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Reply on RC2

Nathan Alec Conroy et al.

Author comment on "Environmental Controls on Observed Spatial Variability of Soil Pore Water Geochemistry in Small Headwater Catchments Underlain with Permafrost" by Nathan Alec Conroy et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-137-AC2, 2022

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Comment on egusphere-2022-137

Anonymous Referee #2

Referee comment on "Environmental Controls on Observed Spatial Variability of Soil Pore Water Geochemistry in Small Headwater Catchments Underlain with Permafrost" by Nathan Alec Conroy et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-137-RC2, 2022

The topic is interesting and within the scope of the journal. Conroy et al. investigated environmental Controls on observed spatial variability of soil pore water geochemistry in two headwater catchments in the Arctic. They collected samples (several geochemical constituents) from two different catchments in vegetation, soil moisture, and other characteristics. The authors performed PCA and Mann-Whitney U-Test to compare inter- and intra-catchment variability in chemical constituents. They also used PHREEQC to examine mineral solubility and other thermodynamic controls. The m/s includes several speculative statements and does not provide a clear understanding of different controls on spatial variability of soil pore water geochemistry. For example, their overarching hypothesis is that vegetation type and hillslope position are the dominant controls on spatial variability of SPW geochemistry. I want to hypothesize that spatial variability of SPW leads to different vegetation in different catchments. Both hypotheses can be shown to be true based on the analysis presented in this m/s. IMO, the problem is the limitation of their methodology. The PCA and non-parametric correlations cannot inform controls of spatial variability of SPW quantitatively. The authors should include coupled physical modeling to explore dominant controls. I have given more specific examples below. The figure quality is not good. For instance, it is hard to read Figure 4. The other minor point is that the m/s should be improved for style and writing.

We appreciate your comments and agree that the cause/effect of spatial variability of vegetation and soil pore water is uncertain and possibly bi-directional. We also agree that the methodology used here would likely be inadequate to robustly determine those causes and effects. It's not entirely clear what the reviewer means by "coupled physical modeling," but we believe they are referring to a physically based transport model. This type of model (ATS specifically) is currently in development but lies outside of the scope for this effort (this manuscript is already ~7500 words). We really appreciate your comments and enthusiasm for a coupled physical model and expect such efforts to be published soon.

Specific comments:

Lines 100-103: This study focuses on two sites with permafrost on the Seward Peninsula of western Alaska, the Teller-27 Catchment and the Kougarok-64 Hillslope (Figure 1).

Figure 1 is confusing. The Teller-27 Catchment, henceforth "Teller,"... and The Kougarok-64 Hillslope, henceforth "Kougarok,"...

I do not understand why Teller is located in the figure twice and so far away from each other. Which one is Teller in the study?

Thank you for pointing this out. If you look at the Legend, you will notice that the red dots are cities and the study sites are enclosed in yellow boxes. "Teller" next to the red dot is the city of Teller, whereas "Teller-27 Catchment" next to the yellow box is the Teller-27 Catchment (study area).

2: Line 107: These are identified as TL# (Teller Station #) or KG# (Kougarok Station #) in Figure 2 and Figure 3, ...

I did not find TL and KG anywhere else in the m/s, except in Tables 1 and 2.

This abridged nomenclature is also used in Figure 2 and Figure 3. We avoided using "TL #" and "KG #" in the main text as we found (through trial and error) that it was difficult to read. It was necessary in tables and figures due to space limitations and to keep the text at a legible font size.

3: Line 108: Teller and Kougarok are not paired watersheds. Why did the authors choose them to compare?

The study sites were selected as part of the larger NGEE Arctic program and were originally selected to provide co-located measurements in a wide range of vegetation types, nested within representative hillslopes and catchments (see lines 64-65). This manuscript was leveraged from the data available from the NGEE Arctic program and we therefore had no say in site selection.

