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Landscape control of uranium and thorium in boreal streams – spatiotemporal variability and the role of wetlands

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Abstract

The concentrations of uranium and thorium in ten partly nested streams in the boreal forest region were monitored over a two-year period. Considerable spatiotemporal variations were observed, with little or no correlation between streams. The export of both uranium and thorium varied substantially between the subcatchments, ranging from 1.7 to 30 g km^{-2} a^{-1} for uranium and from 3.2 to 24 g km^{-2} a^{-1} for thorium. Airborne gamma spectrometry was used to measure the concentrations of uranium and thorium in surface soils throughout the catchment, but could not explain the variability in the export. Instead, the extent of lakes and mires within each subcatchment was found to be a stronger predictor for the transport of uranium and thorium. The results indicate that there is a predictable and systematic accumulation of both uranium and thorium in boreal mires. Approximately 65–80 % of uranium and 55–65 % of thorium entering a mire is estimated to be retained in the peat. Overall, accumulation in mires and other types of wetlands is estimated to decrease the fluxes of uranium and thorium from the boreal forest landscape by 30–40 %. The atmospheric deposition of uranium and thorium was also quantified and its contribution to boreal streams was found to be low compared to weathering.

1 Introduction

Uranium and thorium are the heaviest elements that occur naturally in appreciable levels on Earth. All isotopes of both uranium and thorium are radioactive, but since the half-lives of the most abundant isotopes, ^{238}U, ^{235}U and ^{232}Th, are long (4.46, 0.704 and 14.0 billion years respectively), they remain ubiquitous in the environment. The average concentration of uranium in continental crust has been estimated to 2.5 µg g^{-1} (Wedepohl, 1995), which means that uranium is as abundant as arsenic and tin. According to the same estimations, thorium is about four times more common with an estimated average concentration of 10.3 µg g^{-1}. Hence, thorium is nearly as abundant

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as copper, cobalt and lead. Uranium and thorium are also the only representatives of the actinide series to occur in significant quantities in the environment, making them interesting as natural analogues, for example for some of the transuranium elements.

Whereas thorium is only present as Th^{4+} in natural waters, uranium occurs in multiple redox states, U^{4+} and U^{6+} being the most common. Th^{4+} and U^{4+} are generally considered to have low solubility, while U^{6+} often is more mobile (Langmuir and Herman, 1980; Andersson et al., 1995). Areas of naturally high concentrations of uranium and thorium are found throughout the world, causing both radiological and toxicological problems. Although ^{238}U, ^{235}U and ^{232}Th themselves are only weakly radioactive, they produce chains of more short-lived radionuclides as they decay, e.g. ^{222}Rn and ^{226}Ra. All together, this implies that the U-Th decay series may cause considerable radiation doses. In addition, uranium and thorium are also chemically toxic. Uranium primarily affects the kidneys, and the World Health Organisation recommends that the concentration of uranium in drinking water should be below 15 $\mu g\,l^{-1}$, a limit that is frequently exceeded in uranium-rich areas (Frengstad et al., 2000; Prat et al., 2009). Although thorium is more abundant, it is considered less of a problem due to its lower solubility in natural waters (Langmuir and Herman, 1980). Nevertheless, thorium can be harmful and has been shown to damage the liver function of mice (Kumar et al., 2008). In addition to the natural occurrence of uranium and thorium, human activities such as uranium mining have left a legacy of contamination of soils and groundwater (Hu et al., 2010; Zoriy et al., 2010). The world's boreal forest regions have not escaped such disturbances; both Canada and Russia are major uranium producers, and increasing uranium prices in recent years have boosted the exploration for uranium throughout the world. Issues regarding the long-term behaviour of uranium and thorium in the landscape are also becoming increasingly important, as many countries, e.g. Finland and Sweden, are planning to build deep repositories of nuclear waste.

Whereas the spatial and temporal variation in concentrations of uranium has previously been studied in larger catchments (Saari et al., 2008; Porcelli et al., 1997), the focus of this study is a network of streams within a 67 km^2 catchment. This provides

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a spatial resolution that enables a detailed assessment of the role of various landscape types. Small streams are not only important as unique and vibrant ecological environments, but also for the biogeochemical cycles of uranium and thorium on larger scales because much of the water in big rivers originates from the fine network of small streams that drains the boreal landscape (Bishop et al., 2008). These smaller streams also represent environments that are more likely to be directly affected by mining or deep repositories of nuclear waste, since they are so much more common than big rivers. With continuous hydrological measurements and frequent hydrochemical sampling, it was possible to follow the temporal responses of different landscape types and estimate the export of uranium and thorium from each subcatchment. These fluxes were compared to the atmospheric deposition of uranium and thorium in the area, landscape characteristics, and the inventories of uranium and thorium in local soils in order to obtain an improved understanding of the transport and accumulation patterns of uranium and thorium in the boreal landscape.

2 Material and methods

2.1 Site description

Krycklan is a tributary to one of Sweden's major rivers, Vindelälven. Part of its catchment, the 0.5 km^2 Svartberget catchment, has been studied and monitored continuously since 1980, but environmental research in the area dates back to the early 20th century. In 2002, the Krycklan Catchment Study (KCS) was initiated with intensified sampling of the hydrochemistry in 18 partly nested streams within an area that was expanded to cover 67 km^2 of the upper parts of the Krycklan catchment. The Krycklan catchment, which also includes the Vindeln Experimental Forests and is a central part of the Svartberget Long-term Ecological Research site (LTER), has a well developed research infrastructure. Extensive research in various fields has lead to a good, process based understanding of the catchment and the hydrological connection between streams and soils (Seibert et al., 2009).

