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Interactive comment on “Landscape control of uranium and thorium in boreal streams – spatiotemporal variability and the role of wetlands” by F. Lidman et al.

F. Lidman et al.

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Received and published: 6 June 2012

Below follows our response to all of the comments of referee #2 on our manuscript “Landscape control of uranium and thorium in boreal streams – spatiotemporal variability and the role of wetlands”. In order to facilitate for all readers to follow the discussion all of the reviewer’s comments are provided as “Comment” below. Our response to each of the paragraphs follows directly after each comment and is labeled “Response”.

Comment: "The paper presents not novel but geochemically-valuable topic, concentrations and migration of uranium and thorium in wetlands. This topic is certainly interesting for geochemists but I am not sure about the pertinence of this work to Biogeo-

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sciences journal (unless there is a special issue). The amount of discussion of organic matter / biota and related mechanisms are minimal."

Response: To begin with, we wish to make clear that this manuscript is not about migration of uranium and thorium in wetlands. Nor does it present any concentrations of uranium and thorium in wetlands as the referee claims. If that is perceived as the topic of the manuscript, we understand that it may come across as neither novel nor original, but the scope of this manuscript is much broader than that and the conclusions reach further. We hope that this will be evident after the following discussion.

As regards the choice of journal, we deliberately chose Biogeosciences, since we believe that our manuscript has a clear biogeochemical perspective. Biogeochemistry, as we perceive it, involves not only the study of biota and organic matter, but is a much wider discipline combining elements of chemistry, geology, earth science, physics – and biology. One of the central concepts in biogeochemistry is biogeochemical cycles, particularly on global scales. Admittedly, this manuscript does not deal with global fluxes of uranium and thorium, but it attempts to describe and explain the cycling of these elements in the boreal forest landscape, which is one of the largest terrestrial ecosystems on Earth. If the conclusions of our study are extrapolated to the whole boreal forest region, as discussed in the manuscript, it is clear that export of both uranium and thorium from the boreal forests areas to the oceans is significantly decreased by wetlands. Hence, the topic is important for the global biogeochemical cycling of uranium and thorium. In the aims and the scope of Biogeosciences it is clearly stated that Biogeosciences is dedicated to papers on "all aspects of the interactions between the biological, chemical and physical processes in terrestrial or extraterrestrial life with the geosphere, hydrosphere and atmosphere". Furthermore, it is explicitly written that Biogeosciences aims to "cut across the boundaries of established sciences and achieve an interdisciplinary view of these interactions". Among the fields that Biogeosciences is meant to cover this manuscript fits well into the category "Biogeochemistry and global elemental cycles". Although biogeochemical studies traditionally often have tended to

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focus on carbon, nitrogen, phosphorus and, to some extent, sulphur, there is no reason to exclude other elements. All elements have individual biogeochemical cycles, and they all need to be further explored. While uranium and thorium traditionally have been discussed mainly in geochemical or radioecological contexts, we think that it is fruitful to apply a more biogeochemical perspective also to these elements – which is what we have tried to do in this manuscript. As far as we know, this is the first attempt to analyze the fluxes of uranium and thorium from a landscape perspective. Therefore, we believe that our manuscript would be met by interest among the readers of Biogeosciences.

Comment: "The motivation and objectives of this work are unclear. Is there any hypothesis to be tested? Without clearly presenting this issue, the paper may appear “of local interest only”. The novelty of main results and main conclusions are unclear. The amount of primary material presented in this work is insufficient. Some data useful for the discussion are in preparation; they should be certainly shown."

Response: We agree that the motivation and the objectives of our work should be possible to understand from the introduction. In the manuscript we mention the increasing exploration for uranium and the approaching construction of deep repositories for nuclear waste in the boreal region. Both these activities call for a better understanding of the long- and short-term behavior of uranium and thorium in these environments. There is also a more fundamental scientific interest to understand how these elements, the only ubiquitous representatives of the actinide series, behave in the boreal forest landscape. As we mention in the manuscript, previous studies have mainly focused on major rivers, e.g. Andersson et al. (1995; 1998), leaving the headwaters essentially unexplored. Our results can be considered as “of local interest” only in so far as headwaters are considered unimportant or uninteresting. We would, however, strongly object to any claims that this would be the case. 80 % of the permanent stream length in Sweden is found in catchments smaller than 2 km². As we argue in the manuscript, small streams are important and vibrant ecosystems. Since they are so small, they

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are sensitive to disturbance, but yet they are most likely to be directly affected by anthropogenic influences, since they are so common in the boreal landscape. The headwaters are also very important for draining the boreal landscape. We know of no good estimates, but a significant portion of the discharge from the boreal landscape should be generated in the type of streams that we investigate. Hence, a large portion of the uranium and thorium that is weathered from the boreal landscape should enter the surface water in small streams.

