

Reviewers' Comments to Author (black text), and our detailed responses to those comments (blue text):

We sincerely thank both anonymous reviewers for their insightful comments and helpful suggestions. We found the majority of the critiques are relatively easy to address and will make this manuscript stronger. We are proud of the work that went into this manuscript and look forward to crafting its final version.

Reviewer #1:

1 Reviewer Decision

This manuscript addresses an important and timely topic, particularly in the context of mountain glacier loss, ecological succession, and its implications for regional and global carbon cycling. The dataset is impressive, spanning multiple spatial and temporal scales, which is a clear strength of the study. The integration of geochemical measurements with isotopic tracers and modelling approaches is also commendable. However, there are several issues, outlined below, related to the modelling approach and overall structure of the manuscript that should be addressed before the manuscript can be considered for publication.

Thank you for the positive critiques, especially regarding the spatiotemporal scale we conducted our research at, which we are particularly proud of. We agree that there are several areas where this manuscript can be improved and believe that the concerns you have with it will be relatively easy to address. Please see below for responses to specific comments.

2 Primary Comments

1. Independence and Consistency of Modelling Approaches

A central concern with the manuscript is the use of multiple modelling approaches that appear to constrain overlapping aspects of the system. This issue is compounded by a lack of clarity in the methods about the overlap of these methods.

An inversion model is used to partition solute sources among carbonate, silicate, evaporite, precipitation, and pyrite endmembers, while the inorganic-organic carbon mass balance subsequently uses many of the same geochemical inputs (e.g., major ions, DIC, and derived quantities) to partition carbon sources using a forward model.

This overlap introduces some ambiguity regarding the independence of the modelling approaches and how overlapping parameter estimates should be interpreted. For example, precipitation inputs are estimated using both models, but there is no comparison between model outputs. The manuscript would benefit from either a clearer justification of model independence, and a direct comparison of overlapping outputs between the modelling approaches, or a streamlined approach that uses a single inverse or forward model approach.

We hope it is understandable that we hesitate to use only one of the modeling approaches because one of the main strengths of our study is that we used multiple approaches to obtain similar geochemical patterns in our ecologically complex study region. We do acknowledge overlap in using the same major ion and DIC data in both the inversion and inorganic-organic carbon mass balance forward model. However, the inversion model relies on $\delta^{34}\text{S}$ - SO_4 and the forward model relies on $\delta^{13}\text{C}$ -DIC, DOC, and $\delta^{13}\text{C}$ -DOC for ultimate partitioning. We can clarify this in text and provide a comparison table or figure showing overlapping outputs side by side as Reviewer 1 suggested.

Further modelling choices complicate this issue. For example, the manuscript interpolates missing major ion chemistry using empirical relationships (Lines 389–395), then subsequently uses those estimated values within the inversion framework. If the number of missing samples is sufficiently small, excluding them may be preferable to estimating them from empirical relationships and subsequently using those estimated values within the inversion framework. Otherwise, the inversion framework becomes partially dependent on assumed empirical geochemical relationships.

The manuscript interpolates major cation data from five sampling events, or ~3% of cases, so we expect the differences to be negligible. However, to address this comment, we propose running the inversion and inorganic-organic carbon mass balance models with and without the interpolated data and comparing the outputs. If the outputs are significantly different, as tested through statistics, we will remove the inverted samples, but if they are not, we will keep them in due to the explanation given in text (i.e., this inclusion was important due to the general lack of weathering data for spring in glacierized regions globally).

Given the overlap of the modelling approaches, a number of other questions need to be addressed and clearly presented in the manuscript. For example:

- Are the same endmembers used consistently between the inverse and forward approaches?

The same endmembers are not used between the inverse and forward models. This is because the models use two independent approaches to determine the most appropriate endmembers, even though we use major ions and DIC as base chemistry in both. This can be clarified in text.

- Can the acidity ratio used in the forward model be constrained directly from the inversion results?

The acidity ratio used in the forward model can likely be constrained directly from the inversion results. Yet, we tried to not use outputs of one model as inputs into the other. This is because we use different endmembers in each model, based on best practices of each model, and as such, consider the outputs independent enough that they verify each other. We are thus hesitant to constrain the forward method's acidity ratio from the inversion output because that would remove the one thing that makes the comparison useful: two independent estimates of the same quantity that we can check against each other.

Additional clarification is also required regarding:

- the origin of the 15% inversion error threshold (Lines 479–480);

The 15% error threshold follows the MEANDIR settings from Kemeny & Torres (2021), who published the model methodology. We will add a sentence to the Method clarifying that point.

- the specific cost function used in the inversion (Line 481);

The cost function follows the MEANDIR settings from Kemeny & Torres (2021), who published the model methodology. We will add a sentence to the Method clarifying that point.

