The mobility of uranium from U-containing bedrock materials as a function of pH: Implications for tunnel construction

Mobilitet av uran fra forskjellige bergarter som funksjon av pH: implikasjoner for tunnelbygging

Tari Anne Helmers

NORWEGIAN UNIVERSITY OF LIFE SCIENCES
Department of Plant and Environmental Sciences
Master Thesis 60 credits 2013

Preface and acknowledgements

This thesis has been submitted as the culminating project for a Master's of Science degree in Radioecology from the Norwegian University of Life Sciences and the Department of Plant and Environmental Sciences. The research was conducted between 2012 and 2013 in collaboration with the Norwegian Public Roads Administration (NPRA) for "NORWAT", a research and development program, established at UMB. The experimental planning was a collaborative effort between Professor Brit Salbu, Professor Lindis Skipperud, and myself, at the Isotope Laboratory and the Center of Environmental Radioactivity.

The aim of the project was to improve the understanding of environmental contamination from road construction in areas with naturally-occurring radioactive material. Hopefully, this research will not only be of use to the NRPA for risk assessment analysis and waste management planning, but also provide information to the scientific community on the practical challenges of environmental radioactivity.

Firstly, I would like to express my sincere gratitude to my main advisors, Brit Salbu and Lindis Skipperud. Your passion and commitment to educating students on the importance of Radioecology is truly inspiring. This project would not have been possible without your dedication to the program, or your insightful inputs.

I would also like to acknowledge Dr. Sondre Meland. Thank you for introducing me to the magic of multivariate analysis. You have forever changed how I will look at large data sets. Also, a special thanks to Karl-Andreas and Solfrid for their help with the ICP-MS, Dr. Per Hagelia for imparting his extensive geological wisdom and providing crucial feedback, Marit Pettersen for her help with experimental setup, and Halldis Fjermestad for sharing data, time and a lab workbench with me. It was truly pleasure to share a project with you. Additional thanks are owed to Kyle Elkin for partaking in many brainstorming discussions with me throughout the process of this project. Your inputs never ceased to be thoughtful and intellectual. I am incredibly grateful for all of your time that I have taken.

Finally, a large bit of gratitude is due to my family (Gerry, Jess, Vicky & Orrin) who has been so supportive of my studies and, also understanding about my being so far from home. I love you all and could not have done any of this without you.

Abstract

According to amendments made to the Norwegian Pollution Control Act in 2011, naturally occurring radioactive material (NORM) is now to be considered as an environmental contaminant, in addition to organic pollutants and trace metals. Alum shale areas are rich in radionuclides and, thus, must now be treated as contaminant sources. The substrate media analyzed in this work was collected from a future tunnel construction site that is being built in the Gran municipality on Highway Rv4. The bedrock in the Gran municipality is rich in U-bearing minerals. Therefore, there is high potential for environmental contamination from the rock material removed for tunnel construction purposes.

Environmental contamination is strongly correlated with the mobility and bioavailability of metals and radionuclides in natural systems. The present work focuses upon the effects of pH and the contact time (substrate media: solution) on the mobility of uranium, in aerobic conditions. In order to identify the effects of pH and contact time on mobility, sample cores collected from an area rich in alum shale were subjected to an extended leaching experiment. In this experiment, the substrate materials were treated with five different pH solutions (2, 4, 6, 7 & 8) and were analyzed for contact times of two hours, one day, one week and one month. In addition, the results were compared to data from a sequential extraction experiment performed by Halldis Fjermestad (MSc student). This data was used to characterize the binding mechanisms (speciation) of uranium in substrate materials of interest. The mineralogical make-up of the substrate material was determined using XRF, XRD and ICP-MS, while the elemental composition of the extracts was determined using ICP-MS.

Of the four sample cores analyzed, two were classified as containing black shale material and two with limestone material. In the leaching experiment, the mobilization of uranium in all of the substrate material was affected by the pH of solution. All of the samples were capable of quickly buffering pH solutions with a pH as low as 4 to neutral-alkaline conditions. This was attributed to the carbonate minerals present in all of the substrate materials studied. However, all of the substrate material had a much lower buffering capacity for the pH 2 solutions. Therefore, the effects of pH on mobility were observed in two groupings: media treated with pH 2 solutions and media treated with pH 4-8 solutions. The black shale materials were particularly sensitive to the pH 2 treatment, mobilizing 25-36% of the total uranium, compared to the 2-21% mobilization noted in the limestone materials. In contrast, the pH 4-8 treatments resulted in the mobilization of 1-15% of total uranium for black shale and 0-12% for limestone.

The kinetics of U-mobilization were further described using principal component analysis (PCA). PCA was performed to illustrate the relationship between U and trace elements in extracts, and the relationship between mobilized U/trace elements and contact-time. The mobilization of these elements produced a logarithmic relationship in relation to contact time, and equilibrium conditions were typically reached around one-month's contact time.

Overall, the results of the present work should have strong implications for the handling of waste materials generated from road / tunnel construction in alum shale areas.

Sammendrag

Ifølge endringene i den norske forurensningsloven i 2011, naturlig forekommende radioaktivt materiale (NORM) er nå å anse som en miljømessig forurensning, i tillegg til organiske miljøgifter og spormetaller. Alunskifer områder er rike på radionuklider, og må dermed behandles som kontaminerende kilder. Bergartene analysert i dette arbeidet ble samlet inn fra en fremtidig RV4 tunnel byggeplass i Gran kommune, Norge. Berggrunnen i Gran kommune er rik på U-bærende mineraler, slik som alunskifer. Derfor er det ett potensial for miljøforurensning fra disse bergartene ved tunnelbygging.

Miljøforurensning er sterkt korrelert med mobilitet og biotilgjengelighet av metaller og radionuklider i naturlige systemer. Dette arbeidet har fokusert på virkningene av pH og kontakttiden (substrat media: løsning) på mobiliteten av uran i aerobe forhold. For å identifisere effekter av pH og kontakttid på mobilitet, ble prøver fra borekjerner innsamlet fra et område som er rikt på alunskifer benyttet i eksperiment. I dette eksperiment ble mineralene behandlet med fem forskjellige pH-løsninger (2, 4, 6, 7 og 8) ved kontakttider på to timer, en dag, en uke og en måned. I tillegg ble resultatene sammenlignet med data fra en sekvensiell ekstraksjon prosedyre utført av Halldis Fjermestad (MSc student). Disse data ble benyttet for å karakterisere urans bindingsmekanismer (spesiering) i nineralene av interesse. Den mineralogiske sammensetning i prøvene ble bestemt ved hjelp av XRF, XRD og ICP-MS, mens elementsammensetningen av ekstraktene ble bestemt ved hjelp av ICP-MS.

Av de fire borekjerner, ble to klassifisert som svart skifer og to som kalkstein. I utlekkingsforsøket ble mobilisering av uran i alle prøver påvirket av pH i løsningen. Alle mineralene var i stand til raskt å bufre pH-løsninger med en pH så lav som 4 til nøytral-alkaliske betingelser. Dette ble tilskrevet karbonatmineraler til stede i alle de studerte prøvene. Imidlertid hadde alle mineralene en mye lavere bufferkapasitet for pH 2 løsningene. Derfor ble effekten av pH på mobilitet gruppert i to grupper: prøver behandlet med pH 2 og media behandlet med pH 4-8 løsninger. Svart skifer materialene var spesielt følsomme for pH-2-behandling, hvorav 25-36% av uran ble mobilisert, sammenlignet med 2-21% i kalksteinsmaterialer. I kontrast resulterte pH 4-8 behandlinger til mobilisering av 1-15% av total uran for svart skifer og 0-12% for kalkstein.

Kinetikken til U-mobilisering ble ytterligere beskrevet ved hjelp av prinsipal komponent analyse (PCA). PCA ble utført for å illustrere forholdet mellom U og spormetaller i ekstraktene, og forholdet mellom mobilisert U / spormetaller og kontakt-tiden. Mobilisering av elementer som funksjon av kontakttid ga ett logaritmisk forhold, og likevektsbetingelser ble vanligvis nådd rundt én måneds kontakttid.

Samlet sett bør resultatene av dette arbeidet kunne gi føringer for håndtering av mineralavfall som genereres fra vei- og tunnelbygging i alunskifer områder.

List of Abbreviations

Bq	Becquerel
Eh	Redox potential
EPA	United States Environmental Protection Agency
ICP-MS	Inductively-Coupled Plasma Mass Spectrometry
Kd	Dissociation constant
LMM	Low Molecular mass
LOD	Limit of Detection
LOQ	Limit of Quantification
NORM	Naturally-occurring radioactive material
NPRA	Norwegian Public Roads Administration
PC1	First Principal Component
PC2	Second Principal Component
PC3	Third Principal Component
PCA	Principal component analysis
ppm	Parts Per Million
PRB	Permeable Reactive Barrier
R2	Correlation Coefficient
RPM	Rotations per minute
RT	Room Temperature
Rv4	Highway “Riksvei” 4
SRM	Standard Reference Material
TENORM	Technologically-enhanced naturally-occurring radioactive material
USA	United States of America
UMB	Norwegian University of Life Sciences
WHO	World Health Organization
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

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1. Introduction & Background

Uranium is an element that is ubiquitous throughout the natural environment. In uranium has been identified in at least 60 different minerals. U-238 constitutes 99.3% of these naturally occurring isotopes. Though uranium poses a weak radiological hazard, it can also be chemically toxic. Also, it decays into very radiotoxic elements, such as radium and polonium, making it an element of ecotoxicological concern (Choppin, Liljenzin, & Rydberg, 2002).

Figure 1 illustrates the decay chain of U-238 (EPA, 2012a). The parent product, U-238, slowly undergoes α-decay with a half-life of 4.5 billion years. This chain of radioactive decay ends with the stable lead isotope, Pb-206, after undergoing eight α-decay steps and six β-decay steps. Along the way, radium, radon and polonium isotopes are produced as daughter products. These daughter products are a source of concern, due to their high radiotoxicities and high environmental mobilities. For example, radium, a chemical analogue of calcium, is easily dissolved in groundwater. In addition, radon is a nobel gas that can be easily released from groundwater infiltrating soils and subsequently the basements of houses. As radon travels through the environment, it deposits its daughter products along the way (Choppin et al., 2002). Following inhalation, the particle reactive (i.e associated with dust) daughter products of radon, Po-210 and Pb-210, can be deposited in the lungs, inducing lung cancer. Historically, radon's daughter products have had a significant effect on health in Scandinavia, due to the abundance of uranium in the region's geological makeup (Strand et al., 2001; Strand, Jensen, Anestad, Ruden, & Ramberg, 2005).

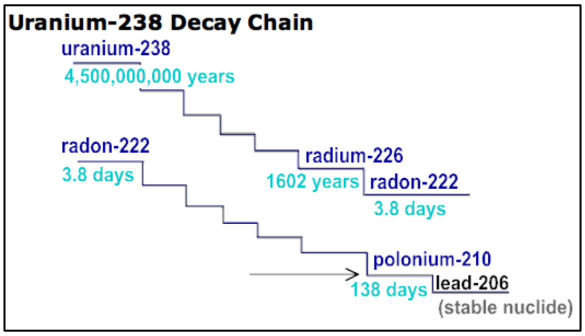


Figure 1: The U-238 decay chain and its daughter products (EPA, 2012a).

In 2011, the Norwegian Pollution Control Act was amended to include radioactive materials as contaminants, in addition to trace metals and organic compounds (Lovdata, 2004). Therefore, regulations on radioactive materials are no longer exclusive to the nuclear industry, but also apply to naturally occurring radioactive materials (NORM) and technologically enhanced radioactive materials (TENORM) or radioactive material derived from non-nuclear industries.

Previously, most of the attention to radionuclides in the environment focused upon anthropogenic sources; however, NORM is ubiquitous and has been present in the Earth's crust since the formation of the Earth (EPA, 2012b). These radionuclides are increasingly ecologically relevant when released into the environment by human activity such as uranium mining, road construction, oil and gas extraction or the processing of phosphate fertilizers (Betti et al., 2004; EPA, 2012b). Increases in NORM, due to processes such as these, was previously referred to as TENORM (EPA, 2012b). Today, TENORM is included in the term, NORM.

Radioactivity from NORM is a matter of concern in all corners of the world. Internationally, research has been conducted on the environmental effects of uranium mining and milling wastes (Carvalho, Oliveira, Lopes, & Batista, 2007; Fernandes, Simoes, Perez, Franklin, & Gomiero, 2006; Hancock, Grabham, Martin, Evans, & Bollhofer, 2006; Landa & Gray, 1995) Even in the artic environment of Svalbard, increases of radionuclides from the Uranium and Thorium series have been documented due to the extraction and processing of coal (Dowdall et al., 2004). In addition, results from the Marina II project suggested that NORM from the oil/gas industries and phosphate processing industries have been larger contributors of radioactivity to the North Sea than the nuclear industry since the mid-1980s (Betti et al., 2004). Findings such as these suggest that it is equally as important to study the effects of NORM on the environment as to study inputs of radionuclides from the nuclear industry.

By amending the Pollution Control Act to include radioactive materials, the Norwegian government has taken the position that NORM is also to be handled as a contaminant. This has significant implications on road construction in Norway, where roads/tunnels are often built through areas with high NORM levels. This study will focus upon one such instance, where a tunnel is to be built through a region containing high NORM levels.

A new tunnel has been planned near Gran, approximately 70 km north of Oslo, in the relocation of Highway Rv4. The geology within the Oslo region is incredibly complex. In this area, the bedrock alternates between uranium-rich alum shales/granites and uranium-poor sedimentary/mafic igneous rocks. In addition, these sediments include sporadic layers of superficial deposits of marine clays and glaciofluvial sands/gravels (Smethurst, Sundal, Strand, & Bingen, 2008). In the municipality of Gran, over 35% of houses have recorded radon concentrations over the Norwegian regulatory limit of 200 Bq/m3 (Smethurst et al., 2008). These high radon concentrations are a direct repercussion of the uranium-rich alum shales and granites in the region.

Alum shale is a sedimentary rock that is more generally classified as “black shale”. These formations are usually comprised of silicate/sulfide minerals, calcite, limestone, organic matter, and are rich in trace metals and radionuclides (Falk, Lavergren, & Bergback, 2006). In addition to having generally higher concentrations of radionuclides and trace metals, alum shales typically have high concentrations of sulfides, making them high risk for acidification. When the reduced sulfides are exposed to moisture and air, they become oxidized and form sulfuric acid (Kjeldby, 2012).

According to the Norwegian Pollution Control Act §2-3, all bedrock material that forms acid or leaches pollutants when in contact with water or air should be treated as contaminants (Lovdata, 2004). Historically, alum shales are known to have acidifying effects and contain radionuclides (Falk et al., 2006), and are therefore required to be treated as contaminants. However, there are immense practical issues related to handling large amounts of waste material, such as the rock material removed during tunnel construction. Thus, road construction in alum shales poses a challenge, due to the high potential for environmental contamination, and the large scale of waste material generated.

In order to determine the risk of environmental contamination, it is of particular importance to determine the mobility of uranium and trace metals found in rock materials from projected road construction sites and their binding mechanisms. By determining the speciation and mobility of uranium and trace metals, better predictions can be made on the transport of contaminants in the environment (Prikryl, Pickett, Murphy, & Pearcy, 1997; Salbu & Skipperud, 2009). The mobility of uranium in the environment has been studied extensively, with most literature suggesting that pH is one of the most important parameters (Echevarria, Sheppard, & Morel, 2001; Langmuir, 1978). This work will also focus upon the effects of pH and contact time between the substrate media and solution.

2. Hypotheses and Objectives

Based on available literature, it is hypothesized that:

(i) Tunnel construction, in the Gran area, will result in the disturbance of large amounts of U-enriched alum shale;
(ii) NORM in the accrued waste will exceed regulatory limits and be classified as radioactive waste;
(iii) The exposure of alum shale to oxygen and moisture will decrease the pH and increase the mobility of U/trace elements;
(iv) The mobility of U/trace elements will be dependent upon pH and contact time with aqueous solution;
(v) The potential mobility of U will influence the risk evaluations of the tunnel waste material, and aid in the selection of appropriate countermeasures for handling the waste material.

The overall objective of the present work is to investigate the mobility of U and associated trace elements as a function of contact time (solution: substrate media) and pH for media collected from an area rich in alum shale. This knowledge will be used to better predict the risk of U-mobilization from road construction on Highway Rv4 and to suggest appropriate waste management techniques. Based on substrate materials collected from the proposed Rv4 tunnel construction site near Gran, the work has been focused on specific research tasks:

(i) Characterize the highly variable sample media with respect to mineralogical properties and chemical composition (U and selected trace elements) using X-ray diffraction (XRD) and inductively coupled mass spectrometry (ICP-MS);
(ii) Determine the buffering capacity of various medias when subjected to various pH levels;
(iii) Measure U concentrations in extracts from leaching and sequential extraction experiments;
(iv) Measure the effect of pH and contact-time on the mobilization of U from the sample media;
(v) Identify the relationship of between mobilized U and Th, S, Al, Ca, Mn, Fe, Co and Mo using principal component analysis (PCA);
(vi) Evaluate the potential mobility of U in alum shale waste from Highway Rv4.

2. Theory

2.1 Speciation of Radionuclides

Radionuclides naturally occur in different physico-chemical forms, varying with respect to nominal molecular mass, charge properties, valence, oxidation state, structure, morphology, density, and degree of complexation (Salbu & Skipperud, 2009). Figure 2 illustrates the various size fractionations of radionuclides and their corresponding mobilization/immobilization mechanisms. The size fractions can be described in three categories: LMM, colloid/nanoparticles, and particles. LMM (low molecular mass) is considered to be highly mobile and potentially bioavailable to organisms, while colloids/nanoparticles are mobile but not readily available for active uptake. Particles, on the other hand, are neither mobile nor highly available. The particle fraction slows down the transfer of radionuclides through the environment by becoming part of the solid-state (Salbu & Skipperud, 2009). However, these fractions vary with time as conditions change. Therefore, mobilization of particles and immobilization of LMM may shift the size fractionations toward more or less mobile and bioavailable species.

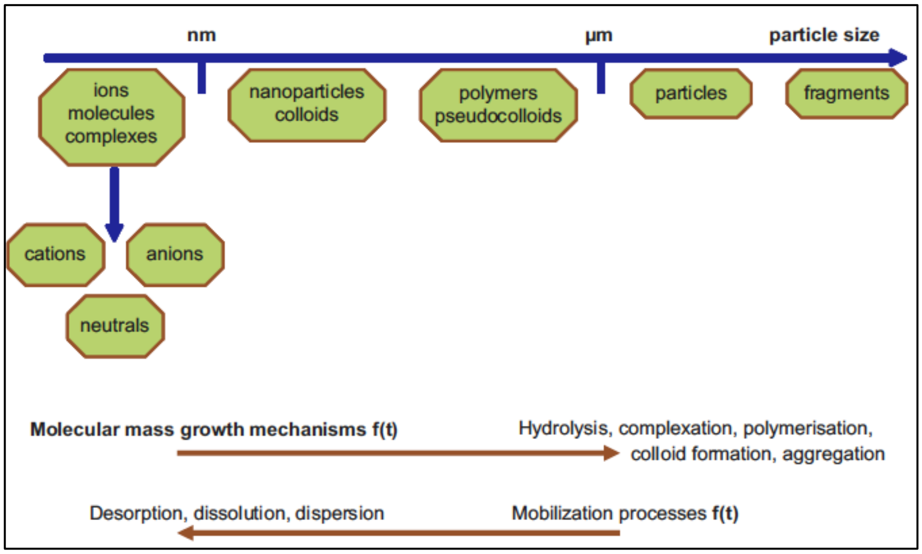
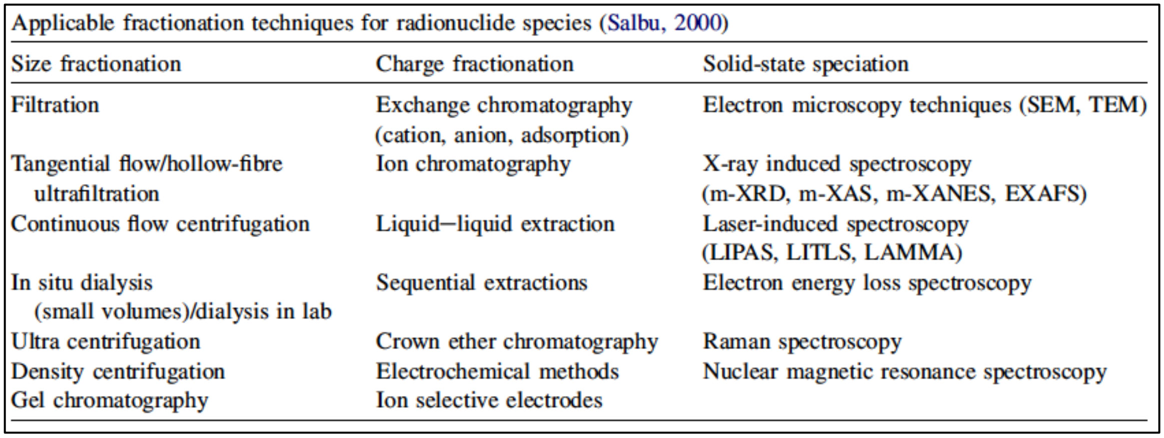


Figure 2: This figure illustrates the three major size fractions (LMM, colloids/nanoparticles, particles) and the various mobilization/immobilization processes that affect the size distribution (Salbu & Skipperud, 2009).

The various species of radionuclides behave and interact with organisms and the environment in very different ways. A better understanding of the bioavailability and mobility of radionuclides in the environment can be achieved by characterizing the speciation of radionuclides (Salbu & Skipperud, 2009). In Salbu & Skipperud 2009, *speciation of radionuclides* is defined as the following: “The speciation of radionuclides is the distribution of a radionuclide amongst defined chemical radionuclide species in a system.” By implementing the “speciation of radionuclides”, radionuclides are described by their physico-chemical properties, rather than their total concentration. This provides a more accurate depiction of radionuclides’ environmental fate.

There are numerous methods currently used to characterize the physico-chemical attributes of radionuclides. A summary of these methods can be seen in Table 1. Filtration and centrifugation techniques can effectively separate radionuclides based upon size. In addition, they can be coupled with ion chromatography to provide information about the charge distribution within fraction. Solid-state speciation illustrates the distribution and size of particles on a microscopic level. This technique provides essential information to determining the future risk of transferring radionuclides to the environment through weathering processes. Lastly, sequential extractions are also commonly used to determine the mobility of radionuclides (Salbu, 2007). This study utilized sequential extraction, in order to illustrate the binding mechanisms of U/trace elements to the solid-phase, and in turn, describe its mobility.

Table 1: Fractionation techniques for radionuclide speciation analysis (Salbu, 2007).



Applicable fractionation techniques for radionuclide species (Salbu, 2000)

Size fractionation	Charge fractionation	Solid-state speciation
Filtration	Exchange chromatography (cation, anion, adsorption)	Electron microscopy techniques (SEM, TEM)
Tangential flow/hollow-fibre ultrafiltration	Ion chromatography	X-ray induced spectroscopy (m-XRD, m-XAS, m-XANES, EXAFS)
Continuous flow centrifugation	Liquid—liquid extraction	Laser-induced spectroscopy (LIPAS, LITLS, LAMMA)
In situ dialysis (small volumes)/dialysis in lab	Sequential extractions	Electron energy loss spectroscopy
Ultra centrifugation	Crown ether chromatography	Raman spectroscopy
Density centrifugation	Electrochemical methods	Nuclear magnetic resonance spectroscopy
Gel chromatography	Ion selective electrodes	

2.2. Alum Shale

2.2.1. Mineralogy

Alum shale is a sedimentary rock that is more generally classified as “black shale”. These formations are usually comprised of silicate/sulfide minerals (i.e. pyrite, marcasite), calcite, limestone, organic matter, and are rich in metals. Additionally, alum shale is an argillaceous, and often carbonaceous material. Alum shale deposits originate from sediment material in shallow ocean areas that were anaerobic and had a high influx of both organic and inorganic material (Falk et al., 2006; Gautneb & Sæther, 2009).

2.2.2. Alum Shale in the Oslo Rift

The bedrock geology of the Oslo Rift alternates between uranium-rich areas (alum shale/granite) and uranium-poor areas (sedimentary/ mafic igneous). Intermittent layers of marine clay and glaciofluvial sands and gravel deposits further complicate this alternation (Smethurst et al., 2008). Figure 3, taken from Smethurst et al. (2008), illustrates the variation in bedrock geology near the Gran municipality. Alum shale is typically found in the Cambrian and Lower Ordovician stratigraphic sequences of the Oslo Rift. While the Lower Cambrian shales were typically deposited in an aerobic environment, the Upper

Cambrian/Lower Ordovician sequences were deposited in an anaerobic environment. The anaerobic environment enabled the formation of black shales, including alum shales. The excess of hydrogen sulfides (H_2S) in the alum shales is indicative of the reducing environment that existed during deposition (Gautneb & Sæther, 2009).

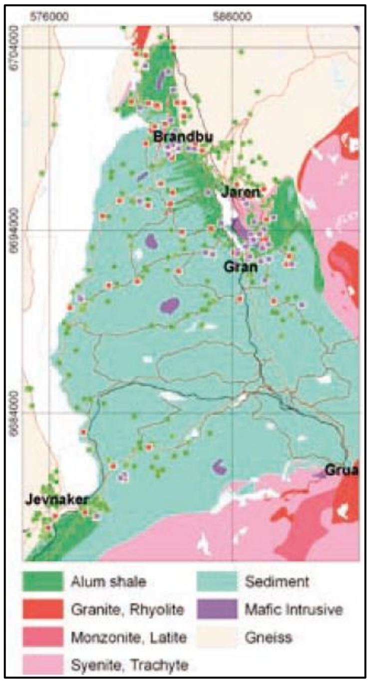


Figure 3: Map illustrating the bedrock geology in the Gran municipality. The green alum shale and red granite regions indicate substrate with high concentrations of radionuclides (Smethurst et al., 2008).

2.2.3. Environmental Concerns from Alum Shale

There are a variety of environmental concerns associated with alum shale. These concerns include radon gas emission, health effects due to radiotoxic radon daughter products, acidification and ecotoxicological effects from trace metals and radionuclides.

The concentrations of radon in Norway are among the highest in Europe. Principally, this has been related to the prevalence of radionuclide-rich alum shale. Some areas in Norway have recorded radon concentrations greater than 10,000 Bq/m^3 (Strand et al., 2005). In a study conducted in the Gran municipality, over 35% of the houses had radon concentrations greater than 200 Bq/m^3, with 3.5% of those registering levels greater than 1,000 Bq/m^3 (Smethurst et al., 2008). Therefore, many of the homes in Gran have radon levels far surpassing the Norwegian regulatory level for radon of 200 Bq/m^3 (NRPA, 2000). A map of the hazard levels for radon gas and placement of alum shale in the Gran region is shown in Figure 4. Long-term exposure to radon and its daughter products can have significant impacts upon health. It has been suggested that this type of exposure is responsible for 14% of all new cases of lung cancer every year in Norway (Strand et al., 2001).

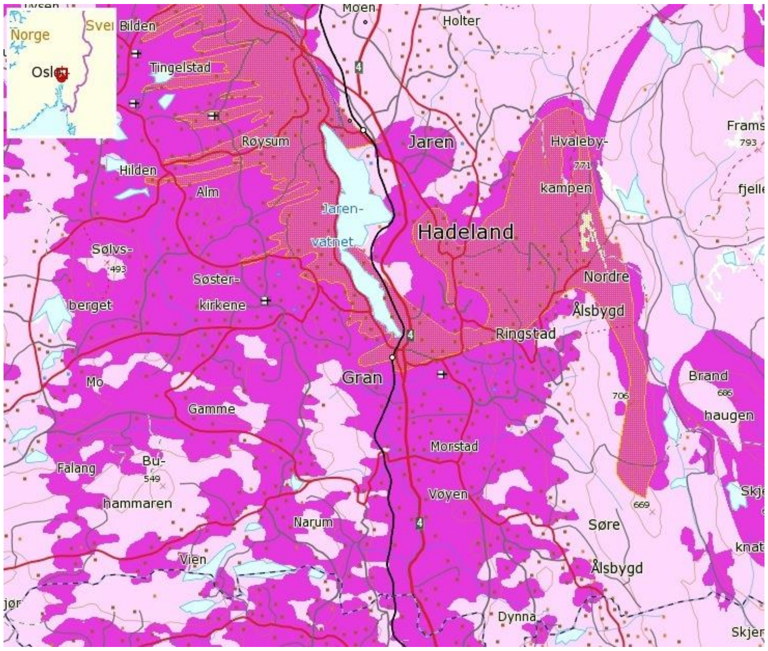


Figure 4: Map of Radon gas hazard. The dark pink represents regions of high concentrations of radon gas, while the light pink represents moderate concentrations. The orange dotted overlay indicates areas of alum shale, which are known to be high in Uranium. (NGI, 2013)

In addition to radon emissions, the high concentrations of sulfides typically found in alum shale, such as pyrite or marcasite, make the material high risk for acidification. Oxidation of pyrite (FeS_2) occurs when the material is exposed to oxygen and water and results in the generation of sulfuric acid (Butler, 1994). This process can be accelerated by the presence of *Acidithiobacillus* bacteria, which produce ferrous iron and sulfate through the oxidation of pyrite (Garcia, Bigham, & Tuovinen, 2007).

$$4FeS_2 + 13O_2 + 2H_2O \rightarrow 4FeSO_4 + 2H_2SO_4 + 2SO_4$$

As large amounts of alum shale are disturbed during road construction, the potential for acidification is increased. Acidification stems from the increased exposure to moisture and oxygen. A case study from Tennessee, USA describes a situation in which road fill (consisting of black shale with high alum contents) was deposited near a stream after road construction was completed in 1963. The exposure of this material to air and precipitation lead to the formation of acid drainage and precipitation of aluminum hydroxides. The combination of changes in aqueous pH and increased aluminum concentrations resulted in a fish kill, stretching eight kilometers downstream from the dumpsite. The ecological effects of this incident were still evident after 25 years (Hammarstrom, Seal, Meier, & Jackson, 2003). This case study demonstrates that while the direct consequences of acidification can be damaging, the secondary effect of metal release due to a lowering of pH has additional ramifications.

