Response to Anonymous Referee #1

General response

We thank the reviewer for the positive assessment of the dataset, the spatial coverage, and the integration of greenhouse-gas, hydrochemical, and colloidal measurements. We agree that the manuscript will benefit from a clearer treatment of colloidal dissolved organic carbon, more cautious interpretation of concentration stability, explicit limitations of dialysis-based fractionation, moderated novelty claims, and a more restrained use of PCA.

Comment 1 - Colloidal DOC dynamics

The manuscript discusses colloidal transport extensively, especially in Sections 3.6 and 4.2.2, yet the review of colloidal DOC dynamics is insufficient. The authors mainly cite studies related to Fe/Al colloids and trace metals. The discussion would benefit from engagement with broader colloid and DOM literature from Arctic and boreal systems, and from treating DOC colloids both operationally and mechanistically.

Response: We agree. The original text focused too strongly on metal-bearing Fe-Al colloids and did not sufficiently explain what the measured colloidal DOC fraction represents. We have explicitly define colloidal DOC as an operational 1 kDa-0.45 um fraction and discuss it mechanistically as a mixture of humic supramolecular assemblies, high-molecular-weight organic macromolecules, microbial/plant-derived polymers, and organic coatings or complexes on mineral surfaces. We have also add broader Arctic and boreal DOM references, including Amon et al. (2012), Mann et al. (2012), Guéguen et al. (2006), Fellman et al. (2010), and Novak et al. (2022), in addition to the existing colloid/trace-metal references.

Comment 2 - Concentration stability versus compositional and process stability

The manuscript's central conceptual conclusion is that DOC/DIC pools are buffered whereas pCO2 remains dynamically regulated. This is interesting. On the other hand, stable DOC concentration does not necessarily imply buffered carbon cycling because DOC composition may vary substantially, DOC lability may shift, and residence time effects are unknown. Concentration stability, compositional stability, and process stability need to be distinguished.

Response: We fully agree. Our revised conclusion is now limited to concentration-level patterns of bulk DOC and DIC, not to stability of DOC composition, lability, residence time, or overall carbon cycling. We have replaced several uses of "buffered dissolved carbon pools" by "stable bulk DOC and DIC concentrations" or "concentration-level buffering". We have added an explicit caveat stating that our dataset does not resolve DOC molecular composition, biodegradability, photoreactivity, or water residence-time effects.

Comment 3 - Novelty and framing as an integration advance

While the combined dataset is valuable, several components have already been investigated individually in the Lena system. The actual novelty lies more in integrating GHG measurements with colloidal geochemistry, obtaining high-resolution longitudinal observations during post-freshet recession, and linking CO2 evasion with trace-element partitioning. The manuscript would be stronger if the authors framed the work as a synthesis/integration advance rather than a fundamentally new conceptual discovery. In addition, the related claims (e.g., first assessment, first evaluation, first colloidal transport, etc.) should be moderated.

Response: We agree. We have moderated claims of "first" assessments and reframe the manuscript as an integrated longitudinal study that combines high-resolution greenhouse-gas observations, solute chemistry, and operational colloidal partitioning under the same post-freshet hydrological conditions. This framing better reflects the actual advance and acknowledges previous Lena River work on individual components.

Comment 4 - Operational limitations of dialysis-based colloid separation

The manuscript heavily emphasizes colloidal controls on trace elements and DOC. However, the colloidal dataset is somewhat limited, relying on one operational cutoff. Are there changes in microbial activity, colloidal aggregation, and metal adsorption/desorption during dialysis over 3-5 days? Although the authors state concentrations changed <10%, this does not guarantee preservation of original colloidal structure. The operational limitations of dialysis-based colloid separation should be discussed a bit.

Response: We agree. The dialysis data provide robust operational partitioning between <1 kDa and 1 kDa-0.45 um fractions, but they do not preserve or identify the exact in situ colloidal structure. In the revised version, we have explicitly stated that dialysis can potentially influence aggregation, adsorption/desorption, and microbial processing during the 3-5 day equilibration. The <10% change in <0.45 um concentrations indicates bulk chemical stability during dialysis, but not necessarily full preservation of the original size distribution or colloid morphology. Note that ideally, dialysis bags should be deployed directly in situ within river or lake waters (e.g., Vasyukova et al., 2010; Pokrovsky et al., 2012; Mikhaleiko et al., 2026a), as this minimizes potential alterations of colloidal structure during sample handling and incubation. However, such deployment was not compatible with the logistics of a continuous ship-based survey covering 1500 km of the Lena River, where prolonged equilibration times (3–5 days) at individual locations were not possible.

