Anonymous Referee #1

General comments:

Thawing of permafrost is one of the most obvious and severe effects of global change and has the potential to fundamentally change ecosystems at higher latitudes and elevations. The release, subsequent transport and biological metabolization of soluble organic carbon entrapped in permafrost layers has drawn substantial scientific interest over the last decades but knowledge on controlling factors is still far from completeness. The present study investigates the role sediment mineral properties in the regulation of amounts, composition, and microbial consumption of soluble/dissolved organic matter at landscape scale.

The study addressed sorptive interactions between sediments and soluble/dissolved organic matter across large gradients in sediment mineral properties. Extensive sorption experiments were combined with incubation experiments and spectroscopic (absorption/fluorescence) analyses. The resulting comprehensive dataset was carefully evaluated and revealed that the fractionation during sorption and desorption control composition and, thus, the bioavailability of dissolved organic matter. Sorptive interactions with minerals in sediments seemingly are important in regulating the fate and ecological impacts of soluble organic matter within permafrost landscapes.

The entire manuscript is well structured. It starts with a focused, still extensive and comprehensive summary of the scientific background, a detailed presentation of the environmental settings in the study area that, and, based on that, a straight-forward justification of the presented study. The Method section is extremely detailed, providing all necessary information to fully understand the scientific approach. The presentation of results, in the manuscript as well as in the supplement, is very neat, comprehensive, and logic. The discussion, as the rest of the manuscript, is also well-structured, easy to follow, with the arguments well presented (I like much the artwork and the figures), and the conclusions/implications well supported/justified by data and literature evidence. I enjoyed the reading very much, likely because it is in line with my own way of thinking. However, other people might consider some of the detailed reflections as too lengthy (see comments below).

Overall, I think the manuscript presents a great contribution to the field of carbon research in permafrost regions, with novel and important findings on organic matter processing at landscape scale. Also, I think it fits very well the focus and style of the journal and therefore recommend acceptance for publication after minor revision.

We thank the reviewer for their thoughtful feedback and assessment of this manuscript.

Specific comments

1. Title: I suggest to small simplification: "Experimental evidence of mineral regulation of dissolved organic matter composition and lability across permafrost landscapes in northwestern Canada".

   Thank you for this suggestion. We would like to keep "organo-mineral interactions" in the title to emphasize the direct interactions occurring between organic compounds and mineral surfaces.

2. Abstract: It is brief and informative, with the key findings and implications highlighted but contrasts a bit the otherwise rather long manuscript. Probably, the abstract could serve as starting point for considering some condensation of text.

   Thank you for this suggestion.

3. l. 19: I like the term "organo-reactive" much, since nicely illustrative.

   Thank you.

4. l. 22/23: Ii might be an idea to directly point out that fractional sorption/desorption as key driver of organic matter remaining in solution.

   We feel that the current text conveys this idea without being overly strong, as requested by reviewer 2. However, we are happy to consider a specific edit that might convey this concept more clearly, via a follow-up from the reviewer.

   Current text:

   Preferential sorption of larger, humic-like compounds and displacement of mineral-bound small, aliphatic molecules enriched the DOM pool in labile compounds.

5. l. 26: It might be worth to mention that this refers to the bioavailability of dissolved organic matter remaining in solution.

   Agreed. We will modify the text as follows: "while increasing DOM bioavailability <u>remaining in solution</u> following exposure to permafrost-origin sediments…"

6. l. 62: Some of these references actually do address sediments but soils and minerals. So, re-phrasing to sentence in l. 61 should be considered.

   Agreed. We will modify the text as follows: "Given that the potential for organo-mineral interactions is largely influenced by ~~sediment~~ substrate properties …"

7. Section 2.1: Very detailed and informative description of the environmental settings but probably a bit too long.

   Thank you for this suggestion. We believe that all information included in the study region description (Section 2.1) is related to the interpretation of the results and therefore necessary to include. However, we will revisit the text in this section and streamline the text for brevity where possible.

8. l. 195: The reference to the supplement material could be better placed at the end of Section 2.3.

