Development of a Standardized Leaching Procedure for the Evaluation of Uranium Mobility in Groundwater in Nova Scotia

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Abstract

Approximately 4% of drinking water wells in Nova Scotia contain elevated concentrations of naturally-occurring uranium. There is demand for a simple and effective procedure to evaluate soil and rock formations for uranium mobility prior to the development of potable water supplies in vulnerable regions. Empirical evidence shows that uranium mobilization in groundwater can be enhanced in the presence of key ions. A series of extractions were performed on uranium-bearing Nova Scotian rocks, noting the impact of calcium, sodium, chloride, and bicarbonate concentrations in the extraction fluid on uranium mobilization. A uranium leaching procedure (ULP) was developed and compared to the general synthetic precipitation leaching procedure (SPLP). The ULP was capable of mobilizing an order of magnitude or more uranium than the SPLP from six Nova Scotian rock samples and shows promise as a tool for choosing groundwater resources to minimize the risk of groundwater contamination through uranium mobilization.

Keywords: uranium, groundwater, mobilization, leaching, sorption, extraction procedure, speciation, complexation, uranyl-carbonate

List of Abbreviations and Symbols Used

ANOVA	Analysis of variance
APHA	American Public Health Association
CMA	Calcium magnesium acetate
DIC	Dissolved inorganic carbon
(NS) DME	(Nova Scotia) Department of Mines and Energy
(NS) DNR	(Nova Scotia) Department of Natural Resources
Eh	Oxidation-reduction potential; redox potential
g	Grams
h	Hours
ICP-CC	Inductively coupled plasma collision cell
ICP-MS	Inductively coupled plasma mass spectrometry
kg	Kilograms
L	Liters
MAC	Maximum acceptable concentration
MB	Millet Brook
MEC	Mining Engineering Centre
mL	Milliliters
μg	Micrograms
μm	Micrometer; micron
mV	Millivolt
NS	Nova Scotia
NSE	Nova Scotia Environment
ORP	Oxidation-reduction potential; redox potential
ppb; ppm	Parts per billion; parts per million
RDL	Reportable detection limit
SMB	South Mountain Batholith
SPLP	Synthetic Precipitation Leaching Procedure
Sv, mSv, μSv	Sievert; millisievert; microsievert
TCLP	Toxicity Characteristic Leaching Procedure

TMP	Three Mile Plains
U	Uranium
U(IV)	Tetravalent uranium isotope
U(VI)	Hexavalent uranium isotope
UEMPA	Uranium Exploration and Mining Prohibition Act
UO_2^{2+}	Uranyl ion
USEPA	United States Environmental Protection Agency

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Chapter 1 Introduction

Uranium is a naturally-occurring element in rock formations throughout Nova Scotia. Some areas of the province are so rich in uranium that they were explored for prospective uranium mines in the 1970s and early 1980s before public concern for environmental and human health pressured the provincial governing bodies to prohibit uranium exploration and mining (O'Reilly, 1982). Elevated uranium concentrations in groundwater have been observed across the province; approximately 4% of wells exceed the Canadian drinking water MAC of 20 μg/L (Drage & Kennedy, 2013; Health Canada, 2009). In Nova Scotia, uranium is the second most common naturally occurring contaminant to exceed its guideline, after arsenic (Drage & Kennedy, 2013). This thesis details the development of a simple procedure for the characterization of the risk of uranium mobilization into groundwater based on an understanding of uranium geochemistry and the mechanisms that allow it to be released from subsurface material. Particular emphasis is placed on uranium mineralization and mobilization in plutonic and sedimentary rock formations in Nova Scotia.

1.1 Uranium Geology and Geochemistry in Nova Scotia

In Nova Scotia, uranium occurs primarily in igneous and sedimentary rock formations; consequently, it is the plutonic and sedimentary groundwater regions in the province that give rise to elevated uranium in wells (Drage & Kennedy, 2013). Parent magma will crystallize common minerals first as it cools; the later crystallization of incompatible elements such as uranium, thorium, tin, and tungsten from a parent magma results in minerals that are rich in these incompatible elements in igneous rock formations and in the fractures and veins within rock formations (O'Reilly, 1982). The most significant of such formations in Nova Scotia is the South Mountain Batholith (SMB). The uranium-enriched rocks found in localized areas of the SMB are the parent material for the formation of sandstones, siltstones and shales in sedimentary rocks such as the Horton Group in Nova Scotia. Additional mineralization of uranium can occur due to the deposition of aqueous uranium from groundwater to aquifer material as the groundwater encounters a reducing environment. Such an accumulation of uranium as a result of changes in redox potential (measured as Eh) and pH in sedimentary sequences is referred to as a roll-front occurrence (Ryan & O'Beirne-Ryan, 2009).

Uranium is a radionuclide of the actinides group (Murphy & Shock, 1999). The uranium decay series includes the isotopes radon and radium, daughter products that, when found in well water, can indicate the presence of elevated uranium in rock formations nearby (O'Reilly, 1982). At concentrations observed in well water, the chemical toxicity of uranium is more dangerous to human health than its radioactive properties; the heavy metal can cause kidney disease in chronically exposed individuals (Drage & Kennedy, 2013; Health Canada, 2009). The daughter products associated with uranium are more of a concern radiologically and have the potential to cause leukemia and lung, bone, breast, and thyroid cancers (Grantham, 1986; Health Canada, 2009).

1.2 Uranium Mobilization

Several mechanisms for uranium mobilization have been proposed in the literature, including weathering of uranium-bearing rocks (O'Beirne-Ryan, 2006; Parsons, 2007; Ryan et al., 2009; Ryan & O'Beirne-Ryan, 2009), ion exchange (Bäckström et al., 2004; Drage & Kennedy, 2013), the formation of soluble complexes between the uranyl ion and other constituents present in groundwater (Dong et al., 2004; Bachmaf et al., 2008; Nair & Merkel, 2011; Drage & Kennedy, 2013), and the changes in pH and oxidation-reduction potential (ORP; Eh) on uranium sorption behaviour (Samolczyk et al., 2010; Nair & Merkel, 2011; Drage & Kennedy, 2013). These mechanisms, particularly the complexation of uranium with other groundwater constituents, are dependent upon environmental conditions such as the distribution of uranium within the mineralogy of the rocks, the pH and Eh of groundwater, and the presence of complexing ions such as calcium, sodium, dissolved inorganic carbon (DIC), sulphate, and chloride.

The literature reports that uranium can be mobilized due to the formation of a zero-valent, calcium-uranyl-carbonate complex $(Ca_2UO_2(CO_3)_3)^0$ and other uranyl-carbonate or uranyl-sulphate complexes (Langmuir, 1978; Dong et al., 2004; Fox et al., 2006; Drage & Kennedy, 2013). The complexing ions required for the formation of these species can be inherently present in the rock formation or can be added to groundwater from both natural and anthropogenic activity. Empirical evidence in Nova Scotia has suggested that dissolved calcium or carbonate leaching from construction and demolition (C&D) waste disposal sites can contribute to elevated uranium levels in aquifers (Drage & Kennedy, 2013). Elevated uranium concentrations have been reported not only near C&D sites, but also in areas under the influence of seawater intrusion or the application of road salt (Drage & Kennedy, 2013). An evaluation of the mobility of uranium from aquifer material could identify regions of Nova Scotia that are vulnerable to uranium mobilization in groundwater and enable proper siting of construction and demolition facilities, allowing decisions to be made regarding drinking water resources in new developments across the province. Procedures exist to evaluate the transport of contaminants from solid waste and soils (US EPA 1992; US EPA 1994), but they do so by simulating landfill and on-land disposal of waste and contaminated soils. Hence, there is a need for a procedure to test the mobility of naturally-occurring contaminants in groundwater.

1.3 Objectives

This project aims to develop a standardized leaching test for determining the potential for uranium mobilization from bedrock. A review of common, existing leachate tests such as the Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP), which are tests that simulate landfill or waste pile conditions to determine whether a sample of solid waste is hazardous or not, will form the basis for the development of this leaching procedure (United States Environmental Protection Agency [USEPA], 1992), (USEPA, 1994). The solubility of uranium in groundwater may be affected by pH, temperature, redox potential, and agitation time. These factors, as well as the presence of complexing ions, were examined during the experimental phase of the project to determine the sensitivity of the test to these conditions.

A series of tests performed on uranium-bearing rock from various locations in Nova Scotia were examined under the influence of extraction fluids containing water chemistry parameters indicative of the influence of seawater intrusion, road salt application, and runoff from C&D processing or disposal sites. The redox potential was maintained approximately constant to simulate the oxidizing conditions conducive to uranium mobilization for each extraction performed. The principal factors under examination in this study were pH, agitation time, and the presence of varying concentrations of calcium, sodium, carbonate (and bicarbonate), chloride, and sulphate, which are known or suspected to influence the dissolution or desorption of uranium.

Chapter 2 Literature Review

The mobility of uranium in the environment is a complex topic that has been explored in a variety of laboratory scale tests, modeling studies, and evaluations of groundwater data. As a result, there is a rich pool of literature from which to develop an understanding of uranium and its environmental mobility. This literature review discusses uranium in Nova Scotia in the context of exploration and occurrences in rock formations and groundwater throughout the province. It then discusses the physical and chemical properties of uranium as a radionuclide, before discussing its geochemical behaviour in the subsurface. This leads to a section on uranium mobilization, in which specific mobilizing factors are discussed. Finally, the existing leaching tests used for contaminant evaluation are explored and the need for a uranium-specific test is reinforced.

