

# Reviewer 1: comments and answers

## General comments

This manuscript, which investigates the pools and export of C, Fe, and Pb in a hemiboreal mire, is generally well written, fits well within the scope of the journal, and will likely be of interest to the audience of Biogeosciences. The findings showing increased DOC and Fe mobilization following drought periods, as well as the role of hydrological connectivity in regulating DOC and Fe export from peatlands, are consistent with previous research. Placing these results within a broader climate change context is valuable. Moreover, the inclusion of the heavy metal perspective is intriguing, and the observation that peat decomposition in peatlands affected by climate change may pose a risk not only through the loss of stored C but also via mobilization of toxic heavy metals to the surrounding environment adds an important and novel dimension to the study.

## Specific comments

### Question 1.1

The study objectives are not entirely clear upon reading the manuscript. The research questions are introduced without a clear structure, and the final paragraph of the introduction provides only a very general statement of the aim of the study. I recommend that the authors present the study objectives more explicitly and potentially include specific hypotheses/predictions in the introduction to better guide the reader.

### Answer

The first paragraph in the introduction will be amended to also introduce the “anthropogenic aspect” as well as DOC, and now more explicitly addresses the overall question we investigate throughout the manuscript: How changes to peatland hydrology and climate affect the export of DOC and metals, in particular Fe and Pb and how their transport is related to DOC

- 1) The objective stated in the end of each paragraph in the introduction sections has been described more explicitly now.
- 2) For the next version of the manuscript, something along the line of: The overall aim of this study is to investigate the export of DOC in relation to Fe and Pb over a 4-year period, will be added.  
Specifically, we might add the hypothesis: Fe and Pb concentrations in stream water leaving the peatland are positively correlated with DOC, and both increase in summer due to warmer and drier conditions that enhance DOC production.

## Question 1.2

The manuscript lacks clear definitions of the topography types and information regarding their spatial scale. It is specified that the topography types were sampled 1-2 m apart, but the typical size or extent of these structures is not described. I furthermore lack a discussion of the observed differences in the physical and chemical characteristics among different topography types.

## Answer

Mycklemossen is composed of a mosaic of hummocks and hollows with transitions zones, called intermediate in our study, but mostly dominated by hummock (Rinne et al., 2022). The hummocks are mainly dominated by *Eriophorum vaginatum*, *Calluna vulgaris* and *Erica tetralix* and the hollows consists of different *Sphagnum* species, mainly *S. rubellum*, *S. fallax* and *S. austinii* as well as *Rhyncospora alba*, and the peat samples were sampled approximately within a square meter plots (Kelly et al., 2021).

The only parameter that was significantly different between topography types was SOM content ( $p=0.04$ ), while pH, N% and C/N was significant when testing for type x depth interaction (Table S6).

SOM content is affected by decomposition contra production of new organic matter. Hummocks are generally harder for microorganisms to degrade compared to hollow species, due to a higher content of recalcitrant components, primarily non-carbohydrate compounds as lignin-like compounds and secondary metabolites (Limpens et al., 2017; Mäkilä et al., 2018; Turetsky et al., 2008). Therefore, the higher SOM in hummock compared to the other topographies, particularly in the top of the mire, is likely due to less decomposition taking place in relation to production of new biomass compared to hollow species.

The formation of secondary metabolites and more structural compounds is likely also the reason for the higher N% in hollow species, as the metabolites and more structural compounds are high in C content.

Kelly, J., Kljun, N., Eklundh, L., Klemedtsson, L., Liljebladh, B., Olsson, P.-O., Weslien, P., & Xie, X. (2021). Modelling and upscaling ecosystem respiration using thermal cameras and UAVs: Application to a peatland during and after a hot drought. *Agricultural and Forest Meteorology*, 300, 108330. <https://doi.org/10.1016/j.agrformet.2021.108330>

Limpens, J., Bohlin, E., & Nilsson, M. B. (2017). Phylogenetic or environmental control on the elemental and organo-chemical composition of *Sphagnum* mosses? *Plant and Soil*, 417(1), 69–85. <https://doi.org/10.1007/s11104-017-3239-4>

Mäkilä, M., Säävuori, H., Grundström, A., & Suomi, T. (2018). *Sphagnum* decay patterns and bog microtopography in south-eastern Finland. *Mires and Peat*, 21, 1–12. <https://doi.org/10.19189/MaP.2017.OMB.283>

