EGUsphere, referee comment RC1 https://doi.org/10.5194/egusphere-2022-137-RC1, 2022

Comment on egusphere-2022-137

Anonymous Referee #1

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-RC1, 2022

Does the paper address relevant scientific questions within the scope of TC?

Yes

Does the paper present novel concepts, ideas, tools, or data?

Yes.

Are substantial conclusions reached?

Yes

Are the scientific methods and assumptions valid and clearly outlined?

Yes

Are the results sufficient to support the interpretations and conclusions?

The authors link water quality to vegetation, however I fell this link is rather qualitative. They have compiled vegetation data from the NGEE Arctic project. This section needs either more description or references to papers and reports on the methods used. Additionally it would greatly strengthen the paper to be more quantitative and descriptive with the vegetation. Are there photos of the sites that can be shown in supplementary material etc.

> We agree that the description of vegetation at these sites needs to be strengthened. We have taken the reviewer's recommendations into consideration and done the following:
>
> - Added plot photos for plant functional types to the Supplementary Materials.
> - Provided percent cover data for dominant plant functional types for each plot in Table 1 and Table 2.
> - Added the following text to Section 2.2:
>   *"Vegetation data were collected at the peak of the growing season in mid to late July 2016 and 2017 at the NGEE Arctic Kougarok and Teller field sites, respectively. The distribution of plant communities in the Arctic is primarily controlled by landscape, topography, soil chemistry, soil moisture, and the plants that historically colonized an area (Raynolds et al., 2019). Soil available rooting depth, which can be limited by shallow depths to bedrock, permafrost, or the water table, can also restrict plant growth and survival of certain species by reducing access to water and nutrients. We surveyed the dominant plant communities along each hillslope, which varied in their shrub abundance, canopy height, and structure, to characterize the vegetation composition at*

the sites following the recommended protocol of Walker et al. (2016). Extensive field site details and vegetation sampling methods are more thoroughly described in previous studies (Salmon et al., 2019; Langford et al., 2019; Yang et al., 2020; Sulman et al., 2021; Yang et al. 2021).

For this study, we provide summary statistics for vegetation plots associated with intensive stations. Vegetation composition plots within each intensive station were chosen subjectively in areas of homogeneous and representative vegetation varying in size from 1 to 25 m2 depending on canopy structure and height. The surveyed plot area was 1 × 1 m for all plant communities except for the taller stature willow-birch tundra, mesic willow shrubland (2.5 × 2.5 m), and alder shrubland (5 × 5 m). For each plot, all plant species (vascular plants, lichens, and bryophytes) were recorded along with visual estimates of their percent cover. For plots with multiple canopies, field cover estimates were recorded as absolute cover, meaning that the total cover per plot can be >100%. We calculated relative cover values (adding to 100%) from the field data and use these for all subsequent analyses.

Plant species were further aggregated into nine plant functional types (PFTs), groupings of plant species that share similar growth forms and roles in ecosystem function (Wullschleger et al., 2014), based on growth patterns and plant traits. PFTs in this study include: (1) nonvascular mosses and lichens, (2) deciduous and evergreen shrubs of various height classes, including an alder PFT, (3) graminoids, and (4) forbs. Canopy height was estimated within each plot for each PFT as the average of 4 measurements, including a maximum canopy height. Active layer depth was measured at the end of the growing season for all plots in September 2018 using a frost probe. A temperature probe was used to determine if the resistive layer was permafrost (≤0 °C) or rock (>2 °C). Thaw depth is an average of 4 measurements from the vegetation plot corners."

Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)?

Overall, yes, however they should provide a data table of their water chemistry dataset in a supplementary material table.

Our water chemistry dataset is very large and (despite our best efforts) was not conducive to a printed format. Therefore, we have provided it in an open-access electronic format which can be downloaded:

Nathan Conroy, Jeff Heikoop, Brent Newman, Cathy Wilson, Carli Arendt, George Perkins, Stan Wullschleger. 2021. Soil Water Chemistry and Water and Nitrogen Isotopes, Teller Road Site and Kougarok Hillslope, Seward Peninsula, Alaska, 2016 - 2019. Next Generation Ecosystem Experiments Arctic Data Collection, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, USA. https://doi.org/10.5440/1735757.

This data product is referenced in the Data Availability Statement (Section 7).

Do the authors give proper credit to related work and clearly indicate their own new/original contribution?

Yes, the authors give proper credit to prior work and outline their contribution.

Does the title clearly reflect the contents of the paper?

Yes.

Does the abstract provide a concise and complete summary?

Yes

Is the overall presentation well structured and clear?