2.1 Uranium in Nova Scotia

The presence of naturally occurring uranium in Nova Scotian rock formations and groundwater has been known for decades. While the province was briefly explored for prospective uranium mines in the 1970s and 1980s (O'Reilly, 1982), concern for public and environmental safety eventually resulted in legislated prohibition of uranium mining and exploration in the province (Uranium Exploration and Mining Prohibition Act [UEMPA], 2009). This thesis seeks to develop an understanding of the mobility of uranium in the environment, with a particular focus on Nova Scotia. This literature review begins with a discussion on the policy surrounding uranium mining and exploration in Nova Scotia, comments on the known occurrences of uranium across the province in igneous and sedimentary rock formations, and explains the known areas of elevated uranium in groundwater.

2.1.1 History of Uranium Exploration and Legislation

The presence of uranium in Nova Scotia has been known since the late 1950s, when Brummer noted the significance of uranium mineralization in northern mainland Nova Scotia (as cited in O'Reilly, 1982, p. 3). Mining the uranium for profit was briefly considered but the low market price of uranium and the high cost and crudeness of exploration techniques at the time would have made the implementation of a uranium mine prohibitively expensive. The refinement of uranium exploration techniques in the mid-1970s, paired with a concurrent increase in the market price of uranium, increased the economic viability of a uranium mining operation in Nova Scotia. Mining companies from all over the world were attracted to the known uranium occurrences in the New Ross, Lunenburg, and Georgeville areas of Nova Scotia (see Figure 2-1). Over the next several years, the testing of wells for uranium and its daughter products in groundwater, coupled with the public release of a radiometric survey by the Geological Survey of Canada, led to the discovery of promising uranium mine prospects in mainland Nova Scotia (O'Reilly, 1982).

Mineral resources in the mid-1970s were governed by the Nova Scotia Department of Mines and Energy (DME), which today operates as the Nova Scotia Department of Natural Resources (DNR). In 1975, uranium was designated a "special license" mineral, requiring the submission of a work proposal under special terms and conditions so the province could monitor the surge of exploration interest. The Uranium Task Force was born out of concern for environmental and public health in 1980 and investigated the presence of uranium in well water. In 1978, the Guidelines for Canadian Drinking Water Quality had recommended that the Maximum Acceptable Concentration for uranium be lowered from 5000 ppb to 20 ppb. The Uranium Task Force reported that 6% of wells exceeded the new recommendation (O'Reilly, 1982).

In 1981, the provincial Minister of Development declared the intent to protect workers, public, and the environment by allowing open discourse between the public, government, and mining companies to determine the terms and conditions, submission requirements, and approval procedures that would comprise provincial regulations. As such, any applications for leases to mine uranium were dismissed on the grounds that any mining of uranium should be conducted under acceptable standards with public input. An official moratorium on uranium exploration came into effect on September 22, 1981. Existing licenses were allowed to continue exploration but no new uranium exploration licenses were issued, such that all exploration stopped when the licenses expired in 1982 (O'Reilly, 1982). That same year, the Uranium Inquiry – Nova Scotia was established to investigate all scientific and technical information related to human and environmental protection associated with uranium mining (O'Reilly, 1982).

This moratorium remained in place until it was legislated in November, 2009 as the *Uranium Exploration and Mining Prohibition Act*. The Act states that uranium ore bodies may not be sought or mined and invalidates any mineral licenses or special leases issued before or after the Act. It states that any mining activity for a mineral other than uranium may extract the uranium as long as it does not exceed 0.01 percent by weight and the appropriate regulations for the mining, treatment, handling and disposal of uranium are followed (UEMPA, 2009).

2.1.2 Uranium Occurrences

Uranium can be found in igneous, sedimentary, and metamorphic rocks in Nova Scotia, although it is more predominant in igneous and sedimentary regions (Drage & Kennedy, 2013; O'Reilly, 1982). An occurrence of any mineral is defined as a locality where an interesting concentration of mineral has been found (O'Reilly, 1982). Uranium occurrences can be found in intrusive igneous rock formations, both large batholiths and smaller plutons, throughout Nova Scotia. In such rocks, the uranium content typically increases as the silica content of the rock increases. Sedimentary rock formations contain uranium in shale or clay rich layers; bituminous material also tends to be rich in uranium. Metamorphism tends to cause a release in fluid and uranium with it; therefore the original uranium content of a metamorphosed rock decreases (O'Reilly, 1982). This section discusses how uranium is mineralized in different rock types in Nova Scotia.

The uranium exploration period in the late 1970s and early 1980s identified a number of uranium occurrences across the province in a variety of environments. **Error! Not a valid bookmark self-reference.** summarizes the exploration efforts and identifies the different types of uranium occurrences across Nova Scotia, indicating the ones that could be profitable as "prospects" (O'Reilly, 1982). The types of deposits described by O'Reilly (1982) are magmatic deposits and vein type deposits in igneous rocks, and sandstone type deposits and black shale deposits in sedimentary rock formations.

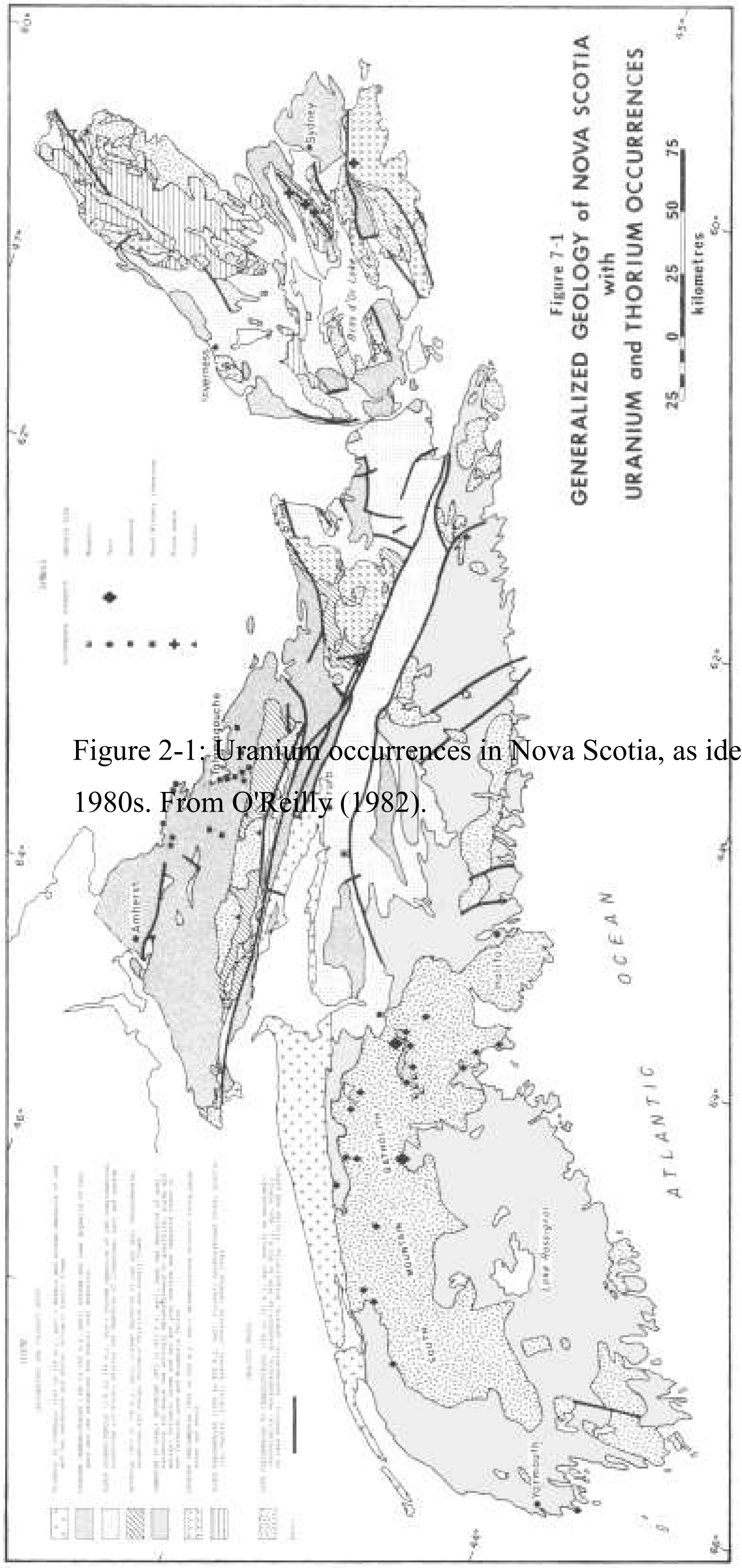

Figure 2-1: Uranium occurrences in Nova Scotia, as identified by mining exploration co
1980s. From O'Reilly (1982).

Magmatic deposits are formed when magma that contains uranium crystallizes. Uranium is an incompatible element and will remain in the liquid magma as the more common minerals crystallize. The incompatible elements remaining in the magma crystallize during the late stages of magma cooling and this results in a rock that is rich in elements such as uranium, fluorine, tin, tungsten, and thorium (O'Reilly, 1982). Vein type deposits are associated with uraniferous granites and form due to changes in temperature of meteoric water as it circulates through a heated batholith (O'Reilly, 1982).