- the exclusion of HCO_3^- from the inversion due to non-conservative behaviour, despite the strong Ca-HCO_3^- relationship discussed elsewhere in the manuscript which is used to justify the modelling of data;

The strong Ca-HCO_3^- relationship is only used in estimating HCO_3^- concentrations for the piper diagram. We consider the piper diagram a first-pass analysis in this manuscript that hints towards the geochemical weathering relationships in the system. When we quantify those relationships, both in the inversion and inorganic-organic carbon mass balance model, we do not use HCO_3^- concentrations. When we calculated the estimation of TDS proportions, we used reaction stoichiometry to determine HCO_3^- concentrations, which is reported in the Methods. We will make these nuances clearer in text.

- the treatment of uncertainty propagation throughout both modelling frameworks.

How we calculated and evaluated uncertainty for both modeling approaches will be clarified in the Methods sections where we describe each model. For the inversion model, we used the uncertainty limits presented in the publication that founded the model – Kemeny & Torres (2021). For the forward model, we used the model published by Voss et al. 2023, which does not explicitly include uncertainties. However, we will include a range of endmembers and do a sensitivity analysis for this to ascertain uncertainty instead.

2. Uncertainty in Sulphur Isotope Endmembers and Pyrite Contributions

The treatment of sulphur isotope endmembers in the inversion model is unclear. Initially, the manuscript appears to use globally compiled $\delta^{34}\text{S}$ endmember ranges to define pyrite, evaporite, and precipitation sources. However, the manuscript also presents data from the Canadian Rockies showing substantial overlap between the $\delta^{34}\text{S}$ of sulphate derived from pyrite oxidation and other sulphate sources.

This introduces an important uncertainty in the inversion framework. If the global endmember ranges are used, it is unclear how representative they are of the local geology. Conversely, if the regional Rocky Mountain sulphur isotope ranges are used, the overlap between sulphate sources may substantially increase the uncertainty associated with the inversion outputs.

At present, it remains unclear in the main text which sulphur isotope ranges were ultimately used in the inversion model and how sensitive the source apportionment results are to these choices. This is particularly important because the inversion relies on $\delta^{34}\text{S}$ as a key constraint for partitioning sulphate sources and interpreting the relative roles of sulphuric versus carbonic acid weathering.

The manuscript would therefore benefit from:

- explicitly defining the sulphur isotope endmember ranges used in the inversion;
- discussing how representative these ranges are for the local geology;
- quantifying the uncertainty in pyrite—evaporite partitioning arising from endmember selection.

The $\delta^{34}\text{S}$ - SO_4 endmember ratio used for pyrite in the inversion model was -40.00 to 40.00‰, as presented in Table 1 and explained in the following Methods Inversion model section, “The elemental and isotopic ratios for the five endmembers were sourced from the global compilation by Burke et al. (2018), which provides representative ranges for major geologic terranes (Table 1). This global dataset was deemed suitable for our study region, which is characterized by a mix of sedimentary carbonate and silicate lithologies.” We followed the global values Burke et al. 2018 reported because we did not have site-specific $\delta^{34}\text{S}$ - SO_4 endmembers available.

The regional Canadian Rocky Mountain $\delta^{34}\text{S}$ -S that was cited in text refers to the sulfur isotope of pyrite/sulfide, and not necessarily the sulfur isotope of dissolved sulfate. Given we are trying to constrain sulfuric acid weathering in the inversion model using $\delta^{34}\text{S}$ - SO_4 , we believe that the relevant measurement is indeed $\delta^{34}\text{S}$ - SO_4 and cannot be replaced with $\delta^{34}\text{S}$ -S values. We will discuss both the global $\delta^{34}\text{S}$ - SO_4 and regional $\delta^{34}\text{S}$ -S values with more clarity in text.

3. Presentation, Structure, and Interpretation of Results

The manuscript contains a large amount of valuable data, but the presentation of results is frequently difficult to follow. In particular, the combined “Results and Discussion” structure often interweaves interpretation with observations, occasionally making it difficult to distinguish between measured results and inferred mechanisms.

Several key findings are also not presented as clearly or prominently as they could be. For example:

- Figure 3 contains central results regarding CO_2 saturation and fluxes, but the multi-panel structure makes trends difficult to interpret;

We agree that these results are central to the story and originally did a multi-panel figure to simplify the spatiotemporal CO_2 data into one figure. However, we understand that it is a lot to interpret at once and can easily amend this into individual CO_2 saturation and CO_2 flux figures. Reviewer 2 has similar concerns with Figure 3 and suggested boxplots (please see below).

- the large oversaturation at BR2 deserves more explicit discussion;