Alum shale, traditionally, has a much higher concentration of NORM and metals than other sedimentary lithologies (Falk et al., 2006; Galindo et al., 2007). Uranium, in particular, has been reported to have an average geochemical background of 2-25 ppm in black shales (Galindo et al., 2007). In the Oslo Rift, the highest total concentration of uranium (126 mg/kg) was found in the Upper Cambrian stratigraphy of the alum shale formation. The average concentration of uranium, however, was found to be 29 mg/kg (Nyland & Teigland, 1984). Abiotic factors such as redox potential (Eh), pH and organic matter content are important for describing alum shale's ability to retain these metals (Kashem & Singh, 2001).

There are two processes that are largely responsible for the mobilization of metals/radionuclides from metal-bearing alum shales. The first process entails the desorption of metals/radionuclides when the oxidation of sulfide leads to more acidic conditions. However, it is important to note that the presence of a buffering agent, such as calcium carbonate, can reduce or even prevent the effects of acidification. The second process is the release of metals/radionuclides from silicate/organic complexes. This form of mobilization occurs when sulfuric acid generated from sulfide oxidation damages the binding of the metal/radionuclide complexes, allowing the metals/radionuclides to be solubilized/dissolved (A. S. Jeng, 1991; B. F. Jeng et al., 1991). The release of metals/radionuclides found in alum shales into the environment can have significant ecotoxicological effects.

2.3. Uranium

2.3.1. Chemistry

Uranium is a naturally-occurring radioactive element that can be found in low concentrations in rock, soil and water samples throughout the earth (EPA, 2012c). In fact, it is one of the most frequently found radionuclides in groundwater and surface waters (Li et al., 2013). There are three major isotopes that comprise naturally-occurring uranium: U-238 (99.3%), U-235 (0.71%), and U-234 (0.01%). The half-lives of these isotopes are 4.51×10^9, 7.13×10^8, and 2.48×10^5 years, respectively (EPA, 1999). Uranium has five valence states (+2, +3, +4, +5 and +6) (Hirose, 2012). Of these five, only two are stable oxidation states U(IV) and U(VI) (Qiao, Hansen, Hou, Aldahan, & Possnert, 2012). Tetravalent uranium, U(IV), is the most dominant form in reduced environments, while U(VI) is more prevalent in oxidized environments (EPA, 1999). Uranium in the tetravalent form is extremely resistant to leaching, while U(VI) has a higher mobility due to its tendency to form strong uranyl carbonate complexes that are easily dissolved (Qiao et al., 2012). Due to weathering, U is also present as mineral particles, along with a series of trace metals.

2.3.2. Mineralogy

When assessing the risk of uranium mobilization, it can be of particular importance to consider which U minerals are present. In fact, the solubility of U-bearing minerals can be more indicative of U mobilization than Kd (dissociation constant) (Elless & Lee, 1998). Table 2 lists commonly found uranium minerals and the oxidation state of U in the mineral species. The U(IV) minerals uranitite and coffinite are essentially insoluble species of U-bearing minerals (Langmuir, 1978). The U(VI) species are all uranyl minerals listed with an increasing solubility. Carnotite has been observed to mobilize less than 1 µg U/L when at equilibrium and at a neutral pH. In contrast, Rutherfordine has been shown to reach 27 mg U/L at a neutral pH, and uranophane can solubilize up to 120 mg U/L at a pH of 8.5 (Langmuir, 1978).

Table 2: Mineral Species of Uranium (Langmuir, 1978; Murakami, Ohnuki, Isobe, & Sato, 1997)

Mineral Species	Formula
U (VI)	
Carnotite	$K(UO_2)_2(VO_4)_2$ x 1-3H_2O
Tyuyamunite	$Ca(UO_2)_2(VO_4)_2$ x 7-11H_2O
Autunite	$Ca(UO_2)_2(PO_4)_2$ x 8-12H_2O
Uranium Phosphate Minerals	$(UO_2)_3(PO_4)_2$ x 4H_2O
Rutherfordine	UO_2CO_3
Uranophane	$Ca(UO_2)_2(SiO_3)(OH)_2$ x 5H_20
U (IV)	
Uraninite	UO_2
Coffinite	$USiO_4$ x H_20

2.3.3. Environmental Contamination

Excessive amounts of uranium in the environment can result in negative ecological and health effects. In humans, the inhalation or ingestion of excessive amounts of uranium (an alpha/gamma emitter) can lead to cancer or kidney damage (EPA, 2012c). In addition, groundwater that is contaminated with uranium can increase radiation exposure through multiple pathways. For example, humans or animals may directly ingest the uranium as drinking water. Also, the contaminated water could be used to irrigate crops, which could then lead to soil contamination or ingestion through plant uptake. Finally, a high water table could introduce the contaminant into soils. Wind and other erosion mechanisms could further distribute the radionuclides and increase risk for inhalation (Koch-Steindl & Prohl, 2001). For these reasons, governments and international organizations have imposed regulations to reduce exposure to uranium.

The United States Environmental Protection Agency (US EPA) established 30 µg U/L to be the maximum acceptable concentration of uranium in drinking water in the Safe Drinking Water Act and 52 mg/kg for uranium in soils (Elless & Lee, 1998; EPA, 2012c). While the World Health Organization (WHO) previously suggested a maximum concentration of 15 µg U/L (based upon extrapolations from animal studies), a new action level of 30 µg U/L (based upon epidemiological studies) has been suggested as a replacement (Hirose, 2012).

Though Norway does not have regulatory levels for uranium in groundwater, a study conducted by Frengstad et al. (2000) determined that 18% of the 476 Norwegian groundwater samples analyzed had concentrations greater than 20 µg U/L and 3% were over 100 µg U/L. The highest concentrations were found in samples taken from granite-rich areas in the Caledonian orogenic belt (Frengstad, Skrede, Banks, Krog, & Siewers, 2000).

2.3.4. Abiotic Mobility Mechanisms

The mobility of uranium in natural waters can be affected by the following mechanisms: sorption/desorption and precipitation/dissolution (Murakami et al., 1997). Oxidation-reduction processes and complexation formations further describe these mechanisms and the mobility of uranium (McLean & Bledsoe, 1992).

Sorption/Desorption

Sorption can be defined as the “accumulation of ions at the interface between a solid phase and an aqueous phase” (McLean & Bledsoe, 1992). In sorption, ions are not incorporated into the solid phase; rather, they are bound to the surface of soil particles. On the other hand, desorption is the release of the surface-bound ion back into solution. There are multiple factors that control sorption processes. Among these, pH and Eh have been found to be the most significant parameters (Langmuir, 1978). In an equilibrium study conducted by Langmuir 1978, sorption mechanisms were determined to be more demonstrative of uranium mobility than mineral precipitation. In non-carbonate, aqueous environments, ferric oxyhydroxides have been found to be the most effective minerals at adsorbing uranium (Milton & Brown, 1987). This effect was observed in a sequential extraction study conducted using two contaminated sediments from a lake in Norway (Øvre Heimdalsvatnet), where 50% of the uranium was associated with Fe-Mn oxides (Qiao et al., 2012).

Precipitation/Dissolution

Precipitation differs from sorption, in that, it involves the incorporation of the metal ion into a mineral structure (McLean & Bledsoe, 1992). It is also dependent upon the solubility constant of the interacting ions. Precipitation mechanisms essentially immobilize uranium and prevent it from entering the aqueous phase. In oxidizing and saturated soil environments, the transport of U(VI) in groundwater can be inhibited by phosphate minerals. Phosphate minerals are able to precipitate uranium from solution as uranyl phosphate minerals and immobilize U(VI) (Jerden, Sinha, & Zelazny, 2003). When these precipitates are formed, the co-precipitation of trace metals may also occur due to sorption mechanisms.

In contrast to precipitation, dissolution is the release of uranium from uranium-bearing minerals. There are a variety of reactions that may induce the dissolution of uranium- bearing minerals. Among these are the complexation of uranium with inorganic/organic materials and reduction/oxidation reactions (Jerden et al., 2003; Luo & Gu, 2011). For example, uranium precipitates can undergo dissolution due to the oxidation of ferric iron and nitrate or the complexation of uranium with organic ligands/humic substances (Luo & Gu, 2011).

Inorganic/Organic Complexation

A complex is a “unit in which a central metal ion [radionuclide] is bonded by a number of associated atoms or molecules in a defined geometric pattern” (McLean & Bledsoe, 1992). The complexation of uranium can either increase or decrease its mobility, depending upon the solubility of its complexing ligands (McLean & Bledsoe, 1992). The most significant complexing species for uranium is carbonate, which is derived from atmospheric carbon dioxide and carbonate minerals (Giblin, Batts, & Swaine, 1981). The complexation of U(IV) from U-bearing mineral to carbonate can result in the increased mobility of uranium (Buck, Brown, & Dietz, 1996). An example reaction is shown below:

$$UO_2 + \frac{1}{2}O_2 + 3CO_3^{2-} + H_2O \rightarrow [UO_2(CO_3)_3]^{4-} + 2OH^-$$

Uranyl ions have also been found to preferentially form carbonate complexes in neutral-alkaline waters, leading to increased U solubility (Echevarria et al., 2001; Elless & Lee, 1998; Sandino & Bruno, 1992). The uranyl-carbonate complexes are not readily sorbed to soil surfaces, having a stronger affinity for the aqueous phase. These complexes may increase the concentration of dissolved uranium (Elless & Lee, 1998). In a study conducted on 13 different soil types by Echevarria et al. (2001), it was shown that soils containing high amounts of carbonate had by far the lowest U-238 sorption ratios, despite their high pH. Echevarria et al. suggested that the amount of carbonate in a system was a better predictor of uranium mobility than any soil properties, including the parameter that historically has been considered the most important, pH.

Oxidation-Reduction

The oxidation-reduction conditions of a system are critical for predicting the mobility of uranium (McLean & Bledsoe, 1992). The hexavalent form of uranium has much higher mobility than U(IV) and primarily exists in aerobic conditions (EPA, 1999). The uranyl (U(VI)) cations are more mobile due to their tendency to form water-soluble complexes with ligands, such as carbonate (Echevarria et al., 2001). In addition to steering complexation, oxidation-reduction conditions can also affect the dissolution or desorption of uranium. In oxidizing conditions, Fe(III) precipitates from solution as highly adsorptive ferric hydroxides. These precipitates are highly effective as scavenging metals out of solution and immobilizing uranium. However, when these precipitates encounter reducing conditions Fe(III) is reduced to Fe(II) and the metals are re-released into solution (McLean & Bledsoe, 1992).

2.3.5. Biotic Mobility Mechanisms

While the abiotic physico-chemical properties of radionuclides play a major role in determining their fate in the environment, there are also biotic factors that affect the transfer of radionuclides. Microbial activity can also greatly influence the mobilization/immobilization of radionuclides (Gadd, 1996).

Biotic Immobilization

There are four major mechanisms through which organisms can immobilize radionuclides, including biosorption, accumulation, reduction and precipitation (Gadd, 1996).

Biosorption describes when radionuclides are bound to microorganisms through physico-chemical mechanisms such sorption. This process is similar to adsorption in soil structures, but binds to nuclides to the cell wall of the microbe instead. This mechanism can lead to the formation of very stable minerals.

Accumulation represents when the radionuclides are incorporated into the biological structure of the microbe. The mechanisms for this vary from radionuclide to radionuclide.

Reduction occurs when anaerobic microorganisms use the oxidized form of a metallic element (or radionuclide) as the terminal acceptor for respiration (such as sulfate-reducing bacteria). The reduced forms of the metallic element can be more soluble than their oxidized forms. The microbes that reduce sulfate and ferric iron can also reduce U(VI) to U(IV). These microbes have been shown to immobilize uranium from uranyl-carbonate complexes through reduction; however, the presence of nitrate/nitrite can inhibit microbes' abilities to immobilize uranium (Senko, Istok, Suflita, & Krumholz, 2002).

Precipitation can occur alongside the reduction mechanism. For example, as sulfate-reducing bacteria reduce metal oxides for respiration, they precipitate metal sulfides such as ZnS, FeS, and CuS.

Biotic Mobilization

Just as microbes are capable of immobilizing radionuclides, they also have the capability to mobilize radionuclides. Two mechanisms that result in the mobilization of radionuclides are autotrophic and heterotrophic leaching (Gadd, 1996). Autotrophic leaching takes place when microbes oxidize mineral ores in aerobic conditions. In fact, microbes are used commercially in this way to extract uranium from mineral ores (Gadd, 1996). Heterotrophic leaching occurs when bacteria or fungi produce protons, organic acids or chelating agents. The chelating agents then form soluble complex molecules with metal ions and carry the ions into solution. The release of organic acids can lead to a localized drop in pH, releasing the metal cations from their bindings to soil. It has been reported that the weathering of minerals and the solubility of contaminants increases drastically in regions with high biological activity, particularly the root-soil interface (G. E. Brown & Calas, 2011). The reasoning behind this is that the high production of organic acids in the root-soil interface, which serves as an energy source for the microbial community, also can lower the pH up to 2 units in comparison to the bulk soil (G. E. Brown & Calas, 2011).

3. Methods & Materials

3.1. Field Site

The field site is located between Gran and Jaren, approximately 70 km north of Oslo. This location is the projected site of a tunnel that will be built in the restructuring of Highway Rv4. Figure 5 is an aerial photo of the region in which the tunnel will be built. The area has large spans of alum shale and high levels of radon gas have been recorded in the houses located in the Gran municipality (Smethurst et al., 2008). Therefore, the site is a potential pollution hazard and investigations are needed to determine the risk posed to the environment from the excavated tunnel material.

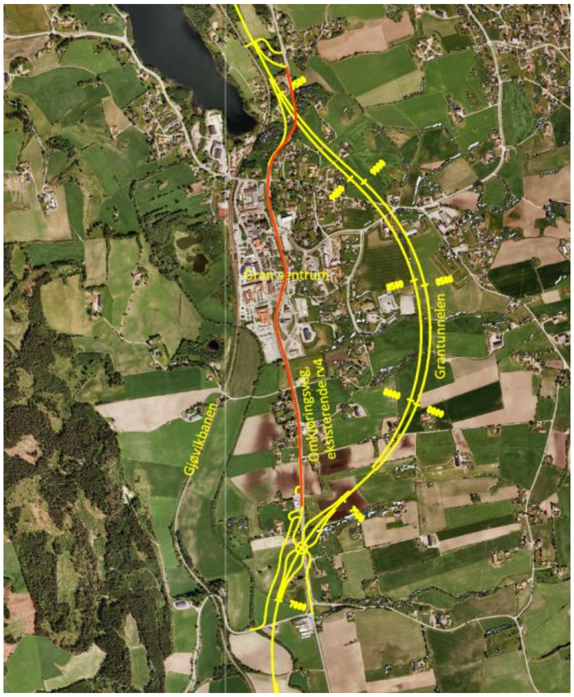


Figure 5: Aerial photo of field site. The red line indicates the current location of highway Rv4, the yellow line indicates the proposed tunnel location.

3.2. Sample Collection

Personnel from NPRA collected the samples alongside the proposed tunnel site between Gran and Jaren in 2005. Ten boreholes were drilled five meters into the bedrock with samples being taken from each meter. At each meter's depth, the material was checked for homogeneity and a subsample was taken. The substrate materials consisted of varying bedrock medium, including limestone, black shale and alum shale. After collection, the substrate media were stored in plastic containers at room temperature.

3.3. Sample Selection

3.3.1. Screening with X-ray Fluorescence (XRF)

X-ray fluorescence (XRF) allows for the analysis of major and trace elements in rocks, minerals and sediments. In XRF analysis, the instrument emits an x-ray beam which then excites and ionizes the atoms in the sample material. The excited atoms then emit a fluorescent x-rays at energies that are indicative of the elemental composition of the sample (Wirth & Barth, 2012).

XRF was implemented in order to conduct a non-destructive, semi-quantative surface analysis of 50 samples (5 depths per the 10 sites). The hand-held XRF analyzer, SPECTRO xSORT, Ametek®, was used to complete the analysis. Each sample was measured five times, providing the mean concentration of elements present in each sample. The results from this analysis were then included in the principal component analysis (PCA).

This was done to select samples for the leaching experiment and sequential extraction procedure.

3.4. Leaching Experiment Method

All of the sedimentary rock samples collected were sieved and the <2 mm portion was collected for analysis. From each sample, 2.00 ± 0.05 grams of material was weighed out five times into centrifugation tubes. Then, unbuffered pH solutions consisting of distilled water, NaOH and H_2SO_4 were created for five pH levels: 2, 4, 6, 7 and 8. Each sample of substrate material was leached using 20 mL of the five different pH solutions (solid:solution = 2 g:20 mL). After the pH extraction solution was added, the samples were continuously agitated on an analog tube roller board (Stuart™ roller mixer SRT6). The roller board operated at a speed of 33 rpm while simulating a rocking and rolling motion. Samples were removed after four different time periods (two hours, one day, one week, and one month) to provide information on the effects of contact time between the substrate media and solution. The samples were then centrifuged at 10000 RPMs using a Beckman Coulter™ Allegra 64R centrifuge. After centrifugation, 18 mL of the 20 mL of solution was pipetted out and the supernatant was transferred to 20 mL plastic vials with plastic caps. The sample material was then immediately re-washed with 18 mL of the freshly prepared, corresponding pH solution, and placed back on the roller board. The supernatants (or extracts) were then analyzed for pH using a pH electrode (WTW inoLab® pH 720), and later analyzed using ICP-MS.

3.5. Sequential Extraction Experiment

In sequential extraction experiments, different extraction reagents are utilized in order to categorize the binding mechanisms between radionuclides/trace metals and the solid-phase of sediments. In addition, the reagents used in sequential extraction provide information about the reversible/irreversible interactions between radionuclides and the solid-phase (Salbu, 2000; Tessier, Campbell, & Bisson, 1979).

The sequential extraction experiment discussed in the present work was based upon the protocol proposed by Tessier et al. (1979) and modified by Salbu (2000). The experimental procedure performed by Halldis Fjermestad at the Norwegian University of Life Science, in the Isotope Laboratory/Center of Environmental Radioactivity. The conditions of the extraction and the reagents that were used are described in Table 3.

Table 3: Fractionation procedure of sequential extraction performed by Halldis Fjermestad. (RT = room temperature).

Step	Fraction	Extraction Reagent	Extraction Conditions	
			Contact-time (hours)	Temperature
1	Water-soluble	H_2O	1	RT
2	Reversibly-bound	1M NH_4Ac - pH 7	2	RT
3	Reversibly bound: associated with carbonate	1M NH_4Ac - pH 5	2	RT
4	Easily reduced compound compounds: (Fe/Mn hydroxides)	0,04M $NH_2OH{\cdot}HCl$ in 25% Acetic acid (pH~ 3)	6	80°C
5	Oxidized Compounds: (Organic material or Uranium oxides)	H_2O_2 30% (pH~2) (15 ml)	5.5	80°C
		3,2M NH_4Ac (5 ml)	0.5	RT
6	Acid-Dissolvable	7M HNO_3	6	80°C

3.6. Analysis Methods

3.6.1 Inductively-Coupled Plasma Mass Spectrometry (ICP-MS)

Inductively-Coupled Plasma Mass Spectrometry combines a high-temperature source (inductively-coupled plasma) with a mass spectrometer in order to analyze the elemental compositions of sample materials. First, the ICP source ionizes the atoms in the sample, then the ions are separated and measured with a mass spectrometer (Wolf, 2013).

The present work implemented an ICP-MS instrument (8800 Triple Quadrupole ICP-MS Agilent Technologies®) for the analysis of extract solutions and substrate materials. An internal standard was added to the extract solutions for instrument calibration, and five aliquots were injected into the ICP-MS, producing a mean value of the elemental composition. In order to measure the elemental composition of the substrate material used in the extractions, two subsamples of each substrate material and three standard reference soils were dissolved using HNO_3 and HF. The samples were then autoclaved until completely dissolved. An internal standard was then added to the samples, and ran on the ICP-MS instrument.

3.6.2. X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) is an analytical technique that is commonly used to identify crystalline stuctures (i.e. minerals) in environmental samples. Each mineral has a unique crystalline structure that can be characterized using XRD. In XRD, an x-ray is directed at a sample and when certain geometric conditions are satisfied (as described by Bragg's Law), the scattered x-rays can constructively interfere and produce a diffracted beam. These beams are detected and counted. The relationship between these beams and the angle in which they are measured provide information about the lattice spacing in a crystalline sample, and in turn, about the mineral present in the sample (Dutrow & Clark, 2012).

For the present work, subsamples of the media used in the leaching/sequential extraction experiments were pulverized with an electric mortar and pestle (Retsch™ Mortar Grinder RM 200) for four minutes. Per Hagelia and Hans-Jørgen Berg analyzed these samples using XRD at the Natural History Museum in Oslo on April 7th, 2013. The samples were analyzed from 2° to 70° on the 2-theta scale at a rate of 0.050° per second. The minerals were further identified using the database of Powder Diffraction Files from the International Center for Diffraction Data.

3.7. Statistical Methods

3.7.1. Principal Component Analysis (PCA)

Principal component analysis (PCA) was implemented as a tool for both the selection of samples and the interpretation of results. PCA is a multivariate statistical method. The method is based upon finding the most descriptive direction of variability, in this case between the samples and their elemental variables. These dimensions of variability are called principal components. By determining the principal components of a data set, PCA allows for the reduction of multidimensionality. One issue with multivariate methods is that missing values cannot be computed in the algorithms. Therefore, when concentrations of certain elements were below the level of detection, the replacement method from Tsanis et al. 1994 was adopted. This method consists of replacing all values lower than the limit of detection with a value that is ½ the level of detection (Tsanis, Xu, & Marsalek, 1994). When presenting the results of PCA , score plots are given to illustrate the relationship between rows of data (samples). The loading plots, on the other hand, describe the relationship between the original variables (elements) (Næs, Brockhoff, & Tomic, 2010). The PCA was conducted using Minitab™ 16 statistical software ("Minitab 16 Statistical Software," 2010).

3.7.1. Linear Regression Analysis

Linear regression analysis was implemented to determine the correlation between principal component score values and the contact time between solution and substrate media in the leaching experiment using Minitab™ ("Minitab 16 Statistical Software," 2010). Linear regression is a modeling technique that predicts the values of a dependent variable (y) in relation to an independent variable (y), and is also commonly known as the “line of best fit” method. This generates a linear equation that can be used to predict the dependent variable in reference to the independent variable, and vice versa (Næs et al., 2010).

In this linear combination, a correlation coefficient (R^2) is also calculated. This coefficient measures how closely associated the two variables are and ranges from a -1 to 1 scale. A negative correlation coefficient denotes a negative linear relationship between the variable, while a positive correlation coefficient denotes a positive linear relationship. The further away from zero that a correlation coefficient is, the more associated the two variables are. A value of 1.0 implies that the linear equation describe 100% of the variation in y as explained by x. This would imply that y was perfectly described by x. Typically, a strong correlation coefficient is anything greater than $R^2=0.80$ (Næs et al., 2010).

In order to determine if the correlation coefficients were statistically significant, p-values were also generated using Minitab™. In science, while it is not possible to “prove” a hypothesis to be true, disproving its opposite can lend support to the hypothesis. This is the underlying theory, which the statistical significance of p-values is based upon. The p-value is related to the null hypothesis. In the case of linear regression analysis, the null hypothesis is that the correlation coefficient is not a truly representative of the relationship between y and x, but has only been generated through chance. The smaller a p-value is, the smaller the probability there is that the null hypothesis is true. Therefore, a p-value of 0.01 indicates that there is a 99% probability that the correlation coefficient was not generated by chance, but is truly representative of the relationship between x and y. Generally, a p-value ≤ 0.05 is the value accepted as being statistically significant (Næs et al., 2010).

4. Results and Discussion

4.1. Quality Analysis

4.1.1. Quality of ICP-MS analysis

The quality of the ICP-MS analysis was determined by including tests for precision and accuracy. In order to test the precision of the analysis, five parallels of material collected from site 8681, depth 3-4 m were prepared in the same manner and analyzed using ICP-MS. The results from this analysis are displayed in Table 4. This table provides the average concentrations (mg/kg), standard deviation and coefficient of variation for the nine elements discussed in this study. The coefficient of variation, which is calculated by dividing the standard deviation by the mean, describes the relative variation observed for each element. The coefficients of variation range between 1-6 % illustrating that the analysis had good precision. Literature has suggested that coefficients of variation less than 30 % are considered indicators of good to fair precision in a data set (C. E. Brown, 1998). The variation observed between the five parallels is most likely attributed to slight variations in the materials collected, rather than the variations in the ICP-MS analysis.

Table 4: Precision of ICP-MS analysis. Results from five parallels.

Analysis of Parallels from Site 8681 Depth 3-4m Substrate Material			
Element	Mean (mg/kg)	Standard Deviation (mg/kg)	Coefficient of Variation
Al	68000	1000	1%
S	3200	200	6%
Ca	29000	1000	3%
Mn	540	10	2%
Fe	50000	1000	2%
Co	26	1	4%
Th	8	0.2	3%
U	6.9	0.1	1%

In addition to testing for precision, the accuracy of the ICP-MS analysis was determined by measuring three standard reference materials. The results of the accuracy test are displayed in Table 5. Table 5 displays the expected values for the reference materials, the measure values, and the % error calculated for each measurement. The percent error was calculated using this following equation:

$$\%\ error = \frac{|Observed\ Concentration - Expected\ Concentration|}{Expected\ Concentration} \times 100$$

The first reference material, SRM® 2709a, was a soil used to test the accuracy of the ICP-MS analysis for Al, Ca, Mn, Fe, Th and U. The analysis of this material provided fairly accurate (< 10% error) measurements for calcium, manganese and uranium. Iron and thorium had a larger percent error and were classified as having fair to poor accuracy. Aluminum, on the other hand, had a very high percent error (118 %). Due to the fact that aluminum was found to have high precision in the ICP-MS analysis and very low accuracy, there appears to have been a systematic error. Some possible explanations for this systematic error include contamination of the standard reference material, or the miscalibration of the instrument.

The other two reference materials, soils NCS DC 73324 & 73325, were used to determine the accuracy of the instrument's measurements of S, Mn, Co, Th and U. The analysis of these reference materials provided results that were highly accurate recording % errors between 0-6 % for the five elements analyzed.

Table 5: Accuracy of ICP-MS analysis. Results from standard reference materials.

Reference Material	Element	Al	S	Ca	Mn	Fe	Co	Th	U
		(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
SRM® 2709a	Expected Range	13000-17000	-	12000-14000	380-450	22000	-	10.7-11.1	3.1-3.2
	Observed	37000	620	15000	490	26000	12	8.4	3.1
	% Error	118%	-	7%	9%	18%	-	21%	0%
NCS DC 73324	Expected Range	-	217-303	-	1368-1532	-	6.5-8.7	21-25	6.0-7.4
	Observed	97000	220	1400	1400	46000	6.1	21	6.9
	% Error	-	0%	-	0%	-	6%	0%	0%
NCS DC 73325	Expected Range	-	214-286	-	1667-1893	-	91-103	8.4-9.8	1.8-2.6
	Observed	160000	220	1100	1600	98000	100	9.2	2.1
	% Error	-	3%	-	4%	-	0%	0%	0%

Limit of Detection and Limit of Quantification

In addition to testing for precision and accuracy, blanks were also included in the analysis to determine the limit of detection (LOD) and limit of quantification (LOQ). The LOD represents the concentration that was measureable by the ICP-MS, while the LOQ represents the concentration that has a high enough confidence level to be subjected to further statistical analysis. The two limits were calculated using the following equations:

$$LOD = 3 \times standard\ deviation(concentration\ of\ blanks)$$
$$LOQ = 10 \times standard\ deviation(concentration\ of\ blanks)$$

The LOD and LOQ calculated for the elemental concentrations of substrate media used in this study are listed in Table 6. Values below the LOQ were not included in the any analysis of the media. These values were also not included in the analysis of data generated from the aqueous extracts of the substrate materials. LOD and LOQ values for the ICP-MS analysis of the aqueous extracts from the substrate materials can be found in Appendix IV.

Table 6: Limit of Detection and Limit of Quantification for the ICP-MS analysis of the elemental concentration of substrate media.

Element	Al	S	Ca	Mn	Fe	Co	Th	U
Limit of Detection (mg/kg)	0.6	17	1.8	0.7	1.0	0.004	0.000	0.004
Limit of Quantification (mg/kg)	1.9	57	6.1	2.3	3.4	0.012	0.001	0.013

4.1.2. Leaching experiment

Contamination from pH electrode

During the leaching experiment, the extracts taken were analyzed immediately using a pH electrode. The electrode was kept in solution until the pH reading had stabilized, which typically took approximately five minutes for the extracts and 45 minutes for the reagent blanks. These same extracts were then analyzed using ICP-MS. Exceptionally high levels of Ag, Cd, Cu and Zn were in the reagent blanks, and this was attributed to the leaking of metals from the pH electrode. Therefore, the data for these elements was rendered obsolete and removed from the analysis.

Carryover Effect

Instead of having four parallels (one for each contact-time) of all samples, each sample had its solution extracted and was re-washed with the reagent pH solution at all four respective contact-times. During this process, 18 mL aliquots of solution were extracted. Then, a fresh 18 mL of pH reagent solution was added to the substrate media. This was done for practical reasons. However, the 2 mL of solution left in the vial, added increased the concentration of analytes in the freshly added solution. In Table 7, an example of this "carryover" effect is shown. While the carryover effect did result in the overestimation of uranium leached from the three later time periods, it was relatively insignificant when compared to the total concentration of uranium in the substrate media. The last two columns in Table 7 represent the percentage of uranium leached with values corrected for carryover and the non-corrected values. There is very little difference between the two, with the non-corrected accounting for no more than 1 % increase in the leached concentration. This was considered insignificant, so concentrations of uranium in extracts were not corrected for carryover.

