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Interactive comment on "Physical and chemical evolution of dissolved organic matter across the ablation season on a glacier in the central Tibetan Plateau" *by* Lin Feng et al.

Anonymous Referee #3

Received and published: 8 February 2018

The authors have conducted an interesting study of the chemical evolution of snow as it undergoes metamorphism from snow-firn-ice. The overall goal was to determine the compositions of DOM in snow samples collected from the Dongkemadi glacier and evaluate the changes in DOM composition during transition of snow to firn and then ice. The tool of choice was the use of fluorescence spectrometer and ESI-FTICR-MS. I think the paper is an interesting read. That said, a lot more information, including significant additional qualification of the interpretations, is required to make the manuscript acceptable for publication. The methods sections should be expanded to include the process "blank" analyses for organic carbon. In several places, the authors do not provide adequate references to back their statements (see minor comments).

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Major comments:

A serious shortcoming is that there is no critical evaluation and discussion of the blanks associated with the DOC measurements. It is well known that snow and ice samples for organic carbon measurements can easily be contaminated (see Preunkert et al., Environ. Sci. Technol. 45, 673-678, 2011). Contaminations can occur due to contact of the samples with sampling materials, during shipping, and storing. Furthermore, a strong source of contamination is the dissolution of organic species during the melting of the samples. The impact of possible contamination during storage, the handling of the samples in the laboratory and during the melting process should have been tested using blanks. The authors provide no information about blank experiments. Did the authors estimate the carbon contamination associated with the filter/ filtration device used for filtering the samples?

Ambiguity in biomolecular compound class assignments – I understand that the van Krevelen plot is a useful tool for the visualisation of complex FTICR-MS data. But classifications in this study are based only on the location of formulae in the van Krevelen diagram. It is important to remember that formulae that plot in a particular area of the van Krevelen plot are not strictly representative of all similar molecules, but rather approximate guidelines for identifying compounds of similar composition. Thus, caveats associated with the descriptions of DOM as proteins, lignin, tannin etc., based only on the H/C and O/C without accounting for the N/C or aromaticity index (AImod) should be appropriately explained in the MS. Somewhere in the initial discussion of the van Krevelen diagrams, the authors need to make it very clear that just because a formula falls into a particular category it is not definitely that type of structure, as you only have formula data, not structural data.

The fact that FTICR-MS only provides elemental formulae and not structural classes needs to be emphasized so that readers know that when the authors refer to something as lignin, it could represent a molecule derived from vascular plants, but that it could also represent a carboxylic rich alycyclic molecule with the same formula. It is critical

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that readers, be made aware of these ambiguities when discussing FTICR-MS data.

The authors state that one of the objectives of this study is to examine the compositions and sources of DOM in snow, yet sources are not adequately discussed. The authors identify through fluorescence measurements protein-like and humic like components and through FTICR-MS several lignin, tannin, condensed aromatic, protein formulae among others. What are the sources of these humic, lignin-and tannin-like compounds in snow? These need to be discussed. DOM that shares the same regions of the van Krevelen diagram with other microbial studies can only suggest similar chemical character, and not microbial production (Line 381). And since microbial production was not directly tested with the current experimental design, this statement is inappropriate. Did the authors measure microbial abundances in these samples? If data for microbial numbers is available, these should be included. If not, are there other papers that have described microbial numbers/diversity in snow or ice from this region? Several samples were collected from each elevation. Were all of the replicate samples also analysed by FTICR-MS? If yes, then the authors should report some value of reproducibility. For example see Sleighter et al., Analytical Chemistry, 2012, 84, 9184-9191.

Minor comments:

Line 46 – one of the

Line 51 – 'they were more efficient to be released'. It is not clear what you mean by that.

Line 55 – How is a discussion on cryoconites relevant to this study? You either need to establish a link, or delete this section.

Line 63 – lost how? to where?

Line 79 – 1.767 km2. Is this correct?

Line 115 - What is the detection limit of the instrument?

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Line 200 – edit ‘methanoland 3’ to ‘methanol and 3’

Line 215 – FI-ICR or FT-ICR?

Line 226 – what is DBE? Expand the abbreviation and provide an explanation as to what it signifies.

Line 229-230 - A description of van Krevelen analysis should be included here.

Line 236- what is CRAM? Please provide the definition and expand the abbreviation.