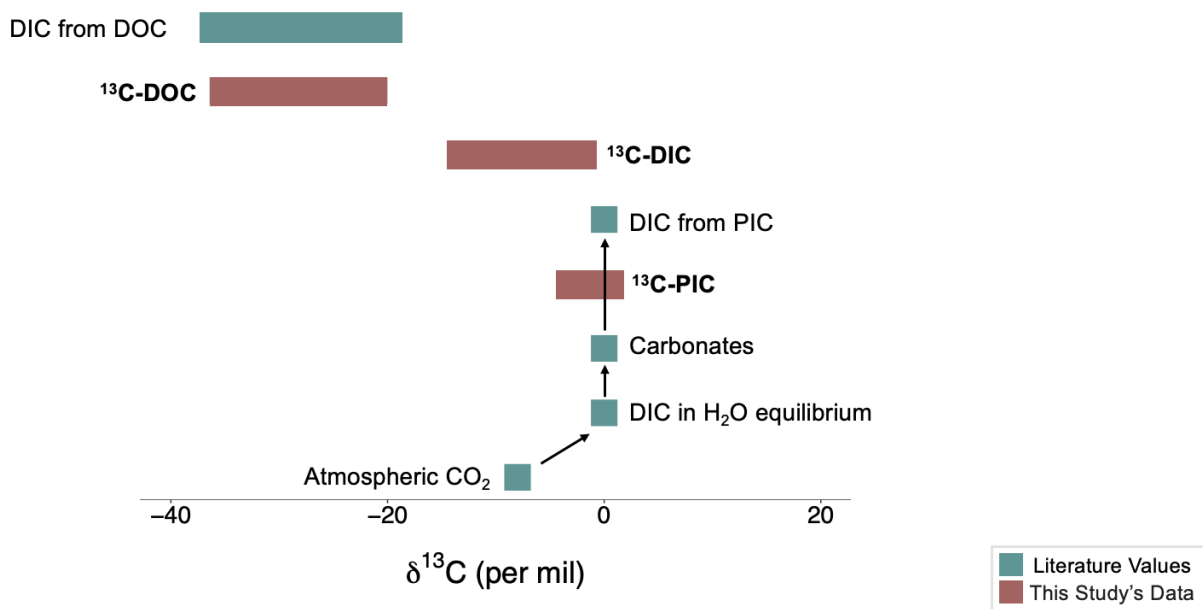
Though it was briefly discussed in relation to flux, the submitted manuscript indeed failed to discuss why BR2 had such large oversaturation. An explanation about this site's wetland ecosystem and how that may relate to CO₂ oversaturation will be added in text.

- downstream trends in Figure 7 are difficult to interpret without uncertainty estimates;

Uncertainty bars will be added for each endmember presented in Figure 7.

- Figure 10 would benefit substantially from inclusion of the raw $\delta^{13}\text{C}$ data alongside the model outputs.

Since the y-axis on Figure 10 is % of total DIC, we cannot directly add the raw $\delta^{13}\text{C}$ data to the existing figure. However, a new panel can be added to the top of Figure 10 that would show the raw $\delta^{13}\text{C}$ data along a δ axis. Something like the following:



The geological framework is also difficult to follow. Figure 1 would benefit from:

- inclusion of the geological cross-section locations directly on the map;

The geological cross-section locations will be directly added to the map

- addition of scale information for the cross-sections;

Scale information will be added to the cross-sections.

- consideration of a simplified geological map for reference.

The geological cross-sections were reproduced from Gadd (2009) with permission, and to our knowledge his book is the only place to find simplified geological map of the region. We will contact him directly and asked for revised permission to also include a reproduction of the map for the Supplementary Information.

Similarly, the XRD analysis would be much more informative if diffractograms were included rather than only presence/absence information. The current presentation makes it difficult to evaluate mineral identifications, especially where poorly crystalline phases or overlapping peaks may occur.

We agree that diffractograms are much more informative than presence/absence information. Yet, we have diffractograms for every sample where enough mineral material was obtained and chose to simplify this information into one figure instead of presenting 112 diffractograms in the Supplementary Information. The XRD data was analyzed and processed by a specialized X-Ray Diffraction Laboratory, and we thus feel comfortable with the interpretation of the peaks and do not believe adding individual diffractograms would necessarily add much additional information.

More broadly, the manuscript would benefit from:

- simplifying figures to better highlight key findings;
- moving secondary figure panels to supplementary material;
- restructuring sections to improve the distinction between results and interpretation;
- reducing the length of the conclusions, which currently contains substantial discussion material.

Given these comments and those of Review 2, we intend to go through the manuscript with a fine-toothed comb to work on simplifying and clarifying our key findings and figures. In response to Reviewer 2 requesting additional information on global comparisons, we will be moving the discussion material from the conclusion into the Results and Discussion discussing the regional and global context more in-depth.

4. Data Treatment, Statistical Handling, and Methodological Clarity

Several aspects of the data treatment and statistical methodology require clarification or stronger justification.

The discharge modelling approach is particularly important because the study relies heavily on modelled discharge at 12 of the 14 sites. However, the manuscript does not clearly present the regression models themselves nor provide observed versus modelled comparisons. This information should be included either in the main text or supplementary material.

The discharge model is definitely important to this study. We did not present the regression models themselves because they are both site- and day- specific. Given that we modeled discharge at 12 sites over two years, this would be 8,760 regression formulas to present in the manuscript, which we do not think is reasonable. We did do figure and mathematical comparisons between observed and modeled discharge in a previous publication (Serbu et al. 2024) but acknowledge that we failed

to repeat them in this manuscript. We will add more information about the comparisons done in previous work in the Methods Discharge section.

Other methodological concerns include:

- the use of half detection-limit substitution without discussion of how this may affect distributions and uncertainty;

We will add additional information about how many half detection limit substitutions were made and why we think this was an appropriate choice, including how they may affect distributions and uncertainty.

