Reviewer 2: comments and answers

This study presents a well-designed and careful investigation of Fe-Pb-DOC dynamics in a boreal mire-lake system affected by historical anthropogenic Pb pollution. The authors integrate peat-core geochemistry, radiocarbon dating, long-term DOC-metal flux monitoring, and Pb isotopic tracing to quantify the coupling between carbon and metal export under variable hydrological regimes. The dataset is of high analytical quality, and the topic is of clear environmental significance. The main conclusions-namely, that hydrological fluctuations promote the co-export of Fe and DOC, and that anthropogenic Pb is remobilized but largely retained within the lake-are well supported by the data.

However, I have several comments that the authors may wish to consider:

Question 2.1

First, the reported Fe-DOC correlation ($R^2 = 0.96$) is striking but insufficiently explained. The term “hydrological connectivity” alone does not capture the underlying chemical mechanisms. Please discuss whether the observed Fe-DOC co-variation results primarily from colloidal co-transport, redox-driven Fe-organic complexation, or other processes.

Answer

In general, Fe in boreal rivers is primarily transported on colloidal form, for instance as Fe-DOC complexes with humic substances, and Fe as Fe^{2+} or Fe(oxy)hydroxides (Heikkinen et al., 2022). The transport of these forms of Fe is primarily affected by redox conditions (oxic/anoxic) and pH, whereas oxic conditions favor co-precipitation of DOC and Fe (Riedel et al., 2013) and acidic pH (4-5) favors soluble Fe-DOC complexes, while a pH of 6 and higher favors precipitation of Fe-DOC complexes (Neubauer et al., 2013).

We believe our reported Fe-DOC relationship is mostly explained by colloidal transport of Fe-DOC complexes, with essentially all Fe bound to an organic ligans and a small proportion as Fe(oxy)hydroxides. It has been reported in a recent study that Fe in northern rivers is dominantly transported on colloidal form (between 1kDa and 0.22µm), and otherwise and to a much less extent found as “truly dissolved” (<1kDa) (Aleshina et al., 2024). Björnerås et al. (2021) investigated Fe inflow to a lake from a Mire, in the south of Sweden. Here, Fe was found bound mainly on colloidal form, but also a noteworthy proportion as Fe(oxy)hydroxides, but here the inflow water had a pH of 6.7 and above, which favors presipitation of Fe-DOC complexes. At the pH we measured (4-5), we would expect a higher fraction of soluble Fe-DOC complexes.

The asynchronous timing of Fe (2018) and DOC (2019) peaks is probably due to a higher soil respiration of DOC in 2018. Both Fe and Pb concentrations were highest in 2018, so the peat degradation was likely highest that year. In 2018, the soil respiration was 15% higher compared to “normal” years (Keane et al., 2021). 2018 was an extreme warm and dry summer in Scandinavia, and therefore it is likely that the larger soil respiration was due to mineralization of DOC, leading the lower DOC peaks in 2018 compared to 2019, which would also explain the higher release of Pb and Fe in 2018.

The large DOC peak in 2019 is harder to explain. One possible explanation is that the stream was supplemented by DOC rich water from the catchment, as suppported by Fig. S2, that shows the the pH in the stream water in 2019 was noteably higher than 2018 (pH 5-6.5) in the summer period. The high pH is not what we expect from water coming from the mire. Furthermore, there was a much higher precipitation in 2019 compared to 2018 (see table below), that could lead to a higher runoff, rich in DOC, from the forested catchment.

SMHI data from Vänersborg	
Year	Precipitation (mm)
2015	875
2016	655
2017	708
2018	599
2019	911

Aleshina, A., Rusakova, M.-A., Drozdova, O. Y., Pokrovsky, O. S., & Lapitskiy, S. A. (2024). Dissolved Iron and Organic Matter in Boreal Rivers across a South–North Transect. Environments, 11(4), Article 4. https://doi.org/10.3390/environments11040065

Björnerås, C., Persson, P., Weyhenmeyer, G. A., Hammarlund, D., & Kritzberg, E. S. (2021). The lake as an iron sink—New insights on the role of iron speciation. Chemical Geology, 584, 120529. https://doi.org/10.1016/j.chemgeo.2021.120529

Heikkinen, K., Saari, M., Heino, J., Ronkanen, A.-K., Kortelainen, P., Joensuu, S., Vilmi, A., Karjalainen, S.-M., Hellsten, S., Visuri, M., & Marttila, H. (2022). Iron in boreal river catchments: Biogeochemical, ecological and management implications. Science of The Total Environment, 805, 150256. https://doi.org/10.1016/j.scitotenv.2021.150256

Keane, B., Toet, S., Ineson, P., Weslien, P., Stockdale, J. E., and Klemedtsson, 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.

