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Interactive comment on "From soil water to surface water – how the riparian zone controls the transport of major and trace elements from a boreal forest to a stream" *by* Fredrik Lidman et al.

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We thank all the Referees for their insightful comments on our manuscript. Our impression is that all Referees found the dataset interesting and worthy of publication, but there were also many comments concerning the presentation and the structure of the manuscript. Having carefully considered all comments, we believe that most concerns could be addressed by slightly revising parts of the manuscript. Below we respond to each of the remarks made by the three Referees:

Comments to Referee #1:

General comments: Referee #1 states that the manuscript is "quite good structured

and provides new ideas/insights on the role of the riparian zone". He/she also thinks that large dataset has been explored in creative ways so that new insights into the functioning of riparian zones are provided. However, Referee #1 also thinks the abstract should be rewritten so that the main findings of the study are better highlighted and the motivation and limitations of the study are clearer. We believe that these are valid remarks, which call for slight revision of the abstract.

Overall, Referee #1 also thinks that clarifications and shortening of sections throughout the manuscript would improve the presentation. Having read our manuscript anew, we feel inclined to agree with Referee #1 that there are parts of the manuscript, which should be shortened and/or clarified.

Small overall comments:

Referee #1 thinks that all graphs are not necessary. It would be helpful to know which ones should be omitted in his/her opinion, but if we are given the opportunity to revise the manuscript, we will try to consider how the number of graphs could be decreased. There is always the option of providing additional graphs as supplementary material.

The title of the manuscript is admittedly quite long, and we agree that a shorter title would be good. We should certainly give this some more thought, but at the same time it is important advertise what can be found in the manuscript.

Referee #1 misses a direct comparison between our results and other papers with a large number of elements. The main reason is that we have not encountered any similar datasets, which could be used for such comparisons. Referee #1 specifically mentions a paper by Lidman et al. (2014), which also was cited in the manuscript. A major difference is, however, that that paper deals with stream water, whereas this manuscript focuses on soil water. We must also emphasize that we used the data published by Lidman et al. (2014) to compare the element concentrations in the uphill soil and the riparian zone to the concentrations in the stream. This can be seen in Fig. 6. It is not obvious to us how further comparisons between these two datasets could

be made.

Specific comments:

1. We agree that the reason for investigating the large group of elements in the riparian zone should be stated in the abstract.

2. We also agree that the main findings of the study should be clearly stated in the abstract. The importance of the affinity for organic C certainly belongs there. This should be emphasized in the abstract.

3. Referee #1 remarks that the final sentences in the abstract are too general. We think that this is a valid observation so we agree that we could be more specific here.

4. Having read the introduction again, we acknowledge that there is a degree of repetitiveness in the introduction. It should be possible to shorten this part a bit, as suggested by Referee #1.

5. Again, we agree that the introduction could be written more concisely.

6. The manuscript includes a large number of elements, which previously have not been investigated in this type of environments. The motivation of the study could be further emphasized by explaining why each if these elements is interesting, as Referee #1 suggests, but at the same time the number of elements is too high to allow a thorough discussion of all of them. In our opinion there are two important reasons to look at all these elements. First, all of them are of interesting in their own right, e.g. as micronutrients, pollutants etc. There are environmental issues related to essentially all elements in the periodic table and the transfer between terrestrial and aquatic systems is often overlooked. Second, including a large number of elements allows the comparison of elements with similar or contrasting biogeochemical properties, which can help to distinguish what processes are important for the fate of various substances in riparian soils. This is for instance illustrated by Fig. 5, where elements with different affinity for organic matter are shown to behave differently in the riparian zone. We

agree, however, that we should try to explain this better in the manuscript.

7. We agree that the objective of the study is to achieve a more over-arching understanding of the riparian zone and its role for different types of elements. As commented above, we might need to put more emphasis on this. We could also try to add more references to previous studies, but a challenge is to find papers, which deal with element transport on a more general level. In our experience, most papers tend to focus on one or a few elements, and we do not think that it is possible to cover all of the included elements in detail.

