Biogeosciences Discuss., 9, C1680–C1686, 2012
www.biogeosciences-discuss.net/9/C1680/2012/

Biogeosciences Discussions

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

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Received and published: 5 June 2012

Response to Dr. C. Noubactep

We thank Dr. Noubactep for his insightful comments on our manuscript "Landscape control of uranium and thorium in boreal streams – spatiotemporal variability and the role of wetlands". We are particularly grateful for the many suggested references (and references therein), many of which should be included in a revised version of our manuscript.

Dr. Noubactep notes that more information on the chemistry of the different streams would make it easier to interpret the data. Quite a lot of information is available in the

references we provide in the manuscript, but a compilation of important characteristics of the streams and the subcatchments would no doubt facilitate the interpretation considerably for the reader. Therefore, we suggest adding a table with key chemical parameters of the stream water (e.g. pH, DOC, carbonate) and key characteristics of their subcatchments (e.g. catchment area, wetland coverage, forest coverage, soil type, soil concentrations of uranium and thorium).

In particular, Dr. Noubactep wonders about the pH of the stream water and its relation to uranium and thorium, respectively. We agree that this is an interesting topic that should deserve more attention in the manuscript. Our original idea was to focus on the fluxes in the landscape, but we realize that a more thorough discussion of the chemistry is needed to convince the readers that it really is the wetlands that control the fluxes of uranium and thorium in this type of systems rather than differences in pH or any other chemical parameter.

There is indeed a significant positive correlation between pH and the export of uranium: $r^2=0.49$ ($p<0.05$, $n=10$), but not for thorium. Hence, higher pH tends to lead to higher export of uranium and higher average concentration of uranium in the stream water. The question is whether this correlation has any causal meaning or not. One of the difficulties when interpreting the data is that many parameters are dependent of one another. There is, for instance, a negative correlation between the pH and the wetland coverage ($r^2=0.43$, $p<0.01$). This does not seem very surprising, since much of the acidity in the streams is related to DOC, for which the wetlands are a major source. The pH is negatively correlated to the DOC ($r^2=0.83$, $p<0.001$), and the DOC is, in turn, positively correlated to the wetland coverage ($r^2=0.55$, $p>0.01$). The question then is whether it is the pH, the wetland coverage, the concentrations of DOC, a combination of these parameters or some entirely different parameters that causes the differences in the fluxes of uranium and thorium. The DOC can quite easily be excluded, since there is no reason to expect the fluxes of uranium and thorium to decrease when the fluxes of DOC increase. On the contrary, if uranium and thorium are bound to DOC,

one would rather expect the opposite relationship – had uranium and thorium been controlled by the availability of DOC. pH is a more likely candidate as a causal agent, since the pH potentially could affect the mobility of both uranium and thorium. This is clearly demonstrated by Kalin et al. (2005). What makes us reluctant to accept pH as the true cause for the varying fluxes of uranium and thorium is the fact that the pH does not seem to have any deeper impact on the speciation of uranium and thorium in these streams. When using thermodynamic modeling (Visual MINTEQ 3.0 (Gustafsson, 2012)) we find that the dominating species are organically bound uranium (>96%). Thermodynamic constants for Th-DOC are not available, but we would not expect the association to DOC to be lower than for uranium. As mentioned in the manuscript, significant association to DOC is also suggested by investigations of colloidal transport of uranium and REEs both in Krycklan (Köhler et al., 2009) and in nearby Kalixälven (Dahlqvist et al., 2007). As a consequence, the pH dependent solubility curves presented by Kalin et al. (2005) may not be relevant in this case, since they do not take DOC into account. Undoubtedly, high concentrations of DOC, which is typical for boreal headwaters, can increase the mobility of both uranium and thorium substantially. Based on the association of uranium and thorium to DOC we therefore dismiss the pH as a cause for the varying fluxes of uranium and thorium within the Krycklan catchment. Our interpretation is that the correlation between pH and the fluxes of uranium is caused by the fact that they both are related to the occurrence of wetlands. More wetlands give more DOC in the streams, which in turn gives lower pH. More wetlands also give less uranium and thorium in the streams both because the area of mineral soils decrease, causing less weathering, and because there is an accumulation of uranium and thorium in the peat. This interpretation is consistent with the well-known ability of uranium to accumulate in peat, although it was previously unknown that this accumulation was so important that it almost entirely controls the fluxes of both uranium and thorium in boreal headwaters, causing an unforeseen degree of spatial variability in these systems. Based on the comments of Dr. Noubactep we intend to develop this discussion further in the manuscript.

