather minor spatial and diel variations in both CO_2 concentration and emission fluxes support the chosen sampling strategy and allow reliable extrapolation of obtained results to full surface of lotic waters of the Ket River basin, during open water period.

3.3. Impact of water chemistry and catchment characteristics on CO_2 concentration and flux

There were generally no strong correlations between CO_2 and CH_4 and the main parameters of the water column (DOC, DIC, POC, TBC and SUVA (**Table 2**). The CO_2 concentration negatively correlated with O_2 concentration ($R_{Pearson} = -0.68$, $p < 0.05$) and FCO_2 positively correlated with $SUVA_{254}$ ($R = 0.34$, $p < 0.05$). Other hydro chemical characteristics of the water column did not impact CO_2 and CH_4 concentration and CO_2 flux. During spring flood, there was no positive correlation between FCO_2 of the river water and various hydrochemical characteristics. During the summer baseflow, there were positive correlations between CO_2 concentration or flux and SUVA and total bacterial number (**Fig. 5 A, B**).

Among different landscape factors, only deciduous light needleleaf forest (larch trees) exhibited significant ($p < 0.01$) positive correlations ($0.6 \leq R_S \leq 0.7$) with CO_2 concentration and flux of the Ket River main stem and tributaries, detectable only during the summer baseflow period (**Fig. 5 C**). The peatland and bogs at the watershed exhibited only weak, although positive ($0.2 < R_S < 0.4$), correlation with pCO_2 and FCO_2 (**Fig. 5 D**). The other potentially important landscape factors of the river watershed (type of forest, riparian and total aboveground vegetation, recent burns, water bodies) as well as lithological parameters (clays, silts, sands with or without of the presence of carbonate concretions) did not significantly impact the CO_2 and CH_4 concentration and measured CO_2 fluxes in the Ket River basin (**Table 2**). The mean annual precipitation (MAP) at the watershed positively correlated with CO_2 and FCO_2 during the baseflow.

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3.4. Carbon emission and lateral export (yield) of the Ket River basin

The C emissions (> 99.5 % CO_2, < 0.5 % CH_4) from the lotic waters of the Ket River basin were assessed based on total river water coverage of the Ket watershed in 2019 (856 km², of which 691 km² is seasonal water, according to the Global SDG database). Given that the measurements were performed at the peak of spring flood in 2019, we used the maximal water coverage of the Ket River basin to calculate the emissions during May and June, and baseflow measurements for July-October period.

For C emission calculation, we used the mean values of CO_2 emissions of the main stem and the tributaries (1.31±0.81 g C m^{-2} d^{-1} for spring flood; 2.11±1.86 g C m^{-2} d^{-1} for summer-autumn baseflow) which covers full variability of both tributaries and the Ket River main channel (**Table 1, Figure 3**). For the month of July which was not sampled in this work and which represents a transition period between the flood and the baseflow, we used the mean value of May and August (1.55 g C m^{-2} d^{-1}). For the two months of maximal water flow (May - June), the C emission from the whole Ket basin amounts to 68±42 Gg. When summed up with July (25±20 Gg) and summer-autumn baseflow period (August to October) emission (32±28 Gg), the total open water season emission flux is 127 Gg. The uncertainty on the total emission over 6 months of the open water period is difficult to quantify but it can be estimated as between 30 and 50 %. This range covers both the uncertainty of the water coverage of the territory and the seasonal and spatial variations of CO_2 emission in the Ket basin.

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**). For this 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. The total annual (excluding ice-covered period) riverine C export from the Ket River basin ($S_{watershed}$ = 94,000 km²) is 0.35 Tg (3.7 t C km^{-2}_{land} y^{-1}), of which DOC, DIC and POC accounts for 56, 24 and 20%, respectively. Therefore, over the 6 month of open water

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period, the C emissions from lotic waters of Ket watershed constituted less than 30% of the dissolved and particulate carbon lateral export from the river basin.

4. DISCUSSION

4.1. Temporal and spatial pattern of CO_2 emissions from the river waters

The first important result of the present study is quite low spatial and seasonal variability in both CO_2 concentration and emissions, as well as in DOC concentration and aromaticity (reflected by $SUVA_{254}$) in the main channel (**Fig. 3, S3, Table 1**). The variability in the tributaries was much larger, with differences in dissolved and gaseous C parameters between spring flood and summer-autumn baseflow (**Table S3**). 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 (**Table S4**). This, together with lack of diel variations in CO_2 concentrations and emissions during spring period of maximal water coverage (**Fig. 4**) suggest rather stable pattern of CO_2 in the river water, not linked to short-scale processes (primary productivity, photolysis, daily temperature variation). Indeed, negligible primary productivity in the water column may stem from low water temperatures (9.3 °C), shallow photic layer of organic-rich waters (DOC of 22 mg L^{-1}) and lack of periphyton activity during high flow of the spring flood. Note that this finding contrasts the recent results of high frequency pCO_2 measurements in tropical and temperate world rivers that show a 30 % higher nocturnal emission compared to daytime observations (Gómez-Gener et al., 2021b).

Concerning spatial variability of C concentrations and emissions during the spring flood, the pCO_2 did not demonstrate sizable variation along the main stem of the Ket River and some of its tributaries, when moving from the mouth to the headwaters. The SUVA also remained highly stable along the river flow. This, together with a lack of pCO_2 or FCO_2 correlation with river watershed area during this period (**Table 2**) suggest relatively modest control of headwater C cycling by 'fresh' unprocessed organic matter from upland mire waters. Much stronger control of mire waters is reported in boreal zone of the Northern Europe (Wallin et al., 2013, 2018). Furthermore, our results on the Ket River main stem and tributaries are in contrast to the

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general view of disproportional importance of headwater streams in overall CO_2 emission from river basins (Li et al., 2021). 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 generally flat orographic context of this part of the WSL (Serikova et al., 2018).

