Author's Response to Referee's

We would like to thank the two Referees for their helpful and constructive comments, which further improved the manuscript. Our detailed responses are listed below. For Author's changes see the attached revised manuscript with mark ups (track changes in MS Word) below. Page and line numbers of changes in the attached manuscript are given in brackets.

Response to Referee #1

 # Specific comments:

 # 1) The paper would benefit from additional editing to address numerous grammatical issues and significant digits. Some of those are noted below (but not all). The paper could also be shortened and focused.

Response: We thoroughly read through the text again and tried to shorten and revise grammar and language errors, as well as unit and significant digit issues.

 # 2) Some additional detail on the sampling would be useful. In addition, it would be helpful to mention the analysis of samples for Fe in the abstract.

Response: We describe the procedure of pore water sampling in more detail now, as we think this part of sampling was the less detailed in the sampling description before. Iron (Fe) is now included in the abstract as suggested by the referee. (p. 2 line 7 and p. 7 line 20-23)

 # 3) The authors note that they are assessing the importance of temp, pH and redox as well as precip for transport. The first two were only occasionally measured, and the third (redox) was inferred, not measured.

Response: The referee is right that we measured temperature and pH only occasionally in the discharging stream, while direct redox measurements are lacking. In terms of the temperature our statement does not relate to stream measurements, but to our weather monitoring on site. The pH is related to our bog pore water measurements also, where redox and pH are important for mobilization processes. Anyway, we do not present this data in our figures. Therefore, we included the temperature record in figure 1 and point out pH measurements within the text. We cut redox from our study description. (p. 4 line 1; Figure 1)

 # 4) The "Years until exhaustion" in Table 2 doesn't appear to be in the text and is confusing. Presumably the calculation is based on the assumption of no new inputs and the measured rates of transport. This obviously doesn't make sense for DOC as production will continue. I'd cut it from the table.

Response: The referee is right and we deleted "Years until exhaustion" from the table. (Table 2)

 # Technical issues:

 # P. 5016, line 5: "one year of continuous"…

Response: We rephrased that sentence. (p. 2 line 5)

 # P. 5016, line 25: %, not ‰ (see also P. 5036, line 24)

Response: We thoroughly recalculated our given number. The ‰ unit is correct. But as the units in Table 2 might be misleading we added the unit kg ha^{-1} for peat inventories in the Table 2 on page 5046. We hope that this will clear out proportion between inventories and fluxes. (Table 2)

 # P. 5018, line 21: over the past centuries

Response: We rephrased that sentence. (p. 4 line 22)

 # P. 5022: Please note the total number of discrete samples used for load calculations

Response: This is a good suggestion and we added the number of samples used for our flux calculations in brackets. (p. 9 line 10)

 # p. 5036, line 2: is that +- really 43%, or supposed to be 43 kgC ha?

Response: The standard deviation unit for carbon was given in percent. But for consistency and to avoid misunderstanding we changed from the percent unit to kg C ha^{-1} now. (p. 25 line 24)

 # p. 5036: These should be referred to as yields rather than fluxes given that they are normalized by area.

Response: According to other studies we changed to the term "export" instead of fluxes now.

 # p. 5027, line 26: That might be "very low" DOC for the bog, but it's high for most places.

Response: We rephrased that sentence to avoid misunderstanding. (p. 15 line 7)

 # p. 5027, line 5: Do you mean "Pb and As…"? Or is it DOC and supposed to be mg/L? line 29 as well.

Response: This is of course misleading. The first concentrations are meant to be DOC concentrations in mg L^{-1}. The unit has been deleted during the editing process by Biogeosciences and slipped our revision. It is corrected. (p. 14 line 11)

 # Figure 3. The plots are difficult to see. I'd suggest making it a multi-panel plot by storms instead.

Response: We reworked the former Figure 3 to present the storm event data. We think that the new version is easier to understand and that the data is better presented now. (Figure 3)

 # Figure 7. Plots are difficult to see. Consider different colors for constituents.

Response: We changed the characters of Figure 7 to highlight the load data in front of the additionally given concentration data. (Figure 7)

Response to Referee #2

 # 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.

Response: This is an important point and we are glad that the referee highlights this issue so we can clear out this requisite of our study. When defining the catchment area by the topographic appearance and permanent water ways we need to partly include a forested hillslope on the northern site of the bog. When it comes to rain events we observed that formerly standing small water pools at the edge of the bog get connected and form a water way around the domed bog. This water way does not discharge to our monitored sampling site. Furthermore, at dry or medium conditions you can perceive those small standing water pools and some minerotrophic peatland vegetation very limited at the peatlands edge. We argue that water movement through the bog peat body is very slow and the distance from the edge to the erosion rill within the bog is large enough to encourage the statement that no minerogenic signal influences our bog discharge through the filtering function of a bog. Next to the presented DOC, As, and Pb concentrations we also measured U, Ca, La and other rather minerogenic elements. We can assure you that these data further supports those assumptions we made.

We addressed this objection by changing parts of the catchment description and a modified study site map (p. 9 line 12-19 and Figure 1). See also specific comments discussing this objection further below.

 # 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.

Response: We thoroughly read through the text again and tried to revise grammar and language errors.

 # 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.

Response: The referee is right that the ombrotrophic nature of bogs is part of their definitions. We pointed this out as this characteristic is very important for our argumentation. Nonetheless, we deleted the expression from the manuscript. Regarding the latter suggestion of the referee, we also broadened the assigned capability to accumulate Pb and As to peatlands instead of bogs. (p. 4 line 18)

 # 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.

Response: From our point of view the statement that the upper part of a bog is the most active part is valid. The context of this introducing sentence is not just a hydrologic point of view, but also a biogeochemical one as further described in the following sentences within the manuscript. It relates to microbial and decomposition processes due to aeration, higher temperatures during summer months and fresh organic material. These conditions are lacking in the deeper parts of the peat body. The acrotelm – catotelm model is of course an abstract assumption, which might be invalid in detail or at specific sites. In blanket bog environments preferential flow through pipes has been described previously (e.g. Holden & Burt 2002). We cannot exclude the occurrence of preferential flow deeper in the bog, but that deeper water within a bog has great influence on discharge is rather an exception than a rule. The solid phase peat analyses do also clearly indicate that the acrotelm is hydrologically isolated. Moreover, we believe that this issue is better to be picked up in the discussion than in the rather general introduction.

 # 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.

Response: The reviewer is right when stating that the surface-near peat layers are the main metal source released from peatlands is too general. However, the assumption on the origin of metals in bogs is a bit speculative, also. We think that this statement is just valid for bogs, which receive elemental input just by atmospheric deposition and not by any minerogenic input. Therefore, we changed the expression to "ombrotrophic peatlands". (p. 5 line 6)

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

Response: As described before to comments from Referee 1: This happened through the editing process by Biogeosciences and slipped our revision. It is going to be corrected again. (p. 7 line 23,24)

 # 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.

Response: We picked up the referee's comment and tried to better describe the catchment characteristics. We modified Figure 1, where we included a rough catchment boundary and the impermanent water flow out of the catchment area. In addition to the new figure we provide a more detailed description in the manuscript. We think that the nature of this particular catchment area is clear now. (p. 9 line 12-19, Figure 1)

 # 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?

Response: The inventories of As and Pb were calculated for the upper 30 cm of the peat as is stated in the text. We rephrased that description to avoid misunderstanding. It is common to calculate inventories just for the upper peat layer (see for example: Rothwell et al. 2010) as this is in general thought to be the most reactive part of the whole peat body. This characteristic is one important factor for element mobilization, next to the hydrologic flow path. In regard of Pb and As contents: The anthropogenic enrichment of those elements in the upper part (~1.2 m) of the Odersprung bog in the Harz Mountains is 10000 times higher than the natural background level in prehistorical peat. Even if the minerogenic part is enriched compared to the ombrotrophic part it would be negligible. Furthermore, in our long core we see a slightly minerogenic part with elevated Fe contents in the deepest part of

the peat profile, but As and Pb are not enriched there (see Fig. 5a in the manuscript). (p. 10 line 5)

 # 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.

Response: As mentioned by the referee, the hydrology is a cornerstone of this study. We think that combining hydrology and geochemistry is the most important approach of our study and we would prefer to leave the description of the hydrological pattern as is. Nonetheless, we tried to shorten this section and eliminate redundancies. We also tried to fit discharge and water level to a simple logarithm, but this was not successful.

 # 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.

Response: At the beginning of this comment we would like to point out that there is no groundwater within a bog. It is part of the bog definition that it is disconnected from the (flowing) groundwater. Therefore, we refer to water level instead. There is the possibility that through changes in the hydraulic head different pathways may be connected, but the possibilities in a domed bog are limited. We cannot exclude preferential flow through pipe systems, but this wouldn't change argumentation as precipitation is then hardly in touch of the peat body as well and is quickly released again just like surface flow. We can exclude seeping from older water deeper in the peat body through water level changes and a possible replacement of older water by newly fallen rain. We measured ^{18}O and ^{2}H isotopes occasionally on discharge samples and pore water, which further supports our assumption. We did not include this data, because it would further enlarge this already complex manuscript.

 # 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.

Response: Regarding the comment on iron sources within the bog, we admit that iron can be enriched in the down most part of the bog, where peat is of minerogenic origin. At our study site we also see elevated Fe contents at the bottom of the peat body. Nonetheless, by the redox induced iron cycling in the upper peat layer, iron gets slightly enriched there as well. As we argue that the deeper peat layer is hydraulically disconnected from surface runoff and discharge, the main iron source here should be the upper peat layer. Additionally, through the former mining activity in the Harz, bogs experienced intense deposition of dust from deforestation and ore roasting, which also contained iron. We agree with the referee that iron can be of minerogenic origin, if other mineral soils would drain into the stream. We hope that we addressed this issue sufficiently earlier.

 # 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.

Response: This has been changed by Biogeosciences. (p. 14 line 11)

 # 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.

Response: Yes, the water level rose from 13 cm to 6 cm depth. We tried to be concise in using no minus before depth data, but apparently some have slipped our revision at the beginning of the manuscript. We changed that. This unit usage is in agreement with the common application. (p. 14 line 14)

 # p. 5027, line 19: Missing unit.

Response: We couldn't find any number with missing unit in this line. Nonetheless, we assure you that we thoroughly revised units in the text again.

 # 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.

Response: We agree with the referee that iron must not necessarily precipitate in this specific system. However, a distinct iron enrichment in the uppermost peat layer (see Fig. 5a in the manuscript) indicates that iron precipitates at the redox boundary. We believe that Fe plays a minor role in this environment, which we also state in the pore water section. We also refer to that section at this commented part of the manuscript. Nonetheless, we think it is important to mention the possibility of Fe precipitation, as this plays a major role in As-binding in peatlands and peatland draining streams in general. (p. 15 line 1-6)

 # 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?

Response: We agree with the general statement of the referee. As our study is more focused on the connection of the geochemistry and hydrology we cannot cover this biogeochemical

question by our data set. This would be a mechanistic study on its own, while we might see this underlying process in our discharge samples. We also express this in the manuscript. (p 17 line 2, p. 18 line 10 and p. 27 line 22-24)

 # 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.

Response: At the time of all three events there was no ice or snow within the catchment area. We included this remark in the sampling description now. (page 7 line 18)

 # 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 appreciate 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?

Response: We rearranged Figure 3 with separate plots for each event. Regarding the correlation of concentrations to water level and discharge, we tried that. The problem is that you have rising and declining limbs of discharge and water level depth, which exhibit completely different concentration dynamics due to exhaustion effects. Furthermore, there are different concentration levels depending on season and a delay between measured stream concentrations and water level. That is what screws a correlation of those parameters in this study.

An oscillating pattern of iron can be seen indeed in one of our high resolution sampling periods. It might be a diurnal pattern, but with that little data it is quite speculative though. We included the iron data just for the sake of improving interpretation of the As data. Therefore, we do not comment this pattern for avoiding enlargement of the manuscript.

