Response letter to the reviewers of the manuscript bg-2022-71

In this response letter, the reviewer's comments are in ***italic bold black,*** our responses are in blue and significant new text added to the manuscript are in *italic green.* Changes made in the manuscript are tracked and referred to the revised manuscript.

Reviewer #2 – Anonymous

We would like to thank the reviewer for the evaluation of our work and for the constructive comments . We appreciate that the reviewer recognized the importance to document the DOM dynamics in peatlands. We have tried to address the remarks and clarify some aspects of the manuscript. The line-by-line comments have been integrated to the text.

1) Regarding the Mat & Meth section

In general, I think the writing of method is a bit lengthy. While it's good to provide such information for readers who want to replicate the method, there are too many details which are not necessary to be included in the main text of the paper. I'd like to suggest the authors to refine this part in a concise manner, combining with references and supplementary materials.

In addition, as various sampling trips, analyse methods, proxy indices are used in this study, I'd like to suggest using a table or diagram to summarise this information, which would make it much easier for the readers to understand the research design and interpretation. For example, how many samples from what sites on which dates, and which were analyzed for what. It'd also be helpful for the readers to understand why dot plots were used in Fig. 2.

We tried to consider reducing the material and methods section. However, numerous methods were used, explaining the density of this section. Also, the detailed method could be beneficial for further studies.

To help the understanding of the sampling and analyses design, a synthesis table with number of samples and analyses performed were realized. It is added to the supplementary information (Table SI.1) and was referred to in the Material and Method section (l. 132).

"Samples collected per campaigns and analyses performed on it were synthesized in table SI.1."

Table SI.1. Synthesis of samples number per analyses per campaigns.

Year	Campaign	Environment	Analyses					
			DOC; DOC:DON	Isotopic	Absorbance	Fluorescence	Molecular	Incubation
2018	June	Porewater	5	1	5			
		Pools	6	2	4			
	July	Porewater	4	2	4		3	
		Pools	6	3	6		3	
	August	Porewater	6		6		3	
		Pools	6		6		3	
	September	Porewater	4	2	4		3	
		Pools	6	3	6		3	
	October	Porewater						
		Pools	6	2	6			
2019	June	Porewater	6	3	6	6	2	x
		Pools	11	3	11	11	2	x
	August	Porewater	6	3	5	5	1	x
		Pools	11	3	11	11	3	x
	September	Porewater	5	5	5	4	3	x
		Pools	11	3	11		2	x
	October	Porewater	5	3	5	5	3	
		Pools	5	3	5	5	3	

2) Differences in DOM Concentration and Composition

Firstly, when comparing the DOC concentrations in porewater and pools in this study with those in other climatic zones, seasonality should be considered, as here DOC samples were collected in the growing seasons which would tend to be higher than other seasons.

Thank you for this remark. It is true that we did not mention that our study presented data sampled during the growing season, which may not be the case for all compared studies. After checking, we observed that sampling periods of all studies except two occurred during the growing seasons (Beer and Blodeau, 2007; Tipping et al., 2010). We annotated those two references and adjust the text in consequence (l. 410; 413; legend of the table SI.3).

"The average DOC concentrations measured in peat porewater at our sites during the growing season are in agreement with the expected range of a subarctic peatland (13.9-28.8 mg L-1; Deshpande et al., 2016)."

"The DOC concentrations in peatland peat porewaters exhibit a latitudinal gradient, from DOC concentrations commonly lower than 20 mg L-1 in boreal and sub arctic zones compared to temperate zones during growing seasons (Table SI.4)."

Secondly, the authors only explained the good correlation between DOC:DON and 13C in porewater, but didn't try so with the pool DOC. The absence of this correlation in the pools could well lead to the discussion in 5.2, and highlights the discontinuity of DOC composition.

Your comments about the use of the correlation between DOC:DON ratio and the d13C DOC ratio points out that it is not necessary to document the discontinuity between peat porewater and pools. We think that the use of the DOC:DON ratio and the d13C DOC ratio independently were more pertinent to discuss the terrestrial source of DOM in pools (according to the high DOC:DON ratio measured in pools) and discontinuity of peat porewater and pools DOM (according to the divergent seasonal trends in d13C DOC). As suggested, and in line with the other reviewer's comments, this figure has been removed.

