Response to Reviewers of bg-2020-472

General response to the Editor

Associate Editor's comments:

Dear Authors,

I thank you for your comprehensive revision integrating all the comments and suggestions from the first review round.

A reviewer involved in the first review round has kindly provided another set of very considerate and constructive comments. This reviewer, like myself, thought that your careful revision would further improve the manuscript while reducing some lingering uncertainties that are detailed in the attached reviewer report. Regarding the issue of the term "headwater streams", your perusal of the hydrology literature, in addition to the reviewer comment, would fix the nonsense in sentences like "The Shaliu River is composed of first- to third-order streams (Figure 1a) and hence a typical headwater stream": in other words, a headwater stream consists of headwater streams.

As you did well during the first revision, please make all the changes easily identifiable in a marked-up manuscript and specify the line numbers of the marked-up manuscript in your responses to the reviewer comments.

Sincerely,

Ji-Hyung Park

Associate Editor, Biogeosciences

We sincerely thank the editor and reviewers for the considerate and constructive comments. Following their suggestions, we have made important changes to our manuscript, including the definition of headwater stream and the description of our study site when referring to headwater stream. Please refer to the track change version of manuscript for details.

For your convenience, the original comments are listed below in black and our replies follow in blue font. Line numbers listed below corresponds to the revised version with track changes. As shown in our detailed responses, we have made every effort to address the concerns of all reviewers. We sincerely hope that our responses have adequately addressed all the comments. Thank you again for your consideration.

Response to Reviewer #1's comments

The revised manuscript is much improved. Well done by the authors. While it could be on track for publication, there are a few important considerations and perhaps one methodological error that must first be addressed. Please see my comments below, which are intended to be positive and constructive. I would be happy to review a revised version of the manuscript and I again commend the authors for the great progress they have made with this manuscript.

We greatly appreciate the reviewer's positive assessment of our (first) revision and manuscript. We have made substantial changes to our manuscript and hope that our responses have adequately addressed all the comments.

Major comments:

1. What were the units for discharge when you modeled constituent fluxes with LOADEST? From your SI dataset, it seems that you used $m^3\ s^{-1}$? As detailed in Runkel et al. (2004),

LOADEST takes discharge in units of $ft^3 s^{-1}$. If you used $m^3 s^{-1}$, then your constituent modeling must be updated and associated values throughout the text corrected (e.g., Sec. 3.1). Of course, this would be relatively easy to do! This being said, I agree with reporting discharge in metric units ($m^3 s^{-1}$) in the main text (e.g., L210), as is commonly done.

Runkel, R. L., Crawford, C. G., & Cohn, T. A. (2004). *Load Estimator (LOADEST): A FORTRAN program for estimating constituent loads in streams and rivers* (No. 4-A5). https://pubs.usgs.gov/tm/2005/tm4A5/pdf/508final.pdf

Thank you! Our original phrase may be vague. The units for discharge were actually cubic feet per second ($ft^3 s^{-1}$) when we modelled constituent fluxes with LOADEST. The daily discharge is reported in metric units ($m^3 s^{-1}$) in the main text and SI dataset. The above explanations are added in *Line 196*.

2. Following on Dr. Park's comment about headwater streams: Headwaters are generally the smallest surficial fluvial component within a stream network. I read Meyer and Wallace (2001) and could not find where they explicitly state that headwaters include 1st to 3rd order streams, as your citation in L34 implies… but please feel free to prove me wrong about this! The lowest stream order is not necessarily a headwater stream, because definitions of stream order are relative and can vary depending on the resolution of the data used to determine stream order. For instance, stream order derived from geospatial data like a DEM (often relatively coarse, e.g., 90 m from Lin et al., 2019 WRR) may be quite different than stream order determined by an expert in the field or using high-resolution satellite imagery to visually map streams. From Google Earth imagery and your Figure 1, sampling points SLH2–5 do not appear to be headwater streams, and I am not convinced that SLH0–1 are, either. All this to say, I am not convinced that the streams in your study are truly headwater streams and I would not use GIS-derived estimates of stream order (or the citation to Meyer and Wallace 2001) to try to assert this. I think it would be appropriate to place less emphasis on interpreting your results as direct measurements of headwater streams. I think this does not require a major rewrite of your paper and can be addressed without too much trouble by modifying the very nice text that you have in the Introduction and elsewhere. For instance, you could reason that your sampling points capture the integrated hydrochemical signal across headwater catchments. This would be compelling and more accurate. Clarifying this, and omitting ‘headwater’ where appropriate, would more accurately represent your study sites without comprising the overall relevance of your research, or its significance for understanding hydrochemical signals within headwaters of the QTP.

