

# ***Interactive comment on “Spatiotemporal transformation of dissolved organic matter along an alpine stream flowpath on the Qinghai-Tibetan Plateau: importance of source and permafrost degradation” by Yinghui Wang et al.***

**Yinghui Wang et al.**

ypxu@shou.edu.cn

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On behalf of my coauthors, I really appreciate Dr. Jaffe to supply his comments on our manuscript. We found most of his comments are reasonable, so we accepted them and made corrections in the revised manuscript. The follows are our responses point by point. I also marked all changes in the revised manuscript and submit related figures and text as attachments.

General Comments: The abovementioned manuscript describes research on the effect

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of climate change on permafrost degradation in the Tibetan Plateau and its potential impact on associated fluvial systems, in particular on the dynamics of dissolved organic matter. This research is of global significance as little is known about permafrost degradation in areas other than the arctic, and nearly 70% of alpine permafrost is located in the geographical area of this study. The research team is composed of highly qualified scientists with ample experience and expertise in the specific field of study, and applying ideal methodologies to reach the outlines objectives of this research initiative. The manuscript is well written, and the data properly presented. The literature is also properly reviewed and well represented. As such, this manuscript is well-suited for the journal Biogeosciences and I recommend it to be published. However, some aspects of the manuscript should be improved prior to acceptance. For example, seasonal variability observed needs to be fully explained; explanations regarding the observed differences in DOM leachate composition between the AL vs PL needs to be better explained; discussion on instream generation of DOM through microbial primary productivity should be enhanced and variations along the sampling transect better described; etc. These pending issues are described in more detail below.

Specific Comments: 1) L43: “: in-stream metabolism:”: Throughout the manuscript make sure DOM degradation via molecular transformations vs mineralization to CO<sub>2</sub> is specified as needed. Similarly, dilution (concentration decrease) vs. ‘dilution’ (change in relative abundance) through mixing with in-stream DOM from microbial PP?

Response: This is a good comment. Since the DOM degradation process is very complex. Besides different types of degradation (photodegradation vs. biodegradation), DOM can be also completely degraded into CO<sub>2</sub> or partially degraded to other compounds. For the former, we prefer to call “transformation”, while for the latter, we used “mineralization”, although in many literatures, “degradation” was simply used for expressing DOM change. In the revised manuscript, we clarify this difference. From line 41-43, we rewrote as “Our study thus demonstrates that hydrological conditions impact the mobilization of permafrost carbon in an alpine fluvial network, the signature

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of which is quickly lost through in-stream mineralization and transformation”. As for the dilution effect, we referred it to concentration decrease at Line 292-304.

2) L 54: As in #1 – bio- and photo-transformation vs. mineralization? Both?

Response: As we mentioned above, we clarify this point in the revised manuscript. We rewrote the sentence as “When permafrost-derived carbon enters aquatic system, it can be rapidly mineralized and transformed by microbes and light” in line 55.

3) L61-62: Not sure ‘hydrologic inputs’ is the best way to word this! Please re-phrase.

Response: We use ‘hydrologic condition’ to replace ‘hydrologic inputs’.

4) L116: Please indicate distance in Km. This can be deduced from Fig. 1, but would be helpful here for the reader to easily gain a grasp of the spatial extension of the study.

Response: That’s a good suggestion. we supplied this information in the revised manuscript. In line 117-118, we wrote as ‘The water in the gully flows southward across the hillslope before draining into Qinghai Lake, and the total length of the stream is around 40 km (Fig. 1).’

5) L120-124: Please add more details on the methodology used for leachate collection.

Response: We already added the more detailed description of the sampling method in the revised manuscript (Line 122-125). We wrote as ‘At each sampling time, both AL and PL leachates were collected at the depth of 60 cm and 220 cm, respectively, of the gullies’ head. 20 L HDPE carboys were cleaned by pure water, 0.1 N hydrochloric acid and pure water prior to use. It usually took 2 days to gather > 15 L leaching waters. After that, the leachate samples were immediately kept on ice and in the dark by aluminum foil. They were transported to the temporary laboratory in the Gangcha County with six hours.’