Rinne, J., Łakomiec, P., Vestin, P., White, J. D., Weslien, P., Kelly, J., Kljun, N., Ström, L., & Klemetsson, L. (2022). Spatial and temporal variation in  $\delta^{13}\text{C}$  values of methane emitted from a hemiboreal mire: Methanogenesis, methanotrophy, and hysteresis. *Biogeosciences*, 19(17), 4331–4349. <https://doi.org/10.5194/bg-19-4331-2022>

Turetsky, M. R., Crow, S. E., Evans, R. J., Vitt, D. H., & Wieder, R. K. (2008). Trade-Offs in Resource Allocation among Moss Species Control Decomposition in Boreal Peatlands. *Journal of Ecology*, 96(6), 1297–1305. <https://www.jstor.org/stable/20143576>

### **Question 1.3**

The depth resolution of the measured variables, especially for the metals, is coarse. Consequently, statements such as that on line 292; “Peat Fe concentrations at the top of the mire were between 606 and 1237 mg/kg and barely changed until below 120” are problematic, as no data are available for the interval between 50 and 120 cm depth. This limitation should be acknowledged in the manuscript.

#### **Answer**

Yes, there will definitely be variation in concentration of metals in the peat cores we do not see with our depth resolution (quite large std. on concentrations, SI table 1), and we acknowledge this. The text will be rephrased to a more neutral language: Peat Fe concentrations at the top of the mire were between 606 and 1237 mg kg<sup>-1</sup> and was measured to between 1434 and 1474 mg kg<sup>-1</sup> in 120cm depth (Fig 4, Table S1).

### **Question 1.4**

The introduction currently lacks a clear motivation for including the lake measurements. The objectives stated at the end of the introduction are rather general and focus solely on the mire.

Interestingly, the substantially higher export of C and Fe from the lake compared to the inflow to the lake points to other sources than the mire. This observation could be explored further in the manuscript, and the relative contribution of the mire to the overall hydrological inflow to the lake could be clarified if this data is available.

#### **Answer**

The lake has more than twice as large catchment area than the mire and the discharge is substantially higher. Hence, a lot of water is coming from the forested land around the lake, and this can be expected to be high in DOC (maybe also Fe, as there are e.g. Podzols in the area). That means the lake receives a lot of DOC and Fe from the forested land, but not Pb.

This corresponds with the low Pb in all other streams in the catchment (mainly forest dominated), where the mire-streams are the exception.

The relative DOC and Fe export from station 1 relative to station 6 follows the ratio of catchment area, see table below.

|   | Station 1        | Station 6                       | St1 / St6 |
|---|------------------|---------------------------------|-----------|
| Catchment area (km <sup>2</sup> )                   | 0.595            | 1.337                           | 0.44      |
| Annual discharge (m <sup>3</sup> yr <sup>-1</sup> ) | 136 155 ± 35 168 | 412 878 ± 181 006               | 0.33      |
| DOC export (kg yr <sup>-1</sup> )                   | 5834 ± 1674      | 12616 ± 9293                    | 0.46      |
| Fe export (kg yr <sup>-1</sup> )                    | 151 ± 39         | 325 ± 232                       | 0.46      |
| Pb export (kg yr <sup>-1</sup> )                    | 0.705 ± 0.193    | 0.681 ± 0.520                   | 1.04      |
| of which from St. 1                                 |                  | 84.2 ± 2.6%<br>= 0.573 ± 0.438* |           |

\* High uncertainty due to the variability in Pb export from Station 6

### Question 1.5 – technical comments

- Line 54: Replace “binds” with “bind”. **Done**
- Line 57: Replace “peatland” with “peatlands”. **Done**
- Line 68: Remove “and” before “can be traced...”. **Done**
- Line 270: I cannot see that the change in N with depth was more extreme for hummock compared to intermediate and hollow. This is not obvious looking at Fig. 3. Should it be the other way around?

#### Answer

Yes, it should be the other way around, and “more extreme” has been changed to “less extreme”. N content increases in a somewhat linear manner with depth in hummock, while for intermediate and hollow, in particular for hollow, N content decreases from the top of the mire to 200 cm depth, from where it increases to 400 cm depth.

- Line 286: Intermediate generally had the highest Pb content, although the largest concentration was found in hummock at 25-50 cm (Table S1).

Yes, that is correct.

