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Interactive comment on "Hydrologic controls on DOC, As and Pb export from a polluted peatland – the importance of heavy rain events, antecedent moisture conditions and hydrological connectivity" *by* T. Broder and H. Biester

Anonymous Referee #2

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General comments:

The authors present a relatively comprehensive dataset comprising stream water concentrations, bog water concentrations and peat concentrations of As, Pb, DOC/(C/N) ratios and Fe. In addition, they also have good background data with precipitation, groundwater levels in the bog and discharge from the bog. The authors clearly have the ambition to investigate their site from a catchment perspective, trying to capture the major fluxes and inventories in the system. This is not easily done, and as the authors recognize there are gaps in their data. However, I appreciate all the work that has been

devoted to the collection of the data, and there are certainly valuable conclusions that can be drawn from the presented dataset anyway.

The manuscript focuses on As and Pb, both of which are associated with serious environmental problems, and the investigated bog represents a system, which has been strongly affected by anthropogenic emissions. Hence, there is little doubt about the environmental relevance of the problem they are addressing, and the site is highly relevant for investigating that problem. In addition, there is also supporting data on DOC and Fe, which are important for the mobility of these elements, and which also are interesting in their own right. Combined I think all these factors – the quality of the data, especially the high-resolution sampling, the comprehensive dataset and the environmental relevance of the problem with Pb and As – speak in favour of the manuscript.

However, although I think that this material as such is worthy of being published in Biogeosciences, I also think that some changes should be made to the present manuscript before it is published. I was not always able to follow all ideas that the authors present so there may be a need for some clarifications. I some cases I feel that the authors may have drawn too far-reaching conclusions based on the data they have, and in other cases I get the feeling that it might be possible to push the interpretation of the data a bit further. This is developed further in the specific comments below.

However, one thing in particular that I would like to know more about is the discharge from the parts of the catchment that is not a bog. The authors seem to completely disregard this factor. Is that because they know that the stream only receives water from the ombrotrophic parts of the wetland? Otherwise, I think they would have to more thoroughly consider the possibilities that other types of water than bog water contribute to the stream water chemistry during parts of the year. This water has to leave the catchment somewhere, and that would have consequences for the interpretation of the data.

Another problem with manuscript in its present form is the language. English is not my

native language so I am a bit reluctant to criticize that part of the manuscript. However, I feel that there are quite a few mistakes in the manuscript, which sometimes also makes it hard to understand exactly what the authors mean. I am not the right person to comment on those things so I would therefore recommend that the language is examined by a native speaker.

So, in conclusion, I think that the authors present good and relevant data, which should be of interest to readers of Biogeosciences, but the authors should be given a chance to revise the manuscript and improve the presentation and the interpretation of the data before publication.

Specific comments:

p. 5018, line 16: Bogs are per definition ombrotrophic so “ombrotrophic bogs” sounds like a tautology to me, but perhaps it is just to be on the safe side? Furthermore, I think the authors may be too careful when then they point out only bogs as capable of accumulating Pb and As. I think they could safely say that all peatlands have this potential.

p. 5018, line 24: The authors state that the surface layer of a bog is the most active part. This may be true in this specific case (and many other cases as well), and the authors also provide some references. However, one should be aware that this is not always the case. There are examples of mires where there is a preferential flow deeper down in the peat and relatively little flow in the acrotelm, e.g. the mire investigated by Sirin et al. (1998) and Peralta-Tapia et al. (2014). These examples refer to minerotrophic conditions, but I suspect that similar situations could occur also in bogs, depending on how they evolved. In addition, there is the question of how the rest of the catchment is drained.

p. 5019, line 1: The authors claim that the surface-near peat layers are the main source of metal released from peatlands. This may very well be true for metals like Pb with a very high atmospheric deposition, but the statement is too general. I do not think it

is valid for all metals. The main source of many metals in peatlands and the streams draining them is weathering of surrounding mineral soils. See for instance Lidman et al. (2014) (Metal transport in the boreal landscape ...). In a bog these metals will never even reach the surface-near peat layers so they can hardly be the main source.