Lastly, while the photo-degradable DOC might have been quickly degraded in the first few days, I'm not entirely convinced that it would be the main reason. DOC from porewater was not exposed to light before being collected so there should be minimal effects from photodegradation. In pools, new DOC inputs would be expected with the increased precipitation, which was observed especially during the summer and autumn seasons. Therefore, there could be continuous supply of photo-degradable DOC during those periods of time. Furthermore, in boreal and arctic areas, the amount of sunlight is less abundant than low latitude areas, limiting the photodegradation of DOC, although I realised it would be less so in summer. Did you have any data on the light? Was any incubation conducted when it was rainy or cloudy? Did the glasses/vials filter out certain wavelengths which cause photodegradation? As it stands now I don't think there is enough evidence to make the argument that there was no photodegradation process in the samples.

Considering photodegradation, we were also surprised when we found out that the DOM photodegradation was not sizeable despite being considered to be a common process in other boreal surface inland waters (Lapierre and del Giorgio, 2014; Jones et al., 2016).

Concerning the amount of sunlight, the study site it at 51° of latitudes and in summer, sunlight duration is longer than 12 h day^{-1} and the photosynthetically active radiation is higher than close to the equator during summer months (see the figure A bellow from Mortensen, 2014) and the downward shortwave radiation increase during summer months in the north hemisphere (see the figure B bellow from Hatzianastassiou et al., 2005). Thus, we believe that sunlight is not limiting in the period of incubation at our study site.

A) Mortessen, 2014

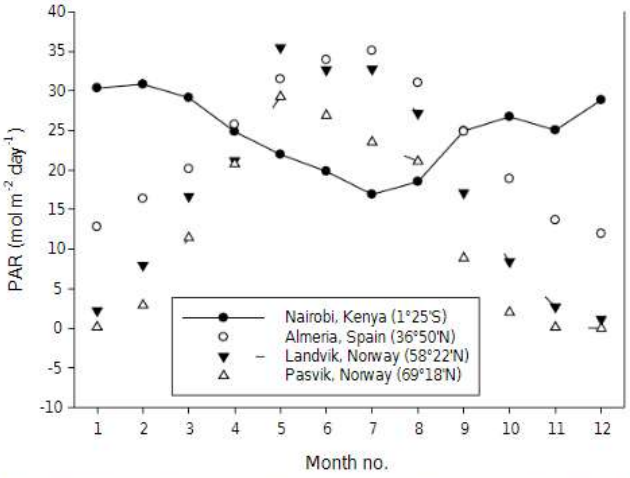


Figure 1. Photosynthetic active radiation (PAR) at different latitudes inside a greenhouse (60% transmission) throughout one year, given as daily means per month [1] [2]. A conversion factor of 7.9 mol per 1.0 kWh was used.

B) Hatzianastassiou et al., 2005 (the star represents the approximative location of the study site)