- selective exclusion of AR1 data when tributary influence was considered large, which would benefit from additional justification;

Additional context will be added to justify the exclusion of some AR1 data. We used high CO₂ concentrations (uM) to assess the tributary influence and resultant non-mixing of waters where we sampled, and this will be explained in detail.

- the interpretation of an R² value below 0.2 as a meaningful correlation without reporting p-values;

We are unable to find what this is in reference to (even with the search and find function) but will be sure to add p-values once we go through the manuscript with a fine-toothed comb and find this case.

- the use of terms such as “strong” for relatively weak relationships;

We can easily remove emphasizing terms like “strong” or “very” from our descriptions.

Additional methodological clarity is also needed regarding:

- whether Cl⁻ is missing from the normalisation described around Line 460;

Cl⁻ is used as a constrained variable in the inversion but is not included in $\Sigma^{\pm}$ because it only derives from precipitation and evaporite endmembers, not from weathering reactions. In the Methods, we would clarify it as such:

“Cl⁻ was included as a constrained variable in the inversion but excluded from $\Sigma^{\pm}$ normalization, as it derives solely from precipitation and evaporite endmembers and would therefore distort the normalization denominator shared across all endmembers.”

- what is meant by “other geology” (Line 802);

We agree that this is vague. We will revise “other geology” to “silicates”.

Overall, the manuscript would benefit from a more rigorous and transparent treatment of uncertainty, statistical interpretation, and data handling choices.

Upon reading Reviewer 1's comments, we understand that we were not as clear as we intended in how we handled the data. We believe these will be relatively easy revisions throughout the manuscript as our data handling choices were justified.

3 Minor Comments

3.1 Introduction

1. Lines 52–54: The wording incorrectly suggests all weathering reactions are acid–base reactions.

Thank you for bringing that to our attention. We will amend the sentence to “However, the direction and magnitude of its influence on the carbon cycle depend on the type of weathering reaction, the minerals involved, and the chemical drivers controlling mineral transformation.”

2. Lines 54–61: The discussion of long-term weathering feedbacks would benefit from additional nuance. The introduction frames carbonate weathering as being balanced over a vague 'geological timescale', but gives comparatively less attention to the longer-term implications of sulphuric acid weathering of carbonates. If the aim is to discuss which fluxes are net transfers of carbon (e.g., carbonic acid weathering of silicate minerals) versus dynamic balances between processes (e.g., carbonate dissolution and precipitation), then a more robust discussion should be included, with specific mention of the timescales of expected steady-state (e.g., the mean residence time of carbon in the ocean).

It was not our intention to discuss net transfers of carbon versus dynamic balances of processes, but to simply introduce the three most common forms of geochemical weathering (i.e., carbonate, silicate, sulfide oxidation-carbonate dissolution) and whether they were net emitters or consumers of CO₂. Since this was not clear to Reviewer 1, we agree that additional details can be added to refine this point. Specifically, we will clarify the geological timescales discussed (i.e., 10⁴ to 10⁶ years) and expand on the sentences relating to silicate weathering and sulfide oxidation-carbonate dissolution over modern and geological times.

3. Equations 1–4 (Lines 66–71): It would be easier to follow the text if the equations were embedded directly within the discussion rather than separated from it.

If we do not misunderstand, Reviewer 1 is suggesting putting the environmental stoichiometry equations directly in text such as: “For instance, carbonate weathering by carbonic acid consumes one mole of CO₂ for every mole of carbonate mineral ($\text{CaCO}_{3(s)} + \text{H}_2\text{O} + \text{CO}_{2(g)} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$) (Mackenzie & Garrels, 1966; Martin, 2017; Meybeck, 1993; Rubey, 1951; Urey, 1952).”

If this is the case, we respectfully disagree with Reviewer 1 because separating the equations from the in-line text removes clutter from the sentence structure and allows those familiar with the stoichiometry to bypass it easier.

4. Lines 82–86: This is a useful point and provides good context for the study.

Thank you!

3.2 Methods

1. Lines 404–448: The estimation of CO₂ fluxes relies on modelled gas exchange velocities (k600) derived from empirical relationships rather than direct measurements. While this is understandable given field constraints, the manuscript does not sufficiently explore the uncertainty introduced by this approach.

Thank you for understanding the field constraints of obtaining k600. We followed Robison et al. 2023 in the CO₂ flux calculations, and they did not account for uncertainty, but we can easily attend to this concern. Ulseth et al. 2019, where we derive the empirical equations for the calculation of k600 provides 95% confidence intervals. We can calculate CO₂ flux with those confidence intervals and give a range of values instead of one estimated value.

2. Lines 411–421: The detailed description of unsuccessful gas exchange approaches would likely be more appropriate in the supplementary material.

This discussion point will be moved to the Supplementary Information.

3. Lines 429–434: Increased discharge alone would not necessarily increase chemical weathering fluxes without considering concentration-discharge relationships.

