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 #1 – Audrey Campeau

This paper presents a large and detailed investigation of DOC concentration and composition in peat 4 porewater and pools in a pristine peatland in northern Quebec. The dataset is interesting. As clearly stated in the title, the study reveals major “discontinuities” in DOC concentration and composition between porewater and pools within a peatland. This could have been done with a single spatially distributed sampling, but the authors complement this dataset by repeating the sampling over 2 different seasons. The seasonal sampling corroborates the initial findings of “discontinuity” in the DOC concentration and composition between these two environments. Whatever hydroclimatic conditions, the DOC in the pools and surrounding peat porewater seems to be considerably different. Overall, I find the dataset presented here to be interesting and the methods and statistics are sound. However, I have some concerns over the interpretation of the findings and how they support the conclusions of the study. In addition, I have made some recommendations to improve the data visualizations and some elements of the text, mainly the discussion.

We thank the overall positive evaluation made on the submitted manuscript and the constructive received. We are pleased to note that the reviewer recognized the contribution of the multiple sampling periods. It is an important aspect of our work that we are very excited to present. The repetition of sampling periods over two growing season is, in our opinion, very important to catch both discontinuities between the peat porewater and the pools but also the temporal dynamics of both DOM concentrations and composition. In the following letter, we hope we addressed all the comments made by the reviewer on the previously submitted version of the manuscript. We hope we clarified the interpretation of our data and the conclusions.

1) Causes of discontinuity

The peat reaches 4 m deep in some locations (line 106) (often near the pools based on the map in Primeau and Garneau 2021), but the porewater sampling considered only the top 2m (Line 125). I expect the reason for that is the assumption that hydraulic conductivity decreases exponentially with depth (stated in discussion 460-466). Therefore, the porewater in the bottom 2m of the peat profile is considered to move very slowly and contribute little to runoff generation or the water contained in pools. However, deep preferential flow areas exist in many
peatlands (often below 2m deep) (e.g. two Swedish studies DOI: 10.1111/gcb.13815, DOI: 10.1002/hyp.10300 [one where I was involved, sorry for citing myself], UK peatlands (e.g. DOI:10.1016/S0341-8162(01)00189-8) and GLAP peatlands (DOI:10.1002/2016GB005397, DOI: 10.1002/hyp.9983 ). These studies have shown that deep peat horizons can contribute to a large fraction of the runoff generation, or at least be hydrologically active. The high hydrostatic pressure in deep peat preferential flow areas can make that water emerge rapidly to the surface in specific locations, for example in streams or pools. Could this also be the explanation here? The water and C found in pools could in fact be feed predominantly from the bottom instead of laterally? This could also explain why the water table is more stable in the pools than the peat porewater (Line 300, Fig SI2). Hence, the discontinuity in DOC concentration and composition observed here could in fact be due to that the sampling didn’t capture the actual source of water and C (if it is located below 2m deep). The difference in specific conductivity between the pools and peat porewater, which here could act as an independent water tracer, indicates different water sources (Line 304-306).

Assuming the authors finds this to be a plausible explanation, I want to highlight that I still find the results of the study to be interesting and relevant by simply highlighting the major and persistent disconnect between surface porewater and pool water. This disconnect possibly arises as a result of the complex hydrology of peatlands. Maybe the paper would benefit from emphasizing this disconnect rather than to suggest a “common source” and find a reason for the apparent discontinuity (which are suggested to be a combined result of hydrological, chemical and biological process) (see my comment on the discussion). Maybe it’s my background showing here, but I believe a missing water source could explain nearly all the observed patterns in this dataset.

We thank you for this comment, suggestion and references. We examined the hypothesis of a deep-water source in pools, explaining the discontinuity we observed. We agree that our experimental design did not allow us to test the hypothesis of a deep source of water supplying DOM to pools. However, we think it is unlikely that the DOM present in pools derives predominantly from deep peat horizons – although it could still partially contribute to fuel the pools with DOM. Upward water movement in peat seems very unlikely at our site. Glaser et al. (2016) partly linked deep horizons water movements with groundwater dynamics at the watershed scale. As the site is surrounded by the Canadian Shield, the aquifers present low conductivity and is unlikely s hydrologically connected to the peat.

The work presented by Holden and Burt (2002) focused on the hydrological dynamics associated with peatland pipe. However, this feature is not present in our site. Thus, the site conditions are very different between our studied peatland and the one from Holden and Burt (2002) which makes the comparison difficult.

