Dear Prof. Steven Bouillon,

Thank you so much for constructive comments. During the past two weeks, we have put together our response to the comments as below. We have also added some minor edits regarding the language of the manuscript to improve ease of reading.

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.

Response: We understand the reviewer's concern here. It is true that high molecular weight ultrafiltrated dissolved organic matter, so called HMW UDOM, usually has a younger ^{14}C age compared to bulk DOM. However, the offset of the ^{14}C age is relatively constant between UDOM and bulk DOM, suggesting that it is still feasible to assess biogeochemical processes of DOM based on HWM UDOM. Actually, because of low carbon concentrations and high salt abundance, it is routine to conduct pretreatment prior to mass spectral and NMR analyses in the literature (e.g., Chen et al., 2016. Structural and compositional changes of dissolved organic matter upon solid-phase extraction tracked by multiple analytical tools. Anal. Bioanal. Chem. 408, 6249-6258). In our manuscript, we used the ^{14}C data of HWM UDOM to discuss the relative contribution of permafrost layer (PL) and active layer (AL) leached DOM to the stream at site Q-1 and compared to the ^{14}C age from headstream to downstream waters. We attempt to trace temporal and spatial changes of DOM along the alpine stream rather than provide an accurate radiocarbon age of bulk DOC at each site. Thus, the extraction biases will not affect our discussion. In order to clarify this point, we have added the reference of "Broek, et al., 2017, Coupled ultrafiltration and solid phase extraction approach for the targeted study of semi-labile high molecular weight and refractory low molecular weight dissolved organic matter, Marine Chemistry, 194, 146-157". We also added the sentence as in line 287-290 as "Broek et al. (2017) found that although the ^{14}C age of HMW UDOM was significantly younger than that of bulk DOM from North Central Pacific Ocean, the offset between them is constant in the whole marine system. This result suggests that HMW UDOM can serve as a proxy for bulk DOM." We also emphasize the HWM UDOM in several places of the revised manuscript. Please see our resubmission for details. Finally, we also note that the recovery of HMW DOM in freshwaters and the material retained on an SPE-PPL cartridge are not opposing to one another (they do not represent 40% and the other 60% as the reviewer suggests). Likely the vast majority of HMW DOM was collected by ultrafiltration, and the same HMW fraction was also retained on the SPE-PPL cartridge, then the PPL retains slightly more in addition (see Mopper et al., 2007; Chem. Rev. 2007, 107, 2, 419-442 for a detailed discussion of this topic).

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 my just be caused by the additional input of GW derived DOC and not by in-stream production of DOM. Similar issues are discussed below.

Response: We did not attribute the increase in the relative abundance or number of molecular formulas to in-stream production only, and we also never say non-existence of groundwater inputs. We mentioned several times in the manuscript about groundwater contribution. For example, 1) In line 329-334, we wrote as “Dilution from groundwater is likely since groundwater discharge sustains baseflow of rivers and streams in the QTP (Ge et al., 2008). Downstream groundwater inputs were further supported by the order of magnitude increase in discharge (1.49 to 24.14 m3/min) and increase in conductivity (37 to 60 μs/cm). Moreover, downstream DOC concentrations remained about 3.0-4.0 mg/L (Q-15 to Q-20), indicative of the low DOC concentrations of groundwater. Conversely, a tributary that originated from another thermo-erosion gully merged into the study stream, however, the different tributaries exhibited similar DOC concentrations (e.g., Q-9 and Q-10 vs. Q-11 and Q-12; Fig. 2d)”. 2) In line 377-383, we wrote 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, an 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}C enrichment in middle and lower-stream (Fig. 3b)**”. However, strong in-stream processes are apparent because 90% of the PL-specific molecular formulas and 59% of AL-specific formulas were lost, which cannot be explained by addition of groundwater or in-situ contribution. In order to trace in-stream processes, we must find some unique tracers that are specific for source of the DOM. That is the reason we used ultrahigh-resolution FT-ICRMS. Ultimately groundwater addition cannot explain the observed trends as we see loss of molecular formula, thus we attribute this to processing of the DOM not mixing with a new source.

