Review of Spatiotemporal patterns in CO_2 fluxes and geochemical weathering in mountain glacial rivers

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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.

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.

   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.

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

   Additional clarification is also required regarding:

   - the origin of the 15% inversion error threshold (Lines 479–480);
   - the specific cost function used in the inversion (Line 481);

- 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 treatment of uncertainty propagation throughout both modelling frameworks.

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 $\delta^{34}S$ endmember ranges to define pyrite, evaporite, and precipitation sources. However, the manuscript also presents data from the Canadian Rockies showing substantial overlap between the $\delta^{34}S$ 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 $\delta^{34}S$ 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.

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;
   - the large oversaturation at BR2 deserves more explicit discussion;
   - downstream trends in Figure 7 are difficult to interpret without uncertainty estimates;
   - Figure 10 would benefit substantially from inclusion of the raw $\delta^{13}C$ data alongside the model outputs.

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

   - inclusion of the geological cross-section locations directly on the map;
   - addition of scale information for the cross-sections;
   - consideration of a simplified geological map for reference.

   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.

   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.

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.

   Other methodological concerns include:

   - the use of half detection-limit substitution without discussion of how this may affect distributions and uncertainty;
   - selective exclusion of AR1 data when tributary influence was considered large, which would benefit from additional justification;
   - the interpretation of an R^2 value below 0.2 as a meaningful correlation without reporting p-values;
   - the use of terms such as "strong" for relatively weak relationships;

   Additional methodological clarity is also needed regarding:

   - whether Cl^- is missing from the normalisation described around Line 460;
   - what is meant by "other geology" (Line 802);

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

3 Minor Comments

3.1 Introduction

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

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).

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.

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

3.2 Methods

1. Lines 404–448: The estimation of CO_2 fluxes relies on modelled gas exchange velocities (k_{600}) 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.

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

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

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

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.

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

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 CO_2 fluxes have been reported in some comparable systems.

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?

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

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.

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.

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 CO_2 evasion and gas exchange. The discussion would benefit from acknowledging both source effects and fractionation processes when interpreting the isotopic data.

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.

3.4 Figures

1. Figure 3: Consider separating CO_2 saturation and fluxes into simpler panels or separate figures to improve readability.

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

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

3.5 Technical Corrections

1. Line 592: replace "whopping" with more formal wording.

2. Line 933: correct "and and".