p. 5021, line 12: The description of the sampling resolution is unclear. There may be some units missing.

p. 5022, line 23: The authors could perhaps clarify this description of the catchment and relate each of the three (?) components of the catchment – open bog X, forested peatland Y and forest soil – to the total catchment area. This description is not entirely clear to me.

p. 5023, line 8: The inventories of As and Pb in the peat are calculated from a number of 30 cm deep cores and one deeper core. Does this imply that that the inventories only refer to the upper 30 cm of the peat or is it the total inventory in the peat? I would assume that there is minerotrophic peat under the bog, which potentially could have quite different concentrations of As and Pb. Is this negligible?

p. 5023, section 3.1: The access to hydrological data is a cornerstone in this manuscript, but I feel that focus should not be on the hydrology but on the studied elements. I appreciate a brief description of the studied time period and the general hydrological behavior of the system, but I think this description might be a bit too detailed. The most interesting part here, which also is relevant for the interpretation of the stream chemistry, is how strongly the discharge is dependent on the groundwater level in the bog. This could perhaps be developed a bit more. If the groundwater level for instance can be related to the logarithm of the discharge or something similar, that would important information, which would support the authors’ conclusions.

p. 5024, line 17: The authors may have good reasons to assume that the runoff generation is dominated by surface-near groundwater flow pathways in this system, but those reasons are not entirely clear to me. For instance, a rapid hydrological response

of the stream does not necessarily mean that this must be the case. Changes in hydraulic head throughout the catchment in connection with rainfall may activate entirely different groundwater flow pathways.

p. 5026, line 18: Based on correlations between As, Fe and DOC the authors argue that As and Fe are mobilized by the same processes and originate from the same source area. As far as I understand, the authors have previously argued that As mainly derives from atmospheric deposition and that the main source is the acrotelm of the bog. If so, this would suggest that the acrotelm also is the main source of Fe. Normally I would not expect that Fe is an element that is so strongly affected by atmospheric deposition, but perhaps there is deposition data to support this? Otherwise it would seem more likely that the primary source of Fe is weathering of mineral soils in the catchment, and that there is a transport of Fe through deeper peat layers.

One alternative possibility that would need to be investigated more closely is that the variability in concentration mainly is controlled by dilution by precipitation. That would also explain the correlation between the all these elements. It might also be useful for the interpretation of the data to compare these elements to a relatively conservative element, which mainly is derived from weathering rather than atmospheric deposition, if the authors have such data available. There is no perfect choice but perhaps Ca, Mg, Si or Na would work, somewhat depending on the precipitation. That would help to determine when the runoff is dominated by other sources than bog water because all runoff cannot be transported to the stream by near-surface or surface flow in the bog. Then it would not be a bog, right? There must also be deeper groundwater flow pathways from other parts of the catchment (everything that is not bog), which have been in contact with mineral soils or minerogenic parts of the peat.

p. 5027, line 6: Missing units. This is a quite common mistake in this manuscript. For instance, if DOC varies from 5 mg L-1 to 10 mg L-1, the unit has to follow after both figures. Alternatively, one could say that it varies from 5-10 mg L-1.

p. 5027, line 9: The water level rose from 13 cm to 6 cm? Is there a minus sign missing? Previously minus was used for depths under the reference level, and the authors should be consistent about this. This is a source of confusion elsewhere in the manuscript as well.

p. 5027, line 19: Missing unit.

p. 5027, line 27: Is there any evidence that Fe-oxides are precipitating in the bog? Given the high DOC concentrations and the low pH it is not evident that Fe-oxides will be able to precipitate. See for instance the study by Neubauer, which is cited in the manuscript.