From the text:

"This study takes advantage of a scientifically diverse array of observations and datasets made available by the Next Generation Ecosystem Experiment (NGEE) Arctic project, sponsored by the US Department of Energy Office of Science. Most of the locations studied herein were selected by the NGEE Arctic project to provide co-located measurements in a wide range of vegetation types, nested within representative hillslopes and catchments. Although selected largely to represent a range of vegetation structure, such as shrub abundance and canopy height, these locations also have considerable variability in other environmental parameters including, but not limited to: soil moisture and temperature, presence or absence of near-surface permafrost, and maximum observed thaw depth (Table 1 and Table 2). The vegetation-delineated sampling approach presented here provides an opportunity to not only quantify the biogeochemical variability of SPW in Arctic environments, but also to investigate the root causes of that observed variability. Data from additional sampling locations, available from a collaborative study, were also utilized when possible."

- It will be better to make a table of similarities and dissimilarities between the two watersheds, as described in Section 2.1.

Thank you, we very much agree. Please see Table 1 and Table 2.

- Line 216: When the authors investigate a permafrost site, why were modeling exercises performed at 25 °C? Shouldn't they do it for the entire range of temperatures observed there? Or the temperature at which samples were collected?

The authors spent significant time deliberating what temperature to run the thermodynamic models but found that selecting a defensible temperature for the purposes of modeling was non-trivial. The temperatures on the Seward Peninsula span a remarkable range, with wintertime lows of – 30 C and summertime highs of 25 C. Meanwhile, freeze/thaw processes (and the accompanying charge exclusion, cryoturbation, ect…) are superimposed on these large temperature swings. 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, it was decided that the "default" value was most suitable; using something other than the default required defensible justification. 25 C is the default temperature for PHREEQC (and for many geochemical thermodynamic modeling efforts). 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.

To address this we have 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)."

- Why was Methane production "turned off"? In the Arctic, several papers (from NGEE itself) have examined methane as GHG variability.

https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2009JG001283

https://bg.copernicus.org/articles/10/5139/2013/

There are several other paper on this.

Methane production was “turned-off” to maintain carbonate availability under reducing conditions to help identify any possible carbonate minerals that could be precipitating. This is described in Lines 250-251. Methane production is very important and of great concern in the Arctic, but not from the thermodynamically predicted reduction of inorganic carbon to methane at low oxidation-reduction potential and pH. Methane emission from Arctic landscapes are predominately the result of methanogens reducing organic carbon as a part of their metabolisms (which is complex and not included in this model or in this manuscript).

7.4.1 Inter-site Variability: Teller versus Kougarok: The authors found that many constituents were significantly different between

Teller and Kougarok. It is unclear how they deduced vegetation, soil moisture, and redox, weathering, water/soil interactions, hydrological transport, and mineral solubility control the difference between the two sites. However, constituents between the two sites will show significant differences anyway. One could measure these constituents in any catchments elsewhere; two catchments would show significant differences almost every time.

Thank you for your comments. Deduction of vegetation, soil moisture, and redox, weathering, water/soil interactions, hydrological transport, and mineral solubility controlling was largely based on expert opinion (a statistical model was not used). The authors are an eclectic group of experts from a broad and diverse range of Arctic fields, and in the Discussion Section are discussing their expert opinion on the likely controls of the observed spatial variability, which are reported in the Results Section.

This is approach is introduced in Section 4.2:

“Our interpretation of the major environmental controls on the observed spatial variability of SPW solute concentrations between stations are shown in Table 4. Each of these controls, including vegetation effects, soil moisture and redox effects, weathering, water/soil interactions and hydrological transport effects, and mineral solubility effects, is discussed in detail in the following sections.”

We very much appreciate your desire for a model-based solution. This “expert opinion” based manuscript is just a first step and models are currently under development and part of a much larger effort.

- Discussion in sections 4.3 to 4.5 is speculative. Comparing observations from two sites and linking several controls using statistical measures like PCA and correlations is not convincing. To come to these conclusions, the authors need to quantify the controls and do physical modeling.

