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# **Speciation of key NORM nuclides in natural waters**

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## **Preface**

This master's thesis is written by Johan Tryti at the Faculty of Environmental Sciences and Natural Resource Management at NMBU.

First, I want to thank my supervisors Deborah H Oughton, Lindis Skipperud and Karl Andreas Jensen. Thank you to Deborah and Lindis for your help with planning my experiment and for your support during my writing phase. Thank you to Karl Andreas for all your help during the practical parts of my MSc, and your great humour that you share with everyone around you.

Thank you to Marti Nandrup Pettersen for helping me during my practical work and answering any questions. I also want to thank Tonje Katrin Strømø for helping me during the rock crushing part of my experiment.

In the end, I want to give a thank you to everyone else that have supported me during my master. Thank you to everyone at the isotope laboratory for a friendly atmosphere. Finally, thank you to my friends and family for your support and encouragement.

## Summary

Naturally occurring radioactive materials are present everywhere in nature. These may cause harm to organisms. Therefore, it is important to know of their behaviour in the environment. The total concentration of an element does not give enough information about the risk, as it says nothing about the elements distribution in a system. This work focuses on several uranium, and how changes in pH and humic acid content affects its distribution. In addition, a few other elements are mentioned, due to the convenience of analysing multiple elements on the ICP-MS.

Alum shale from two different locations were mixed with water for metals to leach into the water. The pH of the two different locations was different after leaching (4 and 8). This difference in pH made it possible to compare the effect of humic acid with low and high pH. After leaching water samples were taken out, and the pH and humic acid content was changed. To compare different sizes, 3 kDa and 45  $\mu\text{m}$  filters were used.

The low P-values obtained for the tests ( $>0.10$ ) meant differences between pHs could not be proven. This was likely due to a low number of observations. To get better results, it would have been beneficial with more observations within each group. The general results from the groups were still used to draw some conclusions. The results showed a decrease in U concentrations with increasing humic acid concentrations. When comparing the two locations, the decrease was much steeper for K34 than RV4G, likely due to the difference in pH. This was expected, and likely a result from the higher charge on the humic acid causing it to have decreased affinity to uranyl ions ( $\text{UO}_2^{2+}$ ).

## Samandrag

Naturleg førekommande radioaktive materiale (NORM) er overalt i naturen. Desse kan påføre skade til organismar. Difor er det viktig å ha kunnskap om oppførselen deira i miljøet. Å vite om eit element sin totale konsentrasjon gir ikkje nok kunnskap om risikoen, då det ikkje seier noko om korleis det førekjem i eit system. Dette arbeidet fokusere på uran, og korleis forandring i pH og huminsyreinnhald kan påverke urans fordeling. I tillegg er eit par andre element nemnd, då dette er lett å praktisk gjere ved bruk av ICP-MS.

Alunskifer frå to ulike lokasjonar var blanda med vatn for at metall kunne lekke ut. Det va forskjell i pH mellom dei to lokasjonene etter utlekk (4 vs 8). Denne forskjellen i pH gjorde det lett å samanlikne effekten av huminsyre ved låg og høg pH. Etter utlekk var vassprøver teke ut, og pH og huminsyreinnhald var endra. For å sjå på fordelinga av ulike element var 3 kDa og 45 µm filter nytta.

Låge P-verdiar fått frå forsøket ( $>0.10$ ) gjorde at ulikheitar mellom ulike grupper ikkje kunne bevisast. Dette er truleg grunna få observasjonar i kva gruppe. Resultata kunne likevel nyttast for å dra sjå nokre samanhengar. Resultata viste ei minking i U konsentrasjon ved auka huminsyreinnhald. Ved samanlikning av dei to gruppene var minkinga mykje brattare for K34 enn RV4G. Dette skjedde truleg grunna ein forskjell i pH, då den lågare pHen i RV4G førte til høgare ladning, og mindre affinitet til uranyl-ionen ( $UO_2^{2+}$ ).

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# 1 Introduction

Naturally occurring radioactive material (NORMs) are present everywhere in nature. When decaying, radionuclides release alpha, beta radiation, and/or gamma radiation. This ionising radiation has the potential to cause harm in organisms. Therefore, knowledge of radionuclides is important as it may be applied to reduce risk. In drinking water, radionuclides might be present, and of concern as they may increase total dose received. In drinking water, the radionuclides contributing to the total exposure are largely from the uranium and thorium decay chains. The focus on this paper is on uranium in drinking water. Uranium in drinking water is mainly a concern due to its chemical toxicity (WHO, 2017b). In addition to uranium, a few other elements are also included in the paper, due to the convenience of analysing several elements at once using the ICP-MS.

Uranium is of particular focus due to its natural abundance and toxicity. In Norway, uranium can be a problem in groundwaters. The concentration of uranium is assumed to be low in surface waters (FHI, 2021), but the levels can be of concern in groundwater. In a test done by NGU of 476 ground water wells in Norway, 18% of the wells exceeded a uranium concentration of 20 µg/L, with maximum concentrations reaching 0.2 mg/L (Midtgård et al., 2007). There is currently no limit set in Norway for amount of uranium in drinking water, however WHO set a limit for Uranium concentration in groundwater to 30 µg/L due to its chemical toxicity (WHO, 2017).

Uranium is of special concern in the Nordic countries due to high amounts of alum shale (Lecomte et al., 2017). Alum shale is known to contain high amounts of uranium, which will release its daughter products into the environment when undergoing radioactive decay. Alum shale also contains several other elements of concern (Lecomte et al., 2017). In Norway, alum shale is common in the areas of Akershus, Oslo, Oppland, Buskerud and Hedmark (NGU & DSA, 2011).

When assessing the risk of elements, only knowing of an elements total concentration does not give enough information to properly assess risk (Skipperud & Salbu, 2015). Therefore, knowing about the speciation of an element is important. The speciation of radionuclides is defined “according to their physicochemical properties such as nominal molecular mass, charge properties and valence, oxidation state, structure and morphology, density and degree of complexation.” (Salbu, 2007). Because of the importance of speciation, this thesis will

focus on the speciation of uranium in natural waters. The focus is on change in distribution with changing pH and humic acid content.

To get radionuclides for the experiment, alum shale from two different locations in Norway was mixed with water, for radionuclides and metals to be leached into the water. The first one was alum shale from Kirkegata 34 in Oslo, while the second stone is alum shale from highway 4 in Gran. Due to differences in the alum shale from the two locations, differences in uranium speciation were expected to occur between the two locations. To see changes in uranium speciation, pH and humic acid content was changed, and the amount of uranium of size  $<45 \mu\text{m}$ , and 3 kDa was measured. The goal of the thesis was to see how the changes in pH and humic acid affected the different size fractions, and to see what differences occurred because of differences between the two different types of alum shale.

## 2 Theory

### 2.1 Alum shale

Alum shale refers to a particular type of black shale formed between the middle Cambrian and early Ordovician period, which is mostly found in southern Scandinavia. Alum shale is known to contain high amounts of Ni, Mo, Cd, Co, Cu, Zn, U, V, As, Se, Ag, Au, PGE (platinum group elements) (Lavergren et al., 2009; Lecomte et al., 2017). Alum shale is of concern as it is a source of radon gas (a daughter product from the uranium decay chain), which is the second biggest contributor to lung cancer in Norway. As radon is a noble gas, it is largely non-reactive, and can permeate through cracks and openings into buildings (NGU & DSA, 2011). In addition, the high amounts of uranium and cadmium in alum shale can be a concern in drinking water (Bjørklund et al., 2020; Midtgård et al., 2007).

#### **Alum shale in Norway:**

In Norway, alum shale is common in the areas Akerhus, Oslo, Oppland, Buskerud and Hedmark. NGU (Geological Survey of Norway) and DSA (Norwegian Radiation and Nuclear Safety Authority) have previously created a map showing abundance of alum shale in Norway (Figure 1). It is noted that the map only shows alum shale near the surface. In addition, alum shale might also be present outside marked areas in the map, due to transportation of alum shale from natural processes (NGU & DSA, 2011).

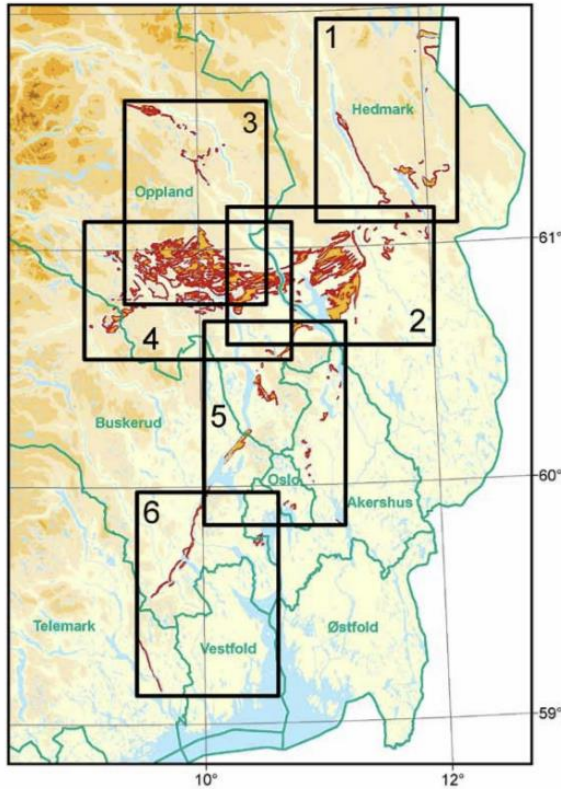


Figure 1: A map showing areas with high concentration of alum shale in Norway (NGU & DSA, 2011).

## 2.2 Radionuclides and metals

### Uranium

Uranium (U) has existed since the formation of the earth. The concentration of uranium is generally low, but geochemical processes cause there to be deposits with heavily increased concentrations (Maher et al., 2013). Uranium exists mostly as U-238 (99.27%), U-235 (0.72%) and U-234 (0.01%) (Waseem et al., 2015). Uranium and its intermediate daughter products undergo radioactive decay until the end product of Pb-206 is reached (Figure 2). U-234 is often the most common isotope in terms of activity in groundwater, due to preferential alpha recoil. U-234 has been found to account for 3-11 times the activity of U-238 in groundwater in Stripa in Sweden, and 1-4 times the activity in bedrock groundwaters around Helsinki (Banks et al., 1995). U-238 is the isotope focused on in this thesis, due to its natural abundance compared to the other isotopes.