Lines 234-238 – please back these classifications with the appropriate reference(s).

Lines 242-245 – How do the values obtained in your study compare with that of other studies that report DOC values for snow from the TP or other mountain glaciers?

Line 251, 311 - Please do not use the word significant if no statistical tests were performed.

Line 264 – what are these obvious differences? State them.

Line 269-272 – this needs to be supported with a reference. Consider changing ‘aromatic components’ to ‘aromatic constituents’

Line 281 – ‘as is described in the Supporting Information section’ is redundant

Line 293 – what do these percentages indicate? Do they refer to the contribution of formulae of a particular biomolecular compound class to the total identified formulae? Please specify.

Line 295 - 298 – why no mention of carbohydrates?

Line 302-303 – Please be advised that the number of molecular formulae can be greatly dependent on sampling method, SPE procedure, ionization mechanism, FTICR-MS parameters, data acquisitions etc. Therefore, when tracking changes in the number of molecular formulae amongst samples, appropriate disclaimers should be provided.

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line 305 – not sure what this line means

Line 307 – did you detect any S containing formulae? If yes, why were these not discussed?

Line 327 – what do you mean by lost DOC?

Lines 331 -332 – consider rephrasing this sentence. A decrease in DOC values do not indicate which compounds/compound categories were reduced in concentration.

Line 337 – edit 'Water-' to 'water-'

Line 342 – what is meant by enrichment of DOM? What contributed to this enrichment?

Line 350-358- It is not clear what point the authors are trying to make by comparing with cryoconite samples.

Line 369 – why is a comparison made to lake Taihu? How is it relevant to your study?

Line 379 – what is meant by more intense microbial signals? I do not understand why a comparison with cryoconite samples is important?

Line 400 – do you mean 'which is the dominant mass fraction'?

Line 401 – How was the chemical composition different? State the differences.

Line 402-404 – Cite a reference to back this claim.

Line 404-406 – it is not clear how you conclude that there is a variation in DOM molecular weight based on the variation in S240-400 values. Please explain and provide appropriate references. Also, please explain how these results suggest the presence of microbially transformed and newly produced DOM.

Line 407 – what other chemical processes?

Line 408 -411 – Perhaps the authors intend to say 'snowpack microbes exhibit diverse enzyme activities and contribute to the degradation of DOM in these environments'?

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But in the previous line, the authors talk about newly produced DOM. This claim needs to be supported with appropriate reference(s) (for example see Smith et al., 2017, Nat. Geosci; Antony et al., 2017, Environ. Sci. Technol.)

Line 414 – please include appropriate references and explain how a change in DBE values suggests the occurrence of oxidation process.

Line 418 – edit 'ranged in' to 'ranged from'

Line 427 – rephrase 'composition of DOM' to 'composition of identified DOM formulae'

Line 431 – edit 'relative contributions of proteins and lignins' to 'relative contributions of proteins and lignins to the total identified formulas'

Line 436-438 – I understand that the authors want to provide a broader perspective to their study, but written as is, this is too general a statement. Consider revising.

Table 1 – Description of component number C1. Do you mean 'tryptophan-like or tyrosine- like'? You need to provide appropriate references to support these classifications.

Line 619 – DOM

Table 2 – You need to indicate in the table, the number of samples analysed for each corresponding SD value.

Table 3 - The authors should not assume that the readers are aware that m/z corresponds to mean mass. Please include m/z in parenthesis next to mean mass. You need to write clearly in the table heading that the numbers in the table correspond to the total number of molecular formulae identified for each sample category.

Table 4 – same comment as above. Please indicate what the numbers reported in the table correspond to. What does total mean?

Figure 2 – please provide error bar/statistical calculation details in the caption

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Figure 3 – same comment as above

Figure 6 – why is the relative intensity of each peak important to show in the figure? Especially since you do not discuss relative intensities of molecular formulae in the main text.

Figure 7 - The overlap of molecular formulae in the venn diagram will be better represented as percentages

Figure 8 – This figure seems unnecessary, given that you only mention the results pertaining to this figure in the main text and do not have a detailed discussion of the same.

Supplementary figure S2. What is Kendrick mass defect analysis? Or Kendrick mass? No description of this has been provided in the MS or in the supporting information. Neither is there a reference to Figure S2 in the main text.

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