Reviewer 3: comments and answers

General Comments

The manuscript investigates the mobilization of Pb, Fe, and DOC from a mire–lake system in southern Sweden, as well as the system's carbon storage, over a four-year period marked by drought events that affected ecosystem dynamics.

The topic is relevant for understanding ecosystem responses to climate change and for the preservation of peatland–lake systems in Europe. However, the scientific conclusions are not entirely novel. As the authors acknowledge, the role of drought–rewetting cycles and hydrological connectivity in controlling DOC, Fe, and Pb export is already well established (e.g., Broder & Biester 2015, 2017; Rezanezhad et al., 2016).

The study presents a comprehensive and valuable dataset, supported by an extended four-year sampling period, which surpass typical studies based on shorter (1–2 year) campaigns. The comparison between the mire and lake compartments provides a broader perspective on the functioning of these common northern European ecosystems.

Overall, the topic is suitable for publication, but several revisions are recommended to improve the presentation and contextualization of the results. The discussion, in particular, needs a deeper and more critical analysis of the controlling processes and factors. Emphasis should also be placed on highlighting the novel aspects of this work and implications.

Answer

The controlling processes and factors for export of DOC, Fe and Pb will be deeper analysed in the discussion, in the next version of the manuscript.

Specific Comments

Question 3.1

The introduction would benefit from a clearer and more concise presentation of the current state of knowledge regarding Fe, DOC, and Pb export from peatlands—particularly the roles of hydrological connectivity, drought, and precipitation events (see Broder et al.). This section could be shortened by summarizing previously established processes collectively, allowing the focus to shift toward how these factors specifically affect the studied system and its long-term dynamics.

Answer

We agree. The paragraph starting at line 105 will be amended with the above comments in mind.

Question 3.2

The statement that "how the export of DOC and hydrology affect the transport of metals is unknown for most peatlands" is somewhat overstated. While some mechanistic details remain uncertain, several key processes are already considered common to peatlands (see previous comment). If previous research cannot be considered indicative for this system, it becomes difficult to reconcile this with the claim in Line 366 that the study site represents northern European mires in the temperate–boreal transition zone. Please clarified.

Answer

Yes, several key processes like hydrological connectivity, precipitation and drought are known drivers of DOC and metal export. The statement "how the export of DOC and hydrology affect the transport of metals is unknown for most peatlands" will be clarified in the next version of the manuscript and will be presented with more context. Our statement in the next version of the manuscript will be more along the lines of:

L50 …. In peatlands exposed to anthropogenic pollution, heavy metals will be found in the upper layers as those metals are primarily sourced from atmospheric deposition. How changes to peatland hydrology and climate affect the export of DOC and these metals is not well understood for most peatlands.

Question 3.3

Several trace metals (Pb, Hg, As, Cd) were analyzed in peat cores as part of previous work (Tchounwou et al., 2012). Since only Pb is discussed in the current manuscript, I recommend omitting mention of the other trace metals in both the methods and the introduction to maintain focus and clarity. If not, I recommend explaining in more detail the implication for other trace metals analyzed. For example, considering the Pb behaviour.

Answer

We will omit the parts about Hg, As and Cd and keep focus on Pb

Question 3.4

The Pb isotope dataset is valuable, covering mire, lake, and forest samples. However, its interpretation is limited. The isotope data suggest a mixing line between European gasoline, coal, and natural geogenic sources, with the lake outflow positioned between the mire and forest endmembers. This pattern likely reflects contributions from both local (forest) and upstream (mire) sources, implying that the lake catchment exerts additional influence (indicated by the forest).

In this regard, please consider:

- Topographic map illustrating the mire and lake catchments (sizes are already provided in the text) and flow directions.

Answer

The catchment areas have been generated based on detailed topographic maps in relation to the location of the measuring stations (out-flow) of the mire and the lake Erssjön. Thus, all the water that are measured at these locations are from these two areas. We do not think we need to add more maps to the manuscript, but will clarify this better in the text, in the next manuscript.