Neubauer, E., Köhler, S. J., von der Kammer, F., Laudon, H., & Hofmann, T. (2013). Effect of pH and stream order on iron and arsenic speciation in boreal catchments. Environmental Science & Technology, 47(13), 7120–7128. https://doi.org/10.1021/es401193j

Riedel, T., Zak, D., Biester, H., & Dittmar, T. (2013). Iron traps terrestrially derived dissolved organic matter at redox interfaces. Proceedings of the National Academy of Sciences, 110(25), 10101–10105. https://doi.org/10.1073/pnas.1221487110

Question 2.2

Second, the Pb isotope work is technically robust, and the evidence for anthropogenic Pb contamination derived from gasoline combustion is convincing. Nevertheless, I recommend that the authors provide propagated uncertainties for the isotope ratios and isotope-mixing model outputs and compare their measured isotope values with established European reference baselines (these appear to be missing from the manuscript). Moreover, please include confidence intervals for the estimated ~33% Pb retention in the lake to substantiate this quantitative conclusion.

Answer

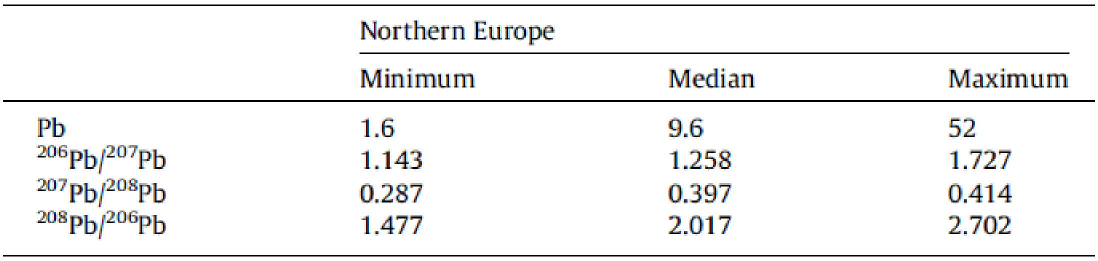
First, we would like to mention that we corrected the export data for the mixing model, we unfortunately had used a wrong value in calculation before. The new results indicate that 19% of lead exported from Mycklemossen is retained in Erssjön.

For the mixing model we now used the IsoError tool (Phillips & Gregg, 2001), which provides also an uncertainty estimate. With the corrected Pb export data, 84.2 ± 2.6% of the lead exported from Station 6 is derived from Mycklemossen. With this, we can estimate how much of the Pb from Mycklemossen is retained in Erssjön, which is 19 % (retained = 0.705 – 0.681 x 84.3% = 0.132). The results are summarized in the table below, also including the other elements, area and discharge.

	Station 1	Station 6	St1 / St6
Catchment area (km2)	0.595	1.337	0.44
Annual discharge (m3 yr-1)	136 155 ± 35 168	412 878 ± 181 006	0.33
DOC export (kg yr-1)	5834 ± 1674	12616 ± 9293	0.46
Fe export (kg yr-1)	151 ± 39	325 ± 232	0.46
Pb export (kg yr-1)	0.705 ± 0.193	0.681 ± 0.520	1.04
of which from St. 1		84.2 ± 2.6% = 0.573 ± 0.438*	

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

Regarding the European reference baselines, data on lead isotopes for agricultural soils across Europe are available (Reimann et al. 2012). For the area around Skogaryd, the map shows a 206Pb/207Pb ratio of 1.245-1-326, which is higher than the data from Mycklemossen of 1.146 (which is actually at the lowest end for Northern Europe, see table). Reimann et al. does not provide a map for 208Pb/206Pb, but the value of 2.112 for Mycklemossen is quite close to the median for N-Europe.