The weathering of uranium-rich granites can contribute to the formation of sedimentary rocks that are similarly high in uranium (Ryan & O'Beirne-Ryan, 2009). Uranium can also mineralize within sedimentary rocks through transport and later deposition of ore-bearing solutions from surface and groundwater (O'Reilly, 1982) under changing pH and redox conditions (Ryan & O'Beirne-Ryan, 2009). This is known as a "roll front" occurrence and forms as dissolved uranium(VI) in groundwater flows through a reducing zone, resulting in the deposition of insoluble U(IV) (Ryan & O'Beirne-Ryan, 2009). Deposits of this type can be found in the large sedimentary basins of northern Nova Scotia in Hants County (O'Reilly, 1982). The clay minerals in the reducing environments in black shales on Cape Breton Island have a similar affinity for fixing uranium. Sedimentary deposits are typically lower in uranium concentration than the granites that the uranium is derived from; in the uranium exploration period, many black shale deposits were considered too low grade to be economical (O'Reilly, 1982).

Of particular importance to this study are the intrusive igneous rocks of the South Mountain Batholith and the overlying Horton Group sandstones and shales that are found in much of south central Nova Scotia, as shown in Figure 2-1 (Ryan & O'Beirne-Ryan, 2009). Known uranium occurrences in the Windsor area of Nova Scotia include the Three Mile Plains (TMP) occurrence, the Millet Brook (MB) occurrence, and the Green Street occurrence in St. Croix. This area was extensively explored for uranium in the late 1970s and early 1980s; cores from the exploration efforts at TMP and MB can be accessed at the DNR provincial core library. As identified in **Error! Not a valid bookmark self-reference.**, there were a number of other interesting occurrences from Yarmouth to Cape Breton Island, including the Northumberland shore, but the most significant prospects were identified in rocks from the Windsor area; these are the rocks on which the laboratory phases of this project were performed.

2.1.3 Uranium in Groundwater

Uranium concentrations in wells throughout the province have been documented by a number of authors (O'Reilly, 1982; Grantham, 1986; Kennedy & Finlayson-Bourque, 2011; Samolczyk et al., 2012; Drage & Kennedy, 2013). Approximately 40% of the population in Nova Scotia relies on private wells as opposed to municipally distributed water. It has been reported in various studies that 4 – 25% of wells sampled across the province exceed the Canadian drinking water MAC for uranium of 20 µg/L (Samolczyk et al., 2012; Drage & Kennedy, 2013; Grantham, 1986). Figure 2-2 shows uranium occurrences in groundwater in Nova Scotia, as compiled by Kennedy & Finlayson-Bourque (2011) and published in Drage & Kennedy (2013). This section discusses the geological environments that are conducive to uranium mobilization and where elevated groundwater uranium concentrations exist in Nova Scotia. The environmental conditions governing uranium mobilization will be discussed in more detail in Sections 2.3 and 2.4.

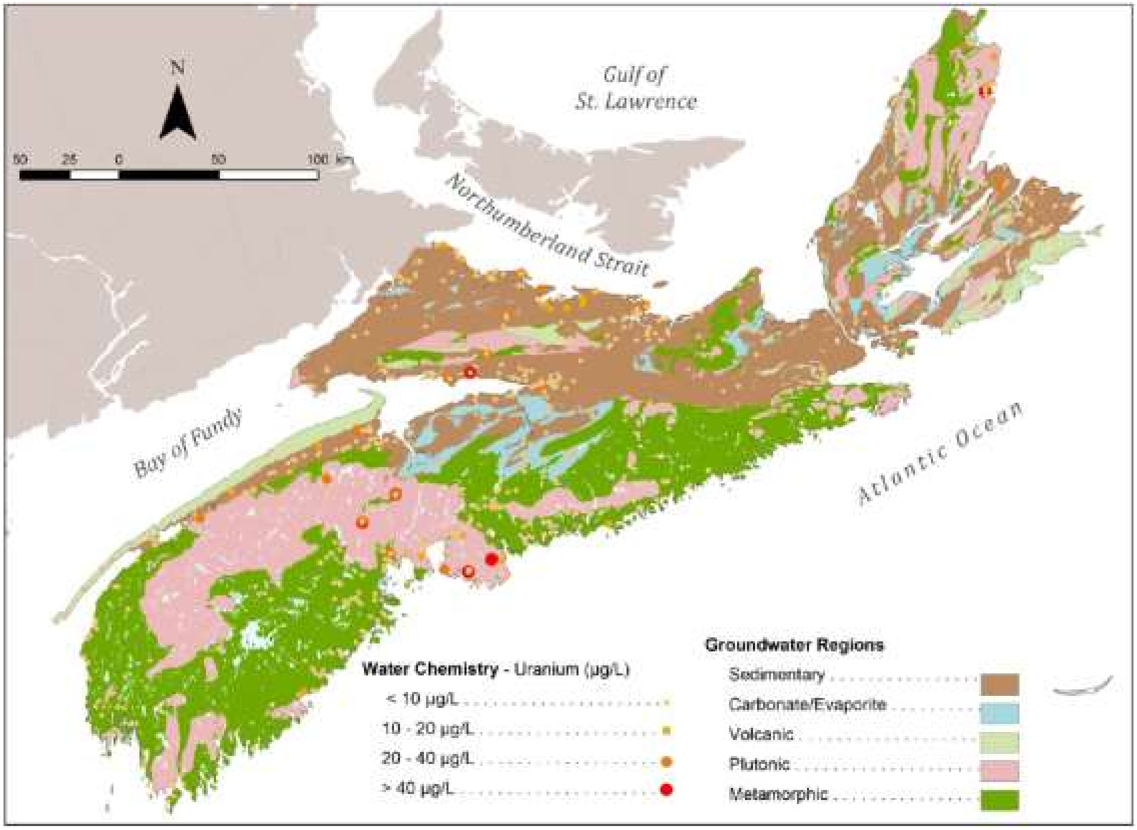

Figure 2-2: Uranium occurrences in well water in Nova Scotia. The occurrences that exceed the uranium guideline are indicated with the larger, orange and red dots and are generally found in the sedimentary and plutonic groundwater regions (Drage & Kennedy, 2013; Kennedy & Finlayson-Bourque, 2011).

In Nova Scotia, the geologic environments most likely to produce elevated uranium in groundwater are the granite batholiths that cover much of mainland Nova Scotia and the alkaline sandstone and shale areas of the Upper Carboniferous basin in the northwest of the province (Grantham, 1986). Uranium-enriched geologic units in Nova Scotia, particularly in the granitic rocks of the South Mountain Batholith, have been associated with anomalous concentrations of uranium and associated radium and radon in groundwater (Drage & Kennedy, 2013; Grantham, 1986).

In general, granitic rock formations produce elevated uranium when the pH and alkalinity are high and complexing ions such as phosphate, silicate, fluoride, and arsenic are present. In the sedimentary rocks of the Carboniferous basin, uranium in groundwater is similarly associated with high pH, high alkalinity, and the presence of silicate, fluoride, and phosphate, but also with hardness and total dissolved solids (Grantham, 1986). This is consistent with observations from various studies that phosphate, carbonate, silicate, and fluoride tend to form soluble complexes with uranium (O’Reilly, 1982; Bachmaf et al., 2008; Dong et al., 2005).

2.1.3.1 Case study: Uranium Mobilization Associated with Construction and Demolition Debris

A construction and demolition disposal site about 15 km outside of Halifax, Nova Scotia, has come under scrutiny in recent years due to an ongoing and escalating increase in heavy metal concentrations, including uranium, in residential wells downgradient of the site. The site operated as a C&D debris disposal site from 1997 to 2013 under different ownership and management. Growing concern about groundwater contamination has led to an environmental assessment and an ongoing court case.

The previous owner and operator of the site accepted and processed construction and demolition waste, but left much of the material in a waste pile exposed to the elements for years because there were no licensed C&D disposal facilities in the province. A containment cell was built to contain the 120 000 tonnes of unrecyclable material on site in 2004, but the operators were still accepting new C&D waste and leaving it on-site. When the current owners took over operation, there were known concerns about the surrounding environment, so they removed the waste left by the previous owners to a proper disposal facility, constructed a concrete pad on which processing was to be done, and continued operation of the disposal facility. Material was removed from the site for disposal in a licensed C&D disposal facility after no more than 30 days. Despite these actions taken to mitigate the impact of the continuing operation, the on-site monitoring wells and residential wells downgradient continued to show increasing groundwater contamination over time. In 2010, seven downgradient wells were identified as "very likely" or "likely" influenced by the plume of contaminated groundwater originating at the C&D site, and three of them required remedial action due to upward trends (Conestoga-Rovers and Associates [CRA], 2011). A geologist with the Nova Scotia Department of Environment (NSE), postulated that uranium on-site is naturally present in the geology but is mobilized through complex chemical and possibly microbial changes as a result of contamination from the site (NSCC 137, 2015).

This case study acts as a catalyst for this project; the operations at this site appear to have led to anomalously high concentrations of uranium in domestic drinking water wells; uranium concentrations have reached concentrations as high as 1200 µg/L. The development of a standardized leach test for uranium could be used to determine the optimum siting of C&D disposal and processing sites considering local geologic conditions, thereby preventing the contamination of residential drinking water and protecting the health of Nova Scotians.

