

**Identification and analysis of low molecular weight dissolved organic carbon in subglacial basal ice ecosystems by ion chromatography” by E. C. O’Donnell et al.**

**Biogeosciences Discussion comments**

**Anonymous Referee #1**

We thank the Reviewer for their thorough review of this paper and constructive comments which have improved the content of this manuscript. In the following, we reply to all referee comments (in italics) point by point.

*This paper by Lawson and co-workers reports very interesting results with regard to low molecular weight DOC (LMW-DOC) speciation and abundance in basal ice from glaciers that have different organic and lithological substrates and thermal regimes. The case is made that these LMW-DOC compounds may support and/or be a product of biogeochemical activity beneath glaciers with consequence to regional aquatic ecology and global biogeochemical cycles.*

*This paper fulfils the basic criteria of Biogeosciences and its topic is suitable for publication in this journal. However, for me, there are several important obstacles that remain before this manuscript is ready for publication.*

- 1. One of the main strengths of this study is the use of ion chromatography for the quantification of an array of LMW-DOC compounds including free amino acids (FAA), extractable carbohydrates (FCHO), and carboxylic acids (FCA) at exceedingly low concentrations. However, given the novelty of this approach (in glaciology anyway) and the lability (volatility?) of many of these compounds, a more rigorous evaluation of the technique with respect to the basal ice samples is required. For example, did you explore if LMW-DOCs changed over the course of the analysis? You state that the FCA analysis of a single sample took 30 minutes (sec 3.3.3). I’m assuming that your samples were analyzed as a batch (not explained in the paper) and that you had 28 samples (Table 1)? Does this mean that the last sample to be analyzed sat in the instrument tray for 14 hours at room temperature? Might there have been any changes in LMW-DOC abundance or composition over the course of the batch analysis due to organic or inorganic processes? For example, is there a trend in acetate increase or decrease over this time in replicates? This would have a significant impact on your interpretation and warrants consideration and/or an explanation.*

The use of ion chromatography for the quantification of trace-level LMW-DOC compounds was a key output from this research. While it is not reported explicitly in this paper, we did rigorously evaluate the ion chromatography procedures and set up relatively short sample runs (12-18 hours, described below) to limit the potential for changes in LMW-DOC abundance and composition while samples were waiting in the autosampler. Prior to running the samples, we assessed the level of instrument drift (which might reflect instrumental changes plus degradation of LMW-DOC compounds) by running 50 µg L<sup>-1</sup> standards, with 5 deionized water samples in between, for a period of 24 hours. We then assessed whether the standard concentration changed over time and used this to determine the optimum number of samples that we could run within the required precision (5-10% for FAA and FCHOs, 5-8% for FCAs, as noted in Section 3.3.3). We found that we could run approximately 21 samples before significant drift (that exceeded the precision of the instrument) was observed. We therefore did not run all of the 28 basal ice samples (and five deionized water blanks) in one run; we set up repeat small batch runs following the sequence described above. Due to the scarcity of sample volume, it was not possible to explore if the LMW-DOC concentrations in the basal ice samples changed throughout the runs. We observed a small change in acetate concentrations (in standards) throughout each run but this was within the reported level of precision. We have added information on how we set up each batch run into the methodology Section 3.3.3 (pgs 10-11, lines 304-312).

- 2. Another issue is that role of basal ice, and its constituent compounds, is confusing and potentially overstated. For example, one could argue that any DOC that is incorporated into basal ice is decoupled from the subglacial hydrologic system and does not get exported to proglacial aquatic ecosystems. Even when subglacial meltwater is exported (polythermal and warm-based glaciers), unless basal ice melt occurs across the entire bed and the subglacial drainage system drains meltwater from across the entire bed (which they don't), then the magnitude of basal ice contribution to the subglacial meltwater is unknown. It becomes negligible when you consider the subglacial routing of supraglacial meltwater during the melt system and the seasonal evolution of the subglacial drainage system from being distributed to being a more channelized "quick flow" system as the supraglacial meltwater flux increases.*

We have revised the manuscript in order to avoid overstating the importance of basal ice in subglacial meltwater export budgets, e.g. throughout Section 1 (Introduction), Section 5.3 (Discussion), and in our conclusion. We accept the Reviewer's point that basal ice melt may be a small component when compared with the larger volume of supraglacial meltwater that travels through some subglacial systems (pg 17, lines 512-516). However, basal ice may be a more significant contribution to glacial export in other glacier systems, e.g. cold-based glacier systems in the Antarctic Dry Valleys, where daily radiation melting of the steep ice cliffs may release solute from the debris-rich basal ice that is exposed on the cliffs. Basal ice can be incorporated into icebergs (Death et al., 2014; Raiswell et al., 2008) and this component subsequently released to ocean waters from marine terminating glaciers. There is also evidence that discrete subglacial channels exist beneath cold-based glaciers, such as Longyearbreen (Yde et al., 2008), which may be in contact with the substrate and hence may represent a mechanism for DOC to be exported from cold-based glaciers. The distributed drainage system beneath temperate and polythermal glaciers may also include a constant source of water from basal ice melt and groundwater in contact with glacial till (Paterson, 1994). We have added some of this information into the manuscript (pgs 19-20, lines 600-605).

It was beyond the scope of this study to estimate the magnitude of basal ice contribution to the subglacial meltwater export and we are unable to do that with the dataset that we have presented. Earlier research has observed a significant contribution from delayed flow to net meltwater export (e.g. Bhatia et al., 2011; 2013), and this delayed flow will include some basal ice contributions. Similar rationale has been used in other published research investigating the DOC signature in basal ice (Barker et al., 2010; Pautler et al., 2011; 2012) and hence we followed their reasoning. In subglacial environments where there is distributed flow, we would expect some basal ice to form by freezing of long residence time water in the distributed drainage system. These waters are difficult to access, and hence, sampling basal ice helps us gain a better understanding of these debris-rich, long residence time waters (though we appreciate that the solute concentrations may change during freezing).

- 3. My understanding of basal ice formation (granted that the authors are by far more authoritative on this point than I am), is that its composition reflects subglacial conditions at the time that the material accreted onto the base of the glacier and subsequent biogeochemical modifications to it since accretion. In the case of the polythermal and warm-based glaciers (Russell, Finsterwalderbreen, Engabreen), subglacially routed supraglacial meltwater would be expected to contribute to the subglacial pool and glacially-overridden material may not be the only source of DOC, as this paper seems to assume.*

The Reviewer is correct that subglacially routed supraglacial meltwater at Russell Glacier, Finsterwalderbreen and Engabreen would be expected to contribute to net meltwater export from the subglacial environment and that basal ice would not be the sole component. We have edited the manuscript to make this clearer (see also point 2). We also emphasize that most subglacial water in temperate and polythermal glaciers derives from the surface. Only in very marginal parts of the glacier bed, where there is no surface melt input, is subglacial meltwater likely to entirely comprise

basally generate meltwater. In cold-based glaciers, the reverse is true, and basal melting should account for all meltwater present at the ice sheet bed.

Basal ice may also form without freezing of meltwater and can be defined as “ice that has acquired a distinctive suite of physical and/or chemical characteristics as a result of processes operating at or near to the bed of an ice mass” (Hubbard et al., 2009). Basal ice formation processes include regelation, adfreezing (freeze-on to the glacier sole), metamorphose of glacier ice into basal ice (Sharp et al., 1994) and post-formational tectonic deformation of basal ice causing intermixing of glacier ice and basal ice (Waller et al., 2000). We cannot be sure of the hydrological conditions at the time of formation for the samples we collected. However, we can assert that composition of basal ice will reflect the parent water plus subsequent modifications. This parent water may or may not include a surface-derived component. We acknowledge that this latter surface component will be an important contributor to subglacial DOC on the warm and polythermal glacier systems we have sampled, but that we cannot be sure that this component is included within our basal ice samples. We have revised the manuscript (e.g. throughout Discussion Section 5.3) to reflect this point and to better describe the various basal ice formation processes. In particular, we have revised the Introduction as our initial description lacked this level of detail (pgs 2-3, lines 48-83).

4. *Finally, I found that the relationship between microbial cell abundance and LMW-DOC and DOC was an interesting result, yet not adequately addressed. If these compounds are biogeochemically significant, either as a substrate or product of in situ activity, wouldn't you expect a correlation between microbial abundance and LMW-DOC concentration?*

The focus of this manuscript was on the LMW-DOC abundance and characteristics in basal ice and hence, we presented the microbial cell counts as supporting evidence of potential microbial activity in the basal ice environment (in line with other cell counts reported in microbially-active subglacial sediments in the literature). The LMW-DOC compounds in basal ice represent viable substrates for microbial growth and/or products of in situ activity, but without conducting incubation experiments we are unable to conclusively show the origin of the different compounds and how they may support microbial activity. We also cannot conclusively separate LMW-DOC derived from biotic and abiotic processes as, at a molecular level, many LMW-DOC compounds are non-specific biomarkers and can be synthesized by both plants and microorganisms (as described previously in Section 5.2, pg 14158, lines 19-29). We therefore would not necessarily expect a correlation between microbial abundance and LMW-DOC concentrations as there are numerous variables that would influence this relationship, such as the difference between production and consumption of different LMW-DOC compounds (dependent on the type of microbes present in the basal ice and the metabolic pathways), the abundance of terrestrial or plant-derived LMW-DOC and the abundance of LMW-DOC released from decaying cells. These factors meant that the microbial cells counts were only presented as supporting evidence.

*More specific suggested corrections are as follows:*

5. *Abstract (line 13): FAA is used but never defined*

FAA (free amino acids) is now defined in the Abstract (pg 2, line 33).

6. *Abstract (line 25): Why “current” subglacial environments? Could you delete “current”?*

The word ‘current’ has now been deleted.

7. *I think that the term “allochthonous” is misused throughout. The overrun OC hasn’t been derived from somewhere other than its present location, as the term suggests. Allochthonous has been used in studies to describe DOC brought in to a system, be it a river or ocean (etc. . .) from somewhere else. This isn’t the case here, and so a different term should be used, perhaps using “microbial” vs. “terrestrial” to make the distinction?*

We take the Reviewer’s comment on board and have changed references to ‘allochthonous’ material. When describing DOC present in overridden material we now use the term ‘terrestrial’, in other cases we have deleted the word as it did not add to the sentence. We now state that “basal ice from all four glacial sites provides evidence that viable substrates for microbial growth, whether derived from a terrestrial or microbial source, are available in subglacial environments” (pg 19, lines 571-574).

8. *Section 3.1 (line 24): What does “BI” and “PR” mean?*

BI and PR refer to ‘Basal Ice’ and ‘Pressure Ridge’, respectively. This was explained in Section 2.5, lines 21-25. We used this terminology to differentiate between the two types of ice that were sampled at Finsterwalderbreen (that had very different mean debris concentrations). However, on the advice of Reviewer 2, we have revised the terminology that we use to describe the two types of Finsterwalderbreen basal ice. Instead of using the term ‘Finsterwalderbreen basal ice (BI)’, we refer to ‘Finsterwalderbreen DB (dispersed banded) basal ice’. Instead of ‘pressure ridge’ ice, we refer to ‘Finsterwalderbreen SB (solid banded) basal ice’, which denotes the fact that these samples were taken from surface outcrops of frozen subglacial material, or thrust bands, with distinct debris layers (pg 6, lines 173-181).

9. *In several locations (e.g. section 4.2, line 13; section 5.3, line 18) the observations that you make have been reported in the literature and you might consider citing them.*

The analyses of LMW-DOC compounds in basal ice from all four sample locations have not yet been reported in the literature. The authors did present DOC, FCHO and FAA concentrations for samples of Russell Glacier basal ice in (Lawson et al., 2013); however, this was for a larger number of samples which were analysed as part of an earlier piece of analytical work. We did not cite this reference as we analysed a new set of Russell Glacier basal ice samples for this current manuscript.

10. *Section 4.2 (line 18): Are these emission or excitation wavelengths?*

These are excitation wavelengths. This has been added to the text (pg 13, lines 391-392) and to Table 3.

11. *Section 4.3 (line 21-23): should it be  $p < 0.5$  rather than  $p = 0.05$ ?*

The p-value determines whether the correlation between the two variables could have occurred due to random sampling and should read  $p < 0.05$ . This has been changed in the caption for Figure 1 (pg 34, line 892).

12. *Page 14157 (line 11): “. . .sources have extensive contact. . .” This would be highly site specific, wouldn’t it? If the water source is part of the well-developed quick-flow component of a channelized drainage system, subglacial contact would be minimal, wouldn’t it? Particularly if it was confined to a scoured bedrock channel (N-channel)?*

The Reviewer makes a valid point that the degree of contact between subglacial material and both the water flowing at the base of the glacier and porewaters in overridden water-saturated sediment will be site specific. Also, we agree that where the drainage system is composed predominantly of N-channels there will be little scope for the fast-flowing waters to acquire dissolved compounds from biogeochemical interactions with the overridden material. We have amended this sentence in the text to explain the site specific nature of these interactions (pg 17, lines 512-516).

*13. Section 5.3 (line 12): Here, and elsewhere, the assumption is made that the Joyce OM is “very labile”. While I agree that it probably is, you never test the source OM for lability, nor do you cite corroborating evidence to support that lacustrine OM is labile.*

The Reviewer makes a valid point that we did not test the Joyce Glacier OM for lability. This has been clarified in the text (pgs 12-13, lines 373-375). We have based the assumption of Joyce Glacier lability on the relatively high proportion of extractable carbohydrates in the basal ice sediment (>17% of the sediment OC) as extractable carbohydrates have previously been used as a proxy for bioavailable OC (Biersmith and Benner, 1998; Pusceddu et al., 2009). In Section 5.1 we do cite that “lacustrine material is generally acknowledged as a source of reactive OC to microorganisms (Meyers and Ishiwatari, 1993)” which implies that it is labile (pg 15, lines 465-466).

*14. Conclusion (line 23): there’s an extra “also” in the sentence.*

This has been removed from the text.

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## Biogeosciences Discussion comments

### Jacob Yde Referee

We thank Jacob for his thorough review and constructive comments which have improved the content of this manuscript. In the following, we reply to all referee comments (in italics) point by point.