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.

Response: We understand the reviewers concerns here. Our major objectives are already stated in the introduction section of the manuscript: 1) determine the dominant sources of alpine stream DOM on the QTP (active layer (AL) vs. permafrost layer (PL)), and 2) trace the persistence and degradation of permafrost-derived DOM in an alpine fluvial network (line 90-97). For the first objective, we used DOC concentration, optical and radiocarbon data to compare AL and PL, and all data showed the predominance of AL contribution (see section 4.1). For the second objective, we found that formulas which are unique to AL or PL leachates in the system, so the degradation of permafrost-derived DOM is significant which was also supported by the optical and radiocarbon data. However, the most important source to the stream is permafrost DOM from AL which is also characterized by high aromaticity. Based on these facts, we merely suggest photo-degradation as a potentially important pathway for the removal of DOM in the QTP stream. We do not attempt to quantify the weight of photo and bio-degradation to the removal of DOM as that is beyond the scope of the current manuscript. But we are conducting the laboratory simulation experiments to assess these two degradation pathways. Ultimately our goal is merely to put forward reasonable discussion of the DOM compositional changes observed in the data and so we have toned back the language to make it apparent that we are suggesting photodegradation may be important as opposed to stating that is the case. We sincerely hope that is clearer in the new edited version.

Detailed comments:

Introduction:

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

Response: “Carbon” in our manuscript is specifically for “Organic Carbon”. In order to clarify this point, we have added “organic” before “Carbon or C” on line 48, 54, 56 in first paragraph and line 93 in the forth paragraph.. Apologies this should have been included.

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.

Response: We have rephrased the statement to “Since the persistence of DOM in aquatic systems is related to chemical composition (Kellerman et al., 2015; Kellerman et al., 2018), it is important for chemical characterization of DOM at different spatial and temporal scales”. (line 67-72)

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?

Response: With the increase temperature on the Qinghai-Tibet Plateau, thermo-erosion and thermokarst occurs widely, resulting in the exposure of deep permafrost layer (PL) to air. Therefore, the leaching from PL is feasible and particularly happens towards the end of the summer (i.e. period of maximal permafrost thaw). We conducted the study along an alpine stream that originates in the thermo-erosion gully and so long frozen material is mobilizing due to increasing temperatures at this location.

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?

Response: Yes, we filtrated leachate samples before further analysis. We also agree with the reviewer’s comment that vertical percolate is possible, reflected by younger ^{14}C age of PL-leachates compared to that of PL-soil organic matter.

L137: The UF filtrate is not mentioned further.

Response: UF filtrate were actually mentioned in ‘Radiocarbon analysis’ part on line 185 as “Freeze-dried retentates from ultrafiltration were fumigated with concentrated hydrochloric acid…” and in the revised manuscript, we have made clear statement on radiocarbon age of HMW UDOM.

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

Response: We have added the related information in the manuscript as “A portable propeller-type current meter was used to measure the flow rate at the stream cross-section, 5–9 measurements were performed. The water flux was calculated according to average flow rate and cross-sectional area of the stream.” (line 147 to 150).

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

Response: We did not check for recovery here, but Ward et al. (2015) have calculated the extraction recovery of permafrost DOM, and Dittmar reported the recovery for different types of DOM by PPL. So, we think their recovery data is applicable to our samples since we used the same types of DOM source materials and methodology. The measurement concentration is 40 µg C/ml and the solvent was MeOH, we have mentioned that on line 170-171.

L168: replace “speed” by “rate”
Response: We accepted this suggestion and replace “speed” with “rate” in line 146 of the revised manuscript.

L169ff: Please report the measurement and evaluation mass range, composition boundaries and applied ppm threshold for formula assignment.
Response We added the requested information. From line 172 to 179, we added as “The direct infusion flow rate was 0.7 µL/min. A total of 100 broadband scans between m/z 150-2000 were co-added for each mass spectrum. After internal calibration in MIDAS Predator Analysis (NHMFL), formulas were assigned based on published rules to signals > 6σ RMS baseline noise (Stubbins et al., 2010) using EnviroOrg®™ software (Corilo, 2015) and categorized by compound class based on the elemental composition of molecular formulas (Kujawinski, 2002; Stenson et al. 2003; Spencer et al., 2014). Formulas with mass measurement accuracy < 0.4 ppm were assigned within the following compositional constraints: C1-100, H2-200, O1-30, N0-3, S0-2.”