Table 7: Effect of 2 mL carryover on the analyzed concentrations of extractions.

Site	Depth	pH	Contact Time (Solution: Media)	Conc. of U-238	Conc. of U-238 Corrected for Carryover	Total Conc. of U-238 in Substrate Media	% U extracted according to non-corrected values	% U extracted according to corrected values
	m		(hours)	mg/kg	mg/kg	mg/kg		
8709	4.0-5.0	2	2	0.65	0.65	29	2%	2%
8709	4.0-5.0	2	24	0.75	0.69		3%	2%
8709	4.0-5.0	2	168	0.96	0.89		3%	3%
8709	4.0-5.0	2	672	0.51	0.42		2%	1%
8709	4.0-5.0	4	2	0.23	0.23		1%	1%
8709	4.0-5.0	4	24	0.18	0.15		1%	1%
8709	4.0-5.0	4	168	0.25	0.24		1%	1%
8709	4.0-5.0	4	672	0.73	0.70		3%	2%
8709	4.0-5.0	6	2	0.25	0.25		1%	1%
8709	4.0-5.0	6	24	0.22	0.19		1%	1%
8709	4.0-5.0	6	168	0.32	0.30		1%	1%
8709	4.0-5.0	6	672	1.06	1.03		4%	4%
8709	4.0-5.0	7	2	0.23	0.23		1%	1%
8709	4.0-5.0	7	24	0.67	0.65		2%	2%
8709	4.0-5.0	7	168	0.32	0.26		1%	1%
8709	4.0-5.0	7	672	0.85	0.82		3%	3%
8709	4.0-5.0	8	2	0.03	0.03		0%	0%
8709	4.0-5.0	8	24	0.18	0.17		1%	1%
8709	4.0-5.0	8	168	0.37	0.36		1%	1%
8709	4.0-5.0	8	672	1.22	1.19		4%	4%

4.2. Sample Selection

4.2.1. PCA Analysis of XRF data

Principal component analysis was conducted on data generated from XRF, in order to select sample materials that offered the greatest variation from the field site. Twelve samples were chosen for the leaching experiment. These samples represented four borehole locations, with samples collected from three depths within each borehole (to represent the variability within the stratigraphy). The four sites chosen were 8921, 9051, 8709, and 8841. The samples chosen are highlighted with circles in Figures 6 & 7 and described in Table 8. While Figure 6 represents the variation between samples, Figure 7 illustrates the variation in chemical composition of the substrate media and the correlation between elemental concentrations.

According to the PCA, site 8709 had a large variation between depth 4-5m and 5-6/6-7m. The shallower depth was relatively high in uranium, thorium and sulfur, while the deeper depths had stronger correlations with a high content of iron and chromium, suggesting a difference in stratigraphy between depths 4-5 and 5-6m. Site 8841 had relatively low uranium, thorium, and sulfur concentrations, and was biased towards iron and chromium. In direct contrast, site 8921, registered very strong correlations with thorium, uranium and sulfur, characteristic of a black shale.

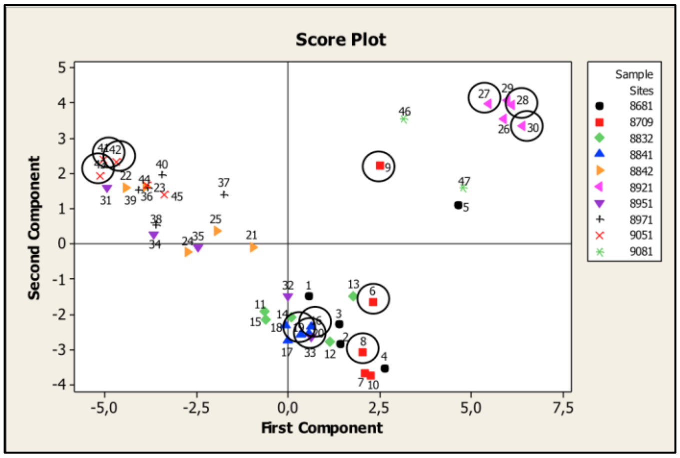


Figure 6: Score plot distribution for PCA analysis of XRF data. The circles represent the samples chosen (3 depths from 4 sites) in order to analyze the greatest variability within the samples. PC1 (48%) & PC2 (28%).

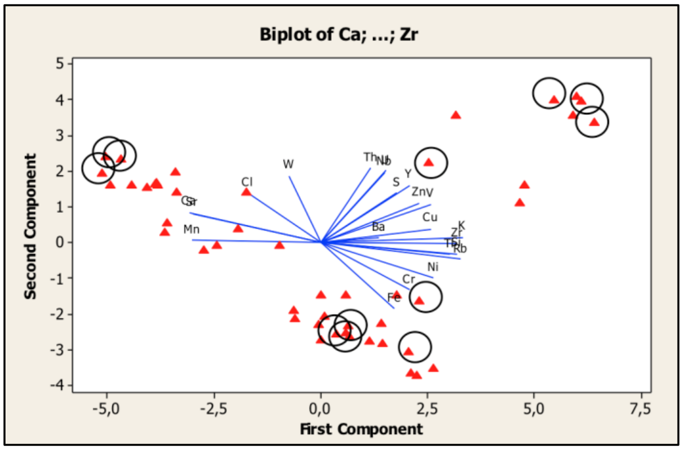


Figure 7: Biplot for PCA analysis of XRF data. The circles represent the samples chosen (3 depths from 4 sites) in order to analyze the greatest variability within the samples. PC1 (48%) & PC2 (28%).

Table 8: Samples selected for leaching experiment.

Sample Site	Sample Depth (m)
8921	3.9-4.9
8921	4.9-5.9
8921	5.9-6.9
9051	5-6
9051	6-7
9051	7-8
8709	4-5
8709	5-6
8709	6-7
8841	3.5-4.5
8841	4.5-5.5
8841	7.5-8.5

4.3. Site 8709

4.3.1. Mineralogy

The mineralogy of site 8709, depth 4-5m was analyzed using XRD. Previously, this area was reported to be a black, carbon-rich shale found in the Ordovician Period (Moen & Kveseth, 2013). The results of the XRD semi-quantitive analysis (Figure 8) showed that the material from this sample largely consists of quartz, calcite, albite, ankerite, pyrite, muscovite and kaolinite. Radionuclides and trace metals can be expected in higher concentrations in these substrate materials, and the pyrite content makes material from this region a potential source of acidification; however, the high concentration of calcite (a carbonate mineral) may serve as a buffer for any acid produced due to the oxidation of pyrite.

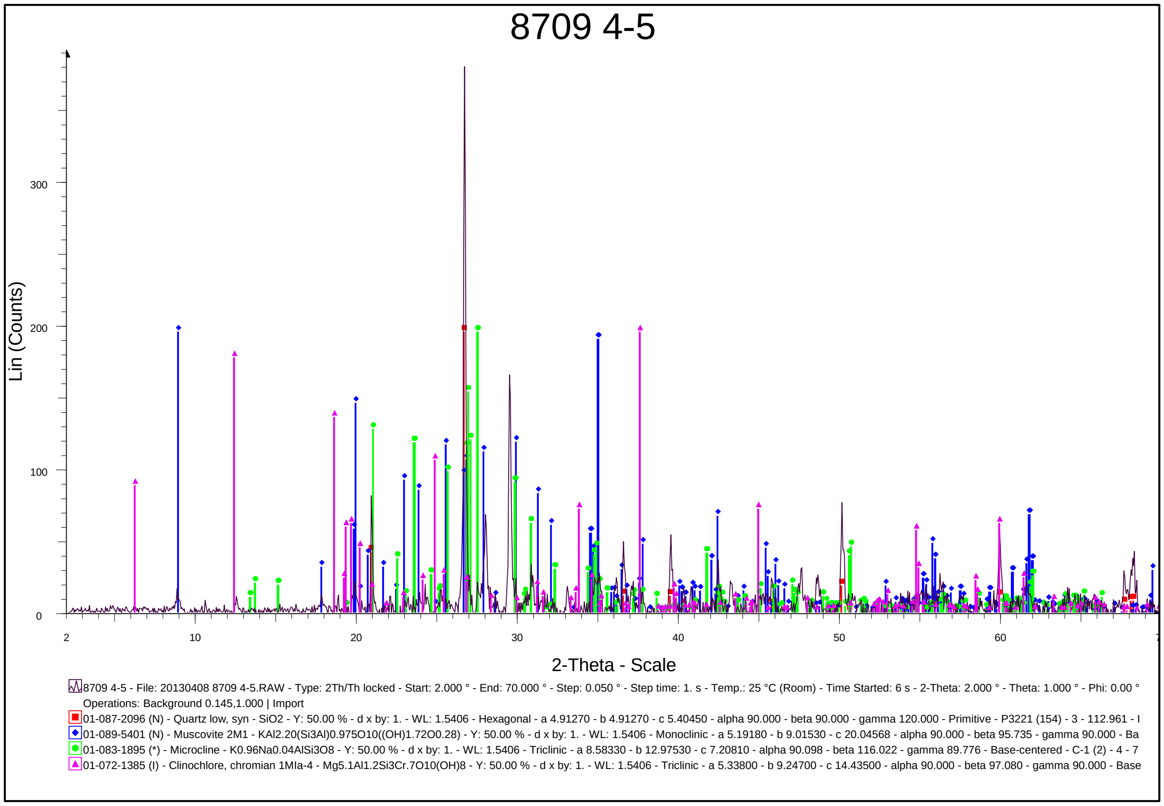


Figure 8: XRD analysis of site 8709 depth 4-5m mineralogy (Hagelia & Berg).

4.3.2. Buffering Capacity

The pHs of the extracts were recorded after 2 hours, 1 day, 1 week, and one month's contact time with the substrate media. After, the media was re-washed with the respective unbuffered pH solutions: 2, 4, 6, 7, and 8. The results are presented in Figure 9, which illustrates that all samples washed with pH solutions between 4-8 were quickly stabilized to alkaline conditions, maintaining pH levels between 8-9.5. The pH 2 solution was also neutralized once coming into contact with the media (ranging from pH 5.5-7.5) and increased logarithmically in relation to contact time. The buffering capacity, exhibited by all three depths of site 8709, suggests that the high levels of carbonate minerals in these materials served as a natural buffering material.

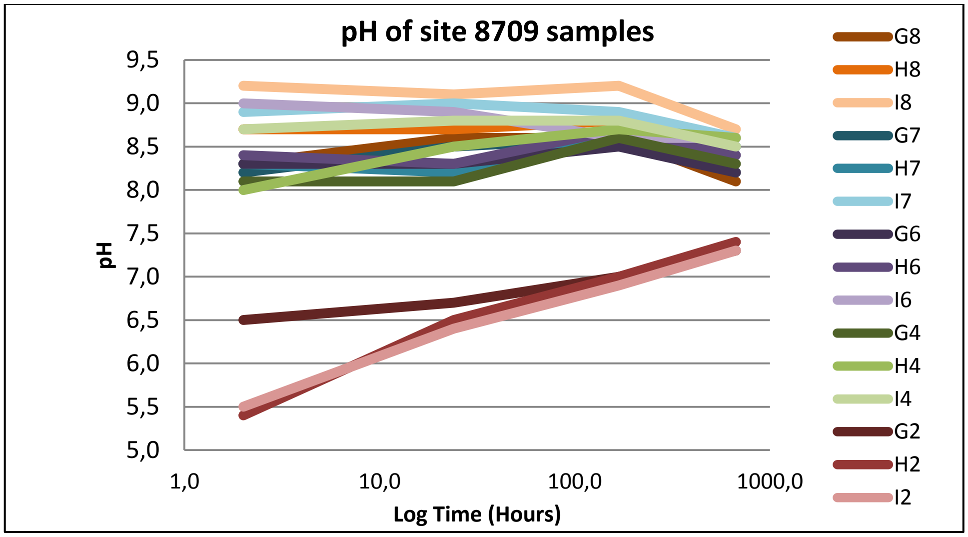


Figure 9: pH of samples from site 8709 in relation to contact time. The orange tinted lines represent samples that were washed with a pH 8 solution at 2 hours, 1 day, 1 week and 1 month, while blue, purple, green, and red represent pH 7, 6, 4 and 2, respectively. G =samples from depth 4-5m, H = 5-6m and I= 6-7m.

4.3.3. Leaching and Sequential Extraction of Uranium

The substrate material from site 8709 was leached using different pH solutions to demonstrate the effect of pH on uranium mobility. As predicted, the materials washed with the pH 2 solution had the highest release of uranium, releasing 25, 21 and 8 % of the total uranium concentration for depths 4-5, 5-6, and 6-7m, respectively (Table 9). The samples collected from depth 4-5m had a much higher total concentration of uranium than those collected from the depths 5-6 and 6-7 (2.6 & 4.8 times higher). This heterogeneity was also illustrated by the XRF analysis.

The relative fraction of uranium mobilized from media treated with solutions of pH 4, 6, 7 and 8 was much lower than was observed in the pH 2 treatment. The extracts taken from media treated with solutions 4, 6, 7 and 8 were grouped together, due to the fact that they had all been stabilized within the range of pH 8-9.5. This grouping represents the fraction of uranium mobilized in slightly alkaline, aerobic conditions. From this pH grouping, the samples from depth 4-5m had an 11 ± 3 % loss of the total uranium in the material, while depths 5-6 and 6-7 had loss of 8 ± 3 % and 3 ± 1 %. Even though this grouping had lower mobilization than the pH 2 treated media, there was still a significant loss of uranium. Thus, mobilization of uranium from neutral-alkaline conditions may still have environmental consequences.

Table 9: Relative fraction (%) of Uranium leached in accordance to pH from leaching experiment over one month's time.

Site	Depth	pH	Range of U Leached	Total U in Substrate Media	% of U Leached
			mg/kg	mg/kg	
8709	4.0-5.0	2	0.65-2.9	29	25
8709	4.0-5.0	4	0.23-1.4		9
8709	4.0-5.0	6	0.25-1.9		12
8709	4.0-5.0	7	0.23-2.1		15
8709	4.0-5.0	8	0.033-1.8		9
8709	5.0-6.0	2	0.15-1.0	11	21
8709	5.0-6.0	4	0.034-0.26		5
8709	5.0-6.0	6	0.046-0.43		7
8709	5.0-6.0	7	0.54-0.40		7
8709	5.0-6.0	8	0.2-0.5		12
8709	6.0-7.0	2	0.021-0.26	6.1	8
8709	6.0-7.0	4	0.025-0.11		4
8709	6.0-7.0	6	0.0015-0.11		3
8709	6.0-7.0	7	0.013-0.094		3
8709	6.0-7.0	8	0.014-0.071		2

Sequential extraction was performed on the samples collected from depth 4.0-5.0 in order to illustrate the binding mechanisms of uranium and to provide further information as to potential sources of mobilization. The results obtained from the sequential extraction performed by Halldis Fjermestad are shown in Table 10 and will be discussed according to step of fractionation.

Table 10: Relative fraction (%) of uranium extracted through the sequential extraction of site 8709 depth 4.0-5.0m.

Sequential Extraction of Site 8709 Depth 4.0-5.0m					
Fraction	Extraction Reagent	Average U concentration (mg/kg)	Total U in Substrate Media (mg/kg)	% of U per fraction	% of U Leached
1	H_2O	0.01	29	0	58
2	NH_4Ac (pH 7)	0.81		3	
3	NH_4Ac (pH 5)	1.20		4	
4	NH_2OH-HCl	3.43		12	
5	H_2O_2	1.60		6	
6	HNO_3	9.73		34	

1) According to the results of the first step of the sequential extraction, the amount of water-soluble uranium is negligible (0 %).

2-3) Fractions two and three, extracted with ammonium acetate of pH 7 and 5, represent the reversibly-bound fraction and the reversibly-bound fraction that is likely associated with amorphous carbonate. These fractions accounted for 3 and 4 % of the total uranium mobilized. The 7 % released from these two fractions is compatible with the 11 ± 3 % found in the leaching experiment.

4) Fraction four is representative of the easily reduced components (Fe/Mn oxides), and 12 % of the total uranium content was mobilized in this fraction. Therefore, it can be assumed that a relatively high portion of uranium had co-precipitated from solution with Fe/Mn oxides under oxidizing conditions. This is in line with previous literature, which also reported that U mobility is often dependent upon the formation of ferric oxyhydroxides in oxidizing environments(Milton & Brown, 1987). When reducing conditions were established, it is very likely that the reduction of Fe/Mn lead to the dissolution of the precipitates and released the sorbed/co-precipitated U into solution.

5) Fraction five enabled the use of hydrogen peroxide, a strong oxidizing agent. This portion is believed to be comprised of uranium that was complexed to organic matter or the U(IV) oxides that were oxidized. Six percent of uranium was released in this fraction. This may be attributed to the oxidation of fairly stable U(IV) to the more mobile U(VI) uranyl cations and their formation of soluble carbonate complexes, or the degradation of organic matter (Elless & Lee, 1998; EPA, 2012c; Sandino & Bruno, 1992; Vandenhove, Van Hees, Wouters, & Wannijn, 2007).

6) The highest fraction of U (34 %) extracted was found in the final fraction, the acid dissolvable fraction. This portion is typically immobilized until subjected to strong acidifying conditions. However, with the high levels in carbonate in the given sample, it is unlikely that such high levels of acidification as the one simulated in the sequential extraction would occur in a natural environment.

Overall, only 58 % of the total U concentration was found to be extractable, with 34 % of that being only extractable when dissolved with a strong acid. Therefore, the sequential extraction of site 8709, depth 4-5 m media implied that 42 % of the total U concentration was completely immobilized and 75 % was extremely resilient to mobilization, unless subjected to acidification. A note of importance from these findings is that an increase of 12 % uranium-mobilization would be expected in the leaching experiment if these materials were subjected to anaerobic conditions.

4.3.4. Experimental Analysis: PCA of ICP-MS data

In order to describe the relationship between the extracts from the media studied and the elements analyzed, PCA analysis was conducted. For the PCA, data from the ICP-MS analysis of the extracts taken during leaching experiment was used. The data constituted of materials from the three depths that were subjected to five pH treatments and agitated for four different contact times, totaling 60 sample solutions for the entire site. The complete ICP-MS data set and PC scores can be found in Appendix IV.

In principal component analysis, principal components are generated in order to describe the greatest range of variability. The first principal component (PC1) describes the largest percentage of variation, while the second principal component (PC2) represents the second highest proportion and so on. In the PCA of site 8709, the PC1 represented 45 % of the total variability (Table 11). PC2 accounted for 29 % of the variability and PC3 accounted for an additional 22 % of the variability. In total, these three components represented 96 % of the total variability.

Table 11: Variables from PCA of extracts associated with media taken from site 8709 and their correlation values to PC1 and PC2.

Variable	PC1 (45 %)	PC2 (29 %)	PC3 (22 %)
Al	0.24	-0.181	**0.515**
Mo	0.272	**-0.369**	**-0.399**
Mn	**0.312**	**0.484**	-0.007
Th	**0.328**	**-0.342**	**0.3**
S	**0.343**	**-0.319**	**-0.352**
Ca	**0.347**	**0.439**	-0.08
Fe	**0.358**	-0.188	**0.431**
Co	**0.383**	**0.385**	0.099
U	**0.388**	-0.046	**-0.398**

Though the correlation values are listed in Table 11, loading plots can be used to visually illustrate the correlation of the variables to PC1 and PC2. PC1 was positively correlated with all nine variables, however, it was most highly correlated with uranium, cobalt and iron. This means that as PC1 increased, so did the concentrations of these elements. PC2 is represented as the y-axis, and describes the vertical spread between variable seen in Figure 10. It was most representative of the variation within Co, Ca, S, Th, Mn, and Mo. Of these six variables, PC2 was positively correlated with Mn, Ca, and Co, and negatively correlated with Th, Mo, and S. Though PC3 is not included in the loading plot, values in Table 11 show that PC3 also explained a significant portion of the variation and was positively correlated with Al and Fe, and negatively correlated with U, Mo, and S.

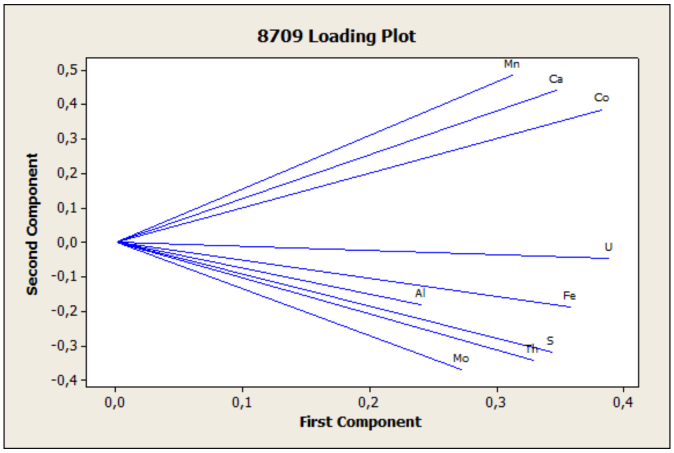


Figure 10: Loading plot illustrating the relationship between the concentration of elements found in extract associated with media from site 8709. PC1(45 %), PC2(29 %).

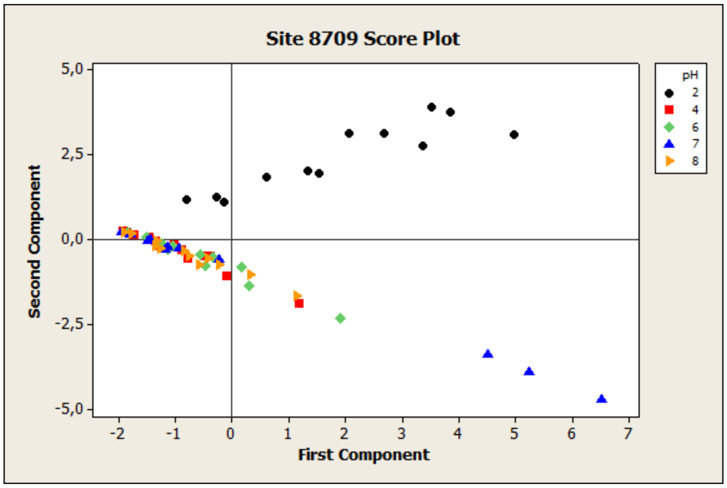


Figure 11: Score plot illustrating relationship between extracts associated with media from site 8709. PC1 (45 %), PC2 (29 %).

While the loading plot illustrates the relationship between variables, the score plot illustrates the variation between samples. Figure 11 shows the score plot generated for site 8709. In this figure, it can be seen that the samples subjected to pH 4, 6, 7 and 8 treatments followed a similar trajectory, while those subjected to pH 2 moved in an entirely different direction. When the score plot and loading plot were compared, it was observed that the pH 2 samples were highly associated with Ca, Mn, and Co, while the pH 4-8 samples are associated with Th, Mo and S.

In addition, the pH 2 treated samples typically had higher PC1 scores than the pH 4-8 samples. There was an exception of three points from pH 7, which had uncharacteristically high score values. These three data points were all derived from the 4-5m depth that had a much higher total concentration of uranium than recorded in the other two depths. It is possible that the sample material from pH 7 included a large particle of uranium that was mobilized causing high score values.

The principal components provide a better understanding of the mobility of uranium in a system. In PC1, the score numbers tend to increase as a function of contact time with the samples agitated the longest, having the highest concentrations of all elements analyzed (discussed further in 4.3.5. kinetics). This includes uranium, which recorded higher concentrations over time. Therefore, it is to be expected that uranium concentration will increase as time and PC1 score values increase.

The PC2 score values represented the variety observed between samples treated with pH 2 and samples treated with pH 4, 6, 7 and 8 (Figure 11). In relation to PC2, uranium was not significantly correlated. This implied that uranium was just as likely to be found in pH 2 samples along with high concentrations of Ca and Mn, or in pH 4-8 samples with high Al or Mn. Uranium was not highly associated with the elements analyzed. One possible explanation is that uranyl-carbonate complexes drove uranium mobility in the samples. However, the samples were not analyzed for carbonate, so it is difficult to prove this association.

PC3 exhibited a different relationship in regards to uranium. According to PC3, uranium concentrations increased as iron and aluminum decrease. This was an observation unique to site 8709. One potential explanation for this relationship may involve the interaction of these elements with phosphate. Uranyl phosphates have been found to have relatively low solubilities (Fuller, Bargar, Davis, & Piana, 2002). Therefore, the combination of uranyl ions with phosphate could reduce the concentration of uranium in solution. However, aluminum and iron have also been shown to have the ability to precipitate phosphates from natural water systems (Kopacek, Ulrich, Hejzlar, Borovec, & Stuchlik, 2001). If aluminum and iron were to out-compete uranium in the complexation of phosphates, it may reduce the amount of aluminum, iron and phosphate in solution. This would allow uranium to more easily complex with the much more mobile carbonate (Langmuir, 1978).

4.3.5. Kinetics

Modeling the kinetics of contaminant mobility is necessary for the prediction of environmental fate. The principal components scores generated from PCA were graphed in relation to time in order to provide a better understanding of the kinetics of the system. Figure 12 depicts the box plots of the PC1 score values in relation to contact time and separated by pH treatment. A clear trend can be observed, with the PC1 scores increasing with an increase in contact time. This trend is particularly strong in the pH 2 samples. The mean PC1 scores of the samples treated with pH 4-8 solutions are also fairly similar, which was to be expected seeing as the solution in all these samples stabilized in the range of pH 8-9.5. However, the large variation from the media treated with pH 7 solution, was once again evident. This may be attributed to the mobilization of a U particle from the material and could have biased the results. Therefore, the linear regression for pH 7 was not considered representative of the kinetics observed for pH 4-8 samples.

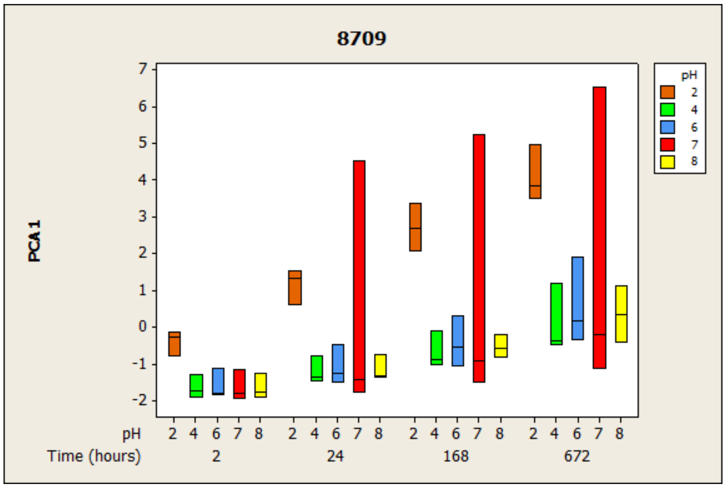


Figure 12: Relationship between PC1 scores and time for site 8709.

In order to further describe the dynamics between score values and time, equations were generated for the two main groupings (pH 2 and pH 4-8). Due to the wide variation in substrate material between depth 4-5m and depths 5-6/6-7, a graph was created for media from the two depths (Figure 13 & Figure 14).

Depth 4-5 m: The extracts of media taken from depth 5-6 m are represented in Figure 13. This figure represents the relationship of PC1 score values and contact time. Media treated with pH 4, 6 and 8 were grouped together and had a correlation coefficient of R^2= 0.78 and p-value <0.005. This implied that the contact time between solution and substrate media was a good predictor of PC1 scores and statistically significant. The samples from pH 7 were not included in the pH 4-8 grouping due to its exceptionally high PC1 score values.

Though the pH 7 grouping was not representative of the pH 4-8 grouping, the PC1 score still had a very high correlation to contact time, which was statistically significant (R^2= 0.92, p-value=0.041). The equation for the pH 7 grouping was in better accordance with the equation calculated for the pH 2 grouping. These two groupings were responsible for the highest PC1 scores for media taken from site 8709.

The pH 2 grouping had a very high correlation coefficient (R^2= 0.99, p-value=0.007) and included samples with relatively high uranium concentrations (maximum concentration = 2.9 mg U/kg substrate material). Due to its high correlation coefficient, this model should be a very good predictor of PC1 scores in relation to contact time.

Overall, all three equations were strong to very strong models of PC1 scores in relation to time, and all were statistically significant. Therefore, these equations can be used to predict the PC1 scores and, in turn, the range of U/trace elements expected to be leached in relation to contact time. It also appeared that all models had approached steady-state conditions after one-month's contact time. This implies that the concentration of elements mobilized from this material should be near equilibrium conditions after one-month's time.

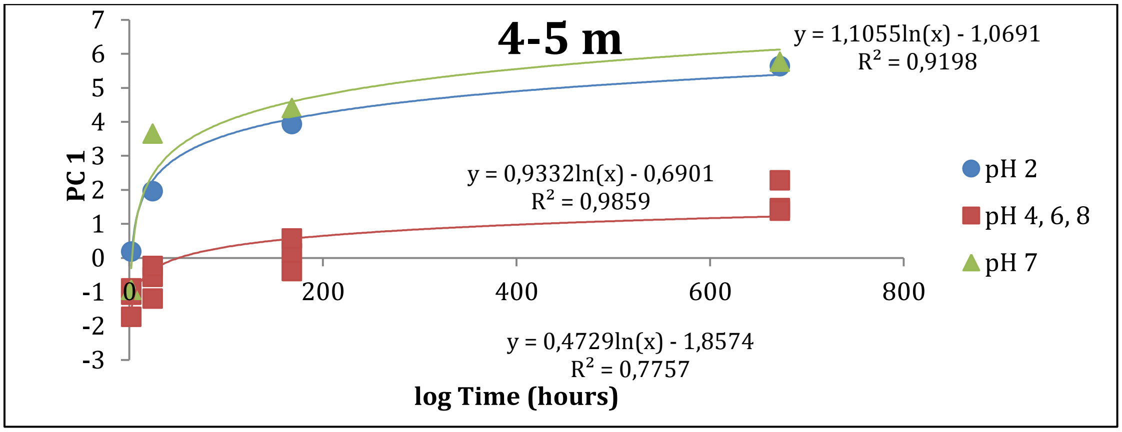


Figure 13: Relationship of PC1(45%) and contact time for extracts associated with media from site 8709, depth 4-5m. pH 2 (R^2=0.99, p-value=0.007), pH 7 = (R^2=0.92, p-value 0.041), pH 4, 6 & 8 (R^2=0.78, p-value <0.005).