*The authors have indeed conducted an interesting and novel study of low molecular weight dissolved organic carbon (LMW-DOC) in basal ice. The text is well written and suitable for Biogeosciences. The authors have good control on the biological and biogeochemical aspects of the study. Therefore, I have focused my review mainly on the glaciological and sedimentological aspects.*

- 1. My main concern is the lack of information about the sampling sites and character of the basal ice (i.e. the basal ice facies). This makes it difficult to know how the basal ice was formed (regelation, adfreezing, thrusting) and to assess whether the authors make appropriate comparisons, interpretations and conclusions. I will like to see a better description of the basal ice at each sampling site, including a figure showing close-up photos of the basal ice.*

We did not conduct an extensive investigation into how the basal ice was formed as we did not possess the necessary information and analytical data to be able to provide a thorough account of the basal ice formation processes at each site. For instance, we lacked data on ice crystallography, sediment grain-size distribution, clast-shape and form analyses, co-isotope analyses ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ), and gas composition of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{O}_2$  in bubbles in the ice, which are typically used to describe and differentiate the basal ice facies. We also did not have detailed accounts of the thickness of individual debris layers or structural measurements of basal ice facies. Instead, we were relying on visual description of the basal ice, sediment concentration (by mass) and published literature to infer how the basal ice formed. This lack of detailed data made us cautious when inferring basal ice formation processes as these are often controversial and basal ice formed by different mechanisms may be indistinguishable (Sleewaegen et al., 2003) and flow related to post- or syn-deformational processes may alter the primary character of the basal ice (Waller et al., 2000).

Nonetheless, we agree with the Reviewer that more information is needed on the location and character of the sampling sites and basal ice facies, which we provide in Section 2.5 (pgs 6-7, lines 156-196). We refer the Reviewer to points 17-25 where we address particular comments on the sample collection and basal ice description in more detail.

- 2. I am also concerned about the coupling between LMW-DOC and debris concentration in basal ice because debris concentration is a poor proxy for the surface area of the debris within a sample. I would have liked to see some data on particle size distributions. Again, this makes me skeptical to some of the interpretations and conclusions.*

We have revised some of our interpretations and conclusions based on the Reviewer's valid comment that debris concentration is a poor proxy for the surface area of the debris (which would be the controlling variable to test whether DOC was leached from the basal debris) (pg 12, lines 360-368). Unfortunately, we do not have data on particle size distribution <2mm or the debris concentration for particle sizes <2mm, and are restricted to presenting only debris concentration (by mass). We have however, removed our hypothesis and revised sections of the results and discussion, while noting the limitations of our dataset when discussing the potential for DOC to leach from sediments (e.g. Section 5.2). We refer the Reviewer to points 28 and 30 where we address the specific comments in more detail.

*Overall, this study is a step forward in the understanding subglacial biogeochemistry and I look forward to read the revised paper.*

- 3. Abstract 14141, L2-4: It seems awkward to start the Abstract by talking about glacial runoff, when the focus of this paper is on basal ice and the subglacial environment. I suggest that you delete the first 2-3 sentences and direct the reader's attention towards the lack of knowledge about DOC in basal ice.*

We take on board the Reviewer's point that the paper is focussed on basal ice and process in the subglacial environment rather than on glacial runoff. Initially, we began the Abstract by mentioning glacial runoff to outline the wider significance of glacial melt and how the export of organic compounds could impact on downstream ecosystems, which is dependent on the composition of the organic material that is released. Basal ice melt is one of the contributors to glacial melt, and so the compounds released in basal ice melt will contribute to net glacial export. This rationale has been used in other published research (Barker et al., 2010; Pautler et al., 2012; Pautler et al., 2011) and hence we followed their reasoning. We have now revised the start of the Abstract to focus more on the lack of knowledge about DOC in basal ice (pg 1, lines 21-26).

- 4. 14141, L7-8: I certainly don't like this definition of basal ice. Several other processes than basal adfreezing may form basal ice, and basal ice may contain incorporated segregation ice or intermixed glacier ice. Here in the Abstract there is no need to define basal ice, but you must present a proper definition of basal ice in the Introduction section.*

Following the advice of the Reviewer, we have removed this definition of basal ice from the Abstract. We have also expanded on our definition of basal ice in the Introduction section (see point 7) (pgs 2-3, lines 48-83).

- 5. 14141, L11: It is unclear what is meant by "basal debris type".*

What we mean is 'different type of overridden material'. We have amended this in the text (pg 2, line 31-32).

- 6. 14141, L13: Make it clear to the wide readership of Biogeosciences that FAA refers free amino acids.*

This has been edited in the text (FAA = free amino acids) (pg 2, line 33).

- 7. Introduction 14142, L2-21: In my opinion, the Introduction section needs to be rewritten. You use 20 lines to talk about glacial runoff, and a single sentence to give a wrong definition of basal ice, which is the environment that you are actually examining. I cannot follow the leap from "Thus, further knowledge is needed to accurately assess the source of LMW-DOC in glacial runoff. . ." to "... and determine the abundance and composition of potentially bioavailable LMW-DOC in basal ice at the base of glaciers and ice sheets". This paper does not accurately assess the source of LMW-DOC in glacial runoff. What is the link between subglacial meltwater runoff and basal ice? At three of the four glaciers that you are studying I will assume that the basal ice is primarily formed at cold-based conditions; at temperate Engabreen, I will assume that the basal ice consists of glacier ice and ice formed by regelation.*

*I recommend that you focus the first paragraph on basal ice. For example, use the definition of basal ice by Hubbard et al. (2009) and inform the readers about metamorphose of glacier ice into*



*basal ice (Sharp et al., 1994) and post-formational tectonic deformation of basal ice causing intermixing of glacier ice and basal ice (Waller et al., 2000), in addition to basal ice formation by adfreezing and regelation. Then, you may continue by describing subglacial entrainment of LMW-DOC into basal ice.*

On the advice of the Reviewer, we have revised the Introduction section and focus the first paragraph on defining basal ice, and have included the references that the Reviewer has helpfully supplied above (pgs 2-3, lines 48-83). We have focussed less on glacial runoff. Our rationale for linking basal ice and subglacial meltwater runoff is that basal ice melt may contribute to the subglacial runoff exported from glaciers with outflow channels. However, we recognise that this is a small component when compared with the large volume of supraglacial meltwater that travels through the subglacial systems within temperate and polythermal glaciers. Nonetheless, the export of subglacially stored meltwater, or basal waters with distinct chemical signatures, which may contain basal ice melt, can be detected in glacial runoff (Bhatia et al., 2013; Hawkings et al., 2015) and thus cannot be excluded from glacial chemical export budgets. We do not overplay this link as the Reviewer is correct in that we did not quantitatively assess the source of LMW-DOC in glacial runoff.

As Russell Glacier and Finsterwalderbreen are classified as polythermal-based, it is possible that the basal ice that we sampled at the margin was formed by regelation in addition to cold-based processes. This has been included in the description of basal ice sampled at each site (Section 2.5).

8. *14142, L22-25: The subglacial environment and the basal ice environment are not synonymous. The basal ice environment is a part of the subglacial environment. Here, it is unclear to me whether you make this distinction.*

We have edited our definition of basal ice in the introduction to make this distinction more clear. The references that we use on pg 2, lines 50-51 all refer to sampled basal ice (and subglacial sediment in (Foght et al., 2004)).

9. *14143, L1: Introduce the abbreviation of free amino acids here.*

This has been added to the text as suggested (pg 3, line 88).

10. *14144, L1-3: You mention that the four glaciers have distinct temperature regimes, but you only list the four glaciers with their assumed substrates. It will be informative to include the temperature regimes in the list.*

The temperature regimes are listed in Section 2.1-2.4 when each of the sample sites is described. On the advice of the Reviewer, we have included these temperature regimes when we introduce the four sample sites towards the end of the Introduction (pg 4, lines 117-120).

11. *Sample sites and basal ice sample collection 14144, L9: What does the reference refer to? It seems superfluous.*

We have rechecked this reference and agree with the Reviewer that it is not necessary and have removed it from the text.

12. *14144, L17: I would say west margin rather than southwest margin.*

We have edited the text and now refer to Russell Glacier as situated on the west margin of the GrIS (pg 5, line 134).

13. 14144, L21: *I think that you mean Archaean, not Achaeen.*

This has been edited in the text (pg 5, line 138).

14. 14144, L21-22: *A more correct reference to the local geology will be Escher and Watt (1976).*

The reference in the text has been changed to Escher and Watt (1976) (pg 5, line 138).

15. 14145, L2-8: *It is relevant to mention that Finsterwalderbreen last surged between 1898 and 1910 (Liestøl, 1969) because the formation of the basal ice is very likely linked to the surge event, as it has been shown at Variegated Glacier (Sharp et al., 1994) and Kuannersuit Glacier.*

We have edited the text to mention the surging of Finsterwalderbreen between 1898 and 1910 (Liestøl, 1969) and how this may have influenced the formation of basal ice (pg 5, lines 143-145).

16. 14145, L10: *Better use the term temperate than warm-based.*

This has been amended in the text (pg 5, line 151).

17. 14145, L16-14146, L2: *The description of the sampling sites is very cursory. It will be difficult for others to find the sampling sites in the field based on these few sentences, and even if they manage to find the sampling sites they will not know which basal ice facies they should sample to replicate your sampling. It is important with a more detailed site description and a characterization of the basal ice in order to get an idea of the differences in the formational processes of the basal ice, as these processes may influence the abundance and composition of LMW-DOC (the aim of this paper). A figure showing photos of the basal ice at each sampling site (both the BI and PR for Finsterwalderbreen) will give an impression of the character of the basal ice. This may also be helpful to readers of Biogeochemistry, who are not familiar with basal ice.*

Following the advice of the Reviewer, we have revised the description of the sampling sites to include greater detail on how, and where, the basal ice samples were collected (pgs 6-7, lines 157-196).

We did not include detailed maps highlighting where the samples were collected, as the Reviewer did in their 2010 basal ice paper (Yde et al., 2010), as we felt that this would make the introduction to the research too long (as we would need to describe four glacial sampling sites) and detract focus from the analytical results and interpretation. We followed the approach of published research that sampled basal ice from multiple locations and restricted the description of the samples to text, e.g. (Pautler et al., 2011; 2012; Sharp et al., 1999; Stibal et al., 2012), and hence, we did not include photographs of the basal ice at each sampling point. While this would help given an impression of the character of the basal ice, unfortunately, we don't have an up-close photograph of the Joyce Glacier or Finsterwalderbreen 'pressure ridge' basal ice samples, and there is not adequate sample remaining to take a new photograph. We believe that it would look odd if there were photographs of three out of the five sample types and opt not to include photographs.

Our research is intended to be an exploratory investigation that aims to; a) test whether ion chromatography is a valid analytical approach for the assessment of trace level LMW-DOC

compounds in glacial samples, and b) investigate whether basal ice from different sample locations with different overridden material types had distinct LMW-DOC signatures. The next phase of research would be to consider how LMW-DOC varied within basal ice facies at each sampling location as we acknowledge that the different formation processes may influence the abundance and composition of LMW-DOC. However, this was beyond the scope of our research and would have required analytical equipment that we did not have access to when we were analysing the samples. For instance, it would have been interesting to describe and differentiate the basal ice facies using ice crystallography, co-isotope analysis of  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , and gas composition of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{O}_2$  in bubbles in the ice; however, this was not possible during the analysis period. Due to limited sample volume, we are unable to run any further experiments on the basal ice samples that we have analysed in this paper

18. 14145, L16-17: *Is this actually basal ice or is it in fact subglacial frozen lacustrine sediment? If it is basal ice, it must have distinct physical or chemical characteristics different from frozen lacustrine sediments (see definition of basal ice by Hubbard et al., 2009). From this single sentence I am unable to assess whether you have actually sampled frozen lacustrine sediment.*

We agree that the phrasing in this sentence is poor and does not adequately explain what we sampled. We sampled basal ice where the facies were composed of frozen debris and only weakly exhibited layers that were >1 mm thick but < 1m thick. According to the classification in (Hubbard et al., 2009), we sampled solid banded basal ice. This has been included in the basal ice description (pg 6, lines 159-161).

19. 14145, L16-19: *A characterization of the sampled basal ice beneath Engabreen will be useful (see Jansson et al., 1996), as the formation of basal ice at Engabreen may differ from the other three glaciers because of its temperate basal regime.*

We have described the character of the ice sampled beneath Engabreen in more detail and thank the Reviewer for recommending (Jansson et al., 1996) which we now cite (pg 7, lines 191-196).

20. 14145, L20: *It sounds a bit dangerous to collect basal ice samples at the calving terminus of Russell Glacier. If you collected the samples at the northern corner of the terminus, you have to be aware that before the 1990s there were some small lakes here, dammed between the moraine and the glacier. When the glacier advanced during the 1990s the lakes were overridden and the glaciolacustrine sediment may have been incorporated into the basal ice. At the southern corner, the glacier advanced into a dune. Detailed information about the location and character of the sampling site is therefore very important, as it may have significant impact on LMW-DOC.*

Our Russell Glacier samples were collected towards the southern corner where the glacier has previously advanced into a dune and hence, we are confident that our basal ice samples did not contain any glaciolacustrine sediment. Our basal ice samples were taken from the same location as those analysed in (Stibal et al. 2012), where biomarker analyses found OC characterised by n-alkanoic acids steroids and other functionalized compounds consistent with a higher plant, and thus, soil organic matter source. We now describe the location and character of the Russell Glacier sampling site in greater detail (pg 6, lines 164-171) and use this information when interpreting the basal ice LMW-DOC signature in the Discussion (e.g. pgs 15-16, lines 469-478).

21. 14145, L20: *Also, it is relevant to mention whether you sampled the solid or banded basal ice facies at Russell Glacier. You make a distinction between two ice facies at Finsterwalderbreen, but the same argument can be used for Russell Glacier. It is okay that you just sampled one ice facies at Russell Glacier, but the readers need to know which one. I will encourage you to do a*

*follow-up study on the horizontal distribution of LMW-DOC in basal ice to examine potential links between genetic basal ice facies and the abundance and character of LMW-DOC.*

We recognise that the descriptions we have given regarding the location and type of basal ice sampled are lacking in detail. As mentioned in point 17, we have revised Section 2.5 (Sample collection). This includes the Reviewer's suggestion that we state which ice facies we sampled at Russell Glacier (pg 6, lines 168-169). We sampled banded basal ice where the debris was generally restricted to narrow sediment layers and large vein networks were clearly evident.