This is correct. We did not intend to imply this was the case and were instead trying to explain the relationship between discharge and velocity in this section. We will clarify these sentences.

4. Lines 281–283: Weathering rates are unlikely to simply peak during daytime conditions, as multiple environmental factors may influence weathering intensity.

We will remove this sentence.

3.3 Results and Discussion

1. Lines 558 onward: The manuscript would benefit from a clearer distinction between observational results and interpretation throughout the combined Results and Discussion section.

We believe that the benefit of a combined Results and Discussion is that one can describe a result and instantly interpret it, instead of repeating the information in the separate Discussion. However, we acknowledge Reviewer 1's concerns and will work to clearly describe results before leading the discussion into the interpretation of those results for clarity.

2. Lines 564–582 and 584–620: Several downstream trends are discussed qualitatively but would benefit from clearer quantitative summaries or uncertainty estimates.

We will add specific values of CO₂ saturation to these sentences to be more quantitative.

3. Lines 588–592: Many of the reported fluxes are modelled rather than directly measured, and the discussion would therefore benefit from clearer presentation of associated uncertainties rather than only mean values. It would also be useful to compare these flux estimates with observations from other permafrost-influenced or mountainous catchments, particularly given that positive CO₂ fluxes have been reported in some comparable systems.

This is an astute observation, and we can more clearly present uncertainties. Additionally, we can add more information about CO₂ fluxes in other alpine systems. Reviewer 2 has asked that there are more comparisons of our data to CO₂ fluxes to other mountain environments so this discussion will be increased considerably to address both Reviewer's concerns.

4. Line 594: The statement that “fluxes quickly levelled” would benefit from more quantitative description. Over what downstream distance does this occur, and what is the magnitude or gradient of the observed change?

We will add specific values of CO₂ fluxes, including changes in magnitude, to these sentences to be more quantitative.

5. Line 629: Consider replacing “first-glance” with more precise scientific wording.

This term will be replaced in the manuscript.

6. Line 610: The manuscript should clarify how seasons are defined within the study (e.g., meteorological, hydrological, or temperature-based seasons). It would also be useful to discuss whether these divisions are the most appropriate representation of seasonal variability within the study region.

We will add information about how seasons were defined in Methods and discuss how these divisions may impact the results in the Results and Discussion.

7. Line 664: A substantial proportion of the Results and Discussion focuses on seasonal variability, but comparatively little quantitative information is provided describing the environmental differences between seasons (e.g., air temperature, precipitation, discharge, or land-cover conditions). If seasonality is a central focus of the manuscript, then the drivers of these seasonal differences should be explored more quantitatively.

We agree with Reviewer 1 that we did not discuss seasonality extensively. We can add information about seasonal air temperature, precipitation, and discharge to the Methods and Results and Discussion.

8. Lines 714–721: This section interprets stable carbon isotopes primarily as source tracers; however, substantial isotopic fractionation may also occur through in-stream processes such as CO₂ evasion and gas exchange. The discussion would benefit from acknowledging both source effects and fractionation processes when interpreting the isotopic data.

This is an excellent point. We will add discussion points regarding in-stream fractionation in the interpretation of the ¹³C-PIC and ¹³C-DIC isotopic data in this section.

9. Lines 738 onwards: The interpretation of changes in weathering processes would be strengthened by more direct discussion of the underlying raw geochemical data (e.g., Na/Ca trends), rather than primarily interpreting MEANDIR outputs.

Reviewer 1 is correct that the outputs are based on underlying basic geochemical data and that the discussion can be explored through this lens as well. Results and interpretation of the raw geochemical data will be added to the MEANDIR output to enhance this section.

3.4 Figures

1. Figure 3: Consider separating CO₂ saturation and fluxes into simpler panels or separate figures to improve readability.

As mentioned above, we originally did a multi-panel figure to simplify the spatiotemporal CO₂ data into one figure. However, we understand that it is a lot to interpret at once and can easily amend this into individual CO₂ concentration and CO₂ flux figures.

2. Figure 7: Include uncertainty estimates (e.g., 25–75% ranges) directly on the figure.

Uncertainty estimates will be added directly on the figure.

3. Figure 9: If these are inversion model outputs, uncertainty ranges from MEANDIR should also be shown.

Reviewer 1 is absolutely correct, and this change will be made.

3.5 Technical Corrections

1. Line 592: replace “whopping” with more formal wording.

The lead author likes to add whimsy to scientific writing but will remove this term if it is deemed necessary.

2. Line 933: correct “and and”.

Thank you, this will be corrected.

Reviewer #2:

This manuscript provides valuable data from a relatively understudied glacial watershed. Focusing on three proglacial rivers in the Canadian Rockies, the study investigates seasonal and interannual variations in meltwater quality and chemical weathering processes. Importantly, it extends the analytical framework beyond the proglacial channels to a downstream distance of 100 km, allowing for an examination of CO₂ dynamics along the flow path—a perspective that is commendable for its spatial breadth. The research clearly demonstrates that glacier-induced grinding enhances chemical weathering, positioning glacial meltwater as a notable sink for atmospheric CO₂. By integrating river water chemistry, inverse modeling, coupled organic–inorganic carbon models, and multiple isotope tracers, the study offers a comprehensive characterization of weathering processes within the catchment. The findings carry significant implications for understanding chemical weathering in glacier-fed hydrological systems worldwide, and the methodological framework presented here holds strong potential for broader application and further development in diverse cryospheric environments.