2.2 Physical and Chemical Properties of Uranium

Uranium is a radionuclide in the actinide group of the periodic table. Radioactive elements have an unstable natural configuration, so they release energy in the form of radiation in order to achieve a stable state. This is called radioactive decay and, in the case of uranium, produces a series of daughter products and different isotopes, many of which are also radioactive. Uranium exists in the environment in three distinct isotopes. The most common isotope is U^{238} (99.3%), and the other two, U^{235} and U^{234} are found in much smaller quantities (0.71% and 0.006%, respectively) (O'Reilly, 1982). The decay series for uranium-238 can be found in Appendix A (adapted from O'Reilly, 1982). The radiation emitted during decay can be in the form of alpha (α), beta (β), or gamma (γ) radiation. Alpha radiation takes the form of two protons and two neutrons and does not penetrate skin; it is usually absorbed by the outer layers of skin, but inhalation and ingestion are serious health hazards. Beta radiation is emitted at a lower energy than alpha particles in the form of negatively charged electrons or positively charged positrons. This type of radiation is only harmful at intense levels, although inhalation and ingestion are still cause for serious concern. Finally, gamma radiation occurs as shortwave electromagnetic radiation and is the most penetrative of the three forms; it can cause significant damage to interior organs without being ingested (O'Reilly, 1982).

The principles of radioactive decay and the half-life of uranium daughter products are considered and used in geochemical exploration for uranium. Two important daughter products of uranium are the gases radon-222, which has a short half-life of 3.8 days, and radium-226, which has a longer half-life of 1620 years (O'Reilly, 1982). The chemical partitioning of these daughter products is highly dependent on geochemical conditions and they are sometimes found at great distances from the uranium source. However, geochemical testing for these two elements can be indicative of nearby uranium sources, especially if there is a large amount of the short-lived radon in well water samples (O'Reilly, 1982).

The presence of uranium and other actinides at "vanishingly low concentrations" in the environment can still have significant consequences to human health due to radiological effects (Murphy & Stock, 1999). However, it is the toxicological effects, rather than the radiological effects of uranium, that are dangerous to human health at concentrations typically found in groundwater. The properties of uranium as a heavy metal can cause kidney damage in chronically exposed individuals (Grantham, 1986). Radon and radium, which are commonly associated with uranium in the environment, are more dangerous from a radiological point of view, causing lung and bone cancer, respectively (Grantham, 1986; Health Canada, 2011).

2.3 Geochemistry

Uranium is a multivalent metal that exists in the environment in either its tetravalent form, U(IV) or U^{4+}, or in its hexavalent form, U(VI) or U^{6+} (Murphy & Shock, 1999). There are at least 200 uranium-bearing minerals known in Canada (Murphy & Shock, 1999). In this section, the general behaviour of uranium in the environment is discussed along with its presence in uranium-bearing minerals.

The hexavalent form of uranium, U(VI) is generally considered the environmentally available form (Murphy & Shock, 1999). It is mobile in the environment as the uranyl ion, UO_2^{2+}, and its complexes (Langmuir, 1978; O'Reilly, 1982;Ryan & O'Beirne-Ryan, 2009; Kumar et al., 2011). When uranium is leached from rocks as the mobile uranyl ion, the concentration of uranium in the rocks decreases. Subsequent uranium enrichment elsewhere can occur when a reducing environment converts the mobile hexavalent uranium to the immobile tetravalent uranium, U(IV) (O'Reilly, 1982). Tetravalent U(IV) is not typically soluble and is present in reducing environments where it readily sorbs to aquifer material (Langmuir, 1978; O'Reilly, 1982; Ryan et al., 2009). This is the mechanism behind roll front occurrences as discussed in Section 2.1.2.

In general, the most abundant uranium-bearing mineral is uraninite, UO_2, which can also be called pitchblende when referring to its oxidized form (Murphy & Shock, 1999). Uranium is also commonly associated with biotite, smoky quartz, iron and titanium minerals (O'Beirne-Ryan, 2006; Nair et al., 2014). In subsurface environments, carbon-rich or pyrite horizons tend to be high in uranium, where it was deposited as oxidizing groundwater encountered reducing conditions there (Samolczyk et al., 2012).

Many actinides are present as colloids in the environment, which complicates the discussion of uranium transport (Murphy & Shock, 1999). The influence of colloids on uranium geochemistry is a complex issue that tends to limit the accuracy of geochemical modeling. It has been argued that no thermodynamic description of solubility equilibria of actinides can be easily obtained because the effect of colloids cannot be quantified (Murphy & Shock, 1999).

In the environment, uranium forms a strong association with organic matter (Murphy & Shock, 1999; Nair & Merkel, 2011). Organic matter can be very influential on actinides in the environment, but information is limited due to the variability of the structures of the functional groups in humic substances that bind the trace metals. Metals such as uranium that form a strong association with organic matter can be expected to be less mobile in aquifers that are rich in organics (Murphy & Stock, 1999).

Uranium can be considered fixed or leachable, depending on the mineral with which it is associated. The amount of uranium that is easily mobilized from any rock sample typically makes up only a small fraction of the total uranium present; the mobile portion tends to be that which is adsorbed to mineral surfaces and the edges of clay minerals (Jurgens et al., 2010). On the other hand, uranium that is present in certain minerals, such as zircon, is not environmentally available because it is tightly bonded within the mineral structure itself (O'Beirne-Ryan, 2006). The uranium in minerals such as biotite is usually present in cleavages and is therefore easily mobilized when the biotite is physically or chemically weathered to clay minerals (Parsons, 2007).

2.4 Uranium Mobilization

Hydrogeological environments are complex and therefore any discussion of uranium mobilization in groundwater is necessarily complex. Mobilization of uranium can occur due to a number of mechanisms, including weathering, ion exchange, pH, Eh, and the formation of soluble or insoluble complexes. This section discusses these mechanisms before exploring the specific complexing ions that could be influencing uranium in Nova Scotia.

O'Beirne-Ryan (2006) discussed the weathering of rocks from the South Mountain Batholith and the consequent mobilization of uranium from the eroded rocks of the region. Parsons (2007) further noted that visibly weathered samples from the South Mountain Batholith contained less uranium than fresh or less weathered samples from comparable areas, indicating that uranium is released during some physical and chemical weathering processes.

Bäckström et al. (2004) and Bachmaf et al. (2008) identified ion exchange as a significant mechanism for the transport of heavy metals in subsurface environments. Ion exchange refers to the competition of ions for exchange sites on the surface of suspended particles, including ion exchange with structural and non-structural minerals as well as with organic matter and any associated metal ions (Schnoor, 1996). Charged media tend to hold some ionic species more tightly than others, depending on pH and Eh conditions (Schnoor, 1996). Below are the general preference orders for cations and anions, respectively, from Reible (1999).

$$Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mg^{2+} > Ag^{+} > Ca^{+} > K^{+} > NH_4^{+} > Na^{+}$$

$$SO_4^{2-} > I^{-} > NO_3^{-} > CrO_4^{2-} > Br^{-} > Cl^{-}$$

Subsurface media may replace an ion of lower preference with one of the same charge that is of higher preference because certain ions are attracted and held more strongly than others by a given medium (Baird & Cann, 2012). The above preference orders do not include uranium ions. Uranium can be present as the uranyl ion, or as a complex between uranyl and carbonate, phosphate, fluoride, sulphate, or other anions (Dong et al., 2005; O'Beirne-Ryan, 2008; Bachmaf et al., 2008, Jurgens et al., 2010). Figure 2-3 shows that two common uranyl-carbonate complexes, $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$, dominate carbonate-rich aqueous systems at circumneutral to alkaline pH (Nair & Merkel, 2011). These anions can participate in ion exchange, depending on where they exist in the anion preference order. Ion exchange can replace the uranyl cation, UO_2^{2+}, or either of the uranyl-carbonate anions, with an ion of higher preference. In this way, ion exchange can directly influence the aqueous concentration of uranium. Ion exchange is also capable of indirectly affecting uranium concentrations in groundwater by liberating ions that will then form mobile species or precipitates with uranyl complexes (Bäckström et al., 2004; Nair & Merkel, 2011). The exchange of ions depends on many water chemistry parameters, including pH and oxidation-reduction potential (ORP).

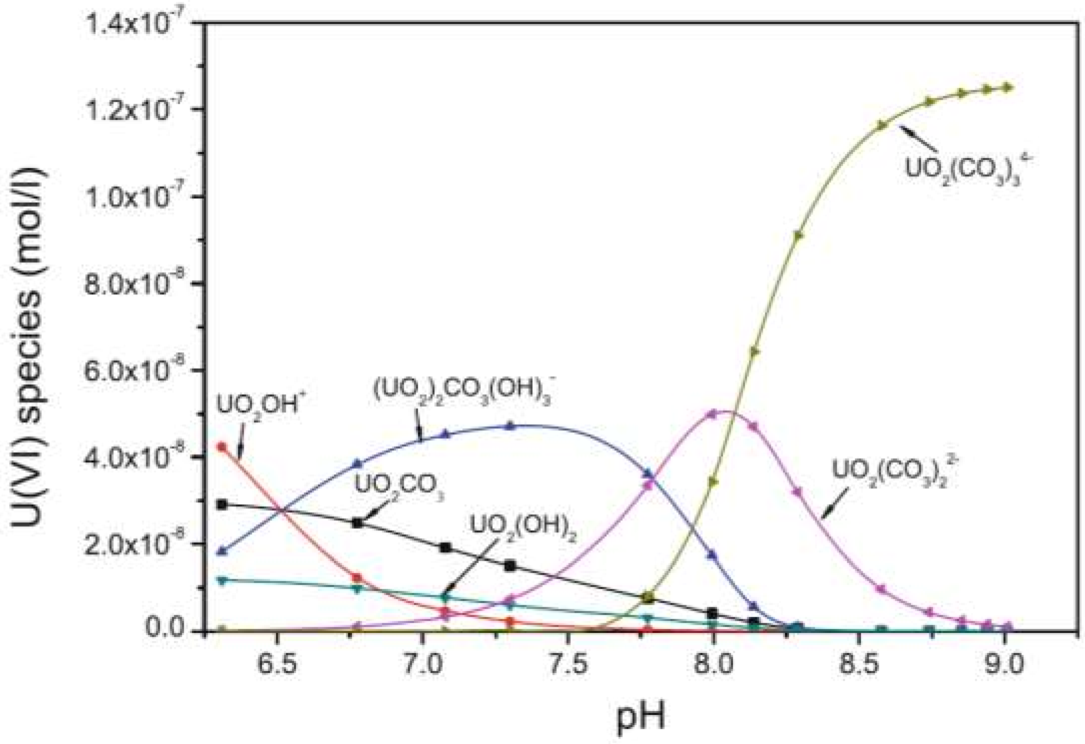

Figure 2-3: Speciation of uranium in the presence of sodium carbonate and sodium chloride, representing typical groundwater chemistry (as modeled by Nair & Merkel, 2011).