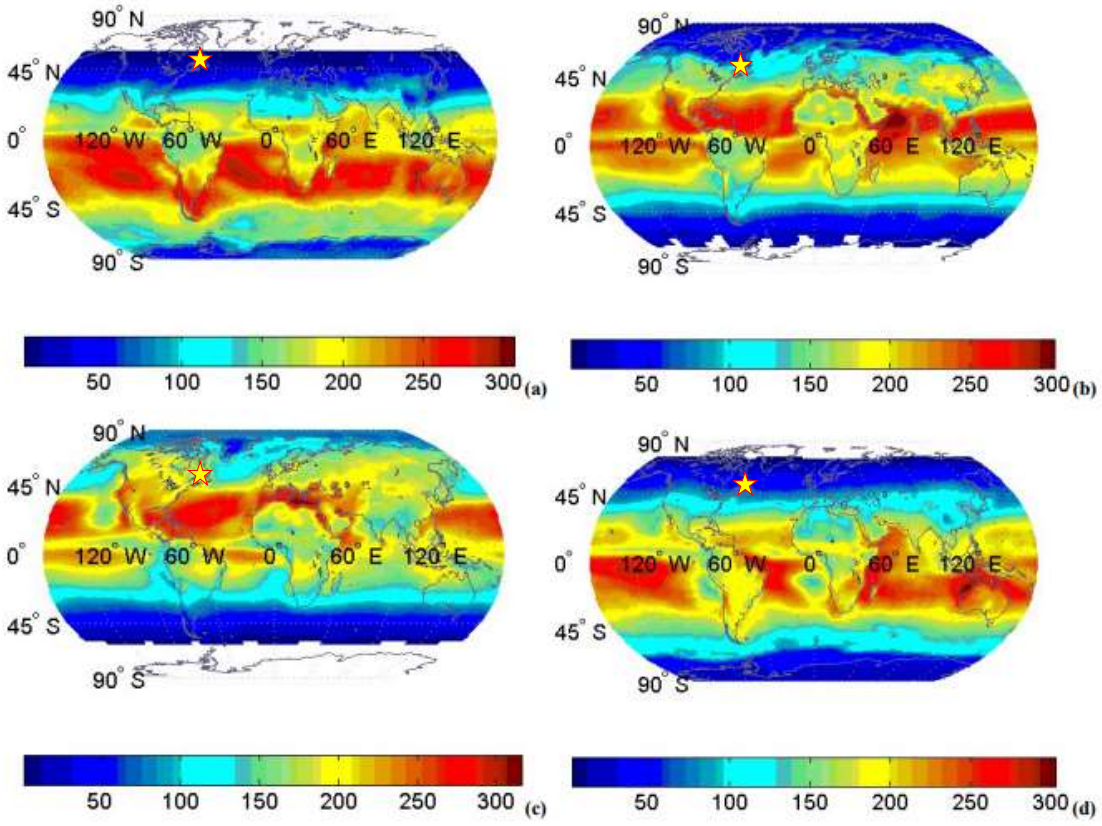
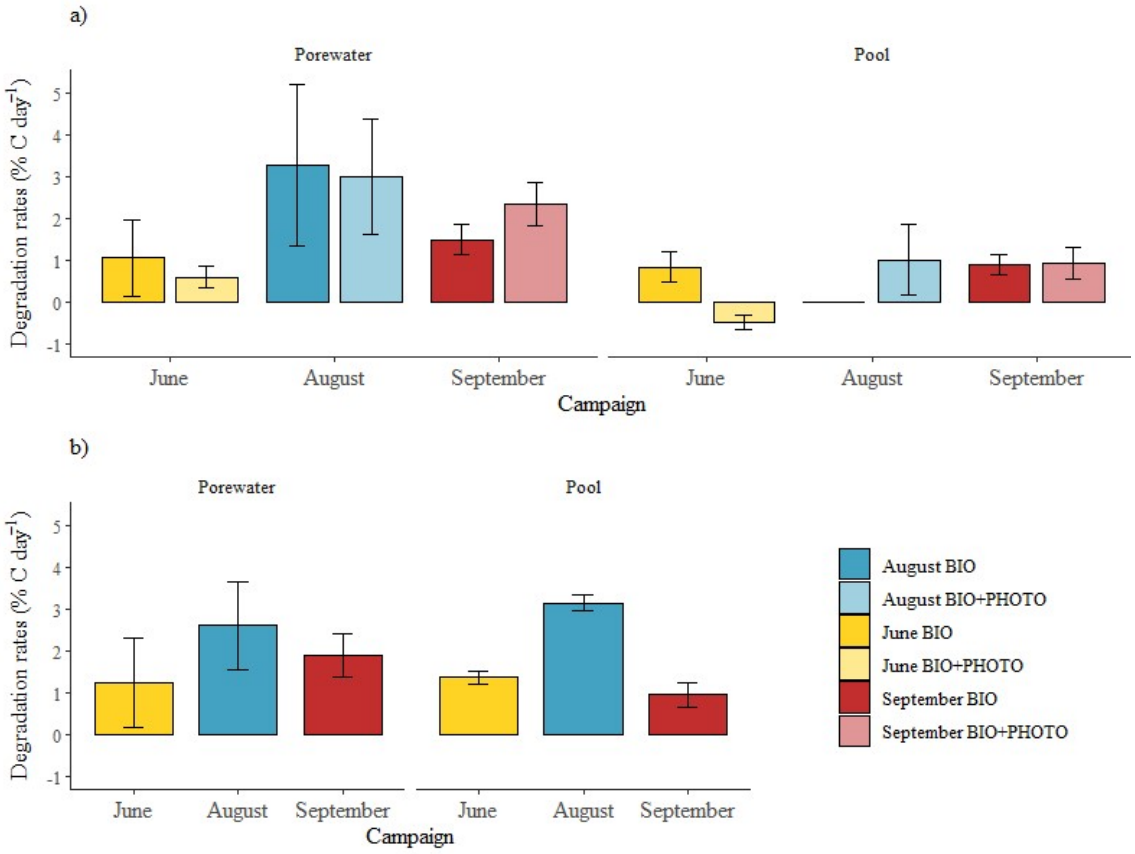