- Exploring implications for DOC origin: how does catchment size and type (forest, agriculture) affect lake outflow composition compared with mire outflow? Do sites S1 and S6 directly receive water from other catchment areas? Relevant literature includes Kaal et al. (2017, 2020), which highlights the contribution of forest organic matter to DOM in similar mire systems and could strengthen this interpretation.

Answer

Mycklemossen recieves almost all its water from rain and some from forested peatsoils, and as we discuss already, the Erssjön has a larger inflow from forest land (there is no agriculture to speak of in the catchment, just a tiny field).

- Clarifying the processes of Pb and in lake outflow. Does it primarily derive from the mire (directly). Estimating or discussing the lake's water residence time could help address this. What are the implications for the lake being a "sink" for Pb from the peatland?

Answer

Yes, it is primarily from the mire, which is calculated by the isotope mixing model. No previous estimates of the water residence time have been made, but given the size of the lake (6.2 ha) and the mean depth of 1.7 m (Milberg et al., 2017)) the volume would be ~100 000 m3, which gives a mean residence time of about 3 month.

- Based on isotopes and Pb. Can any kind of extrapolation be made about the role played by the mire-lake system depending on the flow (precipitation, drought period, etc.)?

Answer

Except for one sampling, the 206/208Pb ratio is always higher in Erssjön than Mycklemossen, proofing that the forest land almost always contributes to the lead in Erssjön. Conducting mixing model on the individual sampling dates (N=10), Mycklemossen contributes by 68 – 100% to the lead in Erssjön outflow.

Milberg, P., Törnqvist, L., Westerberg, L. M., & Bastviken, D. (2017). Temporal variations in methane emissions from emergent aquatic macrophytes in two boreonemoral lakes. AoB PLANTS, 9(4), plx029. https://doi.org/10.1093/aobpla/plx029

Question 3.5

Although CN ratios are presented, their implications for organic matter degradation are not discussed in sufficient depth. Given the importance of decomposition in DOM formation in peatlands, I recommend expanding on the observed CN trends and discussing how they reflect mass loss or varying degradation intensities within the cores. (See Biester et al., 2014 and Zeh eta l., 2020 for comparison between proxies for OM decomposition.

And

Question 3.6

The results for $\delta^{13}C$ and $\delta^{15}N$ show clear variations, yet their interpretation remains superficial. The authors should elaborate on how these isotopic shifts relate to organic matter degradation, plant sources, and CN ratios, and what they reveal about peat formation and transformation processes. See Zeh et al., 2020; Gandois et al., 2019.

Answer

Question 3.5 and 3.6 will briefly be discussed here, but will be further elobarated in the next version of the manuscript

Looking at the top part of Mycklemossen where we observe the largest differences in C/N between hollow and hummock ranging from a median value of approximately 25 to 75 for hollow and hummock respectively. (Fig. 3). First, there are differences in the vegetation between the two topographies, with the hummock being mostly dominated mainly by vascular plants (*Eriophorum vaginatum*, *Calluna vulgaris* and *Erica tetralix*) and the hollows mainly consists of different *Sphagnum* species as *S. rubellum*, *S. fallax* and *S. austinii* as well as *Rhyncospora alba* (Kelly et al., 2021). The higher median value of C/N in hummock can therefore be explained differences in the dominant vegetation, meaning the higher C/N in hummocks is likely explained by higher lignin content from vascular plants and by the presence of roots (Biester et al., 2014; Zeh et al., 2020).

The depletion of $\delta^{13}C$ in hummock contra hollow, in particular in top layer, is a common tendency and in our case, the most likely explanation is likely that hummock is dominated by vascular plants (Biester et al., 2014; Zeh et al., 2020) or a higher degree of grasses, “the Suess effect”, as mentioned in the manuscript.