L177ff: How did you derive theses 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 change 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.
Response: We understand the reviewers concern here thus the use of “like” terminology which we have adopted now throughout. This is the same for the fluorescence community, I don’t think they are saying it for example is “tryptophan” fluorescence but “tryptophan-like” and thus it fluoresce in the same part of optical space as tryptophan. We understand the reviewers concerns with similar terminology for FT-ICR MS data and we are merely trying to make the data more accessible for the non-specialist. We agree N-containing aliphatic might be more appropriate than “peptide-like” but we clearly define several groups based on molecular composition – the group names are broad and hopefully help the reader assess what’s generally present, just like many previous studies do, and this kind of classification is helpful for us and readers to understand the change of DOM compositions. In our study, we used the most widely used classification and current standards.

L184: Not clear which samples were used for radiocarbon analysis

Response: This is a good point. We marked the samples for ^{14}C measurement in figure 4, including spatial distribution of DOM from the sites Q1, Q5, Q16, Q19, AL and PL leachates, as well as temporal variations of DOM from the site Q1.

L199: Please define AD
Response: AD is "Average Deviation" and has been clarified.

L227: By "molecular chemodiversity" you just mean number of assigned formulas. Really??
Response: Yes, and this is a commonly used term.

L228: Was the molecular weight calculated as weighted average? And if not, why not?
Response: We calculated mean molecular weight based on relative abundance of FT-ICR MS signals. We have added this information in the methods on line 186-188 as "The relative abundance of the defined compound class, mean molecular weight and AI_{mod} of each sample were all weighted by relative abundance in each spectrum."

L234: "polyunsaturated" was not previously defined.
Response: Here "polyunsaturated" means "highly unsaturated compounds (Uns.)" which is defined as AImod < 0.5, H/C < 1.5 in section 2.3. We have revised this in the manuscript.

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.
Response: We have added the reference of Wang et al. (2017, JGR: Biogeosciences) in the introduction and results sections. On line 78-81 we wrote as "Consequently, the permafrost soils on the QTP have begun to thaw and collapse, causing abundant carbon loss from in-situ degradation (Mu et al., 2016) and relocation (e.g., selective leaching in different soil layers; Wang et al., 2018).", and on line 113-114, we wrote as "detailed description on the collapse can be found in Wang et al. (2018).".

L278: Please explain equation variables. As no Δ^{14}C values were reported (which I thought was good practice), the equation is of no great use to the reader.
Response: This is a good comment. In the equation, f_{AL} and f_{PL} are the fraction of AL and PL-derived C in the DOM, and we have added Δ^{14}C values in the results section supplementary table S1 in the revised manuscript.

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.
Response: This is a good concern, changes of source ^{14}C values do change the AL and PL contribution, but in the binary mixing model we used the fixed end-member value

for AL and PL, because these values will not change a lot throughout the whole season, as the depth of the collapse did not change.

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?
Response: We don't agree with reviewer on this comment. With the relative contribution of PL increases, although total DOC concentration decreased, the proportion of PL-derived C increased. We already reported increased old carbon contribution and change in optical property during this process. In line 297-304, we wrote as "Headwater ^{14}C age of HMW UDOM increased from summer to fall (Fig. 4b), reflecting an enhanced contribution of old carbon from the deeper soils (i.e., PL), however, the AL still accounted for ⩾ 72% of total DOC exported (Fig. 6a). This binary mixing model may overestimate the contribution of AL to stream DOC since PL-derived DOC may be degraded faster than AL-derived DOC, due to the high biolability of ancient permafrost carbon as shown in Arctic ecosystems (Vonk et al., 2013). Nonetheless, the AL appears as a major contributor to stream DOC in the QTP." Both support enhanced contribution of PL-derived C from summer to fall.