6) L124-127+: Please add distances in m or Km as needed.

Response: We added this content in the revised manuscript, which is 8.5 km long for

the first order stream and 6.9 km long for another order stream.

7) L156-160: Leachate/Water volumes used for the SPE? How did you avoid breakthrough?

Response: We actually realized this point. Before SPE, we estimated the maximum volume before loading samples based on the SPE recovery (60% in our case) and the final eluate concentration 40  $\mu\text{g C/ml}$ . The exact loading volumes vary among samples, but the eluate concentration is similar that might help reduce the selective ionization. In the revised manuscript, we added detailed information on this issue. From line 160 to 166, we wrote as ‘They were solid-phase extracted (SPE) using the Bond Elut PPL (Agilent Technologies, 100 mg PPL in 3 ml cartridge), following the procedures of Dittmar et al. (2008). In order to avoid overloading of the SPE column, the aliquot volume of SPE DOM was calculated based on an average SPE recovery (60% for permafrost DOM; Ward, et al., 2015) and a final eluate concentration of 40  $\mu\text{g C/ml}$  (in ca. 2 ml methanol).’ We also cited a reference ‘Ward, C. P. and Cory, R. M.(2015) Chemical composition of dissolved organic matter draining permafrost soils. *Geochimica Et Cosmochimica Acta*. 167, 63-79.’.

8) L180: ‘Freeze-dried retentates’? Meaning SPE-DOM? Explain or rephrase accordingly.

Response: We already changed into ‘Freeze-dried retentates from ultrafiltration’.

9) L206-207: Does that mean the in-stream microbial generation of DOM is negligible?

Response: In this section we use optical properties to show DOM characteristics, in that way we could quick screen the inter-annual variation between year 2015 and 2016. The lack of inter-annual change did not mean insignificant microbial generation of DOM in stream. Actually, from headwater to downstream water, we observed apparent change in optical parameters of DOM, suggesting substantial transform of DOM by photo or bio-degradation. We discussed this point in section 3.3 Spatiotemporal



change of 14C-DOC age through fluvial networks.

10) L213-216: I do not see any detailed discussion on this inter-annual variability. Please add.

Response: We added the discussion on inter-annual variability in the revised manuscript. From line 204-211 as 'Paired t-test based on S275-295 and SUVA254 of water samples showed no significant inter-annual variation between year 2015 and 2016 ( $p = 0.716$  and  $p = 0.321$ , respectively). The mean S275-295 of 2015 and 2016 samples was  $(14.5 \pm 0.48) \times 10^{-3} \text{ nm}^{-1}$  for the AL leachates and  $(18.3 \pm 1.3) \times 10^{-3} \text{ nm}^{-1}$  for the PL leachates. In the stream waters, the S275-295 ranged from  $15.8 \times 10^{-3}$  to  $22.5 \times 10^{-3} \text{ nm}^{-1}$ , increasing in downstream reaches." In the stream waters, the S275-295 ranged from  $15.8 \times 10^{-3}$  to  $22.5 \times 10^{-3} \text{ nm}^{-1}$ , increasing in downstream reaches. Mean SUVA254 was  $3.52 \pm 0.24 \text{ L mg C}^{-1} \text{ m}^{-1}$  for the AL leachates and  $0.95 \pm 0.14 \text{ L mg C}^{-1} \text{ m}^{-1}$  for the PL leachates, and decreased in the stream from Q-1 to Q-10 ( $3.06$  to  $1.27 \text{ L mg C}^{-1} \text{ m}^{-1}$ ), and then remained low (Fig. 3). ', but for the radiocarbon age of the DOM, actually we did not do inter-annual analysis, here we discussed just temporally change in different months in 2015 as showed in line 219-221.

11) L243: Please expand on the discussion of these differences in chemical composition between AL and PL leachates. The information shown in the discussion is highly selective to age and very limited with regards to molecular composition and optical properties. In the first paragraph on page 11 there is some discussion on this with regards to sample Q-1, but nothing much else (i.e. along the sampling transect).