8. The flow pathways in the transect were identified in tracer experiments before the lysimeters were installed in 1995. According to previous studies (cited in the manuscript), the flow pathways are strongly dependent on the hydrological conditions, in particular the groundwater levels. This is illustrated in the Fig. 2 (bottom). Perhaps it would also be helpful to add a photograph of the transect in the supplementary material.

The reason for using stream chemistry sampling 300 m downstream of the transect is that this is the closest sampling location in the Krycklan catchment. Note that it is a first-order stream that does not receive water from any other landscape type. We must also emphasize that even if the stream chemistry would have been sampled right next to the transect, the would still not guarantee that the transect would have been more representative for the catchment of the stream at that location. On the contrary, the current setup with the stream stretching both upstream and downstream from the transect might even make it more representative for the catchment as whole, since the stream gets increasingly larger further downstream.

9. The reason that S22 was described in more detail than the other two soil profiles was that S22 unlike the others has distinct soil horizons. We agree, however, that we could elaborate more on how the organic content of S12 and S4 varies. Note that this also is presented in Fig. S1.

10. There are soil data from the Swedish Geological Survey (SGU) for the area, but unfortunately it does not provide much insight into what the soils really look like. The catchment is dominated by till (100% according to the maps) because the organic soils of the riparian zone are not mapped. One reason is certainly that the importance of riparian zone historically has not been recognized, and this also makes it hard to assess the importance of organic-rich riparian soils on larger scales. We have investigated the soils along this stream and know that the accumulation of organic matter near the stream occurs all along the stream channel. This is illustrated in Fig. S2. However, we do not think that it is a good idea to add this information to the map because the riparian zone is too narrow in comparison to the catchment as a whole. The width of these organic soils is likely to vary depending on the local typography and the hydrology, and attempts to model this are being made. We hope that this will lead to a better description of the extension of organic riparian soils.

11. The reference to Table S1 is clearly incorrect, as Referee #1 has commented. We agree that it may not be crucial for the manuscript to show that soil porosity at different depths. We added this information to the supplementary material just to make it accessible and citable. The depth of these samples as well as the depth of the lysimeters are based on the sampling and the installation of the lysimeters in 1995. As regards Fig. S2, we need to add some more information concerning how the data was collected and describe more thoroughly what it illustrates. One alternative might also be to add the investigated transect to the figure.

12. It might be more logical to present general information about the area before presenting the transect, as suggested by Referee #1. Since the transect is the focus of the manuscript, we thought it would be easier to start by describing the lysimeters etc., but this could easily be changed.

13. In order to limit the number of figure in the manuscript, we tried to include most the requested information in the subplots of Fig. 2. We could prepare a separate illustration of the transect, if it does not suffice with a reference to Fig. 2.

14. We agree that ANOVA could be used to further analyze the data statistically, but the question is whether it is motived to include that in this manuscript. We feel that we would not be able to go through all the results for all the elements. Perhaps this is something that can be kept in mind for future studies that focus more on specific elements?

15. We agree that Figs. S6 and S7 are not necessary. They were included because we thought that some people might be interested in those elements, but the figures could certainly be excluded without loss of context. We will not insist on keeping them if they are perceived as unnecessary.

16. We think that it would be a good idea to add more information to Table 1 so that it becomes clearer how different elements behave. The only limitation is that the table already is quite large, but we could certainly see if it is possible to find space to add the information that Referee #1 requests.

17. We agree that Fig. S4 is interesting. It would certainly be an option to transfer it to the main figures, as Referee #1 suggests.

18. Referee #1 thinks that the title of section 3.6 is a bit misleading and that parts of the text could be shortened or moved to section 4. We agree that section 3.6 should be renamed and slightly revised.

19. “More or less” is not a good wording. We should remove such unprecise descriptions from the manuscript.

In addition to these comments, Referee #1 has a number of technical remarks, which we agree need to be addressed.

