Report #1
Submitted on 28 Feb 2023
Anonymous referee #1

Please add a reference to line 445, to support "Barite solubility can exhibit a redox dependence in conditions are sufficiently reducing to reduce SO4 to sulphide. "

The following reference has been added:

Neff, J. (2002). Barium in the Ocean. In Bioaccumulation in Marine Organisms (pp. 79–87).

Report #2

Submitted on 06 Apr 2023
Anonymous referee #2

In their response to the first round of questions, the authors adequately addressed many of the concerns raised. However, they missed key questions that are essential to prove their conclusions. While the argument that word count limitations prevented including a physically based transport model is reasonable, they should have used a statistical model to determine the controlling factors of vegetation, soil moisture, redox, weathering, water/soil interactions, hydrological transport, and mineral solubility. While expert opinion is valuable, it should not be relied upon exclusively as it can introduce subjective bias.

We do apologize that we were unable incorporate the physically based transport model that Reviewer 2 requested during the previous review into this manuscript. That effort is currently underway by a several modeling-focused colleagues and is likely to result in several manuscripts (it is a massive effort!). I am also sorry that Reviewer 2 felt inclined to change their rating to “Poor” and reject this version of the manuscript, following what was a mostly positive review of the previous draft. I do think the Reviewer 2 is the overlooking value of the novel approach taken here: recognizing that the data available to us was insufficient to produce a defensible physically based transport model, we creatively combined statically analyses, semi-generic thermodynamic models, spatial analyses, and expert opinion to produce a manuscript that is reasonably novel and likely to have some impact for the community of scientists who do work in Arctic soils (according to the reviews of both reviewers).
We also acknowledge Reviewer 2s comment with respect to including vegetation, soil moisture, and redox, weathering, water/soil interactions, hydrological transport, and mineral solubility in a statistical model. Unfortunately, after some research and discussions with more statistically savvy colleagues, we concluded that the multi-variable dynamics influencing contributions of vegetation, soil moisture, and redox, weathering, water/soil interactions, hydrological transport, and mineral solubility to soil pore water solute concentrations do not readily fit into a statistical model.

Regarding temperature dependence, the authors acknowledged some but stated that differences between 4 °C and 25 °C did not impact their results. However, given the extreme temperature range observed in the Arctic, it would have been better to run several thermodynamic simulations covering a broader range of temperatures. This is easily achievable.

This was performed and addressed in the previous review, when we added a temperature dependency figure to the Supplementary materials and added the following text to Section 2.4:

"Modelling exercises were performed at the default PHREEQC modelling temperature (25 °C), as the selection of an alternative defensible temperature was non-trivial; temperatures on the Seward Peninsula span a very wide range and it is unclear what temperature would be most suitable for mineral solubility limitation modelling. Ultimately, because the thermodynamic models were used as a tool understand what could be controlling soil pore water solute concentrations and were not intended to model the system or to predict future concentrations, the default temperature was decided to be the most suitable. While there is some temperature dependence of mineral solubility, the differences in predicted solubility between 4 °C and 25 °C did not impact the interpretation of our results (Supplementary Figure 8)."

It seems from their comment that Reviewer 2 is requesting a broader range of temperatures, presumably to much colder, as temperatures on the Seward Peninsula span – 30 C to 25 C and we covered up to 25 C. Reviewer 2 is certainly correct that this would be easily achievable from a modeling perspective, but it is unclear what the value of a mineral solubility model would be at temperatures where the pore water is frozen. Below ~4C, freeze/thaw processes (and the accompanying charge exclusion, cryoturbation, ect…) are superimposed on solubility and the solubility models are less valid. Therefore, we chose to keep the model to non-frozen temperatures.

It is important to note that the conclusions drawn from this study are based on field data collected in the Arctic with actual methane production taking place. The authors' argument for turning off methane production to maintain carbonate availability may not be convincing, as methane emissions in Arctic landscapes are predominantly the result of methanogens reducing organic carbon, which was not included in the model or manuscript. They should have shown both scenarios to build confidence in their interpretation. Again, this was easily doable.

There are many reactions that are thermodynamically favorable but are kinetically-limited or do not occur spontaneously. As noted in the previous response-to-reviews inorganic reduction of carbonate to methane is not a significant source of methane in the arctic. Therefore, including this reduction pathway in the model amounts to including a pathway that we know does not exist in any appreciable way. Methanogenesis in the Arctic is much more complex than inorganic reduction and is dependent on, among many things, the microbial communities (who is eating) and their source of carbon source (what they are eating). Many excellent scientists have spent their careers working to understand and model these processes, which is not easily doable, as suggested.