Environmental parameters such as pH and Eh have significant effects on uranium (Murphy & Shock, 1999). pH is one of the major controlling factors of uranium speciation (Kumar et al., 2011; Nair and Merkel, 2011) and can also influence ion exchange due to changes in available ions. Figure 2-3 demonstrates the influence of pH on some uranium species. Since pH has a significant effect on the form that dissolved inorganic carbon takes, uranium speciation with carbonate and bicarbonate also depend on pH (Samolczyk et al., 2012). Changes in pH and Eh can occur naturally, but they can also be influenced by anthropogenic factors including de-icing practices in roadside environments (Bäckström et al., 2004) and extensive aquifer withdrawal (Jurgens et al, 2010). In Nova Scotia, groundwater pH typically ranges from approximately 6 to 8.5 with a median pH of 7.7 (Kennedy & Bourque, 2011).

As discussed in Section 2.3, redox potential directly influences the oxidation state of uranium. Under reducing conditions, uranium is generally in its insoluble tetravalent form, but even small changes in ORP can cause it to be oxidized to the mobile hexavalent form (Murphy & Shock, 1999). Bachmaf et al. (2008) argue that the greatest influences of uranium mobility in the environment are pH and redox potential, rather than mineral solubility. In evaluations of existing groundwater data, Jurgens (2010) and Samolczyk et al. (2012) noted correlations between oxidizing groundwater and elevated uranium concentrations, stating that uranium tends to be deposited in reducing environments. Samolczyk et al. additionally noted that ion solubility is sensitive to changes in redox potential, which can in turn influence ion exchange and speciation. Redox conditions in natural systems depend on the presence of oxygen in groundwater and are therefore influenced by rainwater recharge, microbial activity (Fetter, 2001), and drawdown due to well pumping (Jurgens et al., 2010). Field measurements of ORP in groundwater are difficult because measurement itself affects the redox potential (USEPA, 2013), so widespread data for redox potential in groundwater in Nova Scotia are not available.

The mobility of uranium depends strongly on the speciation or complexation of uranium with other constituents of the groundwater (Nair & Merkel, 2011). Uranium speciation may enhance its mobility in groundwater (Dong et al., Fox et al., 2006) or reduce it by inducing precipitation, sorbing to aquifer material or forming surface complexes (Bachmaf et al., 2008).

2.4.1 Complexing Ions

This literature review has revealed several ions that enhance the mobility of uranium in the environment. This section discusses why these factors have such an influence and refers to previous studies that have attempted to confirm or quantify this influence through laboratory tests, modelling studies, or analysis of existing groundwater data. The typical concentrations of each ion of interest found in natural groundwater in Nova Scotia are presented, along with an indication of what concentrations might exist in contaminated groundwater.

2.4.1.1 Calcium

Calcium has been shown to enhance the mobility or inhibit the sorption of uranium in lab, field, and modeling studies. The inhibition of uranium adsorption to various media by the presence of calcium was noted by Fox et al. (2006) and Nair & Merkel (2011) at circumneutral pH, and the presence of calcite powder in solution demonstrated a similar mobilizing effect (Dong et al., 2005). Blume (2016) noted an almost twofold difference between uranium concentrations extracted in the presence of calcium chloride compared to sodium chloride. Bäckström et al. (2004) noted that heavy metal concentrations (cadmium, copper, lead, and zinc) in soil solutions were increased under the influence of de-icing agents such as sodium chloride (NaCl) and calcium magnesium acetate (CMA) in Sweden. Samolczyk et al. (2012) evaluated groundwater data from Grand Pré, Nova Scotia and found that calcium-dominant groundwater tends to also have high uranium concentrations. Jurgens (2010) similarly found a strong correlation between uranium and calcium in groundwater in California. A modeling study observed calcite inhibiting uranium sorption (Dong et al., 2010). Nair and Merkel (2011) found that 90% of uranium sorbed to porous material in the absence of alkaline earth metals, but the presence of calcium, magnesium, and strontium (as chloride salts in the presence of sodium bicarbonate) increased uranium mobilization.

It has been suggested that the bivalent calcium ion, Ca^{2+}, competes with the bivalent uranyl ion, UO_2^{2+}, for sorption sites, or that it changes the surface charge of minerals in the aquifer (Fox et al., 2006). However, it is widely believed that calcium enhances uranium mobilization and suppresses sorption in subsurface environments due to the formation of calcium-uranyl-carbonate complexes (Dong et al., 2005; Fox et al., 2006; Nair & Merkel, 2011; Drage & Kennedy, 2013). Figure 2-4 demonstrates the speciation of calcium-uranyl-carbonate species as predicted by a geochemical model from Nair and Merkel (2011). Drage and Kennedy (2013) postulated that the majority of aqueous uranium in a speciation study of Nova Scotian groundwater is comprised of the zero-valent calcium-uranyl-carbonate species $Ca_2UO_2(CO_3)_3^0$ and the anionic species $CaUO_2(CO_3)_3^{2-}$. The importance of $Ca_xUO_2(CO_3)_3$ species in uranium uptake to groundwater from aquifer media is further emphasized by Fox et al. (2006) and Dong et al. (2005).

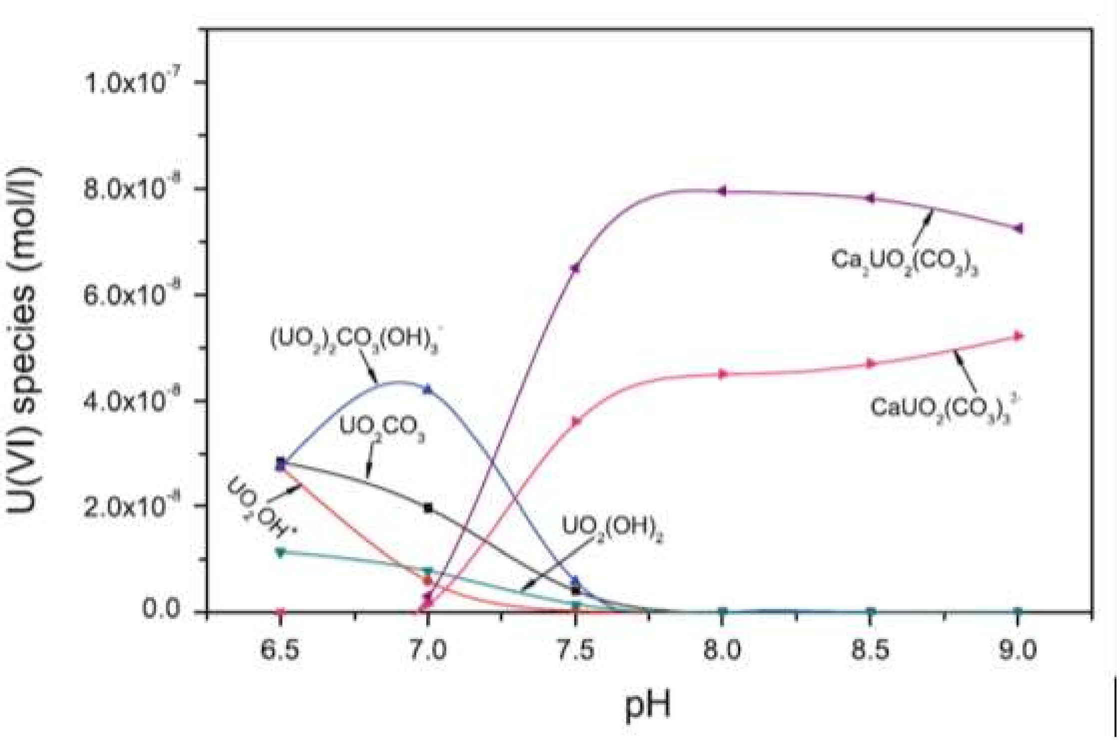

Figure 2-4: Speciation model of uranium in a calcium, sodium, bicarbonate, and chloride environment (from Nair & Merkel, 2011).

Calcium is naturally present in many soils as calcite, dolomite, gypsum, or other calcium-bearing minerals (Samolczyk et al., 2012). It can also be introduced to aquifers through de-icing efforts (particularly if CMA is used) (Bäckström et al., 2004), the application of gypsum to agricultural soils (Jurgens et al. (2010), and the improper disposal or handling of construction and demolition debris, which in Nova Scotia contains high proportions of drywall, which is calcium sulphate, $CaSO_4*2H_2O$ (Drage & Kennedy, 2013). In Nova Scotia, the mean concentration of calcium in groundwater is 44.6 mg/L and the median is 29 mg/L, but concentrations approach 700 mg/L in some samples (Kennedy & Finlayson-Bourque, 2011). Calcium concentrations in leachate from the C&D disposal cell discussed in the case study (Section 2.1.3.1) ranged from 300-1200 mg/L (CRA, 2011).