Comments to Referee #2:

Referee #2 is arguably the most critical of the three referees, expressing a certain disappointment with the results of our study. Nevertheless, it is acknowledged that the dataset is “very good”, but Referee #2 has concerns regarding the presentation,

both because the text is considered too repetitive and because it is not sufficiently to the point. In this respect, Referee #2 largely echoes the comments of Referee #1. As authors, it is hard to argue with such statements so we evidently need to think about how to present the results and structure the manuscript to make it more readable. Having read our manuscript anew, we agree that there is a certain degree of repetitiveness that should be addressed.

We do not fully understand what Referee #2 means when he/she states that the methods "are not really reproducible". The results are obviously not reproducible in the sense that we cannot collect samples under exactly the same conditions as when these samples were collected, but this is of course the case for nearly all environmental studies. The suction lysimeters are, however, still left in the soils and would be possible to sample again. Indeed, they are still being used for other studies. More importantly, however, it would be possible to install similar equipment at other sites and do corresponding measurements. Whether that would reproduce the results of this study or not can obviously be known in advance, but it would certainly be possible to design and conduct a similar study. As for the description of the sampling and the statistical analyses, however, we arguably need to be more specific, as Referee #2 thinks that they we are too vague. This is certainly something we could improve.

Referee #2 states that he/she expected more from this study, particularly raising two questions that he/she evidently thinks we should have answered. The first question concerns the difference in water quality between the riparian zone and the stream. Perhaps there is a need to collect samples even closer to the stream, but with the current data we can only compare the water chemistry 4 m from the stream to the water chemistry in the stream. It is possible, as Referee #2 discusses, that there are filtering/mediating processes that we fail to see with the current experimental setup, but it is also possible that the differences are caused by variations along the stream. One must keep in mind that we only sampled a single transect along ca. 1 km long stream. As shown in Fig. S2 and discussed in the manuscript, there are longitudinal variation

in the composition of the riparian zone, which means the investigated transect may not be entirely representative for the catchment as a whole. Furthermore, there may be scale-dependent differences along the stream even at these scales, e.g. more inflow of older and deeper groundwater further down in the system. By the transect we have identified a compact till layer at ca. 1 m, which seems to limit the exchange with deeper groundwater, but this may not be the case throughout the entire catchment. Therefore, the lack of an exact agreement between the water quality of the stream and that of one single riparian profile should not raise too much concern in our opinion. Nevertheless, we believe that the gradient from uphill podzol soils to organic soils in the riparian zone describes something important about the functioning of boreal headwater catchments. We do not see how it would be possible to settle this question based on the dataset we present, but hopefully the observations of this study will lead to more research on the role of riparian soils, which eventually can shed more light on these issues.

The second question concerns the functioning of the riparian zone and its long-term mass-balance. Again, Referee #2 raises a highly relevant question, but we do not see how it would be possible to resolve that question based only on soil water data. As suggested by Referee #2, modelling and sampling of soil would be possible strategies to gain more insight into this matter. Indeed, the are modellers now working with this data, trying to integrate a hydrological transport model with a thermodynamic chemical model. We are also working with soil samples that could reveal more about what is going on in the riparian zone. It is not included in the manuscript, however, partly because we have not finished the analyses, partly because it would result in a very lengthy manuscript. Even in its current state, this manuscript is fairly long, and then it must also be acknowledged that we do not discuss any of the elements in detail. Nor do say much about the temporal variability in the soil water chemistry, although such information can be found in the dataset. Therefore, we do not think that it is a good idea to add even more data. It is already challenging enough to generalize the current results into a coherent manuscript.

Overall, however, we think that these two questions are highly relevant, and we hope that the research in the Krycklan catchment eventually can help to solve them. We can assure Referee #2 that this manuscript in no way was intended to be the final word on this matter. As mentioned, there are currently multiple on-going efforts to model the hydrology and the biogeochemistry of this particular transect. One reason why we think that is important to publish these results is that they should become available and citable for on-going and future research. Getting all the mass-balances right – both in the present and historically – is, however, not an easy task. It requires more data and more work, and therefore goes beyond the scope of this manuscript in our opinion. Therefore, we believe that this study must be seen as part of a greater effort to understand the long-term functioning of riparian soils and their impact on stream water quality.