Good point! Definition of headwater streams is a long-standing conundrum for researchers. Admittedly, we made a mistake in citation of the correlation of headwater stream with stream order. Headwater streams are considered to be first- and second-order streams (Meyer and Wallance, 2001), while they are grouped into first- to third-order streams in the report of Vannote et al. (1980). Anyway, use of stream order to define headwater streams is problematic because, as you mentioned here, stream-order designations vary depending upon the accuracy and resolution of the stream delineation.

Given the lack of a universal and spatially-explicit definition of headwater streams, we revise the texts on the definition of headwater streams, the description of our study site, and the discussion of Shaliu River as “a typical headwater stream”. In addition, the title is revised to “spatial-temporal variations in riverine carbon strongly influenced by local hydrological events in an alpine headwater catchment”, because our study site captures the integrated signal across headwater catchments (rather than a stream within a narrow channel). Detailed revisions are in *Lines 17, 28, 31, 34, 71, 84, 88, 91-92, 396, 405*. We sincerely appreciate your considerate comments!

Reference:

Meyer, J. L. and Wallace, J. B.: Lost linkages and lotic ecology: rediscovering small streams, Ecology: Achievement and Challenge, The 41st Symposium of the British Ecological Society of America, 295-317 pp.2001.

Vannote, R. L., Minshall, G. W., Cummins, K. W., Sedell, J. R., and Cushing, C. E.: River continuum concept, Can. J. Fish. Aquat. Sci., 37, 130-137, https://doi.org/10.1139/f80-017, 1980.

Minor comments:

1. Also related to LOADEST: I see now (from the text in Sec. 2.5 and Table S1) that you consider all possible LOADEST regression equations when modeling C flux. i.e., It appears that you selected Model 0 and let LOADEST automatically choose the most parsimonious model (lowest AIC) from models 1–9. However, model #s 3, 5, 7–9 include covariates for long-term change, which are arguably more appropriate to use when you have measurements from across multiple years (even five years of observations is not considered long enough by some studies, e.g., Zolkos et al., 2020). Because your study period is not multi-annual, and you are not investigating long-term trends, it would be more appropriate to estimate fluxes using the best model from 1, 2, 4, or 6.

Zolkos, S., Krabbenhoft, D. P., Suslova, A., Tank, S. E., McClelland, J. W., Spencer, R. G., ... & Holmes, R. M. (2020). Mercury Export from Arctic Great Rivers. *Environmental Science & Technology*, *54*(7), 4140-4148.

Thank you! The more appropriate LOADEST regression model with lowest Akaike Information Criterion (AIC) and without variables for long-term change during the calibration period (i.e., Model 1, 2, 4, 6; Zolkos et al., 2020) is re-selected to estimate fluxes. Relevant revision is added in *Lines 190-192, Line 195, Figure 2 and Table S1*.

Additional comments:

L14: “dynamics” is vague. Avoiding it generally improves clarity. If there is more to the story than just C ‘transport’ / fluxes, consider clarifying how ‘dynamics’ relates to it.

The word “dynamics” is revised to “fluxes”, “transport”, or “spatial-temporal variations” as needed. Please refer to the track change version of manuscript for details.

L17: What do you mean by “in-depth”? Please clarify.

The word “in-depth” means that we conducted sampling at a high spatial resolution in both pre-monsoon and monsoon seasons. This is clarified in *Line 18*.

L22: “… thawed frozen…”. Are the soils thawed or frozen? I see what you are trying to say here. It would be clearer to just say ‘thawed’.

Revised in *Line 22*. Thank you!

L30: “dynamics”- see comment for L14.

Revised in *Line 30*.

L30: What exactly do you mean by “cascading effects”? i.e., that thaw effects in headwaters might propagate downstream, across watershed scales? (especially for dissolved inorganic carbon, in your region) If so, you might consider recent work from the western Canadian Arctic exploring this topic: https://bg.copernicus.org/articles/17/5163/2020/bg-17-5163-2020.html, but also recognize that thaw effects on fluvial C cycling (especially DIC) across watershed scales vary across permafrost regions. For Siberia, see: https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2017JG004311. Perhaps worth considering in the Discussion, and how your work adds to this understanding.

Our original phrase might be misleading. We actually mean that carbon variations in headwater streams might critically affect the biogeochemical cycles of the downstream watersheds (such as high-order rivers) when facing permafrost thawing and precipitation events. This phrase is revised at *Lines 30-31* and *Line 404* as follows:

> *"...thawing of permafrost and alterations of precipitation regimes may significantly influence the alpine headwater carbon transport, with critical effects on the biogeochemical cycles of the downstream rivers."*

L63-4: Why is it important that there are different C sources? It would be interesting and helpful to clarify the biogeochemical relevance of the C sources, and doing so could help to justify the rationale for your Ad/Al ratio measurements. For instance, do the sources have varying degrees of recalcitrance?