Response: This is good comment. Actually, we have addressed this issue previously. Please see Wang, et al., 2018, Selective leaching of dissolved organic matter from alpine permafrost soils on the Qinghai-Tibetan Plateau. J. Geophys. Res. Biogeosci., 123, 1005-1016, doi: 10.1002/2017jg004343. In this article, we examined and compared the chemical composition of DOM leached from AL and PL. We found the se-

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lective leaching in Permafrost soils that upper AL leachates are enriched in aromatic components, whereas deep PL leachates are enriched in alkyl components. In current work, we focus on instream processes of DOM rather than leaching process from soil to headwater. Nevertheless, we added some sentences (line 249-252) as “This difference is likely attributed to selective release of aromatic components from upper AL soils and carbohydrate/protein components from deep PL soils during the thawing process which was observed in our previous study (Wang et al., 2018).” We also cite the reference of Wang et al. (2018) in the revised manuscript.

12) L256: How were STDs obtained from  $n=2$ ?

Response: We are sorry for this mistake. Here we calculated the average value and the average deviation based on two samples. In the revised manuscript, we corrected all the calculated data throughout the manuscript, and here rewrote as “The mean DOC concentration of the AL leachate based on samples from 2015 and 2016 ( $11.57 \pm 0.77$  mg/L) is similar to that of the headstream (Q-1; ca.  $11.69 \pm 0.60$  mg/L), but substantially lower than that of the PL leachates ( $126.40 \pm 14.80$  mg/L), supporting a predominance of AL-leachate DOM in stream waters. In addition, the SUVA<sub>254</sub> is  $3.52 \pm 0.17$  L mg C<sup>-1</sup> m<sup>-1</sup> for AL leachates and  $0.95 \pm 0.10$  L mg C<sup>-1</sup> m<sup>-1</sup> for PL leachates, whereas the S<sub>275-295</sub> is  $(14.49 \pm 0.34) \times 10^{-3}$  nm<sup>-1</sup> for AL leachates and  $(18.05 \pm 0.94) \times 10^{-3}$  nm<sup>-1</sup> for PL leachates”.

13) L260: Remove the ‘(‘ before ‘and’

Response: we deleted “(“.

14) L261-264: idem as above – explain differences in composition between AL and PL.

Response: We have added some brief information about AL and PL leachates at Line 267-269, but as mentioned above (response to comment 11), we did not give much detailed information in this study.

15) L280: What about seasonal variations in the optical properties and MS data? Miss-

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ing important information here. Please add.

Response: It is a pity that we did not conduct FT-ICR MS analysis for seasonal samples. But a seasonal variation of DOM could be revealed by our optical analyses. In the revised manuscript, we added the sentence as 'Our result also shows seasonal variations in 14C age and optical parameters of headstream DOM. From summer to fall, the SUVA<sub>254</sub> of stream DOM at Q-1 decreased from 2.79 to 2.36 mg C-1 m-1, whereas the S<sub>275-295</sub> increased from  $16.33 \times 10^{-3}$  to  $16.96 \times 10^{-3}$  nm-1. These temporal changes indicated that the proportion of aromatic components and high molecular weight compounds decreased with the deepening of permafrost thawing.' Please see the details from line 292 to 297.

16) L285-288: This statement seems to make sense, but at the same time the DOC concentration from PL is significantly more elevated compared to AL. How much is 'percolation' due to freezing reduced?

Response: We agree it would be helpful to distinguish leaching and percolate if we could separate them. Unfortunately, it is very difficult to monitor percolation in fieldwork. So we just separate the whole soil profile into active layer and permafrost layer and discussed combined effects by collecting leaching waters at the Q-1. Nevertheless, several lines of evidence from optical, DOC concentration and FT-ICRMS support our statement that active layer is a major contributor to leachate DOM.

17) Section 4.2: I encourage the authors to actually calculate physical dilution to see if it indeed agrees with the estimation determined based on age variation. Mineralization and in-stream contributions could be roughly estimated by difference based on dilution only.