As for any environmental study, which is carried out at a specific site, there is always the question of whether that study is representative for larger areas or whether it is “of local interest only”. The fact that this is the first detailed study of uranium and thorium in boreal headwaters should be motivation enough, but ultimately this question is best answered by the conclusions that the study produces. We will return to the question of what the main conclusions of this study are and how representative they are below.

The reviewer also asks for specific hypothesis to be tested. A posteriori it is of course easy to suggest hypotheses to test, but it would not be honest to present such hypotheses as a priori hypotheses, motivating this study. The truth is that so little was known about the spatiotemporal variability of uranium and thorium in this type of streams that it was not possible to suggest any meaningful hypotheses. We may be narrow-minded, but we would not have anticipated that the export of uranium would vary by as much as a factor 18 within the relatively small (67 km²) Krycklan catchment. And if someone would have told us that this really was the case, we would probably have guessed that it was caused by some uranium mineralization in parts of the catchment – not that wetlands could cause such spatial variability. Instead we will emphasize more clearly in the revised manuscript that the main objectives of this study were to (1) describe the spatiotemporal variability of uranium and thorium in boreal headwaters and to (2) try to explain that variability based on stream water chemistry, catchment characteristics and seasonality.

We are also quite surprised to hear that the amount of primary material is insufficient.

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It is the result of an ambitious sampling program involving a large number of people, not only the authors of this manuscript. We present detailed concentrations of uranium and thorium from no less than ten streams covering two years. Only the stream water samples represent 342 observations each for uranium and thorium. Especially in connection with major hydrological events such as the spring flood we have a high resolution of the sampling in order to capture the full range in stream water concentrations of uranium and thorium. It is hard to see that anyone with any experience in hydro-chemical sampling and hydrological measurements would fail to recognize the amount of work that has been devoted to gathering the data we present in our manuscript. If there are publications with a comparable spatiotemporal resolution, we would very much like to know where to find them. The publications that the reviewer seems to suggest are either from the Kalixälven study (Andersson et al., 1995; 1998), but it does not provide a comparable spatial resolution and operates on different scales, or the study by Astrom et al. (2009), which provides an impressive amount of data covering large areas but little temporal resolution.

Finally, the reviewer argues that there are data still in preparation, which could be important for interpreting the results presented in this manuscript. It is hard not to agree with this, since this manuscript is intended as a first part in a bigger project addressing various aspects of the fate of uranium, thorium and related elements in the boreal landscape. However, it is not always possible to include everything more or less remotely important into one single paper – not only would that paper be unreasonably long, it would also be quite unfocused and, presumably, more or less unreadable. We are indeed currently preparing material dealing with the colloidal transport of a wide range of elements, among all uranium and thorium. It would certainly have been nice, if that material already had been published, but since the material is too disparate and too extensive to fit into a single paper, we have to begin somewhere. When preparing this manuscript and deciding what to include we followed the guidelines of Biogeosciences concerning extensive work on a system so that this paper will “give a complete account of a particular aspect of the general study”

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(http://www.biogeosciences.net/submission/obligations_for_authors.html).

Comment: "Introduction: The authors should formulate the objectives and scientific questions of this work. What is new in this paper compared to previous study of Anderson et al., 1995, 1998? Only the choice of the catchment? Then this study is of local interest only. Secondly, the authors achieve the same conclusion on the correlation between element concentration in soils and in streams as that of Astrom et al., 2009. The question of novelty and originality is, again, becomes important."

Response: As for the objectives of our work, we believe that we already have answered these questions, and they can certainly be developed further in a revised manuscript. In that sense we see no problem to motivate this study. We have already touched upon the differences between our work and the previous work of Andersson et al. (1995; 1998) and Astrom et al. (2009), but let us take a closer look at this issue, since it apparently is not explained clear enough in the manuscript.

It is important to realize that Kalixälven, which was investigated by Andersson et al. (1995, 1998), is one of Sweden's largest rivers. Its catchment covers an area of more than 18,000 km² and covers not only boreal forests but also parts of the Scandinavian mountains, including various types of bedrocks. This is 270 times bigger than the entire Krycklan catchment and more than five orders of magnitude bigger than the smallest subcatchment in our study (0.13 km²). Hence, the work by Andersson et al. (1995; 1998) represents a fundamentally different type of system, although we also must recognize that there are connections. However, as should be evident after reading our manuscript, knowledge about uranium or thorium in downstream rivers or streams provides no information about the spatiotemporal variability at upstream sites. This is probably true for many more elements and is related to the much discussed problem of scaling in environmental studies. This aspect has probably never been discussed in relation to uranium and thorium, quite possibly due to lack of data, but it is well-known in hydrology and in relation to more well-studied substances such as DOC. Thus, one important difference between Krycklan and Kalixälven is the size – Andersson et al.

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(1995; 1998) studied a large river and what happened when it reached the sea; we studied small first order streams in close contact with the terrestrial environment and followed the stream water up to a fourth order stream. This difference alone between Kalixälven and Krycklan study should be enough to justify our work.