Comment 5 - Direct colloidal characterization and future work

Is there any colloidal characterization in the present study or planned research to better strengthen conclusions regarding Fe-Al-organic colloids? For example, particle size distribution, zeta potential, Fe speciation, organic ligand composition, and DOM molecular composition.

Response: In the present study, direct characterization of colloid size distributions, surface charge, Fe speciation, organic ligand composition, or DOM molecular composition was not performed. The inference of Fe-Al-organic colloidal carriers is based on operational dialysis, strong co-variation of trace elements with Al, Fe, and DOC, and previous Lena River studies that directly characterized Fe-bearing particles and colloids. In the revised version, we have made this limitation explicit and proposed specific future measurements.

We agree that a multidisciplinary characterization of colloidal material, including in situ spectroscopic techniques, would greatly improve understanding of the structure of organic matter–trace metal complexes and the composition of organic ligands. Examples of such approaches have been provided in previous studies by our group, including nuclear magnetic resonance characterization of Al–DOM associations in Central Siberian rivers (Pourpoint et al., 2017) and Fourier-transform ion cyclotron resonance mass spectrometry analysis of DOM molecular composition in western Siberian rivers (Kurek et al., 2025). However, applying these approaches to Lena River colloids was beyond the scope and budget of the present study, although such analyses are clearly desirable for future work.

A major technical limitation is the need to concentrate large volumes of river water to obtain sufficient colloidal material for resolving molecular and structural organization, because most microscopic and spectroscopic methods have relatively low sensitivity at natural riverine concentrations. Such pre-concentration can itself introduce artefacts, including aggregation, restructuring, coagulation, and conformational changes of organic–mineral colloids. Consequently, although advanced structural analyses would be highly valuable, the resulting material may not fully preserve the original colloidal state present under natural river conditions.

Kurek, M.R., Pokrovsky, O.S., Krickov, I.V., Lim, A.G., Korets, M.A., McKenna, A.M., Spencer, R.G.M.: Assessing the molecular-level controls of dissolved organic matter cycling in Western Siberia Lowland rivers, J. Geophys. Res.: Biogeosciences, 30(4), Art No e2024JG008537, DOI:10.1029/2024JG008537, 2025.

Pourpoint F., Templier J., Anquetil C., et al. : Probing the aluminum complexation by Siberian riverine organic matter using solid-state DNP-NMR, Chemical Geology, 452, 1-8, 2017.

Comment 6 - PCA variance explained and moderation of dominant controls

In the PCA interpretation, the first two components explain only 23% and 13% of variance. As such, >60% of variability remains unexplained. Statements regarding dominant controls should be moderated.

Response: We agree. The current wording was too strong, especially where PCA is said to "confirm" or identify "dominant controls". The first two components explain 36% of the total variance and should be interpreted as the most interpretable axes of covariation, not as an exhaustive description of the dataset. We will revise the Methods, Results, Discussion, and Conclusions accordingly and present PCA as exploratory and complementary to pairwise correlations, longitudinal trends, and dialysis results.

Comment 7 - Interpretation of low methane concentrations

The low CH_4 values are interesting. Are they related to floodplain connectivity, oxidation, or sediment processes?

Response: We agree that the low and spatially uniform CH_4 signal deserves more interpretation. We have added a short discussion emphasizing that the post-freshet recession period likely reduced connectivity with anoxic floodplain habitats relative to peak flood, while high oxygen concentrations and turbulent main-channel transport likely favored methane oxidation and atmospheric loss. Limited exchange with anoxic sediments in the deep, fast-flowing main stem may also contribute. The floodplain lake sample with elevated pCO_2 and CH_4 supports this interpretation, because hydrologically disconnected or weakly connected floodplain waters can retain stronger methanogenic signatures.

Comment 8 - Terminology: "Low Lena" versus "Lower Lena"

Low Lena may read Lower Lena or use consistently?

Response: We agree. We changed to "Lower Lena River" consistently when referring to the studied river sector and "lower Lena reaches" only in descriptive lower-case usage. This also aligns with the manuscript title.

Response to Reviewer # 2

Overall assessment. The review is strongly positive and does not require a structural rewrite or new field/laboratory work. The comments can be addressed by targeted methodological clarification, cautious interpretation of tributary anomalies and PCA, a short expansion of the DOC/DIC discussion, and several figure and terminology corrections. The current revised Word version already partially addresses the low PCA variance and DOC-composition caveat; the wording below sharpens these points and aligns them with the reviewer's exact concerns.

