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Interactive comment on "Identification and analysis of low molecular weight dissolved organic carbon in subglacial basal ice ecosystems by ion chromatography" *by* E. C. Lawson et al.

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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-1 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.

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. 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). These examples highlight the importance of studies into basal ice composition.

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 northern hemisphere 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 Antarctica, 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.

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.

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

rent"?

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" (Section 5.2).

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.

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 (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 text.

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 (Section 5.2.2).

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 (e.g. Section 4.1, Results). 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.

14. Conclusion (line 23): there's an extra "also" in the sentence.

This has been removed from the text.

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Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/12/C7550/2015/bgd-12-C7550-2015-supplement.pdf

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