Good point! It is reported that the aged permafrost carbon and modern carbon released following permafrost thawing may have different degradation potentials (Mann et al., 2015), and this sentence is added in *Lines 63-64*.

Reference:

Mann, P. J., Eglinton, T. I., McIntyre, C. P., Zimov, N., Davydova, A., Vonk, J. E., Holmes, R. M., and Spencer, R. G. M.: Utilization of ancient permafrost carbon in headwaters of Arctic fluvial networks, Nat. Commun., 6, 7, https://doi.org/10.1038/ncomms8856, 2015.

L89: The value for mean annual daily discharge is interesting. It would also be interesting to know total annual discharge (e.g., km^3 y^{-1}), from your daily Q measurements.

According to our daily discharge measurements, a total annual discharge of 2.4×10^8 m^3 during 2015 to 2016 is estimated and added in *Line 213*.

L90-1: Please see my Major comment #2.

Revisions on headwater stream is shown in *Lines 17, 28, 31, 34, 71, 84, 88, 91-92, 396, 405*.

L95-6: No carbonate lithologies? Why are your DIC concentrations so high? This should be discussed a bit more. My recollection is that some of the recent work by Song et al. discusses carbonate lithologies on the QTP.

Thank you! Our prior description on bedrocks in the Shaliu River is incomplete because Zhang et al. (2013) mainly focused on the lithology comparison between Buha and Shaliu River and their effects on silicate weathering. However, besides the Triassic sandstone, late Cambrian metamorphic rocks (schist and gneiss) and granites, there are actually abundant late Paleozoic marine sedimentary rocks rich in carbonates (Bissell and Chilingar, 1967) in the upper and lower reaches of the Shaliu River when searching more related literatures (Jin et al., 2009; Xiao et al., 2012; Xiao et al., 2013). To keep consistency with our subject on carbon transport, we revise the lithology characteristics by adding "late Paleozoic marine sedimentary rocks" in *Lines 97-98*.

Reference:

Zhang, F., Jin, Z. D., Li, F. C., Yu, J. M., and Xiao, J.: Controls on seasonal variations of silicate weathering and CO_2 consumption in, two river catchments on the NE Tibetan Plateau, J. Asian Earth Sci., 62, 547-560, https://doi.org/10.1016/j.jseaes.2012.11.004, 2013.

Bissell, H.J., Chilingar, G.V.: Classification of sedimentary carbonate rocks. In: Developments in Sedimentology, vol. 9, pp. 87–168, 1967.

Jin, Z. D., Yu, J. M., Wang, S. M., Zhang, F., Shi, Y. W., and You, C. F.: Constraints on water chemistry by chemical weathering in the Lake Qinghai catchment, northeastern Tibetan Plateau (China): clues from Sr and its isotopic geochemistry, Hydrogeol. J., 17, 2037-2048, https://doi.org/10.1007/s10040-009-0480-9, 2009.

Xiao, J., Jin, Z. D., and Zhang, F.: Geochemical and isotopic characteristics of shallow groundwater within the Lake Qinghai catchment, NE Tibetan Plateau, Quatern. Int., 313, 62-73, https://doi.org/10.1016/j.quaint.2013.05.033, 2013.

Xiao, J., Jin, Z. D., Zhang, F., and Wang, J.: Major ion geochemistry of shallow groundwater in the Qinghai Lake catchment, NE Qinghai-Tibet Plateau, Environ. Earth Sci., 67, 1331-1344, https://doi.org/10.1007/s12665-012-1576-4, 2012.

L202: Please specify: What post-hoc test did you use?

The "post-hoc Duncan test" is added in *Line 205*.

L239: Would be good to consistently include valencies for calcium and magnesium throughout, as you do here (e.g., L156).

Revised in *Lines 157-158*.

L307: Pardon the editorial comment, but it would be more appropriate for dissolved 'bicarbonates' and 'carbonates' to be singular, not plural.

Revised in *Line 307*.

L311-12: Please see my comment for L95-6. Are there carbonate lithologies? Consistency in the message would help.

Carbonate lithologies are added in *Lines 311-312*. Thank you!

L313: Technically, high Ca^{2+} and Mg^{2+} concentrations and a strong association with DIC reflect greater availability of carbonate-bearing lithologies for chemical weathering, not necessarily high rates of weathering. So, I am not sure that I would say "proved" here. Perhaps say "reflected" or "indicated by".

The word "proved" is revised to "reflected" in *Line 314*.

L318-320: Rainfall should enhance carbonate weathering, no? (e.g., Zeng et al., 2019) Perhaps clarify and elaborate on this.

Zeng, S., Liu, Z., & Kaufmann, G. (2019). Sensitivity of the global carbonate weathering carbon-sink flux to climate and land-use changes. *Nature Communications*, *10*(1), 1-10.