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The Krycklan catchment is located in northern Sweden (64°14′ N, 19°46′ E). The mean annual temperature is +1.7 °C, and the mean annual precipitation is 625 mm, of which on average 35 % falls as snow. The total annual discharge is about 325 mm, of which approximately one third leaves the catchment during a few weeks in the spring (Cory et al., 2009). The landscape is dominated by coniferous forests with Scots pine (*Pinus sylvestris*) and Norwegian spruce (*Picea abies*). These forests cover 83 % of the total catchment area, and the rest is made up of wetlands (12 %), clear cuttings (2.1 %), arable land (0.2 %) and lakes (0.1 %). These other landscapes types may, however, be major constituents of some of the subcatchments (see Table 1). Whereas the upper parts of the catchment are dominated by till and peat, large areas of glaciofluvial silt and fine sand deposits are present in its lower parts (Fig. 1). The forests are dominated by well-developed podzols, but more organic soils are common in wetter areas. The quaternary deposits are underlain by gneissic bedrock of svecofennian metasediments, mainly metagraywacke. The investigated subcatchments are denoted C1, C2, C4, C5, C6, C7, C9, C14, C15 and C16, and are shown in Fig. 2. The stream water is generally characterised by high concentrations of dissolved organic carbon (DOC) and low pH, but the heterogeneous landscape allows for considerable hydrochemical variability both within and between streams. The average pH ranges from 4.3 (C4) to 6.4 (C16) and average concentrations of DOC vary from 11 mg l^{-1} (C16) to 31 mg l^{-1} (C4). If the temporal variation also is taken into consideration the variability is of course even greater. Average concentrations for major ions and other hydrochemical parameters in the investigated streams have been published by Björkvald et al. (2008).

2.2 Sampling and analyses

Concentrations of uranium and thorium were monitored in ten partly nested streams within the Krycklan catchment in 2004–2005. In total, 356 samples were analysed for ^{238}U and ^{232}Th at Stockholm University using ICP-MS. Details on the sampling and analyses of the stream water samples can be found elsewhere (Lidman et al., 2011; Björkvald et al., 2008). Concentrations of uranium and thorium in precipitation

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were analysed in bulked volume weighted monthly samples collected at the Svartberget LTER in the in centre of the Krycklan catchment during 2004 (Klaminder et al., 2006). The samples were analysed using ICP-MS at the Swedish Defence Research Agency.

Discharge was measured using a 90° V-notch weir located in C7 in a heated hut to avoid ice formation in wintertime. The water level was recorded every ten minutes and averaged to produce hourly measurements using a pressure transducer connected to a data logger (Campbell, USA). The discharge for the other subcatchments was estimated by assuming that the specific runoff was the same throughout the entire Krycklan catchment (Laudon et al., 2007). It has been shown that the overall mean differences between streams are less than 12 % and that the streams are highly synchronised during the spring flood (Buffam et al., 2008). To estimate the export of uranium and thorium, daily concentrations were interpolated over the cumulative discharge, multiplied by the daily discharge and summed.

The concentrations of uranium and thorium in soils were measured by the Swedish Geological Survey (SGU) using airborne gamma spectrometry (Thunblom et al., 2005; Antal Lundin and Bastani, 2007). Flight lines had a separation of 200 m and the sampling interval was 40 m, resulting in at least 14 observations in each subcatchment and a total of 3851 observations throughout the entire Krycklan catchment. Each observation represents an integrated value over an area described by an ellipse with transverse diameter approximately 200 m, perpendicular to the flight path. Thus, these measurements provide more information about the average concentrations of uranium and thorium than feasibly could be obtained from point measurements (Viscarra Rossel et al., 2010). Kriging was used to interpolate the concentrations of uranium and thorium and to estimate the average concentration within each subcatchment. The values presented for uranium are based on gamma emissions of ^{214}Bi, a daughter of ^{222}Rn. Due to transport of radionuclides throughout the uranium decay chain, e.g. ^{226}Ra and ^{222}Rn, ^{214}Bi may not always be in equilibrium with ^{238}U. Although the measurements should give a reasonably good idea of the concentrations of uranium in surface soils, the results should be interpreted with some care. The chemistry and the half-lives of

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the daughters of ^{232}Th do not suggest similar disequilibria throughout the thorium decay chain, wherefore the concentrations of thorium in surface soils are less uncertain.

3 Results and discussion

3.1 Uranium and thorium in stream water

Figure 3 shows the concentrations of uranium and thorium together with the discharge for the investigated streams. Compared to the average concentration of uranium reported for Europe (0.32 µg l^{-1}), the concentrations in Krycklan are low (Astrom et al., 2009). It is also clear that there are considerable differences between the streams. Particularly low concentrations are found in C4, a mire outlet, and C5, a lake outlet. Higher concentrations are found in predominantly forested catchments. It is noteworthy that small forest streams such as C1 (0.60 km^2) and C2 (0.13 km^2) during baseflow conditions have similar concentrations of dissolved uranium and thorium as larger catchments like C14 (13 km^2) and C16 (67 km^2). Hence, the catchment area does not appear to have any clear effect on the concentrations in the streams. As could be expected, mixed catchments like C7, which receives water from both C2 (forest) and C4 (mire outlet), have intermediate concentrations of uranium and thorium.