> We thank the reviewer for the positive and constructive assessment of the manuscript. We have revised the Methods, Results, Discussion, and figures to clarify the independent pCO_2 control measurements, provide cautious explanations for tributary-scale anomalies, improve the PCA presentation and temper its interpretation, add references supporting the proposed seasonal mechanisms, and distinguish stability of bulk DOC/DIC concentrations from possible changes in carbon composition, lability, and carbonate speciation. We also corrected the terminology and technical issues identified by the reviewer.

1. Independent pCO_2 control measurements and their discrepancies

> *More detail is needed about the methods for the control measurements for pCO_2 in Figure 3A. And a brief discussion why at some places the control measurements are very different than shipboard measurements for pCO_2 methods?*

> We thank the reviewer for identifying this omission. We have expanded Sect. 2.4 to describe the second, independently calibrated pCO_2 system and clarified that the red symbols in Fig. 3A are stationary field-validation measurements rather than exact analytical replicates of the moving shipboard record. We also added a short explanation in Sect. 3.2 and revised the figure caption. The underway system integrates water delivered through the Kingston intake over moving ~1.25-km segments, whereas each control measurement is a local snapshot obtained at a different time and potentially a slightly different depth. The largest discrepancies occur where pCO_2 changes rapidly, particularly near tributary mixing zones, and can therefore reflect real spatial/temporal heterogeneity, incomplete mixing, and different membrane response times rather than a systematic analytical bias. No consistent positive or negative offset was evident.

2. Potential causes of tributary-scale anomalies

> *You mention regional differences in several parameters, for example high Mn in Undyulyung River, or CO_2 from certain tributaries. Can you add details about potential drivers of this variability or anomalies?*

> We agree and have added a concise, explicitly hypothesis-based interpretation of the tributary anomalies. We now relate the Fe-Mn enrichments to local reducing end-member waters and the contrasting pCO_2 signals to differences in floodplain/wetland connectivity, residence time, biological processing, and prior degassing. We also state that the available dataset does not permit definitive source attribution.

3. PCA presentation and confidence of interpretation

> *PCA figure and analysis: Can you add color, grouping, or annotations to this figure that increases interpretability? Also, the cumulative amount of variance explained is relatively low, can you amend statements about the confidence of these findings to reflect this?*

> We have redesigned Fig. 7 using colored interpretive envelopes and explicit variance percentages on the axes. We also revised the Methods, Results, caption, and Discussion to state that the first two rotated components explain only 36% of total variance and that the PCA is an exploratory ordination rather than a definitive classification or causal test. The PCA interpretation is now retained only where it agrees with pairwise correlations and independent dialysis results.

4. Citations for the proposed seasonal CO_2 mechanisms

> *Discussion of drivers of seasonal differences CO_2 on lines 561–566 could use some citations.*

> We agree and have added references supporting snowmelt flushing, seasonal changes in lateral inputs, in-stream production, and degassing. We also clarified that this is a mechanistic interpretation rather than a direct within-year comparison, because the spring and post-freshet estimates derive from different campaigns and river sectors.

5. DOC/DIC concentration versus composition, lability, and speciation

> *While absolute DOC/DIC concentrations appear to be stable the study doesn't present specific evidence that there are no changes to lability, source, or composition of DOC over the river transect. A short discussion of this is warranted, especially when linking DOC to pCO_2. I also think a short discussion of any previously observed DIC speciation data could strengthen the DIC buffering statements.*

> We agree and have revised the text to make clear that "stability" refers only to the limited longitudinal variability of bulk DOC and DIC concentrations during the sampled period. We now explicitly state that no molecular, optical, isotopic, or incubation data were obtained to assess DOC source, composition, or lability. We also added Lena carbonate-system context showing that bicarbonate dominates total DIC under open-water, near-neutral conditions, whereas the dissolved CO_2 fraction and pCO_2 can vary rapidly. Finally, we clarify that the DOC-FCO_2 correlation indicates covariance and does not establish direct mineralization of DOC as the CO_2 source.

6. Technical corrections requested by the reviewer

We have also performed all requested technical corrections. Thus, we used pCO_2 whenever the quantity is expressed in µatm or ppm-equivalent partial pressure. However, we retained CO_2 for molecular dissolved CO_2, total CO_2 emissions, or FCO_2. We increase hydrological-station markers by approximately 2–3×, used a high-contrast fill with a black outline, and labelled Tabaga and Kyusyur directly. On the issue of climate wording, we clarified that the statements concern seasonal distribution versus annual amount, not different contradictory basins. We edited "kkk" typo and corrected other small orthographical and stylistical issues.