Response: This is a good comment. We qualitatively discussed the dilution effect in line 305-312. Several lines of evidence from DOC concentration, total water discharge and water conductivity all supported the existence of dilution effect in downstream waters. However, it is difficult to quantify this effect because the lack of DOC and water flux

data of tributaries and groundwater. We may conduct more comprehensive survey in next year and address this issue in future. In current study, we circumvent this problem by tracing unique peaks of DOM by using FT-ICRMS. If these unique peaks disappear along the stream, it suggests the occurrence of biodegradation or photodegradation for the specific type of compounds.

18) L304-314: Not clear why the authors make comparisons with values observed in coastal systems. Seems irrelevant in this case.

Response: We accepted this suggestion and removed related contents in the revised manuscript.

19) L314-318: The size-reactivity continuum (Amon and Benner, 1996) applies well for marine systems. However, it is controversial for terrestrial systems as both similar and opposite trends have been reported in the literature. Considering this, I would focus on the photo-degradation process, which is more likely dominant in this case.

Response: We agree with this suggestion and deleted these sentences. In line 343-344, we rewrote the sentence as 'A strong negative correlation between S275-295 and SUVA254 ( $R^2 = 0.73$ ,  $p < 0.01$ ) indicates that photodegradation of high molecular weight aromatic compounds (like lignin) may play a role in the decrease of mean molecular weight of DOM along the stream, despite that microbial degradation might also contribute the molecular modification in stream to less extent.'

20) L346-353: I would like to see an effort by the authors in enhancing the interpretation of the MS data here. Can molecular formulas generated/added along the transect through microbial in-stream activity be identified? What about photo-transformation products? I assume not all photo-degraded DOM is mineralized to CO<sub>2</sub>.

Response: Yes, besides the mineralized molecules and new produced molecules, the partial transformations of DOM can also contribute the change in molecular characteristics in stream. This kind of transformations is a result from combined factors such as

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microbial degradation, photo degradation, and also new input from base flow and in-stream generation, among others. In the revised manuscript, we have added a supporting figure (Fig. S1) that shows the change of DOM molecular formula between Q-1 and Q-17, with the decrease of aromatics and the addition of highly unsaturated molecules. From line 363 to 369, we rewrote the sentences as “Concurrent with the rapid loss of AL-specific formulas, some new molecular formulas were detected by FT-ICR MS, which was mainly attributed to in-situ production by stream algae/microbes, and import from groundwater and molecular transformation of leachate DOM. The van Krevelen diagram showed that the new products were mainly composed of highly unsaturated molecules (Fig. S1). The addition of new molecular formulas was also reflected by the  $^{14}\text{C}$  enrichment in middle and lower-stream (Fig. 3b).”

21) L392-393: This seems to make sense, but is still mainly speculative. Can you find partial evidence for this from your MS data (i.e. in-stream DOM)? Not sure it is possible.

Response: We identified some new formulas which give some evidence for in-stream production of new DOM, but as mentioned above, these new compounds could be also partially transformed from leachate DOM from bio-, and photo-degradation. In order to distinguish the different pathways, we are currently doing a series of incubation experiments in the laboratory, and wish we can publish those data soon..

22) L413: As above – seasonal variations discussion needs to be enhanced.

Response: We have added the discussion about seasonal changes in the revised manuscript. Please see our response to comment 15.

23) Figure 5: Color code ‘dots’ are VERY hard to see. Please enlarge accordingly.

Response: we have changed the figure legends and provide a new figure 5 in the revised manuscript.

Please also note the supplement to this comment:

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<https://www.biogeosciences-discuss.net/bg-2018-182/bg-2018-182-AC1-supplement.zip>

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Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2018-182>, 2018.