Areas of the paper should be restructured, see detailed comments.

Is the language fluent and precise?

Yes.

Are mathematical formulae, symbols, abbreviations, and units correctly defined and used?

Yes.

Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated?

I have specific questions about parts of the discussion, see specific comments.

Are the number and quality of references appropriate?

Yes.

Is the amount and quality of supplementary material appropriate?

Yes.

Overall Comments

The paper "Environmental Controls 1 on Observed Spatial Variability of Soil Pore Water Geochemistry in Small Headwater Catchments Underlain with Permafrost" presents an evaluation of water chemistry data collected from two catchments underlain by permafrost terrain. Overall, the paper presents interesting data on a topic which is important given the changing environment in permafrost terrain caused by anthropogenic warming. While the paper is well written I think there are some significant changes needed prior to publication. I think the suggested changes are needed to be able to strengthen the conclusions of the paper and will result in a significantly better paper.

Two general areas for improvement are here and detailed comments are below.

The information on the vegetation could be more quantitative, or at least include some photos etc. A significant portion of the discussion rests on the information provided in Table 1. The authors need to provide more information on how the vegetation assessment was done, and more information on the results of that, I have made a few more detailed comments on this below.

Please see above response plant functional type photos added to the Supplementary Materials, inclusion of dominant plant functional type cover to Table 1 and Table 2, as well as additional text added to Section 2.2:

> *"Vegetation data were collected at the peak of the growing season in mid to late July 2016 and 2017 at the NGEE Arctic Kougarok and Teller field sites, respectively. The distribution of plant communities in the Arctic is primarily controlled by landscape, topography, soil chemistry, soil moisture, and the plants that historically colonized an area (Raynolds et al., 2019). Soil available rooting depth, which can be limited by shallow depths to bedrock, permafrost, or the water table, can also restrict plant growth and survival of certain species by reducing access to water and nutrients. We surveyed the dominant plant communities along each hillslope, which varied in their shrub abundance, canopy height, and structure, to characterize the vegetation composition at the sites following the recommended protocol of Walker et al. (2016). Extensive field site details and vegetation sampling methods are more thoroughly described in previous studies (Salmon et al., 2019; Langford et al., 2019; Yang et al., 2020; Sulman et al., 2021; Yang et al. 2021).*
>
> *For this study, we provide summary statistics for vegetation plots associated with intensive stations. Vegetation composition plots within each intensive station were chosen subjectively in areas of homogeneous and representative vegetation varying in size from 1 to 25 m2 depending on canopy structure and height. The surveyed plot area was 1 × 1 m for all plant communities except for the taller stature willow-birch tundra, mesic willow shrubland (2.5 × 2.5 m), and alder shrubland (5 × 5 m). For each plot, all plant species (vascular plants, lichens, and bryophytes) were recorded along with visual estimates of their percent cover. For plots with multiple canopies, field cover estimates were recorded as absolute cover, meaning that the total cover per plot can be >100%. We calculated relative cover values (adding to 100%) from the field data and use these for all subsequent analyses.*
>
> *Plant species were further aggregated into nine plant functional types (PFTs), groupings of plant species that share similar growth forms and roles in ecosystem function (Wullschleger et al., 2014), based on growth patterns and plant traits. PFTs in this study include: (1) nonvascular mosses and lichens, (2) deciduous and evergreen shrubs of various height classes, including an alder PFT, (3) graminoids, and (4) forbs. Canopy height was estimated within each plot for each PFT as the average of 4 measurements, including a maximum canopy height. Active layer depth was measured at the end of the growing season for all plots in September 2018 using a frost probe. A temperature probe was used to determine if the resistive layer was permafrost (≤0 °C) or rock (>2 °C). Thaw depth is an average of 4 measurements from the vegetation plot corners."*

And at Line 75:

> *"Indirect effects would include vegetation canopy impacts on soil moisture (through evapotranspiration and snow trapping). Direct effects of vegetation would include nutrient cycle changes resulting from the annual deposition of plant litter. Such a direct effect can be augmented at sites populated by alder shrubs due to this genus of*

deciduous shrubs ability to form a symbiotic relationship with nitrogen-fixing Frankia that they host in underground root nodules. Nitrogen fixation associated with alders has been shown to accelerate local nitrogen cycling (Binkley et al., 1992; Clein and Schimel, 1995; Bühlmann et al., 2014)."

The authors conduct numerous geochemical calculations which is great, however were samples collected of the soil for mineralogical analysis? It would greatly support the paper if there were some XRD analysis of the soil, or other relevant information (other reports, papers discussion the soil minerology in the study areas). If you have this or can easily do it, it would greatly improve the paper. I think your geochemical discussion needs to better reflect that the water chemistry suggests these are the mineral phases present, however this you don't actually know this.