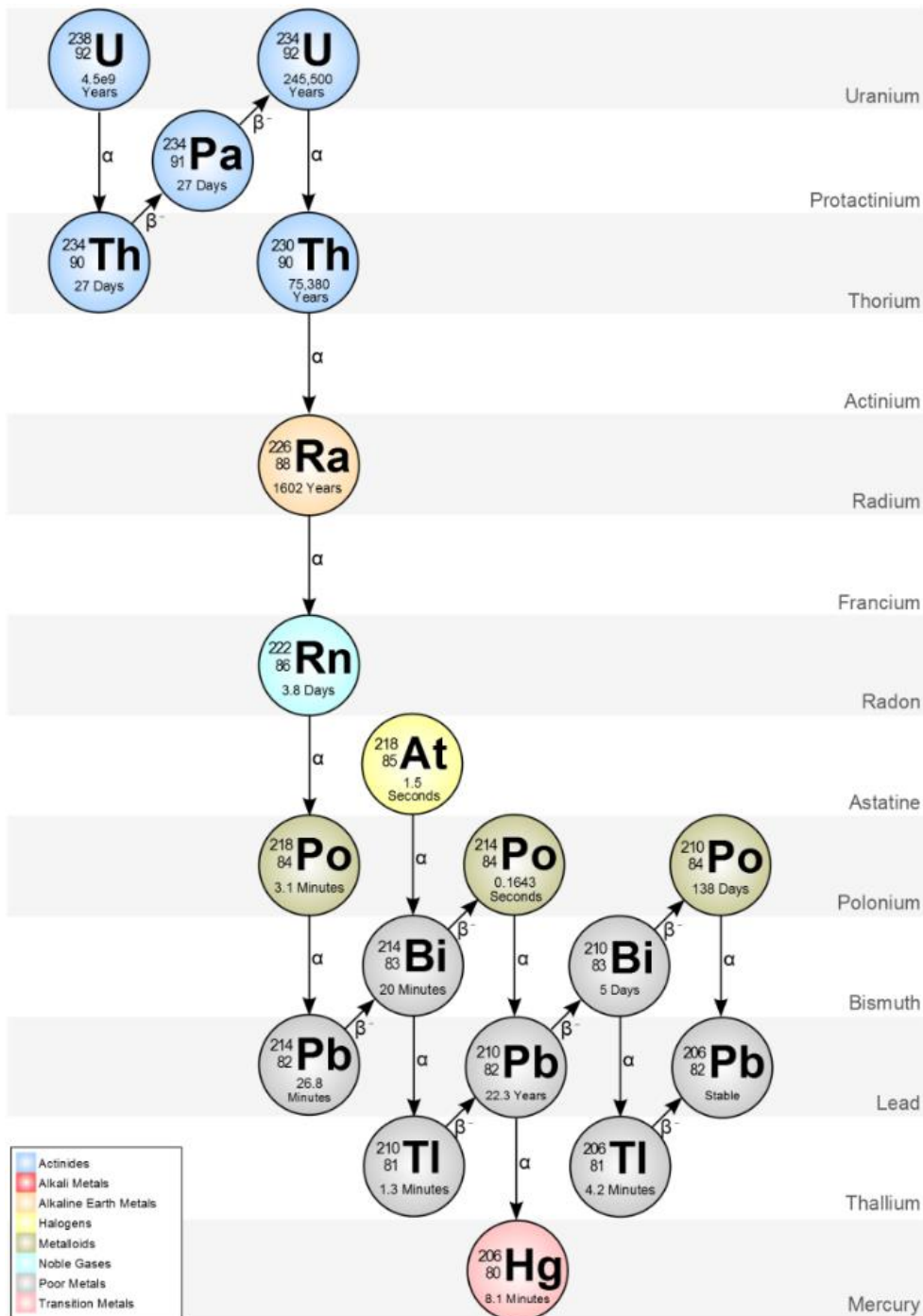


Figure 2: The uranium decay series (PhysicsOpenLab, 2016).

In drinking water, uranium is mostly of concern in groundwater (Skeppström & Olofsson, 2007). Uranium has been found in high concentration in groundwater in several location both in Norway (Midtgård et al., 2007) and Sweden (Skeppström & Olofsson, 2007).

Uranium is of concern both due to its chemical toxicity and its radiotoxicity. In Norway, the total dose of radionuclides allowed in drinking water per year is 0.10 mSv/year, with the exception of radiation from tritium, potassium-40, radon and the daughter products of radon (Forskrift om visse forurensende stoffer i næringsmidler, 2015). There is no official limit for the concentration of uranium in drinking water in Norway, but WHO (2017b) has a recommended guideline of 30 µg/l, due to its chemical toxicity. Uranium is known to be toxic to the kidney, and also functions as an active redox catalyst for the reaction between DNA and H<sub>2</sub>O<sub>2</sub> (Bjørklund et al., 2020). Uranium in the blood is deposited in the bone, and most of it is excreted after 1.5 years (Brugge et al., 2005).

When looking purely at the radiotoxicity of uranium, 0.14 mg/l U would cause the concentration to exceed the limit for radioactivity in drinking water in Norway, according to FHI (2021). From calculations done in this paper (see 7.1.1), a concentration of 0.24 mg/l U-238 would be needed to exceed the limits for radioactivity in drinking water. However, due to the presence of other uranium isotopes which may account for more of the activity than U-238 (Banks et al., 1995), the limit for uranium in total would be lower than the calculated limit for U-238. In addition, when looking at the dose received from water, it is important to include all radionuclides in the water (WHO, 2017b).

Uranium in rock is mostly present in the +4-oxidation state, which is mostly insoluble. When it has access to oxygen, uranium can be oxidized to uranium +6  $UO_2^{2+}$ , which is a more mobile form. Uranium(IV) can be transported in groundwater and can form complexes with several ions including OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, F<sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>. Uranium has also been found to form complexes with organic matter (humic and fulvic acid (Chen & Yiacoumi, 2002). In anoxic waters, U(+4) is the most common form, while U(+6) is the major for in oxic surface waters (Waseem et al., 2015).

### **Cadmium:**

Cadmium has a guideline limit in drinking water given by WHO of 3 µg/l (WHO, 2017a), and a limit in Norway of 5.0 µg/l in drinking water (drikkevannsforskriften, 2016). Drinking water in Norway might contain significant amounts of Cd in areas with low pH, but in areas with newer drinking water facilities, cadmium is generally not a problem (FHI, 2021).

The water chemistry of cadmium is relatively simple. Cadmium is generally insoluble in water, but can be released when due to either low pH or high nitrate concentrations (Xue & Sigg, 1998).

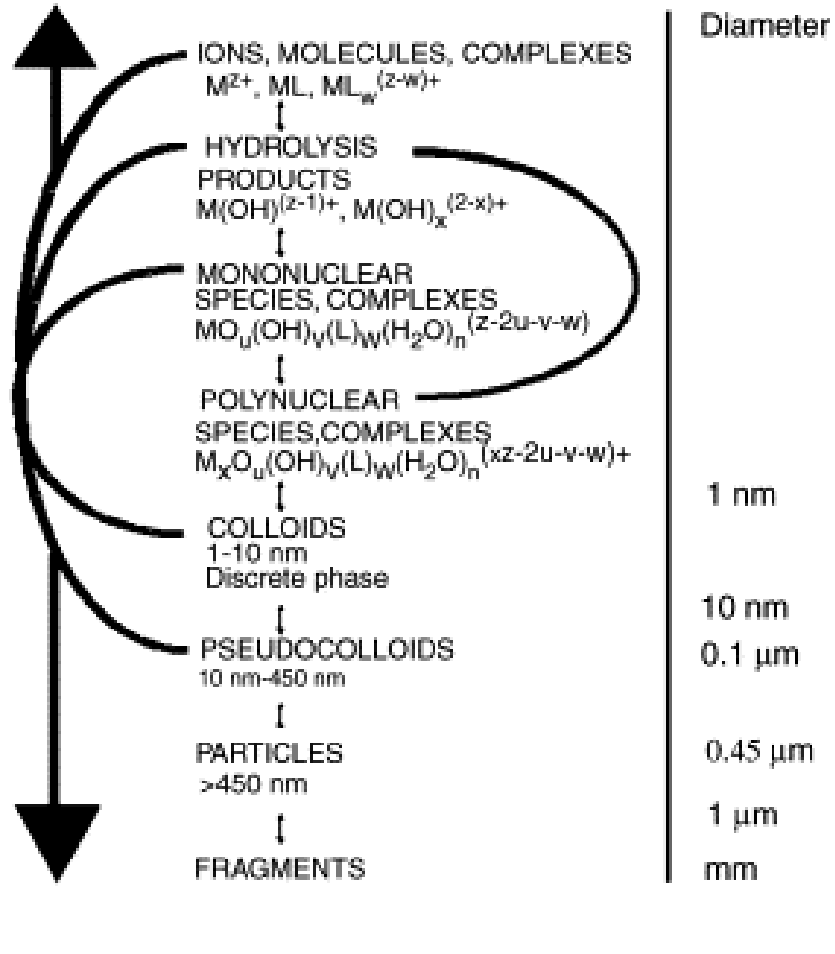
### 2.3 Speciation

Speciation is used to explain the distribution of an element in a system. One definition by Salbu, B and Skipperud, L (2009) define radionuclide species:

according to their physico-chemical properties such as nominal molecular mass, charge properties and valence, oxidation state, structure and morphology, density, degree of complexation. The speciation of radionuclides is the distribution of a radionuclide amongst defined chemical radionuclide species in a system. Speciation analysis is the analytical activity of fractionating, isolating, identifying and quantifying one or more individual radionuclide species in a sample, and include in situ, at site, on line, in laboratory fractionation techniques applied prior to analysis (p. 281).

Knowledge of the speciation of chemical elements is of high importance. The total concentration of an element cannot explain the mobility and biological uptake of elements. Knowledge of the speciation of an element can help explain changes in mobility and biological uptake (Salbu, 2009). As an example, the total dissolved concentration of Cd in water does not explain its toxicity, as the  $\text{Cd}^{2+}$  concentration is the toxic Cd species (Xue & Sigg, 1998). Low molecular mass (LMM) species are more mobile than high molecular mass (HMM) species. HMM are also more biologically inert than LMM species. The distribution of different species in a system can change over time by several different processes, as shown in figure 3 (Salbu et al., 2004).

**Mobilization mechanisms:  
desorption  
dissolution  
dispersion**



**Molecular mass growth mechanisms:  
hydrolysis  
complexation  
polymerisation  
colloid formation  
aggregation**

Figure 3: relation between the size and physico-chemical form of radionuclides, and examples of transformation progresses that decrease or increase size (Salbu et al., 2004).



## 3 Material and methods

### 3.1 Overview

Alum shale was crushed and then mixed with synthetic rainwater to get water containing radionuclides. After a few weeks of leaching, the levels of different elements in the water were determined. This was done to check if concentrations had reached a high enough level for the rest of the analyses. This water was then manipulated by changing pH and humic acid content. The speciation of radionuclides in the resulting water was analysed using a combination of <45 µm and <3 kDa filters and inductively coupled plasma mass spectrometry (ICP-MS).

The alum shale samples used for this experiment were previously collected by a master and PhD students at NMBU. The alum shale was from the locations of Riksveg 4 Gran (RV4G) and Kirkegata 34 (K34) in Oslo. These two different types of rock were chosen as they have somewhat different properties, which can be interesting when looking at factors influencing radionuclide speciation. At the end of the experiment, untreated water samples were also measured for radium using ICP-MS. Figure 4 shows an overview of the entire process.

All parts of the experiment were carried out at ca. 20°C unless otherwise stated.

The pH was measured using a Multi 3420 from WTW with a SenTix 41 probe from WTW. The pH-meter was calibrated using two-point calibration with pH 7.00 and 4.01 buffers from Hamilton.