Thank you for the complimentary summary of our manuscript. We are particularly proud of its spatiotemporal reach and appreciate Reviewer 2 commenting on this strength. We acknowledge Reviewer 2's concerns about aspects of the manuscript and have addressed them below.

Major concerns:

1. The MEANDIR model employed in this study relies on global average endmember values rather than locally measured endmembers. Although the authors acknowledge this limitation (Lines 467–468), the potential uncertainty introduced by the use of non-local endmembers is not sufficiently discussed, particularly in light of the near-equal partitioning of Na⁺ among atmospheric precipitation, evaporite dissolution, carbonate weathering, and silicate weathering (Fig. 7). To better constrain the model outputs and validate the source apportionment, the authors are encouraged to supplement the analysis with endmember values derived from 2–3 locally collected rock or soil samples. Such site-specific constraints would substantially strengthen the robustness of the weathering budget calculations.

We absolutely agree that region-specific endmembers would increase the robustness of the MEANDIR geochemical weathering calculations presented in the manuscript. However, it is not possible for us to collect and analyze new samples as the data collected for this manuscript was from 2019 and 2020, and it has been many years since the research program that funded this work has existed. In lieu of new samples being collected and analyzed, we will include additional sentences about the assumptions associated with using global endmembers and what this may mean for the results.

We want to acknowledge that the benefit of doing multiple models in the manuscript is that the results from MEANDIR were independently verified with the forward model. In the inorganic-organic carbon mass balance model, we do use Ca_{nss}/Na_{nss} samples collected directly from this study as endmembers (please see **Text S1, Figure S6** in the Supplementary Information). We also used the endmember of the fraction of sulfuric acid involved in weathering from the nearest point

we could find in the literature – the western side of the Canadian Rocky Mountains, as found in Spence & Telmer 2005 (please see **Text S1** in the Supplementary Information).

2. In the absence of direct in situ velocity measurements, the estimation of FCO_2 using hydraulic geometry and empirical rating curves is inherently subject to considerable uncertainty—a common challenge in proglacial and headwater environments. Substantial spatial variability in flow velocity was observed among the glacial river sampling sites, spanning contrasting channel types—including a high-gradient riffle, a plunge pool below a waterfall, a lake outlet, and a low-gradient wetland-influenced reach.

However, the authors applied a single nominal regression (Eq. 5) across all sites without stratifying by reach-scale hydraulic characteristics (e.g., slope, bed substrate, and cross-sectional morphology). This uniform treatment likely leads to systematic bias: at the same discharge (Q), the model assigns identical velocity (V) to both high-gradient torrents and low-gradient slow-flowing reaches, thereby underestimating V at steep sites and overestimating it at quiescent sites. Such aggregation may compromise the accuracy of reach-scale gas exchange estimates and warrants careful consideration.

Authors should revisit the velocity–discharge relationship by grouping sites according to their dominant hydraulic typology, or alternatively, incorporate reach-specific coefficients where feasible. If direct velocity measurements are unavailable, we recommend a sensitivity analysis to evaluate how the assumed velocity–discharge parameterization influences the overall FCO_2 budget, and to explicitly discuss the associated uncertainties in the context of inter-site comparisons.

The velocity–discharge relationship could be refined by stratifying sites based on hydraulic typology or, where possible, by incorporating reach-specific coefficients. Given the lack of direct velocity measurements, a sensitivity analysis would be useful to assess how the current parameterization affects FCO_2 , and the resulting uncertainties merit explicit discussion across sites.

We thank Reviewer 2 for acknowledging that the quantifying CO_2 fluxes is particularly difficult in headwater rivers. We did use a single power relationship because, from 2019 to 2021, Water Survey of Canada only measured 56 matching Q and V points at the four sites along the study rivers on which the equation is based. Instead of doing each river separately, or assuming that the relationship at one site along the Sunwapta River, for example, explains all the sites along that same river, we pooled the 56 points into one equation. As such, in Methods, we expressed that any velocities derived from the power relationship were estimates only, but we will add more information about what this means for the subsequent flux calculation uncertainties.

Due to the lack of information regarding the hydraulics of our study reaches, we agree that it is likely that while some velocities are overestimated, others may be underestimated. However, we want to clarify that velocity is only used, *along with with slope and gravity*, to determine the energy dissipation rate (eD), or quantification of turbulence. $eD = 0.02$ is a turbulence threshold for $k600$, above or below which the value of eD does not bear significance for further calculations (based on Ulseth et al. 2019). In looking back at our data, the only sites that had $eD < 0.02$ were SR2 and

NSR2. An $eD > 0.02$ is expected in steep mountain proglacial rivers, and as such, nearly all of the k600s were calculated with Eq. 8 (in text). To ensure that Eq. 8 is the appropriate calculation for the majority of our sites, we will take Reviewer 2's suggestion to do a sensitivity analysis for how changes in velocity estimations may impact CO₂ fluxes. Additionally, in response to Reviewer 1 above, we will be adding uncertainties in our flux calculations based on the 95% confidence intervals presented for k600 in Ulseth et al. 2019.