(Figure 3)

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

Response: We tried to rephrase part of this paragraph for better readability and tried to clarify the discussion of this specific point. (p. 18 line 12-18)

 # 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.

Response: We did include the approximate ages of those peaks now. (p. 18 line 24 – p.19 line 2)

 # p. 5030, line 28: Missing units.

Response: The requested units were partly deleted by Biogeosciences during the editing process. We reentered units in the manuscript. (p. 19 line 7)

 # 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).

Response: The referee is right stating that the word "immobile" is not completely suitable here. We are aware of the described problem. In our revised version we tried to rephrase the sentence to avoid this misleading adjective. (p. 19 line 9-12)

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

Response: The comparison of element to DOC ratios is a useful tool to track changes in export dynamics from the bog. We evaluated those, but decided to exclude them from this manuscript during preparation.

 # 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.

Response: We think this confusion is caused by the catchment problem we tried to unravel and improve earlier. The assumption we made is not contradicting, but is rather a matter of scale. When the water level is low and low discharge occurs we still deal with a water level depth of 40 cm maximum, which is still high in comparison to the whole water saturated peat body of about 3 meters depth. We state that the water discharge from the upper part of the peat body, meaning at water level depth. Even during low discharge we do not see water seeping from deeper down the peat body, what we proofed by the chemistry of the pore waters and stream samples. This is also consistent with the As, Fe and DOC data.

To address the question of pore water samples being representative for the whole bog, we include this aspect into the manuscript now, because this is of course a valid concern we cannot disprove. Nonetheless, not published peat core data of this bog – and also peat cores from other bogs in close vicinity – prove that As and Pb depth distribution profiles are very similar with dominating peaks induced by mining activity. Therefore, we assume that the pore water profile is quite similar with depth in the whole bog, but concentration levels are very likely varying. (p. 27 line 2-4)

 # 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.

Response: We thank the referee for this constructive comment. We created a new figure, which illustrates element load to discharge plots. After plot separation in different season and rain events this figure turned out to be very helpful in explaining different fluxes depending on season and rain events. Nonetheless, we kept the Figure 7 (slightly modified) within the manuscript. We think that it gives an important overview of the whole annual

record and further helps to understand the discussion about fluxes separated by season and rain events. (Figure 7 and Figure 8)

 # 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.

Response: The referee is right stating that 10% of discharge represents a volume. The referee's assumption is correct, that we actually meant 10% of time span with highest discharge values, which is different. We corrected this. We also want to point out that the hydrograph separation is not arbitrary, but set to a value where discharge is only very slowly declining anymore. As we have no constant groundwater flow it is more complicated to set a baseflow threshold. Nonetheless, we think it is important to try to separate hydrologic conditions between "event water" and water which is not directly influenced by a rain event. Nonetheless, we tried to identify redundancies and thereby shortened this section. (e.g. page 24 line 1)

 # p. 5035, line 3: Missing percent signs.

Response: The requested percent signs were deleted by Biogeosciences during the editing process. (page 24 line 2)

 # 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.

Response: The main idea of this section is to show how much of the elements are actually transported by rain events, regardless of the amount of water. This means - even if it seems quite simple - that through the rain event more As and Pb is mobilized as if there would be no rain event. Describing this and the different pattern of export in spring and fall is important in view of changing weather conditions in the future. More rain events would export more As and Pb and it is also important at which time of the year rain events agglomerate. We tried to reformulate this part of the manuscript. (p. 24 line 18 and p. 25 line 5-7)

 # 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?

Response: It is a good objection to mention winter export in this section. We included a small explanation why it is not possible to survey winter fluxes. We also changed the specified sentence which tries to explain seasonal flux differences. (p. 25 line 25 – p. 26 line 1-3 and p. 25 line 10-12)

 # 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.

Response: We added this particular reference. As it mainly focuses on mineral soils this publication failed our literature search. (p. 25 line 3)

 # 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?

Response: This aspect has been discussed before (see comment on p. 5034 line 8). As this is a point we cannot disprove we implemented this limitation in the manuscript. (p. 27 line 2-4)

#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.

Response: The measurement of As and Pb deposition was beyond the scope of this study. That is why we cannot provide any information whether the bog is a current net source or sink even so this is a very interesting subject. We did not consider to add further elements to this study, as we focused on As and Pb export dynamics here and additional elements would disproportionally enlarge the manuscript. A comparison with literature is difficult as those studies the referee refers to are in different peatland systems, which exhibit a completely different hydrology. We deleted the information "years until exhaustion" from Table 2 and added a short notice in the text instead, which considers mentioned concerns. (Table 2 and p. 26 line 25 - p.27 line 2)

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

Response: We included an approximate catchment area boundary in Figure 1 now. (Figure 1)

 # 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?

Response: We modified Figure 3 with separate plots for each event. (Figure 3)

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

Response: Yes, we corrected this to µg L^{-1}. (Figure 5)

1 **Hydrologic controls on DOC, As and Pb export from a polluted peatland – The**

2 **importance of heavy rain events, antecedent moisture conditions and hydrological**

3 **connectivity**

4 T. Broder, H. Biester

5 Institut für Geoökologie, AG Umweltgeochemie, Technische Universität Braunschweig,

6 Langer Kamp 19c, 38106 Braunschweig, Germany

7 Correspondence to: T. Broder (t.broder@tu-bs.de)

Abstract

Bogs can store large amounts of lead (Pb) and arsenic (As) ~~attributed from~~ to atmospheric deposition of anthropogenic emissions. Pb and As are exported along with dissolved organic carbon (DOC) ~~in from~~ these organic-rich systems, but it is not yet clear which hydrological (pre-)conditions favor their export. This study combines a one year ~~continuous~~ monitoring of precipitation, bog water level and pore water concentration changes with bog discharge~~,~~ and DOC, iron, As and Pb stream concentrations~~.~~ ~~and fluxes~~From this data annual DOC, As, and Pb exports were calculated. Concentrations ranged from 5 mg L^{-1} to 30 mg L^{-1} for DOC, 0.2 µg L^{-1} to 1.9 µg L^{-1} for As~~,~~ and 1.3 µg L^{-1} to 12 µg L^{-1} for Pb with highest concentrations in late summer. As and Pb concentrations significantly correlated with DOC concentrations. Fluxes depended strongly on discharge, as 40% of As and 43% of Pb were exported during ~~by the upper~~ 10% of time with highest discharge, pointing out the over-proportional contribution of short-time ~~heavy rain and~~ high discharge events to annual As, Pb and DOC export. Exponential increase in element export from the bog is explained by connection of additional DOC, As and Pb pools in the acrotelm during water table rise, which is most pronounced after drought. Pb, As and DOC concentrations in pore water provide evidence of an increase of the soluble Pb pool as soon as the peat layer gets hydrologically connected, while DOC and As peak concentrations in runoff lag behind in comparison to Pb. Our data indicates a distinct bog-specific discharge threshold of 8 L s^{-1}, which is thought to depend mainly on the bogs size and drainage conditions. Above this threshold element concentration do not further increase and discharge gets diluted. Combining pore water and discharge data shows that As and Pb exports are not only dependent on the amount of precipitation and discharge, but on the frequency and depth of water table fluctuations. Comparing the annual bog As and Pb export with element inventories indicates that As is much more mobilized than Pb, with annual fluxes accounting for 0.85 ‰ and 0.27 ‰ of total As and Pb inventory, respectively.

1 Introduction

Peatlands ~~inherit~~ provide important ~~functions~~ services in the environmental system. They play an important role in the storage of carbon and other elements such as heavy metals. On one hand the filtering function of peatlands partly prevents the input of these pollutants to streams. On the other hand, peatlands can release heavy metals as soluble DOM-metal complexes. Even though, acting as major carbon sink, peatlands are also the greatest source of dissolved organic carbon (DOC) to the aquatic system (Aitkenhead et al., 1999). Several studies demonstrated runoff, water level fluctuations and temperature to be the most important controls on terrestrial DOC production and export (Freeman et al., 2001; Hongve et al., 2004; Köhler et al., 2008; Seibert et al., 2009; Laudon et al., 2011). ~~Lately~~Recently, numerous studies describe the emerging problem of rising DOC levels in streams and lakes especially in catchment areas comprising peatlands (e.g. Worrall et al., 2004; Monteith et al., 2007), which might cause severe problems for aquatic biota and in drinking water production (Chow et al., 2003). ~~Next to~~Besides the observed general increase in concentrations, which has been attributed to the decrease in acid rain deposition or temperature rise (Freeman et al., 2001; Evans et al., 2005; Monteith et al., 2007), a flushing effect, which produces high instantaneous DOC loads during high discharge events after a summer dry period has been described (e.g. Worrall et al., 2002; Clark et al., 2007). Even though temporally limited, the high concentrations might affect the aquatic system even stronger. This effect gains more importance through the predicted climate change with enhanced dry periods and more frequent heavy rain events (IPCC, 2013). How these high DOC concentrations after re-wetting of the peatlands surface-near layer built up is not yet fully understood. Fenner and Freeman (2011) proposed that the microbial DOC production is stimulated after a drought period by reduced concentrations of phenolic compounds through an enhanced phenol oxidase activity. Moreover, release of DOC adsorbed to Fe-(oxy)hydroxides through Fe-

(oxy)hydroxides dissolution after re-wetting and decreasing redox potential has shown to be an important process for DOC dynamics in peatlands (Bauer and Blodau, 2009; Knorr, 2013; Riedel et al., 2013), as well as DOC ~~solution~~solubilization through pH rise (Grybos et al., 2009). Similar~~ly~~, Clark et al. (2012) described a decrease of DOC solubility due to acidification during droughts.

Although the general focus in most studies is set on changing DOC dynamics, it is also known that some elements are mainly exported by transport with DOC to the discharging stream. Lead (Pb) strongly binds to organic matter (Tipping, 1998; Rothwell et al., 2007) and high DOC concentrations increase Pb mobility (Jordan et al., 1997). In spite of the high affinity of arsenic (As) to iron(oxy)hydroxides, recent mechanistic studies revealed a strong binding of As to sulfhydryl groups of organic matter in the anaerobic peat layer (Langner et al., 2011, 2014). Due to the low pH (<4.5 pH) and the low amount of mineral phases in peat, a correlation of DOC and As concentrations in bog draining streams has been observed (Rothwell et al., 2009; Neubauer et al., 2013). ~~Especially~~Moreover, As is known to be subjected to post-depositional mobilization due to water level fluctuations and resulting redox changes (Blodau et al., 2008; Rothwell et al., 2009; Langner et al., 2014).

~~Ombrotrophic b~~Bogs, which receive element inputs exclusively by atmospheric deposition, and also other peatland types have the potential of accumulating As and Pb in the peat. The anthropogenic deposition rate of those two elements largely exceeds pre-industrial background fluxes (Shotyk, 1998; Bindler, 2006). Mining activity, fossil fuel combustion, especially emissions from burning of leaded gasoline, often resulted in high As and Pb concentrations in peat layers, which developed over ~~of~~ the past centuries. Based on observed metal concentrations some peatlands especially those influenced by mining areas would even have to be classified as highly contaminated soils.

The near surface layer of a bog, the acrotelm, is the most active part, and conducts most of the bogs discharge (Evans et al., 1999; Holden and Burt, 2003) and DOC production (Clark et al., 2008). Due to ~~its~~ high porosity, the acrotelm has a high hydraulic conductivity and is characterized by recurrent~~ly~~ water table drawdowns and aeration resulting in higher biological activity. Moreover, this surface-near peat layer, which often hosts large amounts of atmospheric derived metals, is the main source of metal release from <u>ombrotrophic</u> peatlands.

Up to now, most studies on heavy metal release from contaminated peatlands have ~~been~~ focused on discharge ~~measurements~~, only. Studies connecting DOC export with *in-situ* pore water chemistry measurements are rare or lacking in regard of Pb and As. Clark et al. (2005) found a strong correlation between peat soil solution DOC and stream water DOC concentrations over a ten-year record. ~~However, a lot of~~<u>Many</u> field or lab<u>oratory</u> ~~experiment~~ studies focused on DOC production in view of water level, redox-state, acidification, temperature or microbial conditions (e.g. Grybos et al., 2009; Clark et al., 2012; Evans et al., 2012) without <u>a</u> connection to discharge measurements or <u>they</u> were conducted ~~with~~in mineral soil~~s~~ <u>environments</u> (e.g. Kokfelt et al., 2009; Singh et al., 2014, for Pb see Vinogradoff et al., 2005). In regard of As, Blodau et al. (2008) found a higher release of As in minerogenic peat mesocosms after a drought period, which is in line with leaching experiments described by Tipping et al. (2003). Rothwell et al. (2009) observed higher As concentrations during late summer storm flow after the summer dry period in a~~n~~ ~~ombrotrophic~~ bog catchment.