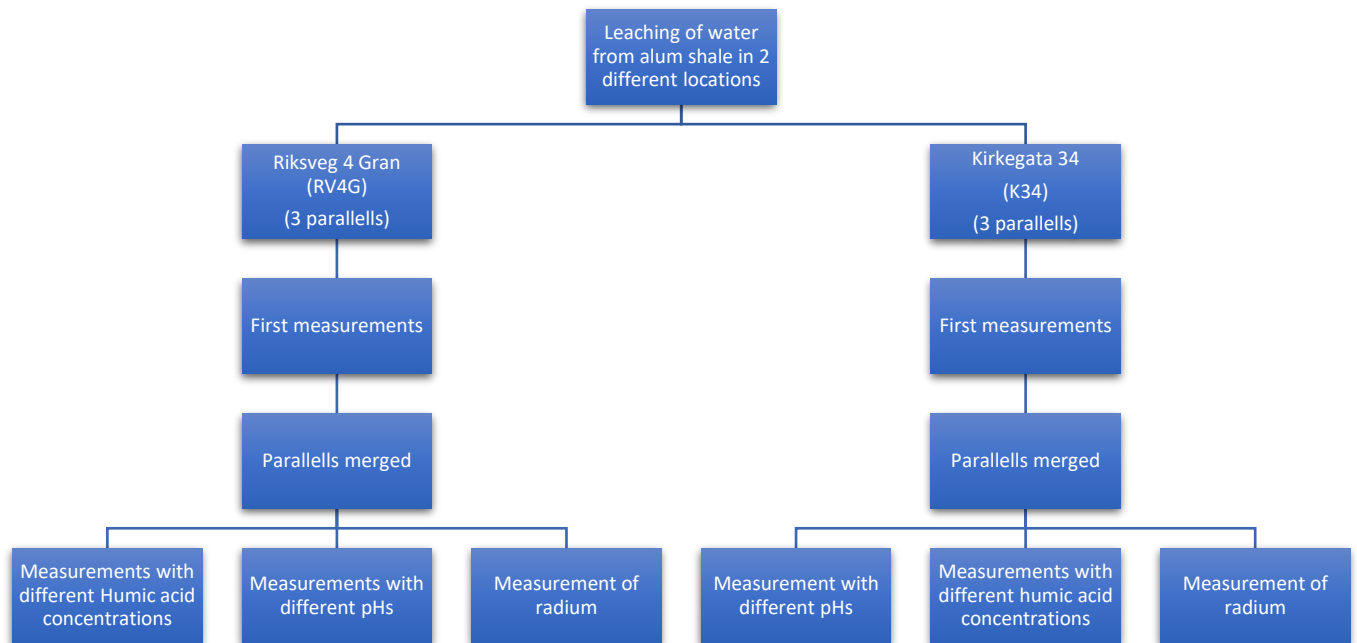


Figure 4: An overview of the different steps done in the experiment.

Description of the alum shale:

The alum shale from Riksveg 4 Gran (RV4G) were from a tunnel construction in 2015. The stone was collected 19/05-2015. The alum shale is described in more detail below. The rock collected was ensured to be U-rich by using handheld XRF (Niton™ XL3t GOLDD+ from thermo Scientific), add a total of about 10 kg material was collected. The stone was crushed using a jaw crusher and was thereafter sieved to filter out stones >2mm (Wærsted, 2019).

The stone from Kirkegata 34 (K34) was non-weathered alum shale, collected from the foundation of an apartment building under renovation. The sample was hacked out of the bedrock before collection. The sample was put in thick plastic bags, and then delivered to the CERAD isotope laboratory at NMBU (Hjulstad, 2015).

For more information about the alum shale from RV4G, see Wærsted et al., (2019).

### 3.2 Sample preparation

Alum shale from two different locations were leached in synthetic rainwater to create the solutions used in this experiment. The alum shale from K34 has been stored at NMBU since 2015, and the stone from RV4G has been stored at the isotope laboratory since 2019.

The rock from Kirkegata was not pre-crushed. Before mixing with water, it was crushed by using a jaw crusher and sieved to filter out stones  $>2\text{mm}$ . Some weathering of the stone was observed (See figure 5). The stone was crushed to decrease the time needed for elements to leach into the water. The jaw crusher and resulting crushed alum shale is seen in figure 6. After being crushed, the stone was stored in plastic bags for one night before being mixed with synthetic rainwater in 3 L bottles.



Figure 5: the stones from K34 that were crushed in the jaw crusher. Weathering can be seen from the yellow tint on some of the rocks. Photo: Johan Tryti, 11/11-2020.



Figure 6: the jaw crusher used to crush the stone (left), and the resulting crushed alum shale (right). Photos: Johan Tryti, 11/11-2020.

A total of 70 mL concentrated synthetic rainwater (see appendix 7.1 for the recipe) was mixed with 7 L deionised water in a 10 L container. This was then mixed with 200  $\mu$ L 0,5 M HCl. This was done to reduce the pH in order to 4.7. The water chemistry was made according to the composition of precipitation at Narbuvollen in 1980 (Overrein et al. 1980).

Three 1 litre bottles were filled with 100 g stone from K34 and three were filled with 100 g stone from RV4G. Afterwards, ca. 1 L water was added to each of the bottles, and 1 L was added to an additional bottle (blank). All bottles were acid rinsed and washed before use.

The bottles were then placed on a steering table with a magnet in each bottle and left to mix for 10 days. They were also manually shaken about once every day, to improve the mixing. After 10 days, the magnets were removed from the bottles and the first measurement of radionuclides in the water on ICP-MS was done. This measurement was done to ensure that there was enough uranium in the bottles to start manipulation, and to see what other elements were present. See 3.5 for details about this measurement.

After the rocks had been leaching for 21 days, it was decided to add the three parallels from each location together, to avoid having to work with uncertainties from different leaching in individual bottles. The three parallels from each location were added to one 5 L container each. Thereafter, 20 ml up concentrated synthetic rainwater was added to each container, before 2 L deionised water was added. The two containers were shaken on a shaker table at ca. 27°C for 2 days.

### **3.3 Size fractionation protocol**

To see the difference in speciation, 2 different fractions were used: <45 µm and <3kDa.

To extract the <0.45 µm fraction, a 20 ml sterile syringe (SOFT-JECT luer from Henke Sass Wolf) was used. The syringe was filled with water from the samples. Thereafter, a 0.45 µm sterile syringe filter from VWR was placed on the syringe. A few drops of solution were squeezed through the filter to clean it. Thereafter, about 2 mL solution was pressed through the filter and added to a 15 mL vial. A new syringe and filter were used for each replicate to avoid any cross-contamination between samples.

To get the 3 kDa fraction, 2 mL vials with 3kDa ultrafiltration filters on top from VWR were used. First, 200 µL solution was transferred from the <0.45 µm fraction to the filter on top of the vial. Thereafter, the vial was centrifuged at 14000 g for 15 minutes, and the filtrate was discarded. This was done to saturate and condition the filter. 500 µL solution was added to the vial and centrifuged at the same speed for 30 minutes. The throughfall from the second centrifugation was used to determine the <3 kDa fraction.

### **3.4 ICP-MS standards and details**

A 50 mL multistandard in a 50 mL vial was created for calibration on the ICP-MS. For details about all added chemicals, see appendix 7.2. The multistandard was made using standards from Agilent Technologies, with the medium being ultrapure HNO<sub>3</sub>. 3 replicates were made, with two of the replicates only being filled to the 40 ml mark. This was done so that concentration of different elements in these replicates could be increased later. This

could have been needed if the concentration of interesting elements in the samples were higher than anticipated. 50 ml multistandard was diluted 10 and 100 times and used for calibration for all measurements on the ICP-MS, except for measuring radium (3.7).

All internal standards used were added with in line addition.

For the ICP-MS, 5% HNO<sub>3</sub> was always used as a carrier.

#### Description of blanks:

Analytical blank: a blank which is treated as the same way as the samples.

Reagent blank: a blank where the reagent is added, in order check for any increase in signal due to the added reagent.

The blanks used in this measurement were ion free water.

### **3.5 Measurements prior to manipulation**

The initial measurements carried out by ICP-MS were done when the samples were still in parallel one litre bottles. To take liquid from the bottle into vials, a 15 mL syringe was used. A pipette tip was placed on the tip of the syringe, so that the syringe could be used to get water from the area slightly under the surface of the water. This was done to avoid getting particles from the surface into the mixture, and get a cleaner mix for the ICP-MS. The tip was removed from the syringe, and a sterile 0.45 µm syringe filter was added to the syringe tip. Afterwards, ca. 3 mL of liquid was pressed through the syringe filter and into a 15 mL vial. For each of the three 1 L bottles from K34 and RV4G, 3 replicates were made. The same syringe was used for each replicate within a group, but a new syringe filter was used for each replicate. Whenever a new syringe filter was used, a few drops were first pressed through the filter to condition it. Three replicates were also made for the analytical blank.

Before analysis, 1 mL unfiltered sample from each replicate was added to a new 15 mL vial. These samples were then diluted 10 times by adding 5% HNO<sub>3</sub>. These diluted samples were then measured on the ICP-MS.

The following elements were of interest when using the ICP-MS: Ca, As, Sr, Mo, Cd, Sn, Pb and U. As internal standards, <sup>103</sup>Rh, <sup>115</sup>In and <sup>209</sup>Bi were used. O<sub>2</sub>, NH<sub>3</sub> and He were used as reaction/collision gasses. For details about the measurement, see appendix 7.3.

The second measurement was also carried out before the parallels had been merged. This was a quick measurement of uranium in each sample, to check that the size fractionation showed different results for 3 kDa and the 45 μm fraction. For this test, one sample was taken from each parallel and the blank. The samples were taken by placing a pipette tip on the end of a syringe, and then using the syringe to get the samples. These were filtrated using the method described in 3.3. 0.3 mL sample from each 45 μm fraction was moved to a 15 mL tube, and 0.3 mL from each 3 kDa fraction was moved to a 15 mL tube. Thereafter, all samples were diluted 10 times using 5% HNO<sub>3</sub>.

The samples were then analysed on the ICP-MS. Th-232 was used as an internal standard. O<sub>2</sub> was used as a reaction gas. The first quadrupole was set to a mass of 238 u, and the second to 270 u (UO<sub>2</sub>).

### **3.6 Measurements of elements in water after manipulation**

The following manipulations were done for this experiment: pH and organic matter content.

#### **pH manipulation:**

pH was changed to see how the different fractions responded with changing pH. To reduce/increase pH, ca. 80 ml water from the two fractions and the blank was moved into a 100 ml plastic beaker. A sterile 50 ml serological pipet with a manual air pump on top was used to transfer the water.

After moving the water to their different beakers, pH was adjusted. After reaching each pH, ca. 15 ml of the mixture was moved to a 15 ml beaker. See table 1 for the different pHs used for each location. The acid and base used to adjust the pH was HCl and NaOH.

For each pH, 3 replicates for the 45  $\mu\text{m}$  fraction and 3 kDa fraction were made using the method described in 3.3.

For the blank, a few drops of NaOH and HCl was added, and the final pH was ca. 6.

Table 1: The different pHs used in the experiment.

pH	RV4G	K34
First extraction	7.70 (“natural” pH)	3.93 (“natural” pH)
Second extraction	6.01	5.03
Third extraction	5.01	6.03

### **Humic acid manipulation:**

The Humic Acid (HA) (Sigma Aldrich, technical grade, batch number # BCCD6371) was available in powder form. The residue of ignition of the humic acid was 28.3 % and the pH 5.9 (from the certificate of analysis, see attachment 7.3). The HA was dissolved in water before being added to the samples.

