

## ***Interactive comment on “Greenland Ice Sheet exports labile organic carbon to the Arctic oceans” by E. C. Lawson et al.***

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Reviewer #2

1. This study relates POC and DOC transport to seasonal ice melt and subsequent discharge from the Greenland Ice Sheet. It demonstrates the variable nature of this process and how it affects the export of carbon from this system to the coastal ocean. Certainly an interesting story to read with implications for biogeochemical fluxes from the ice sheet and the coastal ocean. I have the following questions/suggestions before the manuscript should be published. 1. Methods. The study uses a number of analytical methods that are inadequately described in the current version of the manuscript, there should be enough information in the main body of the manuscript to reproduce how the analysis were carried out. I suggest describing the methods for carbohydrates

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and amino acids more thoroughly.

We thank the Reviewer for their comments and have edited the methods section in the manuscript and the Supplementary Information to provide the relevant information, which we have presented in a clear and concise way. We agree that describing the methods for carbohydrate and amino acid analyses in more detail would be beneficial, however, this methods section accounts for 317 words and some technical information that may be more appropriate for the Supplementary Information (e.g. precision, accuracy, limit of detection).

We have thus explained the methods in more detail in the manuscript and have moved the technical details to the Supplementary Information.

2. From reading the CHO method section it seems like the authors carried out a hydrolysis step, was that done for POM and DOM? If so, the neutral sugars don't necessarily represent LMW DOM but rather are the hydrolysis product of polysaccharides. If no hydrolysis was done on DOM samples, then the carbohydrate concentrations are likely underestimated. It is not clear from the current version. These methods need to be described for both, DOM and POM fractions.

The hydrolysis step was only done for POM.

Carbohydrates in the DOM represent the free carbohydrates in the samples (mainly monosaccharides and two disaccharides, a list is given in Supplementary section 2.2). The carbohydrate concentrations we present do not include polysaccharides and large disaccharides that could not be resolved by the chromatography column we used. We refer to the measured carbohydrates and amino acids as “free” concentrations to account for the potential underestimation, e.g. lack of measuring combined carbohydrates. These data represent the first quantification of free carbohydrates and amino acids by ion chromatography in glacial runoff.

We have described the hydrolysis step for POM in more detail in Supplementary

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section 2.1 and described what the carbohydrates represent (hydrolysis product of polysaccharides).

We have also clearly noted that dissolved carbohydrates were not determined after a hydrolysis step and so likely underestimate the total dissolved carbohydrates (lack of polysaccharides and larger compounds).

3. A similar lack of detail is found with the description of the fluorescence analysis, why did the authors choose an offset of 18 nm for the synchronous scans?

We chose an offset of 18 nm as this has previously been used in synchronous scans of glacial samples (Barker et al., 2006) and humic substances (Miano and Senesi, 1992; Miano et al., 1988).

We appreciate that the choice of wavelength offset differs for each application and for natural waters may be complicated, as discussed in (De Souza Sierra et al., 1994). However, 18 nm resulted in high spectral resolution and a clear discrimination between DOM of different origins in the (Barker et al., 2006) study, and hence, we followed this method. We have made this clearer in the manuscript.

4. The incubation studies also need to be described in more detail. With a volume of 100 ml the bottle effect might potentially be significant. Why was there no control treatment in the experiments? Why not show the actual DOC concentrations but % DOC losses during the experiment?

On the Reviewers advice, we have developed the incubation section and described the studies in full. We have split the Discussion section 4.2 into two parts, the second to address the bioavailability incubations, as suggested by Reviewer 1. Here, we have described the results from the incubation experiment in more detail and included the points suggested by Reviewer 2.

We also agree that presenting the % DOC loss during the incubation experiment would more clearly represent the trend for DOC loss over time and have amended Figure

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4 and the accompanying text in the manuscript accordingly. We have also plotted % bacterial cell loss and added information about the bacterial control to the Discussion (decline in bacterial cells in the glacial and proglacial controls averaged 99% and 100% for the marine control).

We ran control treatments for proglacial runoff, glacial runoff and the marine inocula (100 mL of each in the glass serum vial, three replicates, stored and sampled according to the live incubations), but did not present the data. The decline in DOC between T1-T22 was 17.1 % and 18.7 % for proglacial and glacial runoff, respectively. DOC concentrations in the marine control increased by 6.3 % between T1-T22. The total % declines in DOC concentration in the live incubations were;

G1 50.8% G2 45.5% G3 64.1% PG1 9.1% PG2 9.6% PG3 41.4%

From this, we can be confident that there is a decline in DOC in the glacial (G) incubations that exceeds the controls, supporting our assertion that DOC decline is due to biotic processes when marine inoculum is added to glacial export. This trend is only illustrated in one of the proglacial (PG) incubations (PG3). This may reflect compositional changes in DOC in the proglacial zone and suggests a topic worthy of further study.