However, the Krycklan catchment also provides additional advantages that lead beyond the conclusions presented by Andersson et al. (1995; 1998). One major advantage is that we study so many catchments that we can use a statistical approach to differentiate between the role of different landscape units. This could also be done on larger scales, quite possibly with different results, but it requires a large amount of data from a sufficiently high number of catchments. It is here that the wetlands emerge as a key unit for understanding the fate of uranium and thorium in the boreal landscape. Thanks to the access to airborne gamma spectrometry we can also rule out the possibility that the spatial variability is caused by differences in the soil and bedrock concentrations of uranium and thorium. None of this is present in the work of Andersson et al. (1995; 1998). Although it certainly is known that uranium easily accumulates in wetlands, it was not known that wetlands could exert such profound control over the fluxes of both uranium and thorium from the boreal landscape before our study. Based on uranium isotope measurements of an individual wetland Porcelli et al. (1997) rejected the hypothesis that wetlands were major sources for uranium, but in comparison our results are more general, since we consider wetlands on the landscape-scale. Thanks to the large number of catchments we can also produce the first estimate of how much uranium and thorium that is retained in boreal wetlands – and as it turns out, this can be quite a lot: as much as 30-40% of the uranium and thorium that is annually weathered according to our estimations. If this is not novel and original, we have apparently missed some key publications concerning the biogeochemical cycling of uranium and thorium. It is certainly not present in the publications mentioned by the reviewer. Needless to say, if the accumulation in boreal wetlands indeed is as extensive as our data suggest, our conclusions can hardly be dismissed as “of local interest only”.

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Having said this, we also want to emphasize that we do not consider the work of Andersson et al. (1995; 1995), Porcelli et al. (1997) and other papers from Kalixälven to be ill performed. Clearly, measurements on different scales are needed to grasp the whole picture of how elements are transported in the boreal landscape. This far, however, the headwaters have not been properly addressed. Just as our conclusions reach beyond what could be concluded from their results, their conclusions reach beyond what could be concluded from our results. This clearly demonstrates that our study is not similar to theirs except for the choice of catchments, as suggested by the reviewer.

As regards the work of Astrom et al. (2009), which we discuss in the manuscript, we are quite puzzled by the reviewer's statement that we come to the same conclusion as Astrom et al. did in their paper – and more precisely that we should present similar correlations. As we understand Astrom et al. (2009), they found no correlation between uranium concentrations in streams and uranium concentrations in soil in Phanerozoic areas, while there was a weak correlation ($r_s=0.45$) in Precambrian areas. However, even in this case most of the variability remained unexplained, indicating that there is some unknown factor causing considerable variability in the streams. Hence, based on the conclusions of Astrom et al. (2009) one might expect a weak correlation between soils and streams within the Krycklan catchment, since it is located on Precambrian bedrock. However, our data shows no such correlation for uranium. In other words, the almost 20-fold variability in the average concentrations of uranium in stream water is not correlated to the concentrations of uranium in the soil. Our work does not necessarily contradict the results of Astrom et al. (2009), since we work on different scales, but it is hard to see how our conclusions could be interpreted as being the same as those of Astrom et al. (2009).

What we did find, on the other hand, is a significant and strong correlation between thorium in soils and thorium in stream water. This has, however, little to do with the work of Astrom et al. (2009), since their work does not consider thorium at all. More importantly, we also reject this correlation as a causal explanation to the variability of

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thorium in stream water. Instead we introduce another, in our opinion, much more credible explanation, namely the different landscape units within the catchments and their area. The wetland coverage also turns out to be strongly correlated to the export of uranium – but this has nothing to do with the finding of Astrom et al. (2009), since they did not consider the role of wetlands at all. We believe that the conclusions of Astrom et al. (2009) are correct in the sense that there is a significant influence from the soil concentration on the stream water concentration on the scales where they operate, but we must also point out that a large part of the variability remains unexplained in their article. It is quite possible that our results provide the key to why that is, since we clearly show that the different landscape units can cause considerable variability. Our guess would be that more of the variability in the dataset presented by Astrom et al. (2009) could be explained if the wetland coverage of each investigated catchment was used.

Having said that, we also wish to point out that even if we would have come to the same conclusion as Astrom et al. (2009), which we did not, our results we still have been interesting, since we are operating on very different scales. Spatial relationships established on regional scales, as in Astrom et al. (2009), do not automatically imply that the same relationships apply on local scales.

Since the reviewer believes that we reached the same conclusions as Astrom et al. (2009), he/she has obviously not understood at least one of the two texts properly. It follows that the criticism concerning lack of novelty and originality is substanceless and cannot be taken very seriously. Hence, what we can learn from this criticism not that our study lack novelty and originality, but rather that we may need to elaborate on the message of the manuscript further so that the conclusions and the message become clearer.

Comment: "The last sentence of the Abstract is rather trivial unless the solid and dissolved fractions(bulk and filtered samples) are provided."

