Author's Responses to Reviewer 1:

Overall response: We would like to thank the reviewer for the helpful and constructive review. We have made extensive changes to the text, particularly the Discussion, in line with the commentary below and that of the other Reviewer. We feel that the manuscript has been significantly improved as a consequence.

Reviewer comments and responses.

GENERAL COMMENTS: Overall, the manuscript by Holland et al. provides some important, hard-fought observations in one of Earth's least studied biomes, and provide some of the first evidence of the biogeochemical role played by the large seasonal algal bloom that develops on Greenland's Ice Sheet, which has recently attracted attention due to its influence on albedo. These data are therefore timely given the projected future mass loss of the Greenland Ice Sheet, and the consequences that these fluxes may have on downstream environments. Lastly, these present data are unique in that they seem to represent a relatively large spatial and temporal extent, and analytically, the methods employed for the data generation appear excellent.

However, I have some concerns with the way the data are described, interpreted, and reported. Firstly, I feel like the authors could do better job in focusing what exactly this paper is about, as the abstract, introduction, and discussion all give slightly different objectives for the study (see detailed comments below). I think that this manuscript would benefit from clarifying and focusing the objectives and hypotheses and making these consistent throughout the document.

- **Response:** We would like to thank the reviewer for their commentary regarding the clarification of the manuscript. We have significantly revised the manuscript and feel that this revision better follows the three main aims and objectives set out in the last paragraph of the introduction. A major restructuring of the results section has been carried out, to make the section more hypothesis driven, as well as to link more clearly to the objectives in the introduction and the subsections of the discussion. The discussion has also been rewritten to clarify meaning and refocus on the objectives of the manuscript.

The second issue is in reference to the biogeochemical cycles/transformations hypothesized to be taking place on the surface of the ice sheet. Some of the language in this regard could be tightened for accuracy and consistency (or at least clarified, see below comments), and I have suggested that the authors could create a conceptual diagram (with all inputs, outputs, transformations, etc) to help in presenting the hypotheses and afterwards discuss the data.

- **Response:** We hope that we have removed terms and phrases that could be misleading to the reviewer about what was actually quantified in the present study. A simple conceptual diagram has been included.

Thus, in revising this article, I challenge the authors to focus this research by asking specific, testable questions, and clearly using the data to answer these questions throughout the different sections of the document, as well as to pay careful attention to the biogeochemical transformations taking place in this special environment. Some specific comments are outlined below by section and line number.

- **General response:** We thank the reviewer for this challenge and hope that the revision now passes muster. Our responses to each individual question are given below.

Title: Is the paper really about nutrient 'cycling'? Maybe something like 'organic nutrients dominate supraglacial environments and correlate with algal cell density...' or similar would better represent the subject matter of this paper.

- **Response:** We agree and have changed the title.

ABSTRACT Line 19: Probably should be nutrient 'abundance' rather than nutrient 'cycling' that is a constraint on algal abundance. Also, do we know if nutrients are indeed a constraint on these communities?

- **Response:** the text has been revised. Nutrient abundance in the Dark Zone has not been investigated in detail enough to definitively determine if it is a constraining factor on the bloom, which is why this manuscript investigates a limiting nutrient.

Line 20: This paper does not really investigate the conversion of dissolved inorganic nutrients to organic ones; it more just investigates the abundance of each. We can of course infer that conversion is the reason for one form of nutrient over another, but most certainly conversion itself was not assessed.

- **Response:** Text changed from 'conversion of dissolved inorganic nutrients…' to 'abundance of dissolved organic nutrients….'.

Lines 21-22: Where are these percentages coming from. . .are these from the entire dataset? There was a gradient of algal abundance sampled over, as well as cryoconite and supraglacial stream categories. . ..it might be appropriate to describe the sampling scheme briefly in the abstract, and state which of these data were used to calculate these numbers.

- **Response:** The authors have added text briefly describing the five supraglacial environments sampled in the study. Please see lines 20-21 of updated manuscript. Text has been added explaining that the percentages have been calculated from across all of the ice surface samples containing low, medium and high visible impurity loadings. Please see lines 21-22 of updated manuscript.

Line 23-24: Can maybe be more specific here to indicate the shift from inorganic to organic forms rather than 'phase shift'.

- **Response:** This line has been deleted in updated manuscript.

Line 24-25: Again, what supraglacial environments are we referring to with these ratios? There are three values given after DON:DOP and DOC:DOP. . ..why three - what do they correspond to? Also, why were these ratios reported and not DOC:DON? Perhaps more importantly, why are only the organic forms being reported and compared with Redfield Ratio as opposed to inorganic forms?

- **Response:** This line has been deleted in updated manuscript.

INTRODUCTION Line 40 and 56: Particles of what? Given the potential importance of these particles in providing nutrients, I think they can be described in a bit more detail here. Are these the same particles described in lines 41-44 as being LAI's?

- **Response:** The particles being referred to are considered to be dust, dated to the late Holocene by Wientjes et al., 2012, melting out of ancient meteoric ice. However, these particles are one example of mineralogic LAIs that could comprise the visible impurities seen in the Dark Zone, which is why the authors have also included a list of other mineralogic LAIs in Lines 53-54 of the updated manuscript. In line 52 of the updated manuscript 'ancient Holocene dust' has been added as a descriptor of the particles being described.

Line 60: Redfield et al., 1963 is an interesting choice for a reference, especially since it is regarded as being specific only to marine plankton in the discussion. Could maybe find something more broad and recent. . .maybe the Ecological Stoichiometry book by Sterner and Elser (2002) would work better?

- **Response:** We have largely removed reference to the Redfield ratio, and note that information on the C:N:P ratio of glacier algae is sparse. We have added Hessen et al., 2013 as a additional reference.

Line 60: Why is carbon in ready supply on the ice sheet surface; where is it coming from? Why would this not also be the case for nitrogen and phosphorus. . .where are these two coming from and in what forms? Perhaps this is intuitive to the authors who are specialists for this ecosystem type but would be good to describe some of these inputs/outputs to non-specialist readers of the journal.

- **Response:** Carbon is in ready supply on the ice sheet surface for two main reasons, the first is that it is scavenged from the atmosphere during snow crystal formation and then is released to the surface ice environments when the snow pack ablates. The second is due to the surface ice environments constant interaction with the atmosphere. Due to the air-water interface during the main ablation season, gas exchange can occur which allows for carbon to be readily available. Both of these forms of carbon are in the dissolved inorganic phase, which includes aqueous CO_2, HCO_3 (bicarbonate), and H_2CO_3 (carbonic acid). Nitrogen is dominantly released to supraglacial environments via snow melt as nitrogen is also scavenged from the atmosphere during snow formation, with a lesser input from ice ablation. N_2 is also a potential source due to the air-water interactions occurring as mentioned before, however it is not very bioavailable and most photosynthetic organisms are not able to fix it from the atmosphere (Falkowski and Raven, 1997). Furthermore, Telling et al., 2012 reported that the overall importance of nitrogen fixation for microbial growth decreases with distance from the margin of the GrIS. Phosphorus is a rock dervived and is therefore only released by physical and chemical weathering of rock derived particles. Typically why it is the limiting nutrient in supraglacial environments. Lines 69-78 have been updated to include a more detailed explination.

Line 63: Does the 'Stibal et al. 2017a' citation go with the cell concentration number? If so, it might be better to move it there. . .I'm not sure that paper suggests that these habitats are nutrient rich (but I could be wrong).

- **Response:** This line has been deleted in updated manuscript.

Line 69: If there are some more examples than the Telling et al. 2012 paper, you should cite them here.

- **Response:** References to Telling et al., 2012 and Wadham et al., 2016 has been added to the end of lines 85-86 of updated manuscript as these presently are the only two studies to have quantified nitrogen concentrations in the Dark Zone of the GrIS.

Line 71: What was the detection limit in this study (i.e. Telling et al. 2012)? Should report before the citation in the same units as your paper.

- **Response:** The LoD for the Telling et al., 2012 study was 0.33µM and has been added to line 89 of the updated manuscript.

Line 73-75: This is more or less what you found for DIN, no? However, for DON, the values were much greater. I think it would be nice to revisit these ideas in the discussion.

- **Response:** Section 4.1 of the discussion revisits these values and discusses the difference between the DIN and DON concentrations for this study.

Line 76-77: This sentence is a little confusing to me. . .how do cycles of uptake and remineralization lead to accumulation of nutrients in biomass? Also, I think there are potentially a lot of systems with microbially-mediated nutrient cycles that can be used as an analogue here. . .Planktonic aquatic systems are nice ones, but I don't think this is somehow the pinnacle of nutrient cycling.

- **Response:** Uptake and remineralization describes what occurs in the microbial loop. As these microorganisms are utilizing and recycling the available nutrients, they become incorporated and accumulate into their cellular biomass as well as to being released back into the meltwater, which leads to nutrients not only existing in the environment in the inorganic phase but also in the organic phase in the form of biotic mass and dissolved organic matter that the cells produce. The authors chose to use planktonic aquatic systems as a comparison as it is similar to the aqueous ice surface environments.

Line 78: Maybe rephrase this. . .'extremely active nutrient cycling' sounds strange and unspecific to me. Would be better to give a rate estimate.

- **Response:** Line 95 of the updated manuscript now cites an NPP rate from Williamson et al., 2018.

Line 79: I think this is something that you need to expand a bit more on, since the whole paper is essentially centered on it. Why are dissolved nutrients concentrating in the organic form, and is this really a sign of 'active' nutrient cycling? Later in the text, the opposite rationale is essentially used to explain the same observation, which is that low mineralization rates are responsible for an accumulation of organic nutrients. I think the authors would do well to describe the major inputs, outputs, and transformations in this unique habitat. Perhaps a conceptual diagram could help here, not only explain the rationale for this nutrient survey, but also help define your hypotheses/predictions?

- **Response:** We argue that DIN and DIP uptake by glacier algae and the production of EPS and other degradation products is the source of DOP and DON. This is the most consistent explanation from the data sets we present. A simple conceptual diagram is now included in the manuscript.

Line 80-82: Isn't there organic nutrient data in Telling et al. 2012? It is likely that there are not so many reports of organic nutrients from the dark zone of the GRIS (it's not so easy to get there, afterall), but what about elsewhere on the ice sheet, or on other glaciers around the world? I think this is something, in concert with my comment above, that needs to be expanded upon ultimately given the content of this paper, an in order to appreciate the finding of this paper later.

- **Response:** Text has been added that now cites Telling et al., 2012 and Wadham et al., 2016 as reporting TN for the Dark Zone, and clarifying that non has been reported for ice populated by Streptophyte ice algae, lines 111-112. Lines 104-107 cite other sources reporting dissolved organic nutrient concentrations in other Arctic environments and the Antarctic.

Line 84: Do you expect that the ice algae are 'recycling' the nutrients, or just taking them up?

- **Response:** This line has been deleted due to edits in the updated manuscript. We do believe that recycling is occurring due to the fact that heterotrophs are present. If heterotrophs are present then they are utilizing dissolved organic matter and therefore remineralization is occurring, albeit at an inefficient rate. Lines 102-118 begin to describe this conclusion.

Line 88: I think you would need uptake data, for example, to actually evaluate the 'importance' of different nutrient forms. Also, when you say 'microbial' recycling, are you only talking about the algae?

- **Response:** Text changed from 'importance' to 'relative abundance' in response to reviewer's comment, line 129 in updated manuscript. 'Microbial' recycling refers to the microbial loop and therefore both the algae and bacteria.

METHODS Line 98: This is an extremely big area. How were sites randomly sampled (line 103) over such a large patch? Is there any sense of the area covered/sampled over this time? Were some sites/areas resampled over the month of fieldwork?

- **Response:** Within each category of low, medium and high visible impurity loadings the sample location was chosen randomly by eye. There was no quantification of visible impurity loading before sampling however, as seen in Figure 2 the differences between the three ice surfaces are very apparent. Figure 3 reinforces this by the significant difference in algal abundance between the three ice surfaces. GPS points were collected at each sampling location within the 500 X 500 m sampling site, however no plots have been made to visualize the total area covered. Sampling areas were destructively sampled by the use of a hand saw to remove the top 2cm of the surface ice as described in the methods, therefore areas were not resampled.

Line 99: Was there any relationship with nutrient concentrations and date sampled? I can imagine that conditions on the ice could be a lot different on the 15 of July than they are on the 15 of August.

- **Response:** There was no clear temporal trend in the data. We believe that this is due to the extremely dynamic and heterogenic nature of these environments making trends over long time series difficult.

Line 100: This explains why you sampled the surface ice in low, medium, and high categories, but did you really sample the cryoconite and streams due to the spatial heterogeneity in ice algae distribution? Algae were not quantified for these two habitats, so this is probably not the case. If it is just as a comparison with the surface ice that is fine, but some justification is warranted.

- **Response:** Lines 144-145 in the updated manuscript adds text for clarification about supraglacial stream and cryoconite hole sampling.

Lines 109-110: Was there any special preparation for the glass stack, bottles and collection jars? Eg. Acid washing, furnacing, etc?

- **Response:** Lines 158-160 in the updated manuscript adds text explaining the sample jar preparation.

Line 131: What was the purpose in assessing the assemblage diversity (as opposed to just a number of cells)?

- **Response:** Reference to assemblage diversity has been removed.

Line 140: What is TON. . ..total oxidized nitrogen? Should probably spell this out the first time.

- **Response:** Line 185 does this.

Line 143: This is a bit confusing as written. . .why not say that DON was estimated by subtracting DIN from TDN since you already defined DIN above? Or would be easier to say DON=TDN-DIN?

- **Response:** Text has been changed for clarification, line 193.

Line 166: Why cite RStudio here. . .Wouldn't it better to cite R?

- **Response:** RStudio is considered an IDE, integrated development environment which cannot be run without R. However, R is an independent program, which can be run without RStudio.

Lines 166-172: In general, I think that it would be better to be more specific about what analyses were conducted and why. For example, can say in order to test hypothesis 'x', we performed test 'y'.

- **Response:** We feel the text does say this. Please push back if you still feel that it doesn't.

Line 170: Similar to the comment above, why test DON and DOC, but not DOP? Why were these parameters chosen, and how to they help you to achieve your objectives? For example, why would you not look at inorganic species, or the ratio of organic to inorganic forms as a function of cell abundance? Would it help to include sample date and spatial coordinates as random variables?

- **Response:** Line 250 of the updated manuscript now state: 'Comparison of DOP surface ice concentrations and algal cell counts were not significant.'. Only significant relationships were reported in the manuscript. The authors chose to compare the average algal abundance to the average DOC and DON concentrations for the three ice surfaces as a way of illustrating a relationship between the glacier algae abundance and the concentration of DOC/DON. We feel that this helps achieve the objective of showing that algae are the main producers of DOC and DON in the ice surface environments.

General comment: Was there any attempt to quantify particulates on the surface ice? While biological activity is no doubt important to biogeochemical cycling, so too would be the density of particulates I would think, especially with regard to phosphorus, since it is usually sediment-bound. While this paper of

course focuses on the dissolved fraction, the particulate fraction is likely also important, and I feel like this would also help answer a similarly important question: are the nutrients in the forms they are because of the biological actors, or because of what the biological actors are sitting upon? This may also play a role in why some patches are in 'high abundance', and others are in 'low abundance', and thus would be collinear with cell abundance. Also, if a given sample was below detection, were they included in the analyses? They seem to be included in the figures, but would be good to know if they were also included in calculations, and if so which ones and how they were treated?

- **Response:** We agree with the reviewer about the potential importance of particulate nutrients in supraglacial environments, however, it was simply outside the scope of this study as we aimed toward understanding the dissolved phase. There is a large companion paper that investigates the mineralogy of the particles that comprise the surface impurities which is about to be submitted for review, and we will make reference to this following its submission and this second review of our manuscript. Investigation into the potential phosphorus input from particles in cryoconite holes has been investigated by Stibal et al. 2008. Text has been added in line 213 that states "Samples resulting below the LoD were considered 0 μM.".

RESULTS General comment: I think it would make more sense if the results section was more hypothesis-lead as well. Right now, it reads more like a list with some carefully chosen significant relationships scattered about and are difficult to understand how they relate to the overall picture.

- **Response:** The text in the results section has been completely reorganized with new sub-headings in order to make the reasoning and hypotheses clearer. Please refer to the results section in the updated manuscript (section 3) for the reworked text.

Line 176: In some ways, I feel like this opening sentence is really only validating the obvious. Transects were chosen based on the abundance of stuff covering them, and the first result is that more stuff was found in these patches covered with more stuff. I think that it would be more helpful to report it in this way such that it is setting up your experimental design rather than a unique result in its own right.

- **Response:** We believe that we need to make this is an important distinction. No quantification of the particulate content of the visible impurities was made. It is therefore important to state that not only did the algal cell abundance increase with the amount of visible impurities but that the differences in abundance were statistically significant. This also provides justification for the sampling method we employed.

Line 179-182: Why are correlations with DOC and DON reported here and not below? Why did you not compare with DOP? Also, while an interesting result, I feel like calling them 'highly significant' is a bit excessive, since the relationships (as far as I can tell anyway) seem to be based upon 3 comparisons apiece (averages of low, mid, high). Would Pearson correlations be the correct test here, or would it be better to test against the categories?

- **Response:** Since the reorganization of the results this correlation is now under the "Links between algal abundance and dissolved organic nutrients" subheading: please refer to section 3.2 of update manuscript. Please refer to above comment regarding the lack of DOP comparison. The Pearson correlation test was used as an initial test to illustrate a relationship between DOC/DON concentration and algal abundance. The term 'highly significant' has been removed.

Line 184 and elsewhere: Noting the number of samples that were over the LOD is great, but out of how many samples? What then happens to these below detection numbers. . .are they included in

calculations? Also, are some of these replicates or from the same patches? Are these also including cryoconites and supraglacial streams? The authors need to be more specific in their reporting of these data.

- **Response:** Text has been added at the start of results section 3.1 noting the total sample number for each nutrient for all five supraglacial environments sampled. Please see above comment with regards to values assigned to samples below the LoD. As stated earlier, sample locations were destructively sampled so the same patch was never sampled again. Two different samples each of the low, medium and high visible impurity ice were collected each sampling day, they are treated as individual samples in the data set.

Line 186: This is interesting. . .why do you think that NH4 was the dominant component of the DIN? Could this be from microbial ammonification of DON? I think this could be potentially also highlighted in a conceptual diagram!

- **Response:** Ammonification was not quantified, and so we are unable to definitively say the cause of the ammonium dominance. Telling et al. 2012 noted that the presence of NH4 in cryoconite hole samples might be an indication of active organic matter remineralization.

Line 194-200: Again, why do you not make comparisons with abundance and DOP? it seems central to what you are trying to find out, whether or not comparisons are 'significant' (in either case its interesting). It is also not clear which samples you are talking about . . .are they all pooled values for the ice sheet as a whole?

- **Response:** Please refer to above comment regarding the lack of DOP comparison. Section 3.1 of the results has been rewritten and text has been added explaining which samples are being referred to.

Line 196: 'The mean concentrations for the remaining 40 DIP concentrations [that were above the LOD] ranged from 0-0.7'. . .the lower limit should be 0.02, since that was the limit of detection, right?

- **Response:** Samples that fell below the LoD were considered to be 0 μM, which is why our sample range begins at 0 μM.

Line 198: 'DOP concentrations in cryoconite hole and supraglacial stream water fell below the LOD'. . .How do you mean this. . .that they fell below the LOD sometimes? In Figure 5, the average DOP for these two habitat types is around 7 uM. DON is a different story. . .Could it be that these two are being confused?

- **Response:** The text has been changed and the comment moved to line 262.

General comment: There are several mentions of nutrient ratios in the abstract and discussion. Why are these not discussed in the results? Also, where is figure 7?

