

Anonymous Reviewer #1

Zolkos et al., present a high quality characterisation of running water chemistry in a sub-catchment of the Peel River where the aim was to determine the effect of retrogressive thaw slump (RTS) on DIC sources and export. The study design, incorporating three transects at different spatial scales (1. retrogressive thaw slump (RTS) runoff water, 2. an intermediate size catchment with direct fed with RTS runoff, 3. A large catchment fed indirectly with RTS runoff through its tributaries), is an interesting and innovative sampling approach. The dataset, including a large number of key variables, is also of very high quality. The research question is also highly relevant to our understanding of the permafrost climate-feedback. The author rightfully stated that changes in carbonate alkalinity export in response to permafrost degradation has been far less studied than those for organic carbon and carbon dioxide. The study is also taking place in a relatively understudied region, which makes it even more valuable. While the subject and design of the study is of high quality, I find that the discussion and conceptualisation of the result need significant improvement. In short, the paper does not make full use of its potential.

The novelty of the paper lies in the approach of scales on the effect of RTSs on DIC export. At the moment, these three scales are taken separately, into three almost individual studies. Is the message simply that we can perceive the RTS effect at each of those three scales or is there a greater interpretation of how these effects integrate with increasing spatial scale and decreasing land-water connectivity? The paper would have more impact if the author could conceptualise these results and formulate how RTSs affect DIC cycling across scales rather than simply testifying that it has an influence. For example, does the “RTS effect” amplify, is conserved, accumulates or becomes diluted with increasing scale. The author already documented that RTSs alter riverine DIC cycling in a previous publication in GRL (Zolkos et al, 2018). At present, this manuscript adds little to this state of knowledge, but this could be remediated by conceptualising further the effect of scales.

I have made a few suggestions to improve the presentation of results and conceptualisation of the discussion.

Thank you for the thoughtful and constructive feedback. Regarding your questions and comments above: Good question about the nature of RTS effects across scales (e.g. is it amplified, conserved, diluted, etc.). Effects on DIC are clearly amplified in headwaters. While CO₂ diminishes rapidly within headwaters, the HCO₃⁻ signal is preserved at broader scales. We use circumstantial evidence to infer the latter point in Zolkos et al. (2018), which focuses on biogeochemical effects immediately downstream of RTSs and leverages long-term Peel River data to assess changes over time. Our current study investigates processes occurring between headwater streams and the larger Peel River. We therefore contend that our current manuscript builds on our 2018 GRL paper and improves understanding of RTS effects on C cycling. We believe our edits help to clarify these points, in part by addressing your helpful suggestion to better conceptualize the effects of scale. Below, please find replies to your comments.

The sampling design is interesting and valuable, but arguably difficult to communicate to the reader. Having the Results and Discussion section together makes it even harder for the reader to put together the key results, and follow the discussion points that are mixed through the text. I recommend to separate these two parts. The first part of the results and discussion section details the changes in water chemistry in each of the three transect. The first part of the Result and Discussion section (section 3.1, 3.2 ad 3.3) details the water chemistry patterns in each transect with discussion points mixed through the text. Having this structure increases the impression that this study actually involves three separate studies rather than one. I suggest to also structure the results by water chemistry variable rather than sites. The study measured a large number of important and interesting water chemistry variables. Each should be presented clearly in the result section for the reader to identify. Each sections should provide, among other things, the overall range in values for the whole study, compare this range between each of the three scales and within each transect.

Great points. Thank you for the helpful suggestion. We restructured the manuscript so that Results and Discussion are presented separately. In the revised Results section we discuss results by hydrochemical parameter and present ranges of values, as you suggest.

Rather than naming the sites by their official river name, why not call them with a more conceptual name that represents the idea behind the sampling design. I like that the symbols in figures have numbers to indicate their position along the transect, but RTS FM2 site DC and SC has little meaning for the reader. I have also provided a few suggestions below to format the figures in a more visually telling way.

We appreciate the suggestion, but will use the official names for continuity with the literature. Our edits were made with this in mind, to improve demarcation between the different watershed scales.

Playing with your dataset I attempted to trace the $\delta^{13}\text{C}$ source with the miller-trans plots, I found a clear difference in that value for the RTS runoff site ($\delta^{13}\text{C}_{\text{source}} -12\%$ and the DC and SC rivers (-22.9%). This suggest two predominant CO_2 sources in this catchment and those end-members could potentially be used for calculations. The RTS site is consistent with a geogenic CO_2 source, while the rivers have a predominant biogenic soil CO_2 source. Would it be worth including this kind of approach to your results?