It would be very interesting to do a follow up study on the horizontal distribution of LMW-DOC in basal ice to examine potential links between genetic basal ice facies and the abundance and character of LMW-DOC.

22. 14145, L21-22: *Again, it will be nice with information about which basal ice facies was sampled.*

Information on the type of basal ice facies that were sampled has now been added to the text as part of the general revision of Section 2.5 (pg 6, lines 173-177).

23. 14145, L22: *Insert the word glacier in front of surface, and delete the word frozen unless you actually mean that the subglacial material was frozen when it was entrained into the shear planes.*

We are referring to outcrops of frozen subglacial material that have been upthrust from the glacier bed and are now evident on the glacier surface. We believe that the original sentence describes the ice that we sampled (pg 6, lines 175-177).

24. 14145, L23-24: *To me the term Pressure Ridge is related to sea ice, making this sentence rather confusing. A more appropriate term could be debris layer, thrust band or shear plane (I am guessing a bit here, as it is unclear to me what you sampled). No matter what you sampled I am pretty sure that the thrusting did not happen "during cycles of (glacier) advance and retreat". As Finsterwalderbreen is a polythermal surgetype glacier, my guess is that primary thrusting occurred during the early surge phase in the subglacial zone between temperate ice and cold ice, and secondary thrusting may have occurred during surge termination due to ice flow compression. This is at least how it is envisaged at the polythermal surge-type Kuannersuit Glacier (Larsen et al., 2010). All this is relevant because it may indicate that the PR debris derives from further upglacier than the BI debris, and that the PR debris may have been glacier-covered for a much longer period than the BI debris.*

We take on board the comments of the Reviewer and have revised the terminology that we use to describe the two types of basal ice that were sampled at Finsterwalderbreen. Instead of using the term 'Finsterwalderbreen basal ice (BI)', we refer to 'Finsterwalderbreen DB (dispersed banded) basal ice'. Instead of 'pressure ridge' ice, we refer to 'Finsterwalderbreen SB (solid banded) basal ice', which denotes the fact that these samples were taken from surface outcrops of frozen subglacial material, or thrust bands, with distinct debris layers (pg 6, lines 173-184).

We agree with the Reviewer's reasoning that the thrusting could have occurred in two phases: primary thrusting during the early surge phase in the subglacial zone and secondary thrusting during the surge termination due to ice flow compression. This has been incorporated into the description of the sampling site at Finsterwalderbreen (Section 2.5). We also make note in the Discussion that this could indicate that the 'PR debris' (now referred to as 'SB debris') derives from further upglacier than the 'BI debris' (now referred to as 'DB debris') (pg 18, lines 550-561). However, we are cautious when

describing the basal ice formation processes as we are limited in the data that we have to be able to interpret these processes, as discussed in points 1 and 17.

25. 14145, L23-24: *It is also unclear to me whether the debris-rich ice in the pressure ridges is in fact basal ice. Maybe it is glacier ice with discrete debris layers (although the debris may derive from the glacier bed).*

We now refer to the ‘pressure ridge ice’ as ‘Finsterwalderbreen SB (solid banded) basal ice’, which we believe is basal ice rather than glacier ice with distinct debris layers, based on its composition according to the classification in (Hubbard et al., 2009). The area where we sampled the ice consisted primarily of solid banded ice in thrust bands and there was a lack of clean (glacier) ice.

26. 14146, L1 and elsewhere: *It is more scientifically correct to write (by mass) rather than (by weight).*

This has been amended in the text (e.g. pg 8, line 242).

27. 14146, L6-7: *Maybe debris-rich basal ice is a better term than “dirty basal ice”. This sentence is awkward because your Finsterwalderbreen BI samples had a debris concentration of 20 +/- 27% and thereby not meet the criteria of having a debris concentration >20%. I suggest that you delete the sentence.*

We have deleted this sentence.

28. 14147, L22-28: *Basal ice debris concentrations are not very useful, as basal ice often contains boulders, stones and sorted gravel lamina. Therefore, the basal ice debris concentration depends on whether you choose to collect your samples in places without large boulders or stones. It will be meaningful to present the basal ice debris concentration for particle sizes <2mm and preferably in combination with data on particle size distribution <2mm.*

We accept the Reviewer’s point. When we refer to ‘basal ice debris’ we are referring to sediment particles predominantly <2mm (plus some small gravel in the Finsterwalderbreen ‘pressure ridge/solid banded’ samples). However, we do not have data on particle size distribution <2mm or the debris concentration for particle sizes <2mm (now stated in the text, pg 12, lines 358-364). While we agree that information on particle size distribution would have been very useful in describing the basal ice facies, this was not the scope of the paper as we were primarily focussed on analysing the LMW-DOC compounds in the basal ice. We accept that the particle size distribution would have aided our interpretations of the potential origins of the LMW-DOC compounds and degree of interaction between the sediment particles and water films within the basal ice matrix. However, we included the basal ice debris concentrations to demonstrate that the basal ice samples from the different glaciers differed in terms of debris:ice ratios, particularly FSB samples (86.5% debris, compared with 20-55% in the other basal ice samples).

29. 14151, L17 and L21: *Here, you use the abbreviations FPR and FBI rather than PR and BI.*

Yes, we used FPR and FBI as abbreviations for Finsterwalderbreen pressure ridge and Finsterwalderbreen basal ice to make it clear which Finsterwalderbreen samples we are referring to. We also used these abbreviations in the Tables and Figures and believe that they are necessary to avoid confusion between the different ice samples. We have now revised the terminology that we use

to describe the two Finsterwalderbreen basal ice types (see point 24) and used the abbreviations FSB (Finsterwalderbreen solid banded) and FDB (Finsterwalderbreen dispersed banded) instead.

30. 14153, L16-23 (and section 5.2): *I am not sure how robust this hypothesis between DOC (and LMW-DOC) and debris concentrations really is, as long as you do not present any data on particle size distributions <2 mm. Assuming that DOC is leached from sediments, the controlling variable will be the surface area of the debris rather than debris concentration. I think that you need to rethink this part of the paper. It is important to present information about debris concentration in the basal ice because it tells something about the material, but it is probably not appropriate to test a hypothesis between DOC and debris content unless you have the appropriate data to do it. As I am skeptical to your hypothesis, I am also skeptical to your use of this hypothesis in the Discussion section.*

We take into consideration the Reviewer's point that while it is important to present information on debris concentration, the fact that we do not have data on particle size distribution < 2mm means that our hypothesis may not be robust enough to test with our existing data. We have therefore removed this hypothesis from the text and incorporated parts of Section 4.3 (Debris concentrations) into Section 4.1 (Basal sediment characteristics) (pg 12, lines 358-368). In this revised section, we state that we investigate possible correlations between DOC (and LMW-DOC) and the debris content of the basal ice, which may provide information on DOC provenance and the potential for DOC to leach from sediments into the basal ice. We acknowledge that if DOC is leached from sediment, the controlling variable will be the surface area of the debris, rather than the debris concentration. However, as a detailed investigation into the particle size distribution was beyond the scope of this study, we use debris concentrations for a preliminary analysis to see if the relationship with debris concentration was different for DOC and LMW-DOC. One of the key observations from Figures 1a and 1b is that no significant associations between LMW-DOC and debris concentrations were observed, which suggests that LMW-DOC in basal ice is not simply leached from the debris, and that there are other sources (potentially microbial) and/or processes (e.g. LMW-DOC cycling) that influences the abundance in basal ice. We have therefore played down our discussion of the potential for DOC to leach from sediments (Section 5.2).

31. 14153, L23: *Where is the presentation of the major ion concentrations in basal ice that you mention in the Methodology section? If you have these data, please show them.*

We did not intend to mention major ion concentrations and have removed this reference (when discussing blank corrections in Section 3.3.4).

32. 14154, L5: *To my knowledge this is the first study to quantify LMW-DOC in basal ice. It not, insert references to other studies.*

To our knowledge, this is the first study to quantify LMW-DOC in basal ice. This has been made clear in the text (pg 14, lines 422-423).

33. 14154, L15: *Specify what you mean by "type of overridden material"? Do you mean differences in lithology or unconsolidated vs. consolidated substrata or differences between pre-entrainment sedimentary types (till, glaciofluvial, lacustrine, soil)?*

By 'type of overridden material' we specifically mean pre-entrainment sedimentary type according to our previous classification of the overridden material at each sampling site, e.g. lacustrine material - Joyce Glacier, paleosols – Russell Glacier. We have made this more specific in the text (pg 14, lines 432-433).

34. 14154, L17: *This is slightly confusing, as one will expect the values in brackets to be the mean values, not maximum limits.*

We agree that this could be confusing and we have removed these values in brackets and instead refer the reader to Tables 1 and 2 where the mean concentrations are presented. This is clearer than presenting all of the mean concentrations in the text.

35. 14154, L18: *Not sure what you mean by comparable. Most things are comparable. Rephrase this sentence.*

We have amended this sentence to read “the mean basal ice DOC concentrations and mean sediment OC content were relatively similar in all basal ice samples despite the differences in the types of overridden material” (pg 14, lines 434-436).

36. 14155, L25-26: *I am not convinced that the GrIS debris in basal ice derives from a soil origin. It all depends on where you collected your samples along the margin of Russell Glacier. It could be of glaciofluvial, glaciolacustrine or aeolian origin, or derive from subglacial erosion.*

We understand the Reviewer’s concern that we are generalising the basal debris type for the entire GrIS based on our samples collected at Russell Glacier. As previous studies have shown, the debris type beneath the GrIS could also contain sediment of glaciofluvial, glaciolacustrine or aeolian origin. We have amended this statement to refer to Russell Glacier only, rather than the GrIS. We also refer the Reviewer to point 20 where we describe where we collected our Russell Glacier samples (towards the southern corner where the glacier has previously advanced into a dune). We are relatively confident that the GrIS debris (in this location) derives from a soil origin and we base this assertion on published literature, e.g. (Stibal et al., 2012) (pgs 15-16, lines 469-472).

37. 14155, L29 and Table 2: *These ages are only relevant if you have collected the samples at the exact same site as Stibal et al. (2012). If you did so, mention it in the text.*

The samples were collected at the same site as Stibal et al. (2012). This has been clarified further in the text (pg 6, lines 185-187).

38. 14156, L4: *No reason to mention again that the Russell Glacier samples were collected from the GrIS margin.*

This has been removed from the text.

39. 14156, L17-20: *Could the lack of organic biomarkers at Engabreen be due to debris entrainment by regelation rather than adfreezing?*

Yes, it is possible that the lack of organic biomarkers in Engabreen basal ice could be due to debris entrainment by regelation, particularly as the glacier is temperate. This has been included in the text as an alternative explanation (pg 16, lines 492-493).

40. 14156, L21: *It seems relevant to distinguish between glacial (ice-contact) lakes and other lake types. Again, I miss information about the chemistry of your basal ice.*

We take on board the Reviewer's comment and have amended this sentence to refer to lacustrine sediments, rather than lakes. We have looked again at the literature which proposes that the recent advance of Joyce Glacier is thought to have resulted in the upthrust and exposure of lacustrine sediments (Hendy, 2000; Stuiver et al., 1981). However, we are unable to find a more detailed description of what specific type of lake was overridden. We know that the Garwood Valley was completely occupied by two large lakes but we do not know if the lakes were bordered by a calving glacier (ice-contact lake) or were located some distance downstream of Joyce Glacier (non-contact glacier fed lake) (Einsele, 2000).

41. 14157, L9-10: *These are not the only sources of parent water. Refreezing of water from pressure melting during the regelation process is important.*

We have revised this sentence to include some of the other sources of parent water as suggested by the Reviewer (pg 17, lines 508-511).

42. 14157, L20: *But you do not have age data from Joyce Glacier and Engabreen, so how do you know that age is a controlling parameter? How can you exclude that other parameters at Russell Glacier are less important?*

The Reviewer makes a valid point that we cannot support the assertion that age is a controlling parameter on DOC acquisition as we do not have age data from all four glaciers. We were originally making the case that, for the two samples that we do have age data for (Finsterwalderbreen and Russell Glacier), where the sediment is relatively young ( $1830 \pm 50$   $^{14}\text{C}$  yrs BP beneath Russell Glacier) there is a stronger relationship between DOC and debris concentration, compared with the older sediment in Finsterwalderbreen basal ice ( $3750 \pm 150$   $^{14}\text{C}$  yrs BP). Nonetheless, we have removed all mention of age as a controlling parameter as we do not have age data for all samples.

43. L14159, L19-21: *In a warming climate the tendency is that temperate/polythermal glaciers become cold-based as the ice thickness decreases, not the other way around.*

We have removed our reference to a warming climate and changing thermal regimes. Instead, we discuss how DOC may be released from cold-based (and warm-based, polythermal) glaciers during the current climate (see point 44) (pgs 19-20, lines 590-605).

44. L14159, L19-21: *Why is a change in basal thermal regime needed? Cold-based glaciers may have discrete subglacial channels where water is in contact with the substrate (e.g. at Longyearbreen).*

We agree with the Reviewer that a change in basal thermal regime may not necessarily be needed to release DOC in basal ice to downstream ecosystems. We have amended this sentence to take into consideration the possibility of discrete subglacial channels beneath cold-based glaciers such as Longyearbreen (Yde et al., 2008) which may be in contact with the substrate and hence may represent a mechanism for DOC release to downstream ecosystems (pgs 19-20, lines 590-605).