- **Response:** Nutrient ratios have now been added to the result section 3.2 in response to the reviewer's comment. Figure 7 from the original version has been removed from the manuscript in response to reviewer 2 comments. Figure 7 is now the conceptual diagram.

DISCUSSION Lines 212-214: This information should be in the results, and it should be specified how they are calculated. For example, are these calculated for only surface ice environments? Furthermore, I think that the ratios of organic to inorganic nutrients would be potentially equally or more interesting to correlate with algal cell abundance than the absolute concentrations.

- **Response:** Percentages have been removed from the discussion and added to results section 3.1 with text added to explain which samples the percentages are referring to. See lines 230-231 in updated manuscript. The revised text discusses the increase of DON:DOP and DOC:DOP ratios with increasing visible impurities, lines 351-354 of discussion.

Line 215: Has this dominance been reported in other glacial systems?

- **Response:** Yes, dissolved organic dominance is commonly reported for cryoconite hole environments (Stibal et al., 2008; Telling et al., 2014). Lines 305-309 in updated manuscript describe dominance of dissolved organic nutrients in other glacial systems and its relation to microbial activity in the environment.

Line 222: Does Tedstone et al. 2017 actually report the timing of this shift in Nitrogen? Actually, has anyone reported this shift in nitrogen?

- **Response:** Text revised.

Lines 223-225: Similarly, how does this Williamson et al. (2018) paper support the shift in nitrogen phase? I think this needs to be rephrased/recast.

- **Response:** The authors have reworded the sentence. Please refer to lines 286-287 in updated manuscript.

Lines 226: But, these other impurities were not quantified, so it's difficult to say this for certain. For all we know, all the impurities could be ice algae! However, I think there may be some other papers showing this these days that you can cite. . .

- **Response:** Text changed in response to reviewer's comment. Yallop et al., 2012 has now been quoted as reporting a particle: cell ratio of 3:2 in the dark zone of the GrIS. Please refer to lines 292-293 in updated manuscript.

Line 227: There is a lot of talk of nutrients 'shifting' to the organic phase. But, it looks like to me that the concentration of DIN is basically the same for all the surface ice habitat types. Might the DON rather be accumulating through time from ice algae taking up DIN and subsequently 'leaking' DON into their habitat, rather than the DIN pool shifting? It would really be nice to see these relationships over time.

- **Response:** The authors would like to clarify that the use of the term 'shift'. With regards to the nitrogen nutrient pool the author's use of 'shift' has to do with the snow and ice core data that show a dominance of DIN with little to undetectable levels of DON. Yet, as the season progresses the dissolved nutrient pool is dominated by the dissolved organic phase, showing that something is occurring at the ice surface to cause the nitrogen pool to change. The authors agree that it is very likely the ice algae up taking the DIN, utilizing it and producing DON, which is the main argument of this paper: ice algae are the drivers in this conversion of nutrients.

Line 228: Furthermore, the big differences in organic/inorganic nutrients with algal biomass seems to only apply to nitrogen, and I think it is important that this distinction is made. Why would this not apply to phosphorus? This should be discussed in detail, and the authors should be more specific whether they are talking about 'nitrogen' or indeed 'nutrients' (ie nitrogen + phosphorus) elsewhere in the manuscript.

- **Response:** The revised text hopefully makes this clear.

Line 230: Do the data really suggest 'efficient' conversion? I think at best there is a correlation between cell counts and organic nutrients, but no data that points directly to conversion, and definitely no data that would suggest that the process is efficient (for example, the DIN concentration seems unchanged with increasing cell abundance). Furthermore, why do you think the same would not be seen for DOP?

- **Response:** Text changed in response to reviewer's comment and the term conversion has been removed. Please refer to line 268 in updated manuscript. Discussion of changes in DOC:DON:DOP ratios can be found in Section 4.4.

Line 232-233: I think this information belongs in the results section. Furthermore, Figure 7 is mentioned for the first time here. Maybe would it be better to put this in supplementary information if it is not going to be used to support the main results? Individual data points could also be superimposed onto bar figures (e.g. 'jittered' points in ggplot2) to illustrate variability between categories, if that is the goal.

- **Response:** Figure 7 from the original version and linear regression relationships have been removed from the manuscript in response to reviewer 2 comments.

Line 239: 'Demonstrate' is strong in this case. . .perhaps 'suggests'?

- **Response:** This sentence has been deleted in revised text.

Line 240-241: Are ice algae assemblages the main producers of dissolved organic nutrients stocks in freshwater and marine ecosystems? Recast this text.

- **Response:** This sentence has been deleted in revised text.

Line 242: Do the ice algae really 'rapidly' take up inorganic nutrients? If there are some numbers to back this statement that is great, but I think this cannot be said without some support.

- **Response:** This sentence has been deleted in revised text.

Line 243: I still think that it would help to somehow organize these sources in a diagram to help guide your thinking and the readers comprehension. What forms of inorganic nitrogen is deposited on the ice sheet and how? How about organic forms? Phosphorus?

- **Response:** The authors have produced a conceptual diagram in response to reviewer's comment. The diagram depicts likely nutrient inputs to supraglacial environments, ice algae producing dissolved organic N, P and C and inefficient remineralization by heterotrophs. The diagram is simple due to the fact that many aspects of nutrient input, cycling and export in the Dark Zone of the GrIS still remain unknown and was one of the main objectives of this paper, to produce a preliminary dataset of dissolved inorganic and organic nutrients for this region. The authors fear

that by making this diagram overly detailed it could be misleading as not enough research has been done in the Dark Zone. Please see Figure 7 for conceptual diagram.

Line 245: Can also be breakage, leakage, or lysis, for example. . .what about extracellular processes?

- **Response:** The authors included 'decomposition of the ice algae' to account for the breakage, leakage or lysis input of dissolved organic nutrients. Extracellular processes such as the production of EPS is addressed in section 4.3 of the discussion.

Line 248: Does bacterial carbon production equate to nutrient-transformation processes like ammonification? If bacteria are really that sparse, I think you could alternatively think that they are really efficient, since they seem to be producing measurable ammonium in excess of uptake.

- **Response:** It is possible that depletion of nitrate and higher levels of ammonium could suggest ammonification, but it would only be speculation within the constraints of this manuscript. Furthermore, the authors would also like to clarify that the manuscript comments on bacterial production rates in comparison to net primary production, not bacterial abundance. Nicholes et al. (2019) reports bacterial abundance as $3.3 \pm 0.3 \times 10^5$ for surface ice samples taken during the same field campaign as the present study. This shows that bacteria are abundant, but not active.

Line 251-254: 'Reduced capacity' is interesting wording. . .were they at higher capacity at some point? I think the production of ON is just outpacing mineralization

- **Response:** This sentence has been deleted in revised text.

Lines 257-259: This is interesting that all of these different habitat types studied by Stibal et al. (2008) also had the organic forms dominate. Why do you think this was not the case for Nitrogen in the supraglacial streams and cryoconites from this study, while it also it seems to hold true for phosphorus?

- **Response:** The authors believe that there could be differences between the two studies due to retention by surface ice microbial communities. One conclusion of this manuscript is a retention ability by the microbes in the surface ice to hold dissolved organic nutrients at the surface via the production of EPS. As EPS contains N, it is likely that N is being retained at the ice surface as opposed to being transported through the water table. DOP is also exuded in the form of EPS, but actually the difference in DOP and DIP in supraglacial streams is not statistically different. The concentrations of DIN/DON and DIP/DOP in cryoconite hole water are not statistically different either.

Line 271: Are ice algae producing EPS? Has anyone tried to quantify this?

- **Response:** To the authors knowledge, quantification of ice algal production of EPS has not been conducted, but Yallop et al. 2012 identified EPS in surface ice samples dominated by ice algae.

Line 279-280: is it possible that DON and DOP are also 'over-wintering' on top of the icesheet? Could any of this be 'leftovers' from a previous season?

- **Response:** We believe that some DON and DOP can remain in the ice surface at the end of the ablation season and remain frozen until the next season. We use Musilova et al. 2017 to provide

an example that this has already been shown for DOC. Please refer to lines 332-340 of updated manuscript.

Line 280: This sentence is vague. . .what exactly about the export of dark zone DOM is unknown. . .the character. . .the quantity?

- **Response:** This sentence has been deleted in revised text.

Line 285: The Redfield Ratio was certainly generated using data from marine systems, but I think its utility over the last decades has been in providing a point of comparison. However, I think it also deserves clarification that the Redfield Ratio is the average molar ratio of biomass under balanced growth. Do we know the elemental composition of ice algae under balanced growth, and how it compares to Redfield Ratio? I'm also not sure that I understand the purpose of the text that follows. While there is certainly a lot of variability across aquatic habitats in dissolved N:P ratios from cold regions around the world (and elsewhere), I'm not sure how useful it is to bring up these numbers here. Furthermore, it is not clear if the ratios from the cited studies are also using the organic fractions-only as done in this study (my guess is that this is not the case). If the purpose of this text was to (presumably) link the reported N:P ratios discussed in the paragraph below to the literature, this makes comparisons difficult, and calls into question the need for this text, or at least would suggest that it needs to be revised to fit the authors' purpose.

- **Response:** We agree that the text following the Redfield Ratio in the original manuscript may cause confusion for the readers and it has been removed. We know of no published literature on the elemental composition of ice algal under balanced growth.

Line 295: This is the first time DOC:DON:DOP ratios have been reported besides in the abstract. . ..I did not see it in the introduction, methods, or results that you planned to look at these ratios.

- **Response:** Text has been added to the updated manuscript to include ratios in the results section 3.2. Line 130 of the introduction now describe our intent to investigate nutrient ratios in the manuscript. We do not believe that it is appropriate to include the ratios in the methods section.

Lines 298-300: Why are you making nutrient ratios for the organic form of these nutrients? Wouldn't you expect that algae would be taking up the inorganic forms primarily (especially NH4)? I feel like these ratios might not be accurately approximating availability for algae, and thus I'm not sure that, based on comparing these ratios with the Redfield Ratio alone, that we can say that the system is P-limited. I think it needs to be carefully explained in the text why this would be the case.

- **Response:** Please see revised Discussion Section 4.4.

Lines 301-304: Would it be possible to more rigorously investigate this statement of different slopes of CP and CN over algal abundance? I think that this could be interesting if better developed, but as written it seems more of an afterthought.

- **Response:** Please see revised Discussion Section 4.4.

Line 313: Is cryoconite the same as the particles talked about in the introduction?

- **Response:** Cryoconite is part of the LAIs discussed in the introduction. Cryoconite holes can melt out or be flushed out throughout the season which causes the cryoconite debris to be washed over the surface. The particles referred to in the introduction describe dust ablating out from meteoric ice as reported by Wientjes et al. 2011.

Lines 326: In order to be able to say 'rapid uptake of dissolved nutrients', you need to have data on the uptake rates to compare. You also do not report rates of organic production.

- **Response:** "Rapid" has since been removed from the sentence. We use the term "high production of dissolved organic production" to refer to the high concentrations of C, N and P produced not to imply any rate at which the production is occurring.

Lines 328-329: These production data are also assumed to hold true here, as production wasn't investigated in this work. Also, why would it be inefficient. . .because there are leftover organic nutrients?

- **Response:** An efficient microbial loop has similar rates of NEP and secondary production, which results in more balanced concentrations of dissolved organic and inorganic nutrients. The fact that there is such a dominance of dissolved organic nutrients implies that remineralization rates are low/inefficient. Nicholes et al. (2019) is cited here because they determined a 30:1 ratio for the same surface ice samples reported in this study, as this manuscript focuses on the geochemistry.

Line 332: Was this the case for phosphorus? Also, I think that the notion of this retention being due to EPS is too speculative to say it this way.

- **Response:** We believe that the retention of dissolved organic nutrients via the production of EPS is a viable hypothesis. Please see revised Discussion Section 4.4.

Line 334: This is vague and repeated from line 280.

- **Response:** This sentence has been deleted in revised text.

TECHNICAL CORRECTIONS

Line 23: Comma after 'nitrogen' not necessary

- **Response:** Text changed in response to reviewer's comment.

Line 30: Should there be spaces between values and "Gt"?

- **Response:** Spaces have been added between values and units throughout the updated manuscript.

Line 36: Similarly, should there be a space between "30" and "km"? This should be fixed throughout.

- **Response:** Please refer to above comment.

Line 160: HCl

- **Response:** Text changed in response to reviewer's comment.

Line 214: comma after "To date"

- **Response:** Text changed in response to reviewer's comment.

Line 241: here and elsewhere, references should be ordered.

- **Response:** Text changed in response to reviewer's comment.

Author's Responses to Reviewer 2:

Overall response: we would like to thank the reviewer for the helpful and constructive review. We have made extensive changes to the text, particularly the Discussion, in line with the commentary below and that of the other Reviewer. We feel that the manuscript has been significantly improved as a consequence.

Reviewer comments and responses.

This paper provides novel information on the chemistry of supraglacial ecosystems. The main finding is that most of the dissolved N and P in these environments is in organic rather than inorganic forms. The authors use their chemical data in concert with measurements of algal cell abundance to make inferences about the role of microbes in supraglacial nutrient cycling. The paper is generally well written and would be of interest to biogeochemists, and to a lesser extent, hydrologists and glaciologists, working in ice-covered ecosystems. There are several sections of the paper that I felt were overly speculative, especially with regards to rates and mechanisms of nutrient retention. In addition, I believe that the authors could better reconcile their findings with previous literature on OM production in supraglacial environments. As a result, I think the paper needs some important revisions before it should be considered for publication in Biogeosciences Discussions. I have provided comments and editorial suggestions below that I hope will be helpful for revising the paper.

- **Response**: The authors would like the thank the reviewer for their in-depth assessment of our manuscript and for providing beneficial comments for the restructuring of the manuscript. We direct them to our responses to each individual question below.

Line 99: It would be appropriate to report the number of samples collected for each habitat type somewhere in this section.

- **Response**: We now include the sample sizes of each habitat.

Line 101: How were sample locations classified into low, medium, and high impurity categories? The figure gives a sense of the density of impurities but there is no indication of whether there was some quantitative aspect to the process (i.e. number of impurities per unit area) or whether the process was

wholly subjective. Also, the nature of the impurities is not well described – are they mineral, biological, or a mixture of both (such as the material found in cryoconite holes)?

- **Response:** Sample locations were determined visually as the difference in the impurity loadings was quite apparent, as the authors tried to show in Figure 2. There was no quantitative process conducted on the ice surface prior to choosing the sample location, however Figure 3 reinforces the validity behind choosing sights visually as there was a significant increase in algal abundance between the low, medium and high visual impurity ice. There was no further analysis of the impurities beyond Yallop et al., 2012, who quantified a 3:2 particle: cell ratio for their samples collected in the Dark Zone. Furthermore, a companion paper is being produced that investigates the mineralogy of the impurities collected.

Lines 179-181: The comparisons between algal cell abundance and organic nutrients are inconsistent. Algal cells and DOC are compared by regression, algal cells and DOC and DON are compared by pearson correlation, and algal cells are not compared at all to DOP. Moreover, these tests do not provide any information about the differences in the relationship between different habitats.

- **Response**: Only Pearson correlation is reported in the revised manuscript, and only significant relationships were reported. DOP did not correlate significantly with algal abundance. ANOVA analysis is included to provide information about the differences in nutrient concentrations between habitats.

Line 184: What was the LoD for DON? Are the sample numbers you report (54 DON samples, 41 DIN samples) out of the 70 samples you included in the data for Figure 4? Also, what value did you use for all of the samples that were below the LoD – half of the LoD or some other value?

- **Response**: LoD for DON is 0.87 μM and is included in the revised text. Lines 229-230 have been added for clarification about the number of samples for each test. Values below the LoD were considered to be 0 μM, line 214 has been added for clarification.

Line 194: What was the LoD for DOP? There were 74 DOP samples above the LoD, however in the legend for Figure 5 it appears that only 70 DOP samples were included in the figure.

- **Response**: LoD for DOP is 0.02 μM and is included in the revised text, as are the correct number of samples.

Line 230: How do you get information about conversion rates from the concentrations you measured?

- **Response:** This sentence has been deleted in revised text.

Lines 232-234: This regression plot is not an effective way to analyze the relationship (or lack thereof) between DOC and algal abundance. The fact that there is any positive relationship is based on the single outlier in the upper right hand corner of the graph. If you removed that outlier, it appears that there would be a negative relationship between DOC and algal cell abundance (or, at best, no relationship). If there is, in fact, no relationship between algal cell abundance and DOC, that does not seem to support your statement that you "interpret these data to demonstrate that ice algal assemblages are the main producers of dissolved organic nutrient stocks within the melts surface ice. . ." (line 239). This may well be true but

it is not what these data show. There are other possible explanations for the lack of relationship between DOC and algal cell counts including that you are comparing data collected across a full month and the relationship may change over the melt season.

- **Response:** We would like to thank the reviewer for pointing out this oversight on our part. The plot and linear regression analysis have been removed.

Lines 234-237: Similar to the comment above, this explanation for the lack of a relationship between algal cell abundance and DOC would be more convincing if it detailed more specifically how these variables could become decoupled rather than just invoking the "highly dynamic nature of the environment" where solutes and gases move around.

- **Response**: We agree and have further elaborated on weathering crust dynamics have been included.

Lines 267-274: It is surprising that cryoconite holes have low stocks of dissolved organic nutrients compared to surface ice. Past research has focused on cryoconite holes as hotspots of C fixation in autotrophic supraglacial environments (e.g. Anesio et al., 2009, Global Change Biology). If this were the case, it seems that the abundant production in cryoconite holes would be reflected in dissolved organic nutrient concentrations, but that is not what these data show. Does this suggest that surface ice habitats are potentially more important for autotrophic production or is there another explanation? Also, if you invoke EPS, which is known to occur in cryoconite holes, as the mechanism by which nutrients are retained in surface ice, wouldn't this also be true for cryoconite holes and drive up dissolved organic nutrient concentrations in the same way in those habitats?

- **Response:** We thank the reviewer for this commentary. We have made substantial revision to the Discussion and decided to concentrate mostly on differences between macronutrient concentrations in the melting surface ice environments. We felt that a discussion of processes in cryoconite holes detracted from the main message of the paper, and so have not included these types of ideas here. However, we fully agree with the reviewer that this is a very interesting idea. It is likely that the melting surface ice does fix more carbon by dint of the greater surface area, but this is not the main thrust of this paper.

Line 277: I don't find the argument for a "large pulse of dissolved organic nutrients" particularly convincing. Particulate organic nutrients are hardly mentioned in this paper. It seems like a more parsimonious explanation for the loss of organic nutrients produced in supraglacial habitats is that they are exported downstream, at least partially, in particulate forms.

- **Response:** We agree and have downplayed this idea in the revised manuscript.

Editorial Suggestions

Line 77: change "to accumulate" to "accumulation"

- **Response:** Text changed in response to reviewer's comment.

Line 101: add "of" after "amounts"

- **Response:** Text changed in response to reviewer's comment.

Line 140: It would be helpful to define the acronym TON. I presume that it represents total oxidized nitrogen here but this acronym is commonly used to refer to total organic nitrogen (dissolved + particulate ON) so you should be clear about how it is being used.

- **Response:** Text changed in response to reviewer's comment, line 186 now reads: "NO_2^- and total oxidized nitrogen (TON) ($NO_2^- + NO_3^-$)…".

Lines 179-180: This sentence refers to data shown in Fig. 7 (currently referenced on line 233), which should be renumbered to Fig. 4 and cited here.

- **Response:** Figure 7 has been removed from the manuscript after review from the above comment and has been replaced with a conceptual diagram.