Thanks for the suggestion. We explored Miller-Tans plots, but do not have enough samples from undisturbed headwaters ($n = 3$) to trace CO_2 sources with this approach. We agree that $\delta^{13}\text{C}-\text{CO}_2$ values reflect at least two predominant CO_2 sources in the catchment. Together, our $\delta^{13}\text{C}-\text{CO}_2$ values and $\delta^{13}\text{C}-\text{DIC}$ vs. pH plot reflect spatial trends in DIC and CO_2 sources (atmospheric, soil biotic, mineral weathering). Building on this plot and following your suggested changes to the conceptual diagram, we clarify the relative importance of biotic versus mineral weathering sources for CO_2 and DIC, and how sources may change with movement downstream.

The effect of scales, with a varying degree of terrestrial connectivity, is only discussed in the context of circumpolar region with, but I believe that the study should also be put in the context of the broader literature, including lower latitude catchments, where many studies have also examined the effect of changing land-water connectivity with size.

Yes, good point. We added brief text towards the end of the manuscript which considers this.

I find it interesting to see the downstream changes in HCO₃ concentration. It could be worth mentioning that studies modelling stream CO₂ evasion based on δ¹³C_{CO₂ value assume that carbonate alkalinity is conserve in river networks (Polsenaere 2012 Geochimica et Cosmochimica Acta and Venkiteswaran 2014 PLOS one).}

Good point. Though, this assumption will not hold true where changes in catchment lithology, groundwater inputs, etc. influence carbonate alkalinity. Nevertheless, it is interesting, so we have added brief text considering this.

The term thermokarst and retrogressive thaw slumps are used interchangeably, I suggest to stick to retrogressive thaw slumps since this was the focus of the study and the findings may not be applicable to all kinds of thermokarst disturbances.

Thank you for the suggestion. We have replaced thermokarst with retrogressive thaw slump where we discuss trends specific to the Peel Plateau. We retain “thermokarst” when we are discussing these effects from a broader perspective.

The term “abiotic-inorganic processes” is a vague term to me, what are the processes included in that? Carbonate equilibrium reaction and CO₂ evasion? Could you be more specific? Either a more specific term should be used or the choice of terminology should be justified in the text.

Clarified.

Abstract: Line 21:26: The results/discussion section of the abstract list changes in water chemistry in each of the three transect. I believe this section, and other relevant section in the main text, should come up with a more unified message of the RTS effect across scales, rather than at individual scales.

Thank you for the suggestion. Please see our reply to your major comment, above.

Line 30: I have trouble with the word “prevalent” here since it implies that one is larger than the other, while such calculations have not been done in the study.

Revised.

Introduction: Lines 32-33: This first sentence would introduce better the second paragraph where the source/sink relationship of DIC is detailed. This first paragraph discusses how the arctic landscape is changing and what is known of its influence on DIC export.

Thanks for the helpful suggestion. Revised.

Lines: 41-44: Since we include CO₂ in this pool, the increase in soil respiration and/or increase in aquatic DOC degradation should also be part of this list. The citations be separated to indicate which if the listed mechanisms have been highlighted by each study.

Revised.

Lines 47-64: This is mostly textbook material and could be synthesised. I think what you want to express is why it's important not only to account for the mass of DIC exported but also to identify its sources DIC. Without this we can't determine whether this is a new sink or source of C in the short and long term perspective. I would suggest to move some of this information in section 2.5 of the methods and rework this paragraph to emphasise the simply the importance of source separation for DIC.

Fair point. We have modified the text but choose to discuss much of the original concepts, because our manuscript intends to target permafrost biogeochemists, who typically consider processes over contemporary timescales and processes associated with organic matter decomposition. So, this "textbook" information is provided – in part – to emphasize to this community the importance of incorporating weathering processes into consideration of the short- and long-term effects of permafrost thaw on biogeochemical (especially carbon) cycling.

Line 65: Could you state the representativeness of this study, which areas across the circumpolar north could be similar to your studied location?

Revised.

Line 94: This is a very important point which I think should be stated earlier in the introduction and given more emphasis.

Text added earlier in the Introduction to elaborate on this point.

Methods Line 133: How deep are those rivers? Can stream order be provided somewhere too.

We were not equipped with instruments to safely measure the depth of the rivers and unfortunately this information is not known. We have added stream order to Appendix Table A1.

Section 2.3 This is a nice way to work around flow measurement scarcity in this region. But should this section come after section 2.6?

Yes, this is more closely related to statistics and logically could be placed just before Sec. 2.7. Revised.

Line 212: What threshold was used in the flow accumulation to delineate the stream lines and catchment boundary? Was it validated with the areal photos mentioned on line 155 or something else?

We have clarified these methods in our ‘Geospatial Analyses’ section. Briefly, geospatial data were validated by modifying as needed to align with stream networks visible in moderate-resolution (10 m) Sentinel-2 satellite imagery, following St. Pierre et al. (2018).