Response to Reviewer # 3

Reviewer report for: *Dynamic CO_2 evasion and colloidal control of trace metals in the Lower Lena River* by Kolesnichenko et al.
Overview and general comments: This study provides an extensive and high-resolution snapshot of carbon fluxes during summer baseflow conditions in the Lower Lena River basin, and connects them to underlying processes through association with the composition and behaviour of solutes, colloids and trace elements. It is an important contribution to our understanding of the probable impacts of climate-associated changes on, and feedbacks from, Arctic river systems and proximate zones of permafrost thaw.

The other two Reviewers have noted the larger-scale questions and concerns associated with the work, which have been addressed by the Authors. The following line-specific comments are thus restricted to more minor, primarily editorial suggestions.
We are grateful for positive evaluation of our work and performed necessary corrections and revisions. We also restricted Results and Discussion presentation as requested by the reviewer.

Line-specific comments:

Lines 105–106: …spatial pattern**s** of hydrological control…?
Revised as "…spatial patterns of fluvial C and metal transport"

Lines 141–150, Figure 1: Should this be Yakutsk to Kyusyur, to correspond to the locations identified on Figure 1? Yakutsk is also not labelled on the map, nor is Samoilov Island. It is recommended to make the map location labels consistent with the locations named in the text.
We strongly revised this map as indicated by this and other reviewers

Line 151: This sentence seems to suggest that there were sampling points along the Aldan, Vilyui and smaller tributaries, but these locations are not identified on the map. Please ensure that the description in the text is consistent with the labelling of sampling points on the map.
We now identified all sampled tributaries and added necessary locations

Line 155: "carbon speciation"… Speciation probably is not the correct term unless the composition and structure of all carbon-containing compounds were identified.
Revised as "carbon, major and trace solutes, CO_2 and CH_4 concentrations…"

Lines 256–263: Should kkk be k_{CH4} or k_{CO2}?
This is transfer coefficient, K_T; revised accordingly as k_{CO_2}

Line 283: Please indicate the supplier for SLRS-6, and it's nature/composition/matrix as a CRM.
Added accordingly: (River Water Certified Reference Material for Trace Metals and other Constituents, Canada)

Figure 1B: Please identify which data the blue and red lines correspond to.
Revised as : "Hydrograph of the Lena River at Kyusur (red line) and Tabaga (blue line)…"

Figures 2A–F: There appear to be one or more potential outliers in each panel. Were these values associated with a single sample, or something anomalous for several samples? If not, is it worth testing them as outliers and removing them if they are?

These are real measurements of specific samples and we cannot identify them as outliers, given rather limited spatially-resolved data set. As such we are not considering removing these data

Results: Much of the material presented in this section seems like it would be better placed in the Discussion section, especially comparisons with other findings. Maybe this could be the title of the first subsection of the Discussion, where all of the results are compared together? There is also a fair bit of interpretation of the results in this section, which might be better moved to the Discussion (e.g. Lines 467–475, 503–509).
We thank the reviewer for this helpful comment. We agree that the original Results section contained several passages that went beyond direct presentation of observations, especially comparisons with previous studies and mechanistic interpretation of solute patterns and PCA results. In the revised manuscript, we have streamlined the Results section so that it focuses primarily on measured values, spatial trends, statistical relationships, and figure/table descriptions. Literature comparisons of carbon fluxes and pCO_2 are now treated mainly in Sect. 4.1, while comparisons of major and trace solute concentrations with long-term datasets are discussed in Sect. 4.2.1. Mechanistic interpretation of the solute groups, tributary anomalies, colloidal carriers, and PCA structure has been moved or consolidated into Sects. 4.2.2 and 4.2.3. We retained only brief interpretive statements in the Results where needed to guide the reader through the observed patterns.
We also agree that Sect. 3.5 contained interpretation better suited to the Discussion. We therefore revised Sect. 3.5 to report only the statistical results: significant pairwise correlations, PCA loadings, explained variance, and figure/table references. Interpretive statements concerning groundwater connectivity, colloidal transport, lithogenic sources, DOC–FCO_2 covariance, and comparison with other Siberian rivers have been moved to Sect. 4.2.3, now framed explicitly as exploratory multivariate support rather than distinct source identification.