Specific comments:

Page 1, line 9: Referee #2 may be right that the concept of riparian zones is limited to streams and rivers. This needs to be clarified in the manuscript.

Page 1, line 10: We agree. This should be rephrased.

Page 1, line 21: We agree that information on the sampling and the sampling location should be added to the abstract and that the problem should be clearly stated. Referee #1 also called for a revision of the abstract.

Page 2, line 5: Strictly speaking, we do not think that "water quality" is exactly the same as "fluxes" of various substances. Water quality is certainly related to fluxes, but when discussing fluxes it relates more broadly to the fate of various substances in the environment and not only in the stream water. However, it may be superfluous to bring up both terms in two consecutive sentences so it is probably a good idea to rephrase this.

Page 3, line 5: Referee #2 observes that the hypothesis is a bit vague. We agree that

we should try to describe the objective and hypotheses more clearly. Site description: The site description indeed contains large amounts of information at different levels. We believe that it is important to provide an extensive background both the area and the specific transect with references to publications where more information can be obtained. In the current version the focus is on the transect, which was investigated, but it would be possible start with background description of the area and then zoom in on the transect, as the Referee suggests.

Fig. 1: The investigated transect is indeed located in the Krycklan catchment, which also is clearly stated in the manuscript. Fig. 1 does not depict the entire Krycklan catchment, but one of the small headwater subcatchments (C2 or Västrabäcken) within the Krycklan catchment, which is where this particular transect is located. As can be seen in Fig. 1, this is an appropriate scale for showing the location of the transect. When using a map of the entire Krycklan catchment, it is hard to even discern the subcatchment (C2), in which the transect is located, let alone the transect itself. Since no data from other subcatchments in Krycklan are discussed in this manuscript, we do not think that a map of the entire Krycklan catchment is strictly necessary in the manuscript itself, but it could be added to the supplementary material for those who are vaguely familiar with the Krycklan Catchment Study and wish to know where the S transect is located. All soils in the catchment (C2) are classified as till in the soil maps so it is not possible to them to map the extent of the riparian zone.

Page 3, line 18: Before the lysimeters were installed in 1995 tracers and a number of groundwater wells were used to determine the flow direction of the groundwater. In reality the direction of the groundwater flow probably varies somewhat over time depending on the groundwater levels, but that is hard to capture in this type of experimental setups that require permanent installation of sampling equipment. The direction also agrees well with what could be expected from the local topography, but that was not decisive when installing the transect.

Page 3, line 25: We agree that it would be good with better references here. To start

with we should include a reference to Fig. S2, which shows that the gradient from inorganic to organic soils is typical for the investigated catchment. There are similar measurements from other catchments in Krycklan, which show that small streams typically have highly organic riparian zones. We will have to check whether that information is citable somewhere or whether we somehow could include it in this manuscript. On larger scales it is quite hard to show that this type of organic riparian soils is common because their importance has not historically been recognized. For example, in soil maps from the Swedish Geological Survey the investigated transect is classified as till – despite its high content of organic matter. Riparian soils have, however, been investigated throughout the Krycklan catchment, and the results suggest that accumulation of organic matter is typical for riparian soils along the smaller (roughly first- and second-order) streams.

Page 3, line 26: Mor is a type of humus, which is typical for coniferous forests. It is not essential information so perhaps it should be removed in order to avoid confusion.

Page 3, line 32: This was an attempt to describe the area upstream of S22, but it evidently needs to be clarified.

Page 4, line 2: We do not entirely understand this comment. A reference is given to Fig. S2, which shows that accumulation of organic matter in the riparian zone is common throughout the catchment where this transect is located and, more specifically, that the LOI at the investigated site is typical for the riparian zone of this catchment. We do not see what other reference we would need to support our claim.

Page 4, line 31: We apparently need to describe the sampling better. There are different types of lysimeters, which can be used to measure different things. These lysimeters are best described as suction lysimeters and consist of small porous ceramic cups, which are buried at different depths in the soil profiles and attached to tubes. When connected to vacuum bottles water is extracted from the soils regardless of whether the cups at that time are in located in the saturated or unsaturated zone. Perhaps an

additional figure of the transect in the supplementary material would be helpful.