The aim of this study is to gain further understanding in the generation and controls of Pb and As export from ombrotrophic ~~bogs~~<u>peatlands</u>. If the export of Pb and As is mainly controlled by DOC production and transport, higher metal concentrations and fluxes are expected during periods of elevated DOC concentrations ~~as well~~. ~~Export~~ <u>Moreover, export</u> dynamics ~~are~~ <u>should</u> strongly depend~~ent~~ on peatland hydrology. This study tries to unravel the importance of hydrologic conditions like antecedent bog water levels, as well as precipitation, ~~and~~

temperature, and pH ~~and redox conditions~~ for the export of As and Pb. <u>We expect that T</u>~~T~~these

factors ~~should~~<u>mainly</u> control hydrologic pathways, DOC production and the hydraulic

connection of different As and Pb pools. We <u>thus</u> aim to investigate to which extent As and

Pb export is constrained by supply of DOC and related soluble metal organic complexes or

discharge quantities.

To tackle these questions we chose a~~n ombrotrophic~~ bog, which is heavily contaminated by

As and Pb through historic mining activities and is known to exhibit high As and Pb

concentrations in the acrotelm. We continuously monitored direct bog discharge at a first

order stream to gain information of the DOC, Pb and As export dynamics dependent on preci-

pitation. To combine discharge generation and element concentrations with (pre-)conditions

within the peat catchment, we sampled pore water to investigate time- and depth resolved

DOC and metal release patterns and monitored temperature, precipitation and water level at

the bog. For an estimation of the overall export and mobilization potential from the bog we

calculated fluxes and peat As and Pb inventories. To examine the importance of storm flow

events we conducted high resolution measurements occasionally during snowmelt and rain

events in spring and fall.

2 Materials and Methods

2.1 Study Area

The Odersprung bog (OS, 52°46.383'N, 10°33.816'E; 800 m asl, 1500 mm mean annual

precipitation and 5°C mean annual temperature) is an ombrotrophic peatland located within

the nature protection area in the Harz Mountains in Northwestern Germany. The treeless part

of the bog covers an area of about 17 ha and has a mean peat depth of 3 m (Beug et al., 1999).

Vegetation is dominated by *Sphagnum magellanicum* and *Sphagnum rubellum*. *Eriophorum*

1 *angustifolium* and *Molina caerulea* occur less frequently (Baumann, 2009). The bog is

2 drained by a small erosion rill, which originates within the bog and further drains adjacent

3 peaty and upslope podzolic forest soils with dominant spruce vegetation. Discharge sampling

4 was conducted at the rill outflow of the bog where all water is exclusively received from the

5 bog. Former studies on the effect of past local mining activities in the Harz Mountains

6 indicate reported Pb and As peat concentrations of up 2300 mg kg^{-1} and 100 mg /kg^{-1},

7 respectively, which is by a factor of 10,000 (Pb) higher than background values (Biester et al.,

8 2012).

9 **2.2 Sampling and Field Measurements**

10 Seasonal discharge sampling was conducted from April 2013 to November 2013 covering the

11 time from snowmelt to begin of snowfall. Water samples were taken in a six day interval by

12 an automated water sampler (ISCO autosampler 3700), equipped with 0.5 L PE bottles and a

13 Teflon hose, which was automatically rinsed with sample water before prior to each sampling.

14 Further grab samples as well as pH and electric conductivity measurements were conducted

15 every two to three weeks. For grab samples new 50 mL PE tubes were used and previously

16 rinsed with sample twice before sampling. For all sampling techniques blank controls were

17 run. Several storm flow events were sampled at high frequency (every 3 hours) over a period

18 of three days, respectively. At all sampled events the catchment was free of ice and snow.

19 Pore water samples at the Odersprung bog were taken using a suction sampler described in

20 Broder et al. (2012). In short, the sampler consisted of PE-sinter slides (5x0.5x1 cm) inserted

21 in a 3.5 m long rod. Slides were connected by tubing to a stop-cock above the peatland

22 surface. Samples were taken by means of PE syringes and transferred to new PE tubes, which

23 were rinsed with sample before. Sampling resolution was 20 cm until 60 cm depth and 30 cm

24 until 210 cm depth. The suction sampler was installed within the catchment area of the

1 erosion rill (Fig. 1). Close to the pore water sampler a peat core was extracted using a Russian

2 peat corer (Eijkelkamp Agrisearch Equipment). Cores were collected down to 300 cm depth,

3 sliced in 2.5 cm sections, frozen and freeze ~~dryed~~dried. For the calculation of As and Pb

4 inventories in the acrotelm 15 short cores (30 cm depth) were sampled by means of a

5 Wardenaar peat profile sampler (Eijkelkamp Agrisearch Equipment).

6 Discharge ~~quantification~~ at the bog outlet was ~~conducted~~ quantified using a V-notch weir.

7 Stage was recorded every 15 min by a water level logger (Odyssey dataflow systems) for the

8 recalculation to the actual discharge. Water level at the bog site was monitored in close

9 proximity to the pore water sampler using PVC piezometer tubes of 4 cm diameter, fully

10 slotted until 120 cm depth and a water level logger (Odyssey dataflow systems). Temperature,

11 relative humidity and precipitation (using a tipping-bucket rain gauge) were ~~individually~~

12 monitored (tinytag tgp 4500 and 4810, Gemini) ~~on~~ at the site.

13 **2.3 Laboratory Analyses**

14 Water samples were filtered with 0.45 µm nylon filters (Merck, Millipore) within the

15 laboratory and stored at 4°C. All water samples were analyzed for total dissolved organic

16 carbon by a thermo-catalytic total carbon analyzer (Analytik Jena multi N/C 2100S) using the

17 NPOC method. As, Fe and Pb concentrations were determined by an ICP-MS (Agilent 7700).

18 Instrumental drift and quality was checked by certified reference materials (SPS-SW 1 and

19 SLRS-4, riverine water, National Research Council, Canada). Detection limits for Fe, As and

20 Pb were 0.01 µg/L, 0.001 µg/L and 0.001 µg/L, respectively.

21 All peat samples were freeze dried, milled and further analyzed with a resolution of 2.5 cm

22 until 50 cm depth and 10 cm resolution below. Peat As and Pb concentrations were

23 determined by an energy-dispersive miniprobe multielement analyzer (EMMA-XRF, see

1 Cheburkin and Shotyk, (1996)). Carbon and nitrogen concentrations in peat were measured

2 using an elemental analyzer (Euro EA 3000, HEKAtech).

2.4 Flux calculations and As and Pb inventory estimates

4 DOC, As and Pb annual fluxes were estimated by calculating the total annual load from

5 analyzed water samples and the continuous discharge record using method 5 according to

6 Walling and Webb (1985) and Littlewood (1992):

$$Load = K \times Q_r \left(\frac{\sum_{i=1}^{n} C_i Q_i}{\sum_{i=1}^{n} Q_i} \right) \tag{1}$$

8 Where K is a conversion factor (here number of seconds per year), Q_r here the annual mean

9 discharge from the continuous record, C_i the instantaneous concentration, Q_i the instantaneous

10 discharge and n the number of samples $(n = 112)$. Load estimates were divided by catchment

11 size to gain fluxes in g ha^{-1}a^{-1}.

12 ~~At the Odersprung bog~~ The rill catchment area is mainly covered by ~~the~~an open and treeless

13 part of the bog~~covers about 65% of the peatland area (8 ha), the remaining is podsolic forest~~

14 ~~soil~~ (8 ha, see Fig. 1). Catchment boundaries were determined by topographic conditions and

15 the occurrence of perennial streams, which required including a part of a hillslope with

16 shallow podsolic forest soils. However, it was perceived that small pools build up between the

17 domed bog and forested areas, which drain downslope during rain events, and do not

18 discharge into the bog (see also Fig. 1). Therefore, the chemical characteristic from the bog

19 stream should not be biased by forest soil draining water. Flux calculations from high-

20 frequency concentration measurements during snowmelt and discharge events were calculated

21 according to method 3 (Walling and Webb, 1985), where instantaneous loads were calculated

22 by the measured concentration and the integrated discharge data of the preceding sampling

23 interval (3h) to obtain a ~~most accurate~~robust discharge estimate. To further improve flux

1. estimates the annual record was separated either by season or by hydrograph and was ~~also~~

2. additionally calculated by method 2 (after Walling and Webb, 1985). Standard error and 95%

3. confidence limits of flux calculations were conducted after Hope et al. (1997). As and Pb

4. inventories for the peatland catchment were calculated from the median value of the upper 30

5. cm As and Pb inventories of all 16 peat cores ~~the long peat core and 15 short cores~~ to estimate

6. an inventory per unit area of the bog surface. Uncertainties of the inventory calculations were

7. estimated by the standard deviation from the mean of all As and Pb inventories of the 16 peat

8. cores.

9.

10. **3 Results and Discussion**

11. **3.1 Hydrologic conditions**

12. ~~Precipitation pattern in~~The year 2013 ~~is~~was characterized by strong snow melt and several

13. intense rain events (Fig. 2). The precipitation record before day of the year (doy) 100 (mid of

14. April) and after doy 289 (end of October) was affected by snowfall, which produces

15. exceptionally high precipitation values that distorts quantification as we used a tipping-

16. bucket. ~~Also, a~~At two other occasions the rain gauge got clogged, ~~resulting in~~thus for a few

17. high flow discharges and water level rises~~, where~~ no rainfall was recorded (doy 150-162 and

18. doy 256-270). During the snow-free record from mid-April to mid-October the catchment

19. received 537 mm rain. Monthly precipitation totals recorded highest rainfall in fall,~~ where~~

20. ~~rain events followed up in short time intervals.~~, while ~~A~~a longer dry period prevailed in

21. summer~~, where only short but intense rainfall occurred~~.

22. In total, 36 discharge events with high flow ~~can~~could be distinguished after the end of

23. snowmelt. High flow events partly followed shortly after a preceding event, especially in fall

24. where rain was frequent.~~ Even though discharge did not return to low flow under those~~

10

1 ~~conditions, event peaks can be clearly distinguished.~~ The two main discharge events of the

2 2013 record triggered by a longer rain fall period, occurred in spring and peaking at a

3 discharge of 44 L s^{-1} and 55 L s^{-1}. The three largest events in fall peaked at 23-24.5 L s^{-1}.

4 High discharge values at the beginning of the record indicate that snowmelt contributed an

5 important portion to the annual discharge (Fig. 2). As a quantification of the complete

6 snowmelt discharge was impossible, calculated annual element fluxes might be

7 underestimated (Dyson et al., 2011). A typical event hydrograph exhibits a steep rising and

8 falling limb with a slow decline as the event subsides. Setting a low flow limit at 0.3 L s^{-1} by

9 thorough visual hydrograph separation, low flow occurred during more than 28% of the time

10 record but contributed only 2.5% of total discharge. This is indicative of an event runoff

11 regime with negligible groundwater contribution. In fact, constant base flow over longer

12 periods could never be observed, as flow steadily declined without rain fall until it almost

13 ceased when the accessible water pool in the acrotelm was depleted. Therefore, we do not

14 refer to base flow conditions, but rather use the term low flow as no steady groundwater

15 component seem to contribute to the bog's discharge. The flashy hydrograph response fits to a

16 rapid runoff generation by surface-near and surface flow. The dominance of this kind of

17 runoff generation is similar to previously reported flashy regimes at blanket bogs (Evans et

18 al., 1999; Holden and Burt, 2003).

19 Lag times from the beginning of rainfall to discharge were ~~rapid~~ short with a mean response

20 time of 1.3 h ±0.5 h. Shortest lag times occurred when discharge was still high at the

21 beginning of a new high flow event similar as has been observed ~~in~~ for ~~a~~n blanket bog

22 (Daniels et al., 2008). This ~~reduced~~ instantaneous response ~~time~~ indicates that at wet

23 preconditions surface runoff prevails as this is the most rapid runoff component.

24 Despite ~~similar~~ high rainfall events in summer, only small corresponding discharge events

25 were recorded. ~~This is attributed to the observation that~~Here, the water pool of the bog's

surface-near layer is recharged before discharge takes place. The process is clearly depicted in

Fig. 2 w~~h~~<u>h</u>ere the water level rose almost immediately after beginning of rainfall at doy 205.