**New sentence:** Intermediate generally had highest Pb content that was more than twice as high as for hollows, while the highest Pb content was measured in hummock at 25-50 cm depth

- Line 288 – 290: Make sure that the correct numbers are presented here. According to Table S1, intermediate has the Pb content of 64.25 mg/kg, and hollow that of 32.21 mg/kg, and not the other way around. Pb contents of 4.41 and 0.05 mg/kg in the 25-50 cm interval do not match with the data in Table S1, nor with Fig. 4. This has been corrected  
**New sentence:** In intermediate and hollow topographies Pb content was highest in 15-20 cm: 64.25 and 32.21 mg kg<sup>-1</sup> and decreased to 58.5 and 14.89 mg kg<sup>-1</sup> at 25-50 cm depth, respectively (p = 0.02, Fig 4, Table S7).
- Line 319: It is not clear why data points for Fe and Pb were removed when discharge was low? It would have been informative to include this data.  
**New sentence:** Data points for Fe and Pb were removed when discharge <0.0001 (m<sup>3</sup> s<sup>-1</sup>), which occurred during summer when the water level was too low to measure discharge, making calculation of export impossible.
- Line 337: Remove “at” before “from Mycklemossen”. **Done**
- Line 402: Incomplete sentence starting with “The strong correlation...” **Done**
- Line 407: I suggest adding “The year of” or something similar before 2017 to avoid beginning the sentence with a number. **Done**

### Question 1.6

Line 390: Please elaborate on what type of interaction with Fe that stabilizes peat. Also in the same sentence, that most Fe in Mycklemossen is placed in deep anoxic peat layers does not rule out that this stabilizing effect of Fe on C is important.

**And**

### Question 1.7

Line 392: What is the “C destabilizing mechanism of Fe”. Please clarify.

### Answer

The text from Line 390 and to the end of that paragraph has been amended with comment 1.5 and 1.6 in mind. Both the stabilizing and destabilizing reactions with Fe has been elaborated.

We suggest including the following elaborated text:

Static oxic conditions during summer could also stabilise peat OM and DOC through adsorption and complexation with Fe (Chen et al., 2020; Riedel et al., 2013; Song et al., 2022), though most Fe in Mycklemossen is placed in deep anoxic peat layers, and therefore the stabilising effect of Fe on peat might be limited. However, regardless of redox regime, the majority of total Fe in peat will interact with peat OM, and Fe-OM complexes are found in both oxic and anoxic peat (Bhattacharyya et al., 2018). Thus, the stabilising effect of Fe

might not be limited to the oxic layer. On the contrary to the C stabilizing role of Fe, under aerobic conditions, oxidative reactions catalysed by Fe can lead to production of hydroxyl radicals that can promote degradation of peat (Qin et al., 2022; Trusiak et al., 2018). These reactions might be driven even by small concentrations of Fe (between 280 - 2.300 mg Kg<sup>-1</sup> peat) (Curtinrich et al., 2022), which is in the range of Fe contents measured in the top part of Mycklemossen. The importance of the stabilizing interactions contra the destabilizing reactions for peatland C dynamics need further investigation.

**The only new references are the ones below here:**

Bhattacharyya, A., Schmidt, M. P., Stavitski, E., & Martínez, C. E. (2018). Iron speciation in peats: Chemical and spectroscopic evidence for the co-occurrence of ferric and ferrous iron in organic complexes and mineral precipitates. *Organic Geochemistry*, 115, 124–137.  
<https://doi.org/10.1016/j.orggeochem.2017.10.012>

Song, X., Wang, P., Van Zwieten, L., Bolan, N., Wang, H., Li, X., Cheng, K., Yang, Y., Wang, M., Liu, T., & Li, F. (2022). Towards a better understanding of the role of Fe cycling in soil for carbon stabilization and degradation. *Carbon Research*, 1(1), 5.  
<https://doi.org/10.1007/s44246-022-00008-2>

**Question 1.8** Line 420: Could this be assessed if there are CO<sub>2</sub> flux measurements from the site?

**Answer**

At the site, CO<sub>2</sub> fluxes have been measured and those show that during the drought year of 2018, soil respiration was higher compared to “normal” years. This would support the statement that DOC production is higher under oxic conditions.

Keane, B., Toet, S., Ineson, P., Weslien, P., Stockdale, J. E., and Klemmedtsson, L.: Carbon dioxide and methane flux response and recovery from drought in a hemiboreal ombrotrophic bog, *Front. Earth Sci.*, 8, 562401, <https://doi.org/10.3389/feart.2020.562401>, 2021.