   We will move the text "Analytical methods and detection limits are summarized in Table S2." to the end of Section 2.3.

9. l. 221/222: The phrasing of the sentence describing the target compounds of the pyrophosphate extraction expresses nicely the rather crude nature of the procedure. I am rather skeptical if it is of any use at all.

   Pyrophosphate extraction at pH 10 chelates polyvalent cations and therefore targets metals (Fe, Mn, Al, and Ca) complexed with organic species. It has been reported that Na-pyrophosphate not only targets organically bonded Fe but also includes nanoparticulate poorly crystalline Fe oxides (Regelink et al. 2014). Therefore, the release of Fe and Al from small particles that have not complexed with soil organic acids is not excluded during pyrophosphate extraction (Rennert et al. 2019).

   For this reason, the sentence L 221-222 specifically mentions "mineral elements complexed with organics and dispersible colloids" to provide clarity on this method for the reader.

10. l. 230: I suggest to re-phrase as follows: "The portion of Al, Ca, Fe, and Mn in existing organo-complexes …". The original text is confusing and not correct.

    We will rephrase the sentence as suggested.

11. l. 232: I guess X-ray diffraction was carried using random powder mounts. This should be mentioned.

    Correct. We will add text to state that samples were processed using front-loaded random powder mounts.

12. l. 238: “Mineral” should be omitted since confusing.

    The text will be modified as follows: “~~Mineral s~~Sorption properties of the selected subset of samples (n = 32) were determined through batch sorption experiments (e.g., Kaiser et al., 1996; Vance and David, 1989) that are designed to examine the proportion of DOC in solution that can be sorbed to minerals in specific sediment samples.”

13. l. 251ff: Very detailed description; could be condensed.

    Thank you for this suggestion. We will streamline this text and/or move details to the Supplementary Information.

14. Section 2.5: I suggest to comment somewhere on possible (or the lack of) anaerobic respiration at dropping oxygen levels.

    We will modify the text in line 282 to provide more clarity:

    “Inoculated samples were incubated in triplicate for 14 days or until a 2 mg L^{-1} dissolved oxygen threshold was met to avoid anaerobic respiration ~~they reached hypoxic conditions (< 2 mg L-1 dissolved oxygen)~~.”

15. l. 358/359: The sorption coefficients are partly rather low as compared to subsoils and also sediments.

    Thank you for this comment. This line refers to our statement of findings in the results. We discuss these values relative to other regions in section 4.2.2 in the discussion. This text in the discussion specifically describes how our measured sorption coefficients compare to those from other regions and sites.

16. 380: I support the idea that correlating no sorption to whatever properties is not really helpful.

    Thank you.

17. l. 390, Figure 6: I suggest to re-label reactive and complexed by according to extraction procedure used (oxalate-/pyrophosphate-extractable), as given the figure caption. Considering the wide spread of overall properties of the tested sediments the correlations are pretty tight, even without any transformation.

    Agreed. Thank you for pointing this out. We will re-label our figure as suggested.

18. Section 4 Discussion: As mentioned, I like it much but some condensation may improve readability.

    We will edit the text with an eye for brevity, where possible.

19. Section 5 Conclusions: Partly more summarizing than conclusive but it reflects well the major findings and implications.

    We agree that the first paragraph of this section is more targeted towards a summary of key findings, which we prefer to keep for readers who might not read the manuscript in detail. The second, and final, paragraph of this section provides high-level conclusions for the work.

20. References: The literature collection is comprehensive and makes full use of the knowledge accumulated over the last decades.

    Thank you.

Anonymous Referee #2

The fate of carbon released from thawing permafrost landscapes is a subject of great concern with potential severe climate impacts, and knowledge on factors determining degradation of organic matter in these landscapes is still incomplete. This study investigates interaction between minerals and dissolved organic matter in a set of different sediment samples collected in geologically different regions of the permafrost zone of northern Canada. An impressive range of experiments and geochemical analyses were conducted. The manuscript is overall very well-written, nicely motivated and explained, and all results are clearly documented.