0.0590 g HA was added to a 50 mL beaker. Thereafter, 40 mL water and 1 mL 0.01 M NaOH mL was added, after which pH was measured to 7.9. A further 0.5 mL 0.01 M NaOH was added to increase the pH to further to increase solubility. The base was added as HA dissolves more easily in basic environments (Kipton et al., 1992). The contents were moved to a 120 mL box, and 40 ml more water was added. The box was then placed in an ultra-wave bath, to suspend the HA colloids. After being in the ultra-wave bath for 32 minutes, the pH of the humic acid solution was measured to 6.84. This was likely due to the HA particles dissolving, causing more of the humic acid to become available to react with the water and reducing the pH. This humic acid (100 mg/l) was used to create two solutions with 10 and 100 times less HA.

To mix the HA with the K34 and RV4G alum shale waters, 15 ml water from each location was added to 4 vials using a sterile 50 ml serological pipet with a manual air pump on top.

1.5 mL HA at the different concentrations was then added to 3 of the vials, resulting in a concentration of 0,1,10 and 100 mg/L humic acid in each of the 4 vials. This was also done



for RV4G. For the reagent blank, 1,5 mL 100 mg/L humic acid was added to a 15 ml vial with 15 mL water from the blank.

The humic acid samples were left in the lab for one day, before each concentration was filtrated using the method described in 3.3. 3 replicates were made for each location. The filtrated samples were then stored until analysis.

### **Measurement of pH and HA samples:**

Before measurement, 0.3 mL of all replicates was moved to a 15 mL tube and diluted to 6 mL using 5% HNO<sub>3</sub>.

All samples manipulated for pH and HA were analysed on the same day of dilution using ICP-MS. The following elements were determined: Ca, As, Sr, Mo, Cd, Sn, Pb, Th, and U. O<sub>2</sub> was used as a reaction gas. <sup>103</sup>Rh, <sup>115</sup>In and <sup>209</sup>Bi were used as internal standards.

### **3.7 Measurements of radium**

At the end of the experiment, unfiltered water from the two alum shales were analysed for radium. This was done to see if there was enough radium in the samples to be able to study speciation following fractionation. Because a different instrument set up was used, radium analysis could not be done while also measuring for other elements. Three samples were taken from each location, and a blank was also analysed. These samples were not diluted, and <sup>169</sup>Tm was used as an internal standard. A standard with 20 and 100 pg/L radium was used for calibration. N<sub>2</sub>O was used as a reaction gas. The first quadrupole only included mass 226, while the last only included 242 (RaO). The method used to measure radon was developed by Wærsted (2019) and has been further improved upon by senior engineer Karl Andreas Jensen.

## 4 Results and discussion

### 4.1 Results from the first measurements.

The first measurements done were done to ensure the concentration of radionuclides was high to continue the experiment. The following table (table 2) shows concentrations of the most important elements found for the first measurement done. For the concentration of all elements found, see appendix 7.4. There are very big uncertainties for all elements for this measurement when comparing different groups within a location. This is suspected to have happened because the 3 different parallels for each location had some differences in leaching. The measurement was mostly done to see if high enough concentrations of the elements had leached to make it possible to continue with the experiment. Since the ICP-MS was able to detect the amount of uranium with low uncertainties within each group, it was decided that the leaching had proceeded long enough to continue the experiment.

One difference between the two types of alum shale is the amount of Fe in the solution. This might be one cause of a difference in uranium behaviour between the two locations, as uranyl ions ( $UO_2^{2+}$ ) has been shown to be strongly sorbed to Fe oxides (Hsi & Langmuir, 1985). M.Izquierdo et al. (2020) has also shown that uranyl ions are probably strongly adsorbed to Fe oxides as inner-sphere complexes.

Table 2. Results for the first measurements done for the ICP-MS. The numbers are given as the average of all observations  $\pm$  the standard deviation. The number of samples for each group was 3.

Element	Ca	Fe	As	Sr
Unit	[ mg/l ]	[ ug/l ]	[ ug/l ]	[ ug/l ]
K34 1	243.3 $\pm$ 2.929	10836 $\pm$ 2.809	1.863 $\pm$ 0.917	2238 $\pm$ 1.243
K34 2	231.6 $\pm$ 0.960	29010 $\pm$ 4.636	2.558 $\pm$ 0.383	2126 $\pm$ 2.152
K34 3	228.5 $\pm$ 2.557	20992 $\pm$ 2.822	2.576 $\pm$ 1.817	2186 $\pm$ 3.644
RV4G 1	351.7 $\pm$ 1.253	<LOD	0.870 $\pm$ 2.011	5240 $\pm$ 1.534
RV4G2	362.1 $\pm$ 1.098	<LOD	0.803 $\pm$ 0.549	5679 $\pm$ 3.111
RV4G 3	335.5 $\pm$ 2.610	<LOD	0.545 $\pm$ 4.204	5323 $\pm$ 1.966

Element	Mo	Cd	Sn	U
Unit	[ ug/l ]	[ ug/l ]	[ ug/l ]	[ ug/l ]
K34 1	17.19±2.739	81.72±1.636	<LOD	105.6±0.753
K34 2	19.83±0.490	84.39±1.064	<LOD	181.0±1.220
K34 3	24.61±2.056	82.38±2.950	<LOD	125.0±2.668
RV4G 1	693.3±1.531	56.17±0.518	<LOD	292.4±1.320
RV4G2	749.6±0.748	59.67±2.019	<LOD	354.9±2.160
RV4G 3	636.5±1.650	61.22±0.938	<LOD	231.9±1.519

## 4.2 Results from size fractionation test

Before manipulation of the samples were done, a size fractionation test was done to ensure that there was a difference between uranium concentration for the different fractions. This measurement was done only for uranium, in order to confirm that the filters managed to separate different fractions. This measurement was only done with one sample for each location. This was due to time constraints, and as a high degree of certainty was not needed, since the test was only done to ensure that the filters worked properly. As the results for all measurements (Table 3) showed a difference between the two fractions, it was decided to continue the experiment. The ratio of the <45 µm fraction divided by the <3 kDa fraction was bigger than 1.25 for all locations, which is also shown in figure 2.

Table 3: The size fractions for uranium for the first filtration done.

	<45µm	<3 kDa	<35 um/<3kDa ratio
RV4G-1	439.83	332.92	1.32
RV4G-2	474.45	368.76	1.29
RV4G-3	342.61	271.08	1.26
K34-1	207.77	166.19	1.25
K34-2	294.23	223.72	1.32
K34-3	415.77	325.46	1.28
Blank	0.001	0.003	0.33

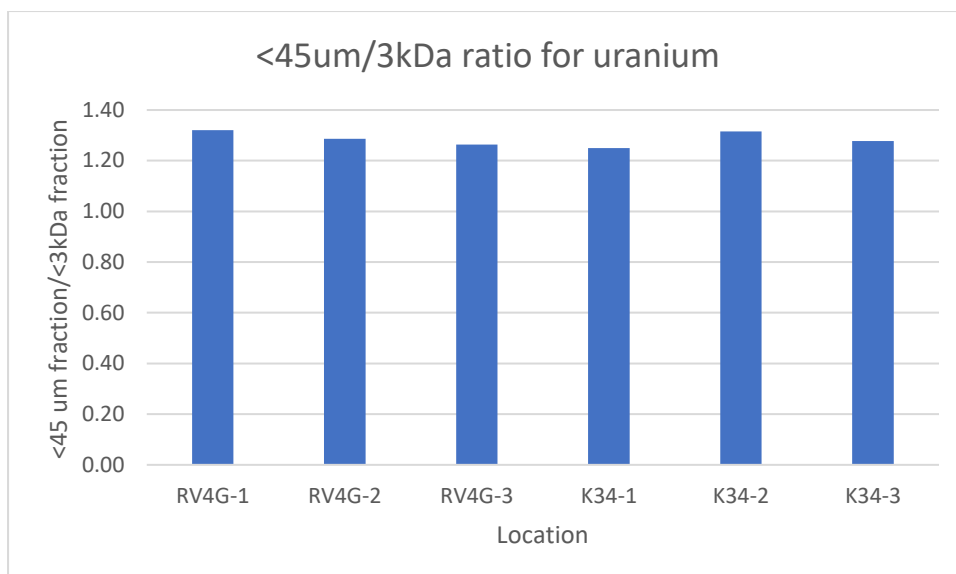


Figure 7: Size fraction ratio for the different locations for the first measurement with filtration for the experiment.

### 4.3 Results from pH manipulation

The results for pH manipulation and uranium concentration showed a general decrease for K34 for both fractions, and an increase for RV4G (Figure 8). For K34 (Figure 9), it showed a general increase for both fractions. However, due to the low sample size, no statistical difference was proven between the different size fractions. For K34, the P-values were between 0.16 and 0.21 for comparison between any groups (Table 6). For RV4G, all P-values found were also above 0.10 (Table 7). See table 4 and 5 for the concentrations of all elements.

Table 4: Measurements from RV4G for <45 µm and <3 kDa fractions with different pHs ranging from 7.5-5. Sample size = 3 for all measurements, apart from Pb for pH 7.7, where n=2 as a Pb-value of 21.89 µg/l was identified as an outlier.

RV4G				
	Ca	As	Sr	Mo
Unit	mg/l	ug/l	ug/l	ug/l
RV4G pH7.7 <45 µm	200±3.7	0.7±0.13	327*10±40	458±2.7
RV4G pH6 <45 µm	201±7.0	0.54±0.027	33*100±1	46*10±13
RV4G pH5 <45 µm	201±1.1	0.544±0.0090	331*10±17	452±2.8
RV4G pH6 <3 kDa	21*10±18	<1.514	36*100±2	50*10±40
RV4G pH5 <3 kDa	21*10±16	<1.514	36*100±3	51*10±42
RV4G pH4 <3 kDa	21*10±16	<1.514	37*100±3	50*10±46
RV4G				
	Cd	Sn	Pb	U
Unit	ug/l	ug/l	ug/l	ug/l
RV4G pH7.7 <45 µm	33.6±0.65	<LOD	<LOD	98±1.5
RV4G pH6 <45 µm	36±1.1	<LOD	<LOD	92±3.0
RV4G pH5 <45 µm	35.7±0.28	<LOD	<0.195	92±3.1
RV4G pH6 <3 kDa	37±2.9	<0.302	<LOD	11*10±13
RV4G pH5 <3 kDa	38±3.1	<0.302	<LOD	6*10±10
RV4G pH4 <3 kDa	38±3.3	<0.302	<LOD	36±8.8

Table 5: Measurements from K34 for <45 µm and <3 kDa fractions with different pHs ranging from 6-4. Sample size = 3 for all measurements, apart from all measurements for K34 pH=6 where n=2.