Lines 189: "increase" should be "increased" to be consistent with the rest of the results which are in the past tense.

- **Response:** Text changed in response to reviewer's comment.

Line 234: Suggest changing "counts were" to "abundance was" since DOC is not plural.

- **Response:** Text changed in response to reviewer's comment.

Dissolved organic nutrients dominate ~~in~~ ~~Nutrient cycling in melting surface ice of the Dark Zone (Greenland Ice Sheet) supraglacial environments of the Dark Zone of the Greenland Ice Sheet~~

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Abstract. Glaciers and ice sheets host abundant and dynamic communities of microorganisms on the ice surface (supraglacial environments)~~.~~. Recently, it has been shown that Streptophyte ~~ice~~ glacier algae blooming on the surface ice of the south-west coast of the Greenland Ice Sheet are a significant contributor to the 15-year marked decrease in albedo~~.~~. Currently, little is known about the constraints, such as ~~the~~ nutrient ~~cycling~~ availability, on this large-scale algal bloom~~.~~. In this study, we ~~present a preliminary data set that~~ investigate~~s~~ the relative ~~conversion~~ abundances of dissolved inorganic and ~~nutrients to the~~ dissolved organic macronutrients (N and P) ~~phase occurring~~ in these darkening surface ice environments~~.~~. Three distinct ice surfaces, with ~~,~~low, medium and high visible

impurity loadings, supraglacial stream water and cryoconite hole water were sampled. Our results show a clear dominance of the organic phase in all ice surface samples containing low, medium and high visible impurity loadings, with 93% of the total dissolved nitrogen and 67% of the total dissolved phosphorus in the organic phase. Mean concentrations in low, medium and high visible impurity surface ice environments are 0.91 µM, 0.62 µM and 1.0 µM for dissolved inorganic nitrogen (DIN), 5.1 µM, 11 µM and 14 µM for dissolved organic nitrogen (DON), 0.03 µM, 0.07 µM and 0.05 µM for dissolved inorganic phosphorus (DIP) and 0.10 µM, 0.15 µM and 0.12 µM dissolved organic phosphorus (DOP) respectively. DON concentrations in all three surface ice samples are significantly higher than DON concentrations in supraglacial streams and cryoconite hole water (0 µM and 0.7 µM, respectively). DOP concentrations are higher in all three surface ice samples compared to supraglacial streams and cryoconite hole water (0.07 µM for both). Dissolved organic carbon (DOC) concentrations increase with the amount of visible impurities present (low: 83 µM, medium: 173 µM and high: 242 µM) and are elevated compared to supraglacial streams and cryoconite hole water (30 µM and 50 µM, respectively). We speculate that the architecture of the weathering crust, which impacts on water flow paths and storage in the melting surface ice, and/or the production of extracellular polymeric substances (EPS), containing both N and P in conjunction with C, is responsible for the temporary retention of DON and DOP in the melting surface ice. The usual presence of measurable DIP and DIN, principally as NH_4^+, in the melting surface ice environments, suggests that factors other than macronutrient limitation are controlling the extent and magnitude of the glacier algae.

1. Introduction

There has been a significant increase in the net mass loss of the Greenland Ice Sheet (GrIS) during the past two decades (Rignot and Kanagaratnam, 2006;Rignot et al., 2011;Shepherd et al., 2012), from 34 Gt yr^{-1} to 215 Gt yr^{-1} between 1992 and 2011 respectively (Sasgen et al., 2012). Surface melt is the primary driver for the increase in ice mass loss (~68%) since 2009, with the remaining (~32%) coming from solid ice discharge or calving (Enderlin et al., 2014). There are two major reasons for this marked increase in surface melting. First, the extent of bare, melting surface ice increased, on average, by 7158 km^2 per year from 2000 to 2014 (Enderlin et al., 2014;Shimada et al., 2016). Second, the albedo of bare surface ice areas declined between 2000 and 2012, with south-west Greenland exhibiting the greatest decrease of up to 18% (Box et al., 2012). A persistent Dark Zone in this region, some 20-30 km inland and ~50 km wide, has reoccurred annually since at least 2001 (Wientjes and Oerlemans, 2010;Box et al., 2012;Stroeve et al.,

2013;Tedstone et al., 2017).~~.~~ ~~Shimada et al., (2016) found that t~~There is ~~was sign~~significant variability in the annual extent of the Dark Zone (Shimada et al., 2016), ~~(Shimada et al., (2016)),~~ which may be the result of both inter-annual climatic variability and factors associated with the ice surface, such as melt-out of ancient Holocene dust particles (Wientjes et al., 2011;Tedstone et al., 2017).~~.~~

Both snow and bare ice albedo are reduced by light absorbing impurities (LAIs), of ~~, which include~~both biological and mineralogical origin~~substances~~ (Gardner and Sharp, 2010), which ~~. Types of LAI~~ includ~~e~~ atmospheric dust and black carbon, cryoconite, and particulates within the meteoric ice that melt out during the ablation season (Warren and Wiscombe, 1980;Warren, 1984;Warren and Wiscombe, 1985;Gardner and Sharp, 2010;Wientjes et al., 2012;Cook et al., 2016a).~~.~~ The importance of biological LAI, ~~specifically~~particularly Streptophyte ~~ice~~ glacier algae, ~~that~~which ~~form significant algal~~ bloom~~s~~ in surface ice environments during summer ablation seasons, as a factor in albedo decline has been identified in recent years (Yallop et al., 2012).~~.~~ The ~~Its~~ effect has become known as "bioalbedo", which is derived from the original term "biological albedo reduction" (Kohshima et al., 1993;Cook et al., 2017a).~~.~~ B~~The b~~ioalbedo ~~effect~~ is attributed to a combination of the ~~the~~ high abundance of cells that grow during the bloom (up to ~10^4 cells ml^{-1} surface ice) and the heavily pigmented nature of ~~the~~ ice algal cells, which includ~~eing production of~~ a unique dark UV-VIS absorbing pigment, ~~UV-VIS absorbing~~ purpurogallin~~-type pigment~~, that~~, purpurogallin, in the ice algae, which is postulated to~~ provide~~s~~ photo-protection from the extreme solar radiation in supraglacial environments~~, and the abundance of cells apparent~~ achieved ~~during bloom progression (up to ~10^4 cells ml^{-1} surface ice)~~ (Remias et al., 2012;Williamson et al., 2018).~~.~~ Tedstone et al., (2017) concluded that ice algal blooms are the main factor responsible for inter-annual variability in the extent, magnitude and duration of the Dark Zone, which ~~and~~ seem to be regulated by climatic drivers, including the June-July-August sensible heat flux anomaly and the timing of snow-line retreat.~~.~~ The spatial extent of ~~heavy~~ ice alga~~e~~l blooms may also be linked ~~also~~ to the availability of mineralogic LAIs, such as late Holocene dust particles melting out of the ~~ancient~~ meteoric ice (Wientjes et al., 2012).~~. ~~, h~~~~H~~owever, the linkage between particles and algae is not presently understood (Tedstone et al., 2017).~~.~~ ~~Furthermore, within the Dark Zone, Yallop et al., (2012) noted significant spatial heterogeneity in the ice algal surface ice colonisation, varying on length scales of cm to tens of meters.~~

C~~arbon~~, ~~nitrogen~~N and ~~phosphorus~~P are essential for all living organisms, ~~as they~~ provid~~e~~ing the basis for cellular mass and all metabolic activity (Redfield et al., 1963;Hessen et al., 2013).~~.~~ ~~As c~~Carbon is usually in ready supply in surface ice environments, both from the atmosphere and from bubbles trapped in snow and ice, and so nitrogen and phosphorus are more likely the limiting factors for growth and activity of microorganisms (Stibal et al., 2009;Lutz et al., 2017). ~~Carbon is readily available in these environments for two main reasons. First, as snow forms in the atmosphere it scavenges nutrients in the form of trace gasses and incorporates them, in the dissolved inorganic phase, into the snow crystal (Kuhn, 2001). The snow accumulates on the ice sheet surface, and during the ablation season, melts and releases dissolved inorganic carbon, to the supraglacial environments (Fig. 7). Second, as the ice surface is constantly open to the atmosphere during the main ablation season, gas exchange can occur across the air-water interface (Liss, 1973). Carbon, in the form of CO_2, dissolves in water pooled on the ice surface and becomes bioavailable to microbes in the form of bicarbonate (HCO_3^-), carbonate (CO_3) and CO_2 (Liss, 1973).As carbon is~~

usually in ready supply in surface ice environments, nitrogen and phosphorus are more likely the limiting factors for growth and activity of microorganisms (Stibal et al., 2009;Lutz et al., 2017).Like carbon, Bioavailable forms of N are less readily available, being largely confined to NO_3^- and NH_4^+ in dry and wet deposition from the atmosphere (Wolff, 2013), and from snow- and ice-melt (Telling et al., 2011). Dissolved inorganicnitrogen is scavenged from the atmosphere by snowfall and released to supraglacial environments by snowpack melt as its main input source (Fig. 7) (Kuhn, 2001). Yet, even though N_2 comprises a large portion of the atmosphere, it is not easily bioavailable and not all photosynthetic organisms are capable of fixing it from the air (Falkowski and Raven, 1997). Telling et al., (2012) even reported that the importance of nitrogen fixation for microbial growth decreased with distance from the margin on the GrISTelling et al., (2012). Therefore, gas exchange over the air-water interface, that assists carbon deposition, is not equally beneficial for nitrogen. Dissolved inorganic phosphorus phosphorous (DIP) is typically the least available nutrient in supraglacial environments (Stibal et al., 2009;Stibal et al., 2008b), assince it is a largely rock--derived and mineral and is only released by chemical and physical weathering or bio-mining (Stibal et al., 2009;Stibal et al., 2008b) of rocks. P sources Consequently, in remote glaciated environmentsareas, such as the Dark Zone, phosphorus input is limitedare largely- confined to the small quantities of particulates deposited from the atmosphere and the melt out of debris in snow and ice (Wientjes and Oerlemans, 2010).

–The presence of such large-scale algal blooms in the Dark Zone, with cell abundances as high as 8.5×10^4 cells ml^{-1} (Stibal et al., 2017a), might suggest that these environments are nutrient-rich. –. This would contrast with However, the the current literature, which suggests that supraglacial environments in the Dark Zone, similar to those found in Svalbard, the margins of the Greenland Ice Sheet and Antarctica, are extremely oligotrophic (Stibal et al., 2008b;Stibal et al., 2009;Telling et al., 2011;Telling et al., 2012;Hawkings et al., 2016;Wadham et al., 2016;Bagshaw et al., 2013). –. Mean A comprehensive review ofdissolved inorganic nitrogen (DIN) concentrations in Greenland ice are ~was conducted by Wolff (2013), who reported that mean dissolved inorganic nitrogen concentrations in ice cores of are 1.4 µMµmol l^{-1}, with NO_3^- and NH_4^+ nitrate and ammonium composing 0.97 µM µmol l^{-1} and 0.3945 µMµmol l^{-1}, respectively (Wolff , 2013). –. There are relatively few measurements of nutrient concentrations in the surface ice environments inof the Dark Zone (Telling et al., 2012;Wadham et al., 2016), but the a. Values of Aaverage NO_3^- nitrate concentrations in surface ice nearalong the K Transect east of Kangerlussuaq, which passes through the Dark Zone, has been are were reported to be 0.6 ± 0.1 µM µmol l^{-1} for surface ice located between 17-79 km from the ice sheet margin (Telling et al., 2012), whilest. DIp PhosphateP concentrations are were reported as being below the detection limit, 0.33µM P (Telling et al., 2012). –. In contrast, dissolved inorganic nitrogenDIN concentrations in snow sampled before the start of the ablation season at the margin of the GrIS had higher were reported as higher than surface ice concentrations, with an average of 1.4 µMmol l-1 (Telling et al., 2012), similar to those of Wolff (2013). Hence, there is no real evidence that neither N nor P concentrations in snow and ice sampled in the vicinity of the Dark Zone are higher than for average Greenland ice. . We anticipate that this average snow concentration may be an upper limit for the Dark Zone during the height earlyof the ablation season, given the high concentrations of ice algae that occur during blooms.

The relatively low concentrations of macronutrient in the snow and ice of the SW Greenland Ice Sheet means that algal blooms are likely to rapidly sequester N and P from snow~~wmelt~~ and ice melt, particularly as the blooms reach their zenith at the height of the ablation season. For example, ~~An efficient balance of nutrient uptake and remineralization occurs in many aquatic environments, specifically for example those with a planktonic system (Dodds, 1993), allowing nutrient to accumulate accumulation in biotic mass over time. Microbial nutrient cycling in polar glacier aquatic environments , such as cryoconite holes, is are also also extremelyhighly active with reported NEP rates as muchhigh as 22±4.8 µg C^{-1} g^{-1} day^{-1} for cryonconitecryoconite holes on the GrIS (Stibal et al., 2012b).~~ NPP (Net Primary Production) values in the wet, melting surface ice (also called rotten ice, or the weathering crust) during blooms range from 21 – 100 µmol C l^{-1} day^{-1} (Chandler et al., 2015;Williamson et al., 2018). Should the mean DIN concentration of the ice melt be 1.4 µM~~µmol l^{-1}~~, this implies a C:N molar ratio of 15 – 71 if all the DIN is sequestered into new organic matter and no other sources of DIN are present. There is no readily available C:N ratio of glacier ~~ice~~ algae in the literature, but typical C:N ratios of sea ice algae are in the range of 12-46 (Niemi and Michel, 2015). It is even more difficult to find C:N:P ratios of glacier ~~ice~~ algae, but should the C:P ratio be in the region of 100:1 to 1000:1, the P demand will be 0.02 – 1 µM~~mol l^{-1}~~.

Blooms in other aquatic ecosystems are associated with efficient recycling of nutrients when new sources of N and P are in scarce supply, often with a balance between nutrient uptake and remineralization (Dodds, 1993), allowing nutrient accumulation in biomass over time~~.~~. This balance does not appear to arise in the surface ice environments of other High Arctic and polar glaciers studied to date. These are predominantly in cryoconite holes, which are water-filled cylindrical holes ~~in the ice surface, which are water-filled and have~~with an organic-rich basal sediment in the ice surface~~,~~ that host ~~to~~ a range of microbes, including cyanobacteria (Christner et al., 2003;Anesio and Laybourn-Parry, 2012;Telling et al., 2012). Dissolved macronutrients tend to become concentrated in organic phases (Stibal et al., 2008b;Telling et al., 2014), suggesting an imbalance in the uptake and remineralization of dissolved inorganic nutrients in cryoconite hole environments. Indeed, the only ratio of primary production to remineralization measured in the Dark Zone is 30:1 (Nicholes et al., 2019)~~.~~. To date, dissolved organic nitrogen (DON) concentrations in the Dark Zone have only been reported in two studies (Telling et al., 2012;Wadham et al., 2016), but neither focus on ice populated by Streptophyte ~~ice~~glacier algae. Telling et al., (2012) reported a near 1:1 relationship between NO_3^- and total dissolved nitrogen (TDN), suggesting that DON comprised only a small portion of the TDN pool in snow and ice samples. By contrast, ~~Whereas~~ Wadham et al., (2016) suggested mineralization of organic matter ~~of cryoconite~~ by microbial activity, either with in the cryoconite holes themselves or in debris- and cryoconite-rich "~~and~~ dirty" surface ice contributed to ~~elevated~~ DON concentrations ~~in runoff from a GrIS margin glacier~~that could reach 0.7 µM and 3.0 µM, respectively. ~~xx~~ No dissolved organic phosphorous (DOP) concentrations in the surface ice environments in the Dark Zone have been reported to date.

Several studies have noted the heterogeneity in the spatial distribution of ~~ice~~glacier algae in the melting surface ice of the Dark Zone (Yallop et al., 2012;Williamson et al., 2018). This heterogeneity occurs on length scales of cm to 10s of m (Yallop et al., 2012). This might well signify that macronutrient concentrations are also variable on this

scale, yet no studies to date have examined variability on these ~~these~~ length scales. We contend that it is important to determine the concentrations and relative proportions of dissolved inorganic and organic nutrients in melting surface ice environments of Dark Zone, particularly during Streptophyte ~~ice~~glacier algae blooms, since a knowledge of both DIN, DON, DIP and DOP may be crucial to better understand how glacier ~~ice~~ algae and bacteria can retain, utilize and recycle their limited nutrients to sustain the large-scale blooms observed in this region of the Greenland Ice Sheet~~.~~. ~~Yet, dissolved macronutrients tend to concentrate in the dissolved organic phase (Stibal et al., 2008b;Telling et al., 2014), suggesting an imbalance in the uptake and remineralization of dissolved inorganic nutrients in cryoconite hole environments. and as a consequence, dissolved macronutrients tend to concentrate into the dissolved organic phase (Stibal et al., 2008b;Telling et al., 2014). To date, dissolved organic nitrogen concentrations in the Dark Zone of the GrIS have only been reported in two studies (Telling et al., 2012;Wadham et al., 2016), yet neither focus on ice populated by Streptophyte ice algae. Furthermore,and phosphorus concentrations for surface ice environments in the Dark Zone have not been reported to date., and Wwe contend that this may be an important omission in our understanding of Dark Zone microbial nutrient cycling, specifically as it relates to the extensive Streptophyte ice algae blooms. Knowledge of both the dissolved inorganic and organic phases of nitrogen, phosphorus and carbon may be crucial to better understand ice surface nutrient cycles and how ice algae and bacteria can retain, and recycle utilize and recycle their limited nutrients to sustain the large scale blooms observed in this region of the Greenland Ice Sheet.~~

The aims and objectives of this study, therefore, are threefold~~.~~. First, we aim to quantify dissolved nutrient concentrations in the supraglacial environments of the Dark Zone during the peak ablation season~~.~~. Second, we determine the relative ~~importance~~ abundance of dissolved inorganic and organic nutrients during the peak ablation season when microbial recycling is likely to have the greatest influence on the dissolved inorganic and organic ratios~~.~~. ~~Last~~Finally, we investigate if there are systematic changes in the relative proportions of dissolved macronutrients during ~~differences in nutrient concentrations in highly~~ increased colonization~~ed~~ of melting surface ice, which might shed light on the limiting nutrient on algal blooms~~environments compared to others with lower levels of ice algal biomass~~.

2. Methods

2.1 Field Site and Sampling

A field camp was established within the Dark Zone, adjacent to Kangerlussuaq, during the summer of 2016~~.~~. The camp was located approximately 30 km inland from the ice margin, near to the 'S6' weather station on the K-transect (Fig 1; 67º04'43.3" N, 49º20'29.7" W)~~.~~. Samples were collected from a designated area of approximately 500 ~~x~~ 500 m, which included surface ice, supraglacial stream and cryoconite hole habitats~~.~~. Sampling occurred at intervals of approximately three ~~-~~days ~~intervals~~ from 15th of July to 14th of August 2016~~.~~. ~~Given spatial heterogeneity apparent in ice algal distributions, a~~A categorical sampling strategy was employed, given the evident spatial heterogeneity apparent in ice algal distributions. Five ~~was employed whereby five~~ three main ice

surfacedifferent habitats were sampled; melting surface ice with three differing amounts of visible impurities, (referred to here as surface ice with "low" (*n=19*), "medium" (*n=19*), and "high" (*n=19*) visible impurities), supraglacial stream water, and cryoconite hole water (Fig. 2) (Yallop et al., 2012). Water from Ssupraglacial streams water (*n=10*) and cryoconite holes (*n=14*) water wereas randomly collected, both to asact as a comparison forwith the melting surface ice and to testexamine how dissolved nutrients were transported through the weathering crust, which is the melting layer of surface ice that has a different physical architecture to the underlying ice (Fig. 2). Surface ice habitats were sampled from a 1 ×x 1 meter area chosen at random, from which the top ~2 cm of ice was removed using a pre-cleaned ice saw.

