Responses to RC2: Muhammed Fatih Sert, 05 Apr 2024

The paper by Doting et al. reveals the DOM molecular composition of a supraglacial micro catchment in the Greenland ice sheet surface with FT-ICR MS analysis. The manuscript is well-written and presents a unique dataset that holds significant value for the scientific community. However, the dataset utilized in the manuscript is solely limited to DOC concentrations and MS analysis and does not provide a comprehensive overview of environmental biogeochemistry in the studied site. Therefore, I would highly recommend to the authors that they may seek additional measurements to document environmental variabilities such as nutrients, isotopic compositions, or microbial diversity. If this is not possible for this manuscript, you should acknowledge this limitation by discussing the potential implications of the dataset's scope and suggesting areas for future research. Additionally, I noticed that the manuscript suffers from complicated nomenclature, which implies different meanings for researchers from other disciplines. Therefore, I would suggest that the terms used in the manuscript be carefully reconsidered for alternatives (see below).

Dear editor and reviewer,

We would like to thank the reviewer for their constructive comments. Please find our responses below (in blue). We agree that additional biogeochemical data on the sample would have been of added value to this study. However, unfortunately this was not within the scope of the study and we do not have samples that can be analyzed for the proposed parameters. We agree that this would be an important avenue for future research, and will acknowledge this limitation in the revised manuscript. In addition, we will revise nomenclate where necessary, and will ensure that any field-specific terminology is defined at first mention throughout the manuscript. We appreciate the time and effort from the editor and all three reviewers, and hope that our responses will be sufficient to be allowed to submit a revised manuscript for publication in Biogeosciences

Please see below for additional comments:
Line 36: if it provides protection from the UV, then it should reflect more and elevate the albedo rather than lowering it.
This is incorrect. The main pigment in Ancylonema nordenskiöldii and Ancyloname alaskanum is purpurogallin carboxylic acid-6-O-β-D-glucopyranoside, as identified by Remias et al., 2012. That same study reports the extensive absorption capacity of this pigment over a wide range from UV B to VIS radiation, suggesting that this phenolic compound shields chloroplasts against a surplus radiation, preventing photoinhibition during high irradiance. As protection is provided via absorption, and the pigment is in part responsible for the biological darkening cause by algal growth on the ice sheet surface, its presence lowers the albedo (the fraction of light that is reflection by a body or surface) as demonstrated by e.g. Cook et al 2017, Williamson et al 2019 and Cook et al 2020.

Line 91: Dark ice resembles ice that is not in contact with the sunlight, which is not the case. You may consider using a different term. Maybe brown ice or just surface ice.
In the revised manuscript, we will make sure to introduce this term clearly or change to biological-darkened ice. Within the cryosphere community, dark ice is commonly used to describe ice surfaces with dust, soot or microbial loading (for example, when searching “dark ice” on Google.com, the top science result describes dark ice in the context of ice sheets and glaciers) - hence, this is the appropriate term to use in the context of this paper.

Line 118: Leachate does not really define what you obtained from your samples. Leachate usually defines liquids that are drained through solids gravitationally or maybe via osmosis. What you did is more like an extraction rather than leaching because of 500 rpm shaking and centrifuging. Therefore, I would use a different term, such as surface debris extract. On the other hand, the component you define as the weathering crust is more like leachate because you let the auger hole fill with meltwater leachate and perform the sampling afterwards.
In the revised manuscript, we will replace ‘laboratory leachate’ with water soluble organic matter (WSOM).

Section 3.3: PCA with dependent variables does not reveal the compositional differences between samples. It is not surprising that the CHON, CHO and CHOS point in different directions on the plot because they are basically the opposite representation of the same variable. The same applies to formula percentages of van Krevelen regions. PCA is usually for independent environmental variables to indicate how environmental conditions differ for the sampling sites. You should consider applying clustering methods on relative intensities for compositional differences between samples then you can add parameters on the ordination plot (e.g. NMDS + envfit in Vegan). You would possibly get a similar separation, but then you may know which cluster of samples is more similar to the other cluster compared to the remaining ones. Then, instead of PCA, you may simply use bar plot or box plot to visualize which parameter infer the bigger variation.
Principal component analysis is commonly used to assess the DOM parameters that distinguish FT ICR MS samples, (e.g. in Riedel et al 2016, Spencer et al 2019, Kellerman et al 2021, Marshall et al 2021, Holt et al 2021) and we therefore consider it an appropriate method to examine our dataset and compare with existing literature. The data suggested for the bar plots are presented in Table 1. We selected a table over bar plots to keep the number of figures in the manuscript to an appropriate number.

Figure 4: The figure caption is unclear, and I did not understand what the individual plots show. You should extend this figure by adding van Krevelen for all the formulas obtained from each sample. For example, 8403 formulas for lab leachate or 7540 formulas for dark ice. You could also involve RAs by symbol sizes.
We will update the figure and figure caption to be clearer in the revised manuscript.

Line 320: What do you mean by high particulate loading? What kind of particulate matter? You may explain more about what you observed with the microscope in the field.
We will elaborate on our observations in the revised manuscript.

Line 326: why preferentially? Are those more soluble?
We assume this is meant to refer to L329. With ‘preferentially’ here we mean DOM that has already leached from the surface debris, and will therefore not leach from the material again when preparing the water extract. We will rephrase this to make it clearer in the revised manuscript.

Line 360: You should have check how molecular intensity of common molecular formulas change between samples. You have done this for several selected formulas, but you could extend this to all common formulas to see if there is indeed hydrological connectivity. Otherwise, number of common formulas do not necessarily indicate hydrological connection. You would have found common molecular formulas in any DOM samples.
Common formulae alone don’t demonstrate hydrological connectivity, but paired with the hydrological data, which suggest hydrological connectivity, the large overlap in shared formulae strengthens the hydrological connectivity argument. Looking at changes in molecular intensity therefore seems redundant and not in line with reviewer requests to streamline the paper.