St. Pierre, K. A., Zolkos, S., Shakil, S., Tank, S. E., St. Louis, V. L., & Kokelj, S. V. (2018). Unprecedented increases in total and methyl mercury concentrations downstream of retrogressive thaw slumps in the western Canadian Arctic. Environmental Science & Technology, 52(24), 14099-14109.

Section 2.4, shouldn't this section be called water chemistry analysis?

Changed to “Hydrochemical Analyses”.

Line 245: Why not model the full carbonate alkalinity pool ($\text{HCO}_3^- + \text{CO}_3^{2-}$)? Arguably the CO_3^{2-} pool is small at this pH range and shouldn't make a much difference to the model, but I find this conceptually more appropriate.

We agree that using $[\text{HCO}_3^- + \text{CO}_3^{2-}]$ is conceptually more appropriate. We re-ran the model using carbonate alkalinity and yes, it is essentially identical to using only HCO_3^- . Nevertheless, we revised the results (Table 2) and text to reflect the updated model.

Results and Discussion

Section 3.1, 3.2 and 3.4 starts with a sentence stating how the author interprets DIC sources and cycling in each transect. This seems odd to me. I would rather the author takes me to that conclusion by presenting the results first.

Thank you for the suggestion. We believe that our revisions, which include splitting the Results and Discussion, address your suggestion.

Line 275: The Miller-tans analysis supports that as well. Again, this statement comes before presenting the key results.

Although we have not done a Miller-Tans analysis, for the reasons described above, our edits were done with an eye to elucidating the processes and sources which contribute to DIC in this system.

Line 290: Is the term “geogenic” more appropriate?

Revised.

Line 285: Probably right, but do you have any measurements or estimates of CH₄ concentration at the source - in the groundwater? The CH₄ might have evaded already, but its imprint on δ¹³C_{CO₂} values might still be there.

Unfortunately, we do not have any measurements of [CH₄] in groundwater.

Line 301: That is also supported with the Miller-tans. But this biogenic soil CO₂ source seems to prevail in other sites as well albeit with some mixing with the geogenic source. Could mixing between the H₂SO₄ weathering and biogenic soil CO₂ be back calculated?

n = 1 in the Dempster Creek headwaters, so it is supported by the Miller-Tans analysis when data from all sampling points are considered. Also, [CO₂] and stable isotopes alone would provide only a very rough estimate of the proportions of biogenic CO₂ and abiotic CO₂, the latter of which may also be sourced from H₂CO₃ carbonate weathering ~ DIC speciation reactions, and atmospheric CO₂. As we lack the measurements (e.g. ¹⁴C of CO₂) to make more robust estimates of CO₂ contributions from these varied sources, we do not attempt this.

Line 314: This is also demonstrated in headwater streams at other latitudes and should be mentioned as well.

Yes, good point. Elaborated and citations added, such as:

*Campeau, A., Lapierre, J. F., Vachon, D., & del Giorgio, P. A. (2014). Regional contribution of CO₂ and CH₄ fluxes from the fluvial network in a lowland boreal landscape of Québec. *Global Biogeochemical Cycles*, 28(1), 57-69.*

*Hutchins, R. H., Prairie, Y. T., & del Giorgio, P. A. (2019). Large-Scale Landscape Drivers of CO₂, CH₄, DOC, and DIC in Boreal River Networks. *Global Biogeochemical Cycles*, 33(2), 125-142.*

Line 314; Again I find this term “abiotic inorganic” to be vague. And what do you mean by dominates? Abiotic dominates biotic, or inorganic dominates organic?

Clarified.

Line 351: What does “amplified inorganic carbon cycling” means?”

Clarified.

Line 371: The term biotic is used here, but could the DOC be degraded photochemically as well?

Although photochemical degradation of DOC could lower $\delta^{13}\text{C-CO}_2$ values (references below), these streams are very turbid and therefore photodegradation is likely limited.

*Opsahl, S. P., & Zepp, R. G. (2001). Photochemically-induced alteration of stable carbon isotope ratios ($\delta^{13}\text{C}$) in terrigenous dissolved organic carbon. *Geophysical Research Letters*, 28(12), 2417-2420.*

*Vähätalo, A. V., & Wetzel, R. G. (2008). Long-term photochemical and microbial decomposition of wetland-derived dissolved organic matter with alteration of ^{13}C : ^{12}C mass ratio. *Limnology and Oceanography*, 53(4), 1387-1392.*

Line 380: Is the model intended only to bring evidence to the fact that RTS increase alkalinity export or for a possibly larger modelling/budget exercises? Could you make use of that model already in this paper for a final “wrap up” exercise?

The model was intended to assess the influence of various landscape characteristics (including RTSs) on carbonate alkalinity yields (please see Section 2.7). We refrain from exercises on larger budgets of carbonate alkalinity, as our model reflects a snapshot of DIC dynamics within a relatively local area.

Line 393: Dominate over what?

Revised.