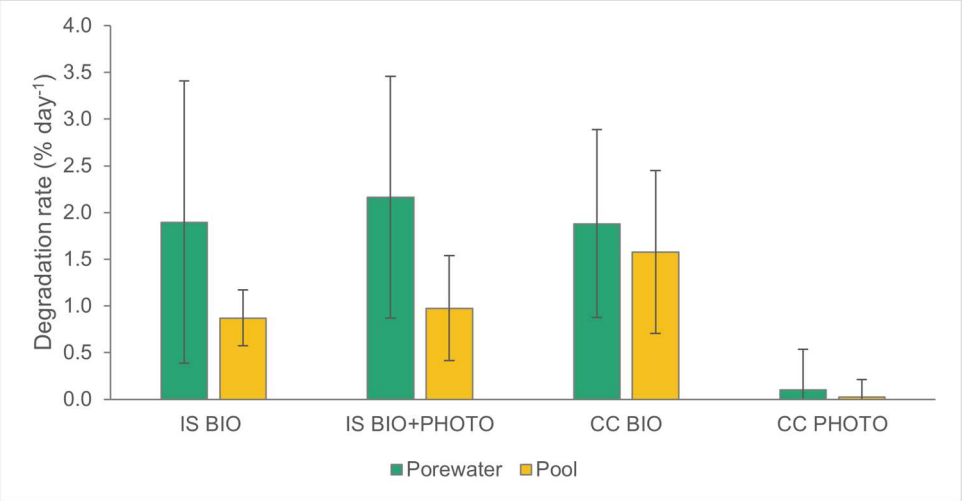
Fig. 2. Long-term (1984–1997) average global distribution of net downward (or absorbed) shortwave radiation (in Wm^{-2}) at the Earth's surface for the mid-seasonal months of **(a)** January, **(b)** April, **(c)** July, and **(d)** October.

To address the comment related to the potential effect of clouds and rain on light exposure variability between the incubation periods, we have looked at the incoming radiation based on a weather station installed at our study site (photosynthetically active radiation using a LI-190R and shortwave incoming radiation using a CNR4). During incubations in August, average photosynthetically active radiation (PAR) was 37.9 mol m^{-2} day^{-1} and the average shortwave incoming radiation (ISWR) was 346.8 W m^{-2} for an average sunlight duration of 15.5 h/day. In September, the PAR was 34.3 mol m^{-2} day^{-1} and the ISWR was 329.5 W m^{-2} for an average sunlight duration of 13.6 h/day. Unfortunately, data was not available for the incubation in June, but during the 6 days before the incubation, the PAR was 48 mol $^{-2}$ m^{-2} day^{-1} and the ISWR was 422.8 W m^{-2} for an average sunlight duration of 16.6 h/day. This suggests that the light conditions during our experiment where similar between one period to another and that cloudy or rainy days do not seem to have affected the overall incoming radiation.

The incubation performed in controlled conditions of temperature and darkness was a way to control the efficiency of amber glass vials to filtrate the light. No significant difference in degradation rates were observed between incubations of amber glass vials in controlled and in situ and with incubation of clear glass vials in situ conditions either as you can see in the figure below.



In addition, incubation performed in a solar incubator at a sunlight exposition equivalent to 6 days of natural sunlight in summer did not reveal significant changes in DOC concentrations, supporting the observation we made with *in situ* photodegradation incubations.



We changed "the DOM was potentially not photolabile" to "the experimental design did not allow the observation of any photodegradation"(l. 445 and the text was adjusted l.451).

"Our data did not evidence any photodegradation during DOM incubation in peat porewaters and pools, suggesting that the DOM photodegradation was not sizeable by our experimental design."

"The absences of sizeable photodegradation suggest that this process did not drive the DOM composition in pools."