Page 5 (?), line 13: Normally there are loggers in groundwater tubes next to the lysimeters, which continuously measure the groundwater levels, but during sampling period the loggers were unfortunately out of order. Therefore, there are no direct measurements of the heads. Instead the groundwater levels (response) were estimated from the discharge in the stream (predictor), which is measured and logged at a weir downstream of the transect (Fig. 1). The full procedure is given in the cited reference, but it could perhaps be clarified also in the manuscript.

Page 5, line 23: The relationship was established based on older measurement because we unfortunately missed to measure pH in this sampling campaign. We should clarify this in the manuscript.

Page 6, line 5: Omega was originally defined in the cited manuscript (Lidman et al., 2014) as an index for how strongly different elements bind to organic matter. It is calculated by modelling the aqueous speciation and equals the fraction of a certain element that is predicted to be bound to DOC. Therefore, the unit is percent, although it can be thought of simply as an index ranging from 0-100, describing how strongly an element is expected to bind to organic matter in a certain environment. This should probably be explained in more detail in the manuscript, although a full description and discussion of this parameter is available in the cited reference.

Page 6, line 6: We agree that we should be clearer concerning the PCA (if it indeed should remain part of the manuscript). The variables were scaled because the concentrations of the included elements vary over several orders of magnitude. We used the average concentrations because that allowed us to include more elements in the PCA – otherwise there would have been more gaps in the data. As stated, Th and Cr were excluded because of missing values, whereas interpolation was used to fill in gaps for U and Zr. In addition, we failed to mention that pH also was excluded, since it was just estimated from other parameters. Since the PCA mainly was used to construct the

biplot (Fig. 3), no Kaiser criterion or other selection criteria was used. Likewise, no rotation was used.

Page 6, line 10: Once it had been observed that certain elements occurred in so much higher concentrations in the riparian zone than in the normal podzol soil, the question was raised whether the riparian zone could be an overlooked exposure pathway for various toxic substances. If the plants are exposed to nearly 100 times higher concentrations of certain elements in the riparian zone, this could lead to much higher concentrations also in, for example, bilberries, which frequently are being picked. This is the reason we made a screening of spruce shoots and bilberry leaves in the riparian zone. The results showed no clear increase in the element concentration in the riparian vegetation, suggesting the elevated element concentrations are present in forms with low bioavailability. We could certainly elaborate a bit more on this introduce the question better in the introduction.

One of the advantages of conducting a study like this in a well-investigated area is that there is plenty of background information available. It is important to put the current study in the context of previous research in the area. It is not always easy to know when it is best to introduce this information, but in some cases we believe that it is best to bring it up in the context where it is most relevant for the interpretation of the data rather than in the introduction or in the site description. One drawback is obviously that it is hard to tell what is based on previous publications and what is based on the present results. We have tried to be careful to cite previous research whenever references are made to older information, but it must also be acknowledged that some of the discussions and conclusions rely both on previous and present results. It should be possible, however, to make a stricter division between previous and present results, as suggested by Referee #2.

Table 1: We agree that the information is exhausting, but nevertheless those are the actual results of this study so it seems important include the table in the manuscript. The general trend is illustrated in

Fig. 4, but we could also see if it is possible to include the enrichment factor in Table 1 (without having to compress it too much). This was also brought up by Referee #1. The temporal trends are not shown in the table (or elsewhere) and are not discussed in any depth in the manuscript. The reason is that we do not know how we possibly could concentrate all that information into something that can be presented in a single manuscript. For some elements there is certainly considerable temporal variability, for others not so much, but we have not been able to discern any simple trend that could summarized in a similar manner as Fig. 5. It is very hard to come up with that type synthesis. Whether or not the average concentration is the most suitable measure over the year is again a very complex question, which ultimately depends on what issues one is trying to address. However, when trying to summarize such large datasets it is necessary to somehow make simplifications. There may very well be interesting patterns that we miss by using averages, but in any case we feel confident that we do not misrepresent the general patterns in the water chemistry by using averages. The idea is to make the dataset available to allow further analyses of, for instance, temporal variations.