Samples from all five categories of surface ice, supraglacial stream water and cryoconite hole water were collected for the analysis of dissolved inorganic and organic nutrients and dissolved organic carbon (DOC). Algal cell abundances were determined on surface ice samples only. Ice collected for nutrient analysis and algal cell abundance was placed into a clean/sterile Whirl-pak™ bag, while that collected for DOC analysis was transferred into a glass jar that was first rinsed three times with sample. Ice samples were left to melt overnight in the lab tent, typically taking 4-5 h. Supraglacial stream water samples for nutrient analysis were collected using high-density polyethylene plastic bottles (Nalgene™), whereas those for DOC analysis were collected in glass jars. Both sampling containers were rinsed three times with sample prior to collection. Cryoconite hole water used for nutrient and DOC analysis was collected using a large pipette and transferred into a Nalgene™ bottle or glass jar, respectively. The large pipette and collection vessels were rinsed three times with sample prior to collection. All high-density polyethylene plastic bottles (Nalgene™) for nutrient samples were acid washed in ~10% HClL solution prior to first use and all glass jars for DOC samples were furnaced at 500ºC for four hours prior to first use.

Ice melt and water samples for nutrient analysis were filtered through a 25 mm, 0.22 µm cellulose nitrate inline syringe filter (Whatman™) and stored in high density polyethylene plastic bottles (Nalgene™; 30mL). The bottles were immediately frozen and stored at a temperature of -20°C, using a Waeco 32L Freezer. Prior to filtration,Some 15 ml of the homogenised, unfiltered ice melt and water samples were subsampled and fixed using 25% glutaraldehyde at 2% final concentration for quantifying algal cell abundance. These fixed samples were stored outside in the dark at ambient ice sheet temperatures. Ice melt and water samples for nutrient analysis were filtered through a 25 mm, 0.22 µm cellulose nitrate inline syringe filter (Whatman™) and stored in high density polyethylene plastic bottles (Nalgene™; 30mL). The bottles were immediately frozen and stored at a temperature of -20°C, using a Waeco 32L Freezer. Ice melt and water samples for DOC analysis were filtered using a glass filtration column and a furnaced 47 mm, 0.7 µm GF/F. The filtration column was washed three times with sample water prior to collection of the filtrate. The filtrate was stored in pre-furnaced amber glass vials and acidified with 100 µL of 1M HClL. They were chilled to a temperature of ~3˚C by storing the samples in a box at ambient air temperature. The samples were maintained at this temperature during transport and in storage at the LowTex Laboratory at the University of Bristol. Nutrient samples were thawed immediately prior to analysis using a ~40˚C hot water bath. Procedural blanks (*n=9710*) were collected over the course of the sampling season, by processing deionised water in place of sample.

2.2 Analytical Methods

Algal cell abundance was quantified using a Fuchs-Rosenthal haemocytometer (Lancing, UK) on a Leica DM 2000 epifluorescence microscope with attached MC120 HD microscope camera (Leica, Germany). For samples containing sufficient cell abundance, a minimum of 300 cells were counted to ensure adequate assessment of assemblage diversity (Williamson et al., 2018).

TDN (total dissolved nitrogen) is the sum of DIN (dissolved inorganic nitrogen) and DON (dissolved organic nitrogen). DIN species include NH_4^+, NO_2^- and NO_3^- and were quantified as follows. First, NH_4^+ was quantified spectrophotometrically using a Lachat QuickChem® 8500 Series 2 Flow Injector Analyzer (FIA; QuickChem® Method 31-10715-061-1-I). Measurements were based on a salicylatephenolate-hypochlorite alkaline reaction method measured at 6360nm (Solorzano, 1969). The limit of detection (LoD) was 0.62 µM. LoD was determined by dividing the standard deviation of the response of the calibration curve by the slope of the calibration curve, then multiplying the result by 3 (Shrivastava and Gupta, 2011). Samples resulting below the LoD were considered 0 µM for all analyses. Precision was ±2.1%, and accuracy was +8.5%, as determined from comparison with a gravimetrically diluted 1000 mg L^{-1} NH_4^+-N certified stock standards to a concentration of 1.1 µM. (Sigma TraceCERT®). Second, NO_2^- and total oxidised nitrogen (TON) (NO_2^- + NO_3^-) were quantified spectrophotometrically using a Gallery Plus Automated Photometric Analyzer (Thermo Fisher Scientific, UK). This combination of analysis allows the original NO_3^- concentration to be determined by subtracting NO_2^- from TON.

TDN (total dissolved nitrogen) is the sum of DIN and DON, andTDN was determined after by digesting the samples with a potassium persulfate, sodium hydroxide and boric acid reagent and autoclaving at 121ºC for 30 minutes and measuring as TON as above (Grasshoff et al., 1999). This process causes the oxidation of organic nitrogen compounds, which can then be measured as TON as above. Purification of the potassium persulfate was conducted via recrystallisation in order to remove any N contamination. DON was then estimated by the difference of DIN from TDN (DON= TDN-DIN). the original TON and NH_4^+ from the TDN of the persulfate digestion (DON=TDN-NH_4^+- NO_2^-- NO_3^-). Measurements were based on the hydrazine-sulfanilamide reaction method measured at 540nm. DON was then estimated by subtracting DIN from TDN (i.e. DON= TDN-DIN). The LoD wasere 0.14 µM (NO_2^-), 0.64 µM (TON) and 0.87 µM (TDN/DON). Precision was ±0.87% (NO_2^-), ±1.17% (NO_3^-) and ±0.63% (TDN/DON), and accuracy was -4.04% (NO_2^-), -8.07% (NO_3^-) and -5.7% (TDN/DON), as determined from comparison with gravimetrically diluted 1000 mg L^{-1} NO_2^-N and NO_3^-N certified stock standards to a concentration of 0.71 µM (NO_2^-), 1.4 µM (NO_3^-) and 7.1 µM (TDN/DON) (Sigma TraceCERT®).

TDP (total dissolved phosphorus) is the sum of DIP (principally PO_4^{3-}) (dissolved inorganic phosphorus, principally PO_4^{3-}) and DOP (dissolved organic phosphorus). The same persulfate digestion method described for TDN was used to measure TDP as PO_4^{3-}. DOP is determined by the subtraction of DIP in the undigested sample from the TDP in the digested sample. PO_4^{3-} in both the undigested and the digested samples was quantified using a Lachat QuickChem® 8500 Series 2 Flow Injector Analyzer (FIA; QuickChem® Method 31-115-01-1-I) using the molybdenum blue method measured at 880nm. DOP was determined by the subtraction of DIP in the undigested

sample from the TDP in the digested sample (i.e. DOP = TDP-DIP).~~–~~. The LoD was 0.02 µM (PO_4^{3-} and TDP/DOP)~~–~~. Precision was ±1.6% (PO_4^{3-}) and ±3.1% (TDP/DOP), and accuracy was +2.3% (PO_4^{3-}) and +5.0% (TDP/DOP), as determined from comparison with gravimetrically diluted 1000 mg L^{-1} PO_4-P certified stock standards to a concentration of 0.65 µM (Sigma TraceCERT®)~~–~~.

~~All DIN, DON, DIP and DOP data were water blank-corrected using values from the respective field procedural blanks (Table 1).~~

DOC concentrations were quantified using a Shimadzu TOC-L Organic Carbon Analyzer, with a high sensitivity catalyst~~–~~. Non-purgeable organic carbon (NPOC) was measured after acidification of samples with HCl~~L~~ and catalytic combustion (680°C) of dissolved organic carbon to carbon dioxide, which was then measured by infrared absorption~~–~~. The LoD was 9.5 µM~~–~~. Precision was ±2.4% and accuracy was -5.9%, as determined from comparison with gravimetrically diluted 1000 mg L^{-1} TOC certified stock standards to a concentration of 83.3 µM (Sigma TraceCERT®).

2.3 Data Analysis

All measurements below the LoD were considered to be 0 for all statistical analyses. All DIN, DON, DIP~~, and~~ DOP and DOC data were water blank-corrected using values from the respective field procedural blanks (Table 1)~~–~~. Additionally, all blank corrected values that were negative were assumed to be 0 for all statistical analyses. S~~All~~ statistical analysis w~~w~~as performed in RStudio v.1.1.414 (RStudio, Inc 2018)~~–~~. Identification of statistical differences between the nutrient content, DOC concentration~~s~~ and algal cell abundance ~~between~~ din different habitats was achieved using 1-way analysis of variance (ANOVA) or t-test comparisons, with post-hoc Tukey HSD analysis applied to all significant ANOVA results~~–~~. Linear regression models and Pearson's product-moment correlations were used to identify correlations between DON, DOC and algal cell abundance~~.~~ ~~–~~Homogeneity of variance and normality of distribution were tested prior to all parametric analyses, and model assumptions were verified by examination of model criticism plots~~–~~.

3. Results

3.1 Dissolved nutrient concentrations in surface ice with differing levels of visible impurities~~Algal Cell Abundance~~

Supraglacial environments are extremely oligotrophic, making ~~the~~ measurements of dissolved nutrients difficult~~–~~. Dissolved nutrient concentrations reported in previous studies of supraglacial environments are typically ~~at~~below or

just above instrument limit of detections~~.~~. Some ~~Fifty-four~~54 DON, 41 DIN, 74 DOP, 40 DIP and 59 DOC samples out of a total of 81 samples for all five supraglacial habitats had concentrations above the LoD ~~in the present study.~~

.

Dissolved organic concentrations were significantly higher than dissolved inorganic concentrations for nitrogen and phosphorus~~.~~. ~~About~~Some 93% of the ~~total dissolved nitrogen~~TDN was in the form of DON and about 67% of ~~the total dissolved phosphorus~~TDP was present in the form of DOP in all three surface ice habitats~~.~~. Mean DON concentrations for the three surface ice habitats range from 5.1~~0~~-14.0 µM, while those for DIN range from 0.62-1.0 µM (Fig. 3~~4~~, Table 1)~~.~~. Overall, mean DON concentrations for the three ice surface habitats~~, which range from 0-14.0 µM~~, were significantly higher ($F_{1,71}$=12.4, p<0.0001) than mean DIN concentrations. ~~, which range from 0-1.0 µM (Fig. 4, Table 1). While~~Similarly, DOP concentrations were usually at least twice those of ~~o times higher than~~ DIP concentrations for the three ice surface ~~samples~~habitats, with mean ~~mean~~ values ranging from 0.10-0.15~~15~~ µM and 0.03-0.07~~07~~ µM respectively (Fig. 4, Table 1)~~.~~. T-tests revealed significant differences between DON and DIN in all three surface ice habitats ~~five supraglacial environments except cryoconite hole water~~ (low: t_{36}=3.6, p<0.001, medium: t_{36}=5.3, p<0.0001, high: t_{36}=7.4, p<0.0001, ~~stream: t_{36}= 2.6, p<0.01)~~ (Fig. 3~~4~~) and DOP concentrations as significantly higher than DIP concentrations for all three surface ice habitats (low: t_{36}=3.1, p<0.01, medium: t_{36}=2.1, p<0.05, high: t_{36}=3.7, p<0.001) (Fig. 4~~5~~)~~.~~. DON~~C~~ and DOC~~N~~ concentrations in the three surface ice habitats showed clear trends with increasing visible impurities (Fig. 3~~4~~ & 5~~6~~)~~.~~. DON concentrations increased significantly from low to medium and low to high visible impurity loadings ($F_{4,71}$=19.8, p<0.05, $F_{4,71}$=19.8, p<0.001, respectively), while DOC concentrations increased significantly in ice with high and low visible impurity loading ($F_{4,74}$=6.8, p<0.01). ~~Algal cell abundance increased significantly with the amount of visible impurities seen on the ice surface, as shown in Figure 3 ($F_{2,54}$=26.1, p<0.0001). The mean (± standard error) concentrations in the three surface ice habitats were: 99.5 ± 23.9 cells mL^{-1} for ice with low visible impurities, 3850 ± 530 cells mL^{-1} for ice with medium visible impurities and 9800 ± 1570 cells mL^{-1} for ice with a high loading of visible impurities. Significant Pearson's product-moment correlations were apparent between average algal cell counts and DON and DOC surface ice concentrations (t_3=3.5, p<0.05, r=0.9 and t_3=5.4, p<0.01, r=0.95, respectively). A significant linear relationship was apparent between algal cell counts and DOC in surface ice habitats (R^2=0.1, p<0.01, n=57). Highly significant Pearson's product-moment correlations were apparent between average algal cell counts and DON and DOC surface ice concentrations (t_3=3.5, p<0.05, r=0.9 and t_3=5.4, p<0.01, r=0.95, respectively).Comparison of DOP surface ice concentrations and algal cell counts were not significant.~~

3.2 Links between algal abundance and dissolved organic nutrients~~Nitrogen~~

A~~No quantification into the mineralogic composition of the visible impurities was conducted., but a~~lgal cell abundance, which ranged from 90 cells ml^{-1} ~~x to~~ to 0.98 × 10^4 cells ml^{-1}~~y~~, ~~e~~ increased significantly with the amount of visible impurities seen on the ice surface, as shown in Figure 6~~3~~ ($F_{2,54}$=26.1, p<0.0001). No determination of the mineralogic composition of the visible impurities was conducted. A Pearson's product-moment correlation was

undertaken ~~conducted~~ to illustrate the relationship between average algal abundance and average DOC and DON concentrations, as DOC and DON concentrations also increased ~~significantly~~ with the amount of visible impurities present~~.~~ ~~–~~. C~~The c~~orrelations between average algal cell counts versus ~~and~~ both DON and DOC surface ice concentrations were significant (t_3=3.5, p<0.05, r=0.9 and t_3=5.4, p<0.01, r=0.95, respectively)~~.~~ ~~–~~. Comparison of DOP surface ice concentrations and algal cell counts were not significant~~.~~ ~~–~~.

Dissolved organic nutrient ratios were assessed to investigate the presence of a limiting nutrient~~.~~ ~~–~~. Molar DON:DOP ratios, ranging from 49~~.3x~~ to 120~~16.8y~~, were elevated for all three surface ice environments compared to the 16:1 Redfield Ratio, and DOC:DOP ratios for all three surface ice habitats, which ranged from 800~~797.8x~~ to 2000~~13.3y~~, were considerably higher, as much as ~19 times the Redfield ratio, 106:1 (Table 1)~~.~~ ~~–~~. ~~Yet,~~ DOC:DON ratios, which ranged from 1~~5.6x~~ to 17~~.2y~~, were, ~~only~~ on average, twice~~2 times~~ the balanced 6.6:1 ratio (Table 1)~~.~~ ~~–~~. DON:DOP and DOC:DOP ratios also increased with the amount of visible impurities present, while DOC:DON ratios remain relatively constant for the three surface ice habitats (Table 1)~~.~~ ~~–~~.

~~Fifty-four DON samples and 41 DIN samples out of a total of 81 samples for all five supraglacial habitats had concentrations above the respective LoD's. Samples resulting below the LoD were considered 0 µM. The field blank corrected mean (± standard error) DIN and DON mean concentrations for all five supraglacial environments are displayed in Figure 44. Nearly all the DIN was comprised of NH_4^+, with little to no presence of NO_2^- or NO_3^-. Overall, mean DON concentrations for the surface ice habitats, which range from 0-14.0 µM, are significantly higher ($F_{1,71}$=12.4, p<0.0001) than mean DIN concentrations, which range from 0-1.1 µM (Fig.ure 44). About 93% of the total dissolved nitrogen in all three surface ice habitats was present in the form of DON. Additionally, DON concentrations increased significantly from low to medium and low to high visible impurity loadings ($F_{4,71}$=19.8, p<0.05, $F_{4,71}$=19.8, p<0.001, respectively). T-tests revealed significant differences between DON and DIN in all supraglacial environments except cryoconite hole water (low: t_{36}=3.6, p<0.001, medium: t_{36}=5.3, p<0.0001, high: t_{36}=7.4, p<0.0001, stream: t_{36}=-2.6, p<0.01). DON concentrations in cryoconite hole and supraglacial stream water fell below the LoD. DON:DOP ratios are elevated for all three surface ice environments compared to the 16:1 Redfield Ratio (Table 1). DON:DOP ratios also increased with the amount of visible impurities present.~~

3.3 Low transport of dissolved organic nutrients within the water table~~Phosphorus~~

Mean ~~Dissolved organic nutrient~~DON and DOP concentrations were ~~decrease~~ significantly lower in supraglacial streams (~~ranging from a to b~~0 µM and 0.07 µM, respectively) and cryoconite hole water (~~ranging from a to b~~0.7 µM and 0.07 µM, respectively) compared to low, medium and high visible impurity ice~~.~~ ~~–~~. ~~DOC concentrations in supraglacial stream and cryoconite hole water were significantly lower than ice with high visible impurities ($F_{4,74}$=6.8, p<0.001, in both cases) (Fig. 6) and a~~All DON concentrations for cryoconite hole and supraglacial stream water were ~~resulted~~ below the LoD (Fig. 34)~~.~~. DIN concentrations were relatively constant over all supraglacial habitats with mean concentrations ranging from 0.62 µM to 1.0 µM~~–~~. ~~Mean~~ DOP concentrations in supraglacial stream (0.07 ± 0.03 µM) and cryoconite hole water (0.07 ± 0.02 µM µM) were not significantly different from ~~mean~~

DIP concentrations ~~(0.07 µM, 0.01 µM and~~ 0.01 ± 0.01~~7~~ µM and~~,~~ 0.06 ± 0.02 µM, respectively)~~.~~. DIP concentrations in low (0.03 ± 0.02 µM), medium (0.07 ± 0.02 µM) and high (0.05 ± 0.01 µM) visible impurity ice were only slightly elevated compared to supraglacial streams, whereas cryoconite hole water concentrations were comparable to the three surface ice habitats~~-~~. Mean DOC concentrations in supraglacial stream and cryoconite hole water (30 µM and 50 µM, respectively~~which ranged from a to b and c to d respectively~~) were significantly lower than ice with high visible impurities ($F_{4,74}$=6.8, p<0.001, in both cases) (Fig. 5~~6~~). ~~Seventy four DOP samples and 40 DIP samples~~ out of a total of 81 samples for all five supraglacial habitats ~~had concentrations above the LoD. Samples resulting below the LoD were considered 0 µM. The field blank corrected mean (± standard error) concentrations for all five supraglacial environments are shown in Figure 5. Half of the DIP values fell below the LoD. Mean concentrations for the remaining 40 DIP concentrations ranged from 0-0.07 µM. DOP concentrations were at least two times higher than the DIP values, with mean DOP values ranging from 0-0.15 µM. DOP concentrations in cryoconite hole and supraglacial stream water fell below the LoD. DOP concentrations were significantly higher than DIP concentrations in all three surface ice habitats (low: t_{36}=3.1, p<0.01, medium: t_{36}=2.1, p<0.05, high: t_{36}=3.7, p<0.001) .with about 67% of the total dissolved phosphorus present in the form of DOP in all three surface ice habitats.~~

~~**3.4 DOC**~~

~~Fifty nine samples~~ out of a total of 81 samples for all five supraglacial habitats ~~had concentrations above the LoD. Samples resulting below the LoD were considered 0 µM. DOC concentrations increased with the amount of visible impurities present in surface ice habitats, as shown in Figure 6, with a significant difference between ice with high and low visible impurity loading ($F_{4,74}$=6.8, p<0.01). The field blank corrected mean (± standard error) values for DOC were 83.0 ± 23.5 µM, 173 ± 29.9 µM and 242 ± 43.6 µML^{-1} for ice with low, medium and high visible impurities, respectively. The corresponding values for supraglacial stream water and cryoconite hole water were 30.3 ± 13.5 µM and 49.6 ± 33.3 µM, respectively. DOC concentrations in supraglacial stream and cryoconite hole water were significantly lower than ice with high visible impurities ($F_{4,74}$=6.8, p<0.001, in both cases). DOC:DOP ratios for all three surface ice habitats were considerably higher, as much as ~ 19 times the Redfield ratio, 106:1 (Table 1). Yet, DOC:DON ratios were only on average 2 times the balance 6.6:1 ratio (Table 1). DOC:DOP ratios also increase with the amount of visible impurities present, while DOC:DON ratios remain relatively constant for the three surface ice habitats (Table 1).~~

4. Discussion

~~**4.1 Dominance of dissolved organic phase over dissolved inorganic phase in ice surface environments.**~~

Dissolved organic nutrients dominate dissolved inorganic nutrients in the surface ice environments of this region of the Dark Zone (Fig. 3 4 &and 45). Ninety three percent of the total dissolved nitrogen and ~ 67% of the total dissolved phosphorus found in surface ice habitats was in the dissolved organic phase. To date, this organic phase dominance has not been documented in studies of fresh snow or ice cores from the GrIS. As previously mentioned, Telling et al., (2012) reports DIN concentrations in snow found in the margin of the GrIS to be 1.4±0.2 μM L^{-1}, with DON concentrations as non-detectable. T Furthermore, the comprehensive review conducted by Wolff (2013) states that mean DIN concentrations in ice cores from Greenland are 1.4 μM L^{-1}, while DON concentrations are also non-detectible. Furthermore, Wadham et al., (2016) reports elevated DON concentrations in debris-rich ice in the Dark Zone of the GrIS during the main ablation season when compared to pre-melt ice and snow. This suggests that potential inputs of nutrients to supraglacial environments, such as fresh snow and melting meteoric ice, are strongly dominated by the dissolved inorganic phase. By contrast, the phase association of dissolved nitrogen at the ice surface shifts primarily to the dissolved organic phase during the peak ablation season (July and August). The timing of this shift in nitrogen coincides with the reported appearance of the annual Dark Zone and ice algal blooms reported byin Tedstone et al., 2017. . The timing of the ice algal bloomis is further supported by Williamson et al., (2018) who conducted a transect across the south-west GrIS Dark Zone and documented the extensive and wide-spread algal bloom comprised of pigmented autotrophs during late July and August of 2016. Figure 3 also also clearly shows that algal abundance increases in the ice with low, medium and high visible impurities, suggesting that algal cells comprise much of the visible impurities. In fact, Yallop et al., (2012) reported a 3:2 particle to cell ratio for surface ice collected in the Dark Zone. We therefore hypothesise that the algae present in these blooms drive the shift in nutrients during the peak ablation season from the dissolved inorganic phase to the dissolved organic phase.