3) Processing leading to the difference

Firstly, the difference in DOC composition, e.g. SUVA254, E2:E3, could be a result of that DOC in peat soil is 'older' than those exported to water, which was not considered in the paper before thinking about the more instant changes caused by hydrological, chemical and biological processes as the authors focused on.

According to the literature, it seems unlikely that the differences in composition between the peat porewater and the pools were due to different ages between the two environments. Several studies have shown that DOM is derived from fresh organic matter produced at the surface (Tipping et al., 2010; Tfaily et al., 2018). The DOM is mostly recent in peatland (Campeau et al., 2018) and older DOM was only observed in deeper horizons and occasionally mobilized through hydrological processes (e.g., mobilization during extreme storm events) and in degraded peatlands (Dean et al., 2019).

Also, the aromatic DOC should be more hydrophobic rather than hydrophilic. If aromatic compounds are hydrophilic, it should be easier for them to flow from peat to pools leading to higher DOC aromaticity in the water, which is contrasting to what was observed.

In our study, we observed significant higher aromaticity of DOM in peat porewater compared to pools. We hypothesized that aromatic DOM is more hydrophobic, which could enhance the exchanges between DOM and partially degraded peat (mentioned in the preprint bg-2022-71 at the l. 472-475). This point supports the idea that DOM was partially retained into peat during its transfer from peat to pools, and partly explains why the aromaticity of DOM decreased from peat porewater to pools.

In addition, in the abstract the authors pointed out the transformation of DOC at the interface led to the production of low molecular weight compounds, which is contrasting to their suggestion that microbial processing would cause the increase in aromatic DOC which is often larger in molecular weight.

The reviewer noticed that we mentioned in the abstract that the DOM microbial process at the interface between peat porewater and pools. This was leading to the production of lower DOM molecular weight compounds AND that we observed an increase in DOM aromaticity during DOM incubation experiments, which is expected to have a larger molecular weight. It is important to understand the DOM in a sum a complex molecular mix. For example, we observed during the growing season an increase in the DOM aromaticity and a lowering of the DOM molecular weight in pools and this was observed simultaneously (Fig. 2 based on SUVA254 for the aromaticity and E2:E3 ratio for the DOM molecular weight). A diversity of DOM compounds were biolabiles and might lead to the production of different degradation products with different properties. As the DOM mix is dominated by lignins, the increase of DOM aromaticity during incubation might be explained by the experimental design that could stimulate their degradation. Also, as we hypothesized that DOM aromatic compounds might be partially retained into peat, it is not contradictory that DOM compounds that were actually transferred into pools were less aromatic, and their degradation productions are less aromatics as well.

In line with this explanation, degradation of DOM compounds occurs at different time scales from few hours to years after its solubilization. For example, some compounds like carbohydrates are preferentially degraded while degradation of aromatic compounds might be longer. This may be why, after the six days of incubation experiments, we observed an increase in the aromaticity. These observations could have been different if measurements were made after the first day of incubation. Hence, the lower DOM molecular weight could result of the rapid degradation of compounds for which the degradation products present a lower molecular weight.

Secondly, DOC does interact with different materials or minerals in peat. For example, the oxidation/reduction of Fe have been observed to be mediated by microbes and affect the solubility of DOC (Mladenov et al., 2010), and tend to coagulate with high molar mass DOC (Ritson et al., 2014). At the interface between peat and pools, particularly when water table is higher in peat, the change from anaerobic to aerobic environment could affect the reduction/oxidation of certain relevant minerals (e.g. Fe) and reduce mobility of certain group of DOC (Nierop et al., 2002).

We have investigated the potential interactions between the DOM and solid and dissolved mineral in peat and peat porewater have been considered. However, boreal ombrotrophic peatlands are relatively poor in mineral elements (%C LOI = 46.7 ± 6.4, Primeau and Garneau, 2021). Then interaction with minerals in peat are limited. Regarding interaction within peat porewater, we collected some data on total trace metals concentration in 2018. Dissolved Fe was about 10 µg L^{-1} . these concentrations are very low compared to the values in the suggested publication (Mladenov et al., 2010), where Fe concentrations ranged between 5 and 10 mg L^{-1} but in a tropical region. The DOC:Fe even decreases from 1080:1 in peat to 62:1 in pools highlighting opposing trends between peat and pools where the Fe seems relatively soluble. The potential of DOM coagulation resulting of interaction with dissolved Fe seems negligible according to the low concentrations in dissolved Fe we measured in both peat porewater and pool.