The second notable result is that, despite sizable variability of CO_2 in the tributaries, especially during the baseflow, there were no correlations between either pCO_2 or FCO_2 and main hydrochemical parameters of the water column (**Table 2**). We believe that main reasons 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. 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. 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 (which also showed positive but less significant correlations, **Fig. 5 D**) during the summer time, and progressive release of CO_2 and DOC-rich waters from the wetlands to the streams. This terrestrial source could be either soil litter leachates (in spring) or bog water (during baseflow, when the river water is substantially derived from wetlands, Ala-aho et al., 2018a, b). Although we did not observe correlations between C emission and bog coverage at the whole Ket River basin, it is known from works in boreal European zone that wetland streams produce about twice higher CO_2 emission flux compared to forest streams (Gomez-Gener et al., 2021). The patterns in CO_2 emissions observed in the present study during summer baseflow thus suggest the importance of allochthonous organic matter from the peatland for CO_2 production in the water column and in soils where the degradation of DOC is enhanced by the presence of bacteria.

Another interesting correlation is that between CO_2 flux during baseflow and the proportion of deciduous needleleaf forest at the watershed (**Fig. 5 C**), which suggests the importance of C cycling by larch

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trees and their possible control on the delivery of degradable organic matter to the river. Similar control of larch vegetation on riverine CO_2 has been suggested for the Lena River, Eastern Siberia (Vorobyev et al., 2021) although we acknowledge that further observations on contrasted Siberian watersheds are necessary to confirm the observation that larch trees litterfall led to export of degradable OM to the river.

During both spring flood and summer baseflow, punctual local variations in CO_2 concentration and emissions along the sampling route of the main stem (**Fig. 2 A**) were not necessarily linked to CO_2-rich tributaries, or variations in water chemistry of the specific segments of the river. Similar to other studies of boreal and subarctic rivers (i.e., Vorobyev et al., 2021; Lundin et al. 2013, Rocher-Ros et al. 2019), these variations likely reflect local processes in the main stem, such as lateral influx from the shores and shallow subsurface waters, sediment resuspension and respiration, or the discharge of underground, CO_2-rich fluids in the river bed (hyporheic zone). Thus, via comprehensive analysis of 187 streams and rivers across the contiguous United States, Hotchkiss et al. (2015) demonstrated that ~60% of CO_2 evasion is from external sources rather than internal production. In view of lack of correlation of CO_2 emissions in the Ket River and tributaries with hydrochemical parameters of the water column, we believe that external source of CO_2 in studied river system represents sizable contribution to total riverine CO_2 evasion across the seasons and sampling sites. In particular, in small peatland streams, the CO_2-rich deep peat/groundwater is known to be the major source of aquatic CO_2 under low flow conditions (Dinsmore and Billett, 2008), whereas in boreal headwater streams of N Sweden the main source of stream CO_2 was inflowing CO_2-rich soil waters (Winterdahl et al., 2016).

At the Ket River basin, the local soil/groundwater effects are certainly more pronounced during baseflow, due to lower impact of dilution, compared to the spring flood period. The hypothesis of deeper flow path in summer compared to spring is confirmed for the WSL (Frey and McClelland, 2009; Pokrovsky et al., 2015; Serikova et al., 2018) and is supported in this study by a strong increase in DIC concentration between spring and summer (**Fig. 3**). Thus, although the pairwise correlations between parameters do not support any particular mechanism, it is not excluded that OM bio- and photo degradation and local mire water feeding drive FCO_2 in spring, and that deeper flowpaths and DIC export drive the elevated FCO_2 in summer.

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Another important factor responsible for higher CO_2 production in the water column in summer compared to spring could be POC degradation. The riverine POC is known to be more biodegradable than DOC (Attermeyer et al., 2018), and the POC concentration in the Ket River basin increased 4-fold between spring and summer (**Table 1**). The origin of summer-time POC and its lability remain elusive, but could be a combination of plankton bloom and mire- or forest-derived DOC coagulation products in the water column (Krickov et al., 2018). Furthermore, pronounced heterogeneity in CO_2 emission during baseflow among tributaries may also reflect the heterogeneity of riverine organic matter which is known to be the maximal during low flow conditions and minimal during high flow (Lynch et al., 2019).

Taken together, the present study demonstrates rather stable and non-equilibrium behavior of CO_2 in the Ket River basin, with minimal role of *hot spots* from various local sources. In this regard, we note high representability of studied riverine system for large pristine zones of taiga forest and bog regions of the WSL - eastern smaller tributaries of the Ob River in permafrost -free zone (Chulym, Tym, Vakh, Agan, Trom'egan), and also western tributaries of the Yenisey River (Dubches, Sym and Kas) with total watershed area of 350,000 km². To which degree the Ket River can serve as an analogue of another eastern tributary of the Ob River, the more anthropogenically and agriculturally - impacted tributary Chulym River ($S_{watershed}$ = 134,000 km²), remains unknown.