We thank the reviewer for their thoughtful feedback and assessment of this manuscript.

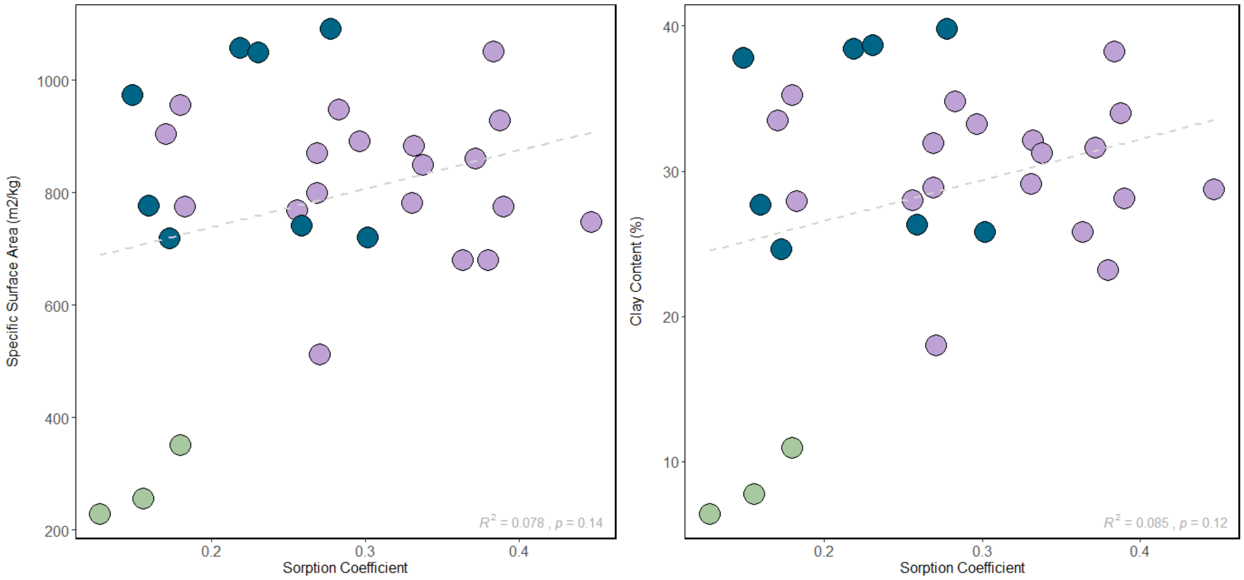
The analyses and experiments performed are extenisive, but nonetheless might fall short of providing sufficient evidence to address the objectives of the study. The large range of geochemical parameters obtained for the large number of samples exhibited broad variability not only between sampling sites but also between samples from the same unit. This is illustrated in Figure S4, where only few panels show significant differences between sample sets (in particular the clay content, here represented by grain-size distribution, not mineral analysis). Within sample set variability appears to be equally large, making it difficult to derive meaningful systematics. On the other hand, some sediment properties with strong impacts on sorption like mineral surface area or quantitative mineralogy are not reported for the sample set. This raises the question whether differences found between the sample sets can be attributed to the differences between the landscapes and are not due to random variability between individual sites. Related to this is the observation that none of the relationships found between sediment geochemistry and sorption coefficient appear to be particularly strong (Figure 6).

Thank you for this comment.

A key finding of this paper is that geochemical variation within regions, and within sediment types, is important to consider. In particular, we emphasize that past thaw increases variability in sediment geochemical properties. This is demonstrated in Figure 3, where more detailed analysis (principle component analysis, compared to boxplots in Figure S4) shows discernible variation between and within sediment types.

Although we did not assess for mineral surface area, we did assess for geometric specific surface area, measured as the total area of the particles divided by the total weight (m^2 kg^{-1}), with an assumed density of $3 g/cm^3$ and the assumption that particles are spherical and non-porous (Malvern Instruments Ltd., 2013). We opted to represent grain size as % clay because % clay has a slightly stronger relationship with sorption coefficient than specific surface area (see figure below), and % clay is a slightly more accessible measurement. For the interested reader, we will add a biplot of specific surface area and sorption coefficient to the supplement of the revised manuscript.