2.4.1.2 Sodium

The influence of sodium on uranium mobilization is documented in the literature less extensively than that of calcium, but is significant nonetheless. When sodium is added to an aquifer, heavy metals can be mobilized by ion exchange and changes in pH

(Bäckström et al., 2004). Elevated concentrations of sodium were associated with high concentrations of calcium and uranium in Grand Pré, Nova Scotia (Samolczyk et al., 2012).

Bäckström et al. (2004) suggested that sodium may influence heavy metal transport in the environment by releasing calcium from soils through ion exchange. In areas affected by road salt application, they reported a 30-fold increase in sodium, but a 250-fold increase in calcium concentrations, which demonstrates some ion exchange. They also suggest that the increase in ionic strength associated with the addition of sodium to groundwater could result in a change in pH due to proton release from the soil, in addition to calcium release (Bäckström et al., 2004). Such a change in pH, as discussed previously, could cause an overall increase in metal mobility and also affect carbonate equilibrium (as shown in Figure 2-4).

Sodium can be naturally present in surficial material in Nova Scotia, or it can be introduced to groundwater through seawater intrusion (Drage & Kennedy, 2013) or road salt application (Bäckström et al., 2004). Groundwater in Nova Scotia can contain sodium concentrations up to 1900 mg/L, with a mean concentration of 45.5 and a median of 40 mg/L (Kennedy & Finlayson-Bourque, 2011). Bäckström et al. (2004) noted sodium concentrations between 100 and 1000 mg/L in roadside environments that were affected by runoff from salt application to roads, so high sodium concentrations could be indicative of contaminated shallow groundwater. CRA (2011) reported sodium concentrations between 108 and 446 mg/L in C&D leachate.

2.4.1.3 Inorganic carbon

Inorganic carbon can be present in the environment as carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), or carbonate (CO_3^{2-}). The prevalence of these inorganic carbon species depends on groundwater pH (Jurgens et al., 2009). Murphy and Shock (1999) proposed that uranium mobilization is controlled largely by carbonate concentration in geochemical environments. Lab and modeling studies have supported this proposition (Dong et al., 2004; Bachmaf et al., 2008; Jurgens et al., 2009; Nair & Merkel, 2011). As discussed in Section 2.4.1.1, solutions that have been equilibrated with calcite ($CaCO_3$) powder have been known to increase uranium mobility in lab-scale tests with circumneutral to alkaline pH. Both the calcium ion and the carbonate ion from the calcite are capable of forming mobile complexes with the uranyl ion (Dong et al., 2004; Nair & Merkel, 2011). Bachmaf et al. (2008) noted a dramatic decrease in sorption at pH 8 or higher, likely due to the formation of uranyl-carbonate species. In an evaluation of well data from California, Jurgens et al. (2009) reported a strong correlation between uranium and bicarbonate.

The primary mechanism attributed to the influence of carbonate and bicarbonate on uranium mobility is the formation of uranyl-carbonate species that reversibly sorb to mineral surfaces. At alkaline pH (>7), carbonate influences sorption because aqueous uranyl-carbonate complexes (Figure 2-3) dominate the groundwater system (Dong et al., 2004; Fox et al., 2006; Bachmaf et al., 2008). The strong dependence of carbonate on pH translates to a strong dependence of uranyl-carbonate speciation on pH (Jurgens et al., 2009). Once formed, uranyl-carbonate species are capable of further complexing to form ternary species or participating in ion exchange (Bachmaf et al., 2008). Other mechanisms of carbonate influence on the mobility of uranium are precipitation reactions and sorption reactions with mineral surfaces (Fox et al., 2006). Murphy and Shock (1999) note that sorption of U(VI) is limited due to the strong affinity of the uranyl ion with carbonate ligands; therefore, carbonate enhances uranium mobility due to the formation of uranyl-carbonate species and the affinity of uranyl with soluble carbonate ligands.

As previously mentioned, inorganic carbon is naturally present in most groundwater, but Jurgens et al. (2009) concluded that bicarbonate concentrations can increase due to excessive groundwater withdrawal causing drawdown in an aquifer. Groundwater concentrations of bicarbonate in Nova Scotia have a mean of 94.4 mg/L and a median of 86.6 mg/L and can reach up to 490 mg/L (Kennedy & Finlayson-Bourque, 2011). Bicarbonate concentrations in C&D leachate reported by CRA (2011) ranged from 27 to 2570 mg/L. Bicarbonate and carbonate are usually measured as alkalinity and a proportion of the total alkalinity is attributed to each ion based on the pH of solution (American Public Health Association [APHA], 2012).

2.4.1.4 Chloride

Chloride has been associated with elevated uranium in groundwater in speciation studies and field groundwater analysis. In a groundwater modeling study, Drage & Kennedy (2013) recorded a positive correlation between uranium and chloride. Similarly elevated uranium concentrations in Grand Pré were found in chloride-dominated groundwater (Samolczyk et al., 2012). The increased mobility of uranium in the presence of chloride could be due to association with other salts or changes in ionic strength (Bäckström et al., 2004). Chloride is high in the anion preference order in many soil types and readily participates in ion exchange, which can release uranyl-carbonate and other anionic species in order to maintain electrical neutrality (Reible, 1999).

Nova Scotian groundwater can contain chloride concentrations up to 3880 mg/L, well above the aesthetic objective (AO) for drinking water, 250 mg/L. The elevated chloride concentrations may be attributed to seawater intrusion or road salt application. Typical concentrations of chloride in Nova Scotia are 69 mg/L (mean) and 24 mg/L (median). Chloride concentrations in C&D leachate have been shown to vary between 83 and 2580 mg/L (CRA, 2011).

2.4.1.5 Sulphate

The effect of sulphate on uranium mobilization and speciation depends on environmental conditions and has led to different conclusions by different authors. Bachmaf et al. (2008) noted that in geochemical environments, sulphate is capable of forming aqueous uranyl species, but there is often competition between sulphate, carbonate, and phosphate for uranyl complexation and in alkaline conditions, carbonate complexes tend to dominate. However, when pH is low (<5), sulphate is capable of forming these ionic species. It has been suggested that uranium that is already mobile in oxidized environments will form stable minerals in sulphate-reducing environments (Jurgens et al., 2009), which would contribute to a decrease in uranium mobility.

In a companion study to this one, Blume (2016) compared the mobilization of uranium from a Horton Group siltstone in the presence of calcium chloride and calcium sulphate. He determined that the sulphate extraction released twice as much uranium from the sedimentary rock samples as the chloride did, indicating that sulphate could be an important factor to consider in the mobility of uranium in the environment. Similar extractions on granite samples revealed no difference between the calcium chloride and calcium sulphate.

Background sulphate concentrations in Nova Scotia were reported by Kennedy & Finlayson-Bourque (2011); the mean concentration is 42 mg/L with a median of 12 mg/L, but concentrations can reach 1930 mg/L. An indication of sulphate concentrations in contaminated groundwater comes from CRA (2011), which reported sulphate concentrations between 890 and 1950 mg/L in leachate from C&D waste.

2.4.1.6 Other Constituents

Groundwater chemistry is an immensely complex subject. The key ions identified above were considered "ions of importance" but there has been evidence of other metals and ions that influence uranium mobility or sorption in the environment. For example, Nair et al. (2014) noted an increase in uranium sorption in the presence of arsenic in a lab-scale study, suggesting that the presence of arsenic decreases uranium mobilization. Samolczyk et al. (2012) used iron concentrations as an indicator of oxidation potential in groundwater (due to the solubility of iron in reducing environments) and found an inverse relationship between aqueous uranium concentrations and iron and manganese concentrations, supporting the earlier discussion about uranium being mobilized by oxidizing conditions. Finally, phosphate is an interesting point of discussion. It can compete with uranium for surface sites, increasing uranium mobility, but it can also form ternary surface complexes with uranyl, decreasing its mobility. Bachmaf et al., (2008) observed this decrease in mobility of uranium in the presence of phosphate and attributed it to the formation of surface complexes and to the precipitation of uranium phosphate solids. O'Reilly (1982) noted that uranium in the Millet Brook region of Nova Scotia are associated with phosphorus as the secondary uranium minerals autunite, $Ca(UO_2)_2(PO_4)_2*8\text{-}12H_2O$, and torbernite, $Ca(UO_2)_2(PO_4)_2*8H_2O$, suggesting the significance of phosphate complexes in mobilizing and redepositing uranium in the South Mountain Batholith.

2.5 Existing Leachate Tests

The United States EPA has standardized leaching tests that have been in use for decades to examine the adsorption-desorption potential of waste materials and determine whether a contaminant would represent an "unacceptable leaching threat" if disposed on land or in a landfill (New Jersey Department of Environmental Protection [NJDEP], 2013). Both tests were formulated for solid waste to determine an appropriate disposal site based on the potential for chemicals of interest to leach out of the waste and into ground and surface water. In these procedures, the sample of solid waste undergoes particle size reduction, if necessary, and is placed in a container with an extraction fluid. The interaction between the waste and the environment is simulated by rotating the vessel in an end-over-end fashion at 30 rpm for 18 hours. After this extraction, the fluid (now called the extract) is removed and analyzed for contaminants of concern. If the concentration in the extract exceeds regulatory limits for any of the contaminants of concern, the waste sample either requires treatment prior to disposal or another disposal option must be considered.