Response: It is of course not unexpected that the atmospheric deposition of uranium

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and thorium is small so it can certainly be discussed whether that information qualifies for the abstract or not. However, it is customary when constructing biogeochemical cycles to include the atmospheric component. We have also had people explicitly searching and asking us for data on the atmospheric deposition of uranium and thorium in this region so we thought it might be nice to advertise a bit that such data can be found in this manuscript. Since the abstract is relatively short and concise, we think it would be worthwhile to keep the last sentence.

Comment: "The sampling and analysis are insufficiently described and as such the quality of experimental approach can not be judged. Describe briefly the methods: sampling, filtration, storage, analysis. What are the uncertainties, detection limits? How good were the analyses of certified samples such as SLRS-4? If the samples were not filtered (what are the bulked volume weighted monthly samples?) then the pertinence of results to biogeochemistry becomes almost nil."

Response: We agree that some clarification of the analyses would be needed. For instance, it should be stated clearly that all water samples were filtered and that all concentrations refer to dissolved uranium and thorium (although this is apparent from the presentation of the results). Particulate transport was not considered at all in this study, since it probably is of little biogeochemical importance. For details about the sampling, filtering, storage, analyses etc. we have referred to other publications, in which this is thoroughly described. We believe that this is common practice and often also explicitly encouraged by many journals, when the information already is available elsewhere. We could of course briefly repeat some of that information in the manuscript if necessary.

The water was sampled in acid-washed high density polyethylene bottles after rinsing them at least three times with stream water. The bottles were completely filled and placed in polyethylene bags directly after sampling. The samples were brought directly from the field to a refrigerator, where they were stored at 4 degrees C in complete darkness until further treatment. The samples were filtered within 48 h in a class 100

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laminar flow hood using 0.4 μm Millipore isotope polycarbonate membrane filters in Millipore SWINNEX-47 filter holders. The filters were rinsed with 50 ml of ultraclean water and then conditioned with 30 ml of sample water. The filtered samples were then acidified with 1 ml suprapure nitric acid per 100 ml of sample and were then stored in the refrigerator again until analyzed. The samples were analyzed for ^{238}U and ^{232}Th at Stockholm University using a Thermo Scientific X Series 2 instrument (ICP-MS). Rhodium was added as an internal standard and SLRS-4 (riverine water; National Research Council; Canada) was used as a control sample. The certified value for uranium in SLRS-4 is 50(3) ng g⁻¹, and the average from our measurements was 48(2) ng g⁻¹. For thorium there is no certified value, but Rodushkin et al. (2005) have suggested 17(2) ng g⁻¹ and Yeghicheyan et al. (2001) 18(3) ng g⁻¹. Our average was 14(3) ng g⁻¹ so it comes close to the suggested values. Hence, no significant deviation from the SLRS-4 standard was found. Field blanks were also prepared at each sampling occasion and analyzed for quality control purposes. For uranium the average was -0.02 ng g⁻¹ and for thorium 0.04 ng g⁻¹. The standard deviation was 0.043 ng g⁻¹ for thorium and 0.16 ng g⁻¹ for uranium. Using three standard deviations as detection limits we get 0.13 ng g⁻¹ for thorium and 0.49 ng g⁻¹ for uranium. This is well below the lowest observed concentrations in stream water, which were 4.1 ng g⁻¹ for thorium and 3.6 ng g⁻¹ for uranium.

“Bulked volume weighted monthly samples” refers to the measurements of uranium and thorium in precipitation. In order to avoid evaporation precipitation must be sampled after each rain episode, but since we had no interest in analyzing each episode individually we bulked mixed water from all episodes during a month into one “bulk sample”. When mixing these monthly samples the amount of sample from each episode was proportional to the amount of precipitation in that episode so that the bulked sample represents the average composition of the precipitation during that month. Hence, we describe this as bulked volume weighted monthly samples. It is perhaps not very elegant, but we cannot think of a better way to describe it. Anyhow, this apparently needs to be clarified in one way or another.

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Comment: "Careful measurements of discharge are certainly appreciated."

Response: This is actually one of the aspects of this study that we are working hard to improve for future studies. Indeed, an appreciable amount of work and money has already been devoted to hydrological measurements within the Krycklan catchment, but we still have not managed to get site specific discharge for all sites. We suspect that this, rather than the uncertainty in the chemical analyses, is a major source of uncertainty in our study. This has been elaborated extensively by others, e.g. Ågren et al. (2007), Björkvald et al. (2008) and Laudon et al. (2001). We could also provide more information on how the hydrological measurements were made, but as for the chemical analyses detailed descriptions can be found in the references provided in the manuscript.

Comment: "p. 2830, line 21: The reference to the Abstract is certainly useless here."

Response: The other two references are certainly more relevant so we will remove it.