Depths 5-6 m & 6-7 m: The PC1 score values generated from extracts taken from site 8709, depths 5-6 & 6-7 m were plotted in relation to contact time in Figure 14. These materials were plotted together, due to their similar mineralogies for pH 2; however, the variability between the pH 4-8 grouping was too large to combine these groupings.

The model generated for the pH 2 groupings of media from both depths had a high correlation coefficient (R^2=0.94) and a low p-value (<0.005), implying statistical significance.

The grouping of pH 4-8 for media taken from depth 5-6 had a much lower correlation than observed in the pH 2 grouping. This model generated a moderate correlation coefficient (R^2=0.64), implying that only 64% of the variation in PC1 scores was explained by the contact time. However, this model was still deemed to be statistically significant (p-value < 0.005).

The same pH grouping for media taken from depth 6-7m, had a much stronger correlation with contact time (R^2=0.78). This model was a strong predictor of PC1 scores, showing that the PC1 scores were strongly correlated to contact time.

As seen in the materials from depth 4-5, all groupings produced models with moderate to strong correlations noted between PC1 scores and the contact time of substrate material to solution. In addition, all of these correlations were found to be statistically significant. Also, all models implied that near equilibrium conditions had been reached after one month's time. This means that these equations, may serve as fairly representative models of PC1 and, consequently, predictors of the mobilization of uranium and other trace elements.

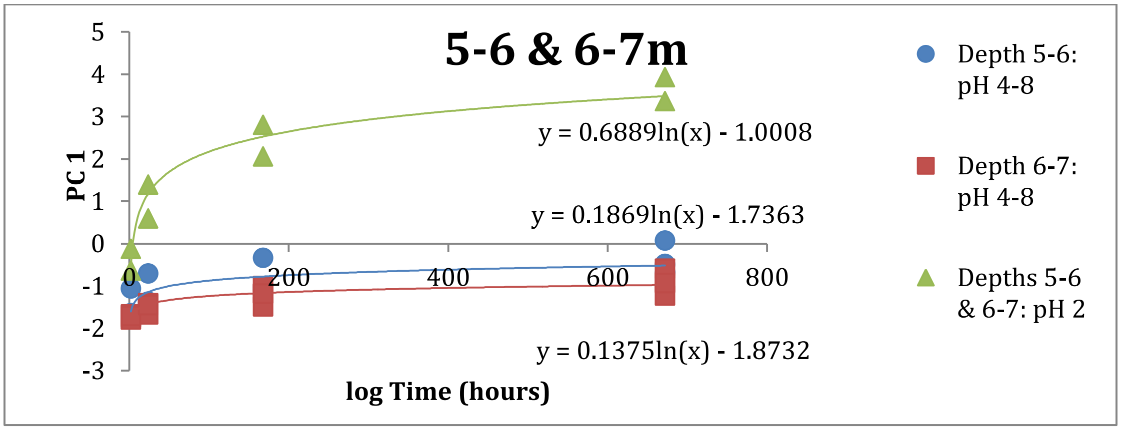


Figure 14: Relationship of PC1(45%) and contact time for samples extracted from media taken from site 8709, depths 5-6m & 6-7m. Depths 5-6 & 6-7m pH 2 (R^2=0.94, p-value <0.005), Depth 5-6m pH 4-8 = (R^2=0.64, p-value < 0.005), Depth 6-7 pH 4-8 (R^2=0.78, p-value <0.005).

4.4. Site 8841

4.4.1. Mineralogy

The mineralogy of site 8841 was determined by analyzing substrate media taken from depth 7.5-8.5 meters using XRD. Previously, sediments at site 8841 were classified as being composed of limestone material established in the Ordovician period (Moen & Kveseth, 2013). The most abundant minerals found during this analysis were quartz, calcite, ankerite, muscovite and pyrite (Figure 17). This detrital mineral had a large variation in its mineral makeup. Additionally, it contained very little uranium.

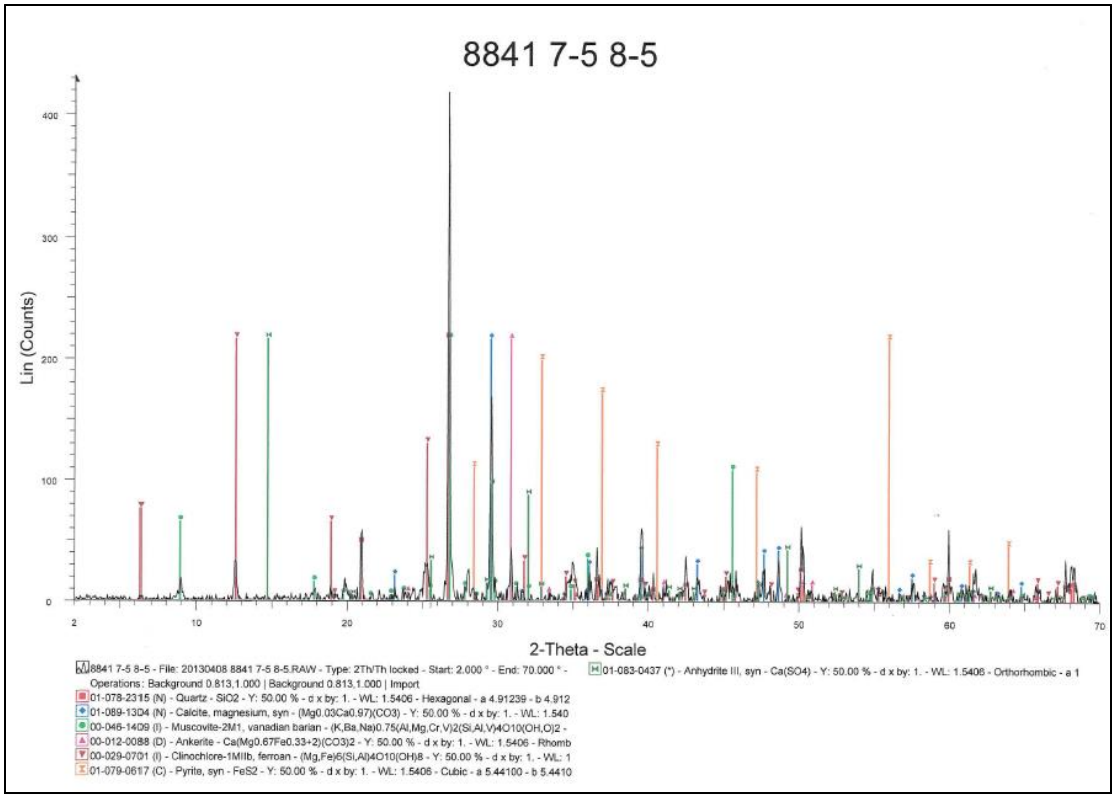


Figure 15: XRD analysis of site 8841 depth 7.5-8.5m mineralogy (Hagelia & Berg).

4.4.2. Buffering Capacity

As was observed in site 8709, the high concentration of carbonate in the substrate material provided a strong buffering capacity for the media collected from site 8841 when subjected to acidic solutions. The samples subject to pH 4, 6, 7 and 8 were all basified and maintained a pH in the range of 8-9.5 (as also seen at site 8709). The samples subjected to pH 2 washings, however, ranged between pH 5.5-7.5, becoming increasingly neutral in relation to increased contact time (Figure 16). This was the same range seen in site 8709. It appears that without the addition of further acidic solution, the pH 2 treated samples would also reach neutral-alkaline conditions, with increased contact time.

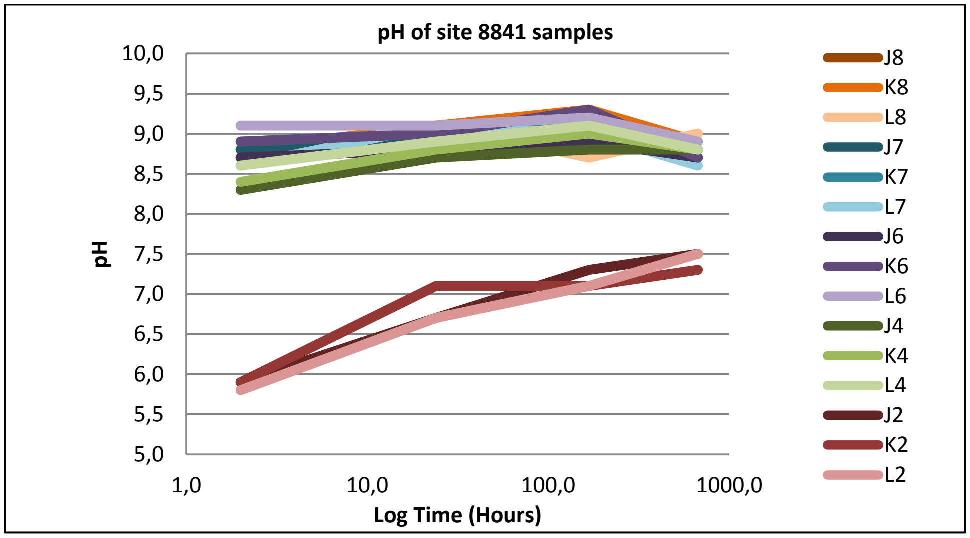


Figure 16: pH of samples from site 8841 versus contact time. The orange tinted lines represent samples that were washed with a pH 8 solution at 2 hours, 1 day, 1 week and 1 month, while blue, purple, green, and red represent pH 7, 6, 4 and 2, respectively. J =samples from depth 3.5-4.5m, K= 4.5-5.5m and L= 7.5-8.5m.

4.4.3. Leaching and Sequential Extraction of Uranium

In order to investigate the mobility of uranium, the substrate materials from site 8841 were used to conduct a leaching experiment. In the results of this experiment, the concentration of uranium was fairly uniform throughout all three depths registering 4.4, 3.9 and 5.3 mg U/kg substrate material for depths 3.5-4.5, 4.5-5.5 and 7.5-8.5 (Table 12). As was hypothesized, the highest leaching was observed from samples washed with a pH 2 solution (9, 13, and 20 % of total U leached over one month's contact time). Because all the materials treated with pH solutions 4, 6, 7 and 8 were quickly stabilized to a pH between 8-9.5, these samples were treated as replicates. For depth 3.5-4.5, the pH 4-8 grouping leached 5±0.2 % of the total concentration of uranium over one month, while the pH 4-8 grouping leached 7±1 % and 8±2%, from the media taken from depths 4.5-5.5 and 7.5-8.5m, respectively.

Table 12: Relative Fraction (%) of uranium leached from site 8841 samples in accordance to pH from leaching experiment conducted over one month's time.

Site	Depth	pH	Range of U Leached	Total U in Bedrock Material	% of Total U Leached
			mg/kg	mg/kg	
8841	3.5-4.5	2	0.025-0.18	4.4	9
8841	3.5-4.5	4	0.013-0.13		6
8841	3.5-4.5	6	0.013-0.13		5
8841	3.5-4.5	7	0.013-0.13		5
8841	3.5-4.5	8	0.012-0.13		5
8841	4.5-5.5	2	0.046-0.19	3.9	13
8841	4.5-5.5	4	0.018-0.15		7
8841	4.5-5.5	6	0.013-0.13		6
8841	4.5-5.5	7	0.018-0.16		7
8841	4.5-5.5	8	0.015-0.13		6
8841	7.5-8.5	2	0.086-0.42	5.3	20
8841	7.5-8.5	4	0.026-0.21		7
8841	7.5-8.5	6	0.017-0.20		6
8841	7.5-8.5	7	0.027-0.29		9
8841	7.5-8.5	8	0.039-0.25		10

In order to determine the speciation of uranium at site 8841, Halldis Fjermestad performed sequential extraction upon the substrate media collected from the depth of 7.5-8.5m. The results of this extraction are presented in Table 13, and shall be discussed in relation to the step of the extraction.

Table 13: Relative fractions (%) of uranium extracted through the sequential extraction of site 8841 depth 7.5-8.5m over one month's time (Fjermestad).

Sequential Extraction of Site 8841 Depth 7.5-8.5m					
Fraction	Extraction Reagent	Average U concentration (mg/kg)	Total U in Substrate Media (mg/kg)	% of U per fraction	% of U Leached
1	H_2O	0.01	5.3	0	58
2	NH_4Ac (pH 7)	0.17		3	
3	NH_4Ac (pH 5)	0.49		9	
4	NH_2OH-HCl	1.47		28	
5	H_2O_2	0.06		1	
6	HNO_3	0.87		16	

1) Very little uranium was found to reside in the water-soluble fraction (0.01 m U/kg substrate media).

2-3) Fractions two and three were treated with ammonium acetate at pH 5 and 7. These fractions represent the reversibly-bound fraction and the reversibly bound fraction associated with amorphous carbonate. The combination of these two fractions accounted for the mobilization of 12 % of the total uranium. This was relatively in line with the 8±2 % of uranium loss noted in the leaching experiment. It is very likely that this portion is associated with the mobile uranyl carbonate complexes, which have been cited as being the most significant agents of uranium mobility in neutral to alkaline waters (Echevarria et al., 2001; Elless & Lee, 1998; Sandino & Bruno, 1992). The high amount of carbonate minerals found in site 8841, lend support to this conclusion.

4) Fraction four represents the uranium species associated with easily reduced components (i.e. Fe/Mn oxides). The highest percentage of uranium was released in this fraction (28 %) suggesting that a large portion of the uranium was associated with Fe/Mn oxide precipitates (Milton & Brown, 1987). It is likely that the introduction of a reducing agent (NH_2OH-HCl) caused the reduction of the precipitates, and resulted in the release of uranium.

5) Fraction five, or the fraction associated with organic matter or U(IV) oxides, was also relatively inconsequential, accounting for the mobilization of only 1 % of the total uranium (0.06 mg U/kg substrate media). Therefore, it appears that there was very little U(IV) to be oxidized into the more mobile U(VI) in media from site 8841.

6) The second highest percentage of mobilized U, came from the acid-dissolvable fraction. At this stage, 16 % of the total U was mobilized. This is likely due to the shift in redox conditions and weakening of u-bindings to organic complexes or minerals.

Overall, only 58 % of the total U was mobilized in the sequential extraction, implying that 42 % was immobile and strongly adhered to the mineral matrix. It is of significance that 28 % of the total uranium was released in the easily reduced fraction, however. Were this media subjected to anaerobic conditions, an increase of 28 % of the total uranium concentration could be mobilized in addition to the fraction mobilized in the leaching experiment (8±2 %).

4.4.4. PCA of Leaching Experiment

The ICP-MS data for the 60 extracts from site 8841 was used to perform PCA. This was done in order to describe the relationship between samples and the correlation between various elemental variables. These samples represent three different depths that were treated with five different pH solutions and subjected to four different contact times. The complete data set and corresponding PC scores can be found in Appendix IV.

In PCA, principal components are calculated to describe the greatest variability within a data set. Each principal component is defined by the variability between the different variables. Therefore, a correlation value describes how strongly a variable is to the principal component in question. Table 14 displays the correlation coefficients for each variable in relation to principal component. The correlation coefficients with the greatest absolute values are most strongly correlated with the corresponding principal component. Also, the positive values imply a positive correlation, while negative values imply a negative correlation.

In the PCA of site 8841, the first principal component represented 55 % of the total variability observed within the data set. In addition, the second principal component represented 32 % of the overall variability. Thus, together PC1 and PC2 described 87 % of the variability within a system.

Table 14: Variables from PCA of extracts associated with media taken from site 8841 and their correlation values to PC1 and PC2.

Variable	PC1 (55 %)	PC2 (32 %)
Fe	**0.419**	0.052
U	**0.396**	-0.004
Th	**0.388**	0.26
Al	**0.337**	**0.38**
S	**0.304**	0.102
Ca	**0.304**	**-0.428**
Co	**0.303**	**-0.394**
Mn	**0.293**	**-0.442**
Mo	0.202	**0.491**

Loading plots can be used to visually describe the correlation between variables and PC1/PC2. The loading plot for the PCA of 8841 is shown in Figure 17. While PC1 was strongly correlated to all of the nine variables analyzed, PC1 was most strongly correlated with Fe, U and Th. In contrast, PC2 had a more diverse representation of the data. PC2 was positively correlated with Al and Mo, but negatively correlated with Mn, Ca and Co. Uranium and iron were relatively neutral in regards to PC2.

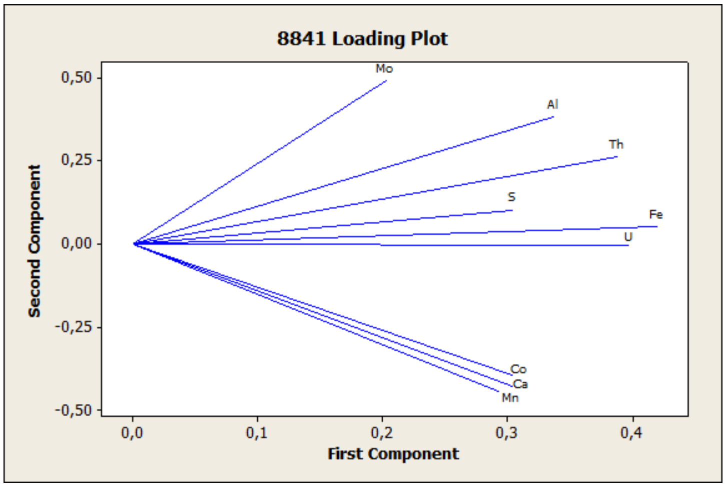


Figure 17: Loading plot illustrating the relationship between the concentration of elements found in extracts associated with media from site 8841. PC1 (55 %) & PC2 (32 %).

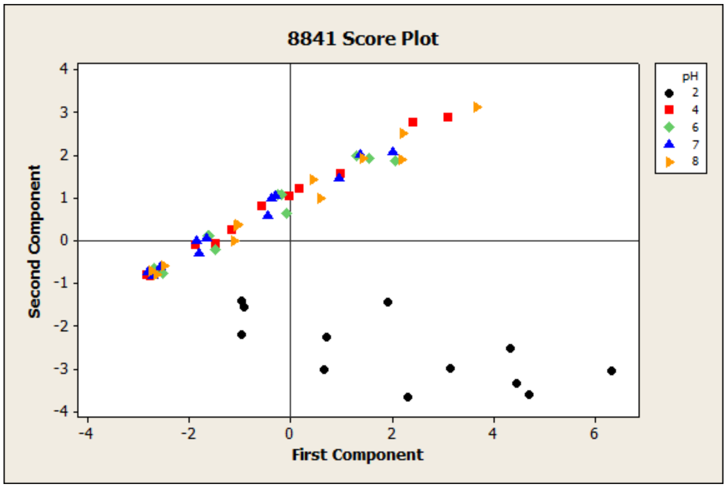


Figure 18: Score plot illustrating relationship between the extracts taken associated with media from site 8841. PC1 (55 %) & PC2 (32 %). Samples have been grouped based upon pH treatment.

While the loading plot represents the relationship of the different variables to one another, the score plot represents the relationship between the different samples analyzed. The score plot for site 8841 is shown in Figure 18. In this score plot, there is a clear difference between samples that were treated with pH 2 solution and samples treated with solutions that had a pH between 4-8. When Figure 18 and Figure 17 are compared, it can be seen that samples treated with pH 2 were very strongly correlated with Co, Ca and Mn. The samples treated with pH solutions 4-8, on the other hand, had a much higher correlation with Mo, Al and Th. Roughly, the same correlation pattern was observed at site 8709.

The principal components can be used to describe the mobility of uranium in a system. In PC1, the score values tend to increase as a function of contact time, with the longer contact times generating higher concentrations of uranium (shown in section 4.4.5. Kinetics). Therefore, PC1 score values can be used to predict the potential range of uranium that will be mobilized in relation to contact time with solution.

While PC1 explains the variation in contact-time, PC2 appears to explain the differences between pH treatments. Uranium was not significantly correlated to PC2. This means that uranium mobilization was not strongly affected by the mobilization of Mn, Ca, Co in the pH 2 solutions, or by Mo and Th in the pH 4-8 solutions. Uranium had a similar correlation pattern to Fe, however. Potential explanations may be that uranium was associated with carbonate, as proposed for site 8709, or that uranium and iron were both mobilized in a similar pattern due to dissolution of precipitates. However, it is important to note that these are merely hypotheses. PCA demonstrates the correlation between elements, not the underlying mechanisms for their mobilization.

4.4.5. Kinetics

Determining the kinetics of a system is important for predicting the fate of environmental contaminants. Figure 19 illustrates the relationship between PC1 scores and contact time (solution: substrate media) for the three depths and five pH treatments at site 8841. There was a visible positive trend between all PC1 scores and time for all pH treatments, however, is strongest for pH 2 treated solutions. The samples treated with pH 4, 6, 7, and 8 all followed a similar pathway, slightly lower than the pH 2 samples, as was expected. Therefore, all the elements analyzed from site 8841 can be predicted to increase in relation to contact time. By modeling the score values versus contact time, it was possible to provide an estimate for the amount of these elements released into solution.

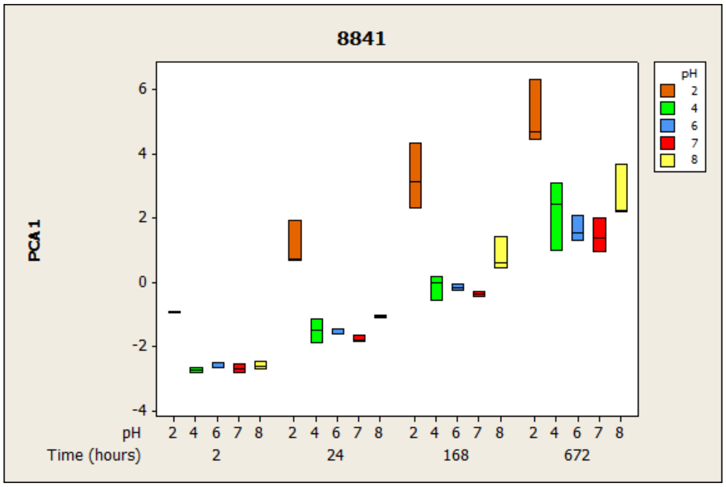


Figure 19: Relationship between PC1(55 %) scores and contact time for extracts associated with media taken from site 8841.

In order to describe the dynamics between PC1 score values and contact time, equations were generated for the two main groupings (pH 2 and pH 4-8). Samples from all three depths were grouped together. Subgroups of samples treated with pH 2 solution and samples treated with solutions that had a pH between 4-8 were further differentiated. Samples treated with pH 4-8 solutions were grouped together, due to the fact that they were quickly stabilized within the same pH range. Results of this relationship are shown in Figure 20. Both groupings increased logarithmically with strong correlation values, $R^2= 0.91$ for the pH 2 grouping and $R^2= 0.87$ for the pH 4-8 grouping. These results suggest that contact-time is the main descriptor for PC1, and that the relationship between the two can be used to model mobilization of elements associated with PC1. In this case of site 8841, PC1 was most highly correlated with Fe, U and Th. Therefore, PC1 can be particularly useful for predicting uranium mobilization.

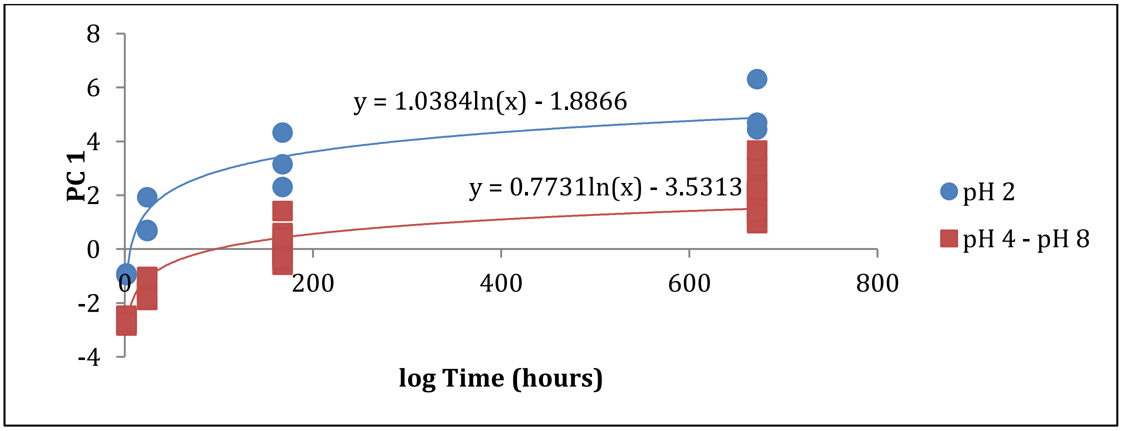


Figure 20: The relationship between PC1 (55 %) score values and the contact-time of extracts associated with media from site 8841. pH 2 (R^2=0.91, p-value < 0.005), pH 4-8 = (R^2=0.87, p-value < 0.005).

4.5. Site 8921

4.5.1. Mineralogy

The mineralogy is of particular importance for identifying areas that may be potential sources of environmental contamination. In previous analyses, the substrate material from site 8921 has been identified as belonging to the “black shale” family (Moen & Kveseth, 2013). XRD was conducted on the pulverized subsamples of the materials used in the leaching experiment and sequential extraction in order to provide a more detailed description of this material. The XRD analysis (Figure 21) illustrated that quartz, muscovite, pyrite, dolomite, and kaolinite were among the minerals of most importance. While the existence of pyrite is often a source of concern for acidification, there was a relatively high amount of carbonate minerals (e.g. dolomite) found at site 8921. The existence of these carbonate-rich minerals may aid in the buffering of any potential acid-formation from the oxidation of pyrite.

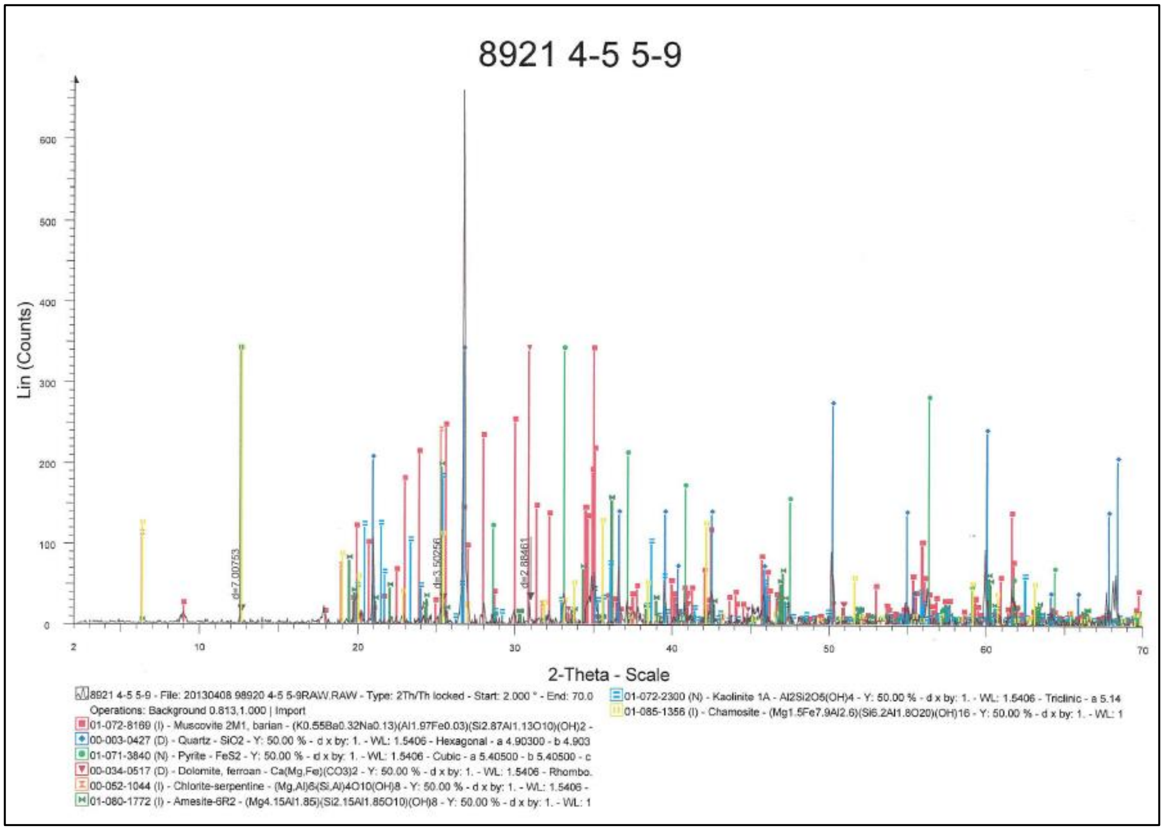


Figure 21: XRD analysis of substrate media from site 8921 depth 4.9-5.9m (Hagelia & Berg).

4.5.2. Buffering Capacity

In order to provide an understanding of the buffering capacity of the substrate media found at 8921, the pH of all extracts were recorded after being in contact with the material. As seen with sites 8709 and 8841, the media was washed with pH solution 4, 6, 7 and 8 was neutralized rather quickly. The samples from site 8921, however, had a slightly lower range than observed in sites 8709 and 8841, remaining between pH 6.5-8.5. The media washed with a pH 2 solution retained their acidity much better than sites 8709 and 8841, staying in a range of pH 2.5-4.5. Though site 8921 exhibited a fairly strong buffering capacity, it was incapable of neutralizing an reagent solution with a pH of 2 over the period of one month (Figure 22). Therefore, substrate media from site 8921 may be more sensitive to acidification effects, than the samples from the other locations.