Figure 3 also shows that the concentrations of uranium and thorium tend to co-vary – both within streams and between streams. Based on all samples from all streams, the correlation coefficient between the concentrations of uranium and thorium is $r = 0.84$ ($n = 356$, $p < 0.0001$). This suggests that uranium and thorium have a common source and that their release into the streams is largely controlled by the same processes. Moreover, Fig. 3 shows that there are considerable differences in the temporal variation between the streams, for instance in their responses to the spring flood. At the mire outlet, C4, there is a sharp decline in the concentrations of both uranium and thorium when the spring flood sets in. The concentrations also decrease in many of the smaller streams. In C16 a clear increase of the concentrations can be observed

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during the spring flood, although no substantial increase can be observed in any of its subcatchments. This implies that the lower parts of C16 must not only support the doubling of the concentrations but also counteract the dilution effects from the headwaters. It is therefore likely that the silt areas in C14 and C16 are responsible for the increasing concentrations of uranium and thorium during the spring flood.

There are significant correlations at the 95 % confidence level in the concentrations of both thorium and uranium between some of the streams, although the correlations are weak in most cases. Generally, uranium is more variable between the streams than thorium, which could be due to the more complex chemistry of uranium. For uranium, there is only one case where the concentrations of uranium in one stream can explain more than 50 % of the variance in another stream. In contrast to what could be expected, this does not occur in any of the streams that are directly connected, but in C1 and C7 ($r^2 = 0.69$). For thorium there are five cases where the coefficient of determination exceeds 0.5. All of them involve only the smaller subcatchments (<1.3 km^2). Overall, the modest or non-significant correlations between the streams, suggests that it is not generally possible to extrapolate knowledge of the temporal variation in the concentrations of uranium and thorium in one stream to another nearby stream. The large variability agrees with previous studies, which have identified uranium as one of the elements whose concentration varies the most in wetland-influenced streams (Kerr et al., 2008).

Hydrological processes have been demonstrated to drive much of the variability in water chemistry of these streams (Seibert et al., 2009; Kohler et al., 2009a, 2009b) and, hence, are likely to also affect the concentrations of uranium and thorium. At the mire outlet, C4, the decreasing concentrations of uranium and thorium during the spring flood are due to dilution by melt water. Using ^{18}O it has been demonstrated that a large proportion of the water in C4 is event water, i.e. recently melted snow (Laudon et al., 2004). Since the concentrations of uranium and thorium in precipitation are low (see below), stream water concentrations will consequently decrease. In forest-dominated catchments like C2 the hydrology functions differently, and hardly

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any event water reaches the stream during the snowmelt period (Laudon et al., 2004). Consequently, there will be no comparable dilution effect. Instead old pre-event water is pushed out into the stream by a so-called transmissivity feedback mechanism. This is generally the case for forest streams, where surface runoff is rare. Therefore, variations in the stream water concentrations of uranium and thorium in small uniform catchments like C2 must be caused by the vertical distribution uranium and thorium in the pore water of the riparian soils (Seibert et al., 2009). On larger scales, in mixed catchments, variations will be influenced by the different characteristics of the landscape, e.g. uranium and thorium exported from mires and forests mixing in different proportions.

3.2 Atmospheric deposition of uranium and thorium

During 2004, thorium concentrations in precipitation varied from below the detection limit (<0.06 ng l^{-1}) to 1.74 ng l^{-1} in monthly bulked samples. Three of the samples had thorium concentrations below the detection limit. Uranium concentrations ranged from 0.03 to 1.23 ng l^{-1}. No clear seasonal trends could be observed for either uranium or thorium. The deposition was estimated to be 0.22 g km^{-2} a^{-1} for thorium and 0.17 g km^{-2} a^{-1} for uranium. During 2004, a total of 607 mm of precipitation was measured at the meteorological station within the Krycklan catchment. This is close to the annual average precipitation for 1988–2008 (598 mm). Therefore, we conjecture that these estimates of the deposition are not biased due to anomalous precipitation.

3.3 Fluxes of dissolved uranium and thorium

The differences in stream water concentrations of uranium and thorium in the investigated catchments will inevitably also be reflected in different fluxes. Our estimates indicate that the export of dissolved thorium varies between 3.2 and 24 g Th km^{-2} a^{-1}.

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The highest export was observed from one of the silt-dominated subcatchments, C14, whereas the lowest export was observed at the lake outlet, C5, and the mire outlet, C4. Hence, C14 exported more than seven times more thorium than C5. However, the variation was even more pronounced for uranium. Here, C14 exported 30 g U km^{-2} a^{-1}, whereas C5 exported only 1.7 g U km^{-2} a^{-1}. This implies that the flux varies by almost a factor 18 only within the Krycklan catchment.

It is evident that export of both uranium and thorium greatly exceeds atmospheric input; even in the subcatchments with the lowest export, atmospheric deposition does not contribute with more than 10 % of the total export at the most. Since much of the deposited uranium and thorium is expected to accumulate in top soils, weathering of mineral soils and, possibly, bedrock must be the dominating source of uranium and thorium in the streams.