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## **Identification and analysis of low molecular weight dissolved organic carbon in subglacial basal ice ecosystems by ion chromatography” by E. C. O’Donnell et al.**

### **List of major changes**

- Revised the start of the Abstract to focus more on the lack of knowledge of basal ice DOC rather than LMW-DOC in glacial runoff (pg 1, lines 21-26)
- Rewritten the Introduction to focus the first paragraph on basal ice including a new description, possible formation mechanisms and subglacial entrainment of DOC and LMW-DOC into the ice (pg 2-3, lines 47-83). The previous paragraph that focussed on glacial runoff and the potential for basal ice to contribute to DOC and LMW-DOC export from glacial systems has been removed
- Added information about glacier surging to the Finsterwalderbreen site description (pg 5, lines 143-145)
- Revised section 2.5 Basal ice description and sample collection to provide more detail on where the samples were taken, the character of the basal ice and the sampling site, and which ice facies were sampled (pgs 6-7, lines 156-196)
- Revised the labelling of Finsterwalderbreen samples from ‘basal ice (BI)’ to ‘dispersed banded (DB) ice’ and ‘pressure ridge (PR) ice’ to ‘solid banded (SB) ice’. These changes have been made to the manuscript, figures, captions and tables
- Added a sentence on basal debris size/type (pg 8, lines 242-244)
- Provided a more rigorous evaluation of the ion chromatography technique used and how we set up batch sample runs (pgs 10-11, lines 304-312)
- Revised section 4.1 Basal sediment characteristics to include results of the preliminary analysis into possible relationships between debris concentration and DOC (and LMW-DOC) (pg 12, lines 358-368). We have removed the hypothesis that if DOC was largely terrestrially derived and leached from sediments there should be a positive correlation between DOC and debris content as we would require data on particle size distribution to fully assess the correlation. We also removed section 4.3 and played down the potential for DOC to leach from sediments in the Discussion (pg 17, lines 508-523)
- Clarified the meaning of ‘type of overridden material’ throughout the text, i.e. the pre-entrainment sedimentary type such as lacustrine material or paleosols
- Edited the Discussion to include more information on how basal ice formation mechanisms may explain the DOC/LMW-DOC character of the basal ice
- Removed section in Discussion that looks at sediment OC age as a controlling parameter for DOC in basal ice as we lack age data from Joyce Glacier and Engabreen
- Included a short discussion on why the LMW-DOC character could differ between FSB and FDB basal ice samples based on the origin of the basal ice and formation mechanisms (pg 18, lines 550-561)
- Revised the section in the Discussion on export of basal melt from glaciers with different thermal regimes (and the impact of changing thermal regimes) (pgs 19-20, lines 590-605)
- Generally revised the manuscript to avoid overstating the importance of basal ice in glacial meltwater budgets (in Introduction and Discussion)
- Edited the manuscript to include the specific (minor) corrections and suggestions from the two Reviewers, e.g. replaced ‘allochthonous’ with ‘terrestrial’ throughout
- Added new references and remove those no longer included in manuscript
- Amended numbering of figures due to changes in manuscript text
- Changed lead authors surname from Lawson to O’Donnell (recent marriage)

1 **Identification and analysis of low molecular weight**  
2 **dissolved organic carbon in subglacial basal ice**  
3 **ecosystems by ion chromatography**

4

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19

20 **Abstract**

21 Determining the concentration and composition of dissolved organic carbon (DOC) in glacial  
22 ecosystems is important for assessments of in situ microbial activity and contributions to  
23 wider biogeochemical cycles. Nonetheless, there is limited knowledge of the abundance and  
24 character of DOC in basal ice and the subglacial environment and a lack of quantitative data  
25 on low molecular weight (LMW) DOC components which are believed to be highly  
26 bioavailable to microorganisms. We investigated the abundance and composition of DOC in  
27 ~~subglacial environments~~basal ice via a molecular level DOC analysis ~~of basal ice~~.  
28 Spectrofluorometry and a novel ion chromatographic method, which has been little utilised in  
29 glacial science for LMW-DOC determinations, were employed to identify and quantify the

30 major LMW fractions (free amino acids, carbohydrates and carboxylic acids) in basal ice  
31 from four glaciers, each with a different ~~basal debris~~ type of overridden material (i.e. the pre-  
32 entrapment sedimentary type such as lacustrine material or paleosols). Basal ice from Joyce  
33 Glacier (Antarctica) was unique in that 98% of the LMW-DOC was derived from the  
34 extremely diverse free amino acids (FAA) pool, comprising 14 FAAs. LMW-DOC  
35 concentrations in basal ice were dependent on the bioavailability of the overridden organic  
36 carbon (OC), which in turn, was influenced by the type of overridden material. Mean LMW-  
37 DOC concentrations in basal ice from Russell Glacier (Greenland), Finsterwalderbreen  
38 (Svalbard) and Engabreen (Norway) were low (0 - 417 nM C), attributed to the relatively  
39 refractory nature of the OC in the overridden paleosols and bedrock. In contrast, mean LMW-  
40 DOC concentrations were an order of magnitude higher (4430 nM C) in basal ice from Joyce  
41 Glacier, a reflection of the high bioavailability of the overridden lacustrine material (>17% of  
42 the sediment OC comprised extractable carbohydrates, a proxy for bioavailable OC). We find  
43 that the overridden material may act as a direct (via abiotic leaching) and indirect (via  
44 microbial cycling) source of DOC to the subglacial environment and provides a range of  
45 LMW-DOC compounds that may stimulate microbial activity in wet subglacial sediments ~~in~~  
46 current subglacial environments.

47

## 48 1. Introduction

49 ~~Glacial runoff is a major freshwater input to coastal waters worldwide, including the high-~~  
50 ~~latitude oceans (Neal et al., 2010). Recent work suggests that this runoff is rich in protein-~~  
51 ~~like, low molecular weight dissolved organic carbon (LMW DOC) (Singer et al. 2012;~~  
52 ~~Stubbins et al., 2012; Lawson et al., 2014a, 2014b; Hood et al., 2015) which, when exported~~  
53 ~~downstream, is rapidly utilised by proglacial and near coastal heterotrophic communities~~  
54 ~~(Bardgett et al., 2007; Fellman et al., 2010). There are at least three different sources of~~  
55 ~~bioavailable dissolved organic carbon (DOC) in glacial runoff. The first source is of ancient~~  
56 ~~terrestrial origin, reflecting allochthonous DOC derived from overridden material at the bed~~  
57 ~~(Hood et al., 2009). The second is derived from anthropogenic aerosol deposition on the~~  
58 ~~glacier surface (Stubbins et al., 2012), while the third is from biological activity in both~~  
59 ~~supraglacial (Anesio et al., 2009) and subglacial (Bhatia et al., 2013) environments. To date,~~  
60 ~~there has been only limited examination of the potential for different bedrock types and~~  
61 ~~overridden organic matter, such as paleosols and lacustrine material (Wadham et al., 2008;~~  
62 ~~Stibal et al., 2012), to act as a source of bioavailable DOC to subglacial meltwaters and~~

63 runoff, either directly (via abiotic leaching) or indirectly (via microbial cycling). Thus,  
64 further knowledge is needed to accurately assess the source of LMW DOC in glacial runoff,  
65 to quantitatively compare contributions from the surface and the bed, e.g. (Stubbins et al.,  
66 2012), and determine the abundance and composition of potentially bioavailable LMW DOC  
67 in basal ice at the base of glaciers and ice sheets.

68 Basal ice is a mixture of refrozen glacial meltwater and sediment entrained from beneath the  
69 glacier. Basal ice forms part of the subglacial environment, which also includes subglacial  
70 sediments and subglacial waters (Hodson et al., 2008). It hosts viable microbial communities  
71 that may play a significant role in the organic carbon (OC) turnover in glaciated regions  
72 (Sharp et al., 1999; Skidmore et al., 2000; Foght et al., 2004). Basal ice is typically defined as  
73 ice that has acquired distinctive physical and/or chemical characteristics due to processes  
74 operating at or near to the bed of an ice mass (Hubbard et al., 2009). Basal ice layers may  
75 comprise ice and debris entrained from beneath the glacier and meteoric ice derived from the  
76 surface and diagenetically modified by hydraulic, thermal and strain conditions at the glacier  
77 bed (Knight et al., 1997). A range of processes can form basal ice, which we highlight  
78 briefly. For instance, new basal ice may form from basal accretion of supercooled subglacial  
79 water, a freeze-on (or adfreezing) mechanism (Lawson et al., 1998), or by regelation, the  
80 localised melting and refreezing of ice at the glacier bed, e.g. around a bedrock obstacle,  
81 which represents an important mechanism to entrain subglacial debris into the basal ice  
82 (Iverson and Semmens, 1995). Sediment may also be incorporated into basal ice by folding  
83 (Hubbard and Sharp, 1989), cavity/crevasse infilling, structural deformation, thrusting,  
84 traction/shearing and metamorphism of existing ice at the glacier bed (Knight et al., 1997).  
85 Metamorphosis of meteoric glacier ice can thicken basal ice layers (Sharp et al., 1994) and  
86 post-formational tectonic deformation of basal ice can cause intermixing of glacier and basal  
87 ice (Waller et al., 2000).

88  
89 The chemical composition of basal ice reflects characteristics of the parent water prior to  
90 being frozen (Knight, 1997). In temperate and polythermal glaciers, this may include  
91 supraglacial inputs, whereas in cold-based glaciers where there is little surface meltwater  
92 penetration, the majority of meltwater at the glacier bed likely derives from basal ice melting.  
93 This water may flow at the base of the glacier, be held in porewaters in overridden water-  
94 saturated sediment or represent refrozen water from pressure melting during the regelation  
95 process. The parent water has potential to acquire dissolved compounds (including DOC and

96 LMW-DOC) via biogeochemical interactions with the overridden subglacial material. To  
97 date, there has been only limited examination of the potential for different bedrock types and  
98 overridden organic matter, such as paleosols and lacustrine material (Wadham et al., 2008;  
99 Stibal et al., 2012), to act as a source of bioavailable DOC to basal ice, subglacial meltwaters  
100 and runoff, either directly (via abiotic leaching or in situ abiotic processes such as dissolution  
101 in water films around basal debris and in liquid water veins (Mader et al., 2006)) or indirectly  
102 (via microbial cycling). Further knowledge is needed to determine the abundance and  
103 composition of potentially bioavailable LMW-DOC in basal ice at the base of glaciers and ice  
104 sheets and the implications this may have on subglacial DOC cycling.

105  
106 OC cycling in the subglacial environment can be investigated by incubation experiments that  
107 monitor DOC decline and/or biogenic gas (CO<sub>2</sub> and CH<sub>4</sub>) production (Montross et al., 2012;  
108 Stibal et al., 2012) and provide a direct measure of bioavailability. Analysis of marker  
109 compounds in the DOC, such as free amino acids (FAAs) (Pautler et al., 2011), may provide  
110 an indirect assessment of bioavailability. These analyses may be complimented by  
111 fluorescence spectroscopy, where fluorescing components (fluorophores) are identified and  
112 associated with particular DOC compounds, e.g. protein-like and humic-like components.  
113 The protein-like compounds are more easily utilized by aquatic heterotrophs when compared  
114 with the more aromatic humic-like components (Fellman et al., 2008) and are indicative of  
115 recent microbial activity (Barker et al., 2006, 2010). More recently, glacial DOC has been  
116 characterised at the molecular level by electrospray ionization (ESI) Fourier transform ion  
117 cyclotron resonance (FT-ICR) mass spectrometry (MS) (Grannas et al., 2006; Bhatia et al.,  
118 2010; Lawson et al., ~~2014b~~2014a), and by solution-state <sup>1</sup>H nuclear magnetic resonance  
119 (NMR) spectroscopy (Pautler et al., 2011; 2012). Both methods have provided unprecedented  
120 high resolution mass spectral information on DOC, but are not fully quantitative. Ion  
121 chromatography has been used to quantify a much smaller range of common LMW-DOC  
122 compounds, including carboxylic acids in ice cores and snow from Greenland, Antarctica,  
123 and alpine glaciers (Saigne et al., 1987; Maupetit and Delmas 1994; Tison et al., 1998). These  
124 LMW-DOC compounds typically represent small fractions of the bulk DOC (Borch and  
125 Kirchmann, 1997), yet are believed to be highly bioavailable to microorganisms owing to  
126 their rapid turnover and uptake rates (Rich et al., 1997; Skoog and Benner, 1997). Ion  
127 chromatography has yet to be widely employed to determine the molecular structure of  
128 glacial LMW-DOC due to the trace analyte concentrations (Lawson et al., 2014b). Recent

129 advances in ion chromatography instrumentation and system optimisation (e.g. greater  
130 column sensitivities, low flow rates, multiple eluents and gradient elution) enabled this study  
131 to identify and quantify numerous LMW-DOC compounds at low (<70 nM C)  
132 concentrations, and demonstrates a novel methodological approach to glacial LMW-DOC  
133 analysis.

134

135 Here, we investigate the abundance and composition of LMW-DOC compounds (free amino  
136 acids, carbohydrates and carboxylic acids) in debris-rich basal ice. We investigate four  
137 different glaciers with distinct temperature regimes, overridden substrates, and hence,  
138 contrasting sources of ~~allochthonous-terrestrial~~ organic matter. These glaciers were Joyce  
139 Glacier (Antarctica – lacustrine organic matter, cold-based), Russell Glacier (Greenland Ice  
140 Sheet, GrIS – paleosols, polythermal), Finsterwalderbreen (Svalbard – bedrock with high OC,  
141 polythermal), and Engabreen (Norway – bedrock with low OC, temperate). We investigate  
142 whether LMW-DOC abundance in basal ice is influenced by the magnitude and bioreactivity  
143 of the OC in the overridden material.

144

## 145 **2. ~~Description of Sampling Sites, and Basal Ice description and Sample~~** 146 **cCollection**

### 147 **2.1. Joyce Glacier, Antarctica**

148 Joyce Glacier (67°06'S, 50°09'W, 90 km<sup>2</sup>) is situated in the Garwood Valley, Antarctica  
149 (~~Elberling et al., 2006~~). A large proglacial lake, dammed by an ice sheet grounded in the  
150 McMurdo Sound >23,000 <sup>14</sup>C yr BP (Péwé, 1960; Hendy, 2000), is thought to have  
151 previously occupied the valley (Hendy, 2000). Joyce Glacier is cold-based, meaning that it is  
152 completely frozen to the underlying substrate. The bedrock lithology includes dolomite,  
153 granite and metamorphic rocks. Joyce Glacier recently advanced over lake sediment (Stuiver  
154 et al., 1981) and hence, the basal material is thought to contain labile OC and algal-derived  
155 organic matter of Holocene age.