We included the hypothesis of upward water movements which supplying pools in DOM in the discussion and included some discussion on DOM composition in deep horizons, based on the work of Tfaily et al. 2018 (l. 471-479).
“The surface flow path could also be supplied by a deep-water source enriched in DOM. It was 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 surface waters (Campeau et al., 2017) and 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 depth 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.”

2) The common source

The section 5.1 of the discussion claims that the differences in DOC concentration and composition hide a common source. The author claims that a common source to be C3 plant-derived, which leads me to wonder - what else could it have been in a boreal peatland? I have several issues with this aspect. 1. It seems obvious to me that the DOC would be predominantly plant-derived in a peatland and therefore doesn’t constitute a hypothesis that needs testing nor a substantial finding out,

One of our first goal when designing this study was to evaluate the contribution of aquatic primary production. Based on our results, the message has evolved towards stressing the importance of terrestrial markers into the pools rather than testing the hypothesis of the plant-derived DOM source into peat porewater.

We have modified the manuscript to remove the ambiguities about the DOM source and the term “hide” was removed from the title of the section 5.1 (l.409).

“5.1 Differences in DOM concentrations and composition between peat porewaters and pools but a similar source”

2. The author hasn’t clearly stated what other possible sources could be, I suppose these are “C4 plants”, which generally are absent at this latitude or “microbial-derived” which are certainly overridden by the decomposing peat material.

We agree that the aspect concerning DOM source needs to be clarified and have made the necessary changes throughout the manuscript. It its particularly clear that no other source than C3 plants was expected in peat porewater DOC. In pools, in situ primary productivity was considered to be a second potential source. However, primary productivity was not observed to be of substantial contribution at our site but still needed to be mentioned. We adjusted different parts when the DOM sources were mentioned:

- in the abstract (l. 21-22)

“The molecular analyses and the DOC:DON ratio showed that DOM in pools was derived from the peatland.”

- in the introduction (l. 58-60)
“The DOM of pools may derive from surrounding terrestrial peat (i.e., allochthonous) or be the result of their internal primary production through phytoplankton and microbial production (i.e., autochthonous).”

- in the discussion (l. 430-431).

“Our results indicate a dominant plant origin of DOM and reflect the dominant contribution in allochthonous DOM in pools.”

3. The vocabulary often changes, sometimes this source is referred to as “terrestrial contribution” “vegetation origin” “plant-derived”. I suggest that the other clarifies both the hypothesis tested here and the vocabulary.

We agree that rather than use the expression of “common source”, we need to emphasize that the results showed that the DOM in pools was derived from the transfer of plant-derived DOM, produced in peat. According to this statement, the terms “referring to the DOM source in pools” were changed and homogenized to “plant derived” or “plant origin” (l. 193; 430; 432; 437; 555).

This leads me to further concerns over the interpretation of the d13C-DOC values and the correlation between d13C-DOC and DOC_DON ratio in Figure 3. The d13C-DOC values reported here varies across a narrow range (-25 to 28‰) and show that DOC originated from C3 plant metabolism. Meanwhile the C:N ratio show that the DOC is strongly terrestrial as opposed to aquatic. This is not surprising. But I doubt that anything else can be said of these values. What is the interpretation of the correlation Fig 3? The discussion mentions this correlation briefly on line 421-423 and Line 434-436 (albeit a missing reference to the figure here). The authors state that this correlation reveals that DOC comes from plant leachates instead of microbial exudates, but I don’t see how this is supported. The study cited here (Magill and Aber, 2000) has no mention of the stable C isotopes. Are you suggesting that there is a fractionation process taking place here, whereby DOC becomes lighter with increasing DOC:DON ratio due to microbial or photodegradation? Below is a typical biplot from a review paper on d13C-DOC and DOC:DON across ecosystem types that puts in context your data

As we can observe in the shared picture, our data clearly present typical $\delta^{13}$C-DOC of both terrestrial plants and freshwater DOC as expected. However, within this range, we think it is relevant to emphasize that our sampling strategy allowed us to capture $\delta^{13}$C-DOC evolution. We observed divergent trends of $\delta^{13}$C over the growing season between the two environments. In peat porewater, an increased contribution of plant-derived DOM seems to be occurring. In pools, we think that the increasing values were related enhanced microbial processing of DOM.

Concerning the use of the DOC:DON ratio, it is worth noting that at our site, we measured DOC:DON ratio exceeding 50 in pools, outside of the range of freshwater DOC presented in the table above. The DOC:DON ratio is also important to document the variations within the pools as a slight but significant increase was observed during the growing season (Fig. 2 and Table SI. 2).