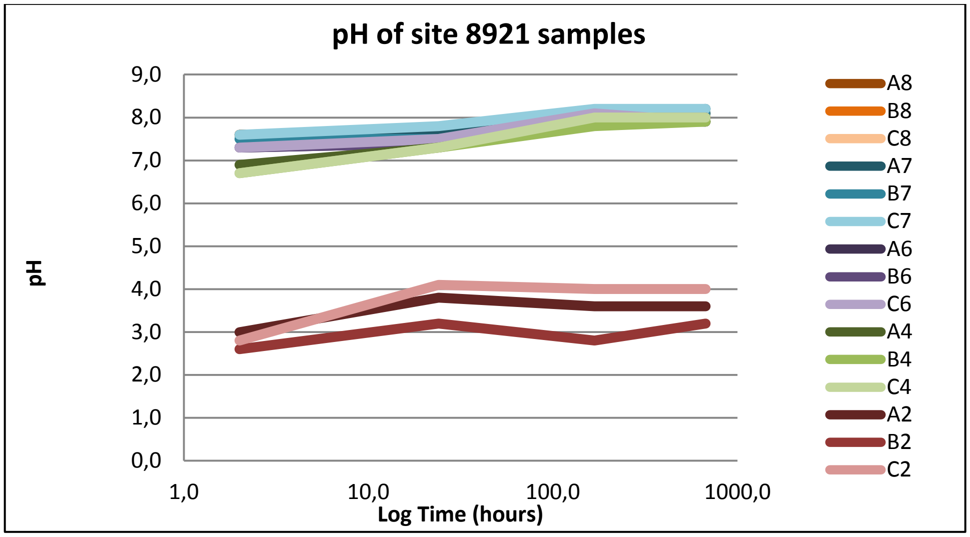


Figure 22: pH of samples from site 8921 in relation to contact time. The orange tinted lines represent samples that were washed with a pH 8 solution at 2 hours, 1 day, 1 week and 1 month, while blue, purple, green, and red represent pH 7, 6, 4 and 2, respectively. A =samples from depth 4.9-5.9m, B= 3.9-4.9m and C= 5.9-6.9m.

4.5.3. Leaching and Sequential Extraction of Uranium

In order to study the mobilization of uranium from site 8921 materials, a leaching experiment was performed. The results of this experiment are listed in Table 15. The sample material from site 8921 had fairly uniform composition between the three depths in terms of uranium (32±2 mg U/kg substrate media). When subjected to leaching over one month's time, the highest release of uranium was noted in the pH 2 samples, as was hypothesized. These samples released 31±5 % of the total uranium in the substrate media. Seeing as samples treated with pH solutions 4, 6, 7 and 8 all were neutralized within a range of pH 6.5-8.5, these samples were treated as replicates. The amount of uranium released on average from all three depths for these five pH values was 2±1 %. The uranium appears to be fairly immobilized in neutral-alkaline pHs, but was mobilized very quickly in acidic conditions.

Table 15: Relative fraction (%) of uranium leached from site 8841 samples in accordance to pH over one month's time.

Site	Depth	pH	Range of U Leached	Total U in Bedrock Material	% of Total U Leached
			mg/kg	mg/kg	
8921	3.9-4.9	2	1.3-4.3	32	36
8921	3.9-4.9	4	0.023-0.33		2
8921	3.9-4.9	6	0.0015-0.26		1
8921	3.9-4.9	7	0.011-0.32		1
8921	3.9-4.9	8	0.014-0.35		2
8921	4.9-5.9	2	1.1-3.2	31	26
8921	4.9-5.9	4	0.033-0.43		2
8921	4.9-5.9	6	0.0015-0.51		2
8921	4.9-5.9	7	0.023-0.48		2
8921	4.9-5.9	8	0.019-0.53		2
8921	5.9-6.9	2	1.4-3.0	29	30
8921	5.9-6.9	4	0.046-0.53		3
8921	5.9-6.9	6	0.017-0.50		3
8921	5.9-6.9	7	0.016-0.49		2
8921	5.9-6.9	8	0.028-0.62		3

In order to characterize the speciation of uranium in site 8921, sequential extraction was performed upon the substrate material from depth 4.9-5.9m. The results are displayed in Table 16 and shall discussed in relation to the steps of extraction.

Table 16: Relative fraction (%) of uranium extracted through the sequential extraction of media taken from site 8921 depth 4.9-5.9m (Fjermestad).

Sequential Extraction of Site 8921 Depth 4.9-5.9m					
Fraction	Extraction Reagents	Average U concentration (mg/kg)	Total U in Substrate Media (mg/kg)	% of U per fraction	% of U Leached
1	H_2O	0.00	31	0	70
2	NH_4Ac (pH 7)	0.15		0	
3	NH_4Ac (pH 5)	0.73		2	
4	NH_2OH-HCl	4.85		16	
5	H_2O_2	1.35		4	
6	HNO_3	14.75		48	

1) The water-soluble fraction of uranium from site 8921 was determined to be negligible (0 % extracted).

2-3) The second and third fractions represent the easily-reversibly bound and reversibly bound/associated with amorphous carbonate fractions. These two fractions accounted for only 2% of the total uranium to be extracted. This is in line with the findings of the leaching experiment that had an average of 1.5 % extraction for a pH in this range.

These findings suggest that very little of the total uranium content exists as uranyl carbonates in site 8921.

4) The fraction of uranium associated with easily reduced components, such as Fe/Mn oxides, was much more significant with 16 % of the total uranium being extracted with NH_2OH-HCl as a reducing agent. This suggests that a good portion of the uranium had been co-precipitated from solution along with Fe/Mn oxides, which act as scavengers. This portion represents the uranium that would be mobilized if these materials were introduced to a reducing environment.

5) After the introduction of an oxidizing agent, 4 % of the total uranium was extracted from the substrate material. A likely explanation for this is that either uranium associated to organic matter was released during its disintegration or that U(IV) was oxidized to U(VI), a much more mobile form of uranium.

6) The final step of the sequential extraction depicts the acid-dissolvable fraction of uranium. This was, predictably, the highest portion of extraction, accounting for 48 % of the total uranium budget. It was much higher than the 36 % release seen in the leaching experiment, however, the acid used in the sequential extraction was much stronger. Therefore, the two values are not directly comparable.

Overall, 70% of the total uranium was extractable through the six steps of the sequential extraction. This was much higher than the extraction rates seen in site 8709 and 8841 (58% for both). Nevertheless, the results suggest that only 22% of the total concentration of uranium could be mobilized unless subjected to an incredibly acidic environment. The largest threat of mobilization, other than acidification, is the potential reduction of easily reduced components such as Fe/Mn oxides. The introduction of this media to an anaerobic environment could lead to the mobilization of an additional 16% than was observed in the leaching experiment.

4.5.4. PCA of Leaching Experiment

In order to describe the relationship between the substrate samples and the elements analyzed, PCA analysis was conducted. For the PCA, data from the ICP-MS analysis of the extracts taken during leaching experiment was used. The data constitutes of samples from the three depths that were subjected to five pH solutions and agitated for four different contact times, totaling 60 sample solutions for the entire site. The complete data set and PC scores can be found in Appendix IV.

In PCA, principal components are calculated to describe the greatest variability within a data set. Each principal component is defined by the variability between the different variables. Therefore, a correlation value describes how strongly a variable is to the principal component in question. Table 17 displays the correlation coefficients for each variable in relation to principal component. The correlation coefficients with the greatest absolute values are most strongly correlated with the corresponding principal component. Also, the positive values imply a positive correlation, while negative values imply a negative correlation.

In the PCA of the extracts associated with the media from site 8921, the first principal component represented 74 % of the total variability observed within the data set and was positively correlated with eight of nine variables. In addition, the second principal component represented 19 % of the overall variability. Thus, together PC1 and PC2 described 93 % of the variability within a system.

Table 17: Variables from PCA of extracts associated with media taken from site 8709 and their correlation values to PC1 and PC2.

Variable	PC1 (74 %)	PC2 (19 %)
Fe	**0.383**	-0.082
U	**0.379**	-0.016
Co	**0.379**	-0.052
Ca	**0.374**	0.003
Mn	**0.369**	-0.09
Al	**0.359**	0.002
Th	**0.353**	0.148
S	0.161	**0.667**
Mo	-0.1	**0.718**

Loading plots visually display the correlation between variables analyzed in PCA. The loading plot associated with the site 8921 samples is displayed below (Figure 23). Eight of the nine variables analyzed had a positive correlation with PC1, with iron, uranium and cobalt having the strongest correlations to PC1. As for PC2, sulfur and molybdenum were the strongest correlated variables, with the other variables being relatively neutral. This means that PC2 mainly described the variations seen in concentrations of Mo and S.

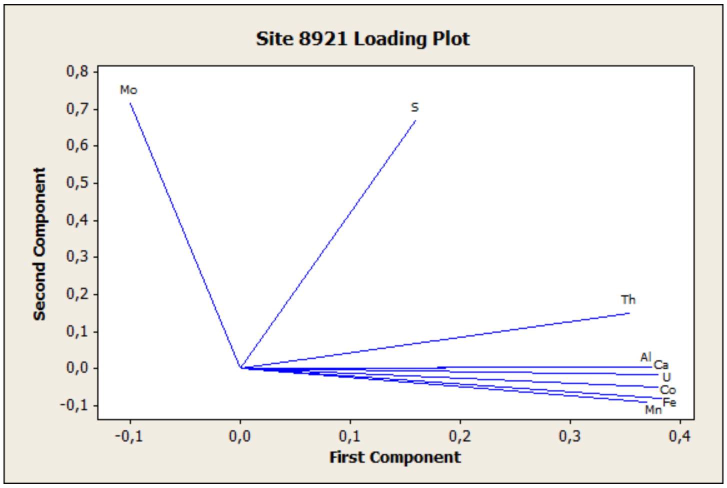


Figure 23: Loading plot illustrating the correlation between the different elements and PC1(74 %) and PC2(19 %) from the extracts associated with media from site 8921.

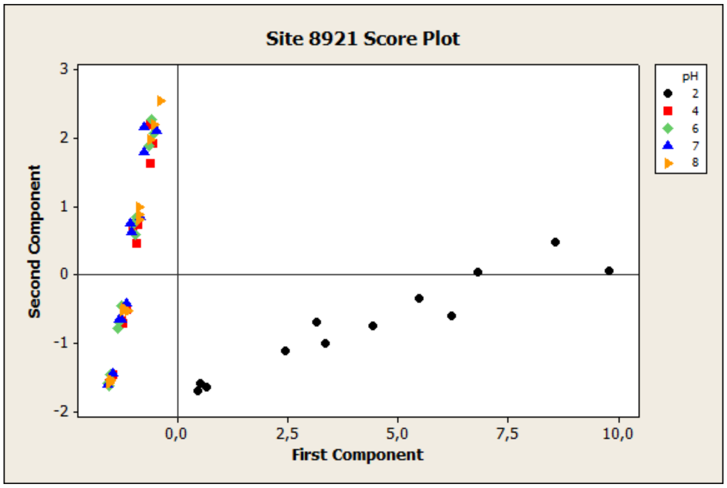


Figure 24: Score plot illustrating relationship between extracts taken associated with media from site 8921.

While the loading plot illustrates the relationship between variables, the score plot illustrates the variation between samples. Figure 24 shows the score plot generated from the PCA of extracts associated with media from site 8921. As was observed in sites 8709 and 8841, the score values generated distinctly follow patterns based on two groupings: media treated with pH 2 solutions and media treated with pH solutions 4-8. The samples treated with a pH 2 solution had exceptionally higher PC1 scores than the pH 4-8 grouping. The pH 4-8 grouping, on the other hand, was much more strongly correlated to the PC2 axis. This implies that the pH 4-8 grouping was more representative of the variables associated with PC2, while the pH 2 grouping was more representative of the variables associated with PC1. By comparing the loading plot (Figure 23) and score plot (Figure 24) of the PCA, it can be incurred that the pH 2 grouping was representative of Fe, U and Co; also, the grouping of pH 4-8 was representative of Mo and S.

The principal components can provide a better understanding of the mobility of uranium. In the case of site 8921, the concentration of uranium was strongly correlated with PC1. The PC1 score values tended to increase as a function of contact time (further described in 4.5.5. Kinetics). Therefore, it can be inferred that uranium concentrations will increase, with an increased contact time (particularly in the pH 2 grouping).

The PC2 score values were more representative of the pH 4-8 grouping. Uranium had a relatively low correlation to PC2, and the pH 4-8 grouping had very low PC1 score values. This implies that the pH 4-8 grouping had very low uranium concentration, and Mo and S were not associated with its mobility.

4.5.5. Kinetics

Determining the kinetics of a system is important for predicting the fate of environmental contaminants. Figure 25 illustrates the relationship between PC1 scores and contact time for the three depths and five pH treatments of the media from site 8921. There was a visible positive trend between all PC1 scores and time for all pH treatments, however, this trend was strongest for the pH 2 treated solutions. The samples treated with pH 4, 6, 7, and 8 all followed a similar pathway, drastically lower than the pH 2 samples, as was expected. Therefore, all the elements analyzed from site 8921 extracts could be predicted to increase with increased contact time. By modeling the score values versus time, it is possible to provide an estimate for the amount of these elements released into solution.

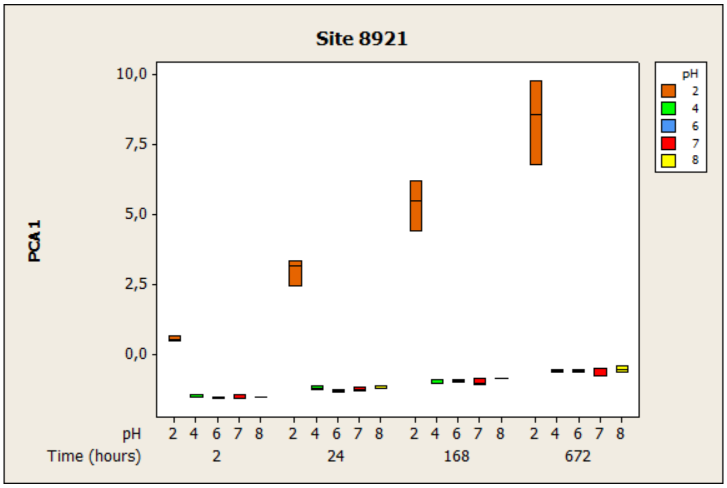


Figure 25: Relationship between PC1 (74%) scores and contact time for extracts associated with media from site 8921.

In order to further describe the dynamics between PC1 score values and contact time, equations were generated for the two main groupings (pH 2 and pH 4-8). Samples associated with media from all three depths were grouped together, due to the substrate material being fairly homogenous. Subgroups of samples treated with pH 2 solution and samples treated with solutions that had a pH between 4-8 were further differentiated. The reason for grouping samples treated with pH 4-8 solutions together was the fact that they were quickly stabilized within the same pH range. Results of these relationships are shown in Figure 26.

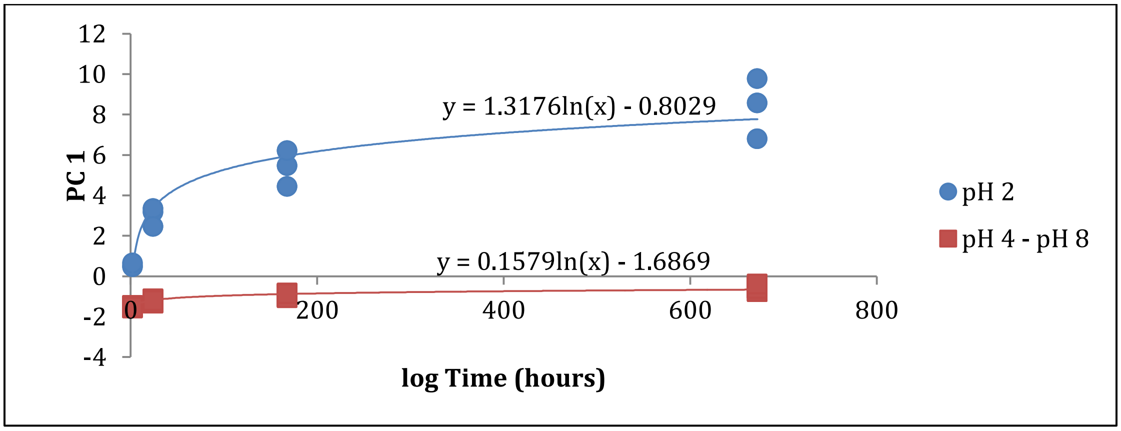


Figure 26: The relationship between PC1 (74 %) score values and the contact-time of extracts associated with media from site 8921. pH 2 (R^2=0.90, p-value <0.005), pH 4-8 = (R^2=0.93, p-value < 0.005).

The equation fitted to the pH 2 grouping suggested that PC1 increased logarithmically relative to the contact time of substrate media to solution. The model demonstrated a statistically significant relationship (p-value <0.005) that described 90% of the variability in PC1 (R^2= 0.90).

The model generated for the pH 4-8 grouping was equally representative, producing a correlation coefficient of $R^2= 0.93$ and p-value <0.005. This showed that the PC1 scores for all media taken from site 8921 washed with solution pH4-8 were highly predictable, in relation to contact time.

These results suggest that contact-time is the main driver behind PC1, and that the relationship between the two can be used to model mobilization of elements associated with PC1. In the case of site 8921, PC1 was highly correlated with Fe, U, Co, Ca, Mn, Al and Th. The media washed with a pH 2 solution released high concentrations of these elements, associating the pH 2 grouping with high PC1 scores. The samples from the pH 4-8 grouping, had very low concentrations of all these elements, and in turn, relatively low concentrations of these elements. Therefore, the influence of pH was quite dramatic. The generation of these equations makes it possible to create a simple model of the kinetics of a system, by knowing the pH and contact time between substrate media and solution.

4.6. Site 9051

4.6.1. Mineralogy

The mineralogy for site 9051 was not analyzed using XRD. Due to its juxtaposition to site 9081 (a site comprised of alum shale), it was initially believed that the substrate material from site 9051 would also be characterized as alum shale. However, further analysis indicates that the 9051 substrate media are most likely comprised of limestone. PCA was conducted on the total elemental concentrations of the media as determined by ICP-MS. This analysis showed that the media from site 9051 was closely related to the media from site 8842, which have been classified as limestone (Figure 27) (Moen & Kveseth, 2013). Also, when the score plot was compared with the loading plot from the PCA, it could be seen that media from site 9051 had very strong correlations to both calcium and strontium, which are characteristic of limestone (Figure 28). Therefore, it is suggested that site 9051, is representative of a limestone layer with an alum shale.

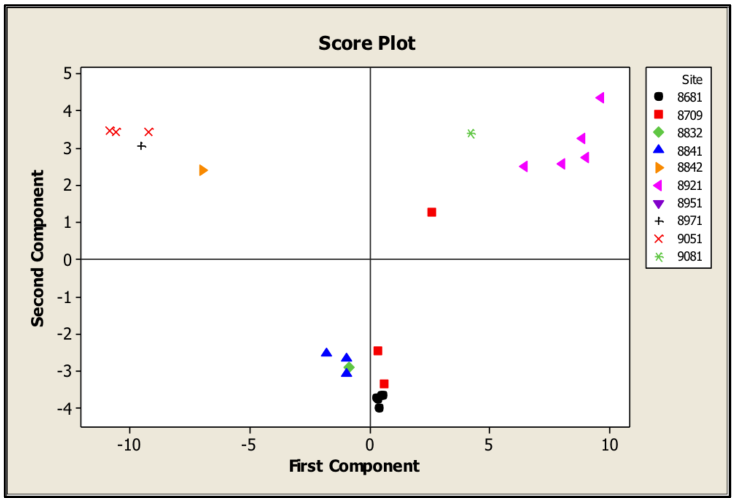


Figure 27: Score plot for total elemental concentrations of the different sample sites, as determined by ICP-MS of acid digested substrate media. PC1(69%) & PC2(19%).

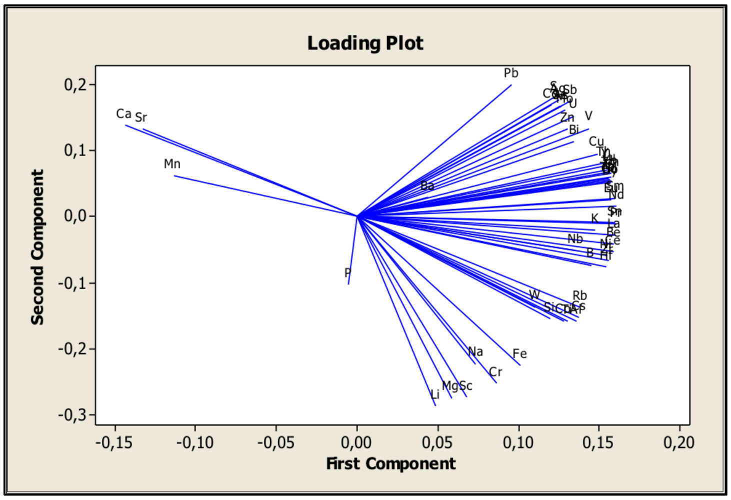


Figure 28: Loading plot for total elemental concentrations of the different sample sites, as determined by ICP-MS of acid digested substrate media. PC1(69 %) & PC2(19 %).

4.6.2. Buffering Capacity

The mineralogy of site 9051 is suggested to consist of limestone material, a carbonate-rich material. The neutralization effect seen in the carbonate-rich materials from sites 8709, 8841 and 8921 was also observed in site 9051 (Figure 29). Media treated with pH solutions of 4, 6, 7 and 8 all were quickly neutralized and recorded pH levels between 8.5 and 9.5 (similar to sites 8709 and 8841). Additionally, the media treated with pH 2 recorded a slightly lower range of pH (6.5-7.5), becoming neutralized quite quickly. The effect of pH on the mobilization of uranium should be quite similar between samples treated with pH 4, 6, 7 and 8, while pH 2 should exhibit a stronger effect from pH.

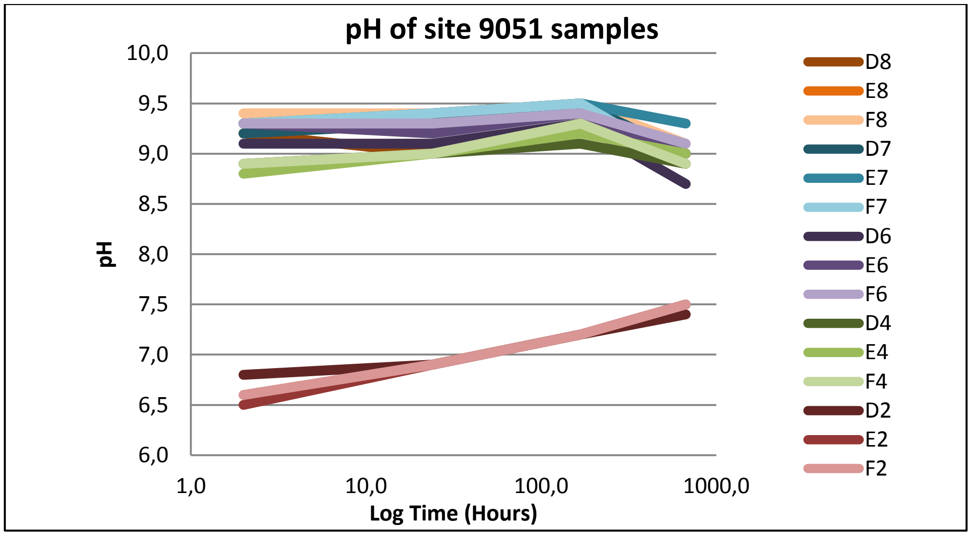


Figure 29: pH of samples from site 9051 versus contact time. The orange tinted lines represent samples that were washed with a pH 8 solution at 2 hours, 1 day, 1 week and 1 month, while blue, purple, green, and red represent pH 7, 6, 4 and 2, respectively. D =samples from depth 5-6m, E= 6-7m and F= 7-8m.

4.6.3. Leaching and Sequential Extraction of Uranium

In order to identify the effect of pH and contact time on the mobilization of uranium, a leaching experiment was conducted on the media collected from site 9051. There were 60 samples for site 9051 taken over one month's time to study the effect of pH on uranium mobility. The samples were the extracts associated with media from three different depths, five different pHs and four different contact times. The results of this experiment are presented in Table 18. The total concentration of uranium in the media from site 9051 was relatively low (3.1±1.9 mg U/kg substrate media). Even though the percentage of uranium mobilized from the pH 2 treated samples was higher than the percentage of U leached from the other pH treatments, the percentage mobilized was still relatively low (6±5 %). The percentage of uranium mobilized from media treated with pH 4, 6 7 and 8 solutions was very low (1±1 %). The low concentration of total uranium and low mobilization rate, imply that substrate materials from site 9051 have a very low potential for environmental contamination in neutral-alkaline, aerobic conditions.

Table 18: Relative fraction (%) of uranium leached from extracts associated with site 9051 media in accordance to pH over one month's time.

Site	Depth	pH	Range of U Leached	Total U in Bedrock Material	% of U Leached
			mg/kg	mg/kg	
9051	5.0-6.0	2	0.029-0.17	3.5	11
9051	5.0-6.0	4	<LD-0.51		2
9051	5.0-6.0	6	<LD-0.04		2
9051	5.0-6.0	7	<LD-0.035		1
9051	5.0-6.0	8	<LD-0.015		0
9051	6.0-7.0	2	<LD-0.01	1.1	2
9051	6.0-7.0	4	<LD-0.013		1
9051	6.0-7.0	6	<LD-0.0015		0
9051	6.0-7.0	7	<LD-0.0015		0
9051	6.0-7.0	8	<LD-0.0015		0
9051	7.0-8.0	2	0.013-0.07	4.8	4
9051	7.0-8.0	4	<LD-0.0015		0
9051	7.0-8.0	6	<LD-0.013		0
9051	7.0-8.0	7	<LD-0.016		0
9051	7.0-8.0	8	<LD-0.021		0

Sequential extraction was also performed on media from depth 5.0-6.0m of site 9051 to characterize characterize the speciation of uranium. The results of the extraction are displayed in

Table 19 and discussed in relation to the steps of extraction.

Table 19: Relative fraction (%) of uranium extracted through the sequential extraction of media from site 9051 depth 5-6m (Fjermestad).

Sequential Extraction of Site 9051 Depth 5.0-6.0m					
Fraction	Extraction Reagents	Average U concentration (mg/kg)	Total U in Substrate Media (mg/kg)	% of U per fraction	% of U Leached
1	H_2O	0.00	3.5	0	83
2	NH_4Ac (pH 7)	0.04		1	
3	NH_4Ac (pH 5)	0.28		8	
4	NH_2OH-HCl	1.26		36	
5	H_2O_2	0.11		3	
6	HNO_3	1.21		35	

1) As with the other three sites, the water-soluble fraction of uranium was found to be negligible (0 %).

2-3) The reversibly bound and the reversibly bound/associated with amorphous carbonate fractions had a combined extraction rate of 9 %. This was much higher than the 1±1% mobilized uranium found in the leaching experiment for pH 4-8. This may be attributed to the sensitivity of the substrate material to different extraction agents (ammonium acetate versus sulfuric acid/sodium hydroxide) and the relatively low total concentration of uranium. Nevertheless, the amount sequentially extracted was relatively small (0.32 mg U/kg substrate media).

4) The fraction associated with easily reduced compounds recorded the highest percentage of mobilized uranium (36 %). This increased mobility is believed to be associated with the reduction of Fe/Mn oxides that co-precipitate uranium from the aqueous phase. As they are reduced, however, uranium is released back into solution.

5) A small portion of the uranium in site 9051 was released when exposed to an oxidizing agent (3 %). This implies that there is very little U associated with organic matter or U(IV) oxides.

6) As was to be predicted, the percent of mobilized uranium from the acid-dissolved fraction was rather high (35 %). Thus, a large proportion of the available uranium has the potential to become mobilized in highly acidic conditions.

Overall, the sequential extraction accounted for the mobilization of 83 % of the total uranium concentration. This was the highest extraction rate seen of all the sites, though only 48% of the total could potentially be extracted without the presence of a very strong acid. Even though this substrate material has a relatively low total concentration of uranium, it could still pose an environmental risk if exposed to reducing conditions.

4.6.4. PCA of Leaching Experiment

In order to describe the relationship between samples of the substrate material and the elements analyzed, PCA analysis was conducted. For the PCA, data from the ICP-MS analysis of the extracts taken during leaching experiment was used. The data constitutes of samples from the three depths that were subjected to five pH solutions and agitated for four different contact times, totaling 60 sample solutions for the entire site. The complete data set and PC scores can be found in Appendix IV.

In PCA, principal components are calculated to describe the greatest variability within a data set. Each principal component is defined by the variability between the different variables. Therefore, a correlation value describes how strongly a variable is to the principal component in question. Table 20 displays the correlation coefficients for each variable in relation to principal component. The correlation coefficients with the greatest absolute values are most strongly correlated with the corresponding principal component. Also, the positive values imply a positive correlation, while negative values imply a negative correlation.

In the PCA of the extracts associated with the media from site 9051, the first principal component represented 63 % of the total variability observed within the data set and was positively correlated with eight of nine variables. In addition, the second principal component represented 23 % of the overall variability. Thus, together PC1 and PC2 described 86 % of the variability within a system.

Table 20: Variables from PCA of extracts associated with media taken from site 9051 and their correlation values for PC1 and PC2.

Variable	PC1 (63 %)	PC2 (23 %)
Fe	**0.392**	0.132
U	**0.386**	-0.009
Th	**0.381**	0.098
Ca	**0.359**	**-0.327**
Mn	**0.345**	**-0.358**
Co	**0.341**	**-0.318**
Al	**0.329**	**0.288**
S	**0.268**	**0.413**
Mo	0.093	**0.619**

Loading plots visualize the relationship between variables analyzed using PCA. The correlation values for each variable generated in the PCA of extracts associated with media from site 9051 are listed in Table 20 and plotted in Figure 30. In this analysis, PC1 was positively correlated with all variables, however, was most strongly correlated with Fe, U and Th. Therefore, samples with a high PC1 value, also had high Fe, U and Th concentrations. PC2 describes the vertical variation between elements. At this site, PC2 was negatively correlated with Ca, Mn and Co, and positively correlated with Mo, S and Al.