4.2 Association of dissolved organic nutrients and algal abundance

CEfficient conversion of dissolved inorganic toProduction of dissolved organic nutrients by ice algal assemblages was initiallyis supported by the strong corroborationcorrelation between average average DON and DOC surface ice concentrations and ice algal abundances measured from the same samples. A closer inspection of the full data set revealed the presence of a high degree of variability, which caused insignificant relationships between the algal abundance and dissolved organic nutrient concentrations. . While t he lack of relationship between algal abundance and dissolved organic nutrient concentrations was an unexpected result, the variability was not surprising. Supraglacial environments are dominated by a shallow, 1-2 m, low density porous ice known as the "weathering crust" (Müller and Keeler, 1969;Irvine-Fynn et al., 2012). Due to the intense short wave radiation, the surface of supraglacial ice decreases in density and melts internally along grain boundaries, resulting in heterogeneous thickness and porosity (Müller and Keeler, 1969;Cook et al., 2016c;Christner et al., 2018). Supraglacial weathering crust has been shown to be extremely dynamic, comprised of infinite flow paths that create an intricate hydrological system, interconnecting different habitats and transporting microbes, particles and nutrients (Christner et al., 2018). Yet, the flow paths are not always a perfect system for the flow of water due to the differential radiance absorption within the ice crystals. In fact, Irvine-Fynn et al., (2012) showed that the weathering crust can act as an inhibitor of

discharge from supraglacial environments. They reported that the weathering crust acted as a filter, particularly for microbes and particles, during times of high discharge. Furthermore, Christner et al., (2018) reported that their predicted values for temperature and water transport in the weathering crust significantly differed with the measured values simply due to the vast number of heterogeneities they did not consider. It is therefore not surprising that over a timescale of two months during the main ablation season in the Dark Zone that the transport of solutes, gases, organic matter and microbial cells both vertically and horizontally within the weathering crust produced variability in the data that caused insignificant relationships.

For example, despite the weak linear association apparent in Figure 7, DOC compared to algal cell counts were significant at the 95% level. The variability within these data is likely driven by the highly dynamic nature of the supraglacial environment. For example, the upper ice surface can be characterised as a perched aquifer, with water percolating through the highly permeable surface ice transporting solutes, gases, organic matter and microbial cells both vertically and horizontally (Irvine-Fynn et al., 2012;Cook et al., 2016c;Christner et al., 2018)W.

We still hypothesise interpret these data to demonstrate that ice algal assemblages are the main producers of the dissolved organic nutrient stocks within the melting surface ice of the GrIS, consistent with previous studies of photosynthetic organisms in glacial, freshwater and marine aquatic environments (Johannes and Webb, 1970;Lampert, 1978;Musilova et al., 2017). Ice algae that bloom in these environments rapidly uptake inorganic nutrients, which are derived from a number of possible sources, including the atmosphere, wet and dry deposition, and snow and ice melt (Fig. 7) (Kuhn, 2001;Maccario et al., 2015). This results in an increase in the mass of nutrients held in the microbial biomass, and an increase in dissolved organic nutrients as a by-product of the vital intracellular processes and decomposition of the ice algae. An efficient microbial loop, which balances dissolved inorganic nutrient uptake by autotrophic organisms and remineralization by heterotrophic organisms, is often reached in more temperate freshwater aquatic environments (Dodds, 1993). By contrast, work on surface ice near the margin of the GrIS demonstrated bacterial production that was 30 times less than the net primary production of ice algal communities (Yallop et al., 2012). A similar 30:1 ratio was also found by a study conducted in the same study area of the Dark Zone during the 2016 ablation season (Nicholes et al., 2019) (Nicholes et al., in review). Dominance of dissolved organic nutrients in surface ice environments highlighted in the present study, in combination with reduced secondary production relative to net primary production in the same environments, indicates an inefficiency inreduced capacity of the microbial loop for remineralization of organic nutrient stocks (Fig. 7) (Yallop et al., 2012;Nicholes et al., 2019)5} (Nicholes et al., in review; Yallop et al., 2012). This assertion is consistent with the findings of previous studies in polar glacier aquatic environments (Stibal et al., 2008a;Stibal et al., 2008b;Stibal et al., 2009;Wadham et al., 2016). For example, as previously stated Stibal et al., (2008) reported that ~70% of the total dissolved nitrogen and ~60% of the total dissolved phosphorus found in supraglacial channel, cryoconite hole and glacier runoff environments of a Svalbard glacier were in the dissolved organic phase.Wadham et al., (2016) found elevated DON concentrations in cryoconite holes and debris-rich ice relative to snow and pre-melt ice in the Dark Zone of the GrIS. They hypothesised that the elevated DON concentrations were caused by either mineralization of organic matter by microbial activity or leaching of allochthonous organic matter in debris.

Furthermore, Stibal et al., (2008) reported that ~72% of the TDN and ~89% of the TDP found in cryoconite holes on a Svalbard glacier were in the dissolved organic phase. This suggests that conversion of dissolved inorganic to dissolved organic nutrients by autotrophs in melting surface ice environments may be a common process on many glacier surfaces.

4.3 Retention of nutrients at ice sheet surface

The intense solar radiation received by glacier and ice sheet surfaces produces internal melting and density reduction within the near-surface ice, resulting in a unique porous surface ice layer also known as the weathering crust (LaChapelle, 1959;Müller and Keeler, 1969;Munro, 1990). The porous nature of the weathering crust allows flow paths to form through the water table that exists within the surface ice (Irvine-Fynn et al., 2012;Cook et al., 2016c;Rassner et al., 2016;Christner et al., 2018). These flow paths serve as important links between different supraglacial environments and are believed to transport microbes and nutrients via subsurface flow (Irvine-Fynn et al., 2012;Hoffman et al., 2014;Karlstrom et al., 2014;Cook et al., 2016c). Overall, the DON and DOC in supraglacial streams and cryoconite hole water were lower than the DON and DOC in all surface ice habitats and significantly lower than the surface ice with high visible impurities (Fig.ures 4 4 &and 6 6). Our data, therefore, likely indicate a retention of organic nutrient phases within surface ice environments. One mechanism of possible retention is the production of extracellular polymeric substances (EPS). Algae and bacteria produce EPS which can alter the physical and chemical environment around their cells (Stibal et al., 2012a;Angelaalincy et al., 2017). For example, it has been shown that EPS are used by cyanobacteria in cryoconite holes to bind mineral particles together creating the cryoconite granules at the bottom of the hole (Stibal et al., 2012b;Yallop et al., 2012;Musilova et al., 2016). EPS exists in the colliodal form and when analysed from melted surface ice samples, it is likely constrained in the dissolved organic fraction (Pereira et al., 2009;Hodson et al., 2010). Yet, it is possible that this retention is transitory, and ice surface habitats have the potential to supply a large pulse of dissolved organic nutrients to downstream ecosystems. For example, Musilova et al., (2017) reported that at the margin of the GrIS, DOC remaining in surface ice at the end of the ablation season likely froze over winter and was released the following ablation season through ice melt. Furthermore, Wadham et al., (2016) produced a time series of DON concentrations in runoff from Leverette glacier, a terminating glacier on the GrIS, showing the highest concentration in early May and decreasing throughout the main melt season. The enrichment of DON concentrations also reported by Wadham et al., (2016) for moulin water in the Dark Zone, suggests acquisition of DON from supraglacial environments while the elevated DON concentrations in runoff water from the base of Leverette Glacier, compared to snow and pre-melt ice during the main melt season, suggest transport of this supraglacial DON to downstream environments . (Wadham et al., 2016)This supports the hypothesis of dissolved organic nutrients being retained at the ice surface over winter and coincidently supplying a large pulse of dissolved organic nutrients at the onset of the following melt season. Yet, For example, Musilova et al., 2017 reported that at the margin of the GrIS, DOC remaining in surface ice at the end of the ablation season likely froze over winter and was released the following ablation season through ice melt. tThe proportional input of dissolved organic nutrients in downstream export of DOM from supraglacial environments in the Dark Zone of the GrIS is currently unknown.

4.4 Stoichiometry of different supraglacial environments

Carbon, nitrogen and phosphorus are required by all cells for balanced growth. The generalised stoichiometry for C:N:P in marine phytoplankton, the Redfield Ratio, is 106:16:1 (Redfield, 1958). It is important to note, however, that while the Redfield Ratio is commonly used as the main stoichiometry reference, this a specific ratio for marine aquatic environments only. Differing stoichiometries have been reported for diverse environments. For example, Barrett et al., (2017) investigated different environments in the Dry Valleys of Antarctica and found average N:P ratios for surface ice and snow environments and cryoconite holes on glaciers to be 21:1 and 15:1, respectively. The average N:P ratios in the same Dry Valley site for streams and lakes fed by glacier melt were 12:1 and 25:1, respectively. The variability and changes in N:P ratios over time were caused mainly by the presence and activity of microorganisms in the environment and the geochemical availability of nitrogen and phosphorus in the area. Furthermore, Lutz et al., 2017 investigated the particulate C:N:P ratios of snow and ice habitats in Sweden and Svalbard. They found high particulate C:N and low particulate N:P ratios, which they concluded as likely N limitation rather than a more common P-limitation.

Here, we examine the DOC:DON:DOP ratios of melted surface ice samples in an attempt to determine the limiting nutrient of supraglacial environments in the Dark Zone. The dissolved organic C:N:P ratios reported for our surface ice samples are notably higher than the Redfield Ratio, indicating that the system could be P limited. For example, DON:DOP (40, 78, 116) and DOC:DOP (797, 1166, 2013) ratios reported respectively for low, medium and high surface ice environments are extremely high compared to their 16:1 and 106:1 Redfield ratio counterparts (Table 1). They also increase as the amount of visible impurities increase. In contrast, DOC:DON ratios are on average only two times higher than the Redfield ratio of 6.6:1 (Table 1). DOC:DOP and DON:DOP ratios increase with the amount of visible impurities, as at a greater rate than DOC:DON ratios, remain relatively stable for surface ice habitats. This indicates that the more algal biomass present, the higher the retention of DOP, in order to achieve and maintain homeostasis, compared to DON and DOC (Table 1), suggesting that P limitation increases with higher algal biomass loading in surface ice habitats.

High DOC:DOP and DON:DOP ratios have been documented in other glacial polar aquatic environments. Stibal et al., (2008) showed that DOC:DOP ratios were ~10 times higher than the Redfield ratio on a Svalbard glacier and that DON:DOP ratios exceed the balanced ratio by a factor of three. This is not entirely surprising as P is a rock derived mineral that is only released into the dissolved phase by chemical and physical weathering. When compared to alpine glaciers, ice sheet surface environments receive less lithological debris via terrestrial and atmospheric processes, due to their relative proximity to source material. It is, therefore, reasonable for dissolved phosphorus to be the limiting nutrient compared to nitrogen and carbon, both of which are more readily available from the atmosphere.

Cryoconite, a rock derived substance with a high organic carbon content, is found in abundance on many polar ice surfaces and covers 0.5% of the surface ice in the ablation zone of the GrIS (Gribbon, 1979; Stibal et al., 2012b; Bagshaw et al., 2013; Cook et al., 2016a; Ryan et al., 2018). Stibal et al., (2008) investigated the potential

~~bioavailability of phosphorus from cryoconite in cryoconite holes on a Svalbard glacier and found the potentially bioavailable pool of phosphorus in cryoconite to be ~0.16mg g^{-1}. Furthermore, Lutz et al., 2017 investigated the particulate C:N:P ratios of snow and ice habitats in Sweden and Svalbard. They found high particulate C:N and low particulate N:P ratios, which they concluded are likely N limitation rather than a more common P limitation. This suggest that the microbiology was able to access the particulate P more readily than the particulate N. While investigations into the targeted ability of microbes to utilize this particulate inorganic phosphorus pool have yet to be conducted, Tedstone et al., (2017) noted that widespread ice algal blooms may only occur where abundant particulates are available as they could be providing necessary nutrients for the ice algal assemblages. Clearly, further investigation into the influence of particulate phosphorus sources and utilization is needed to fully understand the nutrient cycle occurring in supraglacial environments as the dissolved nutrient input might only represent a portion of the existing cycle.~~

4.1 Dominance of dissolved organic over dissolved inorganic phases in melting ice surface environments

Dissolved organic nutrients (DON and DOP) dominate dissolved inorganic nutrients (DIN and DIP) in the melting surface ice environments of this region of the Dark Zone (Fig. 34 & ~~45~~), in contrast with the dominance of DIN in studies of fresh snow or ice cores from the GrIS (Telling et al., 2012;Wolff, 2013)~~ (Wolff, 2013)~~, which has a mean concentration of 1.4 µM~~.~~. Further, DIN also dominates on the margins of the ice sheet, where Telling et al., (2012) found DIN concentrations in snow to be 1.4±0.2 µM, but DON concentrations to be non-detectable~~.~~. Wadham et al., (2016) reported relatively similar DIN (1.3 µM) and DON (~1.6 µM, assuming DON = TDN-DIN in their tabulated data) concentrations in a small number (n = 7) surface, debris-rich ice in the Dark Zone of the GrIS during the main ablation season., but these values were thought likely to be associated with dispersed cryoconite, the dark organic-rich sediment that accumulates in the bottom of cryoconite holes and larger supraglacial water bodies. Otherwise, DON was not measurable in snow and surface ice, prior to melting. In summary, this suggests that potential input of dissolved N-species to supraglacial environments from fresh snow and melting meteoric ice are dominated by DIN, rather than DON. There is too little data on DIP and DOP to be confident that the this is also the case for P species. By contrast, dissolved N-species in the melting ice surface of the Dark Zone shifts to a domination of DON during the peak ablation season (July and August), when blooming of glacier ~~ice~~ algae occurs. We therefore hypothesise that the algae present in these blooms drive the shift in nutrients during the peak ablation season from the dissolved inorganic phase to the dissolved organic phase.

4.2 Association of dissolved organic nutrients and algal abundance

Figure ~~63~~ shows that algal abundance increases in the ice with low, medium and high visible impurities. The blooming of the algal cells is also associated with trapping of other mineral particulates at the surface. Yallop et al.,

(2012) reported a 3:2 mineral particle to algal cell ratio for surface ice collected in the Dark Zone, although these particles have only a minor impact on the albedo reduction at the surface (Cook et al., 2019). It is clear from Fig. 34 that the mean DON concentration increases from low to high visible impurities, consistent with DON formation being linked to ~~ice~~glacier algae blooms. This is ~~perhaps by-product of vital intracellular processes and decomposition of the ice algae~~most likely due to a combination of extracellular exudation of polymeric substances and the decomposition of glacier algal cells within the supraglacial system~~.~~. Concentrations of NO_3^- and NO_2^- are zero (Table 1), and NH_4^+ is the only measurable DIN species (mean values range from 0.6 to 1 µM ~~L~~$^{-1}$). The absence of measurable NO_3^- and NO_2^- is consistent with the uptake of these species by ~~ice~~glacier algae, and the emergence of NH_4^+ as the dominant DIN species is consistent with heterotrophic ~~degradation of the primary producers~~remineralization of organic matter (Telling et al., 2012). We note that the mass of N held in the microbial biomass is likely increasing over time, since the sum of the mean DIN and DON concentrations (1.0 µM and 0.0 µM ~~L~~$^{-1}$respectively) in the supraglacial stream water, which is the ultimate sink of macronutrients from the melting ice surface, is less than~~t~~ the average DIN concentration of the melting ice (1.4 µM ~~L~~$^{-1}$) (Telling et al., 2012;Wolff, 2013;Wadham et al., 2016)~~; xxx)~~. The only measurable DIN species in supraglacial meltwater is NH_4^+, ~~and~~which ~~this~~ points to ammonification being an important process in terms of N dynamics and loss of labile N from the melting surface ice. Previous studies of the relative rates of primary production and bacterial production in both the margins and the Dark Zone have produced ratios of 30:1 (Yallop et al., 2012;Nicholes et al., 2019)~~(xxx).~~ The dominance of dissolved organic nutrients and NH_4^+ in surface ice environments documented here, in combination with reduced secondary production relative to net primary production in the same environments, indicates an inefficiency in the microbial loop for remineralization of organic nutrient N-stocks (Fig. 7).

There is less data in the literature on the relative abundance of DIP and DOP in snow and ice, but ~~there~~ we show that there are similarities ~~with~~ between the accumulation of dissolved N into DON and P into DOP species (Fig. 3 & ~~5)~~4). Mean DOP concentrations in the five sampled environments are higher than mean DIP. This is consistent with uptake of P by ~~the ice~~glacier algae and ~~the~~ subsequent recycling of P into organic forms~~.~~. An interesting observation is that there is usually some measurable DIP found in the particulate-rich environments that were sampled (surface ice and cryoconite hole water), whereas the mean DIP in the supraglacial stream water is the lowest value recorded and below the limit of detection. This suggests two things. First, that particulates are the source of DIP, and second, that export of P from the melting surface ice is largely by DOP. We noted above that particulates are associated with ~~ice~~glacier algae in the melting surface ice, and it appears that as algal blooms develop, more particulates become trapped in the surface layer (Yallop et al., 2012). It may well be that there is an "inorganic symbiosis" between the ~~ice~~glacier algae and the trapped particulates, which provide a P source for algal growth.