### 156 **2.2. Russell Glacier, GrIS**

157 Russell Glacier (67°03'N, 50°10'W, >600 km<sup>2</sup>), situated on the ~~south~~west margin of the GrIS,  
158 is polythermal-based. Warm ice, with a temperature at the pressure melting point, in the



159 interior is surrounded by a frozen layer beneath the thinner ice of the margins. Surface  
160 melting delivers supraglacial meltwaters to the subglacial system from the onset of the spring  
161 thaw. The bedrock is predominantly Archaean gneiss ([Escher and Watt, 1976](#)). Basal debris  
162 contains overridden Quaternary deposits (including paleosols), and relatively fresh organic  
163 matter (Knight et al., 2002), which was buried during the Holocene (Simpson et al., 2009).

### 164 **2.3. Finsterwalderbreen, Svalbard**

165 Finsterwalderbreen (77°28'N, 15°18'E, 44 km<sup>2</sup>) is located on the southern side of Van  
166 Keulenfjorden, south Svalbard, and is a polythermal surge-type glacier. [Finsterwalderbreen](#)  
167 [last surged between 1898 and 1920 \(Liestøl, 1969\) which may have influenced the formation](#)  
168 [of the basal ice as has been shown, for example, at Variegated Glacier \(Sharp et al., 1994\).](#)  
169 The glacier is currently retreating at a rate of 10-45 m a<sup>-1</sup> (Wadham et al., 2007). The bedrock  
170 consists of Precambrian carbonates, sandstones, limestones and shales (Dallmann et al.,  
171 1990). Shales exposed to water may provide a steady source of DOC (Schillawski and Petsch,  
172 2008). The shale beneath Finsterwalderbreen contains up to 2.3 % OC (Wadham et al., 2004).

### 173 **2.4. Engabreen, Norway**

174 Engabreen (66°41'N, 13°46'E, 40 km<sup>2</sup>) is ~~warm-based~~[temperate](#) and part of the western  
175 Svartisen ice cap, northern Norway. Engabreen bedrock consists mostly of schist and gneiss,  
176 with calcite filled cracks (Jansson et al., 1996), and contains relatively little OC. A  
177 combination of in-washed material from the glacier surface and overridden soils of Holocene  
178 age may be the principal OC sources (Stibal et al., 2012).

### 179 **2.5 Basal ice description and sSample cCollection**

180 ~~Joyce Glacier basal ice samples were collected in the austral summer of 2010 from recently~~  
181 ~~exposed, upthrust bands of frozen lacustrine sediment. Basal ice samples from Engabreen~~  
182 ~~were collected in autumn 2009 from an underground tunnel system excavated through~~  
183 ~~bedrock beneath 210 m of sliding ice (Cohen, 2000). Basal ice blocks from the Russell~~  
184 ~~Glacier terminus were collected in spring 2008. Finsterwalderbreen was sampled in autumn~~  
185 ~~2008. Basal ice blocks were collected from the glacier terminus (referred to as basal ice, BI)~~  
186 ~~and from surface outcrops of frozen subglacial material upthrust from the glacier bed during~~  
187 ~~cycles of advance and retreat, otherwise called pressure ridges (PR). Finsterwalderbreen PR~~

188 ~~and BI data are reported separately due to the very different mean debris concentrations (by~~  
189 ~~weight);  $86 \pm 6\%$  and  $20 \pm 27\%$  for PR and BI, respectively.~~

190 ~~Basal ice blocks ( $\sim 40 \text{ cm}^3$ ) were collected by chain sawing. The outermost  $\sim 0.5 \text{ m}$  of the ice~~  
191 ~~surface was removed before the blocks were cut. The blocks were wrapped in pre-combusted~~  
192 ~~foil and stored at  $\leq 20 \text{ }^\circ\text{C}$ , before being transported frozen to the University of Bristol and~~  
193 ~~subsequently stored at  $\leq 20 \text{ }^\circ\text{C}$ . We focus this study on “dirty basal ice” (hereafter referred to~~  
194 ~~as basal ice) containing  $>20\%$  sediment (by weight).~~

195 Joyce Glacier basal ice samples were collected in the austral summer of 2010 from recently  
196 exposed, upthrust bands of debris-rich basal ice at the margin on the southern flank of the  
197 glacier. Basal ice was sampled where the facies were composed of frozen debris and only  
198 weakly exhibited layers that were  $>1 \text{ mm}$  thick but  $< 1 \text{ m}$  thick, classified as solid banded  
199 basal ice (Hubbard et al., 2009). We assume that the basal ice was formed under cold-based  
200 conditions.

201  
202 ~~At Engabreen, bedrock and basal ice are accessible by a system of underground tunnels~~  
203 ~~leading from Svartisen Subglacial Laboratory to the bed of the glacier. Hot water drilling was~~  
204 ~~implemented to create a basal cavity underlying 200 m of glacier ice. Block- and wedge-~~  
205 ~~shaped samples ( $\sim 25\text{--}35 \text{ cm}$  side), consisting of sediment laden basal ice and clean glacial~~  
206 ~~ice, were chain sawed from the ice in this cavity (from Stibal et al., 2012 so edit).~~

207  
208 Debris-rich basal ice blocks from the Russell Glacier margin were collected in spring 2008.  
209 Samples were collected from the southern corner of the glacier where it has previous  
210 advanced into a dune and from within 1.5 m of the ice-bed contact. The basal ice samples  
211 contained subglacial sediment that had been extruded up from the glacier bed via fissures  
212 near the terminus. This comprised banded basal ice where the debris was generally restricted  
213 to narrow sediment layers and large vein networks were clearly evident. As Russell Glacier is  
214 polythermal, we assume that the basal ice was formed by a combination of regelation and  
215 cold-based processes such as basal adfreezing onto the glacier sole.

216  
217 Finsterwalderbreen was sampled in autumn 2008. Basal ice blocks were collected from the  
218 terminus on the northern flank of the glacier from sections of dispersed banded basal ice  
219 (referred to as DB basal ice), within 1.5 m of the ice-bed contact, and from surface outcrops  
220 of frozen subglacial material, or thrust bands, with distinct debris layers (referred to as solid  
221 banded (SB) basal ice). It is probable that the thrust bands were formed during the most

222 recent surge during two phases of thrusting: primary thrusting during the early surge phase in  
223 the subglacial zone between temperate ice and cold ice, and secondary thrusting during the  
224 surge termination due to ice flow compression, as envisaged for the similar polythermal  
225 surge-type Kuannersuit Glacier (Larsen et al., 2010). Finsterwalderbreen DB and SB basal  
226 ice are reported separately due to the very different mean debris concentrations (by mass): 20  
227 ± 27% (DB basal ice) and 86 ± 6% (SB basal ice, where the debris component was much  
228 higher). As Finsterwalderbreen is polythermal, we assume that the basal ice was formed by a  
229 combination of regelation and cold-based processes. Basal ice samples from  
230 Finsterwalderbreen and Russell Glacier were collected from the same sites as the samples  
231 that were analysed in Stibal et al., (2012) and hence, we use their <sup>14</sup>C ages (Table 2).

232  
233 Debris-rich basal ice samples from Engabreen were collected in autumn 2009 from an  
234 underground tunnel system excavated through bedrock beneath 210 m of sliding ice (Cohen,  
235 2000). The basal ice stratigraphy comprises sediment-rich ice layers overlain by clean  
236 sediment-free and bubble-free ice (Jansson et al., 1996). We collected samples from sections  
237 of banded basal cryofacies from within 1.5 m of the ice-bed contact. Hot-water drilling was  
238 first implemented to create a basal cavity and the ice subsequently extracted by chain-sawing  
239 (described below). As Engabreen is temperate, we assume that the basal ice was formed  
240 primarily by regelation (Jansson et al., 1996).

241  
242 Basal ice blocks (~40 cm<sup>3</sup>) were collected by chain-sawing in all sample locations. The  
243 outermost ~0.5 m of the ice surface was removed before the blocks were cut. The blocks  
244 were wrapped in pre-combusted foil and stored at ≤-20 °C, before being transported frozen to  
245 the University of Bristol and subsequently stored at ≤-20 °C.

### 247 **3. Methodology**

#### 248 **3.1. Basal icemelt and sediment sample preparation**

249 Subsamples of the basal ice were prepared for analysis by chipping ~15 ~~cm<sup>2</sup>~~-cm<sup>3</sup> chunks from  
250 the main block using a flame sterilised chisel. The outer ~10-30 mm of the chips was  
251 removed by rinsing with ultrapure (≥18.2 MΩcm) deionized water (DI) (Millipore), and the  
252 remaining ice was transferred into a pre-combusted glass beaker covered with foil. The ice  
253 was allowed to melt inside a laminar flow cabinet (Telstar Mini-H) under ambient laboratory

254 conditions, which allowed any sediment to settle out of suspension. The icemelt was then  
255 decanted into smaller pre-combusted beakers. Icemelt was filtered through Whatman  
256 polypropylene Puradisc™ 0.45 µm syringe filters. Water samples for subsequent OC analysis  
257 were stored in clean pre-combusted borosilicate glass bottles (thrice rinsed with the sample  
258 before storage) ~~and those for major ion determinations were stored in clean, thrice-rinsed~~  
259 ~~Nalgene bottles. Melting and filtration of snow, to be used to correct for the snowpack~~  
260 ~~contribution to the basal ice major ion concentrations, followed the same protocol as~~  
261 ~~described for basal ice.~~ Five samples of filtered icemelt were taken from the ~15  $\text{cm}^2\text{-cm}^3$   
262 chunks cut out of the Joyce Glacier basal ice block, the Finsterwalderbreen ~~BF-DB~~ ice block,  
263 and the Finsterwalderbreen ~~PR-SB~~ ice block. Slightly larger volumes of icemelt permitted six  
264 samples of filtered icemelt to be collected from the Engabreen basal ice chunk, and seven  
265 from the Russell Glacier chunk. DI procedural blanks (n = 5) were subject to identical  
266 processing as the samples from the filtration stage onwards to monitor for possible  
267 contamination during processing and storage. Sample concentrations were subsequently  
268 blank corrected (see Sect. 3.3.4).

269  
270 Sub-samples from each ice block were also collected for free carboxylic acid (FCA)  
271 determination. Ice was melted in an inert gas ( $\text{O}_2$ -free- $\text{N}_2$ , OFN) atmosphere to limit potential  
272 contamination during the melting process (Saigne et al., 1987). The OFN gas first travelled  
273 through a hydrocarbon trap (HT200-4, Agilent) to remove any volatile OC compounds.  
274 Icemelt was filtered through Whatman polypropylene Puradisc™ 0.45 µm syringe filters into  
275 1.5 mL vials with PTFE caps (Chromacol). Samples were analysed within 24 hours of  
276 melting to minimise losses due to the volatile nature of the FCA compounds. Procedural  
277 blanks were collected in concert.

278  
279 The subglacial sediment OC content was derived from analysis of the settled particles, which  
280 were transferred from the beakers with clean, ethanol-rinsed metal spatulas and stored in  
281 sterile 0.5 L Whirl-pak bags (Nasco). Every effort was made to collect as much of the finer  
282 sediment as possible from the bottom and sides of the beakers. However, some fine sediment  
283 may have remained in the beaker and were thus excluded from the OC determinations. We  
284 were also unable to collect the fine particles that remained in suspension owing to the use of  
285 syringe filters to filter the icemelt. The total mass of this finer sediment was small compared  
286 to the mass of the settled sediment; therefore OC determinations were not unduly

287 compromised. Sediment and filtered samples were stored in the dark at  $\leq -20^{\circ}\text{C}$  until  
288 analytical processing.

### 289 **3.1.1 Basal ice debris concentration**

290 Basal ice debris concentrations (% by weight-mass) were determined by mass subtraction.  
291 Basal ice debris typically comprised sediment particles predominantly <2 mm plus some  
292 small gravel in the Finsterwalderbreen SB samples. First, the melted basal ice samples  
293 (sediment + icemelt) were weighed and the sediment extracted according to the procedure  
294 described above. The sediment was dried in a hot air oven ( $105^{\circ}\text{C}$ ) for a minimum of 12  
295 hours and weighed. The basal ice debris concentration was expressed as a percentage of a  
296 massweight (of sediment) to massweight (total weight-mass of ice and sediment) basis.

### 297 **3.2. Basal sediment analysis**

#### 298 **3.2.1. Elemental analysis**

299 The subglacial sediments were first dried in a hot air oven ( $105^{\circ}\text{C}$ , 12 hours) and then  
300 manually homogenized by grinding. Total carbon (TC) was measured on an EA1108  
301 Elemental Analyser (EuroVector). Inorganic carbon (InC) was determined by a modified  
302 Coulomat 702 Analyser (Strohlein Instruments). Total OC was calculated as the difference  
303 between TC and InC. The precision of determinations was  $<5\%$ . Samples were calibrated  
304 using external reference standards at a detection limit of  $0.1\text{ mg g}^{-1}$  (or  $0.01\%$ ).

#### 305 **3.2.2. Carbohydrate sediment extractions**

306 Previous studies have estimated sediment OC bioavailability based on the concentration of  
307 extractable carbohydrates (Biersmith and Benner, 1998; Pusceddu et al., 2009). We employed  
308 this method to provide a conservative estimate and acknowledge that this is not a  
309 comprehensive assessment of bioavailable OC in the subglacial material, as other  
310 compounds, such as enzymatically hydrolysable amino acids, were not quantified.  
311 Operationally-defined minimum estimates of extractable carbohydrate concentrations in basal  
312 sediment were quantified by ion chromatography following an acid-extraction protocol to  
313 convert any polysaccharides and sugar derivatives to lower molecular weight components  
314 (Jensen et al., 2005). We followed the protocol described in (Stibal et al., 2010) and  
315 conducted each extraction procedure in triplicate. Monosaccharide losses occurred during  
316 hydrolysis, including the total loss of fructose, and were not compensated for (Borch and

317 Kirchmann, 1997; Jensen et al., 2005). This methodological limitation means that some of the  
318 variability between samples will be due to procedural effects, rather than a true disparity  
319 between sediment carbohydrate concentrations.