Comment: "Discussion on p. 2832 on relative mobility of U and Th. Much lower mobility of Th compared to U is fairly well known for long time. One would not question, for example, lower mobility of Al compared to Mg, although their concentrations in rock-forming minerals may be similar. The export of U from different watersheds should be placed in the context of dominant lithological substrates (silicate rocks and their weathering products; carbonates: : :)"

Response: We agree that uranium generally is more mobile than thorium due to the low solubility of thorium in most environments. However, it is important to consider each environment based on the local conditions and not generalize where it may not be proper to do so. Boreal waters, especially headwaters, are often characterized by high concentrations of DOC. Since both uranium and thorium have a high affinity for DOC the low solubility of thorium may not apply as limiting factor for the transport of thorium. It has been observed that the transport of both uranium and thorium in boreal waters is dominated by colloids, either Fe colloids or DOC. Hence, the statement that

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thorium is more mobile than uranium may not be valid in this type of waters. In fact, Figure 4 shows that there is no difference between the mobility of uranium and thorium once that they have left the forest soils - the retention in wetlands is equal for uranium and thorium. Since the reviewer's statement that thorium has much lower mobility than uranium is disproved by our observations, it is clearly too general. It follows that the issue is not as trivial as it may appear given the common opinion that thorium always is much less mobile than uranium. This alone should be enough to motive a brief discussion of the matter, but we also note that the other reviewer, Dr. Noubactep, thinks that this discussion should be elaborated further. We do not think that the preferential export of uranium compared to thorium is a major issue in our study. As reviewer #2 points out, it is hardly unexpected. On the contrary, given other observations it seems quite surprising that the differences are so small – only a factor 4 as compared to a factor 40 in Kalixälven for instance. Our opinion is therefore that the issue merits a brief discussion in the manuscript. We can add that the low solubility of thorium may still be important, since it could limit the mobility of thorium in the uphill podzol soils, which are the ultimate source for thorium.

We are not sure what the reviewer means by placing the different watersheds “in the context of dominant lithological substrates”. We could of course add a more detailed description of the minerals in the soils, but to our knowledge there are no clear differences in the mineralogy of mineral soils between the catchments. This could perhaps be clarified in the manuscript, since it is essential for understanding our conclusion. The till soils were brought to the catchment by the inland ice from an area northwest of Krycklan. The only exceptions are the peat and silt areas, which has a difference particle size distribution. However, the silt was probably largely derived from the same type of till that is found in the rest of the catchment. The airborne gamma spectrometry measurements also show that there are no significant differences between uranium, thorium and potassium throughout the catchment (except for the wetlands), which indicates that there are no major differences in the mineralogy. It is possible that the reviewer is suggesting that the differences in the export of uranium and thorium be-

tween the catchments could be caused by the occurrence of different minerals in different catchments, but there is nothing that supports such an assumption. All available evidence point in the opposite direction, i.e the composition of the soils is relatively homogeneous with exception of the peat. This is an important prerequisite for our conclusion that the variability is controlled by the landscape. It is also the reason why we reject the soil concentrations as cause for the observed variability.

Comment: "Section 3.4. Airborne gamma spectrometry. How well comparable these data with the bulk soil/rock analysis by wet chemical methods? At least some comparison should be given here."

Response: We can add data from individual soil cores, but it is hard to make direct comparisons, since airborne gamma spectrometry integrates the radiation from large areas and also somewhat undefined depths. There is a significant variation in the soils – both vertically and horizontally. It is well-known that this type of measurements involves some uncertainties, especially for uranium, but what we think is most important to focus on here is not the actual concentrations that were measured, but the relative differences between the investigated catchments. If the soil concentrations would have been the driving variable behind the variability in the stream water we would have expected much more variability in the soils. Even if there are inherent uncertainties in the method of airborne gamma spectrometry such big differences (a factor 18 judging from the stream water concentrations) should be possible to observe – had they been there.

We will hopefully acquire more soil data in the future, but if we look at C2, which is were we currently have data, the airborne gamma spectrometry records an average concentration of $2.2 \mu\text{g U g}^{-1}$ (std= $1.2 \mu\text{g U g}^{-1}$) and $7.0 \mu\text{g Th g}^{-1}$ (std= $3.4 \mu\text{g Th g}^{-1}$) for the entire catchment. Total concentrations as measured by ICP-MS in three soil cores ranges from $1.5\text{--}2.9 \mu\text{g U g}^{-1}$ and $10\text{--}22 \mu\text{g Th g}^{-1}$. Hence, the concentrations of uranium seem to agree well, while the concentrations of thorium are somewhat lower when measured by airborne gamma spectrometry. However, the deviations are small

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and may very well be caused by the spatial variability within the soils. We see no reason to distrust the results of the airborne gamma spectrometry. Had there been problems, we would expect them to occur primarily for uranium. Hence, what the data suggest is that the high variability in stream water fluxes observed within the Krycklan catchment cannot be caused by differences in the composition of the mineral soil. It follows that there must be some other controlling factor, which we identify as the wetlands.