For example, in Line 304: it is unclear why Teller Station 2 [SHOULD it not be TL2 as mentioned in Section 2.1] did not exhibit elevated NO3 while Station 7 did, but we suspect that higher 305 seasonal moisture content and greater microbial denitrification at

Teller Station 2 likely played a role.

Line 313: The lack of a clear correlation between vegetation and soil moisture...

These are speculative statements. Modeling would need to demonstrate the real cause.

Thank you for noticing this. We kept our language deliberately speculative in order to most honestly represent our interpretation of our dataset. For example, lines 334-336:

“Therefore, we believe the lack of elevated NO3- concentrations at Kougarok Stations 1, 2, 6, 10, and 11 is a combination of less alder leaf litter and greater denitrification, than at Kougarok Stations 3, 5, or 12.”

Models can be extremely useful (which is why we used some geochemical modeling), but models are only as good as the data/equations that govern them (i.e. the old modeling adage “garbage in, garbage out”) and we do not currently have sufficient hydrological knowledge of these sites to develop a robust ATS model. These efforts are currently underway and will be a “next step” in our overall efforts. This work was a “first step” and has resulting in a manuscript that is quite dense and over 7500 words. We would ask this reviewer to allow us to pursue the additional modeling efforts in our next manuscript (it is a very large effort that will result in multiple manuscripts).

- Section 4.4: Did the authors do thermodynamic modeling to investigate their results? It is not clear how they came up with some conclusions. For example, what was the source of Iron (III) and Mn? They talked about different redox species; what was the mineralogy there?

Yes, we did do thermodynamic modeling to investigate our results. In particular, PHREEQC and PhreePlot were used to deduce which soil pore water solute concentrations might be controlled by solubility limitations. This is discussed in the “Mineral Solubility Effects” section (Section 4.5). Briefly, ranges of pH and EH were defined for each site (Figure 6) and then models were used to explore possible mineral formation under the EH/pH conditions present at either Teller or Kougarok using the soil pore water solute concentration data (Figure 7). The concentrations for these diagrams were taken from filtered aqueous concentration data, thus, predicted mineral precipitation was an indication of nearly saturated or over-saturated conditions. Once mineral phases that might be control solution concentrations were identified, sweeps of mineral solubility limits were plotted with pH/ORP/solute concentration data to see if soil pore water solutes followed similar trends (Figure 8). Our modeling efforts suggested that Fe(OH)3(am) was likely a significant control on soil pore water Fe concentrations. We do not know what the source of Mn is at those sites, nor do we know the mineralogy underlaying the site, but our results as well as the data from XRF suggest than the source of Mn is limiting Mn soil pore water concentrations.

Unfortunately, we did not perform XRD nor are we aware of any studies that did. 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.

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)."

- Line 345: weathering, water/soil interactions, and hydrological transport were clear drivers of hydrogeochemical variability for some solutes?

How is this so clear? I guess the authors need to perform physical modeling to prove these statements. They are mostly true, as the author cited several papers, but that brings the question of novelty. What is new here?

An excellent point, "clear" is too strong of language for this statement.

"A combination of weathering, water/soil interactions, and hydrological transport were clear drivers of hydrogeochemical variability for some solutes."

Changed to:

"A combination of weathering, water/soil interactions, and hydrological transport were identified as probable drivers of hydrogeochemical variability for some solutes."

We believe by physical modeling you mean models like the Advanced Terrestrial Simulator (ATS). ATS modeling efforts are underway, but they are non-trivial and very large efforts (and thus, will likely result in multiple papers themselves). The novelty of this work lies in assembling a group of subject matter experts to identify the likely dominant controls on solute concentration variability within each catchment and across catchments. The dataset presented herein provides new data in a sparsely studied region of our planet and the combined use of statistical difference testing, thermodynamic modeling, and subject matter expert interpretation, provides valuable insight into the dominant controls on soil pore water solute concentrations in permafrost landscapes.

Please also note the supplement to this comment:
https://egusphere.copernicus.org/preprints/2022/egusphere-2022-137/egusphere-2022-137-AC2-supplement.pdf