<u>Over the entire record</u> ~~T~~<u>t</u>he water table ranged between 3.5 <u>cm above</u> and ~~-~~36 cm <u>below</u>

~~related to~~ the peat surface ~~over the entire record~~ with a median depth of 10.~~48~~<u>5</u> cm. The

lowest water level occurred during the summer drought (~~-~~36 cm <u>depth</u>) after 20 days without

precipitation. ~~Water level recession varied between 0.6-2 cm d⁻¹ with a median value of 1.2~~

~~cm d⁻¹, but no seasonal or water level depth pattern could be observed within recession~~

~~variation~~. From the 36 discharge events 22 ~~can~~ <u>could</u> be ~~determined~~ <u>classified</u> as following

wet and 13 as following dry precondition<u>s</u> based on the median water level of 10.5 cm as

threshold value. Estimated ~~precipitation to~~ runoff <u>to precipitation</u> ratios for discharge events

~~are~~ <u>were</u> lowest for those events with exceptionally dry preconditions following the summer

drought ~~and a low water table of up to -36 cm~~. In general, dry precondition events exhibited

lower runoff <u>to precipitation</u> ratios than wet precondition events. ~~Absolute values are not~~

~~shown here, as no exact event water determination could be conducted based on our data set.~~

~~However, this estimation should be an additional indication for how the bog generates runoff.~~

3.2 DOC, As and Pb stream concentrations

DOC release patterns from the Odersprung bog were similar than those reported from other

peatlands (e.g. Worrall et al., 2002; Laudon et al., 2004; Clark et al., 2008). Lowest DOC

concentrations (5 mg L⁻¹) were observed in the middle of April during snowmelt when

dilution was highest, whereas highest DOC concentrations (~30 mg L⁻¹) occurred in late

summer to fall when DOC production was highest and mostly low flow conditions occur (Fig.

2). DOC concentration decreased ~~then~~ <u>thereafter</u> until begin of winter and the end of the

annual record. This general seasonal trend with lower concentrations in winter and spring and

increasing concentrations during summer can be attributed to reasons unrelated to discharge,

but to the seasonal temperature ~~gradients~~ <u>dynamics</u> and therefore<u>,</u> enhanced biological

1   activity, organic matter decomposition and solubility. ~~Additionally, t~~The low DOC

2   concentrations during snowmelt can be ~~mainly~~ attributed to a dilution effect, ~~here and~~ but also

3   to a smaller extent to the low DOC production and storage during winter (Dyson et al., 2011).

4   Concentrations of As ranged from 0.2 μg L^{-1} to 1.9 μg L^{-1}, whereas Pb concentrations were

5   significantly higher (1.3 μg L^{-1} to 12 μg L^{-1}) and in some cases even exceeded the WHO

6   threshold value for drinking water (10 μg L^{-1}; WHO, 2011). Highest Pb concentrations

7   occurred during a rain event in fall, which is discussed further below. Concentrations of As

8   ~~concentrations~~ showed the same seasonal trend as observed for DOC with highest

9   concentrations in summer (Fig. 2). This trend was recognizable for Pb as well, but less

10   pronounced ~~as for DOC and As~~ (Fig. 2). Both, As and Pb concentrations significantly

11   correlated with DOC (r²: 0.96 and 0.87, respectively), which supports the assumption that

12   both elements are mainly transported along with DOC within and out of this organic-rich

13   system. Pb is known to strongly bind to organic matter (Tipping, 1998)~~,~~. ~~while~~ As forms

14   soluble DOM-complexes (Buschmann et al., 2006), ~~too, it~~but also shows sorption to

15   iron(hydr)oxides or formation of As-Fe-NOM colloids or complexes (Ritter et al., 2006;

16   ThomasArrigo et al., 2014). ~~This is supported by the observation that~~Accordingly, Fe

17   concentrations significantly correlate with DOC and As (Fig. 1; r² Fe/DOC: 0.86; r² Fe/As:

18   0.80). At the bog's outflow, acidic conditions (< pH 4.5) prevail over the whole sampling

19   period. Under ~~this~~ these conditions iron-DOM complexes such as a ternary complex of As-Fe-

20   DOM, dominate the soluble fraction (Tipping et al., 2002; Lofts et al., 2008; Neubauer et al.,

21   2013). ~~However,~~Exports of As, Fe, and DOC ~~export~~ thus seem to be strongly linked and it is

22   likely that both elements are mobilized by the same processes and originate from the same

23   source area within the bog.

24   **3.3 DOC, As and Pb concentrations during storm flows**

1   Three high frequency samplings of storm flows were conducted at the bog outlet in 2013. The

2   first spring event started after a longer low flow period and a low water level within the bog

3   of around 13 cm below surface, indicating dry preconditions (doy 137; 18/5/13; Fig. 3). The

4   second event followed shortly after the first, but with wet preconditions (doy 150; 31/5/13).

5   The third sampled storm flow event occurred in fall with again dry preconditions and a water

6   level of around 12 cm below surface (doy 251; 9/9/13; Fig. 3). In general, concentration

7   changes of all elements during high discharge events were rather small compared to the

8   annual variations indicating that high precipitation and increased runoff do not necessarily

9   cause dilution, but seem to mobilize or connect additional pools of DOC, As and Pb.

10   At the first event, DOC and As concentration started to decrease immediately after the onset

11   of high flow from 26.8 mg L^{-1} and 1.5 µg L^{-1} to 21.8 mg L^{-1} and 1.0 µg L^{-1}, respectively at the

12   end of the event. No flushing effect with increasing stream water concentrations was visible

13   (Fig. 3). Pb concentrations however, immediately increased with rising water level and

14   discharge. Water levels rose from 13 to 6 cm depth, while Pb concentrations increased from 5

15   µg L^{-1} to 7 µg L^{-1}. With the falling limb of the hydrograph Pb concentrations also decreased

16   to concentrations of about 4 µg L^{-1}. The reason for the different behavior of Pb compared to

17   As and DOC is unknown. The increase in Pb concentrations with increasing water level

18   indicates that there is no dilution but that additional Pb pools are mobilized as surface-near

19   peat layers gets hydrologically connected to discharge. It is still unknown how the Pb pool

20   evolves during the winter months, probably by mineralization of organic matter in the

21   acrotelm. In case of DOC concentrations, which did not increase with increasing water level,

22   we assume that a readily mobilizedpotentially mobile DOC pool hasd not yet been built up in

23   spring when temperature and thus biological productivity are were still low. The role of redox

24   induced formation or dissolution of mineral Fe-phases for As mobilization during water level

25   changes is not yet understood. One explanation could be that As and DOC, as well as As-

organic complexes are adsorbed to precipitated Fe-oxides when water levels are low ~~and Fe-oxides are precipitated~~. The ~~Re-installation~~re-establishment of anoxic conditions after water level rise~~,~~ causes a reductive dissolution of Fe-oxide~~s dissolution~~ and a release of DOC and As. However, these processes ~~after water level rise~~ are assumingly too slow to be ~~visible~~ effective within a storm flow event (Grybos et al., 2007). ~~However, t~~This hypothesis will be further discussed in the pore water section further below.

~~-~~The second storm flow event exhibited ~~very~~ low concentrations compared to the annual concentration record at this site, starting with concentrations of 13 mg L^{-1} DOC, 2 µg L^{-1} Pb and 0.7 µg L^{-1} As ~~in the beginning~~, ~~where~~ when low flow conditions ~~have~~ had just re-established after a greater rain event. During the low flow regime~~,~~ concentrations slightly increased until the onset of the high discharge event. DOC and As concentrations peaked at 18 mg L^{-1} and 1 µg L^{-1}, respectively at the onset of the event, while Pb concentrations only peaked 3 hours later coinciding with maximum flow and a water level rise from 9.5 cm to 5.6 cm depth. Regardless of further smaller discharge peaks, DOC, As and Pb stream concentrations decreased to former low flow concentration~~s~~ levels until the end of the discharge event. Even though a distinct rise in concentration~~s rise~~ of DOC, As and Pb caused by this rain event was evident, concentration ranges for all three elements were ~~comparable to the~~low and of the same magnitude as lower concentrations before the first event in May. This indicates a strong depletion of all three elements through the directly preceding event, which exhibited the highest recorded discharge of the whole record. The obvious exhaustion of ~~readily mobilized~~potentially mobile DOC, As and Pb here, induces an element export constrain~~t~~ed by production rates. ~~While~~ As low flow established again after this rain event, concentrations started to slowly rise again ~~slowly in the same way~~as it has been ~~recorded~~ observed under low flow just before the rain event.

1   At the fall event concentrations before the event were higher than in spring with 33.5 mg L^{-1}

2   DOC, 8 µg L^{-1} Pb and 1.5 µg L^{-1} As. ~~Here~~During this event, DOC, Pb and As behave

3   differently (Fig. 3). DOC concentrations first decreased at the onset of the rising limb of the

4   hydrograph and rising water level within the bog, but thereafter DOC concentrations started to

5   rise ~~again~~ until discharge peaked (Fig. 3) and remained high ~~with~~ at 35 mg L^{-1} to 37 mg L^{-1}

6   until discharge increased ~~again~~even further. Unfortunately, the automated ~~auto~~sampler failed

7   to sample a part of the following main event, but DOC concentrations after the event were

8   again much lower (27 mg L^{-1}, doy 255) than concentrations before the whole event. The As

9   concentration~~s~~ dynamics during this fall event ~~were similar to~~followed that of DOC with a

10 peak concentration of 1.9 µg L^{-1}. For Pb, the first decrease in concentration was not apparent,

11 but an immediate rise to higher concentrations and a second discharge peak resulted also in

12 distinctly higher Pb concentrations of up to 11.9 µg L^{-1}. After the event As and Pb

13 concentrations were ~~again~~ slightly lower than before the event (6 µg L^{-1} Pb and 1.2 µg L^{-1}

14 As). ~~According~~ In line with the different discharge peaks, the water level responded

15 immediately to rain fall with a stepwise rise up to a level of 1 cm above the peat surface. DOC

16 and As concentration~~s~~ evidently peaked shortly after the discharge peak and even decreased

17 with increasing discharge, which can be indicative of a fast runoff component with less

18 intense DOC and As mobilization or dilution. However, Pb concentrations ~~got~~ were not

19 diluted, but increased with first discharge peak, which is contradicting the pattern observed

20 for DOC and As. Similar~~ly~~, Rothwell et al. (2007) also observed variable peak dynamics for

21 Pb amongst other metals over several fall discharge events. ~~Taking together~~Summarizing the

22 response of Pb stream water concentrations ~~at this~~for all three rain events, Pb concentrations

23 seem to respond immediately ~~on~~ to water level rise within the bog with an

24 ~~increasing~~increasing in concentrations. ~~When~~ As fast surface runoff at the beginning of the

25 event can be ruled out as a reason for the initial decrease in As and DOC stream

16

concentrations, the different behavior of the three elements indicates that DOC and As

seemed to be controlled by different mobilization processes than Pb. ~~In general,~~Concentrations of DOC, As and Pb ~~concentrations did~~thus do not respond entirely

similar ~~during the high resolution sampling of~~to rain events. This difference in the dynamics

cannot be explained ~~by~~ based on our data set ~~alone~~ and prompts the question why the strong

correlation of DOC ~~to~~ with As and Pb concentrations observed for the annual low resolution

record is not valid for the rain events.