Good point! We do agree that increasing rainfall should enhance carbonate weathering carbon-sink flux (CCSF) as reported by Zeng et al. (2019), since fluxes are calculated as the function of alkalinity concentration and discharge. This discharge (or rainfall) effects on DIC flux is displayed in our study as well (Figure 2b). However, it is more complicated when referring to rainfall effects on DIC (alkalinity or bicarbonate) concentration. Previous studies show that increased discharge (due to increasing rainfall) could enhance alkalinity concentration yet at five-decade scale (Raymond and Cole, 2003) or at north-south profile through humid belts (Strakhov, 1967). By contrast, instantaneous alkalinity concentration is negatively correlated with discharge (Raymond and Cole, 2003 and Figure 3 therein) or precipitation (Figure R1; Zeng et al., 2016) at short-term or small-region scales, which is normally attributed to a pronounced dilution effects of rainfall (Raymond and Cole, 2003; Zeng et al., 2016) due to the lower DIC concentration in rainwater than stream water (Song et al., 2019). Since our study is conducted at a relatively short-term scale during 2015 to 2016, we postulate that the negative relationship between DIC concentration and discharge is caused by a dilution effect. The above explanation is added in *Lines 320-321*.

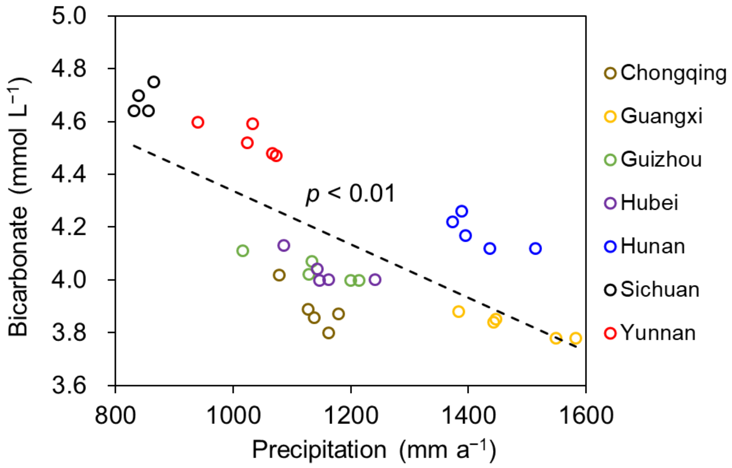

Figure R1. Relationship between mean annual precipitation and bicarbonate equilibrium concentration in karst region (seven provinces) of Southwestern China from 1970s to 2010s. Modified from Zeng et al. (2016).

Reference:

Zeng, S. B., Liu, Z. H., and Kaufmann, G.: Sensitivity of the global carbonate weathering carbon-sink flux to climate and land-use changes, Nat. Commun., 10, 10, https://doi.org/10.1038/s41467-019-13772-4, 2019.

Zeng, S. B., Jiang, Y. J., and Liu, Z. H.: Assessment of climate impacts on the karst-related carbon sink in SW China using MPD and GIS, Global Planet. Change, 144, 171-181, https://doi.org/10.1016/j.gloplacha.2016.07.015, 2016.

Raymond, P. A. and Cole, J. J.: Increase in the export of alkalinity from North America's largest river, Science, 301, 88-91, https://doi.org/10.1126/science.1083788, 2003.

Song, C. L., Wang, G., Mao, T. X., Chen, X. P., Huang, K. W., Sun, X. Y., and Hu, Z. Y.: Importance of active layer freeze-thaw cycles on the riverine dissolved carbon export on the Qinghai-Tibet Plateau permafrost region, PeerJ, 7, 25, https://doi.org/10.7717/peerj.7146, 2019.

Strakhov, N.M.: Principles of lithogenesis, vol.1, Tomkeieff S.I., Hemingway J.E., Eds, Oliver & Boyd, London, 1967.

L352: "headstream"- i.e., "headwater stream"?

The word "headstream" is revised to "stream" in *Line 353*.

L398: You could simply and clarify by saying "DIC" instead of "dissolved carbon (especially DIC)".

Revised in *Line 397*.

L401: Suggest deleting "frozen" (related to my comment for L22).

Deleted in *Line 399*.

L402: "levels" = "concentrations"?

Revised in *Line 400*.

L402: Apparently higher sensitivity of DIC concentration than DOC concentration, but also very interesting that DOC source appears to change. Worth mentioning here.

This sentence is revised accordingly in *Lines 401-402*.

Figure 2: Are the y-axis units metric 'tonnes' per day, rather than imperial 'tons'? For easier

comparison with other figures and values, it would help state the y-axis in metric units (e.g. Megagrams, Mg, or in grams if desired) and re-scale as needed.

The y-axis units in Figure 2b are revised to Megagrams carbon per day (Mg C day^{-1}).