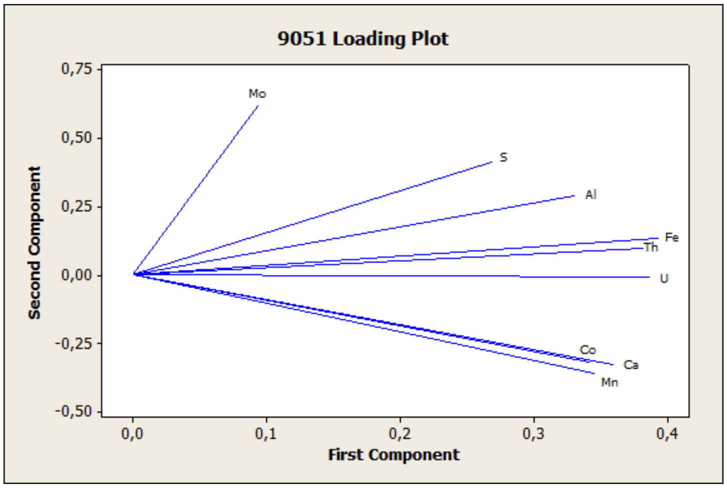


Figure 30: Loading plot illustrating the relationship between the concentration of elements found in extracts assiocated with media from site 9051. PC1(63 %) & PC2(23 %).

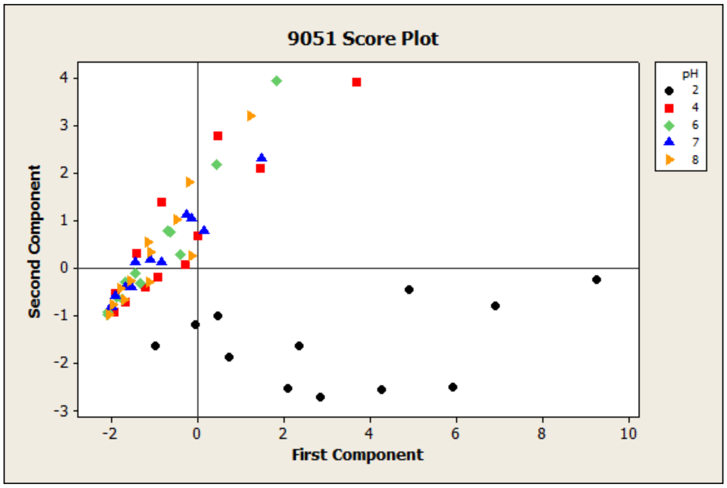


Figure 31: Score plot illustrating relationship between extracts taken associated with media from site 9051. PC1(63 %) & PC2(23 %).

While the loading plot illustrates the relationship between variables, the score plot illustrates the variation between samples. Figure 29 shows the score plot generated from the PCA of extracts associated with media from site 9051. As was observed in all the other sites, the score values generated distinctly follow patterns based on two groupings: media treated with pH 2 solutions and media treated with pH solutions 4-8. The media treated with a pH 2 solution had exceptionally higher PC1 scores than the pH 4-8 grouping. The pH 4-8 grouping, on the other hand, had exceptionally higher PC2 scores. Therefore, media treated with pH 2 solution had a stronger correlation to PC1, and media treated with pH solutions 4-8 had a stronger correlation to PC2.

By comparing the loading plot (Figure 30) and score plot (Figure 31), it was deduced that the pH 2 grouping was strongly correlated to higher concentrations of Fe, U and Th. In contrast, the grouping of pH 4-8 was more strongly correlated to Mo, S and Al. This illustrates the effect that pH has on the mobilization of different elements.

The principal components can provide a better understanding of the mobility of uranium. In the case of site 9051, the concentration of uranium was strongly correlated with PC1. The PC1 score values tended to increase as a function of contact time (further described in 4.6.5. Kinetics). Therefore, it was inferred that uranium concentrations should increase, with an increased contact time (particularly in the pH 2 grouping).

The PC2 score values had a stronger correlation to the pH 4-8 grouping. Uranium had a relatively neutral correlation to PC2, and the pH 4-8 grouping. This implies that the pH 4-8 grouping had much lower uranium concentrations than found in the pH 2 grouping, and that Mo and S were not associated with the mobility of uranium.

4.6.5. Kinetics

Determining the kinetics of a system is important for the prediction of environmental contaminants' fate. Figure 32 illustrates the relationship between PC1 scores and contact time for the three depths and five pH treatments of media from site 9051. There was a visible positive trend between all PC1 scores and time for all pH treatments, however, is strongest for pH 2 treated solutions. The samples treated with pH 4, 6, 7, and 8 all followed a similar pathway, with average PC1 scores that were much lower than in the pH 2 grouping. As stated previously, all the elements analyzed had a positive correlation with PC1. Therefore, all the elements analyzed from site 9051 extracts could be predicted to increase with increased contact time. By modeling the score values versus time, it would be possible to provide an estimate for the amount of these elements released into solution.

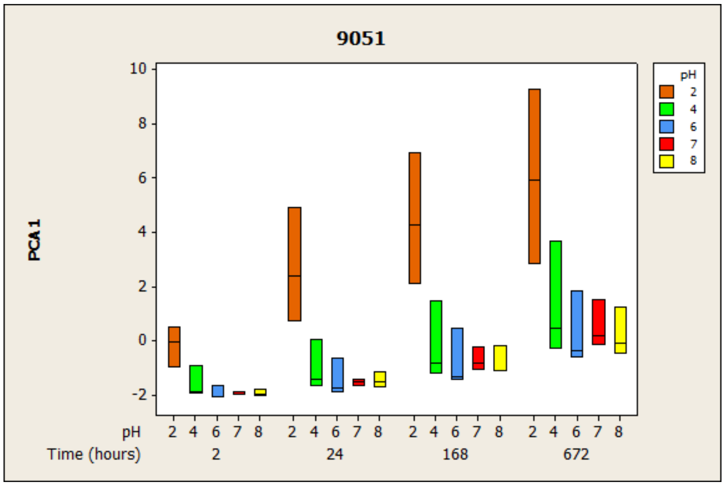


Figure 32: : Relationship between PC1 (63 %) scores and contact time for extracts associated with media from site 9051.

In order to further describe the dynamics between PC1 score values and contact time, equations were generated for the two main groupings (pH 2 and pH 4-8) for all three depths (Figures 33, 34 & 35). Each depth was plotted separately, due to a high heterogeneity of the media collected. The results will be discussed by depth.

Depth 5-6 m: The extracts taken from sediments of depth 5-6 were described in terms of contact time and PC1 scores in Figure 31. In the pH 2 grouping, the model fitted described 98% of the variation in PC1 in relation to contact time. This relationship was also found to be statistically significant with a p-value of 0.008. The equation for the second grouping, pH 4-8, also had a fairly strong correlation coefficient of $R^2=0.73$ and a p-value <0.005. The pH

4-8 grouping had a much gentler slope than the one observed in the pH 2 grouping. Since PC1 was most strongly correlated with Fe, U and Th, Figure 31 illustrates that these elements were mobilized at greater rate from the pH 2 treated media than the pH 4-8 treated media. These equations provide information as to how quickly uranium was and can be released in relation to contact time.

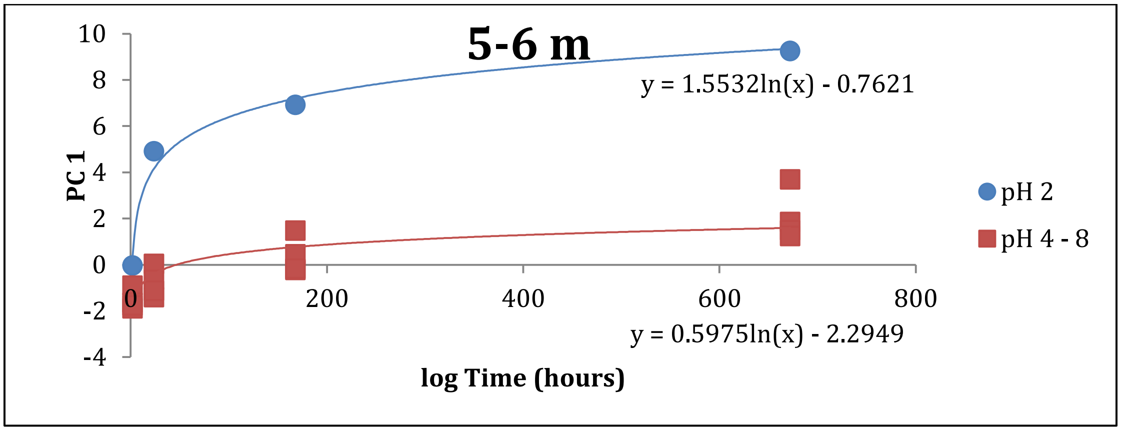


Figure 33: The relationship between PC1 (63 %) score values and the contact-time of extracts associated with media from site 9051 depth 5-6m. pH 2 (R^2=0.98, p-value=0.008), pH 4-8 (R^2=0.73, p-value <0.005).

Depth 6-7 m: Media from depth 6-7 m had the same differentiation between pH 2 treated samples and pH 4-8 treated samples as observed in depth 5-6. Both produced strong correlation coefficients between PC1 and contact time (R^2=1.0, p-value <0.005 for pH2; R^2=0.78, p-value <0.005 for pH 4-8). The media from depth 6-7m had much lower PC1 scores for both groupings than observed in depth 5-6m. These results demonstrated that media from depth 6-7m had a much lower mobilization of Fe, U and Th, than depth 5-6. Results, such as this, can help in the identification of stratigraphies that are higher risk for the mobilization of contaminants.

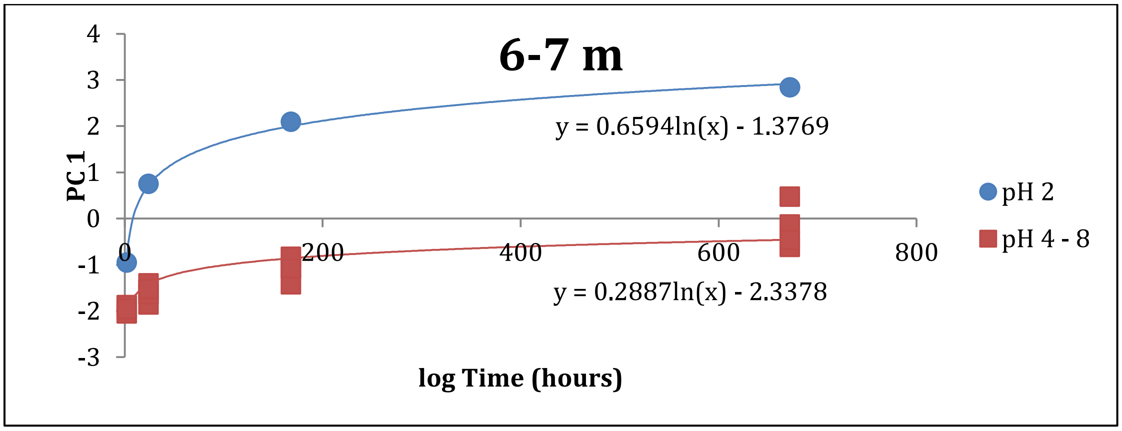


Figure 34: The relationship between PC1 (63%) score values and the contact-time of extracts associated with media from site 9051 depth 6-7m. pH 2 (R^2=1.0, p-value <0.005), pH 4-8 (R^2=0.78, p-value < 0.005).

Depth 7-8 m: Once again, equations generated for the 2 groupings based upon pH produced strong correlation coefficients that were statistically significant (R^2=0.99, p-value <0.005 for pH2; R^2=0.85, p-value <0.005 for pH 4-8). While the pH 4-8 grouping for depth 7-

8m was generated a very similar equation to the one observed in depth 6-7, the pH 2 grouping increased at a much higher rate than was seen in depth 6-7m.

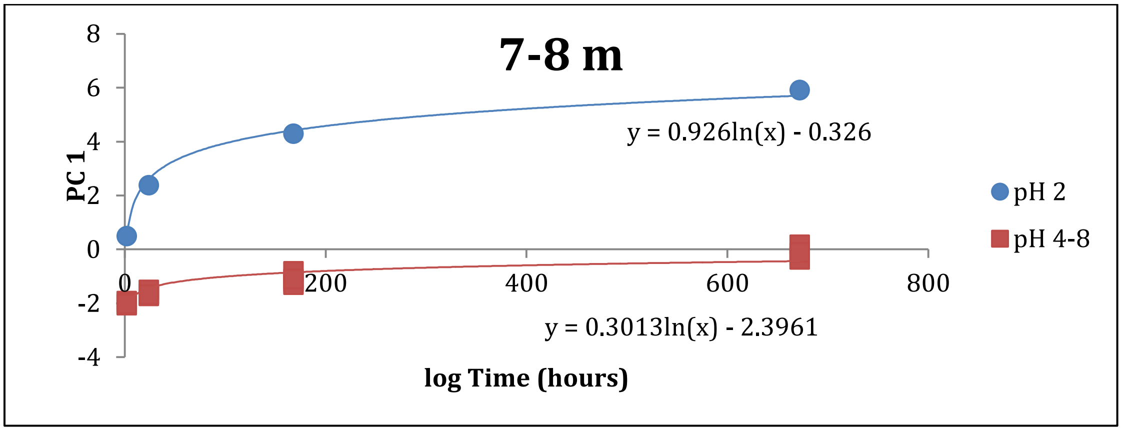


Figure 35: The relationship between PC1 (63 %) score values and the contact-time of extracts associated with media from site 9051 depth 7-8m. pH 2 (R^2=0.99, p-value<0.005), pH 4-8 (R^2=0.85, p-value < 0.005).

Overall, the media from the three depths had different rates of mobilization. This may be attributed to the substrate materials at site 9051 being heterogeneous and having different mineralogies/elemental compositions. Samples from depths 5-6 m and 7-8 m had higher concentrations of uranium than samples from depth 6-7m (3.5 mg U/kg, 4.8 mg U /kg, and 1.1 mg U/ kg, respectively). Therefore, it is of importance to identify the level of heterogeneity of the substrate media before applying any of the models generated. It can also be expected, that unless these substrate samples were subjected to acidic conditions, relatively little uranium would be mobilized. In an alkaline, aerobic scenario, these materials pose little threat to the environment.

4.7. Counter-measures for U-containing waste materials

The results of the present work suggest that neutral-alkaline conditions are inadequate for immobilizing uranium. Therefore, additional counter-measures shall be briefly discussed. There has been extensive research conducted on the remediation of uranium-contaminated soils and groundwater. These methods include bioremediation, interception and containment techniques. It has been shown that sulfate-reducing bacteria can be used to reduce the mobile hexavalent uranium to the rather immobile tetravalent uranium (Senko et al., 2002). This may occur naturally to some extent, if the substrate material was kept in anaerobic conditions; however, applied bioremediation can be time-intensive and expensive. The advantage in this project is that there is an opportunity for a preventative, rather than reactionary approach. Another well-studied approach for the immobilization of uranium includes precipitating uranium from groundwater through the addition of apatite. The phosphates in apatite bind U (VI) ions, and reduce their mobility in an ecosystem (Buck et al., 1996; Jerden et al., 2003; Schindler, Durocher, Kotzer, & Hawthorne, 2013). This method has also been found useful for the removal of lead and cadmium from groundwater (Ma, Traina, Logan, & Ryan, 1993; Valsami-Jones et al., 1998) Containment techniques are often the most low-cost solutions. These techniques could include the installation of an impermeable layer around the waste material, or possible a permeable reactive barrier (PRB) installed downstream of a site (Gavrilescu, Pavel, & Cretescu, 2009). These barriers cross-cut the flow of contaminant transport and precipitate metals from the groundwater.

Overall, there are many established counter-measures that could be implemented to prevent environmental contamination from the rock extracted during tunnel construction.

Conclusions

The results of the present work have characterized the mobility of uranium and its binding mechanisms to sample material collected near Gran, Norway. This was accomplished through an extended leaching experiment and sequential extraction. Of the four sample cores analyzed, two were classified as black shales and the other two were classified as limestone. The black shale samples had a much higher total concentration of uranium (30 mg/kg on average) in comparison to the limestone samples (4.2 mg/kg). Additionally, all of the substrate material analyzed contained moderate to high concentrations of carbonate minerals.

The carbonate-rich minerals in these samples of substrate media served as natural buffering agents, preventing the formation of acid due to pyrite-reduction. All of the sample materials analyzed in this work were capable of quickly establishing neutral-alkaline conditions after being exposed to pH solutions as acidic as pH 4. The samples were also able to neutralize a pH solution of pH 2 at a slower rate, with the exception of the black shale material from site 8921. Samples from this site had the lowest carbonate concentrations of all the material analyzed, and the lowest buffering capacity. Overall, the pH of the extract (after exposure to substrate media) was a better descriptor of U-mobilization than the pH of the extracting solution (before exposure to substrate media). Therefore, it is important to know the buffering capacity of the substrate media to make better predictions about U-mobilization.

The leaching experiment was conducted in order to determine the effect of pH and contact time (substrate media: solution) on the mobility of uranium. Typically, the effect of pH varied between two grouping: media treated with pH 2 solution and media treated with pH solutions between 4-8. The second grouping provided similar results, because all were quickly neutralized within the same range of pH.

Between these two groups, U-mobilization was highest in substrate media treated with pH 2 solution, as was hypothesized. The black shale media were the most vulnerable to the acidic treatment, mobilizing 25-35 % of the total concentration of uranium (a release of 7.3-10.4 mg/kg of uranium). The release of uranium from the limestone media had a much larger variation, mobilizing anywhere between 2-21 % of the total uranium concentration.

While the highest mobilization occurred in the pH 2 treated media, there was still a significant amount of uranium released in the neutral-alkaline conditions of the pH 4-8 treated media. The relative fraction of uranium mobilized in these conditions had a similar range for both black shale and limestone media, releasing 1-15 % and 0-12 %, respectively. Though the relative fractions of uranium released were within a similar range, the amount of uranium leached from the black shale media was much higher, due to a higher total concentration of uranium. In the neutral-alkaline conditions, the highest uranium mobilization occurred in black shale media that contained relatively high carbonate concentrations (site 8709). For these samples, carbonate served not only as a buffer, but also as a mobilization agent. Therefore, black shale media that were mixed with high amounts of limestone media were more likely to mobilize uranium under neutral-alkaline conditions.

Sequential extraction was also performed on the substrate material, in order to characterize the binding mechanisms of uranium to the solid phase. The sequential extraction classified the fraction of uranium mobilized between a pH of 5 and 7 as being either reversibly bound to the surface of minerals or present as amorphous carbonate. The relative fraction of uranium mobilized in this step of the sequential extraction was in good agreement with the results of the leaching experiment for all sites, except for the limestone media from site 9051. This sample had very low total concentrations of uranium (3.5 mg/kg), which was believed to cause the disagreement. Even so, the overall agreement between these two experiments implied that the amorphous carbonates and desorption were the primary mechanisms for uranium mobilization in the neutral-alkaline conditions of the leaching experiment.

The sequential extraction also described another binding mechanism of uranium that was of particular importance. The proportion of uranium bound to easily reduced components such as Fe/Mn hydroxides was very high for both black shale media (12-16 %) and limestone media (28-36 %). While Fe/Mn hydroxides are very efficient at co-precipitating uranium from solution, they are also easily reduced. The reduction of these compounds re-mobilizes uranium. The high proportion of uranium associated with these compounds suggest that if these samples were subjected to anaerobic, reducing conditions, then a strong increase of mobilized uranium could be expected.

Principal component analysis was conducted on the elemental concentrations of the extracts from the leaching experiment. This was done in order to demonstrate the correlations between uranium and trace elements in solution. The first principal component was positively correlated with all elements for all the substrate material (except for molybdenum in site 8921) and had a particularly strong correlation for uranium. The first principal component score values were plotted against contact time to visualize the kinetics of uranium mobilization, and typically divided into two groupings: extracts from substrate media treated with a pH 2 solution and extracts from substrate media treated with pH 4-8 solutions. The relationship between the score values and contact-time was logarithmic for both groupings and indicated that steady-state conditions were approached after one month’s contact time. These equations aid in the prediction of the mobilization of uranium and trace elements analyzed using principal component analysis.

Overall, the greatest potential risk of environmental contamination from uranium was attributed to black shale media in aerobic, acid conditions. Nevertheless, neutral-alkaline conditions were still highly capable of mobilizing uranium, and may lead to environmental contamination. This was especially true for black shales that were associated with high levels of carbonate. Therefore, it is suggested that neutral-alkaline conditions, alone, are inadequate for the immobilization of uranium in these substrate materials. However, it is recommended that further experimentation be done to characterize the mobilization of uranium under anaerobic conditions, which may lead to the reduction of the more mobile hexavalent uranium to the more immobile tetravalent uranium. Also, a risk analysis should be conducted to better define the potential risk associated with the excavated tunnel material.

In addition, there are multiple remediation efforts that may reduce the risk of environmental contamination from these substrate materials. These include immobilization techniques (such as the addition of apatite), containment technique techniques (such as capping the material with an impermeable layer) or interception techniques (such as installing a permeable reactive barrier (PRB) downstream of the waste site). These are relatively low-cost solutions that may reduce the risk of environmental contamination from uranium.

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Appendix I: Elemental composition of substrate media as determined by XRF

The following data was recorded using a hand-held XRF analyzer, SPECTRO xSORT, Ametek®. The values presented are the mean of five replications. The red numbers illustrate the values that were below the level of detection.

Site	Depth	Ca	Sr	K	Rb	Ba	U	Th	Cl	S	Si	Zn	Cu	Ni	Fe	Mn	W	Cr	V	Nb	Ti	Y	Zr
	(m)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
8681	2.0-3.0	22625	119	27167	135	7008	28	18	3618	3573	92280	100	189	107	26714	361	15	113	354	21	5439	33	153
8681	3.0-4.0	15731	96	21193	145	2586	3	11	2511	554	75870	79	52	90	62914	429	5	137	188	13	6676	18	125
8681	4.0-5.0	63453	195	16098	117	6243	6	11	3196	1084	53089	76	37	72	52239	688	13	62	236	13	4279	20	121
8681	5.0-6.0	12862	85	18776	136	2656	3	11	4058	147	42970	70	28	79	57105	313	10	148	159	8	5576	23	123
8681	6.0-7.0	29324	157	19083	123	2777	14	10	3789	227	57186	69	43	87	53036	521	13	122	116	8	7300	25	105
8709	4.0-5.0	33204	233	20896	118	9091	41	18	5382	3297	56661	159	59	114	36334	438	13	60	145	28	4442	34	165
8709	5.0-6.0	22388	179	19000	127	7132	8	11	3209	2733	65752	89	62	108	51409	598	12	114	202	14	5501	26	123
8709	6.0-7.0	42011	124	16556	137	2316	5	9	2625	1476	47218	84	54	112	59432	568	10	133	169	9	7374	23	113
8709	7.0-8.0	13560	100	19658	142	1988	3	8	3515	652	60279	75	55	105	61640	378	5	145	149	8	7418	21	114
8709	8.0-9.0	30428	101	18307	143	2046	8	11	2906	638	52059	86	64	101	60912	381	5	145	150	6	6479	17	115
8832	3.0-4.0	38079	178	16758	114	3346	3	9	4207	299	56011	63	29	62	46884	964	10	100	133	7	5056	26	93
8832	4.0-5.0	27406	123	19812	140	3221	6	8	3871	340	50675	66	147	84	47424	737	19	117	137	14	5208	28	113
8832	5.0-6.0	91509	237	13687	106	2609	3	10	4571	487	38365	64	21	76	44955	1297	12	126	119	5	5175	26	81
8832	6.0-7.0	74610	226	11625	93	2730	3	6	3863	263	49839	49	23	77	45226	948	16	108	60	6	4732	29	79
8832	7.0-8.0	55557	167	17677	121	2645	8	8	2957	178	64762	174	31	96	53497	808	13	119	148	7	5203	20	114
8841	3.5-4.5	38779	115	16810	121	3721	3	11	3980	315	53156	68	28	70	49810	854	12	117	133	9	5417	20	120
8841	4.5-5.5	36158	172	17112	114	3494	3	9	3331	293	63904	56	30	54	50463	931	10	109	132	9	5831	22	115
8841	5.5-6.5	64913	197	15820	103	3487	3	10	3736	265	55525	57	20	67	46830	885	5	112	123	8	5079	18	98
8841	6.5-7.5	53967	153	16041	114	2840	3	8	3874	308	54502	71	24	63	48083	1059	15	108	142	6	5108	20	103
8841	7.5-8.5	53886	161	17769	125	3338	3	7	3037	785	55456	53	28	44	48460	732	13	116	135	7	5168	20	102
8842	3.2-4.2	219940	351	8612	57	1100	8	8	3937	811	27485	78	22	39	18756	794	21	79	133	6	3252	21	46
8842	4.2-5.2	285611	460	6772	35	665	11	13	5057	833	20240	44	15	26	10662	987	22	76	44	16	2193	28	22
8842	5.2-6.2	128650	267	11549	90	2740	10	11	3725	2141	47346	56	33	38	28877	751	15	59	62	7	3421	33	98
8842	6.2-7.2	202533	349	9486	69	1497	5	12	4843	752	28941	54	32	20	15006	813	19	88	30	13	7856	25	80
8842	7.2-8.2	293487	530	4521	26	659	18	13	5352	884	15395	41	17	24	12867	1441	22	92	78	13	2223	21	26

Site	Depth	Ca	Sr	K	Rb	Ba	U	Th	Cl	S	Si	Zn	Cu	Ni	Fe	Mn	W	Cr	V	Nb	Ti	Y	Zr
	(m)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
8921	1.9-2.9	3589	47	33321	171	1967	40	24	5493	3437	74192	516	92	69	25286	77	24	128	684	30	9410	42	184
8921	2.9-3.9	4011	64	31108	166	1796	37	20	2259	1520	67536	710	85	65	28650	118	36	114	720	25	8424	46	171
8921	3.9-4.9	5284	53	31445	173	1922	42	21	3585	6151	87718	390	108	72	31487	140	21	123	666	26	8014	46	181
8921	4.9-5.9	4431	57	31773	177	1694	51	25	4859	2075	80902	369	81	50	26641	105	19	109	637	28	7535	49	185
8921	5.9-6.9	5415	63	30796	176	1450	46	29	3911	8294	78086	188	66	78	44539	82	15	81	498	32	8991	49	179
8951	1.5-2.5	83414	193	15492	97	2729	3	10	4355	242	55085	65	48	60	43665	1352	11	99	119	6	5082	35	128
8951	2.5-3.5	72396	155	15033	108	3028	3	7	3753	159	53954	87	34	75	46895	1157	12	149	140	10	5426	21	157
8951	3.5-4.5	167016	334	7694	64	1725	6	11	5291	522	39593	51	20	43	23028	1492	20	94	74	8	3950	23	106
8951	4.5-5.5	225001	375	8151	48	1242	6	13	4911	679	16396	38	13	29	12220	1755	20	85	44	7	4303	20	64
8951	5.5-6.5	331457	415	3519	20	673	15	14	5075	1436	14322	41	13	23	10581	2004	21	65	30	11	1502	22	26
8971	3.7-4.7	253083	377	6952	40	2454	14	14	5401	1308	20498	43	23	21	15692	1564	20	51	137	14	2433	21	38
8971	4.7-5.7	292507	444	4786	28	1003	17	18	4887	1281	15621	31	15	24	20393	1264	17	84	381	18	1909	25	34
8971	5.7-6.7	285689	462	5398	33	631	18	14	5131	931	17937	50	13	24	19924	1209	22	73	73	14	1654	22	32
8971	6.7-7.7	242634	444	7551	47	937	14	11	4840	779	22633	47	12	22	15972	977	18	72	80	7	2484	22	59
8971	7.7-8.7	187931	307	7555	55	978	20	15	4035	708	38698	80	23	31	17925	690	22	69	66	19	2685	27	115
9051	3.0-4.0	294636	400	4136	24	554	16	16	5006	1293	21782	52	20	30	30301	1389	20	101	80	20	1916	24	47
9051	4.0-5.0	285956	383	4095	22	546	21	15	4799	1130	18877	43	18	35	30943	1599	19	50	54	19	1797	26	33
9051	5.0-6.0	311845	438	3868	24	453	18	19	5061	885	13367	30	9	9	15576	1455	20	51	25	18	811	25	19
9051	6.0-7.0	321974	416	4003	21	518	16	16	4835	1094	13026	28	12	16	9454	1795	24	30	26	16	835	25	25
9051	7.0-8.0	312021	473	4241	20	335	17	14	5318	1219	13257	33	13	12	10647	2154	20	54	28	13	2326	22	24
9081	9.5-10.5	36865	371	23578	137	22458	33	23	4836	1818	57067	202	80	85	17906	487	22	73	407	27	6228	42	144
9081	10.5-11.5	21065	155	30353	148	8332	27	19	4704	3262	88739	164	82	100	23072	349	14	127	931	21	7091	29	158

Appendix II: pH of Sample Solutions in Leaching Experiment

The following data notes the pH of solution used to wash substrate media and the pH of the extracts taken after agitation and centrifugation.