Line 376: Should use the longer "en dash" to separate numerical ranges, rather than the shorter hyphen (e.g. – vs -).
Corrected as noted

Lines 379–382 and Figure 3: Please add all tributaries listed here onto the general area map (Fig. 1) so that readers can identify their locations and visualize the discontinuities in the longitudinal pattern that are discussed.
We revised Figure 1 A and made sure all the tributaries are depicted as necessary

Lines 397, 402, 426 and elsewhere: Should be "Low**er** Lena"? Or "lower Lena", as on line 432?
Yes, we corrected to Lower Lena throughout the manuscript as also noted by other reviewers

Lines 417, 419, 436 and elsewhere: Should be mainstem instead of main-stem and main stem?
We retained "main stem" as most stylistically correct and revised the text accordingly.

Line 478 and Figure 6: Line 478 states that this analysis was restricted to the mainstem of the Lena R., but the caption of Figure 6 states "Lena River and its tributaries".
We thank the reviewer for pointing out this inconsistency. Yes, Figure 6 plots the Lena River main stem; corrected accordingly.

Figure 8: The y-axis scale has cut off the top ends of some of the error bars.
The comment is well taken. We revised the Y axis presentation as noted.

Lines 513–515: Better/clearer to write "dissolved (<0.45 μm) colloids with sizes >1 kDa", instead of "colloidal (1 kDa–0.45 μm) fractions within the dissolved pool (<0.45 μm)"? It may also be better to represent the next sentence as a ratio formula, instead of describing it with words? The term "total dissolved concentration" is strange given that dissolved is a subset of total.
We agree with this remark and revised as recommended.

Lines 521, 525: Suggest changing "are" and "is" to "were" and "was" for consistent tense.
Corrected accordingly

Line 529: Should Al-rich (organo)mineral particles be mentioned here if Al was in the mixed colloidal group (~ 50%).
We agree: these are essentially Fe-rich particles; revised accordingly

Discussion: Much of this section is presented in the present tense, but is best written in the past tense since it is based on measured variables that are likely to change under different freshet conditions, and generally over time with climate change.
We agree with this pertinent remark and we changed the verb tense in the Discussion, where appropriate.

Line 596: Although it is implied by "increased channel width" with all else being equal, is decreasing depth also worth mentioning?
To our knowledge, there is no clear decrease of the channel depth in the Low Lena River. This sentence describes the patterns not yet affected by the delta itself; it is just northward direction which is being discussed

Lines 613–617: Is it worth also considering the impact of any observed decreases in temperature from south to north on the rate of in-stream carbon processing by microorganisms and associated abiotic reactions that may produce CO_2?
We thank the reviewer for this useful suggestion. We examined the water-temperature pattern along the south–north transect and found only a modest downstream decrease, from approximately 18 °C in the middle reaches to about 15–16 °C in the lower reaches. Across all main-stem samples, water temperature averaged 17.6 ± 1.3 °C, with a range of 15.3–20.2 °C (Table 1). Such a decrease could moderately reduce microbial respiration and other temperature-sensitive in-stream processes, but it is unlikely to be the primary driver of the observed pCO_2 pattern. Assuming a typical Q_{10}-type response, a 2–3 °C cooling would change biological rates by only ~15–25%, whereas pCO_2 varied much more strongly over short distances and was also shaped by tributary inputs, lateral carbon supply, and hydrodynamic degassing. We therefore now mention temperature as a possible secondary control, while retaining hydrological connectivity and gas exchange as the dominant explanations for the south–north pCO_2 decrease.

Lines 652–654: Better to say "…dissolved (<0.45 μm) low-solubility trivalent and…", since the particulate fraction (>0.45 μm) was not accounted for?
Agree and corrected as suggested

Line 661: Negative correlation vs negative relationships?
Revised as "correlation"

Line 665: Humic acids typically form more stable complexes with divalent cations like Cu, compared to fulvic acids. They are also known to stabilize Fe and Al (oxyhydr)oxides.
We agree that generally humic organic compounds strongly comple Cu and are capable of stabilizing Fe and Al oxy(hydr)oxides. Revised for clarity.

Line 681: Better to say colloidal versus truly dissolved, and/or include the size ranges?
It is more precise to say « Low Molecular Weight” to reflect the background processes

Line 701: Better to say relatively inert instead of rather inert? Certainly colloid-stabilized DOC is inert relative to more labile forms, but it is also more reactive than other forms of carbon-mineral associations (e.g. allophane).
We agree with this remark and strongly revised this part of the text for clarity

Line 728: Better to say that continuous permafrost **did** not alter transport architecture, and specifically for the studied and reported rivers/area (rather than **does** not in the general sense for all Arctic and boreal rivers), since that may change with time and may be different in other river systems?
Agree and revised as recommended