K34				
	Ca	As	Sr	Mo
Unit	mg/l	ug/l	ug/l	ug/l
K34 pH 6 <45 µm	142±2.8	0.12±0.014	1371±10	0.59±0.062
K34 pH 5 <45 µm	139.3±0.77	<0.075	1348±7.1	0.5±0.13
K34 pH 4 <45 µm	138±1.9	0.131±0.0014	1340±10	0.6±0.13
K34 pH 6 <3 kDa	135±9.9	<1.514	1381±98	<0.785
K34 pH 5 <3 kDa	135.1±0.87	<1.514	1373±16	<0.785
K34 pH 4 <3 kDa	145.1±0.49	<1.514	1488±2.8	<0.785
K34				
	Cd	Sn	Pb	U
Unit	ug/l	ug/l	ug/l	ug/l
K34 pH 6 <45 µm	53.4±0.48	<LOD	<0.195	169±2.8
K34 pH 5 <45 µm	54.3±0.26	<LOD	0.71±0.026	350±2.2
K34 pH 4 <45 µm	54.2±0.31	<LOD	1.93±0.030	379±2.7
K34 pH 6 <3 kDa	52±3.7	<0.302	<LOD	40±17
K34 pH 5 <3 kDa	53.3±0.71	<LOD	<0.905	305±10
K34 pH 4 <3 kDa	57.95±0.013	<0.302	2.21±0.048	415±31

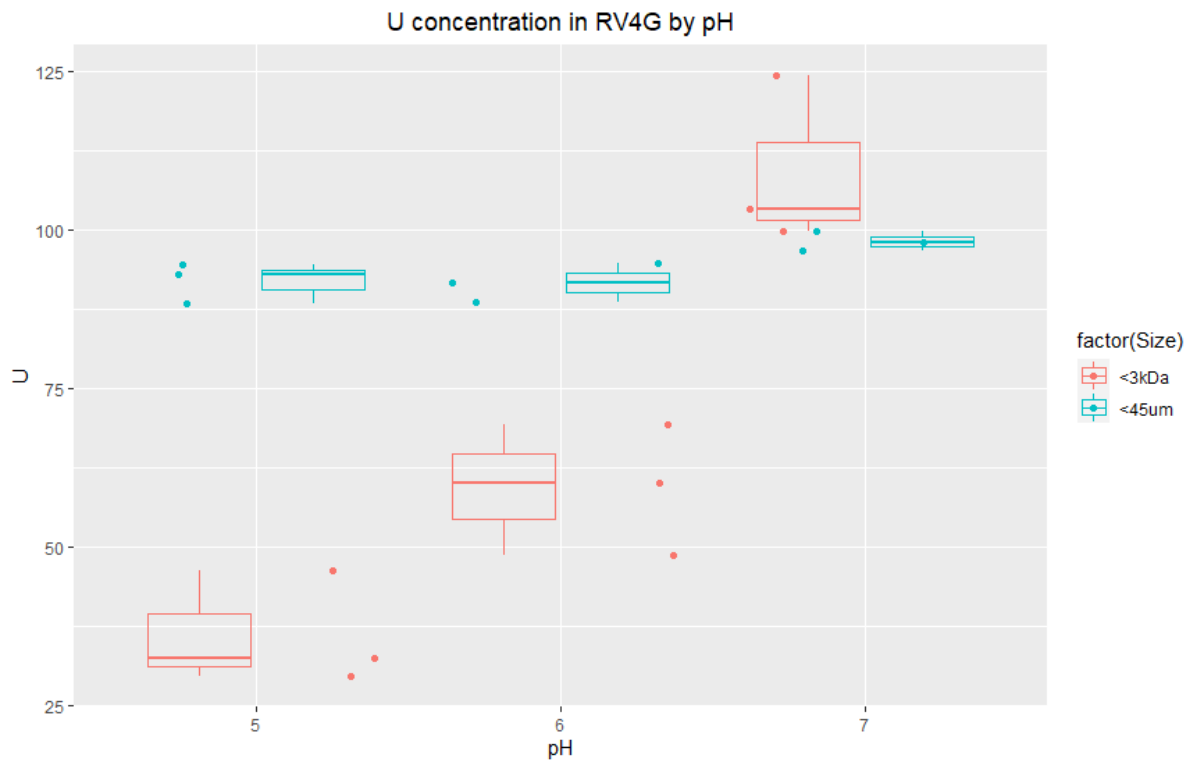


Figure 8: The change in uranium concentrations for size fractions <3kDa and <45μm with increasing pH for pHs 5, 6 and 7 for RV4G.

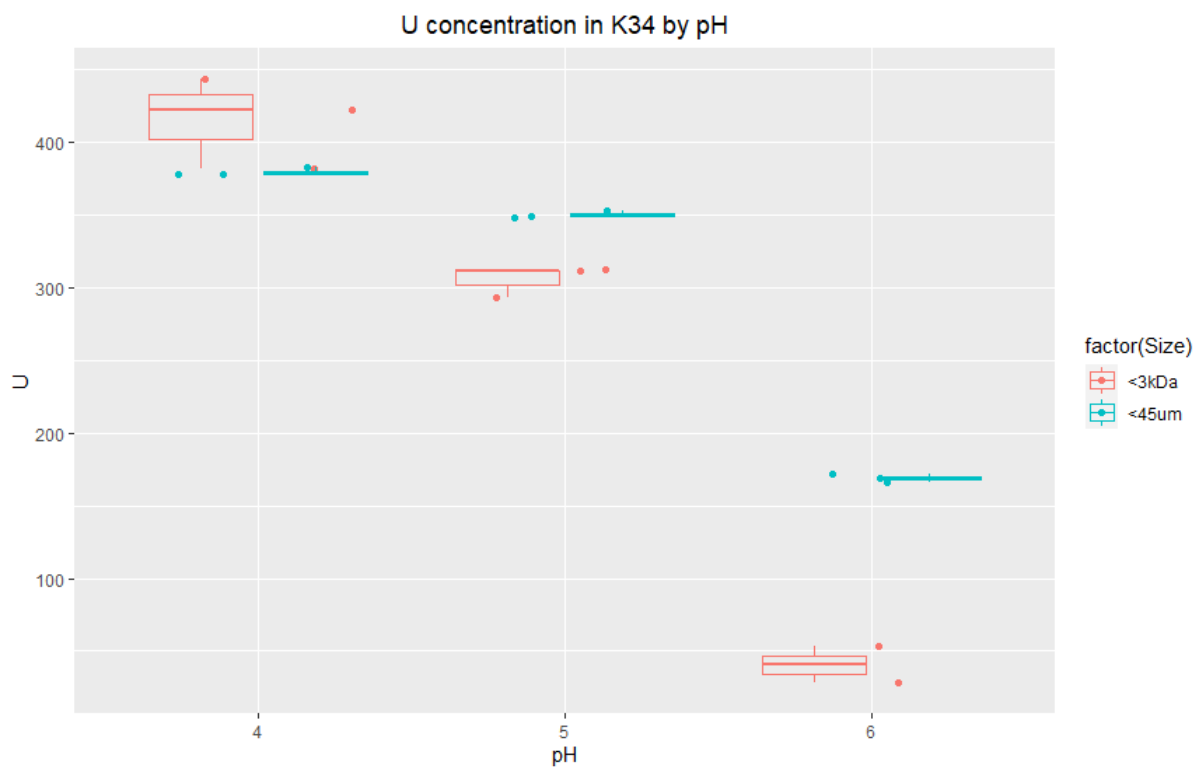


Figure 9: The change in uranium size fractions with increasing pH, for pHs 4, 5 and 6 for K34.

Table 6: P-values when doing a pairwise Wilcoxon rank sum exact test between the different groups for K34, with different pHs between groups.

		K34 pH4<3kDa	K34 pH4<45µm	K34 pH5<3kDa	K34 pH5<45µm	K34 pH6<3kDa
K34 pH4<45µm	0.20	-	-	-	-	-
K34 pH5<3kDa	0.17	0.17	-	-	-	-
K34 pH5<45µm	0.17	0.17	0.17	-	-	-
K34 pH6<3kDa	0.20	0.20	0.20	0.20	-	-
K34 pH6<45µm	0.17	0.17	0.17	0.17	0.20	-

Table 7: P-values when doing a pairwise Wilcoxon rank sum exact test between the different groups for RV4G, with different pHs between groups.

		RV4G pH5<3kDa	RV4G pH5<45µm	RV4G pH6<3kDa	RV4G pH6<45µm	RV4G pH7<3kDa
RV4G pH5<45µm	0.12	-	-	-	-	-
RV4G pH6<3kDa	0.12	0.12	-	-	-	-
RV4G pH6<45µm	0.12	1.00	0.12	-	-	-
RV4G pH7<3kDa	0.12	0.12	0.12	0.12	-	-
RV4G pH7<45µm	0.12	0.12	0.12	0.12	0.21	-

#### 4.4 Results from humic acid content manipulation

The size of the Humic Acid (HA) was not categorized for the experiment. As HA changes size and shape in water depending on factors such as pH and HA concentration (Klučáková, 2018), it might also be different between the locations and HA concentrations. However, the results still indicate a decrease in metal concentration with increased HA concentration, showing a very probably retention above the filters. In addition, pictures taken for the HA blank show a clear difference in colour above and below the filters (Figure 10), showing that HA was likely retained to a substantial degree.



Figure 10: Filtration of humic acid for the blanks. The left picture shows the filters for the <0.3 kDa fraction and the right shows the filters for <45  $\mu\text{m}$  filters. A difference in humic acid concentration can be seen from the difference in colour above and below the filters.

Photos: Johan Tryti, 08/01/2021.

The results for uranium concentrations for RV4G (Figure 11) and K34 (Figure 12) both showed a general decrease with increased HA concentrations. It can be noted that the decrease in uranium concentration RV4G appears less steep than K34. This is likely due to the fact that RV4G has a high pH ( $\approx 7.7$ ), compared to K34 ( $\text{pH} \approx 4$ ). Uranyl ( $\text{UO}_2^{2+}$ ) has previously been found to bind strongly to HA, with a difference in binding strength depending on pH (Lenhart et al., 2000). Uranyl ions have previously been shown to bind more easily to organic matter at higher pHs ( $< 5$ ), which supports the results from this experiment (Li et al., 1980).

When doing a pairwise wilcox test, no difference could be shown between the groups ( $P > 0.10$ ) (Table 10 and 11). Therefore, it has only been concluded on the general trends. Table 8 and 9 shows all concentrations measured for the different elements.



Table 8: Measurements from K34 for <45  $\mu\text{m}$  and <3 kDa fractions with different added humic acid (HA) concentrations ranging from 1-100 mg/l. Sample size = 3 for all measurements.