Our results on the dominance of DON and DOP are consistent with ~~the~~ findings of previous studies in polar glacier surface aquatic environments (Stibal et al., 2008a;Stibal et al., 2008b;Stibal et al., 2009;Wadham et al., 2016)~~.~~. For example, Stibal et al., (2008) reported that DON (~72%) and~~-~~ DOP (~89%) in waters in cryoconite holes on a Svalbard glacier dominated the total dissolved N and P pools. Wadham et al., (2016) found elevated DON concentrations in water in cryoconite holes and debris-rich surface ice in the Dark Zone, suggesting ~~they arose from~~ either mineralization of organic matter by microbial activity or leaching of allochthonous organic matter in debris~~.~~. These observations suggest that conversion of dissolved inorganic to dissolved organic nutrients by microbial communities in melting surface ice environments may be a common process on glacier surfaces.

4.3 Retention of nutrients at ice sheet surface

The low concentration of DIN, DIP, DON and DOP in the supraglacial meltwaters relative to the melting surface ice suggests that ~~the~~ macronutrients are retained in these surface environments. Melting ice surfaces in the Dark Zone often have a veneer of low density, wet porous ice, which may reach depths of 1-2 m, known as the "weathering crust" (Munro, 1990;LaChapelle, 1959;Müller and Keeler, 1969;Irvine-Fynn et al., 2012). The intense short wave radiation during summer often causes internal melt along ice crystal boundaries, resulting in a surface ice layer with heterogeneous thickness, density, porosity and water content (Müller and Keeler, 1969;Cook et al., 2016b;Christner et al., 2018)~~.~~. The porous nature of the weathering crust allows flow paths to form through the water table that exists within the surface ice (Irvine-Fynn et al., 2012;Cook et al., 2016b;Rassner et al., 2016;Christner et al., 2018), which act as important links between different supraglacial environments and are believed to transport microbes and nutrients via subsurface flow (Irvine-Fynn et al., 2012;Hoffman et al., 2014;Karlstrom et al., 2014;Cook et al., 2016b)~~.~~. Water is often in temporary storage in the weathering crust (Irvine-Fynn et al., 2012) ~~Irvine-Fynn et al., (2012)~~, particularly at depth where connectivity of ~~the~~ flow paths can be low. It follows that the first explanation for retention of dissolved organic nutrients in the weathering crust is that they ~~are~~ accumulate in water stored in the weathering crust.

DOC concentrations in supraglacial stream water were lower than the DOC in all surface ice habitats, particularly surface ice with high visible impurities (Fig. 5~~4 & 6~~). This suggests a second possible mechanism of retention of DON and DOP in the weathering crust, via the production of extracellular polymeric substances (EPS)~~.~~. Algae and bacteria produce EPS which can alter the physical and chemical environment around their cells (Stibal et al., 2012a;Angelaalincy et al., 2017)~~.~~. For example, it has been shown that EPS are used by cyanobacteria in cryoconite holes to bind mineral particles together creating the cryoconite granules at the bottom of the hole (Stibal et al., 2012b;Yallop et al., 2012;Musilova et al., 2016). EPS is often colliodal (here, operationally defined as passing through 0.4 µm, but not 0.02 µmfilter membranes) (Raiswell et al., 2018)~~; raiswell ref)~~, and when analysed from filtered (through 0.4 µm membranes)~~.~~, melted surface ice samples will be ~~-~~in the dissolved organic fraction (Pereira et al., 2009;Hodson et al., 2010)~~.~~. The chemical composition of EPS exuded by glacier ~~ice~~ algae is unknown. We note that the EPS of bacteria living in sewage sludge can have a molar C:N:P ratios that approaches 100:101:14 (Guibaud et al., 2008)~~. (Guibaud ref), but his is~~in order to illustrate that EPS can contain N and P ~~only~~. It is likely that the EPS of glacier ~~ice~~ algae contains relatively more C than N and P, given the depauporate nature of the

melting ice surface. ~~The~~ EPS certainly seem~~s~~ to be associated with the binding and retention of particulates in the weatheirng crust, and it follows at least some of the DON and DOP may also be associated with this EPS.

These two mechanisms of retention of dissolved organic nutrient in the weathering crust, either in temporarily stored water or as EPS, mean that DOC, DON and DOP storage in the weathering crust is transitory, and ~~that~~ given the dynamic response of the weathering crust to climatic perturbations, it is very likely that export of these species from the weathering crust will be pulsed, rather than constant. For example, large melt events, accompanying summer storms, may result in wholescale melting of the weathering crust (Tedstone et al., In Review), and export of a significant quantities of the dissolved organic phases contained within them. By contrast, that stored in the weathering crust towards the end of the ablation season, when the crust is freezing and water flow paths are closing, may be retained in the frozen ice surface overwinter. For example, Musilova et al., (2017) reported that at the margin of the GrIS, DOC remaining in surface ice at the end of the ablation season likely froze over winter and was released the following ablation season through ice melt~~.~~.

4.4 Stoichiometry of different supraglacial environments

~~The~~ DOC:DON:DOP ratios in ~~the~~ melted surface ice samples may provide information on whether N or P is the limiting nutrient within supraglacial environments in the Dark Zone~~.~~. For example, Table 1 shows that ~~the~~ DON:DOP ratios increase~~s~~ systematically, from 49, 78 to 120, for low, medium and high impurity surface ice environments respectively, as do DOC:DOP ratios (800, 1200, 2000)~~.~~. By contrast, DOC:DON ratios remain relatively stable for the surface ice habitats (16, 16 and 17 respectively). This could indicate that P is limiting for the glacier ~~ice~~ algal community~~, since the DOP produced by heterotrophic activity and/or as EPS has decreaseds~~. However, this does not quite tie in with the DIP data presented in Fig. 4~~, x~~, which shows that measurable, if low, concentrations of P are usually present in the melting surface ice. Rather, NO_3^- and NO_2^- are below detection, presumably as a result of uptake by phototrophs, and NH_4^+ is the only measurable DIN species, presumably as a result of heterotrophic activity. Phototrophs ~~are usually thought to favour~~preferentially ~~the uptake of~~ utilize both NH_4^+ and ~~over~~ NO_3^-, and the presence of both DIN~~P~~ and DIP ~~N~~ in ~~the~~ melting surface ice environments, irrespective of visible particulate loading, and therefore of algal cell ~~counts~~abundance, suggests that a factor other than macronutrient concentration is limiting algal growth. Table 1 shows that mean NH_4^+ concentrations in the melting surface ice are in the range of 0.6 – 1.0 µM ~~L~~$^{-1}$. We noted above that there is no readily available C:N ratio of glacier ~~ice~~ algae in the literature, but typical C:N ratios of sea ice algae are in the range of 12-46 (Niemi and Michel, 2015). This implies that somewhere in the range of 7.2 – 26 µM ~~L~~$^{-1}$ of C could be additionally fixed, if all the N was~~ere to~~ taken up by phototrophs with ~~the~~ this range of C:N ratios. We also noted that it is even more difficult to find C:N:P ratios of glacier ~~ice~~ algae, but should the C:P ratio be in the region of 100:1 to 1000:1, then P demand will be 0.007 – 0.46 µM ~~L~~$^{-1}$. Table 1 shows that the mean concentration of DIP in melting surface ice is in the range of 0.03 to 0.05 µM, which suggests that P is not a limiting macronutrient on primary production. The systematic change in ~~the~~

DON:DOP and DOC:DOP ratios with increasinge ~~in~~ visible impurities, ~~which is~~ a proxy for algal cell ~~counts~~abundance, could be driven by the amount of P per cell that is potentially available at the high light intensity of the ablation season (> 1500 µmol photons m^2 s^{-1}). The DIP content of the surface ice is relatively constant (Table 1) given the much larger change in cell ~~counts~~abundance as the visible impurities increase. The combination of lower P availability at high light intensity results in an increase in the C:P ratio of phototrophs in other aquatic environments (Hessen et al., 2013).~~(xx).~~ It is plausible that this too happens with glacier ~~ice~~ algae, and that subsequent decomposition products and EPS will likewise have higher DOC:DOP ratios as a consequence.~~—~~.

5. Conclusion

We conclude that DIN and DON -concentrations in the melting surface ice of the Dark Zone on the GrIS are markedly different from those documented in ice cores to date. Wolff et al., 2013 reported DIN, principally in the form of NO_3^-, dominating~~s~~ the initial composition of ice melt~~{Wolff, 2013 #32}~~, yet in the present study, DON dominates ~~in~~ the melting surface ice ~~evironments~~environments which host blooming glacier ~~ice~~ algae. ~~The~~Furthermore, ~~ice algal assembl~~DIN in these environments is exclusively present as~~t~~ NH_4^+, and NO_3^- is below the detection limit (0.64 µM)~~xx).~~ ~~—~~. ~~ages that bloom in the Dark Zone of the GrIS during the ablation season are the main drivers of the nutrient cycling occurring in melting surface ice environments.~~There is relatively little data on the P content of Greenland ice, but we find that DOP dominates DIP in ~~the~~ melting surface ice habitats, although DIP is usually present in measurable quantities (~~the detection limit is~~LoD = ~~-~~0.02 µM~~xx~~). ~~—~~. The presence of both NH_4^+ -and DIP, even in ~~even~~ heavily colonised melting surface ice, suggests that factors other than macronutrient limitation control the blooms. We speculate that dissolved macronutrients are held in the melting surface ice because of the architecture of the weathering crust, and/or because EPS is retained within the melting ice latticework. The former controls the hydrology and the connectivity of water flow paths and water storage in the surface ice, and the latter may be involved with the retention of particulates in the surface. There is currently no data on ~~the~~ C:N:P ratios of ~~the~~ EPS exuded by glacier ~~ice~~ algae, but ~~the~~ EPS of other autotrophs does contain both N and P in association with C. ~~The~~ DOC:DON ratios are~~is~~ relatively constant in ~~the~~ melting surface ice, but ~~the~~ DOC:DOP ratios increase~~s~~ markedly with increasing algal cell counts. This may be attributable to the increasing~~ly~~ ~~higher~~ cell~~s~~ to DIP ratio, which, at high light intensity, increases the C:P ratio of autotrophs in other freshwater environments (Hessen et al., 2013).~~—~~. This could be seen as a~~is a~~ beneficial adaption to algal life in melting ice surfaces, where P sources are limited, since blooms are not so dependent on P as a consequence.~~should this adaptation also be found in glacier ice algae.~~~~Our data indicates a rapid uptake of available dissolved inorganic nutrients and a high production of dissolved organic carbon, nitrogen and phosphorus. The relatively high concentrations of dissolved organic nutrients found on the ice surface, combined with reduced secondary production relative to net primary production, suggests an inefficient or inhibited microbial loop for the remineralization of organic nutrient stocks (Yallop et al., 2012;Nicholes et al., 2019) (Nicholes et al., accepted) . Furthermore, the contrast in dissolved organic nutrient concentrations in surface ice environments compared to supraglacial streams and cryoconite hole water point to~~

~~retention of nutrients by ice algae. This is~~ could be ~~due to EPS comprising a portion of the dissolved organic nutrient pool, and its adhesive properties. This retention could result in supraglacial environments acting as large sources of dissolved organic nutrients for downstream ecosystems~~ during the onset of the following ablation ~~season. ,~~ ~~Yyet, the proportion of DOM export from supraglacial environments of the Dark Zone compared to DOM inputs from subglacial processes in outlet glaciers requires further research. export of DOM from the Dark Zone it is still unknown.~~

Data Availability

All data will be made available upon acceptance and publication of the article~~.~~. Data will be inputted into an open access file.

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Author contribution

MT, AA and MY conceived and designed the study~~.~~. AH, CW, MT, AA, AT, JM, JC and the Black & Bloom group collected the samples~~.~~. CW provided algal counts for the mid to late ablation periods~~.~~. AH conducted all the

nutrient analysis and was aided by FS in the instrument maintenance and data analysis. AH wrote the paper with inputs from MT, CW, AT and AA. All authors reviewed the final manuscript.

Competing Interests

The authors declare they have no conflicts of interest.

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Figure 01. Map showing location of Camp BLACK & BLOOM 2016 (67°04'43.3"N, 49°20'29.7"W). Background image sourced from Sentinel 2, taken on 26/7/2016.

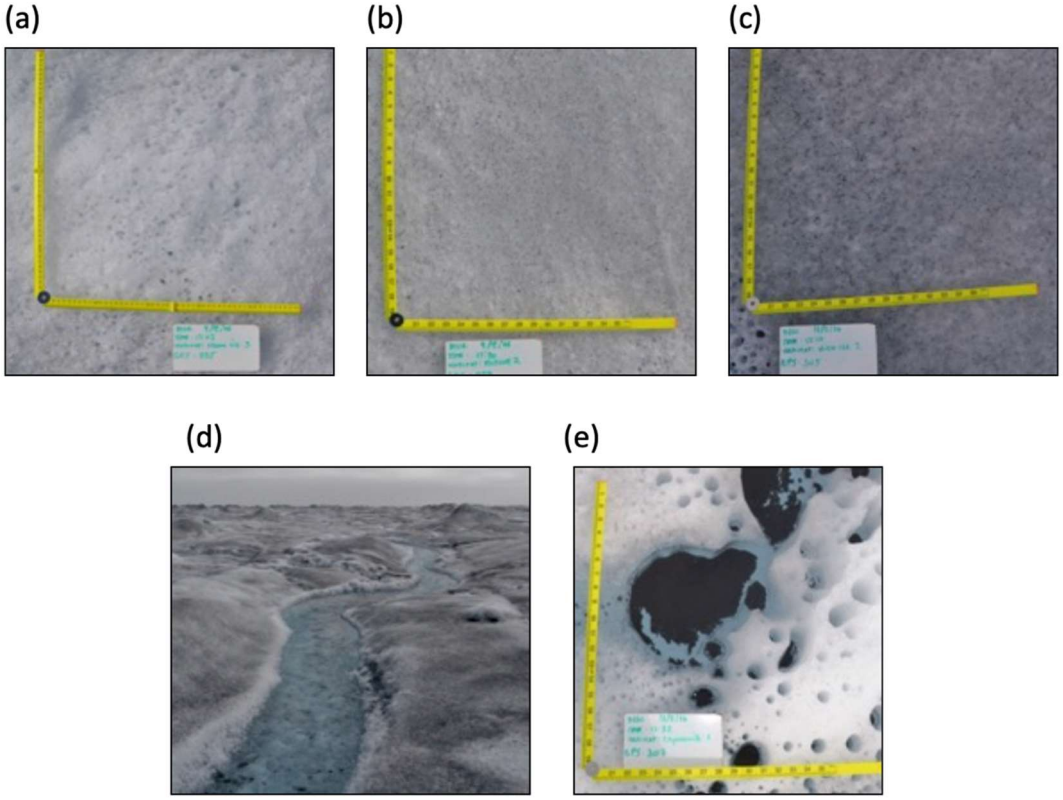
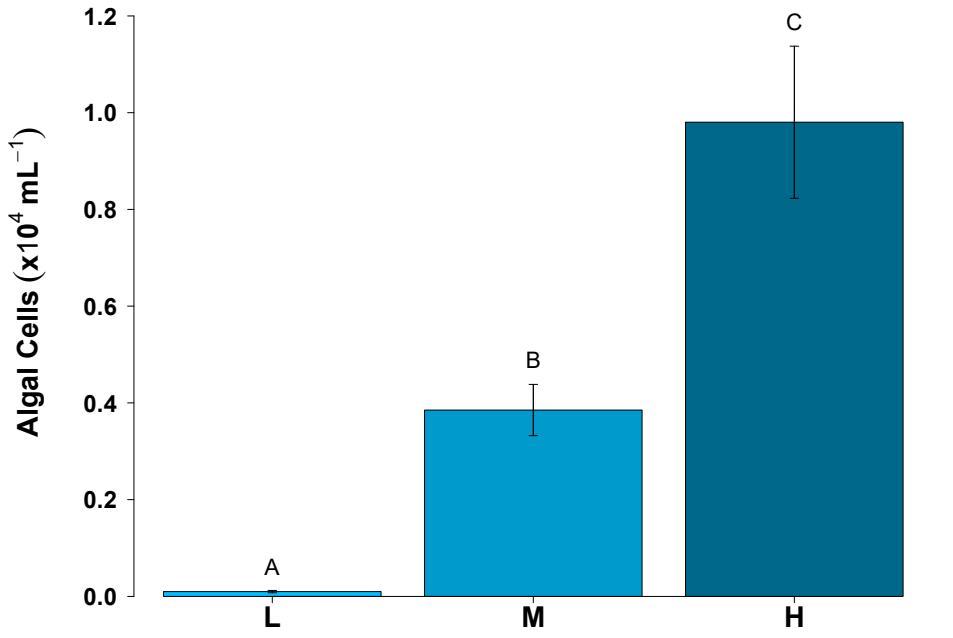


Figure 02: The five supraglacial habitats sampled: **(a)** ice with low visible impurities, **(b)** ice with medium visible impurities, **(c)** ice with high visible impurities, **(d)** supraglacial stream, **(e)** cryoconite hole.



~~Figure 03: Algal cell abundance in ice surface ice habitats (mean ± SE, n=19 for each habitat). **L** ice with low visible impurities, **M** ice with medium visible impurities and **H** ice with high visible impurities. *Uppercase letters* denote homogeneous subsets derived from post-hoc TukeyHSD analysis on a significant 1-way ANOVA~~

in relation to habitat type.