Comparing the export of uranium and thorium with their respective abundance in the local soils, it is clear that there is a preferential export of uranium. In Kalixälven, the U/Th ratios in river water were about 40 times higher than the ratio in detrital matter (Andersson et al., 1998). The differences are not as pronounced in Krycklan: while the export of uranium and thorium are approximately the same, thorium is approximately four times more common than uranium in surface soils. Based only on stream water analyses it is not possible determine the reason for the lower export of thorium, but there are several possibilities, e.g. lower weathering rates of thorium bearing minerals, precipitation of secondary thorium minerals or preferential sorption of thorium to some phase in the soils.

Attempts to estimate the export of uranium from the world's major rivers have revealed large geographical differences. Among the ten rivers in the world with the highest discharge, the export of uranium ranges from 3.0 g U km^{-2} a^{-1} in the Paraná River to 950 g U km^{-2} a^{-1} in the Brahmaputra River. The export of uranium from the Krycklan Catchment is comparable to, for example, the Amazon River (29 g U km^{-2} a^{-1}), the Zaire River (18 g U km^{-2} a^{-1}) and the Orinoco River (30 g U km^{-2} a^{-1}), although European rivers generally tend to export more than 100 g U km^{-2} a^{-1} (Dunk et al., 2002).

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The nearby Kalixälven has been estimated to export 80 g U km^{-2} a^{-1}, but its catchment includes alpine regions and other types of bedrock (Andersson et al., 1998).

3.4 Concentrations in surface soils

The concentrations of uranium and thorium in surface soils throughout the Krycklan catchment are shown in Figs. 1 and 2. The average concentrations of uranium and thorium in the entire Krycklan catchment were 1.7 µg g^{-1} and 6.6 µg g^{-1} respectively. In the subcatchments, the average concentrations of uranium in the soil varied between 1.0 µg g^{-1} (C5) and 2.2 µg g^{-1}(C2). The corresponding range for thorium was 4.4 µg g^{-1} (C4 and C5) to 8.2 µg g^{-1} (C6).

Given the considerable differences in the fluxes of uranium and thorium from the investigated subcatchments, it is pertinent to ask whether any of this variation could be explained by varying concentrations of uranium and thorium in the soils. Since weathering is the major source of uranium and thorium, a straightforward hypothesis would be that the fluxes are dependent on the release of uranium and thorium from local soils. Generally one would expect the release of uranium and thorium to increase with increasing concentrations in the soils, although there may also be other factors such as varying mineral composition and particle size that affect the weathering rates. However, comparing the concentration of uranium in the local soils in the independent subcatchments (C1, C2, C4, C5, C14 and C15) to the export of uranium for each subcatchment reveals that no significant correlation is present at the 95 % confidence level ($n = 6$). If the remaining subcatchments (C6, C7, C9 and C16) are included, there was a significant correlation ($r = 0.67$, $n = 10$, $p = 0.034$), but in that case it must be acknowledged that the observations are not entirely independent. Hence, the correlation, if significant, is not particularly strong with 55 % of the variation remaining unexplained. For thorium there is a significant positive correlation between the concentrations of thorium in the soil and the export of thorium at the 95 % confidence level ($r = 0.87$, $n = 6$, $p = 0.0235$). If the dataset is expanded to include the four dependent

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subcatchments, the correlation is weakened to $r = 0.80$ ($n = 10$, $p = 0.005$). Hence, although a bias is introduced into the data set, which should strengthen the correlation, it actually becomes weaker, whilst also becoming more significant.

A similar approach has been used to study the concentrations of uranium in streams and groundwater throughout Finland and northwest Russia (Astrom et al., 2009). In Precambrian areas in Finland and Russia there was a significant, albeit rather weak, correlation between the concentration of uranium in surface soils and the concentration in stream water ($r_s = 0.45$, $n = 660$). However, in Phanerozoic areas in Russia, no significant correlation was found ($n = 674$). A difference between that study (Astrom et al., 2009) and the present one is that correlation analyses were based on observations of stream water concentrations of uranium at one time point rather than on the total export of uranium. Given the substantial temporal variation that was observed within the Krycklan catchment, the sampled water on one occasion may not be representative of the overall stream chemistry. Furthermore, soil concentrations were obtained from discrete soil samples within the investigated area, which probably does not give as representative results as airborne gamma spectrometry. It is possible that these two factors may have reduced the apparent strength of the relationship between the concentrations in stream water and soils on a regional scale (Astrom et al., 2009). Nevertheless, the weak or non-existent correlations between soil concentrations and stream water concentrations/fluxes on both regional and local scales indicate that there must also be other factors governing the fluxes of uranium.