The increase of $\delta^{13}C$ towards 200cm depth, where hummock reach similar values to hollow and intermediate might indicate aerobic degradation of lignin in the hummock and preservation of carbohydrates from below the water table. The lower median value of $\delta^{15}N$ in hummocks at the top of the mire contra hollow and intermediate, might be because microbial denitrification have removed light N isotope components (Biester et al., 2014). In general, the $\delta^{15}N$ increased with depth and is likely because of an uptake of the lighter N isotopes (Zeh et al., 2020).

Biester, H., Knorr, K.-H., Schellekens, J., Basler, A., & Hermanns, Y.-M. (2014). Comparison of different methods to determine the degree of peat decomposition in peat bogs. Biogeosciences, 11(10), 2691–2707. https://doi.org/10.5194/bg-11-2691-2014

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

Zeh, L., Igel, M. T., Schellekens, J., Limpens, J., Bragazza, L., & Kalbitz, K. (2020). Vascular plants affect properties and decomposition of moss-dominated peat, particularly at elevated temperatures. Biogeosciences, 17(19), 4797–4813. https://doi.org/10.5194/bg-17-4797-2020

Question 3.7

The differentiation among hollows, hummocks, and intermediate positions yields interesting insights into trace metal accumulation and peatland heterogeneity.

The discussion could be strengthened by integrating findings from Pérez-Rodríguez et al. (2025), who examined degradation dynamics under aerobic versus anaerobic conditions in similar microtopographies.

Additionally, it would be helpful to clarify whether the hollow–hummock pattern is assumed to have remained consistent throughout the peatland's development. And what are the possible implications. See Nungesser (2003).

Answer

The most interesting results in Pérez-Rodríguez et al. (2025) in relation to our study, is the leaching of phenolic compounds from the hummock topography, which could have implications for how metals are mobilised and transported. While data explaining the degradation patterns of hollow contra hummock seems interesting, the apparent selective preservation of lignin-like compounds in hollows seems a little curious. Bryophytes do not contain S-type lignin (Weng & Chapple, 2010), as otherwise shown by the paper, so the source of lignin-like compounds measured in hollows is a little unclear. The preservation og lignin-like compounds could othererwise have positive influence on metal sequestration.

Hummocks and hollows are generally relative resilient to climate shifts and the average environmental conditions (hydrology, temeperature, species composition) over time determines the topography, that said, hummocks and hollows are formed by the species themselves (Nungesser, 2003). The time scale for development of hummock and hollow is long compared to other ecosystems, so we would assume the topography has remained the same in Mycklemossen during the time when Pb pollution was ongoing. It could imply that Pb is better sequestered in hummocks as overall slower decomposition rate is observed compared to hollows. Also, it might be worth considereing that hummock makes up most of the Mycklemossen topography (Rinne et al., 2022) and together with the hight of hummocks is more exposed to atmospheric deposition.

Nungesser, M. K. (2003). Modelling microtopography in boreal peatlands: Hummocks and hollows. Ecological Modelling, 165(2), 175–207. https://doi.org/10.1016/S0304-3800(03)00067-X

Pérez-Rodríguez, M., Alten, A., Miler, M., & Kaal, J. (2025). Explicit microrelief-controlled decoupling of initial aerobic decay and leaching (in hummocks) and anaerobic decay (in hollows) in surface layers of a Sphagnum-dominated peatland. Journal of Analytical and Applied Pyrolysis, 192, 107295. https://doi.org/10.1016/j.jaap.2025.107295

Weng, J.-K., & Chapple, C. (2010). The origin and evolution of lignin biosynthesis. New Phytologist, 187(2), 273–285. https://doi.org/10.1111/j.1469-8137.2010.03327.x

Question 3.8 The suggestion that Pb toxicity may inhibit microbial degradation of organic matter deserves further consideration. Where is the Pb located in the moss and moss-derived organic matter, and is this Pb likely to be bioavailable to microorganisms?

Answer

We got a similar question from reviewer 2, that also got a similar answer.