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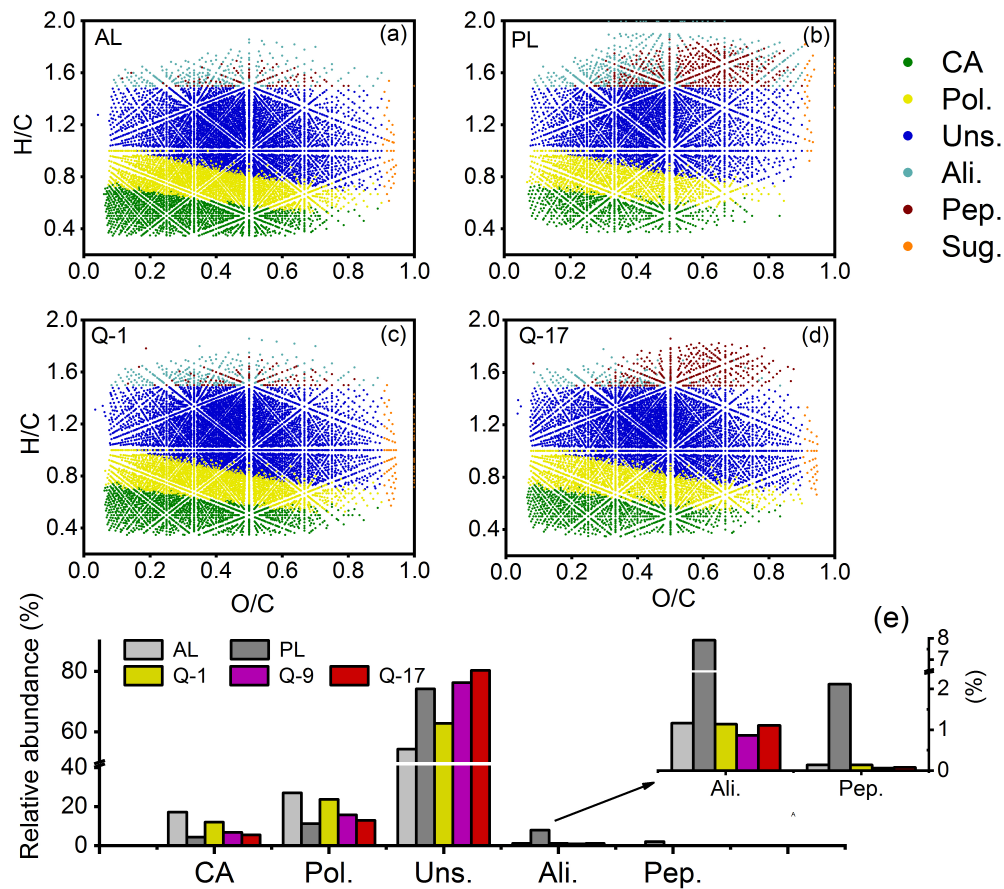


Fig. 1.

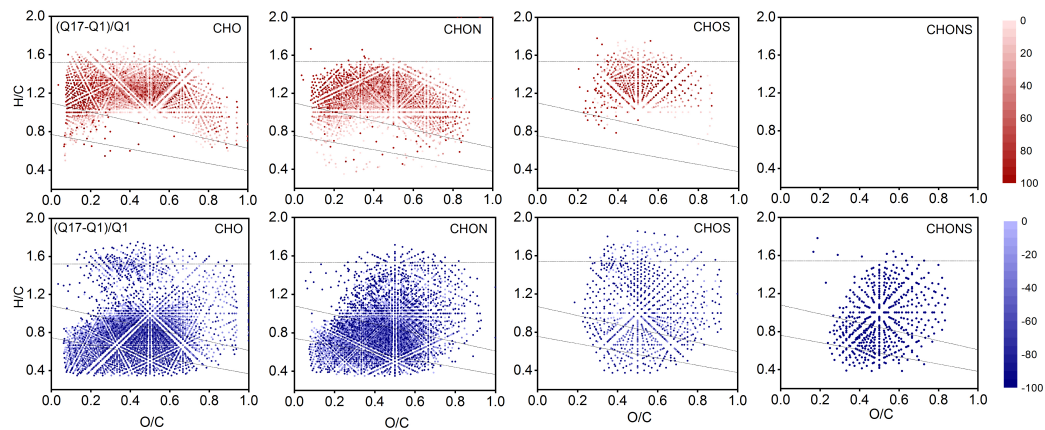


Fig. 2.

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