	Northern Europe		
	Minimum	Median	Maximum
Pb	1.6	9.6	52
^{206}Pb/^{207}Pb	1.143	1.258	1.727
^{207}Pb/^{208}Pb	0.287	0.397	0.414
^{208}Pb/^{206}Pb	1.477	2.017	2.702

Regarding propagated uncertainties: The Pb isotopic data in the provided data table include the following uncertainties propagated in quadrature: the standard error of the 10 replicates, the excess scatter of the primary reference solution NIST SRM 981 for the respective ratio from the measurement session and the uncertainty in the 204Hg correction. The ratio uncertainties from the published ratios for the primary reference material (NIST SRM 981, NIST, Cantanzaro et al. 1968) would need to be propagated to add systematic uncertainties. These uncertainties are 0.04% for the 208Pb/206Pb and 206Pb/207Pb ratios used to in Figure 7 and are thus considerably smaller than the total analytical uncertainties of approximately 0.30 % for both ratios. Thus, propagation of this systematic uncertainty would not significantly change the total uncertainties for both ratios (4th or 5th digit behind the comma for the absolute ratios).

Phillips, D.L. and J.W. Gregg (2001). Uncertainty in source partitioning using stable isotopes. Oecologia 127: 171-179 (see also erratum - Oecologia 128: 304)

Reimann et al. (2012) A Lead and lead isotopes in agricultural soils of Europe – The continental perspective. Applied Geochemistry 27:532–542

Question 2.3

Third, the finding that surface peat Pb concentrations exceed ecotoxic thresholds (>90 mg kg^{-1}) is both important and policy-relevant. However, the manuscript does not adequately discuss Pb speciation or its geochemical associations, which are critical for assessing Pb mobility and ecological risk.

Answer

Total Pb concentrations exceeded ecotoxic threshold of >90 mg kg^{-1}, as outlined by Sjöberg, B. (2016), in the hummock topography, and we believe the Pb originated from atmospheric deposition. Total Pb content is not the same as bioavailable Pb, but the toxicological risk can be estimated in different ways with different ecological risk assessments (Hoang et al., 2025). We believe assessing 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.

In peatlands, Pb is mostly found strongly bound to organic matter and minerals with a low available fraction (Lu et al., 2025). The soil characteristics: pH and organic matter content (including CEC), 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). Under aerobic conditions, as in hummock, the most prevalent ionic form of Pb is Pb^{2+} that will be found in association mainly with organic matter.

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)

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

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

Lu, Z., Ning, Y., Liu, C., Song, X., Pang, Y., Li, Q., Yang, M., & Zeng, L. (2025). Geochemical Regulation of Heavy Metal Speciation in Subtropical Peatlands: A Case Study in Dajiuhu Peatland. Land, 14(6), 1256. https://doi.org/10.3390/land14061256

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

Sjöberg, B. (2016). Miljögifter i vatten – klassificering av ytvattenstatus. Miljögifter i Vatten – Klassificering Av Ytvattenstatus.

https://www.havochvatten.se/download/18.6d9c45e9158fa37fe9f57c25/1708800059479/vagledn-miljogiftsklassning-hvmfs201319.pdf

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

Question 2.4

Given that the studied mire is strongly Sphagnum-dominated, the biochemical characteristics of Sphagnum mosses likely play a central role in the observed Fe-DOC-Pb interactions. Sphagnum tissues contain abundant polyphenolic compounds and organic acids, all of which can influence Fe and Pb cycle and modulate DOC chemistry. Could the authors elaborate on how these unique Sphagnum traits might govern the tight Fe–DOC correlation and the substantial Pb retention observed in this system? For example, does the acidity and high ligand density of Sphagnum-derived organic matter affects the stability of Fe-DOC-Pb complexes? A brief discussion along these lines would substantially enhance the ecological and mechanistic relevance of the study.

Answer

We are not aware of the specific type of DOC that leaves the mire contra the lake, but the relationship between Fe and Pb with DOC seems a little stronger in the stream leaving the mire contra the lake.

A study that investigated chemical characteristics of DOM downstream of a bog, found that the water leaving the bog was rich in polyphenolic DOM, which binds strongly to metals like Fe and Pb and was seemingly derived mainly from *Sphagnum* (Kaal et al., 2017). A pH above 6 will increase co-precipitation of both Fe and Pb with OM, while Pb-OM complexes are more mobile under acidic conditions (pH ~4.5) (Rothwell et al., 2008). These two findings could support the tight relationship of Pb and Fe with DOC leaving the mire.

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. https://doi.org/10.1016/j.jaap.2017.06.025

Rothwell, J. J., Evans, M. G., Daniels, S. M., & Allott, T. E. H. (2008). Peat soils as a source of lead contamination to upland fluvial systems. Environmental Pollution, 153(3), 582–589. https://doi.org/10.1016/j.envpol.2007.09.009