This project focuses on groundwater in Nova Scotia that has been contaminated by some mobilizing factor, as discussed in Section 2.4. The key difference between the TCLP and the SPLP methods are the extraction fluids. Because the TCLP simulates landfill conditions and the SPLP simulates un-impacted environmental conditions, the SPLP will be the focus of the leaching procedure developed in this undertaking.

2.5.1 Toxicity Characteristic Leaching Procedure (TCLP)

This leaching test was developed to simulate the conditions of waste sitting in a landfill for a number of years by extracting the solid waste with an acidic extraction fluid composed of acetic acid at either a pH of 4.93 or 2.88, depending on the pH of the sample itself. When 5 grams of the solid sample is mixed with 96.5 mL of water and stirred for five minutes, the pH is measured. If it is less than 5, the extraction fluid is adjusted to pH 4.93. If it is greater than 5, 3.5 mL of hydrochloric acid is added and the tube is covered with a watch glass and heated to 50 °C for ten minutes. After cooling to room temperature, if the pH is now less than 5, the extraction fluid is adjusted to pH 4.93, whereas if the pH is still greater than 5, the extraction fluid is adjusted to pH 2.88.

Following TCLP extraction, the constituents of concern are compared to the appropriate regulatory limits (USEPA, 1992).

2.5.2 Synthetic Precipitation Leaching Procedure (SPLP)

This leaching test was developed to simulate the conditions of waste that has been disposed of above ground and exposed to acidic rainwater. This test is commonly used to evaluate contaminated soils. This test partitions the contaminant of concern between the sorbed and aqueous phase, producing an extraction solution that can be compared to the leachate concentration of that contaminant under natural conditions in the field. Depending on the source of the sample, the extraction fluid for this procedure is either: 1) reagent water adjusted to a pH of 4.20 using a mixture of sulfuric acid and nitric acid, 2) reagent water adjusted to a pH of 5.00 using the same acid mixture or 3) reagent water. If the sample was taken east of the Mississippi River, the pH of the extraction fluid is 4.20. If the sample was taken west of the Mississippi River, the pH of the extraction fluid is 5.00. If the contaminant of concern is cyanide or a volatile contaminant, the extraction fluid is filtered or distilled water. As with the TCLP test, concentrations in the extract are compared to the appropriate regulatory limits (USEPA, 1994).

2.5.3 Interpretation

The NJDEP points to SPLP as a useful tool for evaluating the leaching capability of contaminants from contaminated soils and for producing appropriate site-specific remediation standards. It also recommends using this test to determine a soil-water partition coefficient (K_d) for modeling and risk management purposes. The NJDEP document provides a link to a spreadsheet that can be used to generate soil remediation standards to protect groundwater. This project deals not with anthropogenic uranium contamination, but with naturally present uranium, which may be mobilized due to anthropogenic contamination by other groundwater constituents. However, the simulation of leaching to groundwater is certainly at the core of this project, so many of the SPLP parameters are carried over to the standardized uranium leaching test.

The limitations of the SPLP are twofold: the possibility of colloid formation and the adjustment of redox potential. Under SPLP methodologies, the leachate is filtered through 0.6 to 0.8 μm filters, which could lead to an underestimation of the inorganics that are associated with colloids above this size range (NJDEP, 2013). According to Murphy and Shock (1999), actinides tend to be found in the environment in colloidal form, so this could be a substantial oversight.

A potentially significant flaw of the test is that the redox potential of the sample is not measured. Through sampling, mixing, and the extraction itself, oxidation is likely to happen, which can convert many metal species to a different oxidation state (NJDEP, 2013). As previously discussed, uranium tends to be mobilized in oxidizing conditions. In order to create a conservative test, the uranium concentration extracted should be maximized to represent a worst-case scenario of uranium contamination. Therefore, performing the extractions under oxidizing conditions maximizes uranium mobility.

It should be noted that the concentrations of contaminants of concern in the leachate from the SPLP test cannot be directly compared to the concentrations that would be found in the field because the proportions of soil and water in the procedure are different from those in a natural system (NJDEP, 2013). The field concentration may be estimated based on a series of equations that are derived in the SPLP guidance document by NJDEP involving partitioning parameters such as soil adsorption coefficients and Henry's Law constants (NJDEP, 2013).

2.5.4 Uranium Mobilization and the Existing Leaching Tests

The SPLP is the standard test for evaluating contaminant transport from a solid matrix. The conditions of extraction by the SPLP simulate acidic (pH 4.2 – 5.0) rainfall on material stored on the ground (USEPA, 1994), which is not necessarily representative of groundwater conditions in Nova Scotia. The application of the SPLP to evaluate mobility of uranium loses validity because, as discussed previously in this literature review, uranium is mobilized in alkaline, oxidizing conditions in the presence of complexing ions. Therefore, there is a need for a more accurate leaching procedure that employs conditions that are conducive to the mobilization of uranium. Both acidic and alkaline conditions exist in Nova Scotian groundwater, depending on rock, soil, and environmental conditions. While uranium can be mobilized in acidic environments as well, this thesis was more focused on alkaline conditions because the median pH in Nova Scotian groundwater is alkaline (Drage & Kennedy, 2011).

A uranium-specific leaching procedure is valuable in its potential for risk analysis and management. The next sections outline the approach to creating a leaching procedure for the evaluation of uranium mobility from subsurface material. By choosing experimental factors that maximize the uranium concentration in the extract, it is possible to create a "worst-case scenario" of contamination of uranium in the environment. The results of such a test can be used to identify local areas with a high risk of uranium mobilization into groundwater that can then be used in land use planning and water resource allocation.

Chapter 3 Methodology

3.1 Safety

3.1.1 Radiation

It is imperative in any project to acquaint oneself with the appropriate safety measures and guidelines. Uranium is known to be a radioactive substance (as discussed in Chapter 2). Health Canada (2011) explains that the natural background radiation that the average Canadian receives each year is between 2 and 4 mSv. The Canadian Nuclear Safety Commission (2015) dictates that the maximum amount of ionizing radiation a person should receive in the workplace is 50 mSv in one year and 100 mSv over five years. This section discusses the radiation levels found in the sedimentary and granite samples collected for this thesis.

The radiation levels of the Three Mile Plains sandstone samples were evaluated using a handheld spectrometer (Model SAIC, GR-135 Plus) from the Department of Natural Resources, and it was found that for the rock dust samples, the maximum radiation dose was 0.11 µSv/h. The manual for this instrument indicates that a user should move away from any source with a dose level greater than 20 µSv/h (Drage, personal communication, 12 March 2015). The 0.11 µSv/h dose would amount to 0.96 mSv in one year and 4.8 mSv in five years, so the radiation levels of these samples were deemed to be safe. The samples collected from St. Croix are similar in origin, location, and uranium content to the Three Mile Plains samples and were also deemed to be safe to work with.

The granite samples collected for this thesis were evaluated using a portable gamma ray spectrometer (Model Exploranium, GR-130 mini SPEC) and the uranium contents were between 1.6 and 5.7 ppm uranium in four of the five samples; the fifth was found to contain 13 ppm uranium. These concentrations of uranium are low; this quantity is considered to be a background level of uranium in rocks and is approximately equal to 0.05 to 0.15 µSv/h (0.44 to1.3 mSv in one year and 2.2 to 6.6 mSv over five years) (Prospectors and Developers Association of Canada [PDAC], 2009).

3.1.2 Laboratory Safety

While the levels of radiation from the samples used in this project are unlikely to cause adverse effects due to proximity, the accidental ingestion or inhalation of these materials would be a cause for serious concern. The crushed, dried rock samples were always handled with safety goggles and gloves while wearing a mask as a barrier to the fine particles that would become airborne during weighing or mixing with extraction fluid.

3.2 Sample Collection and Preparation

The rock material collected for this project came from areas of known uranium-enriched bedrock in Nova Scotia. A sample of uranium-bearing rock was required for the first two phases of experimentation and a variety of types of additional rock material samples were required for the third phase. The samples for all phases came from one of two sources: the NSDNR Core Library, where two granite and one sedimentary sample were taken, and from an outcrop of sedimentary material in St. Croix, NS, where three samples were taken. The DNR Core Library is located in Stellarton, NS and contains thousands of drill core archives from across the province collected over several decades. Samples are permitted to be taken from the Core Library on request as long as half of what is there is left behind; a Norton Clipper wet saw is available for cutting core into halves and quarters. The material from St. Croix was taken with permission from the land owner and was weathered enough that it was possible to take material using a small pickaxe. All samples were placed in carefully labeled zip-top plastic bags for transportation back to the lab at Dalhousie University in Halifax. The sampling locations are identified in Figure 3-1.

3.2.1 Sample Descriptions

3.2.1.1 Millet Brook Granite

Granite samples were collected from the DNR Core Library on May 13, 2015. The samples came from drill hole MB-80 C2-1 at depths ranging from 37.7 to 41.8 m. Much of the desired sampling interval was whole, so they were cut in half, but some depth intervals had already been sampled; therefore, the cores were quartered. This bore hole was an NQ core (47.6 mm diameter) drilled in the spring of 1980 in Millet Brook, Nova

Scotia by Aquitaine Company of Canada, Ltd. The depth intervals containing high uranium were approximated from the drill report by Robertson & Duncan (1981) and the radiation energy and uranium content was later approximated using an XRF from the Dalhousie Earth Science Department. Approximately 4 kilograms of granite was collected in total and labeled as MB. Spectrometry analysis revealed that one of the five zip-top bags containing the MB samples contained an order of magnitude more uranium than the other four, so it was kept separate from the other four. These were labeled MBL and MBH for the low and high uranium content samples, respectively.