Although a quantitative XRD analysis is outside of the scope of this manuscript, we will undertake a semi-quantitative analysis (i.e., using reference intensity ratios; Hubbard and Snyder, 1988) and will compare mineralogy to sorption potential.



Sorption experiments were conducted on freeze dried, disaggregated and homogenized sediments. These were agitated with a DOM solution in a dilution series and the decrease in DOC concentration was used to determine sorption coefficients. I wonder how this can be unambiguously ascribed to sorption alone. Can biodegradation during these experiments be excluded? Were sediments sterilized before the sorption experiments? Initial biodegradation would be consistent with the observed enrichment of labile compounds in the DOM solution (or the loss of humic-like, aromatic compounds). Even in frozen till or Yedoma sediments, resting microbial communities can be readily re-activated when thawed and exposed to water.

We ran our experiments at 10°C to limit biological activity and constrain changes to DOC concentration or DOM composition to mineral sorption. Additionally, previous work with similar sediments from the Peel Plateau has shown that biodegradation potential on regional sediments is quite low (Shakil et al. 2022). The linear relationship between ΔDOC and initial DOC concentration in our sorption experiments (i.e., Figure S7, left column), despite a consistent 10% w/v addition of sediment to all experimental replicates, is similarly consistent with sorption.

We also note that biodegradation of DOM of permafrost leachates will typically preferentially consume aliphatics, leaving the resultant solution enriched in aromatics (e.g., Drake et al., 2015). This contrasts the effects of sorption, which preferentially involve aromatic compounds and enrich the remaining solution in aliphatics (e.g., Kaiser and Zech, 1997, Groeneveld et al., 2020), as observed in our experiments (Figure S7, centre and right columns).

Rather sophisticated statistical analyses were performed. The typical reader of a biogeochemical journal might appreciate more details on the methods.

Thank you for this suggestion.

We will modify the text in Section 2.6 to include further details on the DOM composition analysis:

Line 291 "Spectral slope (275–295 nm; S275–295) and slope ratio (275–295 nm slope:350–400 nm slope; SR), and specific ultraviolet absorbance at 254 nm (SUVA254) were calculated from absorbance data as proxies for molecular weight…"

Line 293: "A parallel factor (PARAFAC) analysis was conducted using EEMs with ~~using~~ the drEEM toolbox…"

We will also add details related to the PARAFAC (as suggested below).

For readers unfamiliar with principal component analysis, we cite the R packages that contain more information on the technique.

In summary, the manuscript presents an ambitious study and an impressive data set. The conclusions drawn from the observations, however, should be formulated more carefully and the rather large unexplained variability observed in the data set should be acknowledged.

We agree that these in situ samples possess substantial variability, in line with their geological history. This natural variability is reflected in some variability in the relationships shown in Figure 6 and the presentation of results in section 3.3. We have been careful to be appropriately soft in our interpretation of these results, particularly in the discussion beginning in line 555 and in the conclusions, but are open to specific suggestions from the reviewer.

Specific comments:

Line 290-300: More details are needed to explain the PARAFAC analysis, including the number of dimensions. Later, in the results chapter, M, A and C peaks are described, which are not properly introduced.

We describe the PARAFAC model results in section 4, but will add text to inform the reader of the number of components at this point:

Line 295-297: "To maximize robustness of the model, EEMs from both the batch sorption (n 295 = 374) and bio-incubation (n = 37; ntotal = 411) experiments were included in model construction. A 6-component model was validated, as discussed in Section 3.4. The relative contribution of each PARAFAC component…"

Line 299-300: "Components were matched (similarity scores > 0.95 for both excitation and emission spectra) to published models on the OpenFluor database (Murphy et al., 2013) and compared to the traditional Coble peaks (B (protein(tyrosine)-like), T (protein(tryptophan)-like), A (humic-like), M (marine or microbial humic-like), C (humic-like); Coble 1996)."