L309: Tributaries also contribute to an increase in discharge.
Response: We agree with this comment. But we already discussed this issue in the manuscript and examined DOM composition of one tributary in the mid-stream. In line 331-337, we wrote: "Conversely, a tributary that originated from another thermo-erosion gully merged into the study stream, however, the different tributaries exhibited similar DOC concentrations (e.g., Q-9 and Q-10 vs. Q-11 and Q-12; Fig. 2d). The similarities in DOC concentrations were attributed to homogeneity in dominant vegetation, soil type and climate, and thus, homogeneity in DOM inputs to the different tributaries in our study area. Therefore, additional tributaries could not explain the spatial pattern of DOC concentration."

L341: Also precipitation, aggregation etc. can remove DOC and selectively alter DOC quality.
Response: We understand the reviewer's concern here. It is true that aggregation and precipitation can potentially change the DOC concentration and quality in many cases. However, in our case, due to very steep hillslope, the sediment and floc deposition is insignificant and we did not observe fine sediments in the stream bed. So, in the revised manuscript, we added the sentences as "The DOC concentration decreased (12.48 to 3.13 mg/L) from upper to mid-stream (Q-1 to Q-5), which could potentially be attributed to several reasons, like aggregation/precipitation, dilution effects, and in-stream degradation of DOM. The aggregation/precipitation is likely unimportant in our case because the steep gradient of sampling sites prevents significant sediment and floc deposition on stream bedrocks, although this effect can't be excluded completely." Please see line 321-327 for details.

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.
Response. This is true, but the loss of unique molecular formulas can't be explained by groundwater dilution. Since the groundwater input can only add molecular diversity, but not reduce the unique PL and AL-formulas. In our study, about 90% of unique PL-formulas and 59% of AL-formulas were lost in mid and lower stream, which strongly suggest active degradation in 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
Response: That's true, it is relative. Here we hypothesize "with enhanced leaching of deep soil C under continued warming on the QTP, DOM in alpine streams will **be more enriched** in biolabile aliphatics/peptide-like groups and depleted in photolabile aromatics". We predict with further climate warming, the deepening of the AL will lead to the relative proportion of biolabile aliphatics/peptide-like groups in leachate DOM to increase whereas the relative proportion of photolabile aromatics in leachate DOM will decrease.

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)
Response: We assume our statements have been misinterpreted here, since we did not intend to claim that sunlight was the only process responsible for the loss of Al-specific formulas. The AL-leachate is enriched in aromatic carbon that is photo-labile but relatively resistant to biodegradation. In addition, the Qinghai-Tibet plateau is characterized by strong UV light and low temperature. These characteristics create a favorable condition for photodegradation of aromatic enriched DOM. So, we draw a conclusion that "Presently, the AL is the major source to stream DOM with relatively high aromaticity. This character, combined with strong solar radiation on the QTP, suggests sunlight may be an important driver for DOM removal in alpine fluvial networks, which was corroborated by an almost 60% loss of AL specific formulas from the thermo-erosion gully head to downstream waters." As noted in the comment above we are merely putting forward a legitimate conclusion from the data presented.

L430: It was not shown in this study that "components with old ^{14}C-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 ^{14}C and MS were measured on different DOC fractions.
Response: We understand this concern here, this highly unsaturated component is extracted by SPE, and the ^{14}C age is from HMW UDOC, so we have identified the specific component as "some components with old ^{14}C-DOC age were recalcitrant to degradation and could be transported downstream" on line 434.

Figures and Tables:

Fig.2: Please report DOC concentration in mg/L like in the main text. (also Fig. 6)

Response: we have made change in the revised manuscript.

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.

Response: The sampling was conducted in 2015 and 2016 rather than 2016 and 2017. We have made correction in the method section.

Table2: Data is presented on a number basis only. How much of the total intensity within each spectrum do the individual groups represent?

Response: In fact, it is impossible to quantify total intensity of peaks by FT-ICR MS. So, we changed the title of table 2 into "The number of specific molecules identified in the AL leachate DOM and the PL leachate DOM within the fluvial network, and the change in the relative abundance of each formula during the transportation".