K34					
Unit	mg/l	mg/l	ug/l	ug/l	ug/l
Sample	HA	Ca	As	Sr	Mo
K34H0 <45 $\mu\text{m}$	0	153 $\pm$ 5.4	0.155 $\pm$ 0.0069	1511 $\pm$ 49	<LOD
K34H1 <45 $\mu\text{m}$	1	136 $\pm$ 2.8	0.19 $\pm$ 0.076	1338 $\pm$ 23	<LOD
K34H10 <45 $\mu\text{m}$	10	135.2 $\pm$ 0.30	0.279 $\pm$ 0.0047	1336 $\pm$ 9.1	<LOD
K34H100 <45 $\mu\text{m}$	100	137 $\pm$ 3.7	1.56 $\pm$ 0.028	1323 $\pm$ 27	<LOD
K34H0 <3 kDa	0	162 $\pm$ 3.1	<2.378	1579 $\pm$ 40	0.6 $\pm$ 0.10
K34H1 <3 kDa	1	137 $\pm$ 1.1	<2.378	1344 $\pm$ 18	1 $\pm$ 0.89
K34H10 <3 kDa	10	138 $\pm$ 1.2	<2.378	1350 $\pm$ 15	0.54 $\pm$ 0.037
K34H100 <3kDa	100	138 $\pm$ 2.0	2.43 $\pm$ 0.018	1342 $\pm$ 16	0.5 $\pm$ 0.12
Unit	mg/l	ug/l	ug/l	ug/l	ug/l
Sample	HA	Cd	Sn	Pb	U
K34H0 <45 $\mu\text{m}$	0	61 $\pm$ 1.8	0.08 $\pm$ 0.031	1.9 $\pm$ 0.14	413 $\pm$ 15
K34H1 <45 $\mu\text{m}$	1	53.7 $\pm$ 0.98	0.09 $\pm$ 0.010	1.4 $\pm$ 0.23	330 $\pm$ 47
K34H10 <45 $\mu\text{m}$	10	53.6 $\pm$ 0.38	0.09 $\pm$ 0.011	1.16 $\pm$ 0.078	281 $\pm$ 2.1
K34H100 <45 $\mu\text{m}$	100	50.8 $\pm$ 0.94	0.11 $\pm$ 0.044	<0.276	51 $\pm$ 1.7
K34H0 <3 kDa	0	65 $\pm$ 1.3	<0.257	2.3 $\pm$ 0.14	424 $\pm$ 14
K34H1 <3 kDa	1	54.8 $\pm$ 0.85	<0.257	1.8 $\pm$ 0.19	349 $\pm$ 4.7
K34H10 <3 kDa	10	55.1 $\pm$ 0.66	<LOD	1.35 $\pm$ 0.064	275 $\pm$ 3.4
K34H100 <3kDa	100	51.4 $\pm$ 0.60	<0.257	0.45 $\pm$ 0.054	35.6 $\pm$ 0.56

Table 9: Measurements from RV4G for <45  $\mu\text{m}$  and <3 kDa fractions with different added humic acid (HA) concentrations ranging from 1-100 mg/l. Sample size = 3 for all measurements.

RV4G					
Sample	HA	Ca	As	Sr	Mo
Unit	mg/l	mg/l	ug/l	ug/l	ug/l
RV4GH0 < 45 $\mu\text{m}$	0	233 $\pm$ 2.8	0.51 $\pm$ 0.0064	3857 $\pm$ 28	570 $\pm$ 5.8
RV4GH1 <45 $\mu\text{m}$	1	223 $\pm$ 13	1.6 $\pm$ 0.22	3677 $\pm$ 2.0	542 $\pm$ 34
RV4GH10 <45 $\mu\text{m}$	10	203 $\pm$ 1.2	0.558 $\pm$ 0.0069	3440 $\pm$ 6.8	506 $\pm$ 0.53
RV4GH100 <45 $\mu\text{m}$	100	193 $\pm$ 5.0	1.23 $\pm$ 0.024	3280 $\pm$ 91	489 $\pm$ 16
RV4GH0 < 3kDa	0	220 $\pm$ 21	<2.378	3611 $\pm$ 3	529 $\pm$ 53

RV4GH1 <3 kDa	1	202±2.4	<LOD	3396±29	499±5.5
RV4GH10 <3 kDa	10	207±3.4	<2.378	3370±31	502±4.9
RV4GH100 <3 kDa	100	199±3.3	2.552±0.0088	3280±53	491±11
Sample	HA	Cd	Sn	Pb	U
Unit	mg/l	ug/l	ug/l	ug/l	ug/l
RV4GH0 < 45 µm	0	41.9±0.34	0.12±0.024	<LOD	143±1.5
RV4GH1 <45 µm	1	41±3.1	<0.054	<0.276	134±9.1
RV4GH10 <45 µm	10	30.3±0.22	0.085±0.0098	<LOD	127±1.1
RV4GH100 <45 µm	100	10.9±0.35	0.07±0.019	<LOD	101±2.4
RV4GH0 < 3kDa	0	40±4.2	<0.257	<0.255	130±13
RV4GH1 <3 kDa	1	36.1±0.52	<0.257	<LOD	125±1.9
RV4GH10 <3 kDa	10	24.4±0.20	<LOD	<0.255	116±1.1
RV4GH100 <3 kDa	100	10.7±0.26	<LOD	<0.255	99±2.0

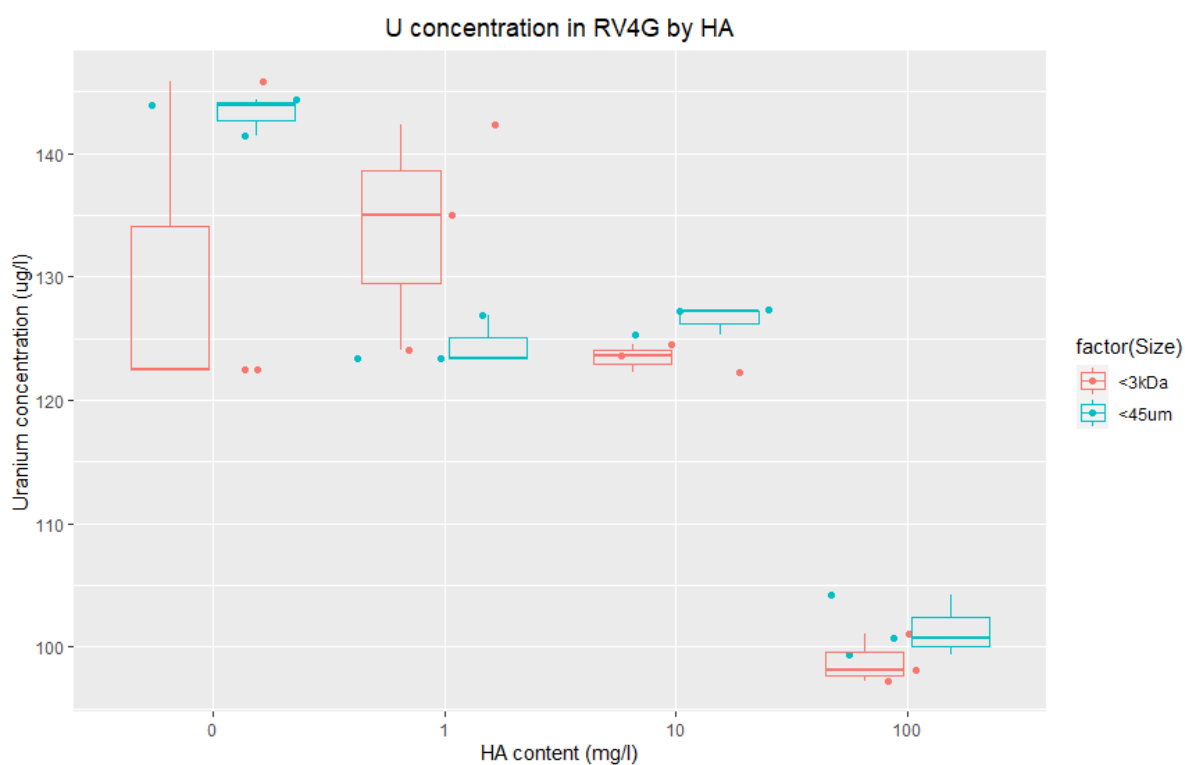


Figure 11: A boxplot showing the difference in uranium fractions for humic acid concentrations of 0, 1, 10 and 100 mg/l HA, for water leached from rocks from RV4G.

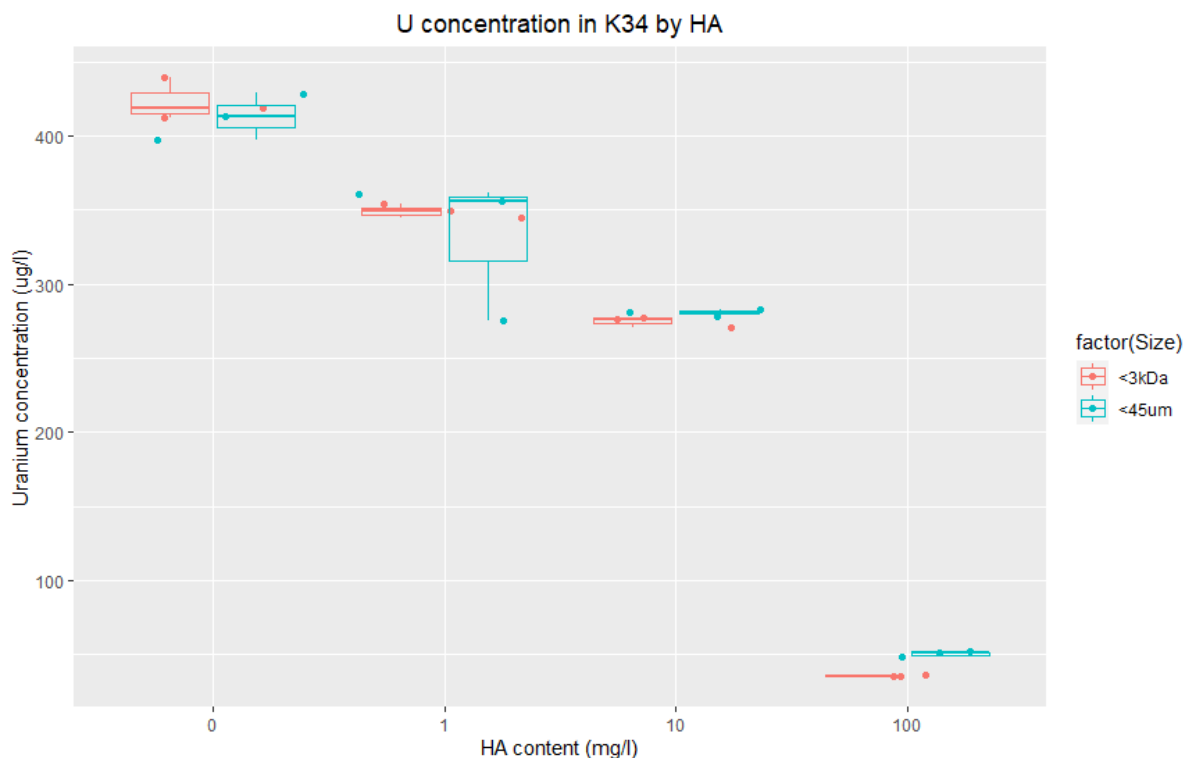


Figure 12: A boxplot showing the difference in uranium fractions for humic acid concentrations of 0, 1, 10 and 100 mg/l HA, for water leached from rocks from K34.

Table 10: P-values when doing a pairwise Wilcoxon rank sum exact test between the different groups for K34, with different HA concentrations between groups.