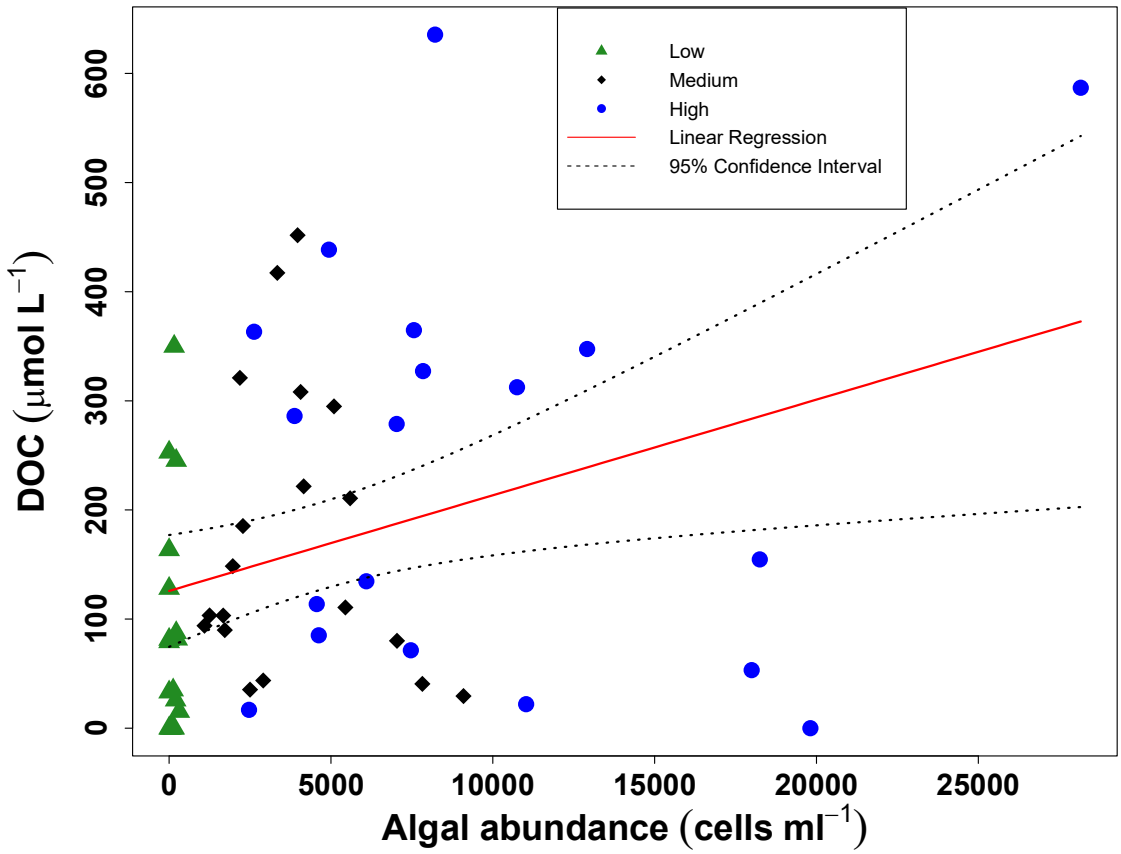
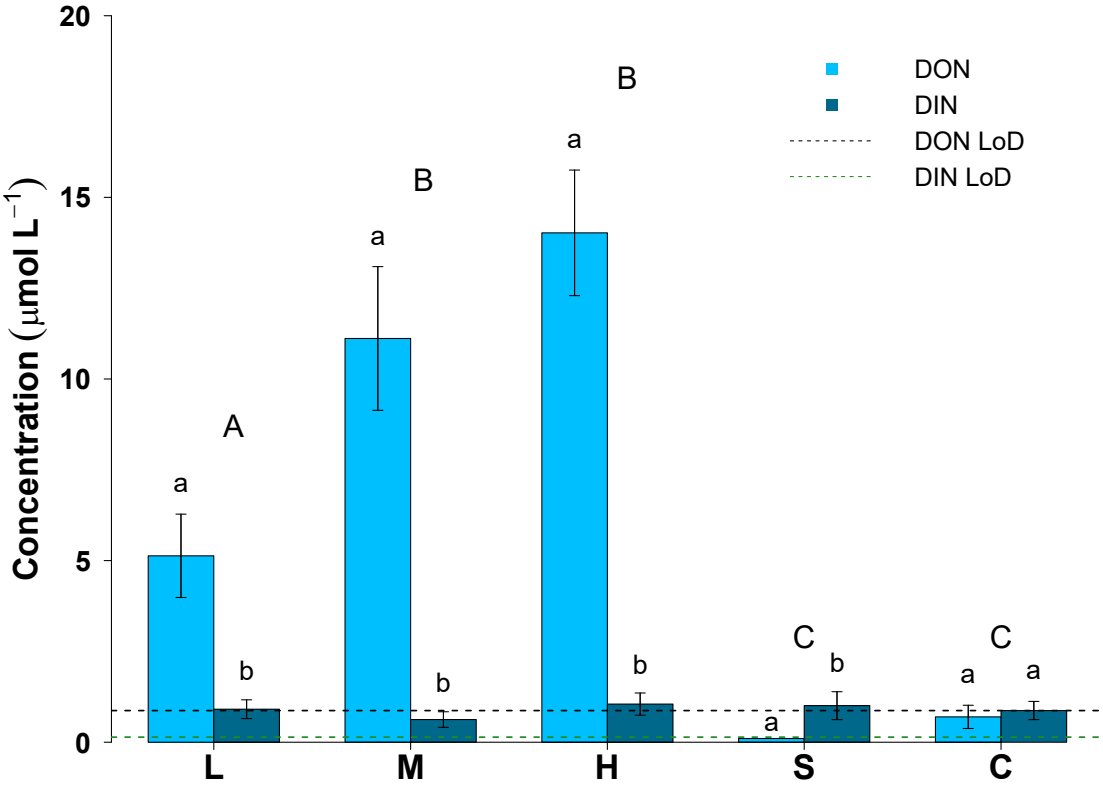


Figure 07: The correlation between DOC concentration and algal cell abundance across ice with low, medium and high visible impurities. R^2=0.1, p<0.01, n=57 for the least squares linear regression.


20
15
10
5
0
Concentration (µmol L⁻¹)
DON
DIN
DON LoD
DIN LoD
A
B
B
C
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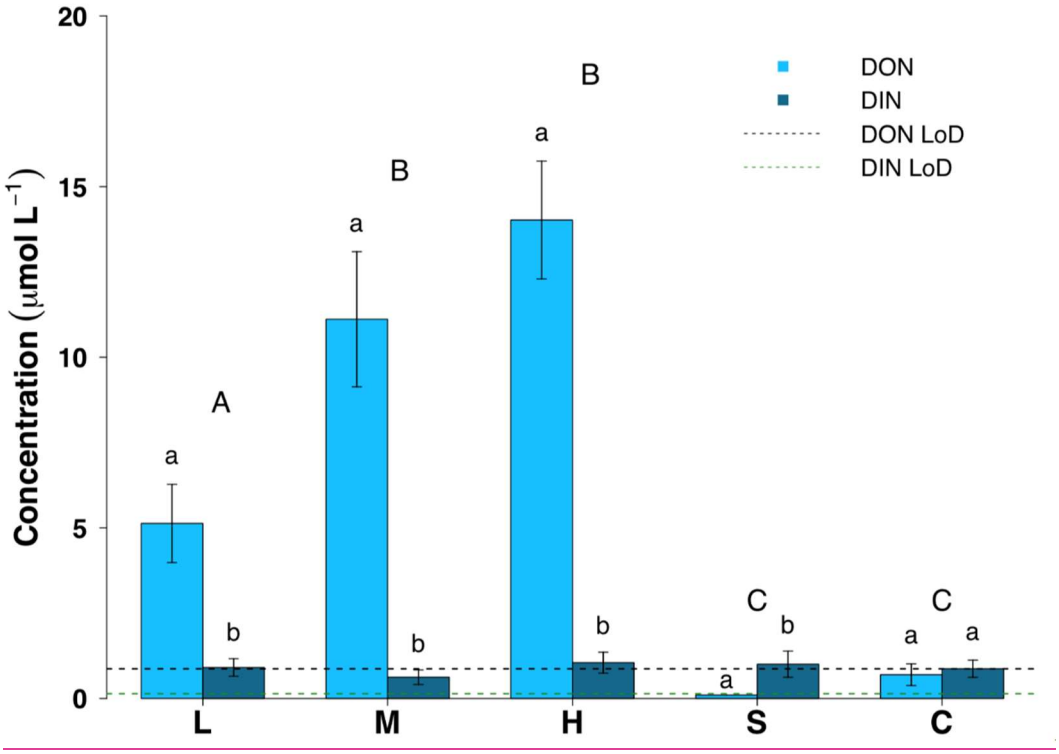
a
b
a
b
a
b
a
b
a
a
L
M
H
S
C

780


20
15
10
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Concentration (µmol L⁻¹)
DON
DIN
DON LoD
DIN LoD
A
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a
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L
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H
S
C

781

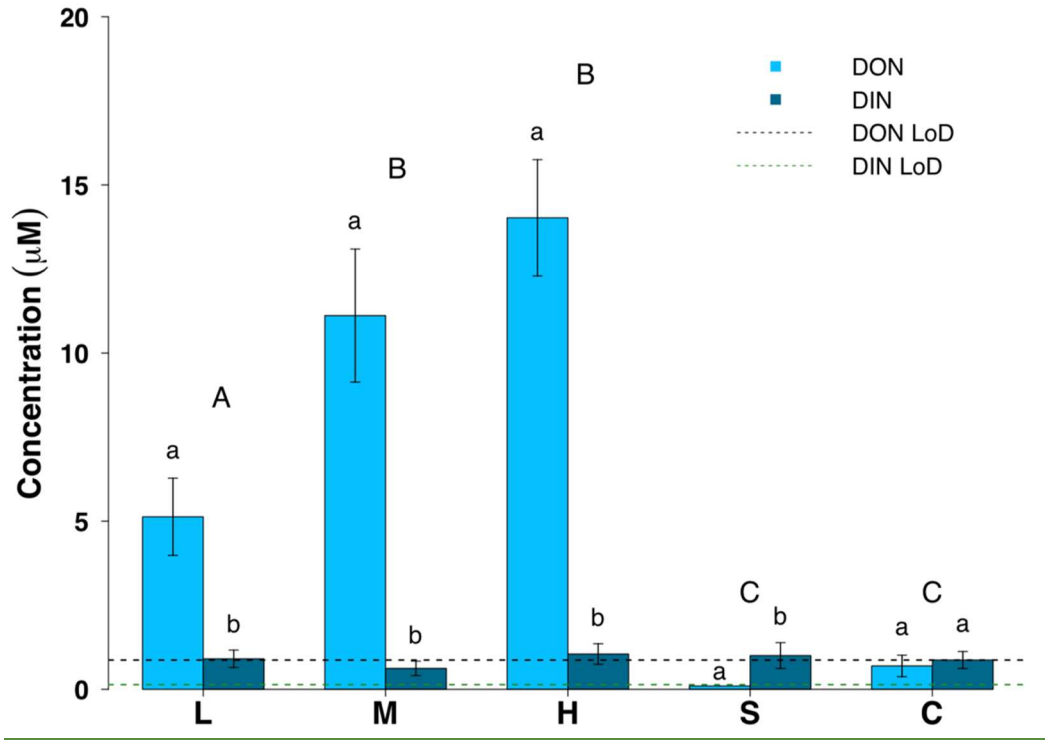
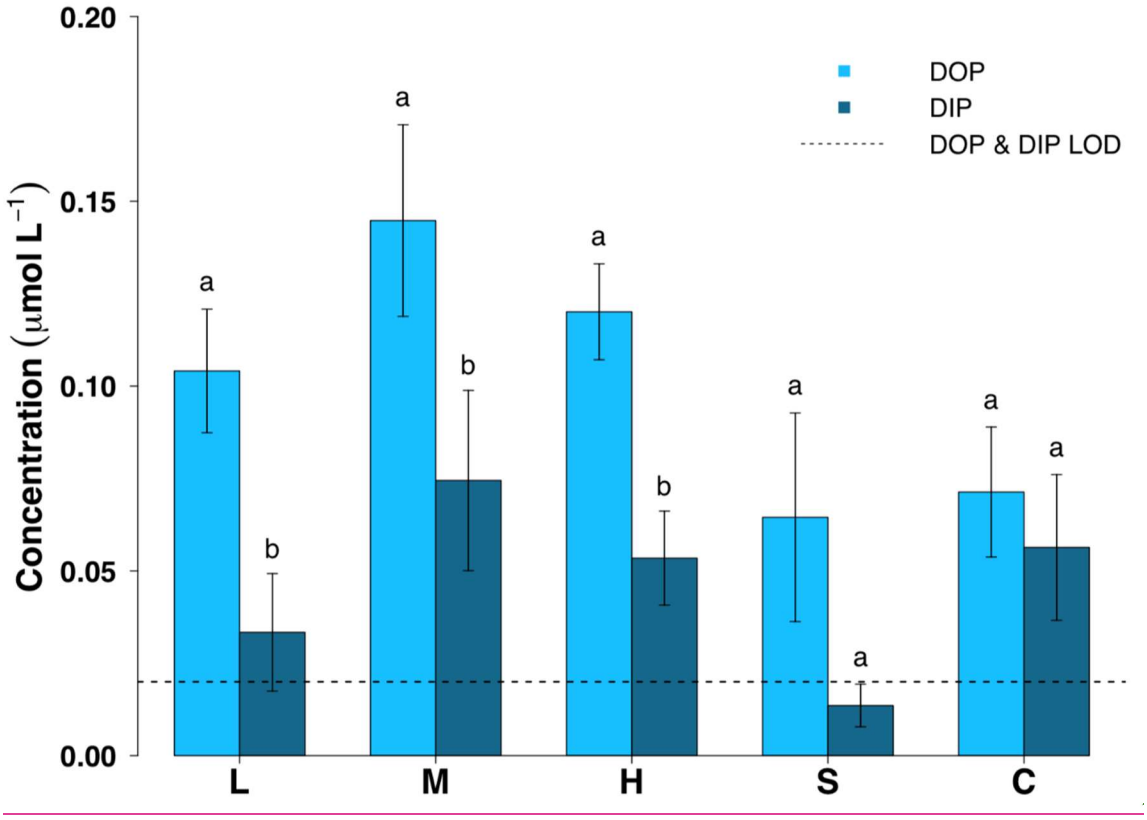
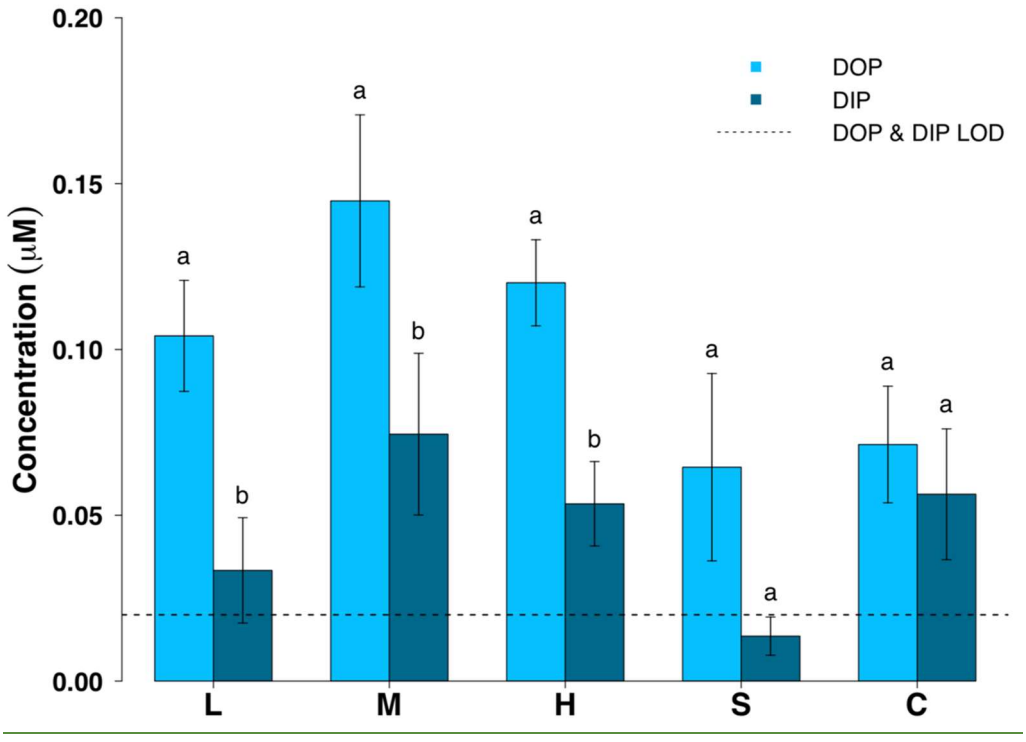


Figure 034: Dissolved Organic Nitrogen (DON) and Dissolved Inorganic Nitrogen (DIN) concentrations for all surface habitats (mean ± SE, n=1197 for **L**,**M**,**H**, n=109 for **S** and n=140 for **C**). **L**- ice with low visible impurities, **M**- ice with medium visible impurities, **H**- ice with high visible impurities, **S**- supraglacial stream water and **C**- cryoconite hole water. LoD line depicts the limit of detection of the instrument. *Uppercase letters* denote homogeneous subsets derived from post-hoc TukeyHSD analysis on a significant 1-way ANOVA in relation to dissolved nitrogen phase. *Lowercase letters* denote T-test comparisons in relation to habitat type.


0.20
0.15
0.10
0.05
0.00
Concentration (μmol L⁻¹)
DOP
DIP
DOP & DIP LOD
a
b
a
b
a
b
a
a
a
a
L
M
H
S
C

789


0.20
0.15
0.10
0.05
0.00
Concentration (μM)
DOP
DIP
DOP & DIP LOD
a
b
a
b
a
b
a
a
a
a
L
M
H
S
C