We agree that the use of the correlation between DOC:DON ratio and $\delta^{13}$C is not necessary to explain the discontinuity we observed between the peat porewater and the pools. As this point, we decided to remove it.

3) The role of biodegradation and photodegradation in peatlands

Are local differences in DOC lability really important for a peatland given that other environmental factors limit the metabolism in peat porewater. It's again interesting to measure the lability of DOC as a tracer of DOC sources, but other possibly more important factors limit the degradation of DOC in peat soils. The author also states that the slow hydraulic conductivity
increases residence time and therefore the potential transformation of DOC. This is true for most surface water environment (e.g. 10.1038/ngeo2720), but other possibly more important factor (e.g. electron acceptor availability) limit microbial metabolism in peat. I am not sure this is a relevant argument here, especially since hydraulic conductivity and water residence time were not quantified here as far as I am aware. DOC will be degraded once the environmental conditions allow it, and that is possibly outside of the peatland catchment boundary.

Concerning the degradation experiments, the goal of this approach was not to trace the sources of DOM but 1) to test the sensitivity of DOM of different environments to the main degradation processes and 2) to document how those processes can impact DOM composition. This was adjusted in the method section (l. 231-233)

“The objective of DOM incubation experiments was to test the sensitivity of DOM to biodegradation and photodegradation and determine how it could affect its composition. The incubation experiments were designed to test the effects of temperature and total organic carbon versus dissolved organic carbon. “

We agree that the degradation of DOM can happen downstream and outside the peatland boundaries. However, many studies point out the degradation of DOM also occurs in peat porewater (Hutchins et al., 2017; Worrall et al., 2017). This is supported by the increase of microbial markers we observed in summer in peat porewater (see fMIC and %LMWFA in Table 1).

As the limitation of microbial metabolism that can occur in peat. The manuscript was modified in consequences (l. 481-483).

“However, the low cations and anions concentration in ombrotrophic peatlands (Gogo et al., 2010) and the low-nutrient availability (Bengtsson et al., 2018) might limit the microbial degradation of DOM in peat porewater.”

I find interesting that the authors quantify the potential photodegradability of the DOC to understand the possible fate of the DOC in downstream environments. But I doubt that photodegradation within this peatland catchment can possibly be an important process for the overall peatland C budget, given 1. the limited amount of light penetrating in peat and pools, and 2. The small areas covered by the pools. The DOC being transported with water will eventually leave the catchment boundary and maybe then photodegradation can then play a role. I find interesting that this aspect was quantified as a way to characterize DOC properties and act as another tracer of DOC sources, but the way it’s presented here, in a context of a mass budget and as a possible mechanism for the disconnect in DOC between porewater and pool seems overstretched.

The incubation experiments under sunlight exposition were a way to test the sensibility of peat porewater and pools DOM to photodegradation within the limit of the peatland catchment. This process is known to affect DOM concentration and composition in boreal surface water (Lapierre and del Giorgio, 2014) and DOM composition in Arctic peatland thaw pools (Laurion and Mladenov, 2013). The key message of our experiment was the absence of sizeable effect of photodegradation on DOM composition and concentration. According to the absence of
significant differences between the condition of biodegradation and photo + biodegradation, the average degradation rate was used in the mass budget we calculated (l. 527). As the photodegradation do not appear to be an important process in DOM concentration differences between peat porewater and pools, we did not discuss the importance of this process in the context of mass balance. It was discussed in the context of differences in DOM concentration and composition between peat porewater and pools for the peatland net C budget.

4) The influence of DOM adsorption

The peat porewater samples were collected through a PVC tube covered with a nylon sock. I would assume that the porewater DOC that is adsorbed to the peat to not sampled then. So can this mechanism really be important to explain the discontinuity between pool and porewater DOC?

We agree that the sampling method used to collect peat porewater potentially exclude a fraction of DOM which could have been adsorbed to the PVC tube. The water collected is the one mobile into peat and thus potentially transferable through the pools and we modified the text in consequence in the method section (l. 126).

“This method allows to collect the mobile water which circulate into the peat.”

The discontinuity was also observed when the peat-pool gradient was performed in 2019 using another sampling method (detailed in the SI). The sampling method was not through PVC tubes but by applying a depression with a peristaltic pump and collected through laboratory-grade plastic tubes. The DOM sampled with this method supported the trends we observed for DOC concentrations, DOC:DON ration, SUVA\textsubscript{254} and E2:E3 ratio, confirming the limiting effect of adsorption processes. However, a limitation of this sampling method is that it was harder to sample porewater at depth below 100 cm into peat.