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)."

Specific Comments:

Line 29: NO3-

Resolved here and throughout the text.

Line 52: I have not reviewed this journals style guide, but is it correct to list Koch, Runkel, Striegl, and McKnight, 2013; most jourlals would be Koch et al. Please check.

Thank you for catching this. Resolved here and throughout the text.

Line 75 to 77: Much of your paper involves discussion about the role of alders and nitrogen fixing but rests on one reference, can you provide more. I think this is a well studied topic, it would be good to show its well established.

Thank you for pointing out this omission and we agree that the role alders play in modifying local nitrogen cycling has been well-studied. We therefore modified text at line 75 to include more references and read as follows:

"Indirect effects would include vegetation canopy impacts on soil moisture (through evapotranspiration and snow trapping). Direct effects of vegetation would include nutrient cycle changes resulting from the annual deposition of plant litter. Such a direct effect can be augmented at sites populated by alder shrubs due to this genus of deciduous shrubs ability to form a symbiotic relationship with nitrogen-fixing Frankia that they host in underground root nodules. Nitrogen fixation associated with alders has been shown to accelerate local nitrogen cycling (Binkley et al., 1992; Clein and Schimel, 1995; Bühlmann et al., 2014)."

Line 100 – 146: This section provides a good general background. I find it lacking in real information about the geology. Based on the locations in Figure 1, I think the two catchments are underlain by different geology. I looked at "Preliminary Bedrock Geologic Map of the Seward Peninsula, Alaska, and Accompanying Conodont Data, By Alison B. Till, Julie A. Dumoulin, Melanie B. Werdon, and Heather A. Bleick, https://pubs.usgs.gov/of/2009/1254/" However you can probably find larger scale maps with more detail. Referencing this would help your description of the site, and can also be made consistent with the geochemical discussion.

Thank you for your efforts in locating the USGS map by Till et al. The final version of the map you referenced is actually already referenced in Line 133:

> *"The upper shoulder of Kougarok is a well-drained rocky outcrop composed of metagranitic rock (Hopkins et al., 1955; Till, Dumoulin, Werdon, and Bleick, 2011)."*

Unfortunately, on the maps both sites are underlain with the same broadly-defined geology: "Surficial deposits, undivided (Quaternary)". We made a significant effort to search for geological maps and old literature that described the region. To the best of our knowledge, we found what was available and have summarized it in Lines 100-146.

Line 101, 103: km2 should be superscript

Resolved here and throughout the text.

Line 108 -109: Reword sentence, it is confusing.

> *"Teller and Kougarok are not paired watersheds in the classical sense, differing in only one major characteristic, which provides the basis for comparison. Instead, Teller and Kougarok differ in many respects and are both representative of the broad range of hillslope conditions common on the Seward Peninsula."*

Changed to:

> *"It should be noted that Teller and Kougarok are not "paired watersheds" in the classical sense, differing in only one major characteristic, which provides the basis for comparison. Instead, Teller and Kougarok differ in many respects and are both representative of the broad range of hillslope conditions common on the Seward Peninsula."*

Line 129 / Figure 3: The figure shows a watershed boundary, however I think the authors are trying to show a boundary of the area studied, as this cannot be a watershed boundary. On the west side the boundary is shown along a contour line which water will continue to flow over.

Thank you for pointing this out, we really apricate your attention to detail. The watershed boundaries were delineated in ArcGIS using the Hydrology Toolbox and using a 5m resolution IFSAR DEM to run the analysis. The ArcGIS Hydrology Toolbox determines the direction of flow by determining the direction of steepest descent from each cell. This mechanism worked very well at Teller-27, which has well-defined drainage divides and pour point, but did not work as well at Kougarok, which is more of a convex hillslope. The legend has been changed to "Hillslope Boundary" to reflect this.

Line 174-178: More information is needed on the methods used for the vegetation assessment. If this assessment is part of this study how was it determined that the dominant plant function type was "Deciduous low to tall shrub (willow)". From the text its sounds like this was done part of another project "NGEE Arctic project", if so the text should reference where we can get information on how this was done, however, even with a reference, a sentence or two is needed to explain roughly how it was done.

We appreciate the reviewer's attention to detail that these methods were missing from the manuscript. We added the text below to Section 2.2 – where noted by the reviewer.

