

Review of manuscript BG-2018-182 of Wang et al, submitted to Biogeosciences to be published as research article, entitled as “Spatiotemporal transformation of dissolved organic matter along an alpine stream flowpath on the Qinghai-Tibetan Plateau: importance of source and permafrost degradation”.

This topic of this MS is alpine permafrost (of the Qinghai-Tibetan Plateau, PRC), which is subject to large scale alteration due to climate change. Especially the deepening of the seasonally thawed surface soil, the active layer (AL), may activate large quantities of frozen soil and connect them to biogeochemical cycles. Of special importance is organic carbon, which can be released by hydrological processes, enter fluvial systems and change regional carbon balance. As such, the topic of the MS is of high relevance to the field and appropriate for the journal Biogeosciences.

Wang and coworker looked at dissolved organic carbon (DOC) sources from two different permafrost soil depths and investigated their fate along a headwater stream and changes within season and years. The authors used a set of complementary methods, optical and mass spectrometric, to characterize DOC quality in their samples.

The main conclusions drawn from their study are that DOC released from the AL contributes most to the stream DOC with seasonal pattern, that this AL derived DOC is rapidly degraded due to in-stream processes and dilution whereas permafrost layer (PL) derived DOC is even faster degraded. Finally the authors use climate predictions of the region to hypothesize about future changes of the alpine stream DOC quality and biogeochemical changes related to this.

This is a re-review of the MS submitted to Biogeosciences and the previous comments by the referees were taken into consideration. The authors of the MS have addressed most of the concerns given by the two previous reviewers and modified the MS accordingly.

However, I have major concerns about the method presentation, the interpretation of the data and the conclusions drawn and cannot recommend publication of this article in its current form.

1. In the study three different types of samples were used, whole water for bulk optical and carbon concentrations, SPE extracts for mass spectrometry and ultrafiltered samples for radiocarbon analysis. Besides a lack of proper description of the methods, no discussion about the potential biases in the interpretation of the results is presented. Especially when combining radiocarbon and mass spectrometry results, this problem becomes evident. In a previous study of the same team of authors (published this year in JGR:Biogeosciences), they acknowledged that ultrafiltration recovers 40% of the total C whereas SPE recovers essentially “the other” 60%. So how should one infer that “the addition of new molecular formulas was also reflected by the ^{14}C enrichment in middle and lower stream” (L362f)? There is a large body of literature dealing with the extraction (biases) of radiocarbon and I encourage the authors to pay more attention to that.
2. The hydrology of the system seems not well considered. E.g. dilution is acknowledged to change the EC and increase the discharge, but this groundwater dilution with a DOC concentration of 3-4 mg/L (L 311ff) is not considered in terms of different DOC quality. In fact, if the discharge increase would be just from GW addition (which is not, as also other tributaries contribute), than the order of magnitude increase in discharge is accompanied by an order of magnitude decrease of DOC concentration between Q-1 and Q16-Q20. How does a plot of discharge vs EC and DOC look like? So when comparing low DOC station Q16-Q20 with high DOC station Q1, an increase of the relative abundance or number of molecular formulas may just be caused by the additional input of GW derived DOC and not by in-stream production of DOM. Similar issues are discussed below.
3. The change of DOC quality along the stream is mainly attributed to photo-degradation, causing depletion of SUVA (aromatics) and increase in spectral slope (molecular weight). The authors argue that due to the high insolation on the QTP, photo-degradation is likely an important process. However, given the high DOC concentration and short water residence time in the headwater (where most changes in DOC concentration and quality occur), make this assumptions at least questionable. Also potential high turbidity of the stream should at least be excluded. But no in-situ light absorption and energy dose was measured, nor was there

an experimental proof of the claimed rapid photo-degradation. In other words, just because in other studies a change in the above mentioned optical properties were observed after experimental UV exposure, not all observed changes in such complex environmental settings can be attributed to the same, single effect.

Detailed comments:

Introduction:

L48ff: No mentioning about organic carbon in the whole first para, is it not important?

L67ff: I don't understand this statement. Please explain better why a "space-for-time" approach should reflect seasonal exported permafrost carbon fate. The authors actually attempted to measure the seasonal pattern.

L90: And later: Please explain how DOM from the PL can actually leach, if the soil is per definition frozen. What are the mobilizations processes?

Materials and Methods:

L122: If the water really percolates through both layers, than the PL leachate is likely a mixture of AL and PL DOM (as also reflected by the much younger radiocarbon age of the PL leachate as compared to PL bulk soil, see Wang et al. 2018). Were the leachates not filtered?

L137: The UF filtrate is not mentioned further.

L144: Given the great detail on DOC measurement, I wonder what the exact method of flow rate determination was?

L165: This is nicely explained, but did you actually check for recovery? Varying extract DOC concentrations may bias subsequent the FT-ICR measurement mass peak intensities. What was the measurement concentration and was only MeOH used as ESI solvent?

L168: replace "speed" by "rate"

L169ff: Please report the measurement and evaluation mass range, composition boundaries and applied ppm threshold for formula assignment.

L177ff: How did you derive these definitions/boundaries of compound "groups"? E.g. a molecule with just 1 N-atom can by definition not be a "peptide" nor is any molecule with > 2 N-atoms automatically a peptide, even if it may by chance have the same H/C and /C ratio as a peptide. This unwary and unnecessary use of compound annotations will get the MS community in the same trouble as the EEMS community with their "tryptophan" and "tyrosine" fluorescence. Same applies to polyphenols.

L184: Not clear which samples were used for radiocarbon analysis

Results:

L199: Please define AD

L227: By "molecular chemodiversity" you just mean number of assigned formulas. Really??

L228: Was the molecular weight calculated as weighted average? And if not, why not?

L234: "polyunsaturated" was not previously defined.

Discussion:

L250: Why is this paper by the same team of authors first cited in the discussion? Much of the sampling site and methods has been described already there.

L278: Please explain equation variables. As no $\Delta^{14}\text{C}$ values were reported (which I thought was good practice), the equation is of no great use to the reader.

L281ff: More critical than fast degradation (where?) is that also source ^{14}C values may change seasonally and bias the interpretation of changes AL and PL contributions.

L302: This sentence is inconsistent. When the relative contributions of PL increases, shouldn't that lead to an increase in DOC concentration? Again ^{14}C values may support this, but are apparently lacking? Any support from optical measurements?

L309: Tributaries also contribute to an increase in discharge.

L341: Also precipitation, aggregation etc can remove DOC and selectively alter DOC quality.

- L343: Also groundwater dilution with different DOC quality can change the relative abundances of peaks. This needs to be taken into account when discussing permafrost DOC quality changes along the stream.
- L398: This depletion may only be relative, not absolute, if the amount of AL derived OC stays constant and only the amount of PL derived OC increases.

Conclusions:

- L419ff: I'm not convinced that one could state that the loss of AL-specific formulas is an indication for sunlight as driver of DOM removal. (see above discussion)
- L430: It was not shown in this study that "components with old ¹⁴C-DOC age (...) were recalcitrant to degradation". It was only assessed based on bulk ¹⁴C values. Further a direct relation to molecular composition as "highly unsaturated" cannot be established as ¹⁴C and MS were measured on different DOC fractions.

Figures and Tables:

- Fig.2: Please report DOC concentration in mg/L like in the main text. (also Fig. 6)
- Fig.3: I'm confused as in the methods section, sampling of PL and AL was conducted in 2016 and 2017, here data from 2016 and 2015 are displayed.
- Table2: Data is presented on a number basis only. How much of the total intensity within each spectrum do the individual groups represent?