4.2. Emissions from the Ket River basin compared to lateral export of riverine carbon

The estimated C emissions (> 99.5 % C; < 0.5 % CH_4) from the Ket River main channel over 830 km distance (0.5 to 2.5 g C m^{-2} d^{-1}) are comparable to those of the Kolyma River (0.35 g C m^{-2} d^{-1} in the main stem and 2.1 g C m^{-2} d^{-1} for lotic waters of the basin; Denfeld et al., 2013), the Ob River main channel (1.32±0.14 g C m^{-2} d^{-1} in the permafrost-free zone; Karlsson et al., 2021), and the Lena River (0.8 to 1.7 g C m^{-2} d^{-1}; Vorobyev et al., 2021). The CO_2 emission in Ket's tributaries (1 to 2 g C m^{-2} d^{-1} in spring; 1 to 5 g C m^{-2} d^{-1} in summer) are within the range reported for small rivers and streams of the permafrost-free zone of western Siberia (0 to 3.6 g C m^{-2} d^{-1} in spring; 4 to 9 g C m^{-2} d^{-1} in summer; Serikova et al., 2018), forest and wetland headwater streams of northern Sweden (0.5 to 5 g C m^{-2} d^{-1}; Gomez-Gener et al., 2021), rivers and headwater streams of the Unites States (2.7 to 3.1 g C m^{-2} d^{-1}, Butman and Raymond, 2011; Hotchkiss et al.,

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2015), small mountain streams in Northern Europe (3.3 g C m^{-2} d^{-1}, Rocher-Ros et al., 2019), boreal streams in Canada and Alaska (0.8 to 5.2 g C m^{-2} d^{-1}, Koprivnjak et al., 2010; Teodoru et al., 2009; Crawford et al., 2013; Campeau et al., 2014).

Total C emissions from the water surfaces of the Ket River basin assessed in this study (148 g C-CO_2 m^{-2} y^{-1}, assuming no emission under ice) are lower than those of the lotic waters of western Siberia (898 g C-CO_2 m^{-2} y^{-1}, Karlsson et al., 2021) but comparable to global C emissions from the Lena river basin (180 to 360 g C m^{-2} y^{-1}, Vorobyev et al., 2021). When normalized to the Ket river basin area ($S_{watershed}$ = 94,000 km²), the C emission amounts to 1.35 g C m^{-2}_{land} y^{-1}. Hutchins et al. (2020) reported 0.63 to 0.29 g C-CO_2 m^{-2}_{land} y^{-1} emission from 50 small streams in boreal biome of Canada, comparable to the headwater stream network emissions in Alaska (0.44 g C m^{-2} y^{-1}, Crawford et al., 2013) and Zolkos et al. (2019) found approximately 0.4 g C m^{-2} y^{-1} in the Northwest Territories. Much higher land area - specific emissions, comparable or exceeding those of the Ket River, were reported in Québec (1.0 to 4.6 g C m^{-2} y^{-1}; Campeau and del Giorgio, 2014; Hutchins et al., 2019; Teodoru et al., 2009), Sweden (1.6 to 8.6 g C m^{-2} y^{-1}; Humborg et al., 2010; Jonsson et al., 2007; Lundin et al., 2013; Wallin et al., 2011, 2018) and boreal portions of the Yukon River (7 to 9 g C m^{-2} y^{-1}; Striegl et al., 2012; Stackpoole et al., 2017). Possible reasons for these differences could be different areal coverage of the territory by river network, the calculated rather than measured CO_2 fluxes, or the higher gas transfer velocity in the rivers from mountainous regions.

The regional assessment of the Ket River basin performed in this study are based on direct chamber measurements of emissions and as such provide rigorous basis for upscaling the CO_2 emissions from currently understudied lotic waters of permafrost-free zone of Western Siberia. The C evasion from the Ket basin assessed in the present work (127 ± 11 Gg y^{-1}, ignoring the emission during the ice breakup in early spring) is 3 times lower than the total (DOC+DIC+POC) lateral export by this river from the same territory (0.35 Tg C y^{-1}). 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 its the middle course at the latitude of the Ket River (3.6 t C km^{-2}_{land} y^{-1}, Vorobyev et al., 2019). Such high C yields in the southern, permafrost-free part of the WSL stem from essentially inorganic carbon originated from groundwater discharge of carbonate mineral rich reservoirs, abundant in this region (Pokrovsky et al., 2015). At the same time, the organic C yield in rivers of this region is quite low and represents less than 20% of total C yield (Pokrovsky et al., 2020; Vorobyev et al., 2019). This can explain anomalously low value of C evasion : C export of the Ket River (1 : 3) measured in this work as compared to the average values for permafrost-free zone of Western Siberia (1 : 1, Serikova et al., 2019). One should also note that the gas transfer velocity measured in thus study provides much lower fluxes than those calculated with K_T = 4.46 m d^{-1} in previous studies (**Table S2**). Another factors potentially leading to underestimation of C evasion in this study is GIS-based minimal water coverage which does not include seasonal oxbow lakes, flooded forest and temporary water bodies of the floodplain which provide sizable emissions (see Krickov et al., 2021). We also do not exclude that some important hot moments / hot spots of C emission were missed in our sampling campaign, such as summer baseflow/autumn peaks (Serikova et al., 2019) or stagnant zones of the floodplain in summer (Krickov et al., 2021; Castro-Morales et al., 2021). This calls a need for higher spatial and temporal resolution monitoring of C emission, with special focus on important events across full hydrological continuum.