	K34H0<3kDa	K34H0<45µm	K34H1<3kDa	K34H1<45µm	K34H10<3kDa	K34H10<45µm	K34H100<3kDa
K34H0<45µm	0.70	-	-	-	-	-	-
K34H1<3kDa	0.12	0.12	-	-	-	-	-
K34H1<45µm	0.12	0.12	0.70	-	-	-	-
K34H10<3kDa	0.12	0.12	0.12	0.45	-	-	-
K34H10<45µm	0.12	0.12	0.12	0.70	0.12	-	-
K34H100<3kDa	0.12	0.12	0.12	0.12	0.12	0.12	-
K34H100<45µm	0.12	0.12	0.12	0.12	0.12	0.12	0.12

Table 11: P-values when doing a pairwise Wilcoxon rank sum exact test between the different groups for RV4G, with different HA concentrations between groups.

	RV4GH0<3kDa	RV4GH0<45µm	RV4GH1<3kDa	RV4GH1<45µm	RV4GH10<3kDa	RV4GH10<45µm	RV4GH100<3kDa
RV4GH0<45µm	0.75	-	-	-	-	-	-
RV4GH1<3kDa	1.00	1.00	-	-	-	-	-
RV4GH1<45µm	0.12	0.12	0.12	-	-	-	-
RV4GH10<3kDa	0.12	0.12	0.12	0.12	-	-	-
RV4GH10<45µm	0.12	0.12	0.12	0.12	0.12	-	-
RV4GH100<3kDa	0.12	0.12	0.12	0.12	0.12	0.12	-
RV4GH100<45µm	0.12	0.12	0.12	0.12	0.12	0.12	0.75

The results for cadmium showed the same trends as uranium, with a steeper curve for RV4G. This is also expected for cadmium, as metals in general have been shown to bind stronger to humic acid with both increased HA concentration and increasing pH (Spark et al., 1997). The P-values for cadmium were  $>0.10$  for comparison between all groups.

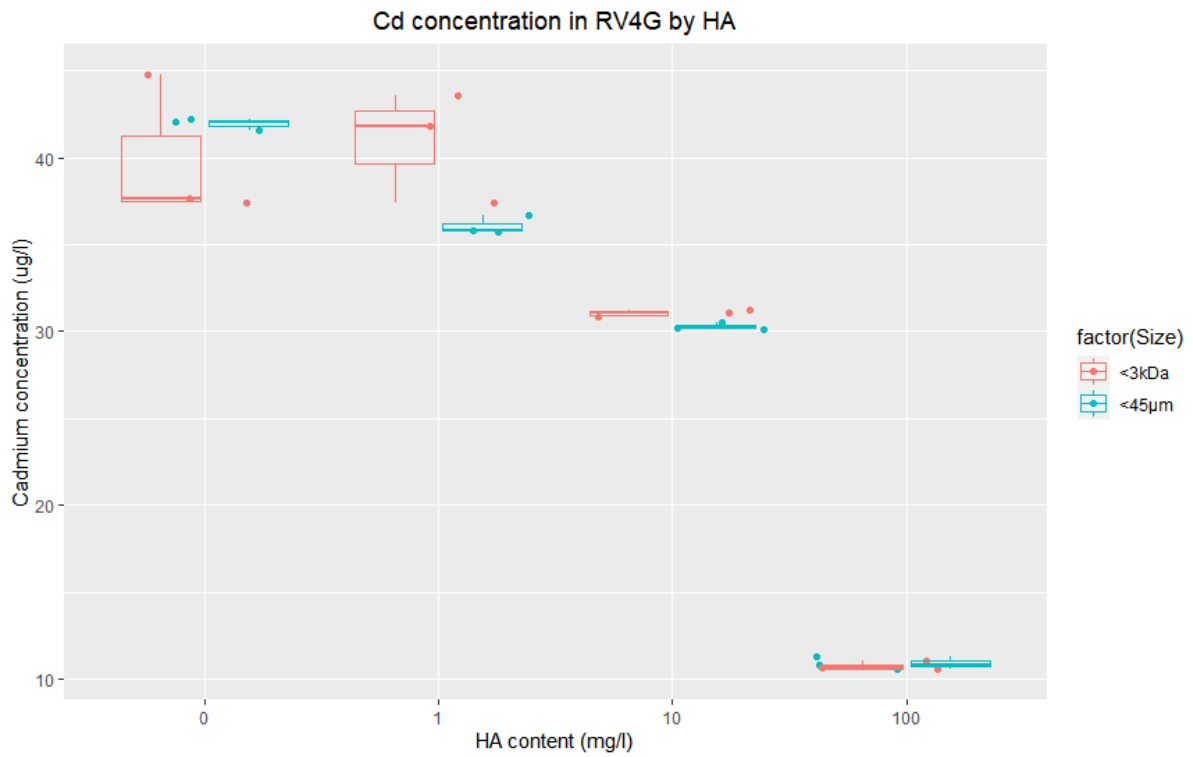


Figure 13: A boxplot showing the difference in uranium fractions for humic acid concentrations of 0, 1, 10 and 100 mg/l HA, for water leached from rocks from K34.

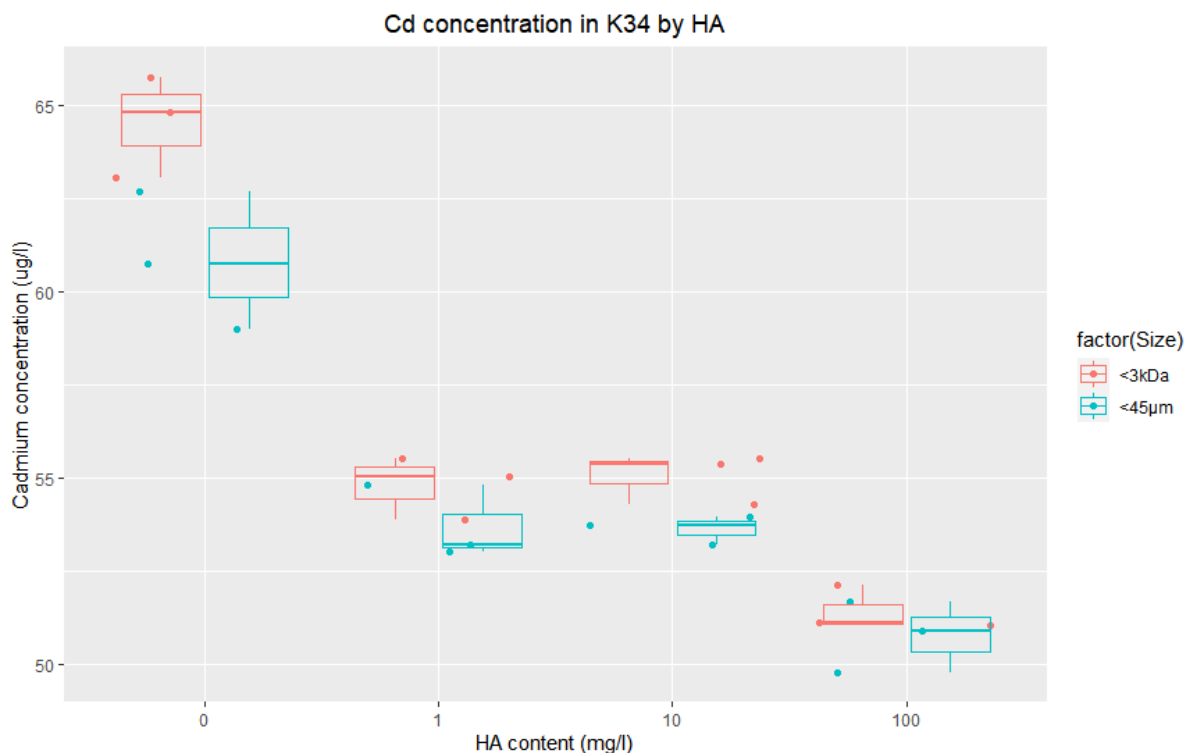


Figure 14: A boxplot showing the difference in uranium fractions for humic acid concentrations of 0, 1, 10 and 100 mg/l HA, for water leached from rocks from K34.

#### 4.5 Results from measurement of radium

The measurements of radium showed radium concentrations of  $7.5 \pm 0.21$  pg/L for K34 and  $8.7 \pm 0.92$  pg/L for RV4G. These results were considered too low to measure radium without doing significant changes on the ICP/MS. Due to the time and effort involved with this, it was decided to not focus on radium for the remainder of the thesis.

After the measurement was done, it was noted that K34 had about 140% internal standard recovery for Thulium. When looking at the earlier measurements for Thulium (4.1), it was found that K34 had around 0.5-1 µg/l Tm. To correct for the thulium in the sample, a very rough manual correction was done. This was decided to be good enough for the current measurement, as the results obtained were only going to be used to see if the levels of radium were high enough to measure radium without changing the instrument.

#### **4.6 Statistical methods**

As normality was not assumed, and due to the low sample size and high number of groups, a non-parametric statistical test was used. Therefore, for all the statistics done, a pairwise Wilcoxon test was done. This caused the power of the test to be quite small, and due to small sample size, the power of the test was too poor to prove any difference between groups.

#### **4.7 Uncertainties and shortcomings**

This experiment has gone over a very short time scale. For risk assessments, knowledge of long term solubility is of importance, and it might differ from short-term results found in the lab (Izquierdo et al., 2020).

This experiment focused on general trends rather than getting very precise measurements. Some steps could have been done to improve accuracy and precision, in particular introducing an internal standard to the samples earlier in the method.

Due to the big number of groups and small number of observations, a type 1 fault is of concern.

## 5 Conclusions

The experiment was not able to confirm any differences when changing pH and humic acid content, due to a statistical test with low power and a low number of samples. Therefore, conclusions are made based on the trends that appeared in the different tests.

The results from the experiment showed trends of increased sorption of uranium and cadmium with increasing humic acid concentration, which is in line with expected results. The sorption was also shown to be stronger in K34 when compared to RV4G. This is suspected to be due to the difference in pH, which is previously shown to be important for the sorption of metals to humic acid.

To improve upon the experiment, it would have been beneficial with larger sample sizes.

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## 7 Appendix

### 7.1 Formulas and calculations

#### 7.1.1 Calculations

These calculations are for figuring out the theoretical amount of U-238 needed in drinking water to exceed the limit for radiological toxicity. The calculations are based on information from the World Health Organizations Guidelines for Drinking Water Quality (2017b), and the limit for dose received from drinking water in Norway (drikkevannsforskriften, 2016). The limit of dose received is the same in Norway as in the guidelines from WHO (2017b).