3.5 What controls the fluxes of uranium and thorium?

It is noteworthy that the lowest export of both uranium and thorium was observed in mire dominated catchments (C4 and C5), while high export was observed from forest-dominated catchments, particularly in the silt areas (C14 and C16). This may suggest that the landscape, i.e. the composition of the catchment, plays a crucial role for how uranium and thorium are transported. Some important landscape characteristics are presented in Table 1. Using multiple linear regression without interaction terms,

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including the wetland and lake coverage as one independent variable and the silt coverage as the other, it is possible to explain 97.6 % of the variance in the export of uranium ($n = 10$, $p = 0.000002$) and 92.8 % of the variance in the export of thorium ($n = 10$, $p = 0.0001$). The export of uranium, U (g km^{-2} a^{-1}), can be estimated as

$$U = 16 - 0.29W + 0.52S \quad (1)$$

where S denotes the silt coverage (%) and W the combined wetland and lake coverage (%). The corresponding model for the export of thorium, Th (g km^{-2} a^{-1}), is

$$Th = 16 - 0.28W + 0.26S \quad (2)$$

It is interesting that the two equations are almost identical, with the exception that the export of uranium is more influenced by the silt. Lakes were added to the wetlands in this case, since they are expected to behave more like wetlands than forest soils in the sense that they limit the contact with mineral soils, which could provide the streams with uranium and thorium. However, the area of lakes in the Krycklan catchment is too small to draw any statistically certain conclusions concerning the role of lakes (Table 1).

The regressions demonstrate that the export of uranium and thorium is strongly dependent on landscape characteristics. Omitting the silt, there are still significant correlations between the wetland and lake coverage and the export of both uranium and thorium at the 95 % confidence level. For the independent dataset the correlation is $r = -0.80$ ($n = 6$, $p = 0.048$) for uranium and $r = -0.88$ ($n = 6$, $p = 0.026$) for thorium. Using all ten subcatchments, the correlation increases to r=-0.84 (n=10, p=0.0059) for uranium and $r = -0.90$ ($n = 10$, $p = 0.00085$) for thorium. Similar relationships between the mire coverage and the stream water concentrations of metals have previously been reported for aluminium during the spring flood (Cory et al., 2006). There is obviously a risk of confounding errors here, since the concentrations in soils are not independent of the landscape type. The average concentration of thorium in forest soils throughout Krycklan is 6.5 µg g^{-1} ($n = 30803$), compared to 3.2 µg g^{-1} ($n = 3987$) in wetlands. The corresponding values for uranium are 1.8 µg g^{-1} in forest soils and 0.68 µg g^{-1} in wetlands. Yet it seems clear that the wetlands, rather than the soil concentrations, must

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be the true causal agents. While the export of uranium varies by a factor 18 within the Krycklan catchment, the average soil concentrations only vary by a factor 2. Although there are uncertainties for uranium when using airborne gamma spectrometry, it is unthinkable that fractionation throughout the uranium decay chain would reduce a natural variation of a factor 18 between the investigated subcatchments that much. It is, however, possible that the differences between forests and mires are slightly underestimated, since airborne gamma spectrometry integrates the gamma radiation from large areas and does not recognise the origin of the detected gamma particles. However, it would not be possible to reproduce the variability observed in export even if the concentrations of uranium and thorium in lakes and wetlands were assumed to be zero. Figure 4 shows that if, for example, 50 % of the catchment area is covered by wetlands, the export of uranium would decrease by 90 %, rather than by 50 %, which would be the expected result if 50 % of the source is removed. This suggests that there must be some additional process, apart from lower release from mineral soils, that decreases the export of uranium and thorium from mire-dominated catchments, presumably accumulation in the mires. Furthermore, Fig. 4 suggests, as confirmed by the multiple regression, that the silt-dominated areas export more uranium and thorium, although they do not distinguish themselves by having higher soil concentrations of uranium and thorium.

3.6 Predicting the retention of uranium and thorium in wetlands

Equations (1) and (2) demonstrate that much of the spatial variability in the Krycklan catchment can be explained by the occurrence of silt and wetlands. In order to highlight the effect of mires for the transport of uranium and thorium focus will be shifted to the till-dominated areas (<6 % silt), since few mires are found in the silt-rich areas (C14 and C16, >25 % silt). This will also remove the heteroskedasticity that prevents the use of a simple linear regression, as suggested by Fig. 4. For the till-dominated subcatchments simple linear regression between the fluxes of uranium and thorium respectively and the lake and wetland coverage indicates that the relative export of

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uranium, compared to a completely forested catchment, U_{rel}(%), can be predicted as ($R^2 = 0.94$, $p = 0.00007$)

$$U_{rel} = 100 - 1.84W \quad (3)$$

As previously, W denotes the wetland and lake coverage (%). The corresponding model for the relative export of thorium, Th_{rel}(%), is ($R^2 = 0.88$, $p = 0.0005$)

$$Th_{rel} = 100 - 1.75W \quad (4)$$

In both cases the extrapolated export from a completely forested catchment has been used to normalise the equations. Equations (3) and (4) indicate that for each percent of wetlands that is replacing mineral soils in a catchment, the export of uranium and thorium decreases by approximately 1.8 %, slightly more for uranium and slightly less for thorium. This 1.8 % could be interpreted as 1 % decrease due to the decreased amount of mineral soils that can provide the streams with uranium and thorium plus an additional 0.8 % decrease due to the accumulation of uranium and thorium in the peat. In reality, it is hardly the mire coverage per se that causes the decreased export of uranium and thorium, but rather the fraction of stream water flowing through significant amounts of peat in order to reach the stream channel. For instance, if a catchment has a mire coverage of 50 %, with all mineral soils located upstream from the mire, it would probably export less uranium than a catchment with the same mire coverage but only half of the mineral soils located upstream from the mire and the rest downstream.