5) Adjustments of Data Visualization

Figure 2 is a key figure presenting the data, but I find the box plot to be an ineffective choice of visualization in this case. There are too many plots and too many things being compared for this type of plot to work. A more effective visualization could be a parallel coordinate plot (e.g. https://datavizcatalogue.com/methods/parallel_coordinates.html). Each vertical axis would represent a different variable (e.g. DOC concentration, DOC:DON etc.), and each line moving laterally would be a different sample location. I would suggest to fade the peat porewater samples in the background and superimpose the pool water samples on top in a darker color to help compare these two environments. You could even make it a three panel figure, one for each season. This would allow to see at a glance, which site/season bear most similarities and differences for all variables. If possible, maybe also indicate the meaning of optical properties on the axis, for example (higher SUVA values is more aromatic and lower is less aromatic etc.).
This would facilitate the visual interpretation. This plot would also give the possibility to merge figure 5 and figure 2, in this case by adding another vertical axis for degradation rates.

If you choose to stick to the boxplot format please add letters on the x-axis to show statistically different groups. (e.g. function multcompLetters in R, library multcompView)

We thank the reviewer for the visualization suggestion. We took the comment into account and obtained this new version of the Fig. 2. We did a parallel coordinate plot with color represents the environments and the line-type the season for centered-reduced means of variables considered in the previous version of the figure.

However, the conception of the figure was challenging, and we were forced to apply a data transformation (centered-reduced means) and to represent average values per environments and per seasons. For this reason, we consider we loose too much information and we decided to keep the first version of the Fig. 2. In the Fig. 2, letters were added to identify the statistical differences between groups (seasons and environments).
Can the symbols in the PCA (Figure 4) be the same as in Figure 6? Also note that all symbols in figure 6 are circles so there is an error here. The figure 4 could also be bigger for better readability.

The size of the fig. 4 was changed and the symbols were homogenized with the fig. 6. In the Fig. 6, all shapes were changed for circles as the season was not a factor we discussed.
6) Line by line comments

**Line 69 to 78:** Those lines might fit better in the discussion if you choose to emphasize the differences in DOC sources between porewater and pools.

We think that this section is important in the introduction as it presents how the differences that have been observed between peat porewater and pools can be the consequences of many processes we actually refer to later in the discussion.

**Line 383:** Is it the “average” or “median” degradation rate that was statistically significantly different?

As the statistical test was ANOVA, it is the average that was is compared. The text was modified (l. 381).

“Statistical tests revealed no significant differences in the average degradation rates between in situ and controlled conditions of biodegradation (section 3.5.1).”

**Line 410:** Be more specific here. Is it the average or range in DOC, porewater or pool water? It can also be helpful for the reader that you write in bracket the number you are referring to, even if they are available in the table SI3.

The text was modified accordingly, and the term average was added (l. 410).

“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).”
Line 412-414: Do you mean here that the subarctic and boreal peatlands have on average 20 mgCl less DOC than temperate ones? Be more clear about what you are comparing here. Also, sentences starting with “A synthesis...” or “a study...” make the text more tedious. You can go straight to the point here and say for example. Porewater DOC concentration in peatlands exhibit a strong latitudinal trend, whereby boreal and subarctic peatlands contain ...

The text was adjusted and simplified in the first paragraph of the section 5.1, thanks to the comment (l. 410-415).

“The average DOC concentration measured in peat porewater at our sites during the growing season is 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 subarctic latitudes compared to temperate latitudes during growing seasons (Table SI.4). This observation, in line with our results, suggests a temperature control on the balance between DOM production and processing (Kane et al., 2014).”

Line 421: Instead of comparing with the name of the study, you could refer to the type of peatland that was studied in this paper Also, why are you making this comparison, again the argument is missing here: The DOC:DON ratios measured in peat porewaters at our study site were up to six times higher than in Austnes et al. (2010) “suggesting that ...

The text was modified and now refers to the study site’s region rather than the paper cited. Also, the text was modified, and an argument supporting the use of this reference was added to justify the reference cited (l. 421).

“The DOC:DON ratios measured in peat porewaters at our study site were up to six times higher than in a Welsh temperate peatland (Austnes et al., 2010). These high ratios suggest a strong signature of plant leachates in peat porewater DOM composition.”

Line 452: This is a hypothesis here, no? The photodegradable fraction of DOC might have already been degraded prior to sampling, but the way it’s written here makes it sound like you are certain that’s the case.