Regardless of the role of methanogens in Arctic soil biogeochemistry, Reviewer 2 seems to be overlooking the role of the thermodynamic model in this section. In this section of the manuscript, thermodynamically modeled Eh/pH diagrams are being used to identify minerals in the soil pore water that are either over saturated or nearly saturated. This is then used to plot SPW concentrations alongside those Eh/pH dependent solubility products to look for trends. The models are not intended to model the system, fit data, or predict concentrations, instead, the thermodynamic models are used as a tool understand what factors were likely to be controlling soil pore water solute concentrations. It is strategic to keep carbonate as carbonate as it makes oversaturation of carbonate minerals more likely, which enables us to identify mineral phases that could be limiting SWP concentrations. In other words, models do not necessarily need to be recreating reality to be useful. This is a case where the model is a tool, not the goal.

Finally, it is worth noting that the authors did not perform XRD analysis to determine the underlying mineralogy of the site, which could limit the accuracy of their thermodynamic models.

We do apologize that we were not able to incorporate the XRD data that Reviewer 2 had requested. Unfortunately, soil samples were not collected when the pore water sampling occurred (2016-2017) and we therefore do not have any samples to analyze for XRD. We did scour the literature and NGEE Arctic databases and we did not find anyone who had performed XRD analyses of the soils. We were able to find some XRF performed at the Teller-27 site, which does not provide mineralogical information, but does confirm the presence of significant amounts of Al, Fe, Si, and Ba, agrees nicely with our thermodynamic models.

To address this concern in the previous review, the following text was added to Section 4.5:
"Although it does not provide mineralogical information, X-ray fluorescence (XRF) data reported by another study at Teller confirmed high concentrations of Al, Fe, Si, and Ba in the organic and mineral soil layers at that site (Graham et al., 2018). We are unaware of any similar studies at Kougarok, nor are we aware of any studies that provide would provide confirmatory mineralogical information, for example by X-ray diffraction (XRD)."

Added references to provide further context:

Jessen, Søren, Hanne D. Holmslykke, Kristine Rasmussen, Niels Richardt, and Peter E. Holm. 2014. "Hydrology and Pore Water Chemistry in a Permafrost Wetland, Ilulissat, Greenland." Water Resources Research 50 (6): 4760–74. https://doi.org/10.1002/2013WR014376.

Patzner, M.S., Kainz, N., Lundin, E., Barczok, M., Smith, C., Herndon, E., Kinsman-Costello, L., Fischer, S., Straub, D., Kleindienst, S., Kappler, A., Bryce, C., 2022. Seasonal Fluctuations in Iron Cycling in Thawing Permafrost Peatlands. Environ. Sci. Technol. 56, 4620–4631. https://doi.org/10.1021/acs.est.1c06937

Raudina, Tatiana V., Sergey V. Loiko, Artyom G. Lim, Ivan V. Krickov, Liudmila S. Shirokova, Georgy I. Istigechev, Daria M. Kuzmina, Sergey P. Kulizhsky, Sergey N. Vorobyev, and Oleg S. Pokrovsky. 2017. "Dissolved Organic Carbon and Major and Trace Elements in Peat Porewater of Sporadic, Discontinuous, and Continuous Permafrost Zones of Western Siberia." Biogeosciences 14 (14): 3561–84. https://doi.org/10.5194/bg-14-3561-2017.

Sjöberg, Y., Jan, A., Painter, S. L., Coon, E. T., Carey, M. P., O'Donnell, J. A., & Koch, J. C. (2021). Permafrost Promotes Shallow Groundwater Flow and Warmer Headwater Streams. Water Resources Research, 57(2). https://doi.org/10.1029/2020WR027463

Park, H., Tanoue, M., Sugimoto, A., Ichiyanagi, K., Iwahana, G., & Hiyama, T. (2021). Quantitative Separation of Precipitation and Permafrost Waters Used for Evapotranspiration in a Boreal Forest: A Numerical Study Using Tracer Model. Journal of Geophysical Research: Biogeosciences, 126(12). https://doi.org/10.1029/2021JG006645

Huang, Q., Ma, N., & Wang, P. (2022). Faster increase in evapotranspiration in permafrost-dominated basins in the warming Pan-Arctic. Journal of Hydrology, 615, 128678. https://doi.org/10.1016/j.jhydrol.2022.128678