### 320 **3.2.3. Cell counts**

321 Cell counts were conducted to quantify the microbial abundance in basal sediment and  
322 determine whether there is potential for subglacial microbial activity. We followed the  
323 protocol described in (Stibal et al., 2012). For Joyce Glacier samples, the method followed  
324 that of (Porter and Feig, 1980) (detailed in the Supplementary Methods).

## 325 **3.3 Analysis of basal icemelt**

### 326 **3.3.1. Bulk DOC**

327 DOC was determined by high temperature combustion (680°C) using a Shimadzu TOC-  
328 V<sub>CSN</sub>/TNM-1 Analyzer equipped with a high sensitivity catalyst. Precision and accuracy of  
329 standard solutions (5-170 µM C) of potassium hydrogen phthalate (C<sub>8</sub>H<sub>5</sub>KO<sub>4</sub>) (Merck) were  
330 < ± 6%, and the limit of detection (LOD) was 5 µM C.

### 331 **3.3.2. Fluorescence spectroscopy**

332 Fluorescence spectra were determined on a HORIBA Jobin Yvon Fluorolog-3  
333 spectrofluorometer equipped with excitation and emission monochromators, a Xenon lamp  
334 (excitation source) and FluorEssence software. Synchronous scans were performed at 1 nm  
335 increments with a 0.1 s integration period, 10 nm bandwidth and an 18 nm offset between  
336 excitation and emission monochromators (Barker et al., 2006). The accuracy of the  
337 monochromators was ± 0.5 nm. Synchronous scans of DI were run under identical scanning  
338 conditions and subtracted from all sample spectra to correct for Raman scattering. All scans  
339 were dark corrected and internally corrected for inner filter effects and variations in lamp  
340 performance. Post-scan data correction followed the protocol described by (Barker et al.,  
341 2006). Fluorophore recognition was based on values reported in the literature (Miano and  
342 Senesi, 1992; Ferrari and Mingazzini, 1995; Coble, 1996; Yamashita and Tanoue, 2003) and  
343 all spectra were normalized to the sample fluorescence peak spectral maximum.

### 344 3.3.3. OC compound determination by ion chromatography

345 Free amino acid (FAA), carbohydrate (FCHO) and carboxylic acid (FCA) determinations  
346 were performed by an ICS-3000 dual-analysis reagent-free ion chromatography system,  
347 employing electrolytic NaOH eluent generation (Dionex™, part of Thermo Fisher Scientific).  
348 Precision and accuracy were monitored by periodically running certified external standards  
349 (Dionex™), and internal standards during each sample run, at concentrations within the range  
350 of sample concentrations (10 - 2000 nM C). The limit of quantification (LOQ) was defined as  
351 the concentration of the lowest standard that could be significantly differentiated from the  
352 next highest. The 28 basal ice samples and five DI blanks were analysed in small batches. To  
353 limit any potential change in analyte abundance or composition over the course of the batch  
354 analysis due to inorganic or organic activity within the sample vial, we typically ran 8-10  
355 samples (plus standards and DI to flush the system) during each run. Prior to running the  
356 samples we assessed the level of drift (which may account for instrumental drift plus changes  
357 in LMW-DOC compounds) in a low level standard (50 µg L<sup>-1</sup>) and found that c. 21 samples  
358 could be run before significant drift (exceeding the precision of the instrument) was noted.  
359 Due to the scarcity of sample volume we were unable to explore whether LMW-DOC  
360 concentrations in each sample changed over the course of the sample run.

361  
362 **FAA:** were separated via gradient anion exchange on an AminoPac PA10 column (2x250  
363 mm) after passing through an AminoPac PA10 guard column (2x50 mm). Pulsed  
364 electrochemical detection with an Au electrode was employed. A gradient mix of 0.25 M  
365 NaOH, 1.0 M Na-acetate (NaOAC) and DI was used to elute 14 FAAs (lysine, alanine,  
366 threonine, glycine, valine, serine/proline, isoleucine, leucine, methionine, phenylalanine,  
367 cysteine, aspartic acid, glutamic acid and tyrosine) at a flow rate of 0.25 mL min<sup>-1</sup>. Serine and  
368 proline were reported together due to co-elution. Precision was typically c. ± 5% for lysine,  
369 alanine, threonine, glycine, valine, serine/proline, isoleucine, leucine, methionine, and  
370 cysteine, and c. ± 10% for phenylalanine, aspartic acid, glutamic acid and tyrosine. Accuracy  
371 was < ± 7% for all analytes (certified external standard, Fluka Analytical). The LOQ ranged  
372 from 10-60 nM C.

373  
374 **FCHO:** fucose, rhamnose, arabinose, galactose, glucose, xylose/mannose, fructose/sucrose,  
375 ribose and lactose were separated isocratically at a flow rate of 0.35 mL min<sup>-1</sup> on a CarboPac  
376 PA20 column (3x150 mm) after passing through a CarboPac PA20 guard column (3x30 mm).

377 Xylose and mannose, and fructose and sucrose, were reported together due to co-elution.  
378 Precision for fucose, rhamnose, arabinose, glucose and xylose/mannose was generally c. ±  
379 5%, and c. ± 10% for galactose, fructose/sucrose, ribose and lactose. Accuracy of a certified  
380 external standard (Dionex™) was < ± 7% for all analytes. The LOQ ranged from 10-80 nM  
381 C.

382

383 **FCA:** acetate, formate, propionate and butyrate were separated via gradient anion exchange  
384 on an IonPac Hydroxide-Selective Anion Exchange AS11-HC column (2x250 mm) with an  
385 AS11-HC guard column (2x50 mm) and Anion Self-Regenerating Suppressor (ASRS).  
386 Electrolytic eluent generation was employed to allow analyte separation along a NaOH  
387 gradient during the 30 minute run at a flow rate of 0.5 mL min<sup>-1</sup>. Precision and accuracy of  
388 the four FCAs in a certified reference standard (Supelco Analytics) was 5-8% (precision) and  
389 3-4% (accuracy). The LOQ ranged from 90-130 nM C.

#### 390 **3.3.4. Blank corrections**

391 Preparation of DI blanks is described in Sect. 3.1. Blank corrections were not required for ~~Cl<sup>-</sup>~~  
392 ~~and~~ FAAs due to the negligible blank concentrations. Minimal corrections were required for  
393 ~~all major ions (≤0.3 μeq L<sup>-1</sup>) and~~ FCHOs (1.3 nM C), but larger corrections were required for  
394 DOC (5.85 μM C) and FCAs (23.06 nM C).

395

## 396 **4. Results**

### 397 **4.1. Basal sediment characteristics**

398 Basal ice debris concentrations (by ~~weight—mass~~) differed between glaciers.  
399 Finsterwalderbreen solid banded (FSB) ~~pressure ridge (FPR)~~ and Russell Glacier basal ice  
400 contained the highest concentration of debris (86 ± 7% and 55 ± 25%, Table 1), which are  
401 similar to percentages in GrIS banded ice (46-57%), solid ice (61%) (Yde et al., 2010) and  
402 debris bands (71%) (Sugden et al., 1987). Debris concentrations in basal ice from Engabreen  
403 (37 ± 21%), Joyce Glacier (21 ± 6%), and Finsterwalderbreen dispersed banded (FDB) ~~basal~~  
404 ~~ice (FBI)~~ (20 ± 27%) were lower than percentages in GrIS and FPR-FSB ice.

405

406 We investigated possible correlations between DOC (and LMW-DOC) and the debris content  
407 of the basal ice, which may provide information on DOC provenance and the potential for



408 DOC to leach from sediments into the basal ice. We acknowledge that if DOC is leached  
409 from sediments the controlling variable will be the surface area, rather than the debris  
410 concentration. However, a detailed investigation into the particle size distribution was beyond  
411 the scope of this study. We thus conducted a preliminary analysis to determine if the  
412 relationship with debris concentration differed for DOC and LMW-DOC. Significant positive  
413 associations between debris concentration and DOC were only evident in Joyce Glacier ( $R^2 =$   
414 0.71,  $p < 0.05$ ) and Russell Glacier ( $R^2 = 0.72$ ,  $p < 0.05$ ) basal ice (Figure 1a). No significant  
415 associations between LMW-DOC and debris concentrations were observed (Figure 1b,  $R^2 <$   
416 0.1,  $p < 0.05$ ).

417  
418 The sediment OC content was low (<0.6%) in all basal ice samples (Table 2). Minor fractions  
419 of extractable carbohydrate (<0.5% of the sediment OC) were measured in Engabreen,  
420 Russell Glacier and Finsterwalderbreen sediments. A higher carbohydrate fraction (17% of  
421 the sediment OC) was measured at Joyce Glacier (Table 2). We use this as a proxy for lability  
422 (Biersmith and Benner, 1998; Pusceddu et al., 2009) and thus make the assumption that Joyce  
423 Glacier sediment is bioavailable. Microbial cell abundance was comparable in all samples (1  
424 -  $7 \times 10^5$  cells  $g^{-1}$ , Table 2).

#### 425 **4.2. Subglacial DOC quantity and complexity**

426 DOC abundance and composition varied between the four glaciers. The highest mean DOC  
427 concentrations were observed in basal ice from Joyce Glacier ( $272 \pm 99 \mu\text{M C}$ ) and  
428 Engabreen ( $114 \pm 106 \mu\text{M C}$ ), with lower concentrations in Russell Glacier basal ice ( $53 \pm 29$   
429  $\mu\text{M C}$ ), FBI-FDB ( $15 \pm 10 \mu\text{M C}$ ) and FPR-2014FSB ( $33 \pm 33 \mu\text{M C}$ ) (Table 1). The  
430 relatively large standard deviations show that subglacial DOC concentrations are highly  
431 variable, even in basal ice from the same glacier. Between 5 and 7 replicate samples were  
432 taken from each of the  $\sim 15 \text{ cm}^2\text{-cm}^3$  chunks cut out of the main ice blocks from each glacier  
433 (detailed in Sect. 3.1). The variability in the DOC concentrations suggests that there is  
434 significant spatial heterogeneity even at the level of the  $\sim 15 \text{ cm}^2\text{-cm}^3$  basal ice chunks  
435 analysed from each glacier.

436  
437 The composition of the subglacial DOC was investigated by spectrofluorescence and ion  
438 chromatography. The synchronous fluorescence spectra of all basal ice samples illustrated the  
439 dominance of three key fluorophores of a marine humic-like/fulvic acid type, at c. 340, 385

440 and 440 nm ([excitation wavelengths](#), Figure [42](#), Table 3), and several unresolved  
441 fluorophores at longer excitation wavelengths. Protein-like peaks (~279 nm [excitation](#)  
442 [wavelength](#)), indicative of tyrosine-like compounds (Ferrari and Mingazzini, 1995;  
443 Yamashita and Tanoue, 2003), were only evident in Joyce Glacier and [FSBFPR](#) basal ice  
444 (Table 3). Ion chromatographic analyses provided a greater level of detail on the molecular  
445 composition of the DOC. LMW-DOC compounds, with concentrations > LOQ, accounted for  
446 <3% of the DOC in all basal ice samples. Mean LMW-DOC concentrations in Engabreen,  
447 Finsterwalderbreen and Russell Glacier basal ice were <420 nM C (Table 1). Mean LMW-  
448 DOC concentrations were an order of magnitude higher (4430 nM C) in Joyce Glacier basal  
449 ice. As with DOC concentrations, the variability in the LMW-DOC compound concentrations  
450 suggests high spatial heterogeneity within the basal ice.

451  
452 LMW-DOC was typically dominated by FCAs (Table 1), except in Joyce Glacier samples  
453 which are subsequently discussed. Overall, acetate was the most common analyte (Figure  
454 [23](#)), being present in 60% of the samples that contained FCAs at concentrations > LOQ.  
455 Basal ice FCHO concentrations were typically < LOQ (<4% of the LMW-DOC, Table 1) and  
456 only detected in Joyce Glacier samples, comprising glucose (16 - 49 nM C) and ribose (16 -  
457 19 nM C, data not shown). Joyce Glacier basal ice DOC was unique in that most (98%) of the  
458 LMW-DOC was derived from the extremely diverse FAA pool (Figure [34](#)). Mean FAA  
459 concentration in Joyce Glacier basal ice ( $4353 \pm 2643$  nM C) was an order of magnitude  
460 higher than mean FAA concentrations in Engabreen, Finsterwalderbreen and Russell Glacier  
461 basal ice (0 - 51 nM C, Table 1). Some 14 FAAs were detected in Joyce Glacier basal ice,  
462 including methionine, glutamic acid, aspartic acid and cysteine, which were not observed in  
463 the other basal ice samples. Serine/proline, alanine and valine dominated the Joyce Glacier  
464 FAA pool. FAAs accounted for 59% of the LMW-DOC in Russell Glacier basal and [FPR](#)  
465 [FSB](#) ice, primarily in the form of alanine and valine, respectively.

### 466 **4.3. Debris concentrations**

467 ~~We investigated the relationships between DOC (and LMW-DOC) and debris concentrations.~~  
468 ~~We hypothesize that if the DOC was largely terrestrially derived and leached from sediments,~~  
469 ~~there should also be a positive correlation between DOC and the debris content of the basal~~  
470 ~~ice. Significant positive associations between debris concentration and DOC were only~~  
471 ~~evident in Joyce Glacier ( $R^2 = 0.71$ ,  $p = 0.05$ ) and Russell Glacier ( $R^2 = 0.72$ ,  $p = 0.05$ ) basal~~

472 | ~~ice (Figure 4a). No significant associations between LMW-DOC and debris concentrations~~  
473 | ~~were observed (Figure 4b,  $R^2 < 0.1$ ,  $p = 0.05$ ).~~

474

## 475 | **5. Discussion**

476 | The application of a novel methodological approach (within the field of glacial science) using  
477 | ion chromatography has allowed the identification and quantification of a range of LMW-  
478 | DOC compounds in debris-rich basal ice, including FCAs, FCHOs and FAAs, at  
479 | unprecedented low concentrations (<70 nM C). This represents, to our knowledge, ~~one of the~~  
480 | first study to quantify LMW-DOC in basal ice from a range of glaciers and ice sheets. We  
481 | demonstrate that ion chromatographic systems that have been optimised for the detection of  
482 | trace level LMW-DOC concentrations, e.g. by using multiple eluents, low flow rates and  
483 | gradient elution, can be utilised as an additional quantitative technique to supplement  
484 | characterisations of glacial LMW-DOC by ESI FT-ICR MS (Grannas et al., 2006; Bhatia et  
485 | al., 2010; Lawson et al., ~~2014b~~2014a) and solution-state  $^1\text{H}$  NMR spectroscopy (Pautler et  
486 | al., 2011, 2012).