Lastly, it was great to see that the authors were trying to explore the biogeochemical processes from porewater, interface and pools, which could be a highlight of this paper. However I'm not entirely sure how big role microbial processing is at the interface as the authors claimed. Indeed, biodegradation could happen within a couple of days, but at the interface I tend to think the physical and chemical interactions, e.g. precipitation and binding via the changes in the physical environment from soil to water is more instant and faster than bio-processing, and might have played a more important role. The soil C is still the dominant input for the pools despite the higher level of microbial activities in water. While the authors did a good job highlighting the difference in DOC concentration and composition, but as the paper is about the discontinuity between pools and peat, it's important to better explore how the water being transported between peat and pools (even vertically), what happens at the interface, what kind of DOC is exported and why.

As mentioned by the reviewer, the goal of the paper is to explore the various ways and processes which can lead to the discontinuity in DOM composition between peat porewater and to pools, within the framework of the sampling and analyses. The paper illustrates well the complexity of the DOM composition and the processes involved. Through this complexity, we tried to identify which processes can explain the discontinuity between peat porewater and pools. Our work led to the hypothesis that biological processes, through microbial degradation, is one of the explanations of the differences we observed. However, we would emphasize that as it is a sum of processes, we cannot totally exclude other processes that can play an important role and are mentioned in the paper. The manuscript was reworked thanks to the comments made by the reviewer. We emphasized and clarified some aspects of our discussion, mostly through the section 5.2 for this particular comment (l. 469-477).

"The surface flow path could also be supplied by a deep-water source enriched in DOM. It has been shown that deep flow path (below 2 m depth) could supply the surface flow (Levy et al., 2014; Peralta-Tapia et al., 2015) This upward movement of water might transport deeper DOM to the surface waters (Campeau et al., 2017). This movement of water might explain the differences in DOM composition observed between peat porewater and pools as it was supplied by a deep horizon rather than lateral transport. However, the DOM composition in deep layers is supposed to be relatively similar to the composition in surface peat with a high aromaticity and average

molecular weight (Tfaily et al., 2018). This is not comparable to the DOM composition observed in pools (Fig. 2) and suggest that this process might only partially contribute to the shift in DOM composition between environments."

4) Technical corrections

21: Please change "If" to "While".

The text was modified (l.20).

39: Please delete "net".

The text was modified (l.39).

49: What processes of organic carbon do you refer to?

The text was adjusted, and processes are now mentioned (l. 50).

"While most studies of peatland carbon dynamics have focussed on terrestrial microforms (Nungesser, 2003; Pelletier et al., 2011; Shi et al., 2015; Chaudhary et al., 2018; Graham et al., 2020), the composition and processes of production and degradation of organic carbon in pools remain poorly documented."

77: This paper presents a study about DOC lability from boreal peatlands with porewater sampling (https://doi.org/10.1139/cjss-2019-0154), so the authors may want to change the argument that no insight about changes in DOM composition in boreal peatlands.

We are thankful for the reference suggestion. But as the reference presents a study that takes place in a site affected by permafrost, the text was adjusted in consequence to be more consistent with our study site which was not affected by permafrost (l.78).

"Studies investigating the changes in DOM composition in peatland porewaters and pools have mostly been focused on temperate (Banaś, 2013; Arsenault et al., 2019), subarctic, and Arctic regions (Laurion and Mladenov, 2013; Deshpande et al., 2016; Burd et al., 2020; Payandi-Rolland et al., 2020; Laurion et al., 2021; Moody and Worrall, 2021), but there is no insight about changes in DOM compositions in boreal peatlands non affected by permafrost."

141: It's not clear what monitoring "among others" refers to.

This formulation was actually not clear and removed from the text as it does not give any pertinent information (l. 144).

178: Both UV and fluorescence are optical analyses.

The title of the section 3.4.2 was corrected in consequence.

3.2.2: Is it better to shorten this part and highlight the key information, as it's effectively repeating what's in each of the graphs in Fig. SI.3.

The section was shortened and only the pertinent part of the text was kept (l. 145-149).