Comment: "Section 3.6. Migration of Th and U in the wetlands. The limiting factor of element migration may be not the source but the carrier availability (Fe colloids, organic colloids, organo-ferric colloids). However there is almost no discussion on these issues, neither on U and Th speciation in streams and their main carriers (Fe, OC). The data on U and Th accumulation in the peat should be shown. Why do the authors fractionate the results? (Line 6, p. 2839 states that the data on Th and U are in preparation(!)) How these data are related to the present study? It is impossible to understand the mechanisms without seeing these data."

Response: The reviewer points out that the limiting factor for the export of uranium and thorium may not be the source but the carrier availability. This is a good point that needs to be clarified further in the manuscript. Since this manuscript was intended to focus on the biogeochemical cycling of uranium and thorium in the boreal landscape, we did not want to get too involved in too specific chemical discussions, but it may be necessary to discuss the speciation in more detail than we did in the original manuscript. As the reviewer notes organic and Fe colloids are often important for transporting uranium, thorium and other metals. In this case we believe that organic colloids are responsible for much of the transport of uranium and thorium. According to measurements by Köhler et al. (2009) Fe colloids are not present in these headwaters. Thermodynamic modeling (using Visual MINTEQ 3.0) also indicates that Fe colloids are not thermodynamically stable at such low pH and high concentrations of DOC. Hence, there are good reasons to exclude the Fe colloids. Köhler et al. (2009) also demonstrated that the transport of REEs is dominated by organic colloids (or DOC), and we would expect

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something similar for both uranium and thorium based on the chemical similarities between these metals. According to Visual MINTEQ 3.0 more than 96% (in most streams >99%) of the uranium should be bound to DOC. There are no corresponding thermodynamic constants for thorium-DOC, but it is hard to envisage that the association to DOC would be lower than for uranium. Consequently, there are good reasons to believe that transport of uranium and thorium in these streams is dominated by DOC, something we also hope to be able to confirm and elaborate further in the future.

We did not include concentrations of DOC for all streams in the manuscript – it may be a good idea to do so in a revised version – but at least we stated that it varies from 11 mg l⁻¹ in C16 to 31 mg l⁻¹ in C4 (the mire outlet). Hence, while C4 has the highest concentration of DOC, it is also one of the sites the exports the lowest amounts of uranium and thorium. If there was not a source limitation, but a carrier limitation, this would hardly be the case. Instead we would expect a positive correlation between DOC on one hand and uranium and thorium on the other. As it happens, there is a correlation between thorium and DOC ($r^2=0.45$, $p<0.05$) and between uranium and DOC ($r^2=0.53$, $p<0.05$) – but the correlation is negative in both cases. In other words, more DOC means less uranium and thorium. This is a strong indication that there is a source limitation on the landscape level rather than a carrier limitation. The underlying explanation to the correlation is probably the wetlands, which are major source for DOC and, as we demonstrate, a sink for uranium and thorium. It is still possible that the carrier availability could limit the export from the forest soils – we do not have the data to test that hypothesis – but evidently it cannot explain the low export from wetland-dominated subcatchments. All evidence suggests that there is a source limitation caused by the accumulation of uranium and thorium in peat. We think it would be a good idea to show these correlations and discuss them further in the manuscript.

Comment: "p. 2839, last line: Why the link between U concentration and alkalinity mentioned in this part of the text is not at all investigated? U-carbonate complexes may indeed compete with Fe-C colloids and this should be certainly addressed."

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Response: This seems to be a misunderstanding that we need to clarify in the manuscript. When we mention carbonate-rich areas, we are discussing how representative our results are on a larger scale. There are, however, no carbonates present in the soils of the Krycklan catchments so the concentration of carbonate in the streams will naturally be quite low – in this case it varies between 1.0 (C4) and 27 (C16) mg l⁻¹. This is a quite large range, but it is not enough to cause any widespread formation of U-carbonate complexes. As we mentioned above, based on thermodynamic modeling more than 96 % of the uranium is bound to DOC in all streams. Hence, it seems unlikely that carbonates would be responsible for any of the variability we observe. When looking beyond the Krycklan catchment, however, we know that there are calcite-rich areas in the boreal landscape, and in this case we would indeed expect U-carbonate complexes to be more common – if not dominating. Since they can be both neutral and anionic, the interaction with organic matter will naturally be lower. Accordingly, one would expect a lower degree of accumulation of uranium in wetlands in such areas. Hence, while we would expect the control of wetlands that we have identified to be valid over large areas in the boreal region, we would not expect this to be the case in calcite-rich areas, where the uranium speciation is dominated by carbonate complexes. We realize that we need to explain this more clearly in the manuscript.

Comment: "One of the main conclusions of this work is that the wetlands are sinks for uranium and thorium. However, this result is not new and the authors cited the relevant papers."