5. Concluding remarks

Via combination of discrete floating chamber and hydrochemistry and continuous CO_2 concentration measurements over 830 km of large pristine boreal river of western Siberia main channel and its 26 tributaries during the peak of spring flood and the summer-autumn baseflow, we quantified spatial and temporal variations, overall emissions of C (CO_2, CH_4) and export of (DOC, DIC and POC) during the 6 months of open water period. The range of CO_2 and CH_4 concentrations in the main channel and tributaries as well as CO_2 emissions were consistent with other boreal and subarctic regions but demonstrated rather low seasonal and spatial variability. The diel CO_2 flux by floating chambers and continuous pCO_2 measurements in the tributaries of the Ket River during spring flood demonstrated negligible impact of day/night period on the CO_2 concentrations and emission fluxes. During spring flood, there were no correlations between concentrations of CO_2 and CH_4, or CO_2 flux and their main potential controlling physiochemical parameters of the water column as well as climatic and landscape parameters of the watershed.

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We hypothesize that homogeneous landscape coverage (bog and taiga forest) provide stable allochthonous input of DOM as confirmed by very weak spatial and seasonal variations of DOM aromaticity. Among possible driving factors of CO_2 production in the water column (bio- and photo-degradation of DOC and POC, plankton metabolism), none seems to be sizably important for persistent CO_2 supersaturation and relevant emissions. The landscape factors of the watershed (bog and forest coverage, soil organic carbon stock) of the tributaries and along the main stem did not sizably affected the C concentration and emission pattern across two seasons. We hypothesize that stable terrestrial input of strongly aromatic DOM, shallow photic layer and humic waters of the Ket River basin preclude sizable daily and seasonal variations of C parameters. Punctual discharge of groundwaters, resuspension of sediments or shallow subsurface influx from mires and riparian zone may be responsible for small-scale heterogeneities in C emissions and concentrations along the main stem and among the tributaries. These effects are much stronger pronounced during summer baseflow compared to spring flood. Overall, deeper flow paths in summer compared to spring enhance the DIC discharge within the river bed and the tributaries, thus leading to elevated CO_2 flux in summer. Additional factor responsible for higher CO_2 emission during this season could be mire-originated particulate organic matter (POM) processing in the water column. Further experiments on POM degradation and isotope tracing of C sources are therefore needed to quantitatively discriminate between surficial "organic" and deep "inorganic" source of CO_2 in the Ket River basin during summer baseflow. In this regard, a reason for relatively low spatial and temporal variability of CO_2 concentration and emissions in this large river basin could be that existing variations in C supply and control of FCO_2 are coupled and counteract each other so that the net FCO_2 remains spatially and temporally stable.

The six month open-water period C emissions from the lotic waters of the Ket River basin were sizably lower than the lateral C export by this river during the same period. We conclude that regional estimations of C balance in lotic systems should be based on a combination of direct chamber measurements, discrete hydrochemical sampling and continuous in-situ monitoring with submersible sensors, at least during two most important hydrological periods of the year which are, for boreal regions, the spring flood and the summer-autumn baseflow. We believe that this is the best trade-off between scientific rigor and logistical feasibility in poorly accessible, pristine and strongly understudied regions.

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Authors contribution.

AL and OP designed the study and wrote the paper; AL, SV, IK and OP performed sampling, analysis and their interpretation; LS performed bacterial assessment and DOC/DIC analysis and interpretation; MK performed landscape characterization of the Ket River basin and calculated water surface area; SK performed hydrological analysis; JK provided analyses of literature data, transfer coefficients for FCO_2 calculations and global estimations of areal emission vs export.

Competing interests.

The authors declare that they have no conflict of interest.

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Table 1. Measured hydrochemical and GHG exchange parameters in the Ket River main stem and tributaries (average ± s.d.; (*n*) is number of measurements).

		Tributaries		Main stem	
Parameter	**unit**	**Flood (*n*=26)**	**Base flow (*n*=12)**	**Flood (*n*=7)**	**Base flow (*n*=6)**
Water temperature	°C	9.48±2.25	14.9±1.24	9.06±1.59	16.5±0.54
pH		6.31±0.45	6.71±0.57	6.2±0.43	7.29±0.26
Dissolved O_2	mg L^{-1}	8.53±1.26	8.02±1.13	8.85±0.83	8.78±0.18
Specific Conductivity	µS cm^{-1}	40.7±22.7	126.9±62.1	39±14.9	181±36.8
DIC	mg L^{-1}	2.83±2.58	17.8±10.4	2.43±1.49	20.5±5.22
DOC	mg L^{-1}	21.7±3.94	15.7±7.04	21.9±4.28	16.6±3.57
$SUVA_{254}$	L mg C^{-1} m^{-1}	4.34±0.33	4.9±0.66	4.29±0.18	4.26±0.52
PON	mg L^{-1}	0.08±0.06	0.64±0.27	0.1±0.07	0.96±0.22
POC	mg L^{-1}	2.41±1.17	8±2.36	2.55±1.2	9.49±1.98
TBC	*10^5 cells ml^{-1}	5.89±3.26	8.69±3.21	5.95±2.83	4.94±2.15
K_T	m d^{-1}	0.53±0.38	1.21±0.52	0.77±0.55	1.22±0.37
FCO_2	g C m^{-2} d^{-1}	1.3±0.76	2.63±2.15	1.35±1.08	1.16±0.5
pCO_2	µatm	2877±679	4005±1494	2405±328	2523±981
FCH_4	mmol C m^{-2} d^{-1}	0.39±0.95	1.38±1.21	0.06±0.05	0.95±0.88
CH_4	µmol L^{-1}	0.65±0.66	1.17±0.81	0.17±0.01	0.86±0.91