Line 405: This “conceptual model of land-freshwater linkages” needs more elaboration. As it stands, this model seems more like a list of DIC sources and sinks across this catchment than a generalisable model. A starting point would be to determine how does it integrates with other models at lower latitudes? How do changes in DIC sources and sinks caused by RTS integrates with other water chemistry properties and C species (organic vs inorganic) that were documented in other studies?

Good point and, as noted in our reply to your comment on Figure 8 (below), we agree that the current conceptual diagram is fairly specific to the Peel Plateau. We believe the revised diagram helps to generalize our findings and, with revisions to the text, address your comments here.

Line 410: What exactly was “striking”?

Clarified.

Line 414-418: How does this conclusion differ from the authors previous publication cited here?

A key difference is the nested watershed/transect approach, which allows us to elucidate mechanisms and how they change downstream. Clarified.

Line 432: Should your model be used to that effect? If so, it should be stated.

Revised.

Line 443: “ change for C cycle in the rapidly changing arctic landscape”

Revised.

Authors Contribution What did D.O. do?

All authors contributed to manuscript writing. Clarified.

Figures and Tables

Table2: Should these values be presented in supplementary and only the model be presented in this table? I find the second part of the table easy to miss.

We feel that the values in the upper panel are important to include in the main text and agree that the lower panel may be easy to miss. To address this, we revised the first sentence of the table caption to draw attention to both the upper and lower panels.

Figure 1: The map feels quite dense, can the photos and context map be placed outside? Could the bedrock lithologies be illustrated on the map?

Thank you for the helpful suggestion. We revised the map and the individual components now have more space. Unfortunately, there are no high-resolution GIS data of bedrock lithology available.

Figure 2: The figures should be placed vertically rather than horizontally since they have the same x-axis. Also in caption, please clearly state that the top x-axis is for the Dempster Creek transect while the second is for the Stony Creek. Could the points for each transect be connected with a line for visualisation. Could HCO₃ and CO₂ concentration be on the same unit? Could there be a third axis for the distance along the RTS runoff transect?

Good suggestion to consolidate x-axes by stacking the figures. Revised. Following your other helpful suggestion, we have also included DOC and SUVA₂₅₄ in Fig. 2.

Caption revised to distinguish between the RTS FM2 runoff, Dempster Creek, and Stony Creek x-axes.

We choose to omit lines connecting the points and, as noted in the caption, instead label consecutive downstream points with their corresponding site numbers; we reserve lines to indicate significant trends.

We like and appreciate your suggestion to report CO₂ in μM , which could help to facilitate a more direct comparison with the HCO₃⁻ concentrations shown in Fig. 1a. However, for Fig. 1b, we choose to report CO₂ in units of partial pressure rather than μM , to make a more intuitive link with atmospheric CO₂. For the readers' reference, CO₂ in μM is reported in Table 1.

We have added a third axes for RTS FM2 runoff and plotted the data (as in Table 1).

Figure 4: Can you give a reference to these end-members

Thank you for the suggestion. In the caption, we added a reference to Methods Sec. 2.4, in which we briefly elaborate on these methods and cite a publication used to derive the end-members (Zhang et al. 1995).

*Zhang, J., Quay, P. D., & Wilbur, D. O. (1995). Carbon isotope fractionation during gas-water exchange and dissolution of CO₂. *Geochimica et Cosmochimica Acta*, 59(1), 107-114.*

Figure 5: Open vs closed symbols would be clearer perhaps?

Thank you for the suggestion. This does appear to help. Figure revised.

Figure 6 and 7: Should these two figures be merged with Figure 2? This would help draw a more complete picture of simultaneous changes in water chemistry along the transects. Why isn't there a similar figure for d¹³C-DIC values?

Good idea. We have included the DOC and SUVA₂₅₄ plots as part of Fig. 2. We choose not to replicate this plot style for $\delta^{13}\text{C}$ -DIC, because the downstream trends in $\delta^{13}\text{C}$ -DIC are shown in Figures 4 and 5.

Figure 8: This is a nice schematic, but it limits the scope of the study. The schematic mostly lists the sources and transformation of DIC in this catchment. Does it only apply to this catchment, i.e. was the goal to map those processes, or can it be generalised to other catchments? I think this figure could be useful if it was to conceptualise the effect of RTS across scales, not just make a summary of all the processes identified in the data for this specific catchment. I have in mind something along the lines of Hotchkiss et al. 2015 NatGeo Figure 3.

Thank you, we agree that the figure is somewhat limiting and we appreciate your suggestion to broaden the scope of our conceptual diagram. We believe the revised conceptual diagram helps to generalize our findings.

Table A1. Why not keep the distance units the same and just add decimals for FM2 site.

Yes, good point! Revised.

Table A2: I find this could be useful in the main manuscript since it also provides a list of the DIC sources you are trying to separate.

Good suggestion. Added to main text.