Response: We clearly do not have the same opinion as the reviewer about what is important in the presented data. From our perspective, the main conclusion is that wetlands control the biogeochemical cycling of uranium and thorium in the boreal landscape. This is not the same as to say that wetlands are sinks for uranium and thorium. What we suggest is that annual fluxes and average concentrations of uranium and thorium in boreal headwater streams is not primarily dependent on the soils, the alkalinity, the export of DOC or any other factor – but on the presence of wetlands. The fact that

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uranium can be accumulated in wetlands is, just as the reviewer points out, well-known (although we do not agree that the same is true for thorium), but it has not previously been described that this accumulation is systematic and predictable on the landscape-scale and, more importantly, that it is so extensive that it controls the fluxes of uranium and thorium in the boreal landscape, causing a previously unforeseen degree of spatial variability. It is symptomatic that although the reviewer seems to think that the accumulation of uranium and thorium in wetlands is trivial, the reviewer still fails to recognize just how profound impact this has on the stream water concentrations and, consequently, on the fluxes of these elements in this type of environment. Instead a wide range of other explanatory variables are suggested. This clearly demonstrates that the problems we discuss in this manuscript are neither trivial nor already explained by previous research. It is regrettable, however, that we have not managed to convey our message in a clear enough way.

As we state already in the introduction, it is well-known that uranium may accumulate in wetlands. We also found one example, where this had been observed also for thorium. There may be more, but the point is that these examples all are based on observations of individual wetlands. Of course the richness of such individual observations for uranium suggests that the accumulation should be quite common, but nobody has previously shown what role they play in the boreal landscape. However, by using a landscape perspective, we place the issue on a much more solid ground. We can for the first time provide significant statistical relationships that are valid on the landscape-scale. This also allows us to present the first estimation of how much uranium and thorium that is accumulated in wetlands throughout the boreal region – and this turns out to be a significant number: as much as 30-40 % of the amount that is released by weathering. This is both novel and original, and it is important not only for the global biogeochemical cycling of these elements, but also for assessing the long-term fate of uranium and thorium released from, for instance, mining or deep repositories of nuclear waste. Hence, simply claiming the observed accumulation of uranium and thorium is the main conclusion of our manuscript is misleading and misses the central points in

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our results.

Comment: "Figure 3 presents the most important part of collected data but it should be better visualized and probably re-drawn. First, a plot of concentration versus discharge for different streams is needed. Comparison of metal flux with DOC flux is certainly needed."

Response: Figure 3 mainly contains the background data, on which the flux estimations are based. In our opinion this is not the most important figure in the manuscript – to a large extent this is only raw data, but we think that it provides a nice illustration of the surprisingly high spatiotemporal variability only within this relatively small catchment. The heart of the manuscript is Figure 4, which summarizes the key conclusions of our study. Yet, we agree that Figure 3 probably could be further improved. Since it represents a large amount of data, it is not easy to visualize it in a good way. One major improvement in our opinion would be if the size of figure could be increased. It is certainly no problem to plot the concentrations versus the discharge, but in general it does not show any particularly interesting patterns so we chose not to include it in the original manuscript. We can elaborate the discussion concerning the discharge further in the manuscript, but if such figures should be included we would prefer to add them as supplementary material. As an example we provide the concentrations of uranium and thorium in C1 as a function of the discharge below (Fig. 1). The concentrations of uranium seem to be independent of the discharge in C1, while there is some tendency that higher concentrations of thorium occur when the discharge is low.

We see little reason to compare the metal fluxes with the DOC fluxes in a figure, since there clearly is no causal relationship. We have already described the negative correlation between metal flux and DOC above. It is probably a good idea to develop this further in the manuscript, but it hardly merits a figure on its own. Instead, we suggest that we add information about DOC, pH, carbonate, U, Th and other important parameters for all subcatchments in a table. As an example we have included a figure with the concentrations of uranium and thorium as a function of DOC in C1 below (Fig. 2).

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We do not think that this figure illustrates any interesting relationship.

Comment: "Figure 4. It remains unclear why the silt was excluded. Just for mathematical convenience? Please provide a sound geochemical explanation."

Response: This is discussed in the manuscript, but we think that the discussion is too long to be included in the figure caption. In the manuscript we provide two models each for uranium and thorium, one including the silt areas and one excluding the silt areas. As we show there is a statistically significant higher flux of uranium and thorium from the silt-rich areas than from the till-dominated areas. In the latter part of the discussion we focus on the role of wetlands, which in our opinion is the major driver of the spatial variability in the fluxes of uranium and thorium. Then we remove the silt-rich catchments because they evidently export more uranium and thorium and because few wetlands are located there - silt is mainly present only in the lower parts of the catchment, while most wetlands are located in its higher parts. Hence, including the silt-rich areas would result in an overestimation of the input of uranium and thorium to the wetlands, thereby leading to an overestimation of the accumulation of uranium and thorium in them. This is because most of the wetlands receive their uranium and thorium from till, not from silt. By removing the silt-rich areas, we can instead estimate the fluxes from the till-dominated areas, which is exactly what we need to properly quantify the role of wetlands. Hence, this is not a trick to make the correlation significant, and is not motivated by mathematical convenience (although it has the advantage of making the data less heteroskedastic). We must also emphasize that the correlation between the wetland coverage and the metal fluxes is significant both with and without the inclusion of the silt-rich catchments. As the statistical analysis shows, there is, however, a higher export from the silt area so the separation of the the silt-rich catchments is based on a significant statistical relationship.