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Table 2. Pearson correlation coefficients of measured FCO_2, CO_2, and CH_4 concentration with hydrochemical parameters of the water column (DOC, SUVA, particulate organic carbon and nitrogen, total bacterial cells) and landscape parameters of the tributaries and the main stem of the Ket River. Significant ($p < 0.05$) values are labeled by asterisk.

	all seasons			flood			baseflow		
	CH_4	CO_2	FCO_2	CH_4	CO_2	FCO_2	CH_4	CO_2	FCO_2
Hydrochemical parameters									
pH	0.2	-0.1	-0.2	-0.1	0.1	-0.2	0.0	-0.6*	-0.6*
Dissolved O_2	-0.1	-0.7*	-0.1	0.0	-0.8*	0.1	-0.2	-0.8*	-0.7*
Specific conductivity	0.3	0.0	0.1	-0.2	0.0	0.1	0.2	-0.3	-0.6*
DIC	0.3	0.0	0.0	-0.1	0.0	0.1	0.2	-0.4	-0.7*
DOC	-0.1	0.0	0.1	0.3	0.0	-0.1	-0.2	-0.1	0.2
$SUVA_{254}$	0.1	0.2	0.3	0.4	-0.3	0.1	-0.2	0.5*	0.6*
PON	0.1	-0.1	0.2	-0.2	-0.4*	0.2	-0.4	-0.5*	-0.5
POC	0.1	-0.1	0.2	-0.2	-0.4*	0.1	-0.3	-0.3	0.1
TBC	0.2	0.2	0.1	0.3	-0.2	-0.1	0.0	0.5*	0.5*
Climatic characteristics									
MAAT	0.2	0.0	-0.5*	0.1	0.0	-0.4*	0.2	0.1	-0.5
MAP	0.0	0.3*	0.5*	0.1	0.0	0.3	0.1	0.6*	0.7*
Land-cover characteristics									
Watershed area	-0.3	-0.3*	0.2	-0.4	-0.5*	0.0	-0.2	-0.1	0.5
Dark Needleleaf Forest	0.1	0.0	-0.3	0.1	0.0	-0.3	0.2	-0.1	-0.2
Light Needleleaf Forest	0.3*	0.4*	0.2	0.4	0.2	0.0	0.4	0.7*	0.6*
Broadleaf Forest	-0.3	-0.4*	0.1	-0.5*	-0.4	0.1	-0.3	-0.6*	-0.2
Mixed Forest	0.0	-0.2	-0.3	0.1	-0.1	-0.3	-0.1	-0.4	-0.4
Peatlands and bogs	0.0	0.2	0.3	-0.1	0.0	0.2	0.1	0.2	0.4
Riparian Vegetation	-0.1	0.0	-0.1	-0.2	0.1	0.0	-0.2	-0.2	-0.5
Grassland	0.1	-0.1	0.0	-0.1	-0.2	0.1	0.3	0.0	-0.5
Recent Burns	-0.1	-0.1	0.2	-0.1	-0.2	0.1	-0.3	0.1	0.4
Water Bodies	-0.2	-0.1	0.3	-0.3	-0.3	0.2	-0.2	-0.1	0.3
Lithology characteristics									
Upper Cretaceous, Maastrichtian – (sedimentary, silicate) Lower Paleocene (sedimentary silicate rocks)	0.1	-0.4*	0.0	0.3	-0.3	0.2	0.0	-0.5*	-0.4
Paleogene. Upper Oligocene (clays and silts)	0.1	-0.2	0.1	0.1	-0.1	0.2	0.0	-0.5*	-0.2
Cretaceous.Coniacian – Campanian (carbonates)	-0.2	-0.4*	-0.3	-0.2	-0.2	-0.2	-0.3	-0.7*	-0.6*
Neogene. Lower -Middle Miocene (clays, silts)	-0.1	0.2	0.3	-0.1	0.0	0.2	-0.1	0.3	0.3
Upper Pliocene-Eopleistocene (sands)	0.0	0.2	0.1	0.0	0.2	0.0	0.0	0.3	0.3
Cretaceous.Cenoman – Turon (clays, some carbonates)	-0.2	-0.5*	-0.3	-0.3	-0.3	-0.2	-0.3	-0.7*	-0.6*
Neogene. Lower Miocene (sands)	0.1	-0.2	-0.1		-0.2	-0.2	0.1	-0.3	0.0