Site Number	Depth of Sample	pH of Solution added @ t=0	pH of supernatant @ 2 hours	pH of Solution added @ t= 2 hours	pH of supernatant @ 1 day	pH of Solution added @ t= 1 day	pH of supernatant @ 1 week	pH of Solution added @ t= 1 week	pH of Supernatant @ 1 month
8921	4.9-5.9	8.0	7.6	8.1	7.7	8.2	7.9	7.8	8.0
8921	3.9-4.9	8.0	7.6	8.1	7.6	8.2	8.0	7.8	8.1
8921	5.9-6.9	8.0	7.6	8.1	7.5	8.2	8.1	7.8	8.1
9051	5-6	8.0	9.2	8.1	9.0	8.2	9.3	7.8	9.0
9051	6-7	8.0	9.3	8.1	9.4	8.2	9.5	7.8	9.0
9051	7-8	8.0	9.4	8.1	9.4	8.2	9.5	7.8	9.1
8709	4-5	8.0	8.3	8.1	8.6	8.2	8.6	7.8	8.1
8709	5-6	8.0	8.7	8.1	8.7	8.2	8.8	7.8	8.6
8709	6-7	8.0	9.2	8.1	9.1	8.2	9.2	7.8	8.7
8841	3.5-4.5	8.0	8.7	8.1	8.9	8.2	9.0	7.8	8.8
8841	4.5-5.5	8.0	8.8	8.1	9.1	8.2	9.3	7.8	8.9
8841	7.5-8.5	8.1	8.7	8.1	9.1	8.2	8.7	7.8	9.0
BLANK 8	-	8.0	7.3	8.1	7.1	8.2	7.1	7.8	6.8
8921	4.9-5.9	6.8	7.6	7.0	7.6	7.2	8.0	6.9	8.2
8921	3.9-4.9	6.8	7.5	7.0	7.5	7.2	8.0	6.9	8.1
8921	5.9-6.9	6.8	7.6	7.0	7.8	7.2	8.2	6.9	8.2
9051	5-6	6.8	9.2	7.0	9.3	7.2	9.5	6.9	9.0
9051	6-7	6.8	9.3	7.0	9.4	7.2	9.5	6.9	9.3
9051	7-8	6.8	9.3	7.0	9.4	7.2	9.5	6.9	8.9
8709	4-5	6.8	8.2	7.0	8.5	7.2	8.6	6.9	8.2
8709	5-6	6.8	8.3	7.0	8.2	7.2	8.7	6.9	8.5
8709	6-7	6.8	8.9	7.0	9.0	7.2	8.9	6.9	8.6
8841	3.5-4.5	6.8	8.8	7.0	8.9	7.2	8.9	6.9	8.7
8841	4.5-5.5	6.8	8.9	7.0	9.0	7.2	9.2	6.9	8.8
8841	7.5-8.5	7.0	8.6	7.0	9.1	7.2	9.0	6.9	8.6
BLANK 7	-	6.8	7.3	7.0	7.2	7.2	7.1	6.9	6.5
8921	4.9-5.9	6.1	7.3	6.1	7.4	6.3	8.0	6.0	8.0
8921	3.9-4.9	6.1	7.3	6.1	7.4	6.3	8.0	6.0	7.9
8921	5.9-6.9	6.1	7.3	6.1	7.5	6.3	8.1	6.0	7.9
9051	5-6	6.1	9.1	6.1	9.1	6.3	9.3	6.0	8.7
9051	6-7	6.1	9.3	6.1	9.2	6.3	9.4	6.0	9.0
9051	7-8	6.1	9.3	6.1	9.3	6.3	9.4	6.0	9.1
8709	4-5	6.1	8.3	6.1	8.3	6.3	8.5	6.0	8.2
8709	5-6	6.1	8.4	6.1	8.3	6.3	8.7	6.0	8.4
8709	6-7	6.1	9.0	6.1	8.9	6.3	8.6	6.0	8.6
8841	3.5-4.5	6.1	8.7	6.1	8.8	6.3	8.9	6.0	8.7
8841	4.5-5.5	6.1	8.9	6.1	9.0	6.3	9.3	6.0	8.7
8841	7.5-8.5	6.1	9.1	6.1	9.1	6.3	9.2	6.0	8.9
BLANK 6	-	6.1	6.8	6.1	6.7	6.3	6.6	6.0	6.2
8921	4.9-5.9	4.1	6.9	4.1	7.3	4.2	7.9	4.1	7.9
8921	3.9-4.9	4.1	6.7	4.1	7.3	4.2	7.8	4.1	7.9
8921	5.9-6.9	4.1	6.7	4.1	7.3	4.2	8.0	4.1	8.0
9051	5-6	4.1	8.9	4.1	9.0	4.2	9.1	4.1	8.9
9051	6-7	4.1	8.8	4.1	9.0	4.2	9.2	4.1	9.0
9051	7-8	4.1	8.9	4.1	9.0	4.2	9.3	4.1	8.9
8709	4-5	4.1	8.1	4.1	8.1	4.2	8.6	4.1	8.3
8709	5-6	4.1	8.0	4.1	8.5	4.2	8.7	4.1	8.6
8709	6-7	4.1	8.7	4.1	8.8	4.2	8.8	4.1	8.5
8841	3.5-4.5	4.1	8.3	4.1	8.7	4.2	8.8	4.1	8.8
8841	4.5-5.5	4.1	8.4	4.1	8.8	4.2	9.0	4.1	8.8
8841	7.5-8.5	4.1	8.6	4.1	8.9	4.2	9.1	4.1	8.8
BLANK 4	-	4.1	4.2	4.1	4.3	4.2	4.3	4.1	4.2
8921	4.9-5.9	2.0	3.0	2.0	3.8	1.8	3.6	2.1	3.6
8921	3.9-4.9	2.0	2.6	2.0	3.2	1.8	2.8	2.1	3.2
8921	5.9-6.9	2.0	2.8	2.0	4.1	1.8	4.0	2.1	4.0
9051	5-6	2.0	6.8	2.0	6.9	1.8	7.2	2.1	7.4
9051	6-7	2.0	6.5	2.0	6.9	1.8	7.2	2.1	7.5
9051	7-8	2.0	6.6	2.0	6.9	1.8	7.2	2.1	7.5
8709	4-5	2.0	6.5	2.0	6.7	1.8	7.0	2.1	7.3
8709	5-6	2.0	5.4	2.0	6.5	1.8	7.0	2.1	7.4
8709	6-7	2.0	5.5	2.0	6.4	1.8	6.9	2.1	7.3
8841	3.5-4.5	2.0	5.9	2.0	6.7	1.8	7.3	2.1	7.5
8841	4.5-5.5	2.0	5.9	2.0	7.1	1.8	7.1	2.1	7.3
8841	7.5-8.5	2.0	5.8	2.0	6.7	1.8	7.1	2.1	7.5
BLANK 2	-	2.0	2.0	2.0	2.0	1.8	1.9	2.1	2.0

Appendix III: Elemental composition of substrate media as determined by ICP-MS

The following data was obtained through ICP-MS analysis of digested substrate media.

Limit of Detection		0.019	0.002	10.089	2.372	0.079	0.566	116.791	0.351	17.184	11.380	1.831	0.000	0.918	0.036	0.019	0.696
Limit of Quantification		0.064	0.007	33.629	7.907	0.265	1.888	389.305	1.170	57.280	37.932	6.104	0.001	3.060	0.119	0.062	2.321
Acid Used for Digestion		HNO3	HNO3	HF	HF	HNO3	HNO3	HF	HNO3	HF	HF	HNO3	HNO3	HF	HF	HNO3	HF
Element Analyzed		Li	Be	B	Na	Mg	Al	Si	P	S	K	Ca	Sc	Ti	V	Cr	Mn
Site	Depth	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
8681	3.0-4.0	76	2.7	99	5200	18000	68000	130000	1300	3300	17000	29000	26	5100	220	120	530
8681	3.0-4.0	80	2.7	100	5400	17000	68000	150000	1300	3300	18000	28000	26	5000	230	120	550
8681	3.0-4.0	77	2.7	99	5300	17000	66000	140000	1300	3300	17000	29000	26	5200	230	110	550
8681	3.0-4.0	81	2.7	100	5200	18000	68000	170000	1300	3300	18000	30000	25	5400	230	120	530
8681	3.0-4.0	69	2.7	97	5100	18000	68000	160000	1300	2900	18000	31000	27	5000	230	120	540
8709	4.0-5.0	23	2.5	77	7100	12000	50000	100000	1100	15000	22000	59000	12	5200	530	66	660
8709	5.0-6.0	60	2.5	97	6600	15000	61000	140000	1600	5500	19000	43000	21	4400	250	100	690
8709	6.0-7.0	73	2.7	100	4700	16000	67000	120000	2500	4800	16000	36000	26	4000	190	120	560
8832	6.0-7.0	62	2.4	100	4500	13000	63000	170000	830	770	21000	63000	26	4000	150	97	1300
8841	3.5-4.5	60	2.4	110	5300	13000	66000	150000	640	1800	20000	43000	24	4300	150	96	760
8841	3.5-4.5	60	2.3	99	4700	13000	60000	120000	590	1800	21000	65000	24	3900	140	88	1200
8841	7.5-8.5	62	2.6	110	3700	13000	67000	170000	710	770	22000	56000	26	3900	150	86	1000
8842	3.2-4.2	13	1.3	50	1900	5900	28000	71000	530	3300	13000	190000	6.2	1800	95	26	940
8921	1.9-2.9	38	3.8	130	3100	8000	76000	120000	820	25000	26000	8800	15	5200	820	74	160
8921	2.9-3.9	28	3.3	130	3500	6900	56000	140000	840	16000	27000	8100	13	5000	790	63	140
8921	3.9-4.9	36	4	130	3300	10000	73000	150000	940	25000	26000	6600	16	4600	880	73	150
8921	4.9-5.9	35	3.8	130	3200	9800	72000	170000	880	31000	25000	7300	15	4900	850	72	170
8921	5.9-6.9	31	3.6	120	3200	9700	71000	160000	1000	41000	24000	8700	16	3800	790	73	180
8951	3.5-4.5	23	1.5	72	3700	7100	36000	94000	480	<450	16000	180000	10	2300	73	51	1800
8971	4.7-5.7	9.5	0.89	33	760	4300	12000	51000	1900	3800	5700	270000	3.7	910	56	18	1300
9051	5.0-6.0	9.9	0.88	30	220	3500	9600	39000	1200	520	4000	280000	3.2	630	19	10	1400
9051	6.0-7.0	7.1	0.64	31	600	4000	9500	32000	570	2000	4600	260000	3.2	740	28	10	1900
9051	7.0-8.0	6.1	0.68	77	2100	3600	12000	89000	700	7200	11000	240000	3.2	1600	49	11	4600
9081	9.5-10.5	20	2.9	97	3000	9000	52000	130000	640	14000	29000	71000	12	4000	770	79	600
blank	-	<0.064	<0.0067	16	20	0.45	<1.89	7100	<1.17	<LD	<17.5	<LD	<LD	1.6	0.034	<LD	1.1
blank	-	<0.064	<LD	24	22	0.42	<1.89	7100	<1.17	<LD	<LD	<LD	<LD	1.3	0.026	<LD	0.75
blank	-	<0.064	<LD	23	22	0.4	<1.89	7200	<1.17	<LD	<17.5	<LD	<LD	1.2	0.05	<LD	0.64
blank	-	<0.064	<0.0067	24	21	0.38	<1.89	7200	<1.17	<LD	<LD	<LD	<LD	0.97	0.036	<LD	0.59
blank	-	<LD	<LD	24	21	0.44	<1.89	7100	<1.17	<LD	<LD	<LD	<LD	0.82	0.018	<LD	0.46
ref. 2709a	-	48	0.91	68	11000	13000	37000	160000	570	620	11000	15000	9.2	2600	96	110	490
ref. 73324	-	36	2.8	62	1100	1500	97000	140000	200	<340	12000	1400	15	3000	110	67	1400
ref. 73325	-	23	2.9	18	280	800	160000	94000	1100	<460	990	1100	39	16000	220	430	1600

Limit of Detection		1.018	0.004	0.038	0.105	0.057	0.021	0.054	0.013	0.013	0.000	0.075	0.029	0.017	0.002	0.000	0.044
Limit of Quantification		3.392	0.012	0.128	0.350	0.190	0.069	0.180	0.045	0.043	0.001	0.252	0.096	0.057	0.006	0.002	0.148
Acid Used for Digestion		HNO3	HF	HF	HF	HNO3	HF	HF	HNO3	HNO3	HNO3	HF	HF	HF	HNO3	HNO3	HF
Element Analyzed		Fe	Co	Ni	Cu	Zn	As	Se	Rb	Sr	Y	Zr	Nb	Mo	Ag	Cd	Sn
Site	Depth	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
8681	3.0-4.0	50000	26	87	50	92	7.1	0.63	120	130	22	100	13	6.5	0.092	0.24	2.1
8681	3.0-4.0	49000	27	87	51	90	7.3	0.66	110	130	23	100	12	6.6	0.094	0.23	2.3
8681	3.0-4.0	50000	27	88	53	87	7.5	0.69	110	130	23	110	13	6.6	0.085	0.25	2.3
8681	3.0-4.0	51000	26	86	52	96	7.5	0.65	100	130	21	100	14	6.5	0.09	0.25	2.2
8681	3.0-4.0	50000	26	85	50	88	6.7	0.68	110	130	21	100	12	6.4	0.099	0.23	2.2
8709	4.0-5.0	35000	19	99	85	180	25	2.7	90	240	27	120	20	41	0.55	2	2.3
8709	5.0-6.0	46000	23	86	51	150	11	0.82	100	150	23	100	14	12	0.17	0.66	2.1
8709	6.0-7.0	52000	29	94	51	70	8.4	0.79	110	120	26	96	10	3.9	0.085	0.17	2.1
8832	6.0-7.0	42000	25	80	31	96	6	0.3	110	180	23	88	10	0.53	0.026	0.045	1.9
8841	3.5-4.5	44000	23	64	41	69	6.5	0.23	110	120	19	100	11	1.2	0.033	0.072	2.1
8841	3.5-4.5	43000	22	58	31	49	5.7	0.2	100	180	20	93	9.7	0.59	0.026	0.0087	1.8
8841	7.5-8.5	41000	22	50	42	80	6	0.19	130	190	21	83	10	0.48	0.031	0.029	2
8842	3.2-4.2	17000	9.8	24	20	54	9.3	0.78	53	450	19	10	6.6	5.1	0.11	0.26	1.1
8921	1.9-2.9	40000	26	120	110	760	40	4.9	140	48	33	150	17	73	0.55	5.8	3.3
8921	2.9-3.9	30000	25	98	93	550	32	2.6	96	30	33	140	16	68	0.48	4.5	3.4
8921	3.9-4.9	38000	25	110	120	510	39	6	130	36	39	140	15	54	0.72	3.7	3.5
8921	4.9-5.9	41000	27	120	130	550	49	6.6	120	37	38	140	15	57	0.82	4.1	3.3
8921	5.9-6.9	48000	33	120	180	360	69	8.6	120	42	42	140	11	71	1.1	2.7	3.2
8951	3.5-4.5	20000	11	29	15	47	7.6	0.31	59	350	18	19	8.2	0.48	0.036	0.047	1.3
8971	4.7-5.7	17000	5.1	9.9	4.5	14	4	0.16	20	500	14	3.3	4.5	0.97	0.038	0.092	0.47
9051	5.0-6.0	13000	3.2	7.8	4.5	10	1.7	0.28	16	570	13	3.6	2.5	0.62	0.022	0.096	0.52
9051	6.0-7.0	8800	3.8	7.9	7.5	14	3.4	0.061	17	500	12	4.1	2.6	0.52	0.03	0.08	0.37
9051	7.0-8.0	10000	8.8	20	19	29	11	0.58	23	630	13	10	7.3	1.8	0.051	0.077	1
9081	9.5-10.5	24000	11	78	94	300	21	2.8	100	470	32	99	15	21	0.86	4.7	2.7
blank	-	<3.4	0.0068	0.1	0.23	<LD	0.052	<0.022	<0.04	<0.04	<0.0007	<0.47	0.033	0.011	<LD	<LD	<LD
blank	-	<3.4	0.0048	<0.091	0.17	<LD	0.046	<0.022	<0.04	<0.04	<0.0007	<0.47	0.021	0.013	<LD	<LD	<LD
blank	-	<3.4	0.0055	<0.091	0.17	<LD	0.048	<LD	<0.04	<0.04	<LD	<0.47	0.01	0.0082	<LD	<LD	<LD
blank	-	<LD	0.0056	<0.091	0.23	<LD	0.044	<LD	<0.04	<0.04	<0.0007	<0.47	0.013	0.0066	<LD	<LD	<LD
blank	-	<LD	<0.0038	<0.091	0.16	<LD	0.033	<LD	<0.04	<LD	<0.0007	<0.47	0.011	0.021	<LD	<LD	<LD
ref. 2709a	-	26000	12	75	30	86	9.3	1.2	43	100	12	54	7	1.4	0.15	0.34	1.2
ref. 73324	-	46000	6.1	53	390	93	170	1.2	130	33	16	110	21	18	0.19	0.13	60
ref. 73325	-	98000	100	270	94	150	5.2	0.43	12	24	26	270	58	2.6	0.048	0.075	3.2

Limit of Detection		0.011	0.002	4.343	0.000	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Limit of Quantification		0.036	0.007	14.476	0.001	0.002	0.000	0.002	0.000	0.001	0.000	0.001	0.000	0.001	0.000	0.000	0.000
Acid Used for Digestion		HF	HNO3	HF	HNO3	HNO3	HNO3	HNO3	HNO3	HNO3	HNO3	HNO3	HNO3	HNO3	HNO3	HNO3	HNO3
Element Analyzed		Sb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Yb	Tb	Dy	Lu	Ho	Er
Site	Depth	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
8681	3.0-4.0	1.1	8.3	550	38	70	8.1	32	5.7	1.2	5	2.2	0.7	4.2	0.32	0.83	2.4
8681	3.0-4.0	1.1	8.5	610	39	72	8.3	33	5.8	1.2	5	2.2	0.72	4.4	0.32	0.85	2.4
8681	3.0-4.0	1.1	7.8	580	38	75	8.5	34	5.8	1.2	5	2.2	0.72	4.3	0.31	0.84	2.4
8681	3.0-4.0	1.1	8.1	610	37	71	8.2	31	5.7	1.2	4.9	2	0.69	4.1	0.3	0.8	2.2
8681	3.0-4.0	1	8.4	610	39	71	8.1	31	5.8	1.2	4.9	2.2	0.71	4.3	0.3	0.83	2.3
8709	4.0-5.0	4.5	6.1	2200	39	76	9.3	38	7.3	1.6	6.3	2.6	0.9	5.2	0.37	1	2.8
8709	5.0-6.0	1.6	6.7	960	37	72	8.5	33	6.2	1.3	5.3	2.2	0.76	4.5	0.3	0.86	2.4
8709	6.0-7.0	1	8.2	540	38	71	8.2	31	6.2	1.4	5.6	2.4	0.82	5	0.33	0.97	2.7
8832	6.0-7.0	0.6	7.2	680	35	65	7.4	28	5.4	1.2	4.7	2.3	0.7	4.2	0.32	0.84	2.4
8841	3.5-4.5	0.97	6.6	790	34	68	7.6	28	5.3	1.1	4.4	2	0.64	3.8	0.28	0.73	2
8841	3.5-4.5	0.71	6.4	770	32	62	6.9	27	5.4	1.1	4.6	2	0.67	4	0.29	0.77	2.1
8841	7.5-8.5	0.48	7.3	920	33	66	7.6	29	5.6	1.1	4.8	2.1	0.7	4.2	0.3	0.82	2.3
8842	3.2-4.2	0.98	2.6	150	19	38	4.9	19	4	0.91	3.8	1.5	0.54	3.2	0.22	0.62	1.7
8921	1.9-2.9	8.6	8.9	560	53	97	11	46	8.1	1.6	6.9	3.8	0.99	6	0.56	1.2	3.7
8921	2.9-3.9	6.7	6.7	550	53	92	11	45	8	1.6	6.9	3.7	0.99	6	0.54	1.2	3.6
8921	3.9-4.9	7.7	8.8	450	59	100	13	51	9.1	1.9	8.1	4.2	1.2	7	0.59	1.4	4.1
8921	4.9-5.9	8.9	8.5	490	51	93	11	47	8.7	1.7	7.7	4.1	1.1	6.8	0.58	1.4	4
8921	5.9-6.9	10	8.7	470	50	93	12	49	9.1	1.9	8.6	4	1.3	7.7	0.59	1.5	4.3
8951	3.5-4.5	0.36	3.6	300	23	46	5.4	21	4.3	0.89	3.9	1.7	0.57	3.4	0.24	0.66	1.8
8971	4.7-5.7	0.55	0.92	210	13	23	3.4	14	3	0.67	3	1.1	0.43	2.5	0.16	0.49	1.3
9051	5.0-6.0	0.23	0.61	74	12	19	3.1	13	2.8	0.62	2.7	0.99	0.39	2.3	0.14	0.44	1.2
9051	6.0-7.0	0.46	0.68	71	11	18	2.9	12	2.7	0.59	2.6	0.97	0.37	2.2	0.14	0.41	1.1
9051	7.0-8.0	1.1	1.2	200	11	19	3	13	2.8	0.6	2.7	1.1	0.39	2.3	0.15	0.44	1.2
9081	9.5-10.5	5.5	5.4	5600	45	81	10	42	8.2	1.7	7.6	3.3	1.1	6.3	0.48	1.2	3.5
blank	-	0.006	<LD	5.3	<0.0009	<0.002	<LD	<LD	<LD	<LD	<0.0004	<LD	<LD	<LD	<LD	<LD	<LD
blank	-	0.0052	<LD	7	<0.0009	<0.002	<0.0004	<0.0019	<LD	<0.0006	<LD	<LD	<LD	<LD	<LD	<LD	<LD
blank	-	0.0041	<0.007	7.7	<0.0009	<0.002	<LD	<LD	<LD	<0.0006	<LD	<LD	<LD	<LD	<LD	<LD	<LD
blank	-	0.013	<LD	5.8	<0.0009	<LD	<LD	<LD	<LD	<0.0006	<0.0004	<LD	<LD	<LD	<LD	<LD	<LD
blank	-	0.0042	<LD	8.8	<0.0009	<LD	<0.0004	<LD	<LD	<0.0006	<LD	<LD	<LD	<LD	<LD	<LD	<0.0003
ref. 2709a	-	1.3	4	660	19	35	4.2	16	3.1	0.64	2.8	1.1	0.4	2.4	0.16	0.46	1.3
ref. 73324	-	61	9.5	89	29	61	5.2	18	3.5	0.6	3	1.8	0.46	2.9	0.26	0.57	1.7
ref. 73325	-	0.46	2.5	130	50	100	11	49	11	3.5	9.9	2	1.3	6.7	0.26	1.1	2.6

Limit of Detection		0.000	0.003	0.034	0.024	0.003	0.000	0.004
Limit of Quantification		0.000	0.010	0.114	0.080	0.009	0.001	0.013
Acid Used for Digestion		HNO3	HF	HF	HF	HNO3	HNO3	HF
Element Analyzed		Tm	Hf	W	Pb	Bi	Th	U
Site	Depth	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
8681	3.0-4.0	0.33	2.9	1.5	11	0.25	8	6.6
8681	3.0-4.0	0.34	2.9	1.2	12	0.25	8.1	7.1
8681	3.0-4.0	0.33	3	1.5	13	0.23	8.2	6.9
8681	3.0-4.0	0.31	3.1	1.6	13	0.24	7.8	7.1
8681	3.0-4.0	0.32	3	1.3	11	0.24	8	7
8709	4.0-5.0	0.4	3.2	1.1	42	0.26	9.4	29
8709	5.0-6.0	0.33	2.9	1.2	14	0.24	8	11
8709	6.0-7.0	0.37	2.7	1.3	14	0.29	7.9	6.1
8832	6.0-7.0	0.35	2.4	1.6	6.1	0.25	6.7	3.4
8841	3.5-4.5	0.29	2.9	1.6	7.9	0.28	7.1	4.4
8841	3.5-4.5	0.31	2.6	1.5	5.3	0.22	6.2	3.9
8841	7.5-8.5	0.32	2.4	1.4	7.3	0.27	6.8	5.3
8842	3.2-4.2	0.24	0.31	0.74	9.7	0.16	5.2	3.6
8921	1.9-2.9	0.55	3.9	1.8	49	0.57	13	26
8921	2.9-3.9	0.54	4	1.6	39	0.51	13	27
8921	3.9-4.9	0.61	4	1.5	52	0.56	14	32
8921	4.9-5.9	0.58	4	1.5	72	0.62	14	31
8921	5.9-6.9	0.61	3.8	0.97	85	0.64	13	29
8951	3.5-4.5	0.26	0.58	0.98	16	0.2	6.6	3.6
8971	4.7-5.7	0.18	0.15	0.68	7.5	0.34	5.5	4
9051	5.0-6.0	0.16	0.14	0.47	4.9	0.18	4.7	3.5
9051	6.0-7.0	0.15	0.14	0.58	14	0.089	3.6	1.1
9051	7.0-8.0	0.16	0.41	1.1	63	0.11	4	4.8
9081	9.5-10.5	0.49	2.8	1.5	46	0.3	13	22
blank	-	<LD	0.0075	0.033	0.075	<0.009	<LD	0.015
blank	-	<LD	0.0057	0.057	0.074	<LD	<LD	0.015
blank	-	<LD	0.005	0.028	0.058	<LD	<LD	0.012
blank	-	<LD	0.0056	0.048	0.068	<LD	<LD	0.015
blank	-	<LD	0.0059	0.042	0.059	<LD	<LD	0.015
ref. 2709a	-	0.17	1.7	1.6	17	0.24	8.4	3.1
ref. 73324	-	0.26	4	76	320	50	21	6.9
ref. 73325	-	0.33	6.3	1.1	13	0.23	9.2	2.1

Appendix IV: Elemental Composition of Leaching Solutions as determined by ICP-MS

Site	Depth	pH	Time (hours)	U	Th	S	Al	Ca	Mn	Fe	Co	Mo	PC1	PC2
				mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg		
8709	4.0-5.0	2	2	0.65	0.00071	260	3300	30	1.9	0.19	1.1	0.1245	-0.15	1.11
8709	4.0-5.0	2	24	1.4	0.00134	343	6300	58	4.4	0.35	2.3	1.5	1.52	1.95
8709	4.0-5.0	2	168	2.36	0.00209	419	9500	86	7.3	0.51	3.9	2.49	3.36	2.79
8709	4.0-5.0	2	672	2.87	0.00293	599	12200	106	9.3	0.63	6.6	3.59	4.97	3.10
8709	4.0-5.0	4	2	0.23	0.0004	240	600	0.74	0.86	0.009	2.4	0.1245	-1.31	-0.16
8709	4.0-5.0	4	24	0.41	0.00101	340	880	0.97	3.26	0.0128	4.5	1.8	-0.78	-0.53
8709	4.0-5.0	4	168	0.66	0.0013	460	1170	1.1	4.76	0.0151	7.9	3	-0.10	-1.06
8709	4.0-5.0	4	672	1.39	0.00188	690	1630	1.39	6.16	0.0184	12.2	4.8	1.17	-1.87
8709	4.0-5.0	6	2	0.25	0.00015	310	680	0.8	1.1	0.011	2.9	0.1245	-1.13	-0.31
8709	4.0-5.0	6	24	0.47	0.00054	450	990	1.05	3	0.0149	5.4	1.5	-0.48	-0.77
8709	4.0-5.0	6	168	0.79	0.00069	590	1270	1.19	3.96	0.0171	9.2	2.36	0.29	-1.37
8709	4.0-5.0	6	672	1.89	0.00122	860	1780	1.71	5.46	0.022	14.3	3.46	1.91	-2.33
8709	4.0-5.0	7	2	0.23	0.0003	300	650	0.65	1.4	0.0082	2.8	0.1245	-1.17	-0.29
8709	4.0-5.0	7	24	0.9	0.1103	580	1360	6.95	321.4	0.2782	5.9	50	4.51	-3.37
8709	4.0-5.0	7	168	1.22	0.11048	700	1610	7.07	322.7	0.2803	9.4	50.9	5.23	-3.92
8709	4.0-5.0	7	672	2.07	0.11076	910	2040	7.37	323.38	0.283	13.9	51.77	6.52	-4.71
8709	4.0-5.0	8	2	0.033	0.000096	92	140	0.19	1.9	0.0061	0.13	1	-1.90	0.23
8709	4.0-5.0	8	24	0.213	0.000556	187	360	0.34	4.4	0.0098	2.53	2.9	-1.36	-0.17
8709	4.0-5.0	8	168	0.583	0.000786	317	640	0.47	5.7	0.0121	6.03	3.9	-0.59	-0.74
8709	4.0-5.0	8	672	1.783	0.004686	567	1220	1.3	13	0.0241	10.43	6.6	1.13	-1.65
8709	5.0-6.0	2	2	0.15	0.0026	100	2400	31	81	0.26	0.034	3.9	-0.29	1.25
8709	5.0-6.0	2	24	0.42	0.0073	150	5100	61	117	0.43	0.097	14.9	1.33	2.04
8709	5.0-6.0	2	168	0.74	0.00775	194	8300	95	124.1	0.57	0.267	17.2	2.67	3.15
8709	5.0-6.0	2	672	1.03	0.00863	246	10900	118	137.1	0.65	0.557	24.2	3.83	3.78
8709	5.0-6.0	4	2	0.034	0.000095	85	180	0.38	1.3	0.0073	0.13	0.1245	-1.92	0.26
8709	5.0-6.0	4	24	0.072	0.002095	132	330	0.97	20.3	0.0353	0.4	8.3	-1.47	0.07
8709	5.0-6.0	4	168	0.13	0.003695	171	490	1.42	37.3	0.0543	0.92	17	-1.02	-0.16
8709	5.0-6.0	4	672	0.26	0.006395	211	690	1.9	60.3	0.0763	1.74	30	-0.38	-0.49
8709	5.0-6.0	6	2	0.046	0.00019	100	190	0.37	3	0.013	0.15	1.4	-1.84	0.23
8709	5.0-6.0	6	24	0.095	0.00086	158	320	0.74	13	0.03	0.47	6	-1.51	0.07
8709	5.0-6.0	6	168	0.192	0.00169	213	480	1.12	26	0.048	1.21	13.1	-1.05	-0.17
8709	5.0-6.0	6	672	0.432	0.00379	276	710	1.6	46	0.07	2.31	23.1	-0.35	-0.52
8709	5.0-6.0	7	2	0.054	0.00024	120	190	0.31	3	0.01	0.15	1.6	-1.81	0.18
8709	5.0-6.0	7	24	0.099	0.00109	173	310	0.68	15	0.029	0.5	7.2	-1.45	0.01
8709	5.0-6.0	7	168	0.189	0.00249	221	470	1.1	32	0.05	1.23	16.4	-0.94	-0.25
8709	5.0-6.0	7	672	0.399	0.00519	279	680	1.56	56	0.075	2.08	28.4	-0.23	-0.60
8709	5.0-6.0	8	2	0.2	0.00083	240	560	0.44	2.5	0.0085	2.9	0.94	-1.27	-0.24
8709	5.0-6.0	8	24	0.258	0.00273	289	680	1.16	23.5	0.0425	3.21	10.54	-0.76	-0.46
8709	5.0-6.0	8	168	0.342	0.00463	333	820	1.78	43.5	0.0665	3.89	20.54	-0.23	-0.72
8709	5.0-6.0	8	672	0.502	0.00603	381	1020	2.16	58.5	0.0815	4.84	29.74	0.32	-1.01