The weak flushing effect during the spring events indicates a lack of supply of DOC and As

caused by a low biological productivity early in the year. The stronger flushing effect of Pb

will be discussed further below in relation to the results of pore water analys~~e~~is. The fall event

followed after the summer dry period and the time of highest productivity. When bog water

level rises to the surface, the entire previously aerated peat layer gets hydrologically

connected and contributes to near-surface flow. Therefore, a much greater amount of DOC,

As and Pb can be mobilized and exported by such discharge events resulting in the highest

discharge concentrations of all three elements of that year. High frequency sampling revealed

a great dependency of DOC, As and Pb discharge concentrations on pool exhaustion within

the bog. This is evident by decreasing concentrations during an event, but also a decline in

DOC, As and Pb concentrations, when rain events follow up over a short time interval. This

exhaustion effect can be explained by a lack of supply of readily ~~mobilized~~ mobile element

pools, when peat layers are hydrologically connected over a longer time period and constant

bog water levels. These results are congruent with Rothwell et al. (2007), who sampled

subsequent discharge events at a bog draining stream in fall. ~~Also, it is important at which time of the year storm flow events occur~~In addition, the observed high concentration levels of

DOC, As, and Pb highlight the role of seasonal dynamics of productivity. ~~These results are~~

Figure 4 displays an element concentration to discharge (c/Q) plot for DOC, As and Pb. Here, it is apparent that above a ~~discharge~~ threshold of discharge~~value~~ of about 8 L s^{-1} concentrations of DOC, As and Pb decrease or ~~stay~~ remain at constant ~~concentration~~. This indicates that at a discharge above 8 L s^{-1} element concentrations get diluted, most likely because all available pools have been connected. As this threshold is distinct and uniform for all three elements, pool exhaustion might be less likely, as the pool size is expected to differ over the vegetation period with a longer supply in summer and fall. Also, mobilization processes are probably different for DOC, Pb and As depending on binding types, which result in different responses depending on moisture and temperature preconditions of discharge events. However, rain water concentrations of DOC, As and Pb are much lower than pore water concentrations and hence dilution by precipitation should affect those elements all in the same way, as was observed here. Assuming that surface runoff takes place after saturation of the entire peat layer, the particular discharge ~~volume~~ at which surface runoff commences and dilution takes place should be similar over the whole year~~, when surface runoff commences~~. This conclusion also implies that at this bog, surface runoff is generated after peat saturation and not through infiltration excess.

3.4 Peat decomposition and solid phase As, Pb and Fe concentrations

Solid phase Pb and As concentration exhibited ~~the same~~a similar general trend with depth with higher contents in the uppermost meter (Fig. 5 A). Pb concentrations peaked in 40 and 72.5 cm depth with 1,200 mg kg^{-1} and 706 mg kg^{-1}, respectively. These two peaks has been ~~seen~~ reported before ~~in~~ for other bogs in the Harz Mountains (Biester et al., 2012) and can be clearly related to mining activities in the past. Kemptner and Frenzel (2000) related those

peaks to regional mining activities in the 12th/13th century and 17th century by 14C dating in a bog within 5 km distance from our sampling site.- Due to the strong historic mining influence the recent decrease in Pb concentrations in the uppermost cm was very pronounced. Also ~~B~~below 75 cm Pb concentrations sharply decreased to non-anthropogenic background levels and < 20 mg kg^{-1} below 100 cm depth. Concentrations of As ~~concentrations~~ were also highest in the uppermost 75 cm and show peaks ~~in the same~~at similar depths as Pb with maximum concentrations of 65 mg kg^{-1} and 38 mg kg^{-1} ~~in~~ at 30 cm and 72.5 cm depth. Peak concentration of Pb and As were high, even compared to other contaminated sites (e.g. Rothwell et al., 2009). While Pb is ~~thought to be immobile after deposition~~no redox-sensitive element, ~~while~~ As ~~is redox-sensitive and~~ might be mobilized after deposition and gets enriched in the surface-near layer due to redox changes, especially, when strong water level fluctuations prevail (Rothwell et al., 2010). As As(V) associates with Fe-(hydr)oxides, As mobility is known to be controlled by the reductive dissolution of Fe-(hydr)oxides, which causes the release of As into pore waters and would lead to an enrichment in the surface-near layer along with precipitated Fe-(hydroxides). Fe enrichment at the redox boundary occurs through the upward diffusion of dissolved Fe(II) and precipitation ~~when~~ where oxic conditions ~~are re installed~~prevail. The Fe depth profile here showed enrichment in the uppermost peat layer with a peak concentration of 5.5 g kg^{-1} at 5 cm depth and decreasing concentrations ~~until~~ down to 1.3 g kg^{-1} at 32.5 cm depth. Lowest Fe concentrations were found below 100 cm depth with concentrations less than 1.3 g kg^{-1}. In general Fe concentrations were low ~~if~~compared to other peatlands (Riedel et al., 2013) and much lower than in studies describing Fe as an important factor for DOC and As retention. Concentrations of As ~~concentrations~~ showed no enrichment in the upper peat layer ~~congruently with~~as did Fe, indicating that As is not coupled to redox induced changes of Fe phases here. We assume that As in our bog is predominately bound to organic matter similar as observed in other

peatlands, where As is mainly bound to organic matter by reduced organic sulphur groups under reducing conditions (Langner et al., 2011).

In previous studies peat decomposition has been found to enrich particular element concentrations through mass loss (Biester et al., 2003; Biester et al., 2004; Biester et al., 2014). Figure 5 A displays C/N ratios of the organic matter as proxy for peat decomposition (Kuhry and Vitt, 1996; Broder et al., 2012; Biester et al., 2014). In the upper 12.5 cm C/N ratios were high (88-128) with a distinct decrease to a value of 54 in 15 cm depth (Fig. 5 A). Further below, C/N ratios remained low between 23 - 50 with higher values between 70 cm and 150 cm (50-100). This indicates that the upper 15 cm are less decomposed, while with decreasing C/N with depth the degree of decomposition increases with again a lower degree of decomposition between 70 - 150 cm depth. A straight influence of decomposition on As and Pb distribution was not found here and concentrations were rather determined by enhanced deposition rates or in case of Fe by redox processes for Fe than by peat decomposition.

3.5 Pore water DOC, As and Pb concentrations

DOC concentrations in the pore water profile ranged from 20 mg L^{-1} to 250 mg L^{-1} (Fig. 5). Highest concentrations were found at the down most sample in 225 cm depth. DOC concentrations in the upper 50 cm, where most discharge is generated, were low in spring under wet conditions (doy 147: 34-41 mg L^{-1}; Fig. 6) and much higher in fall after rewetting following the dry summer period with concentrations of 119 mg L^{-1} in 20 cm depth and 100 mg L^{-1} in 40 cm depth (Fig. 6, doy 254). In late fall concentrations decreased again, but were still much higher than in spring. This is in line with the recorded seasonal trend of DOC concentrations at the discharging stream and the fact that DOC stream concentrations are dependent on temperature and microbial activity to built up potentially mobile pools (Clark et

al., 2005) ~~through pool size built-up~~, but also ~~next~~ to the hydraulic connectivity of the surface-near peat layers. Normally, within a couple of weeks after rewetting ~~after a drought period a higher pH develops~~acidity is consumed in pore waters through anaerobic respiration processes, like sulfate- or iron reduction ~~within a couple of weeks after rewetting~~ (Fenner and Freeman, 2011). This should favor DOC solubility through higher pH, but also by release of formerly Fe-(hydr)oxid-bound DOM (Grybos et al., 2009). Moreover, anaerobic conditions suppress peat mineralization and the described enzymatic latch of phenol oxidase activity favors DOC production after rewetting (Fenner and Freeman, 2011). In line with these assumptions, DOC concentrations were highest several weeks after the summer drought in fall, ~~where~~ when the water level ~~was~~ had fully recovered again (doy 254, Fig. 6). However, the lower DOC concentrations measured during this rewetting, ~~with~~ at an intermediate water level depth of 14 cm, probably reflect ~~rather~~ a limitation in DOC supply and an exhaustion of the DOC pool through export, as the sampling just followed ~~after~~ two rain events, which ~~also~~ already had triggered ~~discharge events accompanied by~~ high DOC stream concentrations.

During the summer drought, the amount of pore water was too low to obtain sufficient sample volume for DOC measurements at 20 cm depth. At 40 cm depth DOC concentrations during drought and following rewetting (doy 254) were higher than in spring and during rewetting (doy 236). On the one hand, this might contradict the concept of Fenner and Freeman (2011) or Clark et al. (2012) who stated low DOC concentrations during drought due to microbial limitations by ~~moisture~~ drought stress and acidification by drought-induced oxidation processes. On the other hand, the measured low pH $(< 4.5$ pH$)$, in all pore water samples at our site might indicate that the drought acidification effect is not pronounced here, as pH in our peat is generally low. Moreover, due to the low Fe concentrations in our peat, the effect of DOC immobilization through binding to Fe-(hydr)oxides during drought and aeration as proposed elsewhere (Riedel et al., 2013) is probably low at our study site. Accordingly, due to

1   the low pH and the low amount of Fe-(hydr)oxides at our site suppression of DOC production

2   by drought events seems to be of low importance here and probably in ombotrophic peatlands

3   in general.

4   Pore water As and Pb concentrations in the Odersprung bog ranged from 1.2 μg L^{-1} to 3.8 μg

5   L^{-1} and 0.5 μg L^{-1} to 8.4 μg L^{-1}, respectively (Fig. 5). Both, As and Pb concentrations were

6   highest in the uppermost sample at 20 cm depth. While As was steadily decreasing and

7   leveled out in 70 cm depth, Pb concentrations peaked again around 60 cm depth with 4-5 μg

8   L^{-1} Pb before it leveled out ~~at~~ in about 120 cm depth. Concentration profiles throughout the

9   year show ~~low~~ only small changes ~~only~~ in the uppermost samples. Lowest As pore water

10   concentrations at 20 cm and 40 cm depth occurred at the first sampling in spring (Fig. 6, doy

11   136) with 2.5 μg L^{-1} and 2.1 μg L^{-1}, respectively. At the end of the summer drought As

12   concentrations remained at around 3 μg L^{-1} (doy 203), while Pb pore water concentrations

13   decreased from about 6 μg L^{-1} (20 cm depth) and 3 μg L^{-1} (40 cm depth) to lowest annual

14   concentrations of 3.3 μg L^{-1} and 1.7 μg L^{-1} Pb~~ during summer drought, respectively. While

15   highest Pb concentrations (8.4 μg L^{-1}) were measured at the beginning of fall, (Fig. 6, doy

16   236) when the water level ~~was~~ had not yet fully recovered, highest As concentrations

17   ~~congruently with DOC~~ occurred after the complete rewetting of the bog in September

18   congruently with DOC concentrations (doy 254). Pb concentrations at 40 cm depth were

19   constant with exception of a slight decrease during summer drought (doy 311: ~3 μg L^{-1}). The

20   very high Pb concentrations measured during water table recovery might be due to

21   mobilization of a Pb pool, which built up during drought in the most reactive surface-near

22   peat layer by microbial decomposition or mineralization processes. This assumption might

23   also explain the decoupling of DOC and Pb export apparent at discharge events after dry

24   preconditions, as a readily solubilized Pb pool is easily flushed. ~~which~~ Moreover, it explains

25   the absence of the initial dilution effect as seen in DOC stream concentrations. Furthermore,

1 the DOC pool increases after drought, when wet conditions prevail again, explaining the lag

2 time of DOC peak concentrations in pore waters.

3 The generally decreasing Pb concentrations with depth allow a determiningation of the source

4 of discharge water source. The hydrologic response of the bog discharge was characteristic

5 for a rapid near-surface runoff. Comparing absolute concentrations in pore water and

6 discharging water, the high Pb concentrations of more than 10 µg L^{-1} in runoff at the fall rain

7 event can only be generated in the uppermost part of the bog, where Pb concentrations were

8 highest. Following this assumption also the low flow concentrations must have been

9 generated in the upper part of the peat profile as Pb concentrations below 1 m depth were too

10 low to generate the observed Pb concentrations in discharge Pb concentrations. The variable

11 Pb concentrations at different flow conditions are attributed to different water levels, which

12 affect variable parts of the Pb pool in the acrotelm and are thus able to mobilize different

13 amounts of Pb. This does also indicate that, in line with the hydrologic discharge response,

14 low flow discharge is generated from upper peat layers and not from seeping water

15 originating from the deep peat sections.

16 **3.6 Fluxes and inventory estimations**

17 As Pb, As and DOC concentrations correlate, fluxes of these elements are necessarily

18 exhibiting the same trends. However, element concentrations and bog discharge were not

19 correlated. Consequentially, fluxes show a different seasonal pattern than concentration

20 records (Fig. 7). While DOC and As concentrations were highest in summer and seemed to be

21 more dependent on temperature, DOC, As and Pb fluxes were not controlled by the

22 concentration changes over the year, but mainly by discharge (Fig. 7). This dependency is

23 valid up to a discharge of 8 L s^{-1}, after whichwhile at higher discharge dilution is observed.

24 Thus, hHighest element fluxes occurred during high discharge events in spring and fall and

during snowmelt ~~also~~. Flux calculations show that~~-~~ 10% of the monitoring time span, when

highest discharge was recorded, ~~the upper 10 % of discharge~~ contributed 39 %, 40 % and 43 %

of the annual DOC, As and Pb export. Similar patterns have been described by Koehler et al.