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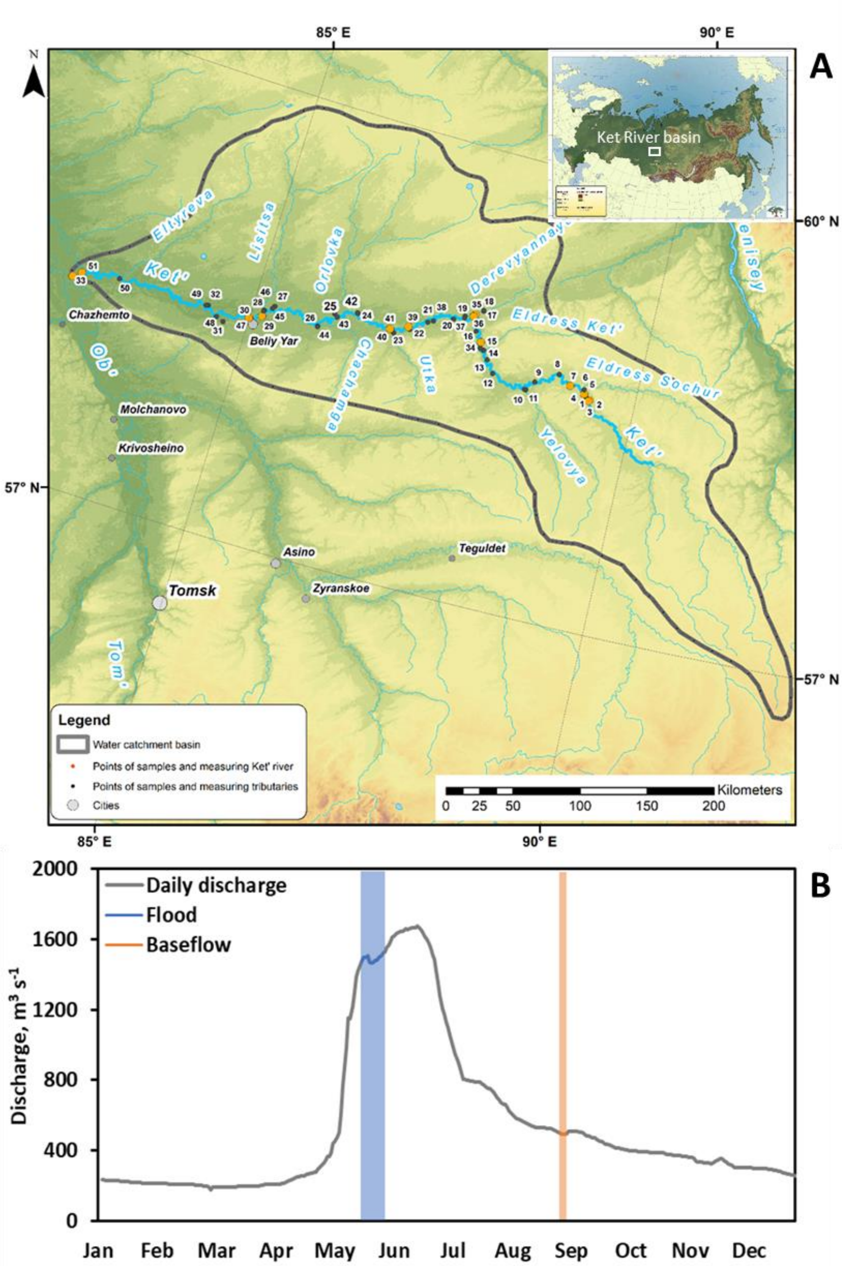

Fig. 1. A: Map of the studied Ket River watershed with continuous pCO_2 measurements in the main stem. **B:** Daily discharge (Q) at the gauging station of the Ket mouth, Rodionovka, in 2019. Highlighted in blue and orange are two sampling campaigns of this study, spring flood and summer-autumn baseflow.

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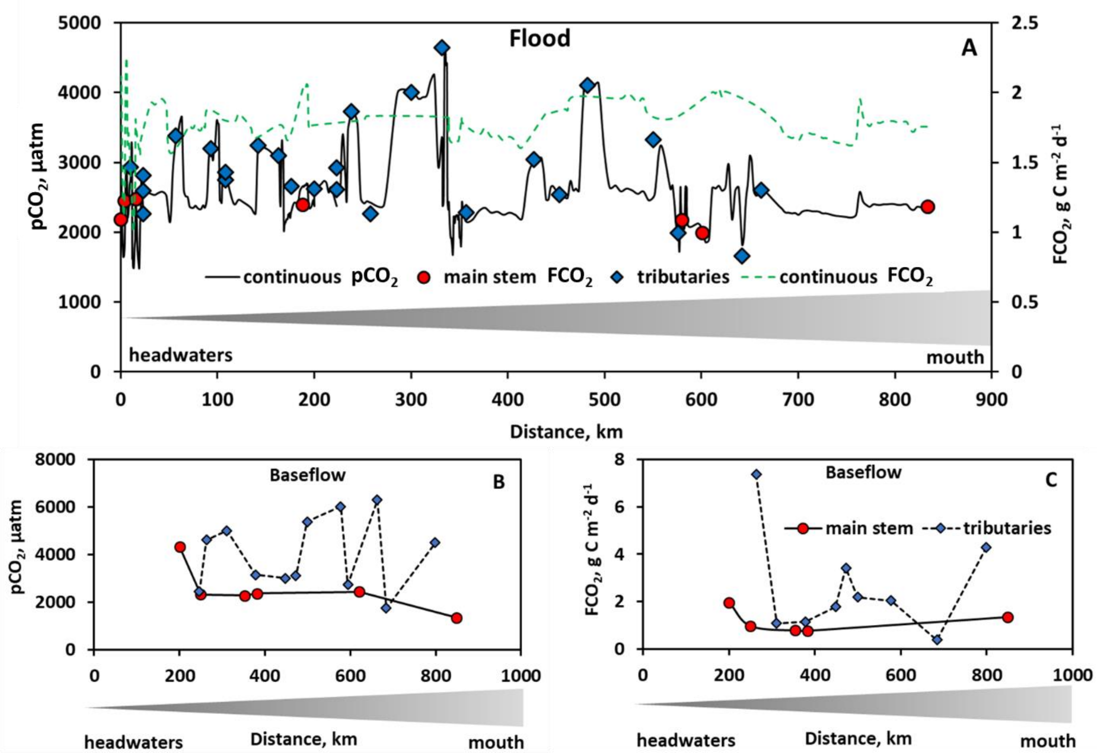

Figure 2. The pCO_2 and measured and calculated CO_2 fluxes during spring (**A**) and summer (**B, C**) of the Ket River main stem and tributaries (over the 830 km distance, from the headwaters to the mouth (left to right). Continuous CO_2 measurements in (**A**) are only for the main stem. Note that during summer baseflow, the water level did not allow reaching the headwaters of the Ket River (first 0-200 km on the river course).