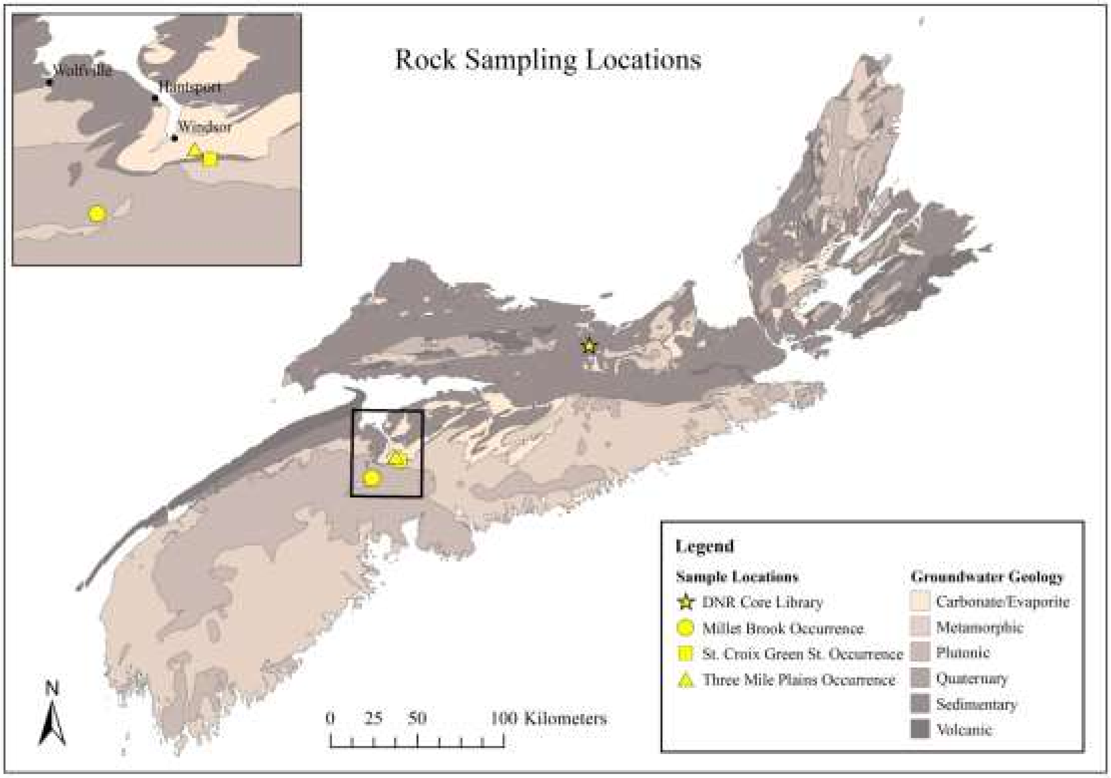

Figure 3-1: Sampling locations of the rocks used for this project. The area of geologic interest near Windsor, Nova Scotia, is shown in the inset map, adapted from Kennedy & Drage (2008).

3.2.1.2 Three Mile Plains Sandstone

A second trip to the Core Library on June 19, 2015 was undertaken to examine sedimentary NQ core samples from Three Mile Plains, drilled by Maritime Diamond Drilling Co. for Saarberg Interplan Canada, Ltd. in 1981 and from River John, drilled by Lacana in 1980. A handheld spectrometer (McPhar, Model 120-G) was used to identify sections of sample that emitted a greater quantity of radiation (measured as counts per second). The Three Mile Plains core number 1/306 was chosen and sampled from a depth interval of approximately 262 to 267 meters, which was identified as an area of high radiation by the spectrometer and in the drill report (Quarch et al., 1981). In many intervals there was only one quarter of the core left, so no more could be taken. Other sections contained core that had already been halved, so it was possible to cut and take one quarter of the core. As a result, the total mass of material taken on this day was approximately 0.52 kg. This sample was labeled as TMP.

3.2.1.3 St. Croix Sandstone and Siltstones

On July 21, 2015, samples of sedimentary material were taken from an outcrop on the side of Green Street in St. Croix, Nova Scotia. The outcrop was clearly weathered, as evidenced by the quantity of loose material near the bottom of the outcrop and by the exposed tree roots at the top of the cliff. The same handheld spectrometer used at the Core Library on June 19 was used to identify a layer of the outcrop with radiation emissions greater than background level. Approximately 9 kg of material was taken; coarser-grained sandstone was kept separate from the finer siltstone because the siltstone had a higher reading on the spectrometer. The sandstone was labeled as Sa and the siltstone was labeled Si. An additional several kilograms of siltstone from this site was collected on September 27, 2015 and the siltstone samples were then labeled S1 (collected on July 21) and S2 (collected on September 27). The key difference between the St. Croix rocks is the particle size. All three rocks when sampled were broken apart easily by hand; however, when crushed to a particle size of less than 2 mm, the sandstone broke into larger pieces than the siltstone samples.

3.2.2 Particle Size Reduction

All samples were oven dried and the particle sizes were reduced to less than 2 mm by the technicians at the Minerals Engineering Centre at Dalhousie University. The particle size of less than 2 mm was modified from the SPLP's requirement that material must fit through a 9.5 mm sieve in order to expose uranium-bearing mineral surfaces. Initial crushing was done using a Braun Chipmunk vd67 Jaw Crusher and secondary crushing was done with a UA Face Plate Pulverizer. Each bag of crushed sample was well mixed and kept in a cool, dry cupboard to await extraction.

3.2.3 Sample Evaluation

An aliquot of each crushed rock sample was sent to Maxxam Analytics for hydrofluoric acid digestion and analysis of 21 different metals using ICP-MS (Agilent 770x ICP-MS), in accordance with USEPA SW846 Method #6020A (H. Macumber, personal communication, 2015). The metals analyzed include common rock elements such as aluminum and iron as well as trace metals of interest including uranium and arsenic.

3.3 Extraction Procedure

The general extraction procedure developed in this research is based on the SPLP test, which is described briefly in Section 2.5.2 and can be explored in more detail in the USEPA Method 1312 (1994). In the SPLP, a sample of solids, liquids, or wastes weighing 100 grams is mixed with 2 liters of an extraction fluid. The extraction fluid depends on the origin of the sample and the motivation for testing. The mixing occurs by fixing the extraction vessel in a rotary agitation device to spin in an end-over-end fashion for 18 ± 2 hours.

The procedures developed for this project are a scaled-down version of the SPLP; 50 g of rock sample was mixed with 1 liter of extraction fluid in a plastic bottle known as the extraction vessel. This change to the standard procedure was made due to limited availability of material for testing. The SPLP is generally used for contaminated soil scenarios, in which there is typically a large mass of material available for evaluation. For the risk characterization of uranium mobility using core samples, it is likely that there will be limited material available for evaluation at the desired depth intervals, so scaling down from 100 g to 50 g reflects the limitations that might be encountered by users. The solid material was reduced to a particle size of less than 2 millimeters prior to extraction, as described in Section 3.2.2. The pH and Eh of the extraction fluid were measured with a Thermo Scientific Orion 4 Star meter (either benchtop or handheld) and an Orion electrode for pH (9142BN or 9156BNWP) and ORP (9179 BNMD) before mixing with the rock samples, as well as after the extraction was performed.

Preparation of extraction fluids was done using clean and rinsed bottles and glassware. The extraction fluids were prepared using powder salts. Calcium chloride dihydrate or calcium sulphate was used to obtain the desired calcium ion concentration, sodium chloride was used to add more chloride, and sodium bicarbonate was used to obtain an approximate amount of bicarbonate ions. The use of these reagents adds sodium to the solution, in addition to the desired ions.

The rotary agitation device on-site is capable of processing eight 1-L bottles at a time, so two experimental treatments were evaluated during each extraction (see Figure 3-2). The extraction fluids were prepared in two 4 L amber jugs; each jug corresponding to four extraction bottles: 1-4 or 5-8. All extractions were performed in triplicate with a blank. Bottles 1 and 5 were blanks for Extraction Fluid 1 and 2, respectively. 50.0 ± 0.1 g of rock sample was measured into the remaining extraction vessels.

The amber jugs were filled with reverse osmosis treated water at least one day before the extraction was to take place to allow them to come to room temperature. 4.1L of extraction fluid was prepared in each jug because 100 mL was required for measuring alkalinity. The appropriate two extraction fluids were prepared according to the experimental conditions provided in Sections 3.3.1 to 3.3.3. The masses of reagents required to obtain this solution chemistry in a 4.1L solution were calculated approximately using dissolution reaction stoichiometry.

After the reagents were mixed, 20 minutes of equilibrium time was allowed before reading the pH and Eh of each jug. If necessary, the pH was adjusted using hydrochloric acid (1N HCl) or sodium hydroxide (0.1N NaOH). The desired pH levels are detailed in Sections 3.3.1 and 3.3.3. 100 mL of each fluid was retained for measurement of alkalinity using Standard Method 2320 (APHA, 2012).

The extraction fluids were added to the extraction vessels. The vessels were closed and wrapped in Parafilm to prevent leaks during extraction. The extraction vessels were secured in the rotary agitation device and surrounded by cloth to prevent agitation in directions other than the desired end-over-end rotation. The rotary agitation device was set to a rotation speed of 30 ± 2 rpm.