Fig. 2: The bottom subplot does indeed show the approximate groundwater levels at different discharge as stated, but we should probably clarify that this is based on the data published by Laudon et al. (2004).

Page 7, line 3: Yes, it should be “at all depths in S22”.

Page 7, line 8: The speciation of Fe is crucial for the mobility of many trace elements because Fe colloids have been found to be one of the most important vectors in boreal waters. The other important vector is organic colloids/TOC. The apparent absence of Fe colloids in the riparian zone is therefore important for the interpretation of the data, since it leaves TOC as the only plausible candidate for trace element transport. This is the reason that we wish to bring up the discussion about Fe at an early stage, which formally should not be a problem because the manuscript does not have strictly separated sections for results and discussion. We are, however, prepared to shorten

this section or move parts of it to the later parts of the manuscript. This would probably be good in some respects, as suggested by Referee #2, but we also think that it would be good to present all evidence that speak against the presence of Fe colloids before we go on and discuss the role of TOC. This is a quite lengthy discussion, which relies on the assumption that there are no Fe colloids present.

Page 7, line 19: The explained variance was only given for the first two principal components, which are the ones that are used in the biplot. The Kaiser criterion was not used to select which principle components to retain, since no further analyses were made using these results. We mentioned the fact that a large number of principle components were needed to explain most the variance just to illustrate that the problem could not easily be reduced to just a few dimensions, but this was perhaps not necessary. Likewise we did not provide or discuss any factor loadings, but all of this could of course be added to the supplementary material. We suspect, however, that anyone who has any interest in such things would be more interested in the full dataset, which we intend to make available. Then it would be possible to proceed with similar analyses for anyone who wishes to do so.

Page 7, line 25: The PCA was done at an early stage of the data analysis, and it is a part of the manuscript that we were uncertain whether to include or not. Referee #2 remarks that we focus too much on the biplot, which probably is why we though that the biplot was the most interesting result of the PCA. We particularly like the way the lysimeters group themselves into the three investigated soil profiles (S4, S12, S22), which is nicely illustrated by the biplot. This provides a good statistical justification for the proceeding analyses of the soil water chemistry, which largely relies on a grouping of the samples according based on the three profiles. To us this was the major reason why we wanted to include the PCA. However, this is no excuse for not providing a full description of the outcome of the PCA. Referee #2 is probably right when stating that we focus to much on the deviations and too little on the general results.

Page 13, line 1: Having read the manuscript anew, we feel inclined to agree with the

opinion of Referee #2 that there is a certain degree of repetitiveness and redundancy in the manuscript. It should be possible to shorten these parts. Referee #2 also thinks that we should focus more on the reasons of high element concentrations in the riparian zone – "weathering, transport . . ." – which is a fair viewpoint, but the problem is that we do not yet have the full picture. In this manuscript we believe that we have demonstrated that TOC plays a key role, but it remains unknown whether the high concentrations ultimately are caused by increased weathering rates in the riparian zone or historical transport to from uphill soils to the riparian zone.

Referee #2 remarks that the inclusion of solid phase samples would make the manuscript much stronger. We certainly understand this viewpoint. In order to fully understand the functioning of the riparian zone it is not sufficient to just look at the soil water chemistry, as we have done in this study. The problem, as we see it, is the length of the manuscript. Already in its present state, Referees are complaining that the manuscript is too long. Although this partly may be related to some repetitiveness in the presentation, it must also be taken into account that the manuscript presents a dataset of considerable size. Most of the included elements are hardly discussed at all and are only briefly shown in tables and figures, and the temporal trends in the soil water chemistry are also largely overlooked, as discussed above. In our opinion there is a lot more that needs to be discussed in more detail in the data we present in this manuscript, and we think that it is likely that more publications will be based on this dataset in the future. The purpose of this manuscript was therefore mainly to present the dataset and try to describe and explain the major trends, thereby making it available and citable. Therefore, we do not think it would be wise to expand the manuscript further at this state by including even more data. However, in the light of these soil water samples we agree that it would be a good idea to also analyze solid samples from the transect. Indeed, such analyses being made, and we hope that the results soon can be published as well. It will hopefully help to answer some of the key questions that Referee #2 raises.