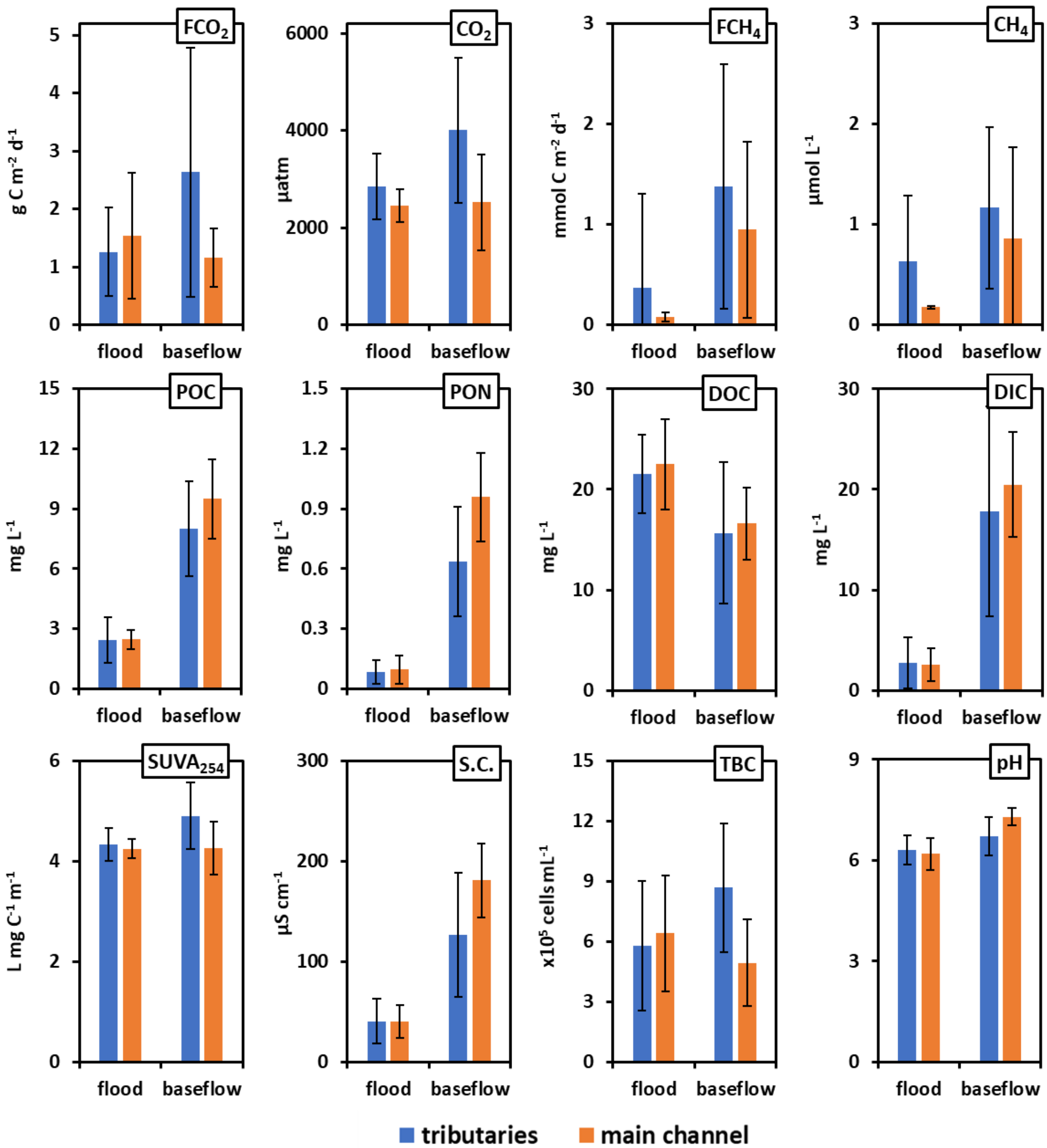

Figure 3. Mean (± s.d.) GHG concentration and fluxes, hydrochemical parameters, particulate organic carbon and nitrogen (POC and PON, respectively) and total bacteria count (TBC), in the main channel (orange column) and the tributaries (blue column) of the Ket River in spring flood and summer (early fall) baseflow.