(2009) for DOC fluxes from a blanket bog in Ireland. Clark et al. (2007) calculated that 10 %

of the monitoring time span including highest discharge contributed 50 % of the annual DOC

export and Hinton et al. (1997) estimated 41-57 % of annual DOC export by the 10 % time of

highest discharge. When separating the annual hydrograph record ~~by hydrograph~~ in storm

flow and low flow conditions (boundary at 0.3 L s^{-1} by visual examination), ~~28~~ 72 % of the

record exhibited ~~low flow~~ high discharge conditions, which contributed ~~2.4~~ 97.6 % of total

annual discharge and about ~~4~~ 96 % of annual As, Pb and DOC export~~, only~~. ~~This means that~~

~~96 % of annual As, Pb and DOC export occur at high discharge conditions, which contributed~~

~~97.6 % of the annual discharge quantity, though.~~ ~~Similar pattern, have been described by~~

~~Koehler et al. (2009) for DOC fluxes from a blanket bog in Ireland. Clark et al. (2008)~~

~~calculated that the upper 10 % of discharge contributed 50 % of the annual DOC export and~~

~~Hinton et al. (1997) estimated 41-57 % of annual DOC export by the upper 10 % of~~

~~discharge.~~

This flux calculations implicate~~,~~ that high discharge events contribute~~s~~ over-proportional to

element exports in a short time period. While low flow conditions generate high element

concentrations, greater discharge not ~~only~~ primarily dilutes element concentrations, but

connects additional pools to discharge, which results in higher fluxes. ~~Therefore, even if the~~

~~upper 10 % of discharge might generate overland flow and a strong concentration dilution,~~

~~fluxes are still highest as all pools contribute to stream discharge.~~ Concluding, as different

DOC, As, and Pb pools, i.e. different peat layers, correspond to different hydrologic

conditions, also different linkages to element export~~s~~ are likely. If low flow discharge is

~~expected to be~~ generated ~~rather~~ in the lower ~~peat layers~~ acrotelm, not only general pool sizes

1. are different, but also mobilization conditions, i.e. different pH, redox, DOC quality. Further

2. insight into differences between low flow and high flow export dynamics might be gained

3. through Pb isotope determinations (see Klaminder et al. 2008), a determination of DOC age

4. ~~specification~~ or DOC characterization.

5. The importance of high discharge events to Pb, As and DOC exports gets more relevant in

6. view of changing climate conditions with more frequent heavy rain events in this region.

7. Furthermore, that it is crucial at which time of the year rain events will occur in the future. A

8. ~~record~~ data separation by season indicates that fall contributes to the largest extend to annual

9. element export followed by spring and similar ranges in summer and snowmelt (Table 1).

10. This pattern is in line with the assumption that higher microbial activity on the one hand, and

11. elevated discharge, which flushes the acrotelm on the other hand favors DOC, As and Pb

12. export.~~This pattern is in line with the assumption that DOC, As and Pb exports were limited~~

13. ~~by production on the one hand, and by high discharge on the other hand, which flushes the~~

14. ~~entire acrotelm~~. The lower fluxes during summer are attributed to prevailing low flow, dry

15. conditions. Figure 8 displays discharge to element loading plots separated by season and high

16. discharge event sampling. It highlights higher loadings at the same discharge volume

17. dependent on season by a steeper increase of the regression line. In general, element loadings

18. are lowest at snowmelt and increase over the year with highest loadings during the fall event.

19. At the end of the year, loadings decrease again. While this general trend is similar for DOC

20. and As, Fig. 8 also shows that Pb loadings during snowmelt and the second spring event are

21. quite similar and that concentrations are less dependent on discharge volume, indicated by

22. lower R^2 values of the regression lines.

23. The annual DOC export from the investigated bog catchment can be estimated to 155 kg C

24. ha^{-1} a^{-1} ~~±43%~~67 kg C ha^{-1} a^{-1} (Table 2) and is similar to values from other studies (Worrall et

25. al., 2003; Koehler et al., 2009). As the upstream catchment is completely snow covered

during winter, including the stream outlet at the bog, no flux quantification during winter is possible. It can be speculated though, that fluxes are probably low due to low temperatures and low flow conditions during winter season.

Aqueous exports of As and Pb ~~fluxes~~ were calculated to 7.8 ± 3.0 g As ha^{-1} a^{-1} and 39 ± 16 g Pb ha^{-1} a^{-1}. Annual Pb export was in the same range ~~than~~ as values reported by Rothwell et al. (2011) with annual aqueous Pb export of 55 ± 18 g Pb ha^{-1} a^{-1} from a contaminated eroded ombrotrophic peatland. ~~They~~ The authors also highlighted the importance of particulate Pb export for peatland systems, which needs to be considered when estimating total Pb export. The calculated aqueous As ~~fluxes~~ export from our site were much lower than ~~fluxes~~ those reported by Rothwell et al. (2011) (47.1 ± 9.9 g As ha^{-1} a^{-1}), in spite of higher As contents in our peat. This might be due to the eroded nature of their sampled bog and the prevailing post-depositional mobilization of As in peat due accelerated water table drawdowns and a consequent binding to Fe-(hydr)oxids (Rothwell et al., 2010).

As and Pb inventories were calculated based on the median element contents in the upper 30 cm of the 16 analyzed cores and were 0.91 g As m^{-2} (0.64-1.17 g m^{-2}) and 13.98 g Pb m^{-2} (7.47-24.02 g Pb m^{-2}), respectively (Table 2). Element contents in the upper 30 cm varied over a wide range pointing out the importance of a multi-core approach for calculating peatland element inventories. Rothwell et al. (2010) calculated a storage of 0.19-0.44 g As m^{-2} and 12.2-13.5 g Pb m^{-2} in another contaminated peatland. While our calculated Pb inventor~~y~~ies ~~is~~ are similar, As inventor~~y~~ies are higher ~~as~~ than those reported by Rothwell et al. (2010). When referring annual fluxes to the bog area of the catchment 0.04 kg As a^{-1} and 0.2 kg Pb a^{-1} were exported in 2013 by the bog drainage. This equals to 0.85 ‰ and 0.27 ‰ of the calculated As and Pb inventories respectively (Table 2). Even though conclusions based on a one year data set are limited and uncertainties are high, it becomes clear that As seemed to be more mobile than Pb. Neglecting future element deposition and changing export

conditions it would take more than 1000 years to deplete As pools and more than 3000 years for Pb pools stored within this polluted peatland. Furthermore, the observed element content variation among all cores might also implicate differences in pore water concentration levels within the stream catchment.

4. Conclusions

Our results highlight the importance of comprehensive field studies to gain further understanding in generation and controls of element exports from peatlands. The cCombination of pore water and discharge data showed that As and Pb exports are not only dependent on the amount of precipitation and discharge, but on the frequency and depth of water table fluctuations, and the extend of pool connectivity in the acrotelm. This has been demonstrated by higher As and Pb concentrations and exponential increase of export at high discharge events, especially after a longer dry period and higher temperature. A distinct bog-specific discharge threshold of 8 L s^{-1} was observed, which indicates a connection of all available pools. and This threshold presumably depends mainly on thebogs size of the bog and drainage conditions. Significant correlations of annual As, Pb and DOC concentrations in discharge hints to transport of As and Pb as organic complexes with decoupling of Pb from DOC concentrations at storm events following dry preconditions. Comparing the annual bog As and Pb export with element inventories indicates that As is much more stronger mobilized than Pb, with annual fluxes accounting for 0.85 ‰ and 0.27 ‰ of total As and Pb inventory, respectively. Results also point out the over-proportional contribution of high discharge events to As, Pb and DOC annual export. The challenge for prospective research is to unravel the biogeochemical effects of short term water level fluctuations on trace element and DOC

mobilization processes within peatlands to further improve parameterization of peatland catchment models.

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6

1 **Tables**

2 **Table 1:** Seasonal distribution of discharge, DOC, As and Pb export fluxes at the Odersprung

3 catchment.

	Record time	Q	DOC export	As export	Pb export
	%	%	%	%	%
Snowmelt	7.6	19.8	7.4	11.1	7.2
Spring	21.3	25.5	19.2	15.3	19.1
Summer	35.6	10.8	12.5	10.2	12.0
Fall	35.6	47.5	60.8	63.4	61.7

4

1   **Table 2:** Estimated mean DOC, As and Pb export in 2013 and element inventories in the

2   upper 30 cm peat. Uncertainties were estimated by the standard deviation of flux calculations

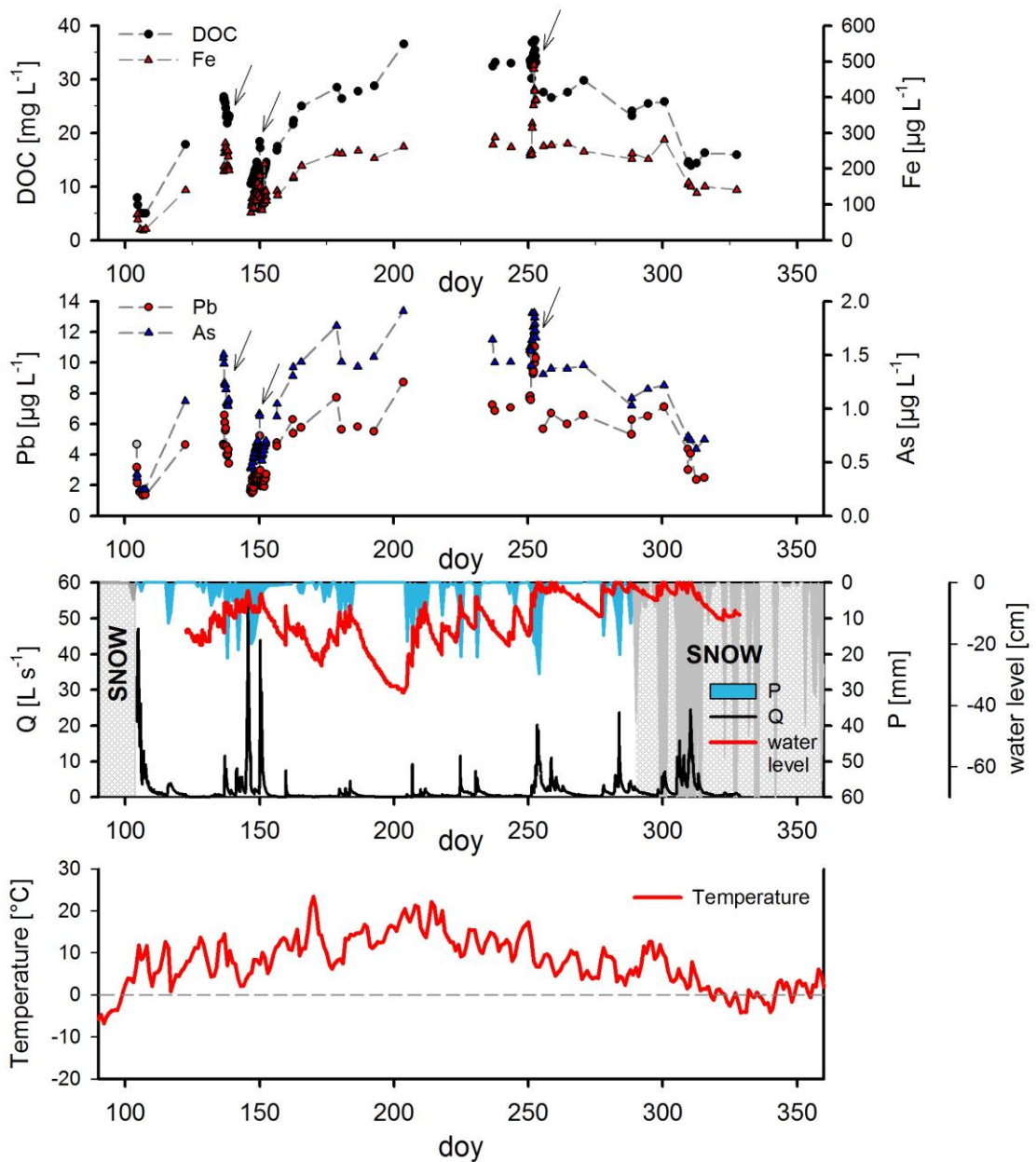3   and element inventories calculated of each core.