There are also some formal problems that Dr. Noubactep noticed in the manuscript, for instance concerning how to denote the oxidation states of uranium and thorium. It is certainly no problem to change the denotation of the oxidation states of uranium and thorium to roman numbers. A disadvantage with this denotation is that U(IV) may look confusingly similar to U(VI), but this is no doubt a minor problem. As for the references, we will make sure that the order of the references is consistent throughout the manuscript. The title of section 3.4 would also become more consistent, if Dr. Noubactep's suggestion is adopted in a revised manuscript.

Further, Dr. Noubactep also indicates that the discussion regarding the relative weathering rates of uranium and thorium should be developed further. (We note that this is contrary to the opinion of the other reviewer.) We agree with Dr. Noubactep that this is an interesting topic, although it may not be a key issue in this manuscript. The main reason why we do not think that it is a good idea to try to develop this further is that we believe that the chemical conditions in the mineral soils, where the weathering takes place, probably are quite different from the stream water. Podzol soils, which dominate the forested parts of the Krycklan catchment, usually have lower concentrations of DOC and higher pH than what we observe in the streams. This is because much of the DOC exported to the streams is produced in the riparian soils. (As a consequence, pH may also be more important for controlling the mobility of uranium and thorium here.) We would presume that the causes to the preferential leaching of uranium are to be found in the uphill podzol soils, but it seems too speculative to try to resolve this issue without proper soil water data. Therefore, we would prefer to stop at the simple statement that there is a preferential leaching of uranium for now and return to the question later when we have more data to support the discussion. In any case, we think that Dr. Noubactep's advice on how to handle this problem is wise. As we have an on-going project about uranium, thorium and other metals in the study catchment, we hope that we can shed more light on this issue in the future.

As regards the discussion on page 2838 concerning whether wetlands temporally can

be sources for uranium and thorium Dr. Noubactep suggests that the flow velocity may be a key issue. Short residence times of the mire water in connection with the spring flood, as demonstrated by 18O analyses by Laudon et al.(2004), could certainly contribute to the low concentrations of uranium and thorium. The relationship between residence time and flux is not simple – as Dr. Noubactep points out long residence times can lead to high concentrations, but slow flow velocities may also lead to low flux due to low discharge. We want to point out that wetlands are never the primary source of either uranium or thorium, but theoretically they could release uranium and thorium that previously has been weathered from uphill mineral soils and subsequently accumulated in the peat. This could potentially lead to higher fluxes of uranium and thorium from wetlands than from forests for a period of time, but, as Dr. Noubactep says, this can only be a temporary peak. However, our data show no indication that wetlands currently would be sources for uranium and thorium during any part of the year. Even when we observe the highest concentrations in the runoff from one of the wetlands, the concentrations are lower than what we observed in forest-dominated catchments. There may of course be individual wetlands temporarily acting as sources for uranium and thorium, but on the landscape-level our data clearly show that they are sinks.

The residence time of the water is also related to the hydrological pathways, which we believe is a central issue for understanding the dramatic decrease in the concentrations of uranium and thorium in wetland-dominated catchments. In the beginning of the snowmelt much of the wetlands are still covered by impenetrable ice so the much of the water cannot flow through the peat. Instead there is a significant portion of surface runoff from the wetlands (Laudon et al., 2005). Since the melt water naturally does not contain much uranium and thorium and does not pass any environments where it can pick up significant amounts of these elements, the concentrations of uranium and thorium in the stream will be low. Hence, we believe that it is proper to describe the lower concentrations as primarily an effect of dilution by melt water.

Concerning the discussion on page 2839 Dr. Noubactep draws attention to the importance of the concentration range, presumably that of uranium and thorium. This is certainly something that must be kept in mind, especially when comparing different sites. In the case of the Krycklan catchment the soil concentrations are not far from the global averages, but relatively low in comparison with many other scientific studies of uranium and thorium, which often tend to focus on sites with high concentrations. As the transport of uranium and thorium in Krycklan apparently is dominated by DOC, we suspect that the actual concentrations may be of minor importance for the mobility of these trace elements, although it of course affects the possibility to precipitate U(IV) minerals for instance.

To summarize, we note that there is little critique concerning the scientific value and the approach of this study. We note, however, that there is a need to provide the reader with more background data and to expand parts of the discussion further, for instance regarding the importance of pH and DOC. We will also consider the possibility to add some modeling results to provide a more sound foundation for discussing the speciation of uranium and thorium in these streams. Based on the comments of Dr. Noubactep we believe that it will be possible to produce an improved version of this manuscript.

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Interactive comment on Biogeosciences Discuss., 9, 2823, 2012.