It is assumed a person drinks 730 litres of water each year. The dose coefficient for uranium is  $4.5 \cdot 10^{-8} \text{ Sv/Bq}$ . The activity concentration needed to reach a dose of 0.10 Sv/year is therefore the following:

Dose coefficient · activity = dose

*Dose coefficient · activity = dose*

$$\text{Activity} = \frac{\text{dose}}{\text{dose coefficient}}$$

$$\text{Activity} = \frac{0.10 \cdot 10^3 \text{ Sv}}{4.5 \cdot 10^{-8} \frac{\text{Sv}}{\text{Bq}}}$$

$$\text{Activity} = 2.2 \cdot 10^3 \text{ Bq}$$

$$\text{Activity concentration} = \frac{2.2 \cdot 10^3 \text{ Bq}}{730 \text{ l}} = 3.0 \frac{\text{Bq}}{\text{l}}$$

This is converted to g/l using the following formula:

$$A = nNa \cdot \lambda \rightarrow n = \frac{A}{\lambda \cdot Na}$$

Where:

A = activity,

$\lambda$  is the decay constant, equal to  $\frac{\ln 2}{t_{\frac{1}{2}}}$ , where  $t_{\frac{1}{2}}$  is the half-life of the radionuclide,

n is the number of atoms and

Na = Avogadro's constant

$$n = \frac{A}{\lambda \cdot Na} = \frac{3.0 \frac{Bq}{l}}{\frac{\ln 2}{1.4 \cdot 10^{17} s^{-1}} \cdot Na} = 6.2 \cdot \frac{10^{17} \frac{atoms}{l}}{6.0 \cdot 10^{23} \frac{atoms}{mole}} = 1.0 \cdot 10^{-3} \frac{moles}{l}$$

$$1.0 \cdot 10^{-3} \frac{moles}{l} \cdot 238 \frac{g}{mole} = 0.24 mg/l$$

### 7.1.2 Formulas

$$STD \text{ (Standard deviation): } STD = \sqrt{\frac{\sum(x-\bar{x})^2}{(n-1)}},$$

where x = a given observation,  $\bar{x}$  = the mean of all observations and n is the number of observations.

$$LOQ \text{ (limit of quantification): } LOD = 3 * STD(blank)$$

$$LOD \text{ (Limit of detection): } LOD = \frac{10 \cdot LOQ}{3}$$

## 7.2 Recipe for the synthetic rainwater

**Water with similar ionic composition as precipitation at Narbuvollen (Overrein *et al.* 1980)**

Reference: Overrein, L.N., H.M. Seip & A. Tolland 1980. Acid/precipitation – effects on forest and fish. Final report of the SNSF project 1972-1980, 175 pp.

### **Stock solution:**

Table 12: the salts and concentrations added for the stock solution for the artificial rainwater.

Salt	µmol/L	mg salt/L	mg salt/5L
$\text{Na}_2\text{SO}_4$	300	42,612	213,06
$\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$	550	120,49	602,45
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	100	25,64	128,2
$\text{NH}_4\text{NO}_3$	1100	88,04	440,2

### **Ionic composition in artificial rainwater (diluted stock-solution):**

Table 13: the ionic composition of the diluted stock-solution used to create artificial rainwater

$\text{Na}^+$	0,136 mg/L
---------------	------------

Ca <sup>2+</sup>	0,217 mg/L
Mg <sup>2+</sup>	0,024 mg/L
NH <sub>4</sub> <sup>+</sup>	0,198 mg/L
Cl <sup>-</sup>	0,390 mg/L
NO <sub>3</sub> <sup>-</sup>	0,806 mg/L
O <sub>4</sub> <sup>2-</sup>	0,290 mg/L

### 7.3 Humic acid certificate of analysis

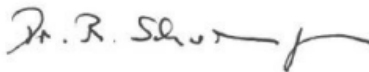
**SIGMA-ALDRICH**

3050 Spruce Street, Saint Louis, MO 63103 USA  
 Email USA: techserv@sial.com Outside USA: eurtechserv@sial.com

#### Certificate of Analysis

**Product Name:** Humic acid  
 technical  
**Product Number:** 53680  
**Batch Number:** BCCD6371  
**Brand:** Aldrich  
**CAS Number:** 1415-93-6  
**Formula:**  
**Formula Weight:**  
**Quality Release Date:** 03 NOV 2020

TEST	SPECIFICATION	RESULT
APPEARANCE (COLOR)	BLACK	BLACK
APPEARANCE (FORM)	POWDER OR CRYSTALS	POWDER
THIN LAYER CHROMATOGR.	CORRESPONDS TO STANDARD	CORRESPONDS TO STANDARD
SOLUBILITY (COLOR)	BROWN TO VERY DARK BROWN	VERY DARK BROWN
SOLUBILITY (TURBIDITY)	TURBID WITH INSOLUBLES	COMPLIES
SOLUBILITY (METHOD)	0.1G IN 10ML WATER	0.1G IN 10ML WATER
PH	--	5.9
RESIDUE ON IGNITION	--	28.3 %



Dr. Reinhold Schwenninger  
 Quality Assurance  
 Buchs, Switzerland

## 7.4 All element concentrations from the first measurement on the ICP-MS

Table 14: all results from the first analyse done at the ICP-MS.

Element	Na	Mg	Al	S	K	Ca
Unit	[ mg/l ]	[ mg/l ]	[ ug/l ]	[ mg/l ]	[ mg/l ]	[ mg/l ]
K34 1	2.03±1.11	45.3±2.42	2.59±1.04	285.3±2.44	27.6±1.42	243.3±2.929
K34 2	2.19±1.93	44.3±3.61	7.20±1.99	286.0±4.83	29.0±3.10	231.6±0.960
K34 3	2.14±4.75	44.5±5.90	3.92±0.99	269.3±2.41	28.9±3.60	228.5±2.557
RV4G 1	6.86±1.10	21.1±2.26	0.09±6.12	311.2±1.98	10.6±1.99	351.7±1.253
RV4G2	7.37±2.28	22.5±2.09	0.07±1.39	308.0±2.10	11.6±3.98	362.1±1.098
RV4G 3	6.86±2.61	21.0±2.85	0.09±22.6	283.9±1.53	8.59±2.83	335.5±2.610

Element	Ti	V	Cr	Mn	Fe	Co
Unit	[ ug/l ]	[ ug/l ]	[ ug/l ]	[ ug/l ]	[ ug/l ]	[ ug/l ]
K34 1	<LOD	<0.12	<LOD	2947±1.641	10836±2.809	366.8±1.012
K34 2	<0.56	0.153±10.11	<LOD	2930±3.934	29010±4.636	375.6±2.400
K34 3	<0.56	<0.12	<LOD	2954±2.329	20992±2.822	368.0±3.857
RV4G 1	<LOD	4.859±0.727	<LOD	2830±1.312	<LOD	<50.8
RV4G2	<0.56	4.274±0.796	<LOD	3068±2.198	<LOD	<50.8
RV4G 3	<0.56	3.129±0.419	<LOD	3030±1.697	<LOD	<50.8

Element	Ni	Cu	Zn	Ge	As	Se
Unit	[ ug/l ]	[ ug/l ]	[ ug/l ]	[ ug/l ]	[ ug/l ]	[ ug/l ]
K34 1	4183.±2.003	<LOD	2311.±1.537	1.181±2.813	1.863±0.917	6.023±2.661
K34 2	4389.±5.275	<LOD	2474.±1.825	2.593±2.928	2.558±0.383	6.143±9.440
K34 3	4472.±4.863	<LOD	2380.±3.191	1.902±3.621	2.576±1.817	5.701±2.569
RV4G 1	<1119	<LOD	497.6±1.892	0.091±2.119	0.870±2.011	8.168±6.011
RV4G2	<1119	<LOD	600.9±2.590	0.098±4.462	0.803±0.549	7.664±5.464
RV4G 3	<1119	<LOD	650.5±2.447	<0.08	0.545±4.204	7.683±7.836

Element	Sr	Zr	Nb	Mo	Ag	Cd
Unit	[ ug/l ]	[ ug/l ]	[ ug/l ]	[ ug/l ]	[ ug/l ]	[ ug/l ]
K34 1	2238±1.243	<LOD	<LOD	17.19±2.739	<LOD	81.72±1.636
K34 2	2126±2.152	<0.01	<LOD	19.83±0.490	<LOD	84.39±1.064
K34 3	2186±3.644	<LOD	<LOD	24.61±2.056	<LOD	82.38±2.950
RV4G 1	5240±1.534	0.014±6.396	<0.04	693.3±1.531	0.043±9.866	56.17±0.518
RV4G2	5679±3.111	<0.01	<LOD	749.6±0.748	<0.03	59.67±2.019
RV4G 3	5323±1.966	<0.01	<LOD	636.5±1.650	0.036±18.17	61.22±0.938

Element	Sn	Sb	Cs	Ba	La	Ce
Unit	[ ug/l ]	[ ug/l ]	[ ug/l ]	[ ug/l ]	[ ug/l ]	[ ug/l ]
K34 1	<LOD	1.296±1.579	0.372±2.668	30.22±2.051	13.06±2.435	25.22±2.141
K34 2	<LOD	1.238±3.919	0.476±6.454	30.59±6.485	17.65±1.687	37.55±1.794



K34 3	<LOD	1.304±3.969	0.538±1.908	33.93±1.895	14.50±3.139	28.69±3.255
RV4G 1	<LOD	7.798±1.548	0.166±5.603	38.04±1.643	<LOD	<LOD
RV4G2	<LOD	7.992±1.428	0.166±5.797	37.40±4.109	<LOD	<LOD
RV4G 3	<LOD	6.012±0.818	<0.12	40.22±5.602	<LOD	<LOD

Element	Tl	Pb	Th	U
Unit	ug/l	mg/l	[ ug/l ]	[ ug/l ]
K34 1	3.44±0.04	0.58±0.01	<LOD	105.6±0.753
K34 2	3.83±0.07	1.15±0.01	<LOD	181.0±1.220
K34 3	3.31±0.10	0.77±0.01	<LOD	125.0±2.668
RV4G 1	0.52±0.00	5.23*E-3±0.54*E-3	<LOD	292.4±1.320
RV4G2	0.51±0.01	5.07*E-3±0.67*E-3	<LOD	354.9±2.160
RV4G 3	0.42±0.00	4.45*E-3±0.49*E-3	<LOD	231.9±1.519

## 7.5 All elements in the standards for ICP-MS analysis

The elements marked A/B come from a multi-standard, either 71 A (Inorganic ventures, IV-ICPMS-71A) or 71 B (Inorganic ventures, IV-ICPMS-71B). All other elements are added using standards from inorganic ventures.

Table 15: the total concentration of all elements added to the multi-standard used for analysis of all samples on the ICP-MS.

Name	Total concentration	unit	71 A-B
Li	20	µg/l	
Be	20	µg/l	A
Na	2	mg/l	
Mg	2	mg/l	
Al	20	µg/l	A
P	220	µg/l	
S	20	mg/l	
K	2	mg/l	
Ca	20	mg/l	
V	20	µg/l	A

Cr	20	µg/l	A
Mn	220	µg/l	
Fe	20	µg/l	A
Co	20	µg/l	A
Ni	120	µg/l	
Cu	20	µg/l	A
Zn	520	µg/l	
As	20	µg/l	A
Sr	520	µg/l	
Mo	520	µg/l	
Cd	20	µg/l	A
Sn	20	µg/l	B
Sb	20	µg/l	B
Ba	120	µg/l	
La	20	µg/l	A
Ce	20	µg/l	A
Pr	20	µg/l	A
Nd	20	µg/l	A
Sm	20	µg/l	A
Eu	20	µg/l	A
Gd	20	µg/l	A
Dy	20	µg/l	A
Ho	20	µg/l	A
Er	20	µg/l	A
Tm	20	µg/l	A
Yb	20	µg/l	A
Lu	20	µg/l	A
Pb	20	µg/l	A
Th	20	µg/l	A
U	20	µg/l	A
Ta	20	µg/l	B
W	20	µg/l	B

Nb	20	μg/l	B
Zr	20	μg/l	B
Tb	20	μg/l	
Hf	20	μg/l	B
Ti	20	μg/l	B
Ge	20	μg/l	B
Se	20	μg/l	A



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