3. Beyond error and sensitivity analyses for FCO₂ estimates, an alternative approach is to bypass the velocity-to-K conversion by using a mass balance model to estimate the FCO₂ exchange potential of glacier-fed runoff, as demonstrated in recent studies (Kleber et al., 2024; Ragnoli et al., 2025). Such methods may provide independent constraints and reduce uncertainties inherent in hydraulic parameterization.

[Kleber G, Magerl L, Turchyn A, et al. Proglacial methane emissions driven by meltwater and groundwater flushing in a high Arctic glacial catchment[J]. *Biogeosciences*, 2024, 22: 659-674.

Ragnoli, M D, Martini J, Jechsmayr B, et al. Probing dissolved CO₂ and CH₄ in glacial streams of the European Alps[J]. *Arctic, Antarctic, and Alpine Research*, 2025, 57(1): 2580737.]

Thank you for these references and providing another means of calculating CO₂ flux in our system. We will certainly discuss this approach in text but are unsure it would lead to less uncertainties than we have with our current approach. If we are understanding correctly, Reviewer 2 is suggesting a mass balance of DIC based on groundwater and tributary inputs, weathering reactions, biological CO₂ production and consumption, and discharge. Unfortunately, we do not have an estimate of groundwater or tributary inputs in our rivers and discharge itself is modeled at 12 of the 14 sampling sites. The quantification of weathering reactions, including carbonate dissolution, silicate weathering, and/or sulfide oxidation-carbonate dissolution all have different uncertainties depending on whether we used the MEANDIR inverse model or inorganic-organic carbon mass balance forward model approach. Additionally, we are in the process of assessing aquatic metabolism in our rivers for another manuscript. While we have found, however, that the majority of the rivers biologically net respire, again given the difficulty of working in proglacial rivers, we are finding direct quantification impossible and estimations with considerable error must be produced.

In short, in using a mass balance approach to avoid the uncertainty of velocity in our current approach of calculating CO₂ flux, we would be adding several major parameters and their potentially large uncertainties. We ultimately agree with Reviewer 2 that there are uncertainties related to the hydraulics in our river systems but believe them to be less egregious than those in the mass balance model for our specific study.

4. The comparison with other glacial catchments worldwide remains insufficient. Only a limited number of sites (e.g., Rhône, Greenland) are referenced, whereas systematic

comparisons with typical glacierized basins in the Himalayas, the European Alps, and the Andes—in terms of weathering styles and fluxes—are lacking.

A comparative table summarizing weathering types and fluxes across global glacial catchments would be valuable, which could help highlight the distinctiveness of the present study, particularly its multi-seasonal sampling and longitudinal gradient design.

We can absolutely add more comparisons of weathering types and fluxes in other global glacial catchments. We are happy to make this relatively easy addition to enhance the strength of the manuscript.

5. A comparative analysis with existing studies on greenhouse gas dynamics in glacier-fed rivers is currently lacking. Numerous investigations have been conducted worldwide on the concentrations and diffusive fluxes of CO₂ and CH₄ in glacial meltwater streams, including those from the Greenland Ice Sheet, the Himalayan glaciers, the European Alps, and Alaska.

It would be beneficial to expand the discussions in Sections 3.1.1 and 3.1.2 by including a systematic comparison of CO₂ concentrations and fluxes observed in the present study with those reported from other major glacial regions. Such a comparison would help highlight the distinctive CO₂ dynamics of the studied glacial meltwater—encompassing concentration magnitudes, flux directions and amplitudes—and facilitate a broader discussion of the underlying controlling factors and mechanisms.

In response to comments made by Reviewer 1 and Reviewer 2, we will add more global comparisons of CO₂ concentrations and fluxes and discuss the global context of our sampling strategy and results more in-depth. To do this, we will conduct a systematic review of Google Scholar, Web of Science, and Scopus databases for published manuscripts and grey literature using key root words like “glacier” and “CO₂” and Boolean operators.

Minor Comments

1. Section 2.3 (Sample collection and analyses) is overly detailed in its current form. A streamlined version highlighting the key methodological approaches would improve readability, while supplementary details could be moved to the Appendix.

We added information to Section 2.3 at the request of the Associate Editor at Biogeosciences, who asked for more details. We can easily remove those details or move them to the Supplementary Information.

2. In Section 3.1.1, dissolved CO₂ is discussed primarily in terms of percent saturation (Line 558). However, the more direct and interpretable metric would be the aqueous CO₂ concentration (e.g., μM). It is suggested that concentrations be used as the primary variable, with the atmospheric equilibrium concentration also plotted in the figures to facilitate clearer visual interpretation.

This is a fair point. We will make the change from CO₂ saturation to CO₂ concentrations throughout the manuscript text and figures.