"Samples from the two studied years were pooled according to seasons. In this study, seasons were defined based on air and water temperatures measured at the site (Fig. SI.3). Spring was defined from the end of the seasonal thaw that occurred in May to the end of June. Summer included the months of July and August when air and water temperatures were at their warmest. Finally, the autumn season corresponded to the months of September and October when air and water temperature decreased to zero."

185: What calibration was conducted after observing the difference in Abs254?

As the differences between the two methods were very low and there were no significant differences between years for absorbance index, we decided to keep it without any post-calibration. This is mentioned in the text (l. 181).

"As no significant effect was observed between years on absorbance indices, no correction was performed on absorbance spectra."

185-230: the description of the method details can be simplified, and information of each index presented more systematically. It's a bit lengthy with much detailed information.

The reviewer can refer to the comment we made on the first section 1) of the present response letter.

233: Can just use DOM as being introduced already. Please check throughout the manuscript.

The first mention of DOM is l.16 in the Abstract and l.51 in the introduction.

238: I'm not fully convinced this mixing was necessary. The variability can be considered in the statistical analysis. And why did the authors only mix the porewater but not the pool samples?

The mixing was performed because the quantity of water in piezometer was limited and not sufficient to perform all incubation conditions. The text was corrected in consequence in the methodology section (l. 238-239).

"This strategy was used because the quantity in piezometer was limited and not sufficient to perform all incubation conditions."

214: Was there additional cover for the amber glasses to completely block out the light? Did you test the light penetration through the vials?

The opacity of amber vials was not tested. However, the reviewer can refer to the comment we made in the section 2) of the present letter. We mentioned that no significant differences were found between the incubation in dark condition and in sunlight condition for amber vials.

246: Why was the porewater samples placed at the outlet instead of inside of the wells? Was it because the authors wanted to monitor the hourly temperature? In addition, the authors didn't provide information on if there was headspace in the glasses/vials, if they were open during the incubation for gas exchange.

The porewater samples were placed at the stream outlet for different reasons. Firstly, because the vials did not fit in wells. Secondly, to test the effect of photodegradation and to monitor the temperature. Finally, because those incubation were also performed in the stream, then the incubation of pore water in the stream simulate the transfer of peat porewater DOM to surface water.

As the bottle used were 125 mL and 100 mL were incubated, a headspace of 25 mL was kept. The bottles were closed.

Thank you for noticing these omissions, and the text was modified (l. 241-243).

"Amber glasses of 125 mL were used to test biodegradation (BIO) only and transparent vials of 125 mL were used for bio and photodegradation (BIO+PHOTO). Each condition was incubated in triplicates with a headspace of 25 mL and bottles were tightly closed."

253: Do you mean both DOC and TN were measured, or a ratio of DOC/TN was examined directly?

It was DOC and TN measured and the text was corrected (l. 352).

"All samples (n = 36) were prepared for DOC, TN and inorganic N quantification, and absorbance analyses, before and after the incubation experiments."

Table 1 and Figure 2: Is it necessary to have both in the results, as they present mostly the same results.

We think that both figure and table are complementary as Table 1 present most of the indices derived from analyses while Fig. 1 present the key results.

Fig.2: Why were there seasons with <5 samples? In the methods, it says 6 pools in 2018, 11 in 2019, and 6 wells in 2019.

Some analyses were not performed systematically on all samples. While it was mentioned from THM-GC-MS analyses (l. 198-199) the omission was corrected for stable isotopes analyses (l. 165-166). The table added in SI. Thanks for the recommendation that will help the understanding.

"Analyses of δ13C-DOC were realised on 41 samples selected from peat porewater (n = 20) and pools (n = 21; Table SI.1) at the Jan Veizer stable isotope laboratory (University of Ottawa, Canada) following the method developed by Lalonde et al. (2014)."

Fig.3: The negative relationship mainly existed in the porewater samples, while the correlation for the combined samples was not that good with cor = -0.53. Maybe it would make more sense to look at the relationship separately, which would help highlight the different C dynamics between the two C sources.

As it was previously mentioned, at this point we decided to remove the figure.

334: There are several cases throughout the paper saying e.g. "As for SUVA254", or 'As for the FI". Do you mean compared to the changes observed in SUVA254? Can you refine this please?