p. 5029, line 11: The lack of correlation between Pb, As and DOC in connection with the rain events to me somewhat contradicts the previous conclusions that these substances are controlled by the same processes and have the same sources. Over the entire sampling period there are large but similar changes in the concentration of all elements, which to me suggests that these correlations reflect some general changes in functioning of the catchment over time. This is likely to be related to seasonality and associated changes in the hydrology throughout the entire catchment, which then would be what governs the large-scale patterns. The lack of correlation in the high resolution data would then suggest that on a biogeochemical level Pb, As and DOC still behave differently, which would not be surprising given what we know about the biogeochemistry of these substances. Would that be a way to unify these observations?

p. 5029, line 15: Was there any ice left at this occasion? That would be a factor that strongly affects the hydrology of the bog. If not, it might be worth to add that information to the site description or the discussion of the hydrology anyway.

p.5030, section 3.3: Overall I think that this is the potentially most interesting part of the manuscript. Somehow, however, I feel that it might be possible to extract more information from the high resolution data that the authors have collected. For instance, I wonder if it would be possible to present the data in Fig. 3 in a clearer way. I ap-

preciate the efforts to focus separately on these events, but it is still quite hard to see the patterns and to compare the changes in concentration to the changes in discharge and groundwater level. One solution might be several sub-plots focusing on each of the events because there is still quite a lot of blank space in the graphs. Furthermore, I am more curious about how the concentrations relate to the changes in the groundwater level and the changes in discharge. It may be worth trying to correlate the concentrations to these changes (if it has not been tried already) both within and between the three events.

In particular Fe has a peculiar oscillating pattern in connection with the second event. It seems to be some sort of diurnal variation. Could that be worth to explore further?

p. 5030, line 13: I do not quite understand what the authors are trying to say here.

p. 5030, line 21: Could you perhaps use this information to provide the reader with an estimation of the age of the peat? It would be interesting to know for how long the contaminants have been in the system.

p. 5030, line 28: Missing units.

p. 5031, line 2: A problem with English is that there seem to be no good adjective for describing substances with low mobility. Immobile seems to suggest something absolute, an incapability of being transported at all. It has been discussed to what extent Pb is mobile in peat, but there is compelling evidence that it is not immobile. Furthermore, it is an implicit assumption in this study that deposited Pb is transported to the stream, which would not be possible if it were immobile.

Two references that may be useful: Mobility and diagenesis of Pb and 210Pb in peat, Urban and Eisenreich (1990). Re-thinking the record: Short-term downwash of Be-7 and Pb-210 in a Swedish peat bog, Hansson et al. (2013).

p. 5034, line 3: Perhaps it would be useful to compare the Pb/DOC ratios between the different compartments?

p. 5034, line 8: This is an interesting idea, but it is a bit surprising that the top layers would be the main source in connection with both rain events and low discharge. Is this model consistent with the variability in As, Fe and DOC as well? Another question is to what extent profile is representative for the bog as whole, which should be commented at some point. Finally, the authors dismiss the possibility that deeper peat sections contribute to the discharge, but in that case I do not quite understand how the rest of the catchment is drained. As far as I understand, there are parts of the catchment, which are not a bog. How does the water from those parts of the catchment reach the stream and what influence does it have on the stream chemistry? If it really is an ombrotrophic bog, that water cannot flow through the ombrotrophic parts of the peat. Or does it enter the stream further downstream? I think this needs further discussion or clarification.

p. 5034, line 25: Given that the variability in discharge is much greater than the variability in concentration it is not at all surprising that the load primarily is dependent on the discharge. Therefore, I do not think that Fig. 7 illustrates anything particularly interesting. If the authors want to focus on the importance of discharge for the load, it might be better to plot the load versus the discharge. That would also indirectly display the effect of concentration on the load.

p. 5035, line 2: It is unclear what the authors mean by “the upper 10 % of discharge”. Since the concentrations of Pb, As and DOC tend to be lower at high discharge, it sounds strange that ca. 40 % of the annual load would be transported by 10 % of the annual discharge (which to me represents a volume). I suspect that the authors may mean that 40 % of these elements are transported during the 10 % of days with the highest discharge or something like that. Note that this does not correspond to 10 % of the discharge.