To summarize, this study was not the first step in trying to understand the riparian zone, and we must emphasize that it is in no way meant to be the last. As mentioned, analyses of the solid phase have been made and are currently being interpreted. We hope that it will be possible to answer some of the questions concerning the functioning of the riparian zone raised in this manuscript using these new results. Particularly, we hope that it will be possible use this data to discern weathering and accumulation patterns in the transect, which might answer the central question raised by Referee #2: "are higher concentrations just a function of mobilization in presence of TOC or locally different weathering rates?" Currently, however, we do not know, but obviously important processes are going on in the riparian zone, as illustrated by the results of this study. That alone we believe justifies their publication.

Comments to Referee #3:

Our impression is that the comments from Referee #3 overall are positive. He/she describes manuscript as "interesting and generally well-written", but also points out that the manuscript is a bit long, partly due to some repetitions that ought to be removed. In this respect, Referee #3 seems to agree with the other two Referees.

Referee #3 brings up the pH, which arguably is a very important parameter. We also regret that pH was not measured in these samples. It was certainly our intent to do so, but due a misunderstanding between the involved laboratories nobody actually did the measurements. When the mistake eventually was discovered, it was considered to be too late to make reliable pH measurements. Luckily there were pH measurements from other sampling campaigns in the transect, which enabled us to establish a relationship between pH on one hand and TOC and Ca on the other. The underlying assumption of this model was that pH mainly was driven by organic acids (TOC) and weathering (in this case represented by Ca). Thus, it was possible to reconstruct the pH with an average prediction error of 0.24 pH units, as stated in the manuscript. The relationship is also illustrated in Fig. S4. Referee #3 calls for an additional explanation about the potential prediction error, and it would of course be possible elaborate further on this

subject in a revised manuscript.

We agree that the prediction error in the pH might cause problems if it were included in further statistical analyses such as the PCA. Therefore, it was not our intent to include pH in the PCA, and as far as we can see pH is consequently absent in the biplot (Fig. 3). The statistics related to the PCA also do not include pH, and should we be mistaken here we agree that it should be corrected. However, we have not stated in the text that pH was not included in the PCA, and that is something that needs to be clarified in the manuscript. Furthermore, pH was included in the discussion about the PCA, although it was not part of the PCA, which is misleading. This should be corrected.

Referee #3 also criticized our approach to look that biological uptake in the riparian zone. We acknowledge that Referee #3 makes a valid point here. What we measured was indeed the concentration of various elements in biota, which is not the same as the uptake in biota. For instance, high uptake may not necessarily lead to high concentrations, since one also needs to consider the release. Therefore, this section has to be rephrased and, as suggested by Referee #3, shortened.

The reason that the element concentrations in biota were measured was that the high concentrations of certain elements in the riparian soil water potentially could lead to higher concentration also in the riparian biota. That would imply that the riparian zone could be an important exposure pathway for animals and humans with respect to many toxic substances. The crucial parameter in this case would be the concentrations in the vegetation rather than the actual uptake. This also brought up by Referee #2 so it is clear that we need to explain these measurements better in the manuscript.

Concerning the organic content of the soils the LOI (loss on ignition) for the three soil profiles is shown in Fig. S1. The variation in organic matter along the stream is further illustrated in Fig. S2. Referee #3 remarks that we need to be more specific when discussing for example the content of organic carbon and be careful to explain all acronyms such as TOC (Total Organic Carbon) and REE (Rare Earth Elements).

We fully agree with Referee #3.

Finally, Referee #3 thinks that the thickness of the organic soil horizon should be indicated in the upper panel of Fig. 2. The current colour background indicating the LOI is based on a regression, but the organic topsoil layer is missing because it was hard to make a good regression when including the topsoils. This is most apparent near S22, but it should be possible to add a thin organic topsoil to the figure.

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