As the Reviewer suggested, we cannot rule out the possibility that there is a bottle effect which influenced the temporal changes in DOC and bacterial cells that would not be apparent in the natural environment. However, the incubation experiments were designed for comparison with previous work, e.g. (Fellman et al., 2008; Hood et al., 2009) who used 23 mL of filtrate and 2 mL inoculum (8.7% of the total volume). We scaled this up as we required a larger sample volume for subsequent analyses (e.g. inorganic ions, DOC, bacterial cells, heterotrophic nanoflagellates, phototrophic nanoflagellates, which are not all presented in this paper), but we maintained a similar ratio of filtrate to inoculum (90:10%).

5. Can you calculate decay rates of DOC to put a timeline on the degradation process?

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How would the decay rate compare to the time it takes the glacial DOC to reach the coastal waters, or would most labile DOC be respired before it hits the ocean?

We could calculate the decay rates of DOC in the incubation vessels but this may not accurately represent decay rates as meltwater travelled from the glacial portal to the ocean, hence, it would be very difficult to accurately put a timeline on the degradation process, and beyond work on glacial OC export that has been done to date, e.g. (Bhatia et al., 2013; Hood et al., 2009).

We approximate that it would take glacial export from Leverett Glacier a maximum of 7 hours (in the peak melt season) to travel from the portal to the coastal waters. Our incubation times were 22 days. Hence, if the incubation vessels accurately simulate biochemical processes occurring during proglacial transport, our data show that longer transit times (>7 hours) would be needed to see the level of % DOC loss that was observed in the incubations. However, we do not have the data to determine how DOC would change compositionally during transit from portal to coastal waters.

6. The high sensitivity catalyst for the Shimadzu TOC analyzer does not work well with salt water, how reliable are your DOC data? These are just a few questions that need to be addressed with a more detailed description of what was actually done, I highly recommend revising the method section.

Samples from the incubation experiments contained 90% glacial runoff and 10% marine inoculum (sea water). We did not run any samples with a higher seawater concentration on the Shimadzu TOC Analyzer.

Previous runs with standards containing the 90:10 (freshwater: marine water) matrix were found to have a similar accuracy and precision to standards made with deionized water. Our standard protocol when running samples was to run a DOC standard after every 6 samples. When running the 10% marine samples, we ran a DOC standard made up with the 90:10 matrix (deionized water: marine water). We found that the peak areas were similar and the precision and accuracy was comparable ( $< \pm 8$  and

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$\pm 9\%$ , respectively) with the daily precision and accuracy determined when running glacial samples ( $< \pm 6\%$ , Supplementary Information 2.2). The method section will be revised to include this additional information.

7. A key point of the manuscript is the estimate of labile carbon export to the marine environment, for this to be a meaningful number, the authors should include a calculation of potential DOC losses before discharge into the coastal area. A substantial fraction of the labile DOM might be removed prior to reaching the coast. Looking at the map, the coast is about 200 km away from the sampling site?

We refer the Reviewer to our comment to their earlier question on DOC decay rates and transport from portal to coastal water. Our incubation experiments suggest degradation of the total DOC is slow relative to proglacial river transit times. We agree that it is possible that a fraction of the labile DOM might be removed prior to reaching the coast, yet with our dataset, we are unable to confirm how the DOC composition would vary.

8. Specific comments: Page 19316, line 1: results for SS should be included in results section.

This has been moved to the results section.

9. The headings in the method section don't make sense.

We have revised the methods section and have changed the headings for greater clarity.

10. Page 19319, line 6 and 7 and Table 1: POC export is given in  $\times 10^6$  mg/l? Milligram per liter?

This has been amended and POC has been converted from mg L<sup>-1</sup> to  $\mu\text{M C}$  for consistency with DOC units (as advised by Reviewer 1).

11. Page 19325, line 13: timing, Page 19329, line 23: POC and DOC flux to these ocean masses (to the ocean) from the GrIS

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These changes to the text have been made.

12. References: for river carbon flux comparisons the authors might want to use more recent references for Arctic rivers (Raymond et al. 2007, Holmes et al. 2012, Amon et al. 2012).

We thank the Reviewer for identifying recent references for river carbon fluxes and have incorporated these into the discussion section of the manuscript.

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