	Mean annual fluxes		Peat inventory[a]		Export
	$g\ ha^{-1}\ a^{-1}$	$kg\ bog^{-1}\ a^{-1}$	$g\ m^{-2}$	$kg\ ha^{-1}$	‰ of inventory
DOC^b	$154.79*10^3$	773.93	16,689	$166{,}89*10^3$	0.93
uncertainty	$88-221*10^3$	441-1107	(15,336-17,417)	$(153.36*10^3-$ $174.170*10^3)$	(0.89-1.01)
As	7.8	0.04	0.91	9.1	0.85
uncertainty	4.8-10.8	0.02-0.06	(0.64-1.17)	(6.4-11.7)	(0.66-1.22)
Pb	39.2	0.2	13.98	139.8	0.27
uncertainty	23.1-55.3	0.12-0.28	(7.47-24.02)	(74.7-240.2)	(0.16-0.51)

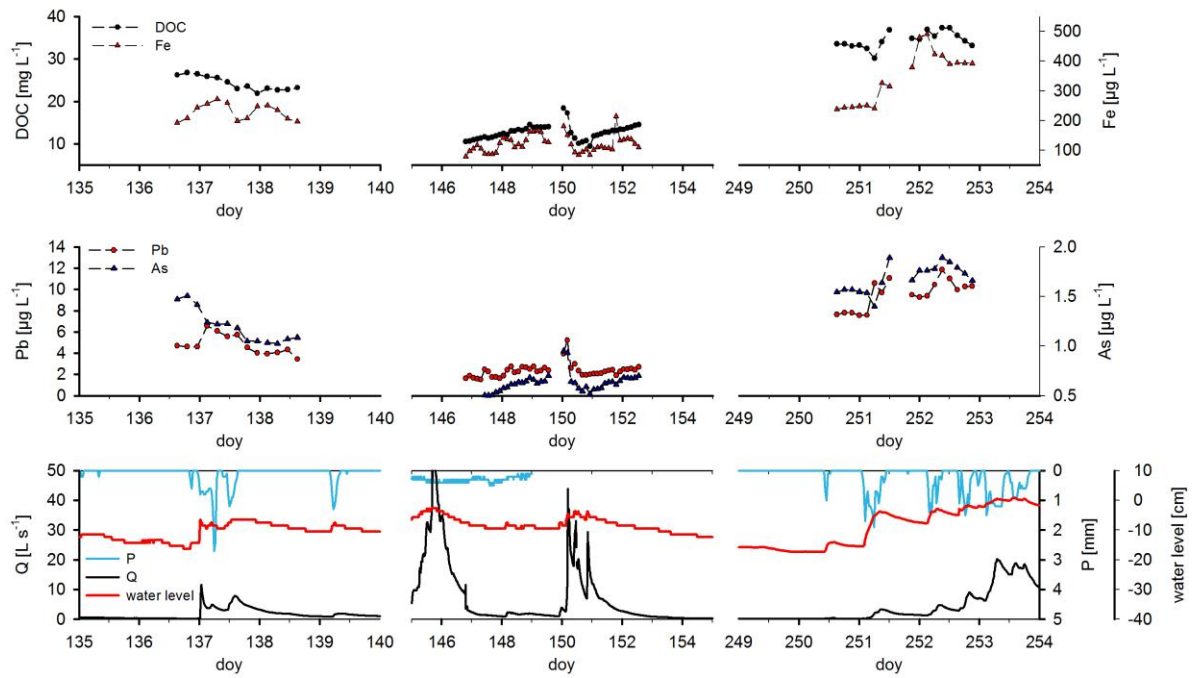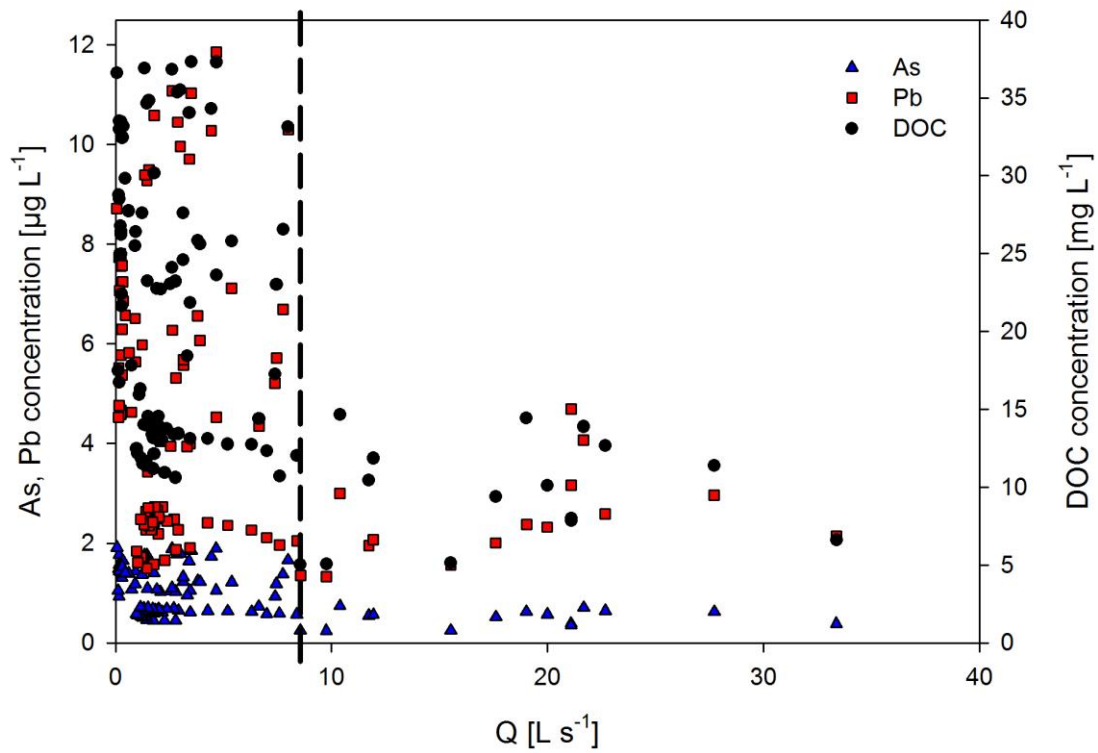4   [a] upper 30 cm [b]total C for peat inventory, respectively

5

1   **Figure captions**

2

3   **Fig. 1:** Location of the study area in the Harz Mountains, northwestern Germany, with

4   catchment boundaries indicated by the dashed light-colored line. Circle denotes discharge

5   monitoring site, triangle marks location of pore water sampling, as well as water level

6   monitoring and peat core retrieval. Crosses mark the location of short cores for inventory

7   calculations. Map Source: Lower Saxony Ministry for Environment, Energy and Climate

8   Protection.

1

Fig. 2: Annual concentration record of DOC, Fe (top), Pb and As (top) (middle) at the bog

outlet. Annual records of bog water level, daily precipitation, and discharge and temperature

(low). Sampled discharge events are highlighted by black arrows. Note that winter
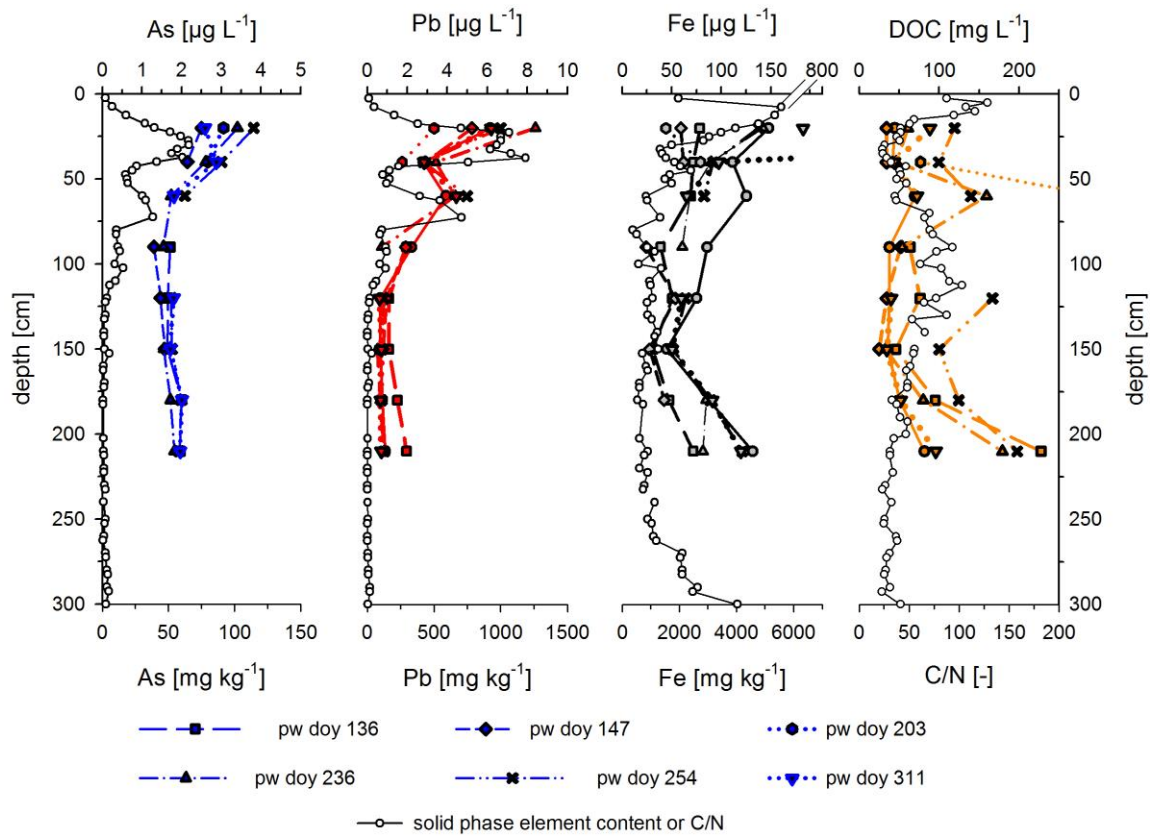
precipitation as snow cannot be quantified.

Fig. 3: High resolution DOC, As and Pb concentrations during recorded spring (doy 135-155) and fall (doy 250-260) events. Records of bog water level, precipitation (30 min resolution) and discharge (low).
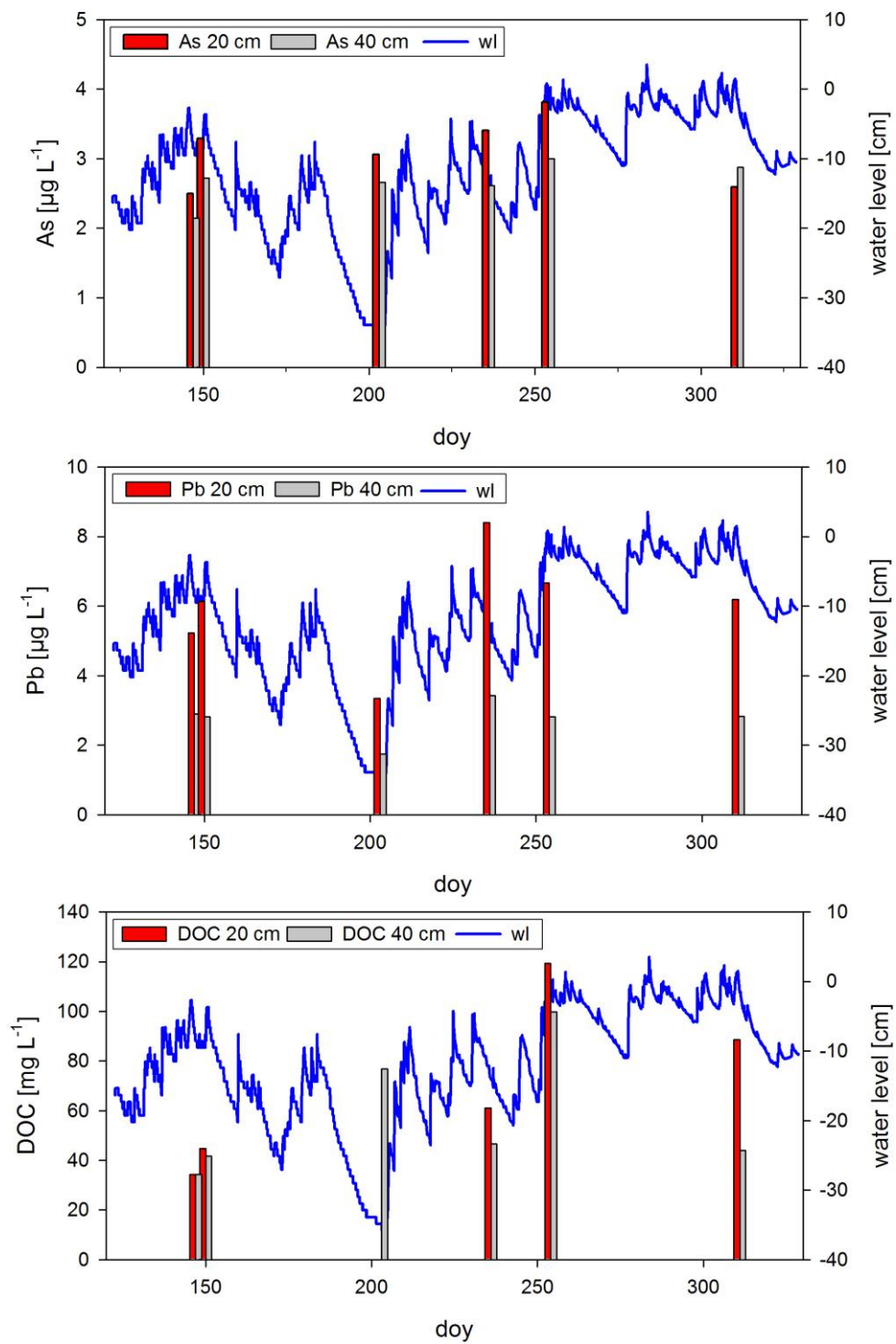
1