3. The presentation of data in Figure 3 (L577–579) is not particularly reader-friendly. It is suggested that the figure be restructured to display boxplots that distinguish among seasons, glacial catchments, and distance from the glacier terminus.

Figure 3 was also commented on by Reviewer 1 for having too much information in one figure. We will first change CO₂ saturation to CO₂ concentration, as suggested by Reviewer 2 above. We will then split the figure into two, as suggested by Reviewer 1 above. We will plot data in boxplots or other simplified figures to allow for spatiotemporal variables to be seen more clearly.

4. In Section 3.1.2 (L586), the units for FCO₂ should be expressed as –149 to 56 mg CO₂ m^{–2} d^{–1} to match the values shown in the figure. The statements in L587–592, particularly the comparison that "the most negative flux was nearly 12 times more CO₂ consumptive than tropical forests and a whopping 166 times more CO₂ consumptive than the tundra," require careful verification. Correspondingly, the relevant discussion in the Conclusions (L945–948) should also be reviewed and revised accordingly.

Thank you for catching the error in units throughout section 3.1.2 – they will be revised accordingly and will match the revised **Figure 3**. The information from L587–592 was taken from the IPCC (2001) report, which have been carefully verified by a panel of expert scientists. We will review the source material again closely and if this information is incorrect, we will remove it from the manuscript.

5. At L609–610, Table S4 is cited in support of seasonal contrasts in instantaneous CO₂ fluxes, but the required data are not presented in the table. Correction or supplementation is advised.

We apologize for this confusion. We were meaning to cite the binned dates that represented each season but see now this was confusing. We will move this citation to Methods where we intend to discuss season more explicitly as per Reviewer 1's comments (please see above).

6. In Figure 10b, silicate contributions show an increasing trend with distance from the glacier, but the correlation is extremely weak ($R^2 = 0.109$). Although the p-value is significant ($p < 0.001$), this significance is likely driven by the sample size rather than a meaningful relationship. In addition, it is suggested that for Figure 10a, the correlation statistics (R^2 and p-value) for the relationship between % of total DIC (from carbonate and atmospheric sources, and from organic matter) and distance from the glacier be included, so as to better quantify the downstream evolution of DIC sources.

We will amend our language in Section 3.4 to more clearly explain that the increase of silicate weathering downstream is a weak relationship and discuss sample size, though we would like to note that this mild trend has been independently verified using the MEANDIR inversion model. The correlation statistics for % of total DIC will be additionally added to panel 10a.

Literature Cited

Burke, A., Present, T. M., Paris, G., Rae, E. C. M., Sandilands, B. H., Gaillardet, J., Peucker-Ehrenbrink, B., Fischer, W. W., McClelland, J. W., Spencer, R. G. M., Voss, B. M., & Adkins, J. F. (2018). Sulfur isotopes in rivers: Insights into global weathering budgets, pyrite oxidation, and the modern sulfur cycle. *Earth and Planetary Science Letters*, 496, 168–177. <https://doi.org/10.1016/j.epsl.2018.05.022>

Gadd, B. (2009). *Handbook of the Canadian Rockies*. Corex Press.

IPCC. (2001). *Climate Change 2001: The Scientific Basis*.

Kemeny, P. C., & Torres, M. A. (2021). Presentation and applications of mixing elements and dissolved isotopes in rivers (MEANDIR), a customizable MATLAB model for Monte Carlo inversion of dissolved river chemistry. *American Journal of Science*, 321(5), 579–642. <https://doi.org/10.2475/05.2021.03>

Robison, A. L., Deluigi, N., Rolland, C., Manetti, N., & Battin, T. (2023). Glacier loss and vegetation expansion alter organic and inorganic carbon dynamics in high-mountain streams. *Biogeosciences*, 20(12), 2301–2316. <https://doi.org/10.5194/bg-20-2301-2023>

Spence, J., & Telmer, K. (2005). The role of sulfur in chemical weathering and atmospheric CO₂ fluxes: Evidence from major ions, $\delta^{13}\text{C}_{\text{DIC}}$, and $\delta^{34}\text{S}_{\text{SO}_4}$ in rivers of the Canadian Cordillera. *Geochimica et Cosmochimica Acta*, 69(23), 5441–5458. <https://doi.org/10.1016/j.gca.2005.07.011>

Ulseth, A. J., Hall, R. O., Boix Canadell, M., Madinger, H. L., Niayifar, A., & Battin, T. J. (2019). Distinct air–water gas exchange regimes in low- and high-energy streams. *Nature Geoscience*, 12(4), 259–263. <https://doi.org/10.1038/s41561-019-0324-8>

Voss, B. M., Eglinton, T. I., Peucker-Ehrenbrink, B., Galy, V., Lang, S. Q., McIntyre, C., Spencer, R. G. M., Bulygina, E., Wang, Z. A., & Guay, K. A. (2023). Isotopic evidence for sources of dissolved carbon and the role of organic matter respiration in the Fraser River basin, Canada. *Biogeochemistry*, 164(1), 207–228. <https://doi.org/10.1007/s10533-022-00945-5>