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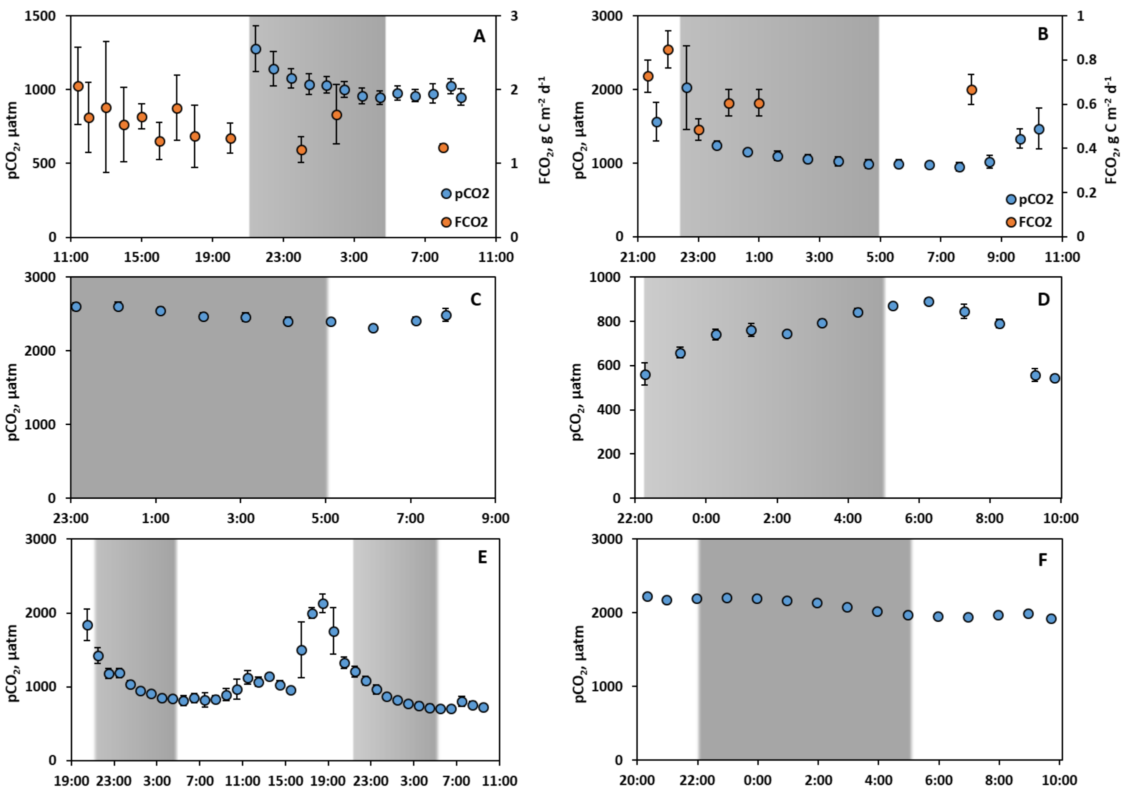

Figure 4. Continuous pCO_2 concentration (**A-F**, blue circles) and chamber-based fluxes (**A, B**) measured during spring flood period in tributaries (**A** Sochur No 3, **B** Lopatka No 8, **C** Derevyannaya No 12, **D** Ob river entrance, **E** Segondenka No 26) and in the Ket River main stem (middle course) near Stepanovka village (**F**) including night time measurements (shaded area). Variations of water temperature were within the range of 0.3 to 0.6 °C and did not exhibit significant correlations with pCO_2 and FCO_2.

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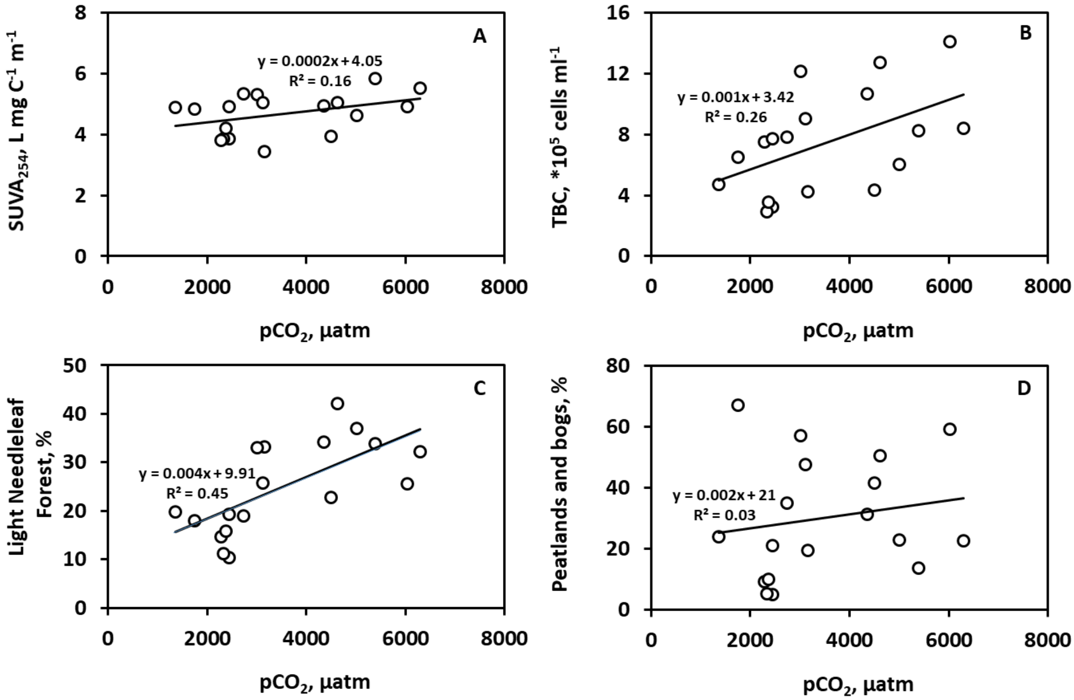

Figure 5. Significant ($p < 0.05$) positive control of SUVA (**A**), Total Bacterial Count (**B**), Light needleleaf forest (**C**) and wetlands (**D**) on CO_2 concentration in the Ket River and tributaries during summer baseflow.