We agree that the phrasing might be confusing. The message here is that we hypothesize that the higher aromaticity we observed during the punctual sampling is in line with the increase of SUVA254 observed during the incubations and support the biodegradation of DOM in peat porewater. The text was modified in consequence (l. 451-456).

“The absence of sizeable photodegradation suggests that this process did not drive DOM composition in pools. The clear pattern of the SUVA254 increase observed during the incubation period was independent of the conditions where DOM was exposed to solar radiation. This is coherent with the biodegradation of non-aromatic molecules (Spencer et al., 2008, 2015; Mann et al., 2015; Worrall et al., 2017) leading to an increase of SUVA254 (Hulatt et al., 2014; Autio et al.,
while photooxidation has been shown to induce a decrease of DOM aromaticity (Laurion and Mladenov, 2013; Ward and Cory, 2016).

**Line 453:** *By consumption here you are referring to the biological pathway, not the photochemical one. Please clarify.*

Indeed, it is biodegradation. The text was corrected (l. 453).

“This is coherent with the biodegradation of non-aromatic molecules (Spencer et al., 2008, 2015; Mann et al., 2015; Worrall et al., 2017) leading to an increase of SUVA254 (Hulatt et al., 2014; Autio et al., 2016) while photooxidation has been shown to induce a decrease of DOM aromaticity (Laurion and Mladenov, 2013; Ward and Cory, 2016).”

**Line 462:** *can they “be explained by” or they can “arise as a result of”. This sounds like you are pleading a case for more “positive” result, while a more “negative” result in this case can be even more interesting.*

That is an excellent remark. We tried to find a better formulation and the sentence was changed as follows (l. 459-460).

“The observed differences in DOM composition between peat porewaters and pools and its persistence during the growing season was driven by a combination of hydrological, chemical, and biological factors.”

**Line 463:** *That doesn’t mean that water cannot be constantly filled from the bottom and just occasionally sourced from surface peat when the water table is high.*

We modified the text according to the general comment you made about the upward contribution of water and DOM (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.”

**Line 410:** *The reference to table SI3 should be placed at the end of the sentence.*

The text was changed (l. 413).

“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).”
Why mention this latitudinal effect? There seems to be an argument missing here. Do you mean that your data fit in with other peatlands at the same latitude? Please clarify.

This part was for contextualizing the results at our study site. We hope that the modifications made in this section make this paragraph clearer (l. 410-415).

“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 subarctic zones compared to temperate zones during growing seasons (Table SI.4). This observation, in line with our results, suggesting a temperature control on the balance between DOM production and processing (Kane et al., 2014).”

If the pools allow old DOC to make its way to the surface and therefore enter the peatland contemporary C cycle then they become very important for the stability of the old peat C stock. But based on the molecular weight indexes, the DOC seems younger in the pools than porewater.

We modified the text according to your comment (l. 532-536).

“This study highlighted that DOM is a highly dynamic component of the carbon cycle in peatlands, with important changes identified in its concentration and composition in both peat porewaters and pools. This discontinuity was persistent throughout the growing season and different hydroclimatic conditions.”
Line 525: Or is the concentration just increasing because it gets drier? Maybe check if this difference persists once the DOC is volume-weighted based on water table position?

The hypothesis of increase in DOM production is based on the postulate that higher temperatures during summer are known to influence DOM production in peat porewater (Laudon et al., 2012; Grand-Clement et al., 2014; Zhu et al., 2022).

Line 534: The term “physicochemical parameters” is vague.

The text was refined (l. 572).

“The rapid modification of physicochemical conditions (e.g., temperature and oxygen availability) between those environments might favour the biodegradation of DOM at the interface between the peat and the pools and within the pool.”

Line 535: What you say here is true, but I find it to be a disappointing end to a paper. The last sentence of the conclusion is very important, and I am sure there is more an interesting take home message to be given here.

We proposed a better take home message centered around the discontinuity (l.571-574).

“The strong discontinuity of DOM concentration and composition observed between the peat porewater and pools and its persistence during the growing seasons, and under different hydroclimatic conditions emphasize the significance of small spatial scales processes.”

Table SI.3: DOC mean and SD?

This is mean and SD and the text was corrected.

Fig S1: If E2:E3 and Sr are both proxies of molecular weight (Line 189), why is it that they correlate so poorly?

This is mainly because even they are both proxies for molecular weight, they are associated with different fractions of DOM. The E2:E3 is also negatively correlated with the DOM aromaticity (see the negative correlation with the SUVA254 in Fig. SI.1) while the Sr is also associated with the microbial metabolism (see the positive correlation with the deoxyC6:CS and the %CARMIC in the Fig. SI.1).