"Vegetation data were collected at the peak of the growing season in mid to late July 2016 and 2017 at the NGEE Arctic Kougarok and Teller field sites, respectively. The distribution of plant communities in the Arctic is primarily controlled by landscape, topography, soil chemistry, soil moisture, and the plants that historically colonized an area (Raynolds et al., 2019). Soil available rooting depth, which can be limited by shallow depths to bedrock, permafrost, or the water table, can also restrict plant growth and survival of certain species by reducing access to water and nutrients. We surveyed the dominant plant communities along each hillslope, which varied in their shrub abundance, canopy height, and structure, to characterize the vegetation composition at the sites following the recommended protocol of Walker et al. (2016). Extensive field site details and vegetation sampling methods are more thoroughly described in previous studies (Salmon et al., 2019; Langford et al., 2019; Yang et al., 2020; Sulman et al., 2021; Yang et al. 2021).

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Plant species were further aggregated into nine plant functional types (PFTs), groupings of plant species that share similar growth forms and roles in ecosystem function (Wullschleger et al., 2014), based on growth patterns and plant traits. PFTs in this study include: (1) nonvascular mosses and lichens, (2) deciduous and evergreen shrubs of various height classes, including an alder PFT, (3) graminoids, and (4) forbs. Canopy height was estimated within each plot for each PFT as the average of 4 measurements, including a maximum canopy height. Active layer depth was measured at the end of the growing season for all plots in September 2018 using a frost probe. A temperature probe was used to determine if the resistive layer was permafrost (≤0 °C) or rock (>2 °C). Thaw depth is an average of 4 measurements from the vegetation plot corners."

We also added this text to Tables 1 and 2 to clarify the dominant species in the deciduous shrub classes:

For Table 1 - Deciduous shrub PFT classes identify the dominant species in the plant community as either willow or willow and birch. There is no alder at the Teller site.

For Table 2 - Deciduous shrub PFT classes identify the dominant species in the community as either willow, alder, willow and birch, or alder, willow and birch.

Line 216: "Modelling exercises were performed at 25 °C utilizing the" why was this done at 25C when your studying water in permafrost terrain? Maybe necessary stability constants were only available at this temp. but you should comment on who it may differ with field temperatures.

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)."*

Line 231, compounds measured as ions should be listed with their charge (eg SO42-, NO3-, however Sr and Ca are likely measured as total concentration (so don't list charge))

Resolved here and throughout the text.

Figure 4: I have had to zoom into 150% to be able to read this. Make it bigger, and you may also be able to use a crisper font.

The authors agree. We hope this will be a full-page figure for the final publication. We used a very high-resolution version of Figure 4, but the quality in the Cryosphere pdf print is less than ideal. We will work with The Cryosphere typesetters and editors to ensure this figure is published at an appropriate size and resolution. As a note: when printed from our Word Document, Figure 4 appears very crisp and clear, and is easy to read. This should be easily resolvable with the Cryosphere editorial team.

Line 282-283: "NO3 concentrations at both sites were generally low, with the exception of Kougarok Stations 3, 5, and 12, and Teller Station 7 (Figure 4). Kougarok Stations 3, 5, and 12 all have a significant alder presence."

Can you back up this statement further? This is very qualitative? Do you have photos of the different sites that you could compare on contrast? Do other papers talk about vegetation density?

Thank you, this is a very good point. The percent coverage of the dominant plant functional types has been added to Table 1 and Table 2. Meanwhile, the text has been changed to make it more precise and quantitative:

> *"NO_3^- concentrations at both sites were generally low, with the exception of Kougarok Stations 3, 5, and 12, and Teller Station 7 (**Figure 4**). Kougarok Stations 3, 5, and 12 all have a significant alder presence."*

Changed to:

> *"NO_3^- concentrations at both sites were generally low, with the exception of Kougarok Stations 3, 5, and 12, and Teller Station 7 (**Figure 4**). Low to tall alder shrubs are the dominant vegetation type at Kougarok Stations 3 and 12. Meanwhile, alders are present at Kougarok Station 5 despite the dominant vegetation type being low willow and birch shrubs."*

Also, plant functional type photos have been added to Supplementary Materials.

Section 4.5 Mineral solubility Effects: Have you measured the presence of the mineral you discuss in soil samples? Perhaps you have done some XRD? If not, have other papers done soil analysis in the area? You can pull in reference to the local geological maps as well. I have had the experience myself where a given mineral is predicted by a geochemical software, but you don't actually have that mineral in your system and something more complicated is going on.

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)."*

EGUsphere, referee comment RC2 https://doi.org/10.5194/egusphere-2022-137-RC2, 2022

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.”*

4. 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.

5. 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)."*

6. 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.

8. 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:
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> > *"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."*
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> 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).

11. 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)."

12. 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.