We are aware that total Pb content is not the same as bioavailable Pb. Toxicological risk can be estimated in many ways with different ecological risk assessments (Hoang et al., 2025). We believe estimating bioavailability is out of scope for this study, as it would require some form of bioassay (Fleming et al., 2013). However, the litterature we refer to presents Pb not as bioavailable, but as total Pb (mg/kg or equivalent unit) and still found an effect on microbial processes. Thus, we believe the same could be the case for peat soils despite peats (and *Sphganum's*) ability to bind strongly to metals.

The soil characteristics: pH and organic matter content, are likely the two most important factors for heavy metal availability, of which a low pH increase availability and high organic matter decrease availability (Hou et al., 2019). In general, Pb binds strongly to the acidic and phenolic compounds of *Sphagnum* moss and its derived organic matter through physiochemical binding. Pb is probably the least mobile heavy metal and even soluble Pb will be bound to DOC because of high affinity for organic matter (Smieja-Król et al., 2022; Vile et al., 1999).

In a study that used *Sphagnum* moss to evaluate air polution of Pb in an urban area, showed by microscopy that Pb is most likely found on the surface of the moss, which includes the inside of the large hyaline cells, in which the degree of Pb absorbtion might be affected by pore size (Dalupang et al., 2023). In *Sphagnum* derived organic matter, Pb might also be found in physical entrapments by the physiochemical binding mentioned above.

The concentration of bioavailable Pb in hummock is therefore certainly lower than the 90 mg kg^{-1}, but Pb can be made available from microbial degradation and lead to accumulation in organisms over time. Our statement "The Pb content of 92 mg kg^{-1}in hummocks at 25-50 cm depth in Mycklemossen are therefore likely to affect the microbial community and the biomass turnover rate", we find suitable, but it will be more adequately discussed in the next version of the manuscript.

Also, the Pb concentrations for water streams will be better explained in relation to bioavailability in the next version of the manuscript including some new litterature ((González & Pokrovsky, 2014; Van Sprang et al., 2016)

Dalupang, X. P., Matias, H. A., Rivera, M. L., & Viz, J. (2023). Biomonitoring of atmospheric lead (Pb) pollutants using Sphagnum moss in Bantay, Ilocos Sur, Philippines. Philippine Journal of Science, 152(6A). https://www.ukdr.uplb.edu.ph/journal-articles/6233

Fleming, M., Tai, Y., Zhuang, P., & McBride, M. B. (2013). Extractability and bioavailability of Pb and As in historically contaminated orchard soil: Effects of compost amendments. Environmental Pollution, 177, 90–97. https://doi.org/10.1016/j.envpol.2013.02.013

González, A. G., & Pokrovsky, O. S. (2014). Metal adsorption on mosses: Toward a universal adsorption model. Journal of Colloid and Interface Science, 415, 169–178. https://doi.org/10.1016/j.jcis.2013.10.028

Hoang, H. G., Hadi, M., Nguyen, M. K., Hai Nguyen, N. S., Huy Le, P. Q., Nguyen, K. N., Tran, H.-T., & Mishra, U. (2025). Assessing heavy metal pollution levels and associated ecological risks in peatland areas in the Mekong Delta region. Environmental Research, 274, 121319. https://doi.org/10.1016/j.envres.2025.121319

Hou, S., Zheng, N., Tang, L., Ji, X., & Li, Y. (2019). Effect of soil pH and organic matter content on heavy metals availability in maize (Zea mays L.) rhizospheric soil of non-ferrous metals smelting area. Environmental Monitoring and Assessment, 191(10), 634. https://doi.org/10.1007/s10661-019-7793-5

Smieja-Król, B., Pawlyta, M., Kądziołka-Gaweł, M., & Fiałkiewicz-Kozieł, B. (2022). Formation of Zn and Pb sulfides in a redox-sensitive modern system due to high atmospheric fallout. Geochimica et Cosmochimica Acta, 318, 126–143. https://doi.org/10.1016/j.gca.2021.11.032