### 487 | **5.1. The influence of debris type on sediment OC and basal ice DOC** 488 | **concentrations**

489 | We find little evidence that the type of overridden material (i.e. the pre-entrainment  
490 | sedimentary type such as lacustrine material or paleosols) and the mean sediment OC content  
491 | has a significant influence on the DOC content in basal ice. Indeed, the mean basal ice DOC  
492 | concentrations (Table 1) (~~<280  $\mu\text{M}$  C~~) and mean sediment OC content (Table 2) (~~<0.6%~~)  
493 | were relatively similar~~comparable~~ in all basal ice samples despite the differences in the types  
494 | of overridden material. Furthermore, the fact that the highest mean DOC concentration was  
495 | observed in Joyce Glacier basal ice (272  $\mu\text{M}$  C) yet the corresponding sediment OC% was  
496 | the lowest (0.01%) of all four sites demonstrates the lack of a relationship between sediment  
497 | OC% and basal ice DOC. This may be due to the particular section of basal sediment that was  
498 | sampled as, in the case of Joyce Glacier, higher OC content has previously been observed in  
499 | other Antarctic lacustrine samples, such as subglacial sediment beneath Lower Wright  
500 | Glacier (0.7% OC) (Stibal et al., 2012), and Antarctic Dry Valley lacustrine sediments  
501 | containing microbial mats (~9% OC) (Squyres et al., 1991). This suggests a more diverse  
502 | basal sediment matrix comprising algal mats and organic lacustrine material that mixed with  
503 | sand and/or other low-OC, mineral-based material during basal ice formation beneath Joyce

504 Glacier. However, we acknowledge that some of the difference in sediment OC (and  
505 extractable carbohydrate concentrations) may be due to the different analytical methods  
506 employed in this and previous studies. The concentrations that we present may also be  
507 conservative as our methodological approach meant that fine sediment fractions, which may  
508 be OC-rich, remained in suspension and were not included in the OC determinations.

509

510 Key differences were, however, observed in the proportions of extractable carbohydrates (a  
511 proxy for bioavailable compounds in the basal sediment) and LMW-DOC concentrations in  
512 basal ice from the four sites. The LMW-DOC concentrations in Joyce Glacier basal ice,  
513 which were an order of magnitude higher than LMW-DOC concentrations in samples from  
514 the other three sites and predominantly due to high FAA concentrations, may have derived  
515 from the relatively large pool of potentially-bioreactive extractable carbohydrates in Joyce  
516 Glacier basal sediment (17% of the sediment OC, compared with <0.5 % of the sediment OC  
517 in samples from Russell Glacier, Engabreen and Finsterwalderbreen). The bioreactive OC  
518 pool in Joyce Glacier basal sediment may have been enhanced by the assimilation of  
519 proglacial algal mats into overridden material during glacial advance, which likely enriched  
520 the basal ice with lacustrine material and associated algal necromass (Pautler et al., 2012),  
521 which may include autochthonous material produced by microorganisms prior to basal ice  
522 formation. Indeed, lacustrine material is generally acknowledged as a source of reactive OC  
523 to microorganisms (Meyers and Ishiwatari, 1993). The lower extractable carbohydrate  
524 concentrations in basal sediment from Russell Glacier, Engabreen and Finsterwalderbreen  
525 (compared with Joyce Glacier) are thought to reflect the more refractory nature of the  
526 overridden material. OC in subglacial material beneath this sampled section of Russell  
527 Glacier~~the GrIS~~ is thought to derive from a soil origin, based on relatively high  
528 concentrations of n-alkanoic acids, steroids, and other soil-derived functional compounds that  
529 have been identified in basal ice samples (Stibal et al. 2012). Due to this, and the relatively  
530 young age of Russell Glacier sediment OC (<1900 <sup>14</sup>C yrs BP), we expected the total and  
531 bioreactive OC concentrations to be higher than 0.44% and 0.47% of the OC, respectively.  
532 For instance, OC content in Greenland soils range from 0.1 - 44.8% in C horizons and peat  
533 soils (Horwath Burnham and Slettern, 2010). The low OC and extractable carbohydrate  
534 concentrations in Russell Glacier basal ice, ~~collected from the GrIS margin~~, may reflect a  
535 heterogeneous sediment matrix that incorporates a lower proportion of paleosols mixed with  
536 other low-OC, mineral-based material. However, as discussed earlier, these differences in  
537 sediment OC concentrations may be due to the conservative nature of our methodological

538 approach that may have excluded the potentially OC-rich fine sediment fractions. The low  
539 extractable carbohydrate concentration (0.04% of the OC) in Finsterwalderbreen basal  
540 sediment is likely influenced by the predominance of OC from kerogen in the overridden  
541 shale bedrock (Wadham et al., 2004) that has been incorporated into the basal ice matrix.  
542 Kerogen is ancient carbon comprising stable carbon macromolecules (Petsch et al., 2001) and  
543 has limited bioreactivity. Similarly, low bioreactive OC in Engabreen basal sediment (0.17%  
544 of the OC comprised extractable carbohydrates) is influenced by the subglacial substrate  
545 comprising overridden continental shield rock depleted in reactive OC, the limited  
546 opportunity for material from supraglacial environments to be in-washed, and the limited  
547 input of overridden paleosols (Stibal et al., 2012). A lack of organic biomarkers (derived  
548 from algal and higher plant inputs) in Engabreen basal ice further suggests that incorporation  
549 of organic material is probably limited (Stibal et al., 2012). Alternatively, the lack of organic  
550 biomarkers may be due to debris entrainment by regelation rather than freezing-on  
551 (adfreezing).

552  
553 In summary, our data suggests that where glaciers and ice sheets override -lakeslacustrine  
554 sediments, there is an injection of particulate and dissolved bioavailable compounds into the  
555 basal ice at the glacier ~~bed-of-the-ice~~, which is less evident where the glacier overrode  
556 paleosols or bedrock. This has implications for subglacial LMW-DOC cycling as this abiotic  
557 input of LMW-DOC (via leaching) has the potential to stimulate microbial activity in wet  
558 sediments in the subglacial environment. We go on to investigate the DOC and LMW-DOC  
559 signatures in basal ice from these contrasting subglacial environments.

## 560 **5.2. Basal ice LMW-DOC signatures and provenance**

561 The presence of LMW-DOC compounds and the similarities in the types of compounds  
562 detected in basal ice samples from the four sites may reflect common sources and pathways  
563 of transformation of DOC in subglacial environments beneath glaciers and ice sheets. The  
564 potential for interactions between basal sediment and subglacial icemelt suggest that  
565 allochthonous—inputs from the overridden subglacial material may represent a key  
566 contribution to basal ice DOC. The chemical composition of basal ice, including DOC  
567 compounds, should reflect characteristics of the parent water prior to being frozen (Knight,  
568 1997), where this water might be either flowing at the base of the glacier, held in porewaters  
569 in overridden water-saturated sediment, or refrozen water from pressure melting during the

570 ~~regulation process.~~ ~~Both~~ These water sources have extensive contact with the subglacial  
571 material and so have the potential to acquire dissolved compounds via biogeochemical  
572 interactions. ~~However, these processes are highly site specific and where there are well-~~  
573 ~~developed quick-flow components and scoured bedrock channels, for instance, there will be~~  
574 ~~less scope for fast-flowing waters to acquire dissolved compounds from biogeochemical~~  
575 ~~interactions with the overridden material.~~ DOC and LMW-DOC components in basal ice may  
576 also be acquired by ~~in situ~~ abiotic processes, e.g. by reactions, such as dissolution, in water  
577 films around debris and in liquid water veins (Mader et al, 2006). It is likely that certain  
578 organic compounds will remain associated with the debris and others will dissociate to  
579 become DOC. ~~We hypothesized that if the DOC was largely terrestrially derived and leached~~  
580 ~~from sediments, there should also be a positive correlation between DOC and the debris~~  
581 ~~content of the basal ice.~~ ~~To fully assess whether DOC is largely terrestrially-derived and~~  
582 ~~leached from sediments, we would need data on the surface area of the debris and~~  
583 ~~information on particle size distribution. As this was beyond the scope of this study we~~  
584 ~~instead used debris concentrations for a preliminary investigation. We find that, in general,~~  
585 ~~for sites where there is a bioavailable OC source in sediments (Joyce Glacier) or the sediment~~  
586 ~~contains relatively young OC (i.e. <1900 <sup>14</sup>C yrs BP) (Russell Glacier), there are significant~~  
587 ~~relationships between DOC and debris content (Figure 4a). This suggests that, at these sites,~~  
588 ~~meltwater contact with the sediments is likely a major control on DOC acquisition.~~ ~~We find~~  
589 ~~that for sites where there is a bioavailable OC source in sediments (Joyce Glacier) there is a~~  
590 ~~significant relationship between DOC and debris concentration (Figure 1a). This suggests that~~  
591 ~~subglacial meltwater contact with subglacial sediment beneath Joyce Glacier, which is cold-~~  
592 ~~based and so has little supraglacial meltwater penetration to the glacier bed, is a major control~~  
593 ~~on DOC acquisition.~~ ~~This suggests that, at these sites, meltwater contact with the sediments is~~  
594 ~~likely a major control on DOC acquisition.~~ We find several additional lines of evidence to  
595 support the leaching of DOC from subglacial sediments, including the presence of fulvic  
596 acids that have previously been associated with terrestrial material (> 440 nm fluorescence  
597 wavelengths) in all basal ice samples (McKnight et al., 2001). The basal ice LMW-DOC  
598 compounds may also be a leached relic of the overridden material that has been preserved in  
599 the ice when frozen. However, the lack of significant association between LMW-DOC and  
600 debris concentration (Figure ~~4b~~1b) is reflective of additional sources and sinks of these  
601 compounds in the basal ice layer and/or in the parent water body from which basal ice  
602 formed. The LMW-DOC signature in basal ice may also be influenced by ~~in situ~~ microbial  
603 production and consumption, as illustrated in earlier work that has proposed a range of

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604 microbial processes to be active in the subglacial environment, including in situ  
605 chemoautotrophic production (Bhatia et al., 2006, 2013), chemoheterotrophic oxidation of  
606 OC substrates to protein-like LMW-DOC compounds (Bhatia et al., 2010) and release of  
607 LMW-DOC from decaying cells. It is probable that subglacial microbial activity cycles  
608 LMW-DOC both before and after the formation of basal ice. For instance, microorganisms in  
609 subglacial sediment porewaters and basal meltwaters flowing at the rock:water interface may  
610 actively utilise OC substrates and energy sources derived from the overridden material. Via  
611 this activity, they may also go on to produce simple LMW-DOC compounds which may  
612 subsequently be incorporated into basal ice. The protein-like peaks that were observed in the  
613 spectrofluorescence spectra in Joyce Glacier and ~~FPR-FSB~~ ice (Table 3) tentatively suggests  
614 that some of the LMW-DOC is ~~derived from of~~ a microbial provenance. Protein-like  
615 fluorescence is linked with recent biological activity (De Souza Sierra et al., 1994) and is  
616 associated with active FAA production during microbial metabolism (Yamashita and Tanoue,  
617 2003). The finding that FSB samples contained larger protein-like peaks and had higher mean  
618 FCA and FAA concentrations when compared with FDB samples may be explained by the  
619 different basal ice formation processes at Finsterwalderbreen. FSB debris, sampled from  
620 surface outcrops of frozen subglacial material, or thrust bands, is expected to derive from  
621 further upglacier than FDB debris and likely formed during the most recent surge c. 1898-  
622 1920 (Liestøl, 1969). This suggests that FSB debris may have been glacier-covered for a  
623 much longer period than FDB debris. These conditions may have led to enhanced leaching of  
624 LMW-DOC from the subglacial material and/or greater production (vs. consumption) of  
625 LMW-DOC by in situ microorganisms. It is also possible that LMW-DOC in basal ice from  
626 the polythermal and warm-based glaciers sampled in this study (Finsterwalderbreen, Russell  
627 Glacier and Engabreen) could derive from supraglacial inputs as glacially-overridden  
628 material is not the sole source of DOC in basal ice.

629  
630  
631 In this study, we were not able to categorically separate LMW-DOC derived from biotic and  
632 abiotic processes as, at a molecular level, many LMW-DOC compounds are non-specific  
633 biomarkers due to their pervasive occurrence in plants and microorganisms (Biersmith and  
634 Benner, 1998). For example, valine, a common FAA in most basal ice samples, can be  
635 synthesized in plants via several steps starting from pyruvic acid (e.g. described in Singh,  
636 1999). Valine can also be microbially-synthesized from pyruvate (Blombach et al., 2007) and  
637 produced by aerobic gram-positive microbes (Valle et al., 2008). Similarly, glucose can be



638 produced by photosynthesis (Kirchman et al., 2001) and chemoautotrophic bacterial activity  
639 (Jansen et al., 1982). The key point is that the presence of numerous LMW-DOC compounds  
640 in basal ice from all four glacial sites provides evidence that viable substrates for microbial  
641 growth, whether derived from ~~an allochthonous or autochthonous~~ terrestrial or microbial  
642 source, are available in subglacial environments. These LMW-DOC compounds may help  
643 support microbial communities within the present-day basal ice, e.g. beneath Russell Glacier,  
644 where recent work has shown that the basal ice may be microbially-active in the current  
645 frozen state (Yde et al., 2010). The microbial cell counts observed in all basal ice samples in  
646 this study ( $10^5$  cells  $g^{-1}$ , Table 2) are comparable to microbial populations ( $10^5$  -  $10^8$  cells  $g^{-1}$ )  
647 reported in other subglacial sediments that have been proven to be microbially-active (Sharp  
648 et al., 1999; Foght et al., 2004; Kastovska et al., 2007; Yde et al., 2010; Montross et al.,  
649 2012).