Chapter 3.1: The way the mineral content is presented is a bit confusing, and I would encourage presentation of minerals in order of decreasing relative abundance. From Figure S3 it is evident that the dominant minerals (as expected) are the silicates (quartz, feldspar, muscovite and clay minerals), which occur in almost all samples. Some samples (dependent on bedrock geology, I presume) contain carbonates and sulfates and sulfites (the latter likely only in anoxic portions of the profiles). Anatase is likely only present in trace amounts, but is presented as one of the first minerals in the list. Overall, mineral occurrence will be tightly linked to bedrock, and may also be related to grain size (with coarser grain size lacking clays). It would be helpful to provide relative abundances of mineral classes, not only report occurrence. Different mineral classes have very different sorption capacities, and their abundance within a sample will determine the effectiveness of sorption. This is particularly true for clay minerals, which have charged surfaces.

As described in the caption of Figure S3, minerals are ordered by weathering susceptibility (following Cornelis et al. 2011), which we prefer to keep to connect to our discussion about the influence of past thaw (and therefore opportunities for weathering) on sediment properties and within-group variability.

In addition, because the relative abundances of minerals would vary across our 35 samples, it wouldn't be possible to order the minerals by decreasing relative abundance.

We will arrange for semi-quantitative XRD analysis with reference intensity ratios. We will present this data in table form in the supplement for this manuscript, and will compare mineralogy to sorption potential.

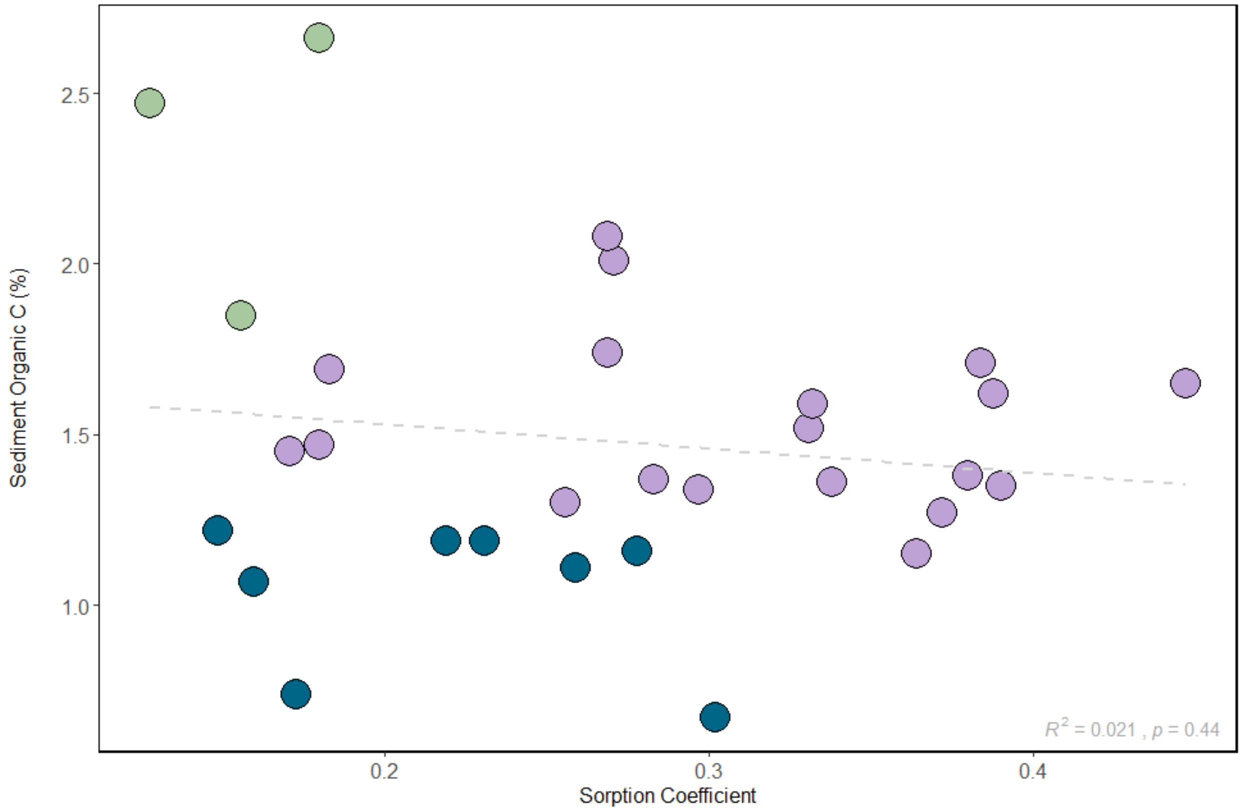
Line 335: Be careful when ascribing causal relationships in a PCA – co-variation does not explain which is the driver and which is the cause. I would expect that high concentrations of Al (high in clay minerals with a high surface charge) and Fe and Mn (in oxides) are the causes for high SOC content, not the result, as those minerals are active sites of OC adsorption.