790

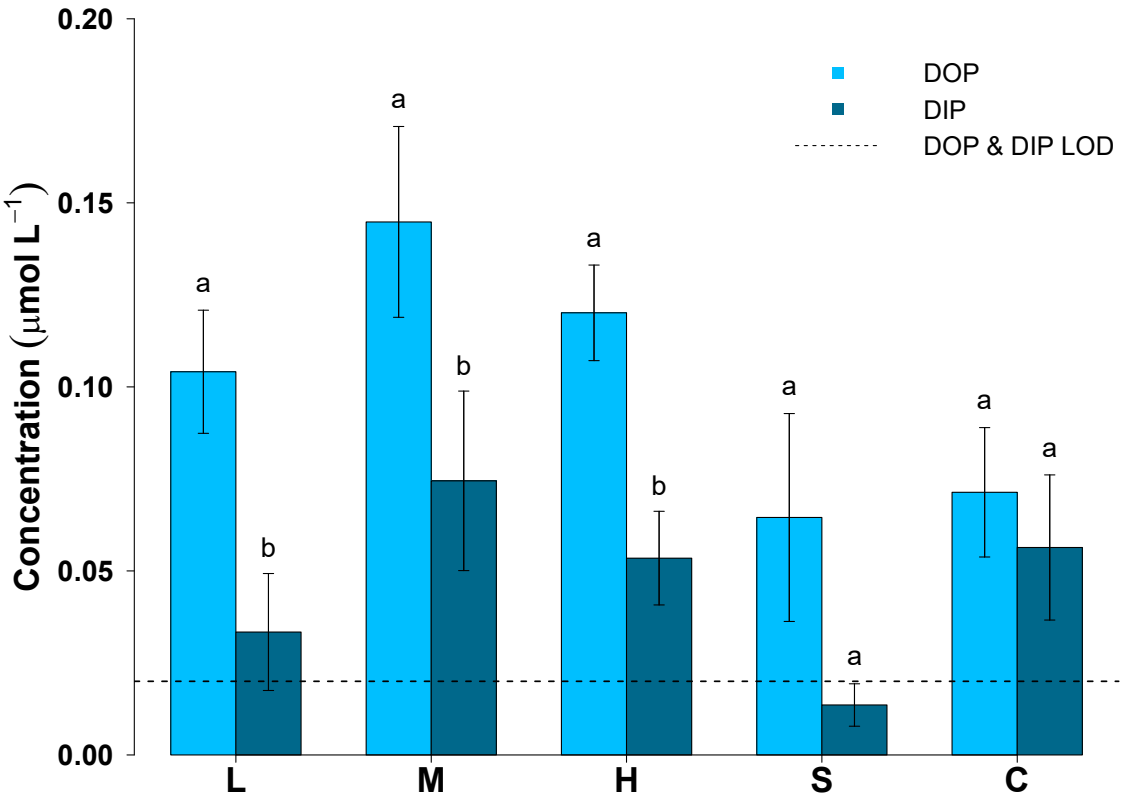
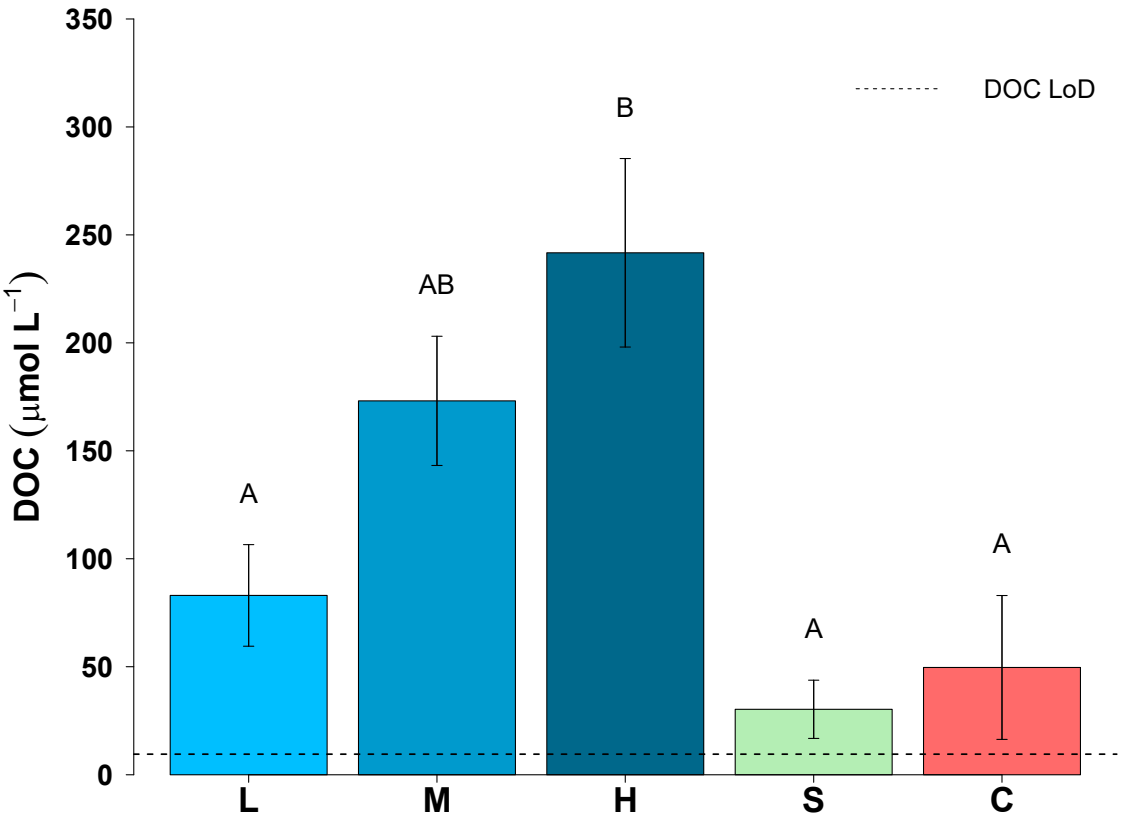
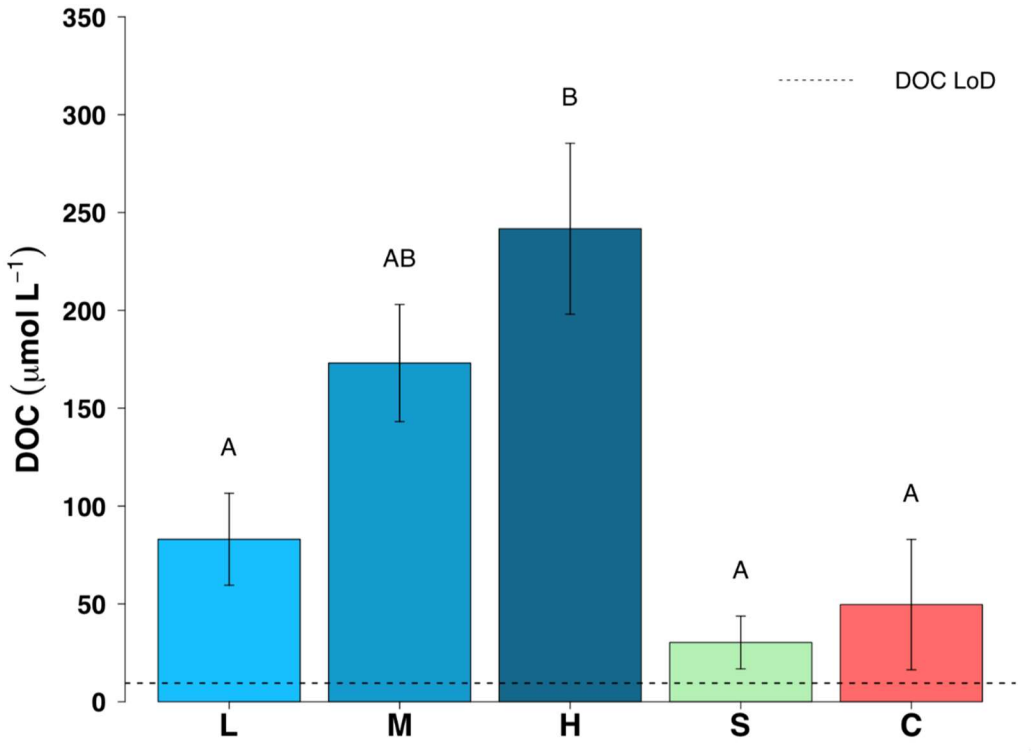


Figure 0~~5~~: Dissolved Organic Phosphorus (DOP) and Dissolved Inorganic Phosphorus (DIP) concentrations for all surface ice habitats (mean ± SE, n=1~~9~~7 for **L**,**M**,**H**, n=1~~0~~9 for **S** and n=1~~0~~0 for **C**)~~.~~. **L**- ice with low visible impurities, **M**- ice with medium visible impurities, **H**- ice with high visible impurities, **S**- supraglacial stream water and **C**- cryoconite hole water~~.~~. LoD line depicts the limit of detection of the instrument~~.~~. *Lowercase letters* denote T-test comparisons in relation to habitat type~~.~~.


DOC (µmol L^{-1})
350
300
250
200
150
100
50
0
DOC LoD
A
AB
B
A
A
L
M
H
S
C

797


DOC (µmol L^{-1})
350
300
250
200
150
100
50
0
DOC LoD
A
AB
B
A
A
L
M
H
S
C

798

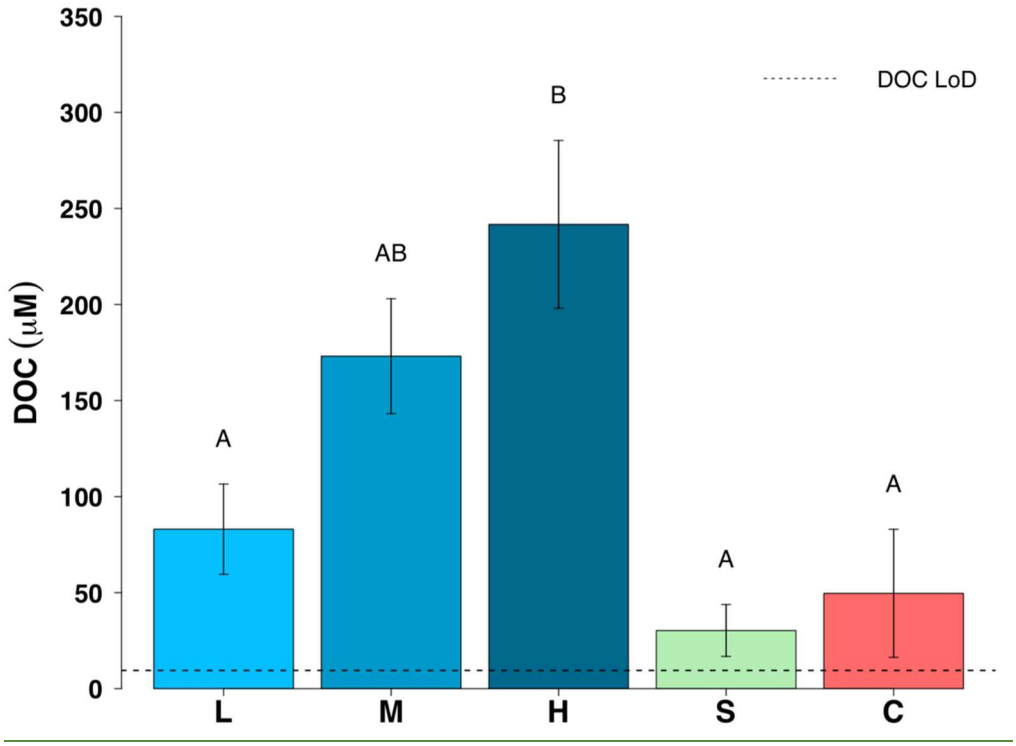


Figure 0~~6~~: Dissolved Organic Carbon (DOC) concentrations for all five surface habitats (mean ± SE, n=19~~7~~ for **L**,**M**,**H**, n=10~~9~~ for **S** and n=14~~0~~ for **C**)~~.~~ . **L**- ice with low visible impurities, **M**- ice with medium visible impurities, **H**- ice with high visible impurities, **S**- supraglacial stream water and **C**- cryoconite hole water~~.~~ . LoO~~D~~D line depicts the limit of detection of the instrument~~.~~ . *Uppercase letters* denote homogeneous subsets derived from post-hoc TukeyHSD analysis on a significant 1-way ANOVA in relation to habitat type.

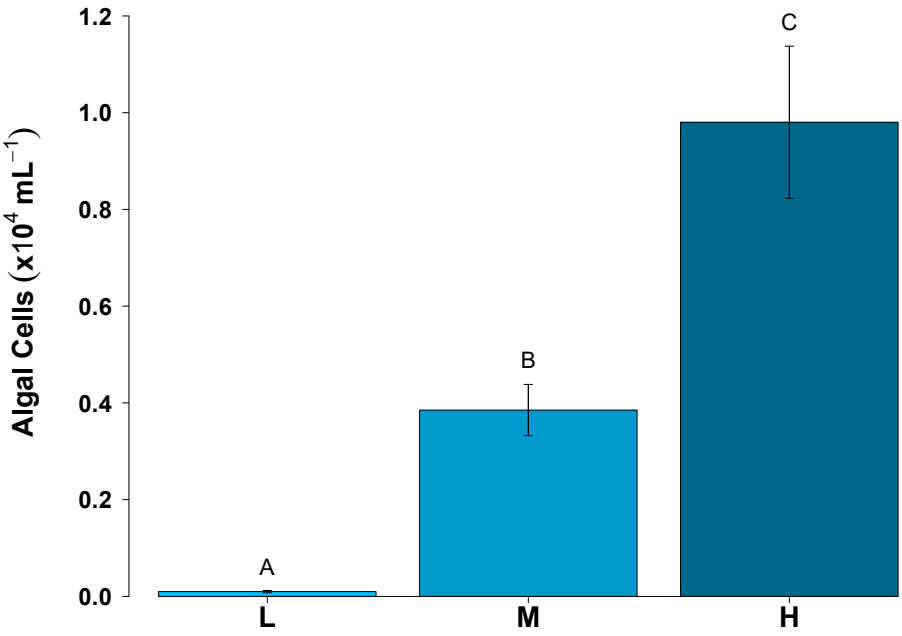


Figure 06: Algal cell abundance in ice surface ice habitats (mean ± SE, n=19 for each habitat). **L**- ice with low visible impurities, **M**- ice with medium visible impurities and **H**- ice with high visible impurities. *Uppercase letters* denote homogeneous subsets derived from post-hoc TukeyHSD analysis on a significant 1-way ANOVA in relation to habitat type.

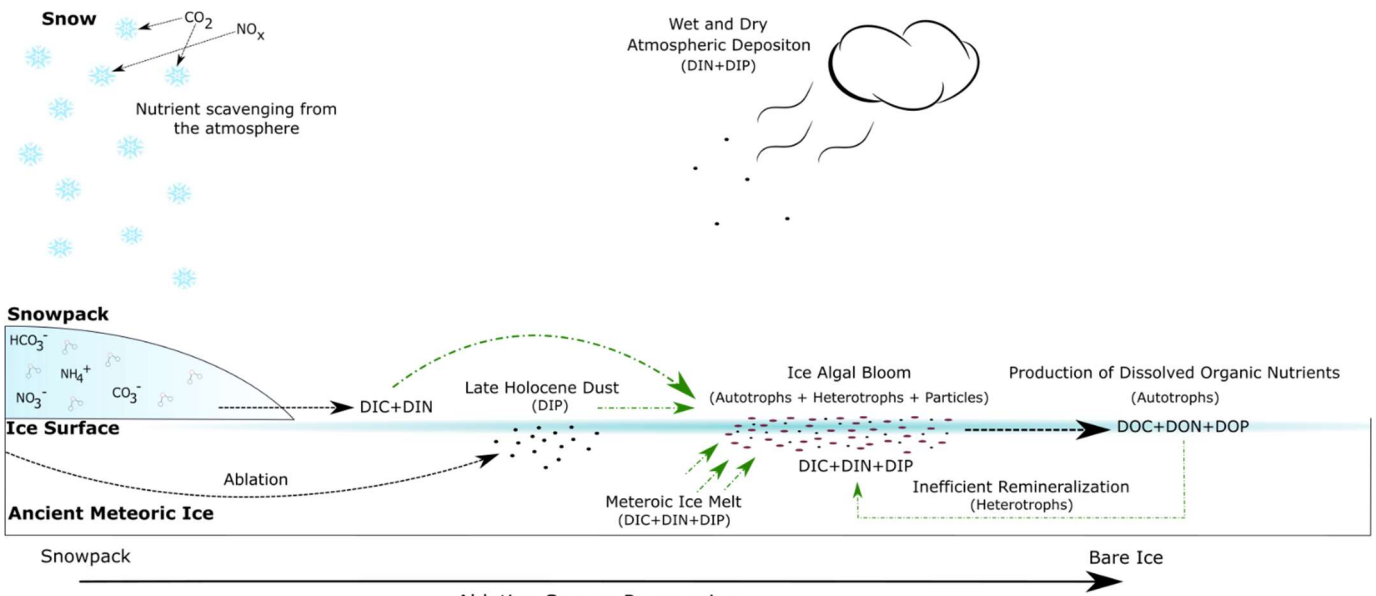
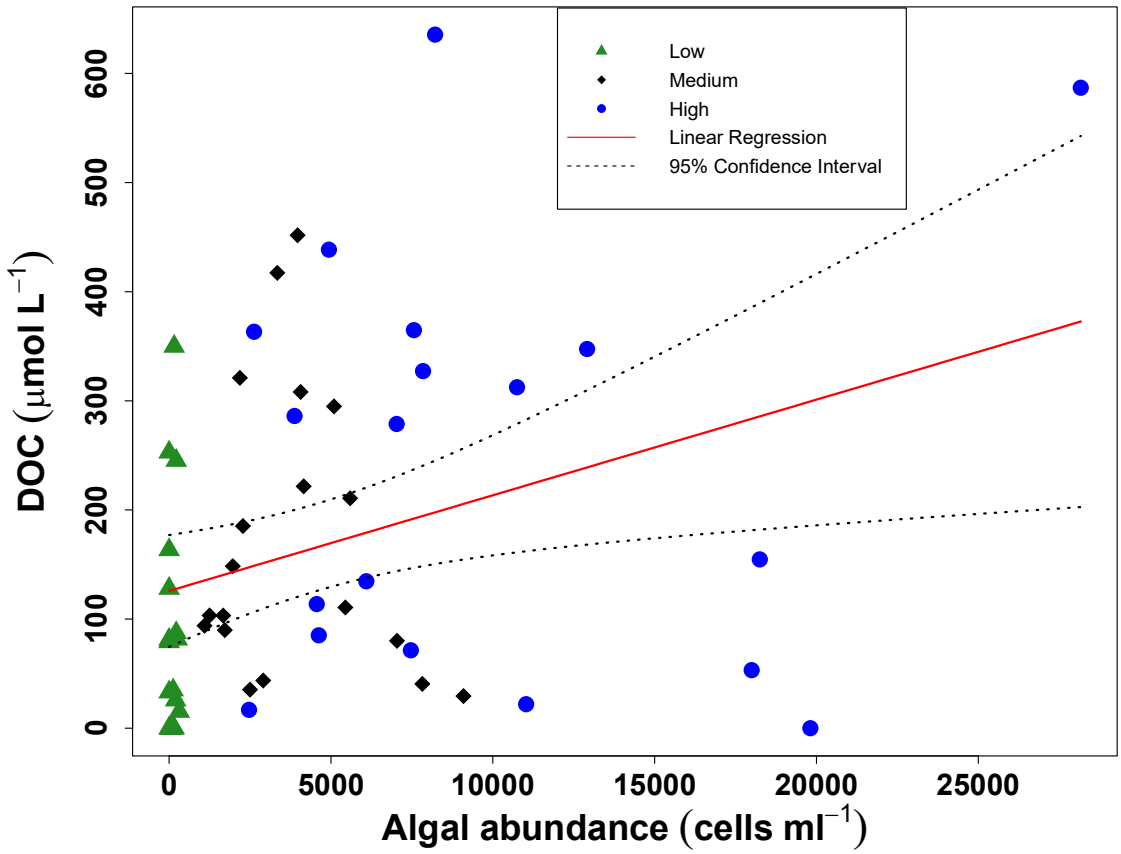


Figure 07: Conceptual diagram of the supraglacial environment in the Dark Zone of the GrIS. Black dashed lines represent nutrient inputs to all supraglacial environments. Green lines represent hypothesized nutrient

inputs utilized by ice algal blooms. Arrow thickness represents relative nutrient concentration.



~~Figure 07: The correlation between DOC concentration and algal cell abundance across ice with low, medium and high visible impurities. R^2=0.1, p<0.01, n=57 for the least squares linear regression.~~

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Table 01: Summary statistics for dissolved macroNnutrient (N and P) and DOC concentrations forin the five supraglacial habitats. DON, DIP, DOP and DOC denote Dissolved Organic Nitrogen, Dissolved Inorganic Phosphorus, Dissolved Organic Phosphorus and Dissolved Organic Carbon respectively.

For each nutrient, the mean ± SD is provided, followed by the range of values. Concentrations are expressed in µMmol; nutrient ratios are in µMmol/µMmol.—.

	Ice Habitat			Supraglacial Stream	Cryoconite Hole	Field Blank
	Low	**Medium**	**High**			
NH_4^+	0.917±0.261.1 0-3.84.0	0.6291±0.211.3 0-2.93.6	1.04±0.311.7 0-4.35.5	1.01±0.381.5 0-3.14.0	0.878±0.251.1 0-2.7-3.0	0.801.1±0.321.4 0-2.63.3
NO_2^-	0.00±0.00 0	0.00±0.00 0	0.00±0.00 0	0.00±0.00 0	0.00±0.00 0	0.00±0.001 0
NO_3^-	0.00±0.00 0	0.00±0.00 0	0.00±0.00 0	0.00±0.00 0	0.0022±0.0071 0-2.2	0.00±0.00 0
DON	54.15±1.13.3 0-10	117±2.010 0-40	1415±1.77.4 3.2-27	0.009±0.0027 0-0.82	0.750±0.321.0 0-3.2	0±0 0
DIP	0.031±0.022 0-0.2709	0.071±0.023 0-0.4414	0.050±0.012 0-0.2006	0.010±0.010 0-0.04	0.060±0.020 0-0.23	0.00±0.00 0
DOP	0.1004±0.029 0-0.27	0.157±0.0215 0-0.48	0.1207±0.0111 0-0.25	0.070±0.030 0-29	0.072±0.0271 0-0.221	0.00±0.00 0-0.04
DOC	836±2410749 0-35049	1783±30135 29-451	2425±44200 0-6366	30±1340 0-84	510±3318 0-4359	12±7.717 0-35
DON:DOP	49.3	78.9	116.8	0.00	9.4	Na
DOC:DOP	797.8	1166.2	2013.3	455.3	671.3	Na
DOC:DON	16.2	15.6	17.2	Na	71.3	Na
DIN:DIP	27.2	8.4	19.6	74.1	15.5	Na
Sample Size (n)	197	197	197	109	140	97

DON Dissolved Organic Nitrogen

DIP Dissolved Inorganic Phosphorus

DOP Dissolved Organic Phosphorus

DOC Dissolved Organic Carbon

1016