Furthermore, I feel that the discrimination between high flow and low may be quite arbitrary so I am not sure what the figures in the rest of the paragraph really tell us. If the authors what to display the dependence of loads on discharge, it might be a better

idea to draw a cumulative graph of the load as a function of the discharge.

p. 5035, line 3: Missing percent signs.

p. 5035, line 13: The authors state that events contribute disproportionally much to the element export. I completely understand what they mean by that statement, but I think that it is misleading in a way. If we compare the discharge on a day by day basis, days with high discharge will inevitably transport more water than days with low discharge because the variability in discharge is so high. Since a hundredfold increase in discharge is not association with a hundredfold decrease in concentration, the days with high discharge will consequently contribute with more element export than days with low discharge. I think this is how the authors have calculated. However, in proportion to how much water that really is transported during the hydrological events the element export is actually lower than usual. This follows from the fact that the concentrations tend to be lower at high discharge. In this sense it is not correct to say that the event contribute disproportionally much (in proportion to discharge that is). However, I think the key point here is that much of the element export takes place in a short periods of time in connection with hydrological events. I think the authors should reformulate this section so that it is clear whether they refer to time or discharge when they discuss proportionalities.

p. 5035, line 29: It is perhaps a bit strange to refer to the mobilization of As and Pb as "production"; as elements they are not produced in same sense as organic carbon for instance. It also sounds strange to say the export was limited by high discharge, when high discharge is a prerequisite for high export. Do the authors refer to the fact that high discharge is associated with low concentrations? Perhaps it would also be good to comment the transport during the winter at this point, since the authors discuss the annual export. Is the winter export negligible?

p. 5035, line 24: A relevant reference on Pb isotopes in a peatland would be Klaimder et al. (2008): The biogeochemistry of atmospherically derived Pb in the boreal forest

of Sweden.

p. 5036, line 17: The authors emphasize the importance of sampling several cores when estimating the inventories of Pb and As, and I believe that their results speak for themselves in this case. However, they might also want to comment on what implications this conclusion might have for the pore water, which only was sampled at one site. Given the large variability in the peat, how representative can we expect the pore water measurements to be for the bog as a whole?

p. 5046, table 2: Calculating the years until exhaustion seems a bit speculative, since is requires a lot of assumptions, for instance that the export would be fairly constant over the next millennia. There are a number of factors that complicate such assumptions, for instance that the export probably would decrease as the inventories decrease or that the burial of the contaminated peat layers will change the biogeochemical conditions as well as the hydrological role of the contaminated peat layers. I think it would suffice to say that with current export rates it would take more than 1,000 years to deplete the bog of anthropogenic Pb and As (but in reality I think it would probably take much longer). As a comparison, in a forest soil Klaminder et al. (2008) estimated that it would take almost 1,000 years even before Pb peaks in the stream water (Flux rates of atmospheric lead pollution within soils of a small catchment in northern Sweden . . .) – although this of course is a quite different system. One could also compare to the mobility in peat of other elements, which bind strongly to organic matter. For instance, Lidman et al. (2013) showed that that transport of U in a minerotrophic mire is extremely slow. Even after thousands of years most of these metals are still found near the edges of the mire, while the more central parts are practically unaffected although they are hydrologically active. (Distribution and transport of radionuclides in a boreal mire- assessing past, present and future accumulation . . .).

It would by the way be interesting to know whether the bog currently is a net source or a net sink for Pb and As. If that information is available it could perhaps be added somewhere.

p. 5047, fig. 1: Would it be possible to also show the catchment boundary?

p. 5049, fig. 3: I appreciate the efforts to show high resolution data in detail, but I still find it quite hard to see exactly what is going on. There is still quite a lot of blank space in between the data so I wonder whether it would be possible to show the time series in even greater detail, perhaps even with separate sub-plots for each of the three episodes?

p. 5051, fig. 5: The unit for Fe (mg/L) seems to be incorrect.

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