Van Sprang, P. A., Nys, C., Blust, R. J. P., Chowdhury, J., Gustafsson, J. P., Janssen, C. J., & De Schamphelaere, K. A. C. (2016). The derivation of effects threshold concentrations of lead for European freshwater ecosystems. Environmental Toxicology and Chemistry, 35(5), 1310–1320. https://doi.org/10.1002/etc.3262

Vile, M. A., Wieder, R. K., & Novák, M. (1999). Mobility of Pb in Sphagnum-derived peat. Biogeochemistry, 45(1), 35–52. https://doi.org/10.1023/A:1006085410886

Question 3.9

While the cited literature on peatlands as trace metal sinks is appropriate, the authors should also consider referencing the extensive work conducted by Bindler's and Kylander's groups on Swedish peatlands, which would provide useful regional context.

Answer

We will consider it, and so far, we will at least include the following work:

Kylander, M. E., Bindler, R., Cortizas, A. M., Gallagher, K., Mörth, C.-M., & Rauch, S. (2013). A novel geochemical approach to paleorecords of dust deposition and effective humidity: 8500 years of peat accumulation at Store Mosse (the "Great Bog"), Sweden. Quaternary Science Reviews, 69, 69–82. https://doi.org/10.1016/j.quascirev.2013.02.010

Question 3.10

The citation (González & Pokrovsky, 2014) in line 64 is not appropriate. Although the authors developed an excellent model to understand trace metal accumulation in mosses, their results are not specifically related to the peatland context.

Answer

Yes, that is a fair point, as (González & Pokrovsky, 2014) the result are obtained under controlled laboratory conditions and not in a peatland – the reference will not be used in line 64.

Reviewer 3 references:

Biester, H., Knorr, K. H., Schellekens, J., Basler, A., & Hermanns, Y. M. (2014). Comparison of different methods to determine the degree of peat decomposition in peat bogs. *Biogeosciences*, *11*(10), 2691-2707.

Gandois, L., Hoyt, A. M., Hatté, C., Jeanneau, L., Teisserenc, R., Liotaud, M., & Tananaev, N. (2019). Contribution of peatland permafrost to dissolved organic matter along a thaw gradient in North Siberia. Environmental Science & Technology, 53(24), 14165-14174.

Kaal, J., Cortizas, A. M., & Biester, H. (2017). Downstream changes in molecular composition of DOM along a headwater stream in the Harz mountains (Central Germany) as determined by FTIR, Pyrolysis-GC–MS and THM-GC–MS. *Journal of Analytical and Applied Pyrolysis*, *126*, 50-61.

Kaal, J., Plaza, C., Nierop, K. G., Pérez-Rodríguez, M., & Biester, H. (2020). Origin of dissolved organic matter in the Harz Mountains (Germany): A thermally assisted hydrolysis and methylation (THM-GC–MS) study. *Geoderma*, *378*, 114635.

Nungesser, M. K. (2003). Modelling microtopography in boreal peatlands: hummocks and hollows. Ecological Modelling, 165(2-3), 175-207.

Pérez-Rodríguez, M., Alten, A., Miler, M., & Kaal, J. (2025). Explicit microrelief-controlled decoupling of initial aerobic decay and leaching (in hummocks) and anaerobic decay (in hollows) in surface layers of a Sphagnum-dominated peatland. Journal of Analytical and Applied Pyrolysis, 192, 107295. https://doi.org/10.1016/j.jaap.2025.107295

Rezanezhad, F., Price, J. S., Quinton, W. L., Lennartz, B., Milojevic, T., & Van Cappellen, P. (2016). Structure of peat soils and implications for water storage, flow and solute transport: A review update for geochemists. Chemical Geology, 429, 75-84.

Zeh, L., Igel, M. T., Schellekens, J., Limpens, J., Bragazza, L., & Kalbitz, K. (2020). Vascular plants affect properties and decomposition of moss-dominated peat, particularly at elevated temperatures. Biogeosciences, 17(19), 4797-4813.