The reason that the regression based only on the till areas is shown in Figure 4 is simply that the inclusion of a second variable, the silt coverage, which appeared in the multiple regression, would require a 3D diagram, which would be much harder to

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interpret. We think that this 2D diagram illustrates the data more clearly – the higher export from the silt-rich areas and the lower export from wetland-dominated areas. It would also be possible to show a regression line for all catchments as discussed above, but since we do not discuss that sort of model in the manuscript, it does not make sense to use that in the figure. With this solution we illustrate both the fact that the wetland coverage decreases the export of uranium and thorium and that the export from the silt-rich catchments is higher. We think that is a good compromise, but it may need some additional explanation.

In summary, we think that the reviewer has identified some key points in the manuscript that need to be clarified or discussed more thoroughly. This will also require the addition of more background data to support more detailed discussions of the speciation, the role of colloids, carbonates, pH, DOC etc. However, we think that the reviewer's apprehension that our manuscript would be uninteresting to the readers of Biogeochemistry is based on a too narrow view of what biogeochemistry is. Although uranium and thorium rarely – too rarely in our opinion – are discussed from a biogeochemical perspective, we think our manuscript complies well with the aims and scope of Biogeochemistry.

The most serious criticism, however, regards the originality and novelty of our work. As is evident from the reviewer's comments, he/she has apparently failed to recognize all major contributions of the manuscript. Hence, this opinion seems to be based on the erroneous belief that the only thing we show is that uranium and thorium are accumulated in wetlands. The reviewer has also failed to recognize the role of scale in environmental studies, suggesting that there would be no difference between previous studies of major rivers such as Kalixälven (Andersson et al., 1995; 1998) and the small streams that we have studied. We hope that our response has refuted this view and demonstrated that our work deal with very different systems. The reviewer has also failed to separate the conclusions drawn by Astrom et al. (2009) from our results, claiming that we present similar correlations. As we have demonstrated in this

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response, this claim is not correct. From these repeated failures and misunderstandings we must evidently draw the conclusion that our manuscript needs to be clarified in certain aspects, but it also follows that the criticism of lack of originality and novelty is unfair and ungrounded.

Since the question of novelty and originality has persisted throughout the comments of this reviewer, we would finally like to summarize what we think are the major contributions of our manuscript:

1. This is the first detailed study of the spatiotemporal variability of uranium and thorium in small boreal streams and headwaters. The headwaters alone stand for 80 % the stream length in Sweden (and probably something similar throughout the boreal region). They represent unique, ecologically important and sensitive environments that merit further studies – this should only be a beginning. There is no way that the described patterns could have been deduced from studies on large rivers.

2. Not only is the considerable spatiotemporal variability of uranium and thorium in these environments previously unknown and unexpected, we also provide the explanation to the variability, namely a substantial accumulation of both uranium and thorium in wetlands. Although it was known that at least uranium could accumulate in wetlands, it was not known that this accumulation was extensive enough to control the fluxes of uranium and thorium in the boreal landscape.

3. This is also the first study to quantify the role of wetlands for the biogeochemical cycling of uranium and thorium in the boreal landscape. We demonstrate that the accumulation is both predictable and systematic on the landscape-scale – which is much stronger evidence than observations of individual wetlands. This also allows us to present the first estimation of how much uranium and thorium that is accumulated in wetlands: as much as 30-40 % of the total annual weathering of uranium and thorium from the boreal forest region. If this is correct, a large portion of the weathering will never reach the headwaters, the rivers or the seas so it would indeed be of importance

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for the global biogeochemical cycling of these elements. It also has far-reaching implications for the long-term fate of anthropogenic uranium and thorium released to the boreal landscape.

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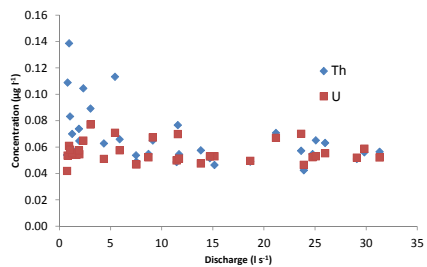


Figure 1: Concentrations of uranium and thorium in C1 as a function of the discharge.

Fig. 1.

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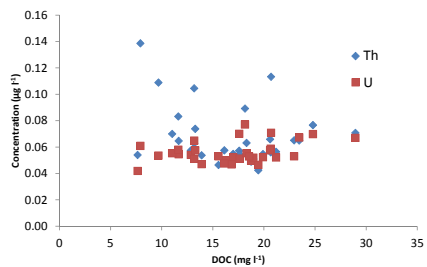


Figure 1: Concentrations of uranium and thorium in C1 as a function of the concentration of DOC.

Fig. 2.

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