Site	Depth	pH	Time (hours)	U	Th	S	Al	Ca	Mn	Fe	Co	Mo	PC1	PC2
				mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg		
8709	6.0-7.0	2	2	0.021	0.0011	64	2400	26	51	0.18	0.023	4.1	-0.80	1.18
8709	6.0-7.0	2	24	0.07	0.0061	105	5000	52	82	0.33	0.06	18.1	0.60	1.86
8709	6.0-7.0	2	168	0.158	0.00658	138	8200	84	95	0.58	0.16	23.8	2.06	3.14
8709	6.0-7.0	2	672	0.255	0.00948	184	10700	108	121	0.78	0.33	36.8	3.51	3.91
8709	6.0-7.0	4	2	0.025	0.0029	58	170	0.53	18	0.014	0.072	7.2	-1.73	0.16
8709	6.0-7.0	4	24	0.04	0.0056	95	320	0.97	35	0.026	0.192	15.1	-1.35	-0.04
8709	6.0-7.0	4	168	0.055	0.0085	120	490	1.38	58	0.041	0.392	27.1	-0.89	-0.29
8709	6.0-7.0	4	672	0.105	0.0103	161	740	1.65	73	0.051	0.612	35.6	-0.49	-0.49
8709	6.0-7.0	6	2	0.0015	0.0019	50	140	0.41	14	0.011	0.07	6.1	-1.82	0.20
8709	6.0-7.0	6	24	0.014	0.0074	80	290	1.15	43	0.033	0.18	19.1	-1.26	-0.10
8709	6.0-7.0	6	168	0.047	0.0131	105	480	1.92	80	0.063	0.44	36.1	-0.55	-0.45
8709	6.0-7.0	6	672	0.106	0.0177	136	670	2.39	115	0.092	0.71	54.1	0.16	-0.81
8709	6.0-7.0	7	2	0.013	0.00014	70	120	0.12	2.4	0.0024	0.13	1.4	-1.95	0.25
8709	6.0-7.0	7	24	0.013	0.00047	108	219	0.24	4.9	0.0044	0.32	4.1	-1.79	0.14
8709	6.0-7.0	7	168	0.035	0.00187	143	349	0.47	14.9	0.0112	0.62	10.8	-1.49	-0.04
8709	6.0-7.0	7	672	0.094	0.00327	193	559	0.67	24.7	0.0183	0.93	17.2	-1.14	-0.23
8709	6.0-7.0	8	2	0.014	0.0013	61	150	0.62	16	0.012	0.075	7.2	-1.77	0.17
8709	6.0-7.0	8	24	0.025	0.0041	94	280	1.24	38	0.027	0.171	17.2	-1.34	-0.05
8709	6.0-7.0	8	168	0.038	0.0077	118	420	1.8	64	0.043	0.311	30.2	-0.84	-0.32
8709	6.0-7.0	8	672	0.071	0.0099	159	590	2.09	80	0.054	0.461	40.2	-0.43	-0.54

				U	Th	S	Al	Ca	Mn	Fe	Co	Mo		
Site	Depth	pH	Time (hours)	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	PC1	PC2
8841	3.5-4.5	2	2	0.025	0.0017	22	3.9	2500	35	26	0.38	0.0045	-0.97	-2.20
8841	3.5-4.5	2	24	0.071	0.00243	38	7.1	5200	69	33.6	0.55	0.0111	0.67	-3.03
8841	3.5-4.5	2	168	0.135	0.00303	53	10.3	8400	104	40.5	0.633	0.0261	2.30	-3.66
8841	3.5-4.5	2	672	0.18	0.00593	74	21.3	10900	127	60.5	0.681	0.0541	4.44	-3.36
8841	3.5-4.5	4	2	0.013	0.00021	17	1.6	190	0.31	3	0.0079	0.011	-2.76	-0.82
8841	3.5-4.5	4	24	0.032	0.00241	26.5	11.6	320	1.61	24	0.0489	0.038	-1.48	-0.07
8841	3.5-4.5	4	168	0.066	0.00441	34.2	23.6	470	2.46	45	0.0789	0.093	-0.03	1.06
8841	3.5-4.5	4	672	0.131	0.00901	43.8	43.6	660	3.66	81	0.1209	0.16	2.41	2.78
8841	3.5-4.5	6	2	0.013	0.00038	29	2	180	0.42	3.8	0.01	0.0083	-2.51	-0.76
8841	3.5-4.5	6	24	0.029	0.00168	43	9.8	290	1.42	17.8	0.043	0.0273	-1.47	-0.20
8841	3.5-4.5	6	168	0.057	0.00388	56	20.8	410	2.52	36.8	0.078	0.0583	-0.08	0.66
8841	3.5-4.5	6	672	0.125	0.00708	77	36.8	610	3.47	64.8	0.116	0.0973	2.05	1.88
8841	3.5-4.5	7	2	0.013	0.00022	18	2.4	160	0.5	4.8	0.013	0.0091	-2.70	-0.82
8841	3.5-4.5	7	24	0.03	0.00112	29	9.7	258	1.41	16.8	0.042	0.0301	-1.81	-0.30
8841	3.5-4.5	7	168	0.059	0.00342	36.9	21.7	378	2.51	36.8	0.078	0.0621	-0.45	0.57
8841	3.5-4.5	7	672	0.125	0.00492	46.9	32.7	558	3.07	53.8	0.099	0.1011	0.96	1.47
8841	3.5-4.5	8	2	0.012	0.0004	23	2.1	150	0.4	3.8	0.01	0.0084	-2.62	-0.78
8841	3.5-4.5	8	24	0.032	0.0028	37	15.1	260	2.4	27.8	0.067	0.0304	-1.11	-0.01
8841	3.5-4.5	8	168	0.067	0.0061	46.7	29.1	380	4.1	54.8	0.114	0.0634	0.60	1.01
8841	3.5-4.5	8	672	0.13	0.0085	58.7	41.1	540	5	74.8	0.144	0.0944	2.18	1.91
8841	4.5-5.5	2	2	0.046	0.0021	23	3.8	2500	33	50	0.14	0.0073	-0.90	-1.54
8841	4.5-5.5	2	24	0.11	0.00303	37	6.7	5300	68	57.9	0.25	0.013	0.71	-2.27
8841	4.5-5.5	2	168	0.167	0.00533	49	17.7	8500	109	84.9	0.46	0.0209	3.14	-2.98
8841	4.5-5.5	2	672	0.192	0.00601	66	22.1	11100	140	92.9	0.61	0.0329	4.69	-3.61
8841	4.5-5.5	4	2	0.018	0.000072	22	1	170	0.31	1.6	0.0022	0.019	-2.67	-0.71
8841	4.5-5.5	4	24	0.039	0.003072	31.6	14	290	1.15	28.6	0.0272	0.048	-1.15	0.27
8841	4.5-5.5	4	168	0.071	0.005072	39.1	26	430	1.72	48.6	0.0432	0.086	0.17	1.23
8841	4.5-5.5	4	672	0.153	0.010472	49.1	58	620	2.92	100.6	0.0812	0.116	3.08	2.91

				U	Th	S	Al	Ca	Mn	Fe	Co	Mo		
Site	Depth	pH	Time (hours)	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	PC1	PC2
8841	4.5-5.5	6	2	0.013	0.000077	23	0.87	130	0.2	1.3	0.0018	0.021	-2.67	-0.67
8841	4.5-5.5	6	24	0.026	0.001577	35	9.17	229	0.67	17.3	0.0148	0.052	-1.61	0.10
8841	4.5-5.5	6	168	0.054	0.003777	46	20.17	349	1.16	36.3	0.0288	0.09	-0.26	1.09
8841	4.5-5.5	6	672	0.129	0.005577	62	31.17	509	1.52	53.3	0.0418	0.123	1.30	2.00
8841	4.5-5.5	7	2	0.018	0.00031	24	1.7	140	0.29	3.4	0.0042	0.021	-2.55	-0.63
8841	4.5-5.5	7	24	0.037	0.00121	36	8.1	232	0.68	14.4	0.0162	0.053	-1.64	0.05
8841	4.5-5.5	7	168	0.077	0.00301	46	19.1	352	1.17	32.4	0.0312	0.097	-0.29	1.06
8841	4.5-5.5	7	672	0.16	0.00511	59	32.1	512	1.57	51.4	0.0462	0.13	1.36	2.03
8841	4.5-5.5	8	2	0.015	0.00048	24	2.9	140	0.4	6.3	0.0078	0.02	-2.48	-0.60
8841	4.5-5.5	8	24	0.034	0.00268	38	13.9	250	1.12	28.3	0.0318	0.055	-1.07	0.35
8841	4.5-5.5	8	168	0.067	0.00498	47.2	26.9	370	1.79	52.3	0.0548	0.098	0.43	1.43
8841	4.5-5.5	8	672	0.125	0.00788	60.2	41.9	520	2.34	77.3	0.0808	0.132	2.22	2.52
8841	7.5-8.5	2	2	0.086	0.0017	12	3.3	2500	30	64	0.057	0.0083	-0.97	-1.41
8841	7.5-8.5	2	24	0.216	0.0065	18.5	17.3	5200	62	105	0.146	0.0128	1.92	-1.43
8841	7.5-8.5	2	168	0.356	0.0077	26.7	23.3	8400	103	120	0.406	0.0198	4.32	-2.53
8841	7.5-8.5	2	672	0.423	0.0088	42.7	32.3	10900	132	132	0.596	0.0328	6.30	-3.04
8841	7.5-8.5	4	2	0.026	0.000079	11	1.2	130	0.15	2.1	0.0017	0.017	-2.84	-0.78
8841	7.5-8.5	4	24	0.053	0.001779	15.9	8.9	240	0.47	16.1	0.0103	0.044	-1.88	-0.09
8841	7.5-8.5	4	168	0.092	0.004179	20.3	20.9	380	0.81	36.1	0.0223	0.076	-0.58	0.82
8841	7.5-8.5	4	672	0.212	0.006079	27.6	31.9	540	1.05	53.1	0.0323	0.1	0.98	1.58
8841	7.5-8.5	6	2	0.017	0.00085	11	2.8	110	0.24	6.5	0.0038	0.018	-2.68	-0.66
8841	7.5-8.5	6	24	0.036	0.00315	15.7	11.8	197	0.54	23.5	0.0124	0.044	-1.63	0.11
8841	7.5-8.5	6	168	0.088	0.00565	21.8	23.8	317	0.87	45.5	0.0234	0.078	-0.19	1.08
8841	7.5-8.5	6	672	0.198	0.00825	30	36.8	457	1.16	67.5	0.0354	0.099	1.53	1.93
8841	7.5-8.5	7	2	0.027	0.00016	12	1.1	87	0.12	1.6	0.0017	0.019	-2.81	-0.74
8841	7.5-8.5	7	24	0.049	0.00226	18.1	8.2	164	0.3	13.6	0.0086	0.047	-1.85	-0.01
8841	7.5-8.5	7	168	0.098	0.00456	23.7	22.2	274	0.62	38.6	0.0206	0.081	-0.37	1.00
8841	7.5-8.5	7	672	0.288	0.00756	32.7	39.2	434	0.92	67.6	0.0346	0.109	2.01	2.08
8841	7.5-8.5	8	2	0.039	0.00016	13	1.2	91	0.12	1.6	0.0017	0.021	-2.73	-0.71
8841	7.5-8.5	8	24	0.086	0.00386	19.3	14.2	188	0.7	30.6	0.0207	0.054	-1.03	0.37
8841	7.5-8.5	8	168	0.142	0.00886	34.3	36.2	338	1.34	67.6	0.0487	0.095	1.41	1.93
8841	7.5-8.5	8	672	0.252	0.01256	44.3	55.2	488	1.81	101.6	0.0687	0.123	3.65	3.13

Site	Depth	pH	Time (hours)	U	Th	S	Al	Ca	Mn	Fe	Co	Mo	PC1	PC2
				mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg		
8921	3.9-4.9	2	2	1.3	0.014	110	22	1100	20	410	0.66	0.4	0.65	-1.62
8921	3.9-4.9	2	24	2.3	0.027	240	58	2400	49	1030	1.4	0.88	3.34	-0.98
8921	3.9-4.9	2	168	3.5	0.0322	340	148	3600	71	1800	2.13	1.43	6.21	-0.58
8921	3.9-4.9	2	672	4.3	0.0371	520	278	4260	86	2900	3.83	1.69	9.77	0.09
8921	3.9-4.9	4	2	0.023	0.00049	120	0.1245	73	0.28	1.5	0.022	0.65	-1.54	-1.57
8921	3.9-4.9	4	24	0.039	0.00389	240	3.1	193	0.82	8.3	0.055	2.65	-1.24	-0.70
8921	3.9-4.9	4	168	0.118	0.00819	340	7.3	383	1.6	16	0.083	7.65	-0.93	0.48
8921	3.9-4.9	4	672	0.328	0.01129	417	11.6	643	2.9	22.2	0.107	13.55	-0.62	1.64
8921	3.9-4.9	6	2	0.0015	0.00024	120	0.1245	67	0.24	0.57	0.026	0.71	-1.56	-1.57
8921	3.9-4.9	6	24	0.016	0.00184	250	2.2	177	0.68	4.77	0.059	2.71	-1.32	-0.67
8921	3.9-4.9	6	168	0.078	0.00694	370	6.7	347	1.26	14.27	0.087	7.61	-0.97	0.60
8921	3.9-4.9	6	672	0.258	0.01104	460	11.7	567	1.98	22.87	0.111	14.01	-0.65	1.90
8921	3.9-4.9	7	2	0.011	0.00054	110	0.1245	65	0.19	1.1	0.017	0.83	-1.57	-1.59
8921	3.9-4.9	7	24	0.032	0.00404	240	2.6	165	0.57	7.1	0.044	3.13	-1.27	-0.63
8921	3.9-4.9	7	168	0.105	0.00654	350	5.2	335	1.08	11.7	0.064	8.63	-1.04	0.63
8921	3.9-4.9	7	672	0.315	0.00914	435	8.5	555	1.74	17	0.081	14.43	-0.78	1.81
8921	3.9-4.9	8	2	0.014	0.0011	110	1.2	59	0.17	2.6	0.014	0.95	-1.54	-1.57
8921	3.9-4.9	8	24	0.044	0.0071	240	5.9	179	0.59	14.6	0.047	3.75	-1.13	-0.51
8921	3.9-4.9	8	168	0.122	0.0106	350	9.2	339	1.06	20.9	0.068	9.65	-0.87	0.82
8921	3.9-4.9	8	672	0.352	0.013	426	12.3	569	1.7	26	0.084	15.75	-0.62	1.99
8921	4.9-5.9	2	2	1.1	0.0089	140	22	1400	24	460	0.52	0.29	0.53	-1.57
8921	4.9-5.9	2	24	1.44	0.0359	280	43	2900	54	910	0.96	0.44	3.16	-0.67
8921	4.9-5.9	2	168	2.2	0.0406	380	90	4400	82	1510	1.49	0.496	5.46	-0.32
8921	4.9-5.9	2	672	3.2	0.0453	600	147	5360	103	2420	3.09	0.565	8.56	0.51
8921	4.9-5.9	4	2	0.033	0.0016	140	1.9	89	0.39	6.5	0.02	0.75	-1.46	-1.45
8921	4.9-5.9	4	24	0.055	0.0044	280	4.8	219	1.02	13.6	0.045	2.65	-1.15	-0.50
8921	4.9-5.9	4	168	0.153	0.0062	410	6.5	419	1.82	17.5	0.063	7.35	-0.90	0.74
8921	4.9-5.9	4	672	0.433	0.0092	500	9.5	689	2.82	24	0.081	12.95	-0.57	1.92
8921	4.9-5.9	6	2	0.0015	0.00055	140	0.1245	87	0.3	1.7	0.016	0.9	-1.53	-1.44
8921	4.9-5.9	6	24	0.024	0.00225	280	2.6	217	0.76	7.7	0.035	3.3	-1.28	-0.44
8921	4.9-5.9	6	168	0.144	0.00665	400	6.6	407	1.31	16.9	0.052	8.5	-0.93	0.85
8921	4.9-5.9	6	672	0.514	0.00925	510	9.6	687	2.18	22.8	0.066	15.3	-0.58	2.28
8921	4.9-5.9	7	2	0.023	0.0022	140	1.7	79	0.27	4.6	0.016	0.91	-1.45	-1.42
8921	4.9-5.9	7	24	0.048	0.0052	280	3.7	199	0.7	10.6	0.035	3.31	-1.16	-0.40
8921	4.9-5.9	7	168	0.158	0.009	400	7	379	1.2	17.9	0.05	8.31	-0.85	0.86
8921	4.9-5.9	7	672	0.478	0.0126	492	10.6	629	1.87	25	0.065	14.31	-0.49	2.11
8921	4.9-5.9	8	2	0.019	0.001	120	1.5	66	0.24	4.4	0.013	0.85	-1.53	-1.54
8921	4.9-5.9	8	24	0.051	0.0036	270	4.8	186	0.75	14.4	0.036	3.25	-1.22	-0.48
8921	4.9-5.9	8	168	0.171	0.0078	400	8.9	376	1.33	25.4	0.055	8.75	-0.87	0.90
8921	4.9-5.9	8	672	0.531	0.01	496	11.8	656	2.15	30.9	0.069	15.15	-0.55	2.20

Site	Depth	pH	Time (hours)	U	Th	S	Al	Ca	Mn	Fe	Co	Mo	PC1	PC2
				mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg		
8921	5.9-6.9	2	2	1.4	0.0079	120	18	1200	25	500	0.36	0.35	0.46	-1.68
8921	5.9-6.9	2	24	1.84	0.0147	260	33	2700	60	1010	0.72	0.437	2.45	-1.10
8921	5.9-6.9	2	168	2.46	0.0169	370	56	4400	96	1440	1.14	0.469	4.43	-0.73
8921	5.9-6.9	2	672	3.04	0.0226	560	81	5800	126	1690	2.44	0.54	6.79	0.05
8921	5.9-6.9	4	2	0.046	0.00057	120	0.1245	81	0.28	1	0.013	0.67	-1.54	-1.57
8921	5.9-6.9	4	24	0.066	0.00267	250	2.3	221	0.85	4.8	0.033	2.67	-1.27	-0.66
8921	5.9-6.9	4	168	0.176	0.00447	380	4.2	441	1.57	8.2	0.046	8.17	-1.03	0.68
8921	5.9-6.9	4	672	0.526	0.00957	475	9.5	721	2.39	19.2	0.063	16.07	-0.61	2.21
8921	5.9-6.9	6	2	0.017	0.00063	110	0.1245	76	0.23	1.3	0.012	0.76	-1.56	-1.60
8921	5.9-6.9	6	24	0.038	0.00213	230	1.8	196	0.6	5.1	0.026	2.66	-1.34	-0.77
8921	5.9-6.9	6	168	0.188	0.00523	380	4.6	426	1.2	11.5	0.04	8.56	-1.01	0.75
8921	5.9-6.9	6	672	0.498	0.01143	480	10.4	676	1.92	25.5	0.058	14.66	-0.54	2.08
8921	5.9-6.9	7	2	0.016	0.00036	110	0.1245	74	0.19	0.95	0.0097	0.87	-1.57	-1.59
8921	5.9-6.9	7	24	0.046	0.00326	230	2.5	194	0.5	6.35	0.0227	3.47	-1.31	-0.65
8921	5.9-6.9	7	168	0.156	0.00506	360	4.9	394	0.84	10.15	0.0316	9.47	-1.08	0.77
8921	5.9-6.9	7	672	0.486	0.00766	453	8.5	674	1.32	16.05	0.0426	16.67	-0.77	2.16
8921	5.9-6.9	8	2	0.028	0.0011	120	1.1	70	0.18	2.3	0.01	0.95	-1.53	-1.52
8921	5.9-6.9	8	24	0.056	0.0046	250	3.7	190	0.54	8.8	0.027	3.55	-1.23	-0.52
8921	5.9-6.9	8	168	0.186	0.0091	390	7.9	390	1.05	17	0.043	9.75	-0.87	1.00
8921	5.9-6.9	8	672	0.616	0.0144	489	14.4	680	1.75	29	0.061	17.65	-0.40	2.55

Site	Depth	pH	Time (hours)	U	Th	S	Al	Ca	Mn	Fe	Co	Mo	PCA1	PCA2
				mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg		
9051	5.0-6.0	2	2	0.029	0.004	26	2.9	3200	18	13	0.032	0.011	-0.03	-1.18
9051	5.0-6.0	2	24	0.073	0.034	38	15.9	6900	38	68	0.068	0.025	4.90	-0.45
9051	5.0-6.0	2	168	0.117	0.0369	46	18.3	10600	54	75.7	0.094	0.041	6.91	-0.79
9051	5.0-6.0	2	672	0.166	0.0442	57	25.5	13300	58.1	93.7	0.1037	0.062	9.26	-0.23
9051	5.0-6.0	4	2	0.0015	0.0061	30	2.9	530	2.5	14	0.0099	0.03	-0.92	-0.20
9051	5.0-6.0	4	24	0	0.0114	41	6.1	840	4	24	0.0161	0.092	0.03	0.69
9051	5.0-6.0	4	168	0.015	0.0178	52	11.6	1190	5.8	36	0.0228	0.212	1.48	2.10
9051	5.0-6.0	4	672	0.051	0.0256	65	22.6	1520	7.4	53	0.0301	0.342	3.69	3.92
9051	5.0-6.0	6	2	0.0015	0.00072	30	0.1245	160	0.33	3.6	0.0021	0.035	-1.65	-0.29
9051	5.0-6.0	6	24	0	0.00392	44	3.1	350	1.22	18.6	0.0069	0.108	-0.66	0.80
9051	5.0-6.0	6	168	0.012	0.00652	56	7.1	510	1.78	30.6	0.0101	0.228	0.45	2.18
9051	5.0-6.0	6	672	0.04	0.00782	83	11.3	700	2	36.5	0.0121	0.348	1.85	3.94
9051	5.0-6.0	7	2	0.0015	0.00027	21	0.1245	110	0.19	1	0.0017	0.03	-1.89	-0.58
9051	5.0-6.0	7	24	0	0.00217	28.8	1.9	240	0.72	4.9	0.0046	0.089	-1.41	0.12
9051	5.0-6.0	7	168	0.011	0.00787	33.9	7.3	450	2.12	15.9	0.0124	0.175	-0.23	1.12
9051	5.0-6.0	7	672	0.035	0.01547	39.7	17.3	690	3.42	28.9	0.02	0.249	1.49	2.30
9051	5.0-6.0	8	2	0.0015	0.00029	27	0.1245	110	0.24	1.7	0.0017	0.03	-1.77	-0.41
9051	5.0-6.0	8	24	0	0.00219	43	1.5	250	0.88	6.6	0.0042	0.096	-1.14	0.55
9051	5.0-6.0	8	168	0	0.00579	57	4.9	460	1.98	16.6	0.008	0.195	-0.18	1.80
9051	5.0-6.0	8	672	0.015	0.01049	75	10.2	730	2.98	28.6	0.0119	0.286	1.23	3.21
9051	6.0-7.0	2	2	0.0015	0.0013	18	0.1245	2900	19	5.5	0.033	0.0066	-0.96	-1.62
9051	6.0-7.0	2	24	0	0.0072	25.6	3.3	6100	37	20.5	0.058	0.0152	0.75	-1.87
9051	6.0-7.0	2	168	0.01	0.0083	29.5	4.5	9700	55	23.5	0.091	0.0234	2.09	-2.54
9051	6.0-7.0	2	672	0.01	0.0094	33.9	6.1	12600	60.6	26.5	0.1006	0.0311	2.84	-2.71
9051	6.0-7.0	4	2	0.0015	0.0001	23	0.1245	150	0.19	0.0605	0.0017	0.033	-1.88	-0.52
9051	6.0-7.0	4	24	0	0.0013	35	0.86	350	0.86	3.5	0.0034	0.103	-1.41	0.32
9051	6.0-7.0	4	168	0	0.0029	42.4	3.26	570	1.61	7.7	0.0051	0.213	-0.83	1.38
9051	6.0-7.0	4	672	0.013	0.0054	52	14.26	820	2.39	14.4	0.0068	0.303	0.47	2.77
9051	6.0-7.0	6	2	0.0015	0.00011	14	0.1245	120	0.14	0.46	0.0017	0.0073	-2.06	-0.93
9051	6.0-7.0	6	24	0	0.00041	22.7	0	230	0.37	1.46	0.0019	0.0213	-1.87	-0.61
9051	6.0-7.0	6	168	0	0.00117	30.4	3.2	370	0.75	3.66	0.0036	0.0443	-1.43	-0.11
9051	6.0-7.0	6	672	0	0.00176	38.2	14.2	510	0.92	5.26	0.0038	0.0673	-0.62	0.76
9051	6.0-7.0	7	2	0.0015	0.00012	18	0.1245	110	0.18	0.67	0.0017	0.012	-1.98	-0.79
9051	6.0-7.0	7	24	0	0.00122	25.3	1	290	0.88	3.67	0.0034	0.035	-1.65	-0.40
9051	6.0-7.0	7	168	0	0.00292	28.9	6.4	470	1.56	7.77	0.0051	0.068	-1.07	0.17
9051	6.0-7.0	7	672	0	0.00442	32.8	19.4	620	1.88	10.87	0.0068	0.092	-0.14	1.04
9051	6.0-7.0	8	2	0.0015	0.00016	19	0.1245	110	0.18	0.73	0.0017	0.012	-1.96	-0.76
9051	6.0-7.0	8	24	0	0.00156	28	1.6	290	0.93	4.53	0.0034	0.04	-1.53	-0.26
9051	6.0-7.0	8	168	0	0.00248	34.4	4.7	430	1.34	7.13	0.0051	0.082	-1.08	0.34
9051	6.0-7.0	8	672	0	0.00348	42.2	10.6	590	1.75	10.03	0.0068	0.113	-0.47	1.02

Site	Depth	pH	Time (hours)	U	Th	S	Al	Ca	Mn	Fe	Co	Mo	PC1	PC2
				mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg		
9051	7.0-8.0	2	2	0.013	0.0042	41	5.9	2900	21	12	0.069	0.0057	0.49	-0.99
9051	7.0-8.0	2	24	0.032	0.0076	49.4	7.6	6100	45	19.4	0.11	0.0102	2.37	-1.63
9051	7.0-8.0	2	168	0.056	0.0096	53.4	9.3	9700	68	24.3	0.167	0.0164	4.28	-2.55
9051	7.0-8.0	2	672	0.07	0.0165	59	14.4	12500	75.4	33.9	0.187	0.0263	5.91	-2.51
9051	7.0-8.0	4	2	0.0015	0.002	14	0.1245	210	0.69	2.3	0.0022	0.005	-1.92	-0.93
9051	7.0-8.0	4	24	0	0.0033	21.2	0	380	1.22	4.5	0.0039	0.0119	-1.67	-0.71
9051	7.0-8.0	4	168	0	0.0061	25	3	560	1.85	7.7	0.0058	0.0188	-1.21	-0.41
9051	7.0-8.0	4	672	0.011	0.0121	29.3	9.2	760	2.56	12	0.0088	0.0242	-0.26	0.06
9051	7.0-8.0	6	2	0.0015	0.00013	13	0.1245	120	0.15	0.44	0.0017	0.0054	-2.08	-0.97
9051	7.0-8.0	6	24	0	0.00183	19.7	1.5	270	0.73	3.14	0.0036	0.0134	-1.73	-0.67
9051	7.0-8.0	6	168	0	0.00353	24.1	5	380	1.01	4.84	0.0053	0.0254	-1.32	-0.31
9051	7.0-8.0	6	672	0.013	0.00743	29.9	12.8	520	1.39	7.54	0.0071	0.0338	-0.38	0.28
9051	7.0-8.0	7	2	0.0015	0.00019	18	0.1245	110	0.17	0.52	0.0017	0.0057	-1.99	-0.83
9051	7.0-8.0	7	24	0	0.00219	30	1.7	270	0.84	3.62	0.0041	0.0127	-1.51	-0.39
9051	7.0-8.0	7	168	0	0.00599	39.8	5.8	440	1.52	7.22	0.0068	0.0204	-0.83	0.13
9051	7.0-8.0	7	672	0.016	0.00979	49.8	12.7	600	1.87	9.52	0.0088	0.0265	0.17	0.77
9051	7.0-8.0	8	2	0.0015	0.00041	13	0.1245	130	0.41	1.7	0.0017	0.0054	-2.03	-0.96
9051	7.0-8.0	8	24	0	0.00171	20.1	1.2	300	1.22	5.1	0.0034	0.0145	-1.69	-0.67
9051	7.0-8.0	8	168	0	0.00481	24.2	4.8	500	2.22	10.9	0.0064	0.0275	-1.10	-0.29
9051	7.0-8.0	8	672	0.021	0.00791	30.1	11.8	670	2.69	14	0.0081	0.0375	-0.12	0.27