### 650 **5.3. Implications for LMW-DOC cycling beneath glaciers with bioreactive** 651 **subglacial sediment**

652 The margin of Joyce Glacier rests upon ancient lake sediments and hence, represents a case  
653 where a very labile organic matter source is overridden. This situation may have been  
654 common in past periods of glaciation, when, for example, the Pleistocene ice sheets advanced  
655 over regions with a high density of lakes, such as in northern Canada and Scandinavia  
656 (Wadham et al., 2008). Hence, the potential for LMW-DOC incorporation in Joyce Glacier  
657 basal ice and sediment may be applicable to these other types of lacustrine-based subglacial  
658 ecosystems. In addition, the abundance of LMW-DOC in Joyce Glacier suggests that  
659 overridden lacustrine material can be sequestered even if the glacier is cold-based. ~~In the~~  
660 ~~case of cold-based glaciers, a change in the 20-melt regime would be needed to release the~~  
661 ~~DOC to downstream ecosystems, which may not be that unlikely in a warming climate. If the~~  
662 ~~glacier was warm-based then the DOC could be flushed out during the summer melt seasons~~  
663 ~~and contribute to the net export of bioavailable DOC to downstream environments. Contrary~~  
664 ~~to traditional assumptions that drainage in cold-based glaciers is entirely supraglacial, it is~~  
665 ~~possible that discrete subglacial channels exist where water is in contact with the substrate,~~  
666 ~~e.g. at Longyearbreen (Yde et al., 2008). This mechanism may enable the release of DOC to~~  
667 ~~downstream ecosystems. If the glacier was warm-based then the DOC could be flushed out~~  
668 ~~during the summer melt seasons and contribute to the net export of bioavailable DOC to~~  
669 ~~downstream environments. DOC in glacial runoff may derive from multiple sources;~~



670 terrestrial DOC derived from overridden material at the bed (Hood et al., 2009);  
671 anthropogenic aerosol deposition on the glacier surface (Stubbins et al., 2012), and;  
672 biological activity in both supraglacial (Anesio et al., 2009) and subglacial (Bhatia et al.,  
673 2013) environments. The contribution from basal ice may be more significant in cold-based  
674 glacier systems, e.g. in the Antarctic Dry Valleys, where daily radiation melting of the steep  
675 ice cliffs may release solute from the debris-rich basal ice that is exposed on the cliffs. The  
676 distributed drainage system beneath temperate and polythermal glaciers may also include a  
677 constant source of water from basal ice melt and groundwater in contact with glacial till  
678 (Paterson, 1999).

679  
680 The dramatic difference in the DOC composition beneath glaciers resting on different OC  
681 substrates that our data have highlighted may have implications for the rate and degree to  
682 which this overridden OC can be cycled to biogenic gases in current subglacial environments,  
683 which in turn, has relevance for the global carbon cycles (Wadham et al., 2008; Stibal et al.,  
684 2012). While the DOC and LMW-DOC signatures of basal ice may arise from several  
685 confounding factors which are difficult to disentangle, identifying the abundance and  
686 composition of DOC in basal ice is an important first step to understanding LMW-DOC  
687 cycling in subglacial environments.

688

## 689 **6. Conclusion**

690 We employ a combined spectrofluorometry and ~~an~~ ion chromatographic methodological  
691 approach to produce the first identification and quantification, at trace level concentrations, of  
692 major LMW-DOC fractions (free amino acids, carbohydrates and carboxylic acids) in debris-  
693 rich basal ice. We demonstrate that ion chromatographic systems that are optimised for trace  
694 level LMW-DOC analyte detection can supplement traditional methods of LMW-DOC  
695 characterisation as a quantitative technique. Our work adds to the growing body of research  
696 addressing sources and reactivity of DOC in subglacial ecosystems and provides a  
697 characterisation of LMW-DOC in basal ice from four different glacial environments with  
698 distinctive basal debris types including lacustrine material (Joyce Glacier), overridden soils  
699 and tundra (Russell Glacier), kerogen in bedrock (Finsterwalderbreen) and bedrock/soils  
700 (Engabreen). We infer that ~~allochthonous~~ terrestrial inputs from the overridden subglacial  
701 material represent a key contribution to basal ice DOC. Our data show that LMW-DOC  
702 concentrations in basal ice are dependent on the bioavailability of the overridden OC, which

703 in turn, is influenced by the type of overridden material. We find that where glaciers and ice  
704 sheets override lakes, such as at Joyce Glacier, there is an injection of particulate and  
705 dissolved bioavailable compounds into the basal ice at the glacier bed ~~of the ice~~, which is less  
706 evident where glaciers overrode paleosols or bedrock. There is also potential for the  
707 overridden substrate to ~~also~~ act as an indirect (via microbial cycling) source of DOC, as the  
708 leached LMW-DOC compounds may stimulate microbial activity in wet sediments in the  
709 subglacial environment. This has implications for the cycling of overridden OC to biogenic  
710 gases in subglacial environments and concurs with recent findings that accelerated melting of  
711 glaciers and ice sheets could constitute a significant source of DOC and other, potentially-  
712 bioavailable dissolved organic matter, to glacially-fed ecosystems. The abundance of LMW-  
713 DOC in Joyce Glacier basal ice suggests that overridden material may be sequestered even if  
714 the glacier is cold-based. ~~A change in the melt regime could release this bioavailable DOC to~~  
715 ~~downstream ecosystems, which has relevance for local carbon cycles and wider ecosystem~~  
716 ~~processes. Identifying the abundance and composition of DOC in basal ice is an important~~  
717 ~~first step to understanding LMW-DOC cycling in subglacial environments, which has~~  
718 relevance for local carbon cycling and wider ecosystem processes.

719 **Author Contributions**

720 JLW and MT conceived the project. ECL, JLW, GPL, MS and SF collected field data. ECL,  
721 GPL, AEP, and MS undertook the lab analysis. PD, GPL and ECL assisted with the Dionex™  
722 ICS-3000 ion chromatography system optimisation and method development. ECL, JLW and  
723 MT wrote the paper with additional comments from the co-authors.

724

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968 **Table 1** Biogeochemical data for basal ice from Engabreen (E), Finsterwalderbreen (F),  
 969 Russell Glacier (R) and Joyce Glacier (J). DB = dispersed banded and SB = solid banded.  
 970 Values given are the mean concentrations for each analyte and the standard deviation is given  
 971 in parentheses. LMW-DOC = free carbohydrates (FCHOs) + free amino acids (FAAs) + free  
 972 carboxylic acids (FCAs). Only values > LOQ have been included.

**Comment [EL1]:** Table and caption have been edited to replace Finsterwalderbreen Basal Ice (FBI) with Debris Banded ice (FDB), and Finsterwalderbreen Pressure Ridge Ice (FPR) with Solid Banded ice (FSB)

973

<b>Sample</b>	<b>% debris (by weight<del>mass</del>)</b>	<b>DOC (<math>\mu\text{M C}</math>)</b>	<b>LMW DOC (<math>\text{nM C}</math>)</b>	<b>FCHOs (<math>\text{nM C}</math>)</b>	<b>FAAs (<math>\text{nM C}</math>)</b>	<b>FCAs (<math>\text{nM C}</math>)</b>
<b>E (n = 6)</b>	36.83 (20.96)	113.56 (106.60)	417.70 (213.07)	0.00	22.41 (24.24)	442.19 (164.00)
<b>FDB (n = 5)</b>	20.22 (26.74)	14.85 (9.91)	169.67 (183.90)	0.00	0.00	169.67 (183.90)
<b>FSB (n = 5)</b>	86.47 (6.58)	33.38 (33.30)	312.67 (502.64)	0.00	46.47 (48.99)	274.91 (549.83)
<b>R (n = 7)</b>	54.89 (24.51)	53.31 (28.89)	343.72 (689.83)	0.00	50.59 (62.97)	365.62 (817.56)
<b>J (n = 5)</b>	21.22 (6.41)	272.09 (99.38)	4429.83 (2625.95)	28.29 (15.83)	4353.30 (2643.59)	0.00

974 Table 2 Mean sediment characteristics. <sup>§</sup>sediment OC age from Stibal et al., (2012), method  
 975 described in the online supporting information. ND = not determined. E = Engabreen, F =  
 976 Finsterwalderbreen, R = Russell Glacier, J = Joyce Glacier. Standard deviation is given in  
 977 parentheses.

<b>Sample</b>	<b><sup>14</sup>C age (years, BP)<sup>§</sup></b>	<b>%OC</b>	<b>%InC</b>	<b>Extractable carbohydrates (µg/g)</b>	<b>Carbohydrate fraction (% of OC)<sup>*</sup></b>	<b>Cell abundance (cell g<sup>-1</sup>)</b>
<b>E (n = 5)</b>	ND	0.19 (0.08)	0.24 (0.18)	3.26	0.17	6.80 x 10 <sup>5</sup>
<b>F (n = 5)</b>	3750 (150)	0.57 (0.12)	1.80 (0.25)	2.34	0.04	1.68 x 10 <sup>5</sup>
<b>R (n=5)</b>	1830 (50)	0.44 (0.09)	0.01 (0.00)	20.83	0.47	2.26 x 10 <sup>5</sup>
<b>J (n= 5)</b>	ND	0.01 (0.02)	0.28 (0.05)	23.95	17.11	1.16 x 10 <sup>5</sup>

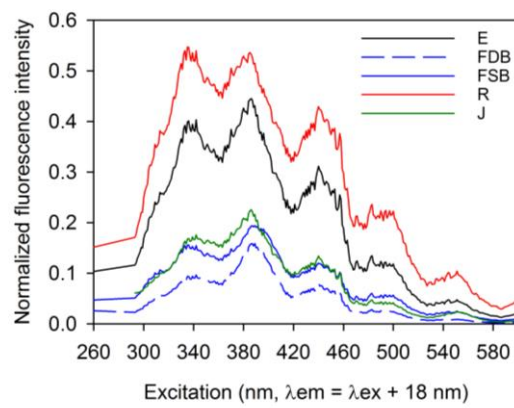
978 **Table 3** Summary of the dominant fluorophores in basal ice from four contrasting glacial  
 979 environments. The dominant fluorophores (denoted by \*) have been identified according to  
 980 previous characterisation of spectral compounds (see Barker et al., 2009 and references  
 981 therein). DB = dispersed banded, SB = solid banded.

**Comment [EL2]:** Table and caption have been edited to replace Finsterwalderbreen Basal Ice (FBI) with Debris Banded ice (FDB), and Finsterwalderbreen Pressure Ridge Ice (FPR) with Solid Banded ice (FSB)

Sample	Fluorophore (peak excitation wavelength, nm)	Dominant fluorophore identification	n
<b>Engabreen</b>	342, 386*, 440, 483	Fulvic acid, marine humic-like	6
<b>Finsterwalderbreen DB</b>	342, 389*, 440	Fulvic acid, marine humic-like	5
<b>Finsterwalderbreen SB</b>	276, 336, 389*, 440	Fulvic acid, marine humic-like	5
<b>Russell Glacier</b>	335*, 385, 440, 483	Protein-like/marine humic-like	7
<b>Joyce Glacier</b>	279, 342, 386*, 440, 460, 551	Fulvic acid, marine humic-like	5

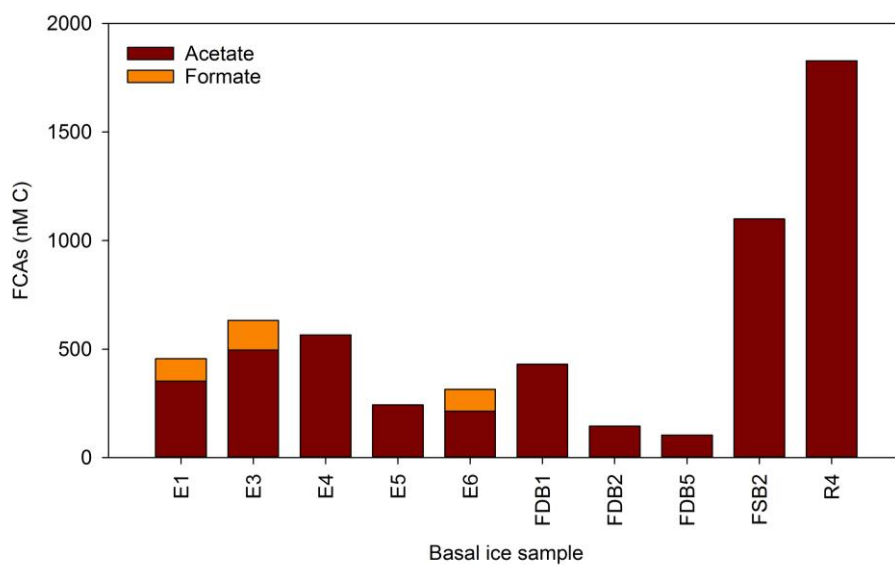


989 Figure 2 Mean normalized synchronous fluorescence spectra for basal ice samples. E =  
990 Engabreen, F = Finsterwalderbreen, R = Russell Glacier, J = Joyce Glacier, DB = dispersed  
991 banded, SB = solid banded.





992 Figure 3 FCA compositions in basal ice samples. E = Engabreen, F = Finsterwalderbreen, R  
993 = Russell Glacier, DB = dispersed banded, SB = solid banded. Samples with zero  
994 concentrations have been excluded from the plot and only values > LOQ have been included.



995 Figure 4 FAA composition in basal ice samples from a) Engabreen (E), Finsterwalderbreen  
 996 (F), Russell Glacier (R) and Joyce Glacier (J), b) FAAs in Joyce Glacier basal ice, plotted  
 997 separately due to an order of magnitude increase in concentrations. Samples with zero  
 998 concentrations have been excluded from the plot and only values > LOQ have been included.  
 999 S/P = serine and proline, reported together due to co-elution. SB = solid banded.