In C4 the sampling site is located close to the outlet of a mire, and in C5 the sampling site is close to the outlet of a lake, which is almost entirely surrounded by peat. Thus, it can be estimated that almost all water in these two streams must have passed through considerable volumes of peat (or possibly to some extent organic sediments) in order to reach the stream. If we assume that the export of uranium and thorium from the mineral soils further upstream in these two catchments is comparable to other till soils in the Krycklan catchment, Eqs. (1) and (2) can be used to estimate the input of uranium and thorium into the mires in C4 and C5. By comparing the estimated input to the

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measured output, we can conclude that at least 65–80 % of the uranium and 55–65 % of the thorium that enters a wetland could be expected to accumulate within it.

3.7 The role of wetlands in the boreal landscape

It is well-known that uranium can accumulate in peat (Schöner et al., 2009; Owen and Otton, 1995; Zaccone et al., 2007; Krachler and Shotyk, 2004; Shotyk, 1988). Natural or constructed wetlands are also commonly used to remove trace elements like uranium from contaminated water, e.g. in the mining industry (Sheoran and Sheoran, 2006; Kröpfelová et al., 2009). The behaviour of thorium in wetlands has been less widely studied, but it has been reported that also thorium can accumulate in peat (Krachler and Shotyk, 2004). This is in agreement with the results of the present study. However, these results demonstrate further that the accumulation of uranium and thorium in mires is systematic and predictable on the landscape-scale and that the distribution of wetlands throughout the landscape greatly contributes to the natural variability of the concentrations of uranium and thorium in boreal streams.

It has been discussed whether mires could also constitute a major source of uranium in the boreal landscape, especially in connection with the spring flood (Andersson et al., 1995; Porcelli et al., 1997). It is thought that a rapid equilibration between melt water and uranium-rich peat could provide much of the uranium during the spring flood. This hypothesis has been questioned previously, since it is unable to explain the $^{234}U/^{238}U$ ratio of river water (Porcelli et al., 1997). It is also not supported by the results of the present study. On the contrary, the measurements show that the concentration of uranium from the monitored mire outlet at C4 decreases drastically when the spring flood sets in, the main reason being dilution by melt water. Instead the highest concentrations of uranium at the mire outlet occur during baseflow conditions. Yet the concentrations of uranium increase further down in the catchment (C16), where few mires are present, in connection with the spring flood. It seems clear that the mires within the Krycklan catchment are not sources of uranium during any part of the year,

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but sinks. The same applies to thorium, although the retention in mires is possibly less pronounced.

It has been demonstrated that a large portion of the uranium (30–90 %) in nearby Kalixälven is transported by organic colloids (Porcelli et al., 1997). It has also been shown that rare earth elements in the Krycklan catchment are associated with DOC to a high degree (Kohler et al., 2009b). (Similar data for U and Th are in preparation.) Therefore, it is likely that DOC also plays a key role for the transport of uranium and thorium in these streams, especially since the concentrations of DOC are higher than in Kalixälven. Olivie-Lanquet et al. (2001) propose that the concentration of DOC could be a key factor for deciding whether a wetland will act as a sink or a source for trace elements. Provided that the wetland is not being ditched or disturbed in some way, we see little reason to expect boreal mires to act as sources for uranium and thorium. However, competition between dissolved and solid organic matter is probably important for regulating how much uranium and thorium that is transported through the wetlands and how much that is accumulated within them. Reduction of U^{6+} to U^{4+} and subsequent precipitation would also be a potential accumulation mechanism, but for example in C4 the redox conditions in the parts of the mire where most of the water is flowing may not be reducing enough (Sirin et al., 1998). Furthermore, with concentrations of DOC in the range 10–50 mg l^{-1} in the mire water the association to organic matter of any U^{4+} present would also be expected to be high, obstructing the precipitation of uranium minerals. For instance, investigations of natural wetlands in Germany have shown that most of the uranium is associated with organic matter and no signs of precipitation or association with mineral surfaces were found (Schöner et al., 2009). The fact that thorium is accumulated in the mires to almost the same degree as uranium also suggests that binding to organic matter may be the most important accumulation mechanism, although this ultimately will depend on the local hydrochemical conditions within mires and other wetlands. Also, in calcite-rich areas the mobility of uranium may increase considerably due to the formation of uranyl-carbonate complexes, thereby decreasing the impact of wetlands.

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To conclude, the present study has demonstrated that there is considerable variability in the spatiotemporal dynamics of uranium and thorium in boreal streams. However, there are still clear trends in the annual export of both uranium and thorium, depending mainly on soil type, particularly the forest-mire gradient, rather than on the concentrations of uranium and thorium in the soils. Thus, our results emphasise the role of the landscape for controlling the transport of uranium and thorium in boreal catchments and suggest that there is a predictable, gradual accumulation of uranium and thorium in boreal mires. Given the appreciable differences in the concentrations of uranium and thorium in the bedrock and quaternary deposits throughout the boreal region, especially when considering areas of uranium or thorium mineralisation, it is doubtful whether the forest-mire gradient would be as decisive for the fluxes of uranium and thorium on regional scales as it is in the Krycklan catchment. Yet, this does not imply that the results are irrelevant beyond the specific catchment, in which these measurements were made. Since the concentrations of both uranium and thorium are comparatively homogeneous throughout the investigated area, it offers a good opportunity to elucidate the role of wetlands for the transport of these elements in the landscape, and our results unambiguously demonstrate the wetlands are sinks for uranium and thorium. The consequences of this accumulation are far-reaching, since mires and other types of wetlands are so common throughout the boreal region. Peatlands across the North American and Eurasian boreal forest zone are estimated to contain one third of the world's organic carbon in soils (Gorham, 1991), which implies that the potential for accumulation of uranium and thorium is substantial. As an example, more than 20 % of Sweden is estimated to be covered by wetlands, a large portion of which are mires (Nilsson et al., 2001). Assuming that this estimate (20 %) is valid throughout the boreal zone, Eqs. (3) and (4) suggest that wetlands may reduce the fluxes of uranium and thorium from the boreal landscape to major lakes and rivers and oceans by as much as 30–40 %. Particularly in isolated basins with a large inflow of fresh water the retention in boreal wetlands is likely to also affect the marine hydrochemistry of uranium and thorium. If the primary immobilisation mechanism behind the accumulation of uranium