We will modify the text for clarity as follows: "PC2 (25.0 % of variation) was ~~driven~~ associated with pH and OC content, with pH plotting positively and %SOC and the ratio of SOC:N plotting negatively along PC2".

Chapter 3.2: Sorption coefficients seem to scale inversely with OC content. This is not mentioned.

We performed a linear regression to express the relationship between sorption coefficients and sediment organic carbon content, and do not see a significant relationship, and therefore chose to exclude this from the manuscript.

We can include this figure in the supplementary, for the interested reader.



Chapter 3.3: None of the relationships displayed in Figure 6 seem to be particularly strong, suggesting that they may not be the primary control on sorption. Did you obtain mineral surface area measurements for the samples? This is likely a strong control on the sorption of OC.

As discussed in response to an above comment, we did not obtain mineral surface area measurements for samples. An assessment of geometric specific surface area relative to sorption potential showed a relationship similar to that for % clay.

Chapter 3.5: Can you provide more details on the "common microbial pool"? Where was it derived from?

The common microbial pool was derived from water from the Mackenzie River, as described in the methods section 2.5 line 278. We will add a few words of text to remind the reader of this in section 3.5.

Chapter 4.3: Can a mechanism be proposed by which organo-mineral interactions may promote biodegradation? Is it perhaps by concentrating OM on mineral surfaces through sorption, while at the same time providing a hot-spot for microbial colonization increasing availability of OM?

Our bio-incubation experiments were conducted with DOM that had been subjected to sorption processes, and then filtered, prior to addition of the microbial inoculum (i.e., no sediments or particulates were present during the incubation). Therefore, we attribute changes in biodegradation to shifts in DOM composition and release of bioavailable nutrients from sediments before the start of the incubation, and there is no potential for hotspots for colonization due to sorption in these experiments. We will reiterate that samples were filtered prior to the experiment in Section 4.3, to ensure clarity for the reader.

We will provide more detail in section 4.3 (line 583-585) to further explain why DOM sorting and the release of mineral-bound labile compounds may promote biodegradation.

Additionally, there no direct evidence in the literature that organo-mineral interactions act as hotspot for microbial colonization. Instead, it is considered that OC is less accessible to microorganisms when involved in mineral-organic complexes.

While it has been demonstrated that Fe can play a role in driving photodegradation (e.g., Bowen et al., 2020), our experiments were conducted in the dark and therefore, photodegradation did not contribute to changes to DOC concentration or DOM composition in our experiments.

Details, typos:

Line 119: what kind of sulfides are contained in the till?

Pyrite and siderite have been previously identified in tills on the Peel Plateau (Zolkos and Tank, 2020). This aligns with the results of the presented study. We will add this detail to the text of line 119 as follows: “This resulted in widespread deposition of ice-rich moraine comprised of fine-grained till containing carbonates, sulfides (pyrite and siderite), and silicates…”

Line 136: shouldn’t this be “siliciclastic“?

Yes, thank you for finding this mistake. We will correct this typo.

References

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