The text was refined where this kind of formulation was written (l.334, l.349 and l.367).

"Compared to SUVA254, the E2:E3 ratio showed no significant trends in peat porewaters, but it slightly increased in pools from 4.02 ± 0.11 in spring to 4.41 ± 0.18 in autumn, suggesting a decrease of the average molecular weight during the growing season (Fig. 2.e)."

"As the changes observed for the FI, variations of the β:α index were limited to a small range."

"Comparatively to the variations observed for the C/V ratio, fVEG remained almost stable in pools, while it decreased in peat porewaters in autumn."

375: DOC:Cl does not seem to be mentioned in the method. I understand the authors may have more data than presented in the paper, but please check and avoid mistakes like this.

The mention of DOC:Cl was removed.

380: Can you include the PCA analysis for the seasonal effect, maybe in supplementary information?

This is the same figure as the one presented in the paper but with colour separation according to the season and no emerging trend. We are not convinced of the pertinence of this figure given the very small weight of the season in the PCA.

Fig 4: Caption was repeating the text in the results so could be shortened. Does DOC:Cl actually refer to DOC: DON? Information on R package for ellipses is not needed here but can be in methods.

The text was shortened in the caption of the figure.

"Figure 3. Representation of the first two dimensions of principal component analysis (PCA) of a) physicochemical, quantitative, and qualitative parameters as variables and b) individuals."

387: Could delete "Statistical tests also revealed that" and replace with "In addition, the..".

The text was simplified according to the comment of the reviewer.

"The degradation rates were significantly higher for the incubation conditions of unfiltered samples (UF) compared to filtered sample (F) conditions (Fig. 4)."

391: Was the absence of filtered samples in August considered, as this could skew the difference between the two treatments?

We are very thankful that this hypothesis has been pointed out. After refining the statistical analyses, no significant differences were found between the degradation rates under filtered and unfiltered filtration a) for samples of spring and autumn season only in peat porewater and pools

(AOV, F = 2.631, p-value = 0.11). However, filtered and unfiltered conditions were significantly different in peat porewater only for all seasons (Welsh AOV, statistic = 6.04, p-value = 0.02).

We adapted the paper accordingly, but we kept the figure per Filtered and UnFiltered condition as the significant differences are still conform when peat porewater was grouped for all seasons (l. 396-397) and adjustment was made in the discussion (l.520-522).

"After excluding the UF condition of August, there was no persistent significant differences between F and UF conditions."

"Degradation rates under unfiltered conditions in pools were two times lower than for peat porewaters and no significant differences were observed in spring and autumn."

412: The sentence needs some changes.

This was noticed and the text was modified.

"The DOC concentrations in peatland peat porewaters exhibit a latitudinal gradient, from DOC concentrations commonly lower than 20 mg L-1 in boreal and sub arctic zones compared to temperate zones during growing seasons (Table SI.4)."

505: Is this 136350m3 the volume of the pools in this study? While it's small DOM degradation in these sites, what would it be if scaling up for the whole Bouleau peatland? It may not only be 'slight effect' if considered collectively. In addition, seasonal variation in DOC concentration and degradability could also mean that in some months, the pools may act as 'hotspots' for GHG emission, which would be important information for peatland management along with global warming.

As the objective was to evaluate the impact of DOM degradation in pools particularly, we did not scale it to the whole peatland surface. The DOM degradation in peatlands is driven by numerous other factors and mainly water table depth variations and is coupled with CO_2 and CH_4 dynamics. It is a larger process the research group will explore in a future paper.

However, the reviewer raised an interesting point. As degradation rates varying during the growing season, it is an important element we considered it in the discussion (l. 533-537).

"It is also important to note that the DOM in pools presents characteristics of recently produced DOM transferred from peat, its biodegradation might not affect importantly C from deeper peat horizons."

515: I may suggest an alternative next step to explore the effects from pools and peat morphology on DOC transport from peat to water, as it is not so clearly assessed yet but could be important as regulating the water and DOC sources.

This point was more detailed, and, in the conclusion, we propose a better coupling of both DOM and hydrological dynamics (l. 561-563).

"As the dynamic of DOM in peat porewater seems closely connected to the hydrology of the peatland, it seems important to better connect it with the water sources and its circulation through the peat."