Fig. 4: DOC, Pb and As stream concentration to discharge (Q) plot (c/Q). The black dashed

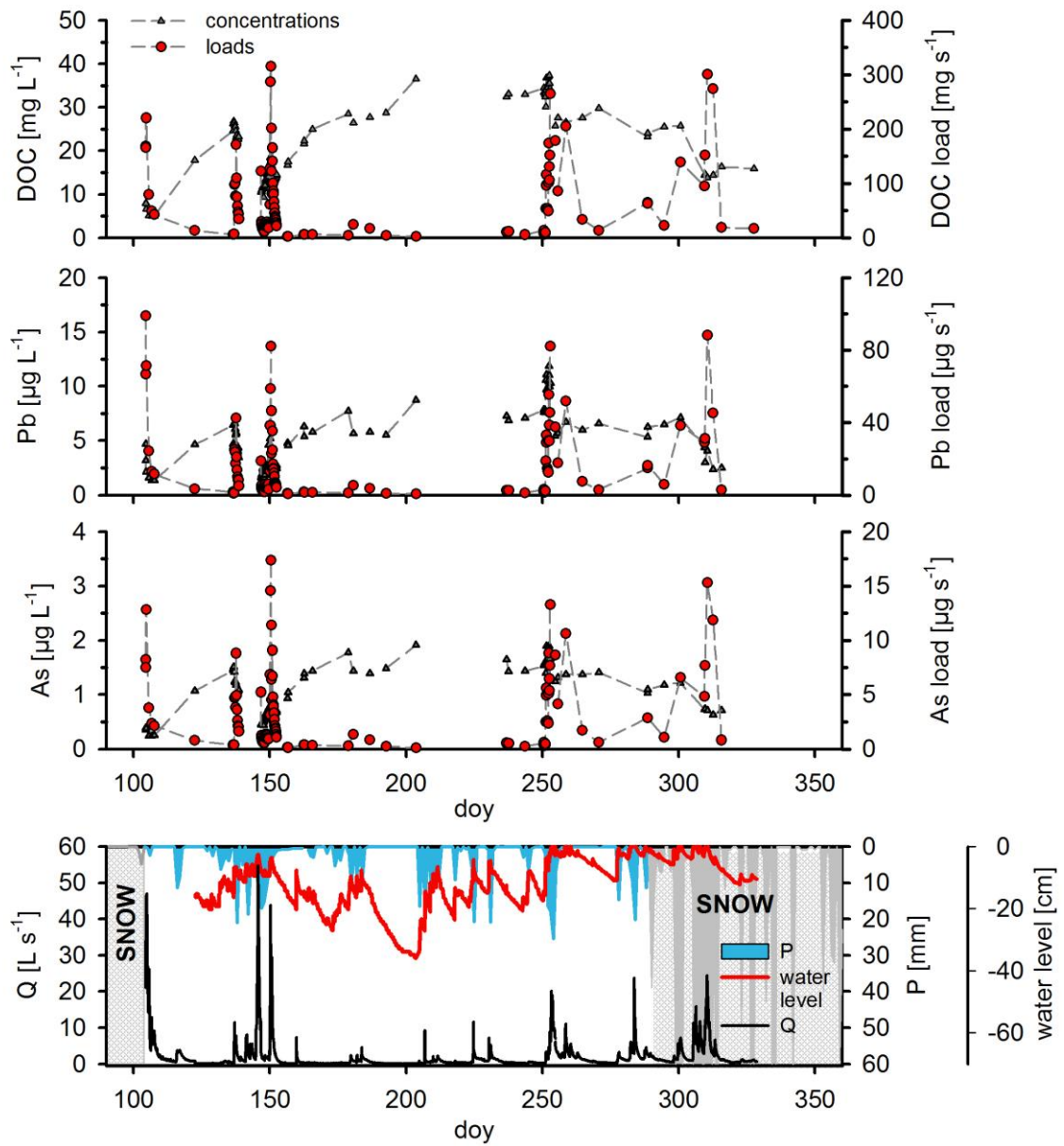line indicates the threshold discharge value for a compulsive dilution effect.

Fig. 5: A) As and Pb contents of the long peat core taken at the Odersprung bog and carbon nitrogen ratios (C/N) as indicators for peat decomposition. B) Pore water concentrations of As (left, blue), Pb (middle, red) and DOC (right, orange) along a depth profile (250 cm).
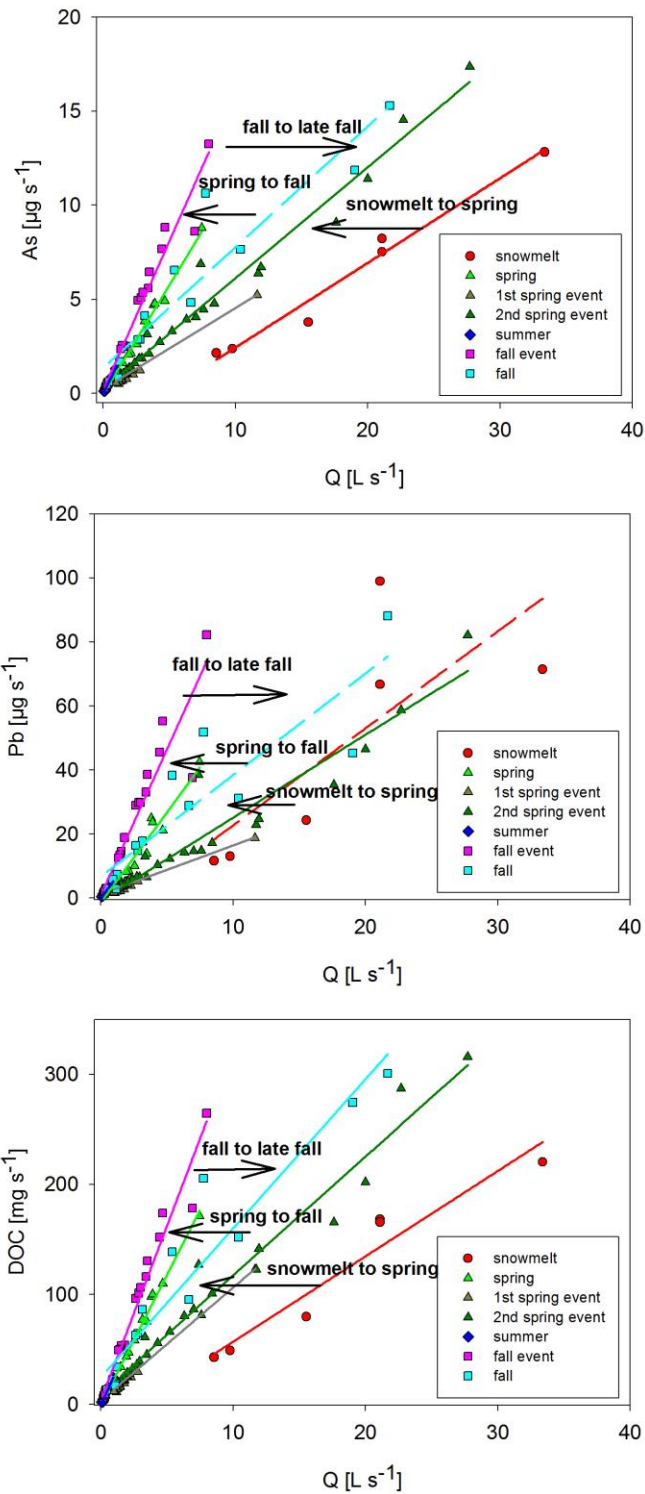
1

Fig. 6: Pore water concentrations of As (top), Pb (middle) and DOC (low) in 20 cm and 40

cm depth over time. The blue line indicates the recorded bog water level (wl).

Fig. 7: Concentration record and instantaneous loads of DOC, Pb and As at the bog outlet.

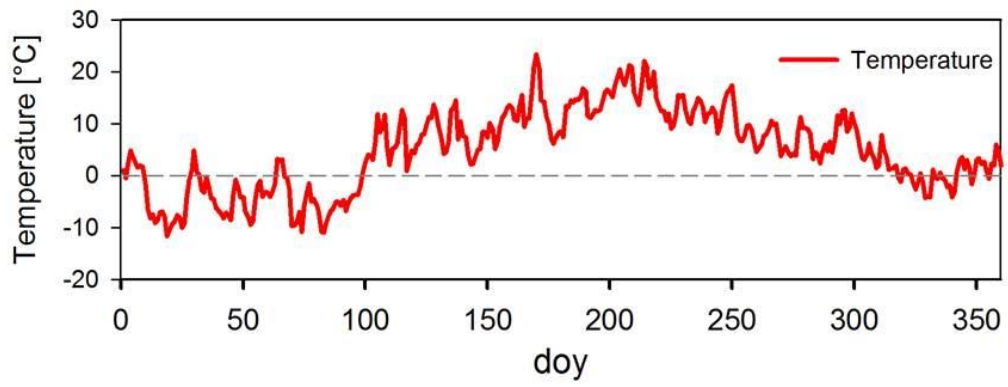Annual records of bog water level, precipitation and discharge (low).

Fig. 8: As (top), Pb (middle) and DOC (low) loadings to discharge (Q) plots divided by season and event sampling. Regression lines with R² > 0,90 are plotted with a solid line, R² < 0,9 are plotted with a dashed line..

1 **Table S1**: As and Pb concentrations of the 30 cm short peat cores used for inventory calculations.

2 Concentrations were determined on sample aliquots of the upper (0-15 cm depth) and lower part (15 -

3 30 cm depth) of each core.

Core	As [mg kg^{-1}]		Pb [mg kg^{-1}]	
	0-15 cm	15-30 cm	0-15 cm	15-30 cm
1	48.74	23.90	1463.78	478.58
2	52.40	8.78	1030.13	45.40
3	70.22	17.77	2097.97	182.20
4	52.08	32.47	965.09	496.84
5	16.54	42.78	229.56	697.67
6	19.96	45.70	198.71	767.60
7	20.98	39.52	232.31	446.55
8	3.64	27.84	23.16	281.85
9	27.24	44.76	320.88	734.68
10	35.99	48.02	568.28	903.72
11	21.66	27.05	397.32	472.32
12	34.41	51.96	839.34	1285.92
13	23.84	53.40	280.36	736.18
14	3.61	25.51	16.57	240.64
15	5.70	28.90	47.14	427.62

4

1

2 **Figure S1:** Annual temperature record at the Odersprung bog in 2013. Gray dashed line highlights

3 0°C line.

4