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and thorium indeed is binding to organic matter, similar patterns are also likely to occur for many other trace elements with a high affinity for organic matter.

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Table 1. Area and landscape characteristics of the investigated catchments.

Catchment number	Area (km^2)	Lake (%)	Forest (%)	Arable land (%)	Wetland (%)	Clear cutting (%)	Till (%)	Silt (%)
1	0.6	0.0	87.2	0.0	2.7	10.1	92.8	0.0
2	0.1	0.0	98.7	0.0	1.3	0.0	90.6	0.0
4	0.2	0.0	49.6	0.0	50.4	0.0	17.1	0.0
5	0.8	5.8	57.5	0.0	42.5	0.0	49.5	0.0
6	1.3	3.7	70.7	0.0	29.3	0.0	58.4	0.0
7	0.5	0.0	82.7	0.0	17.3	0.0	68.0	0.0
9	3.1	1.5	83.8	0.0	16.1	0.1	68.9	5.9
14	12.6	0.1	86.4	3.0	5.7	4.2	50.2	30.8
15	19.7	2.0	77.6	0.2	13.7	5.0	65.7	2.0
16	66.8	0.7	84.0	1.9	8.6	3.7	51.9	25.7

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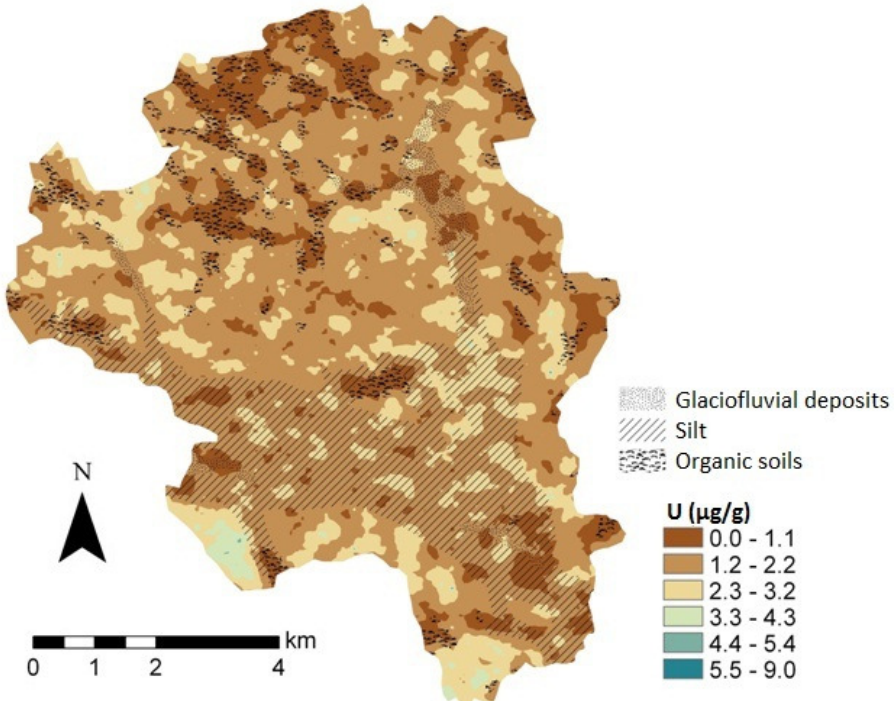

Fig. 1. Concentration of uranium in surface soils and soil type in the Krycklan catchment (SGU, consent Dnr: 30-495/2008).

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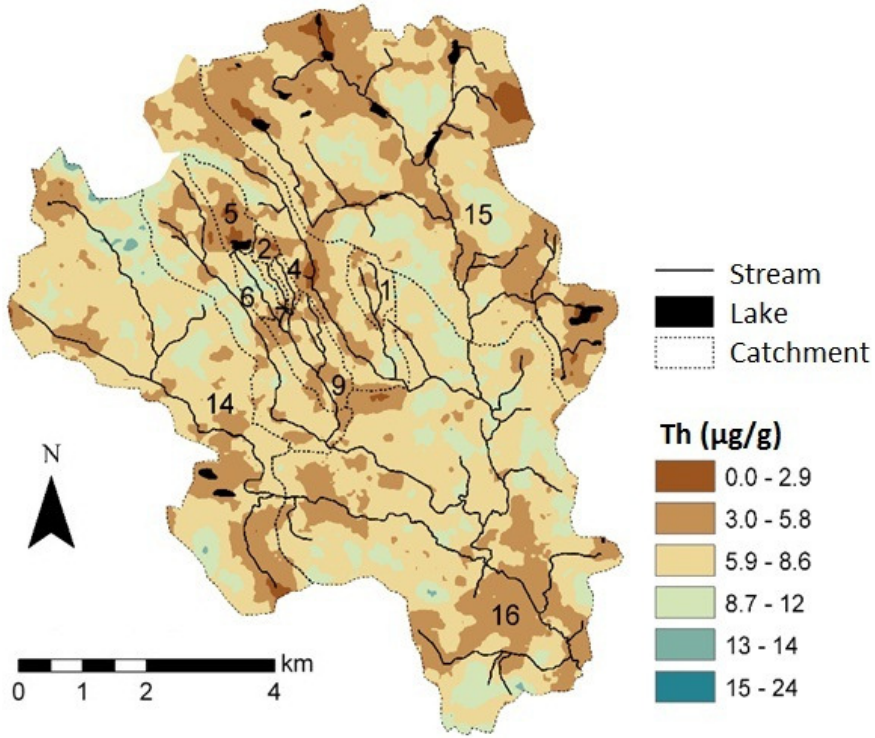

Fig. 2. Concentration of thorium in surface soils in the Krycklan catchment. The investigated subcatchments are indicated by numbers. (SGU, consent Dnr: 30-495/2008).

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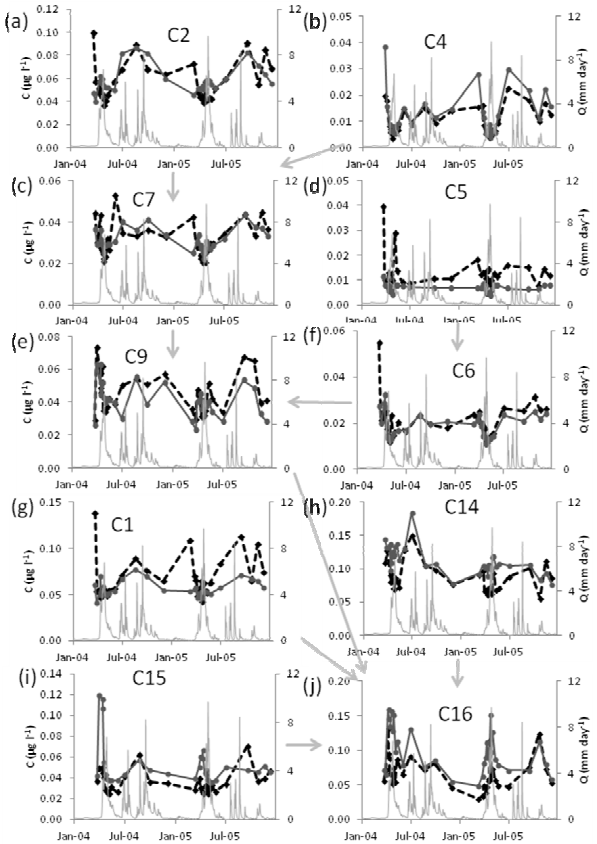

Fig. 3. The concentrations of uranium (diamonds, dashed lines) and thorium (circles, solid lines) in C2 **(a)**, C4 **(b)**, C7 **(c)**, C5 **(d)**, C9 **(e)**, C6 **(f)**, C1 **(g)**, C14 **(h)**, C15 **(i)** and C16 **(j)**. The discharge is shown in light grey. The arrows show how the streams are interconnected and indicate the direction of flow. Note that the scale of the primary vertical axis (concentration) differs between the streams.

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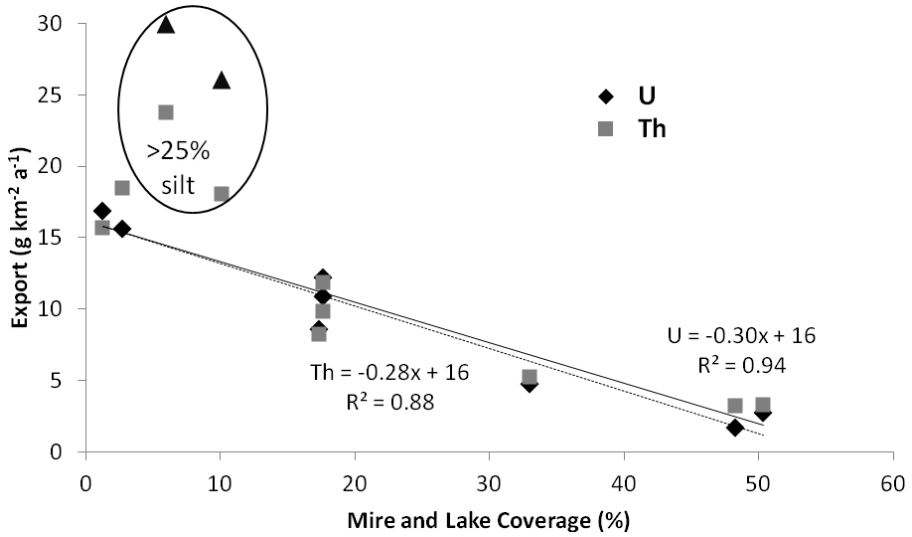

Fig. 4. Export of uranium and thorium as a function of the wetland and lake coverage. The regression lines are based only on the catchments with less than 6 % silt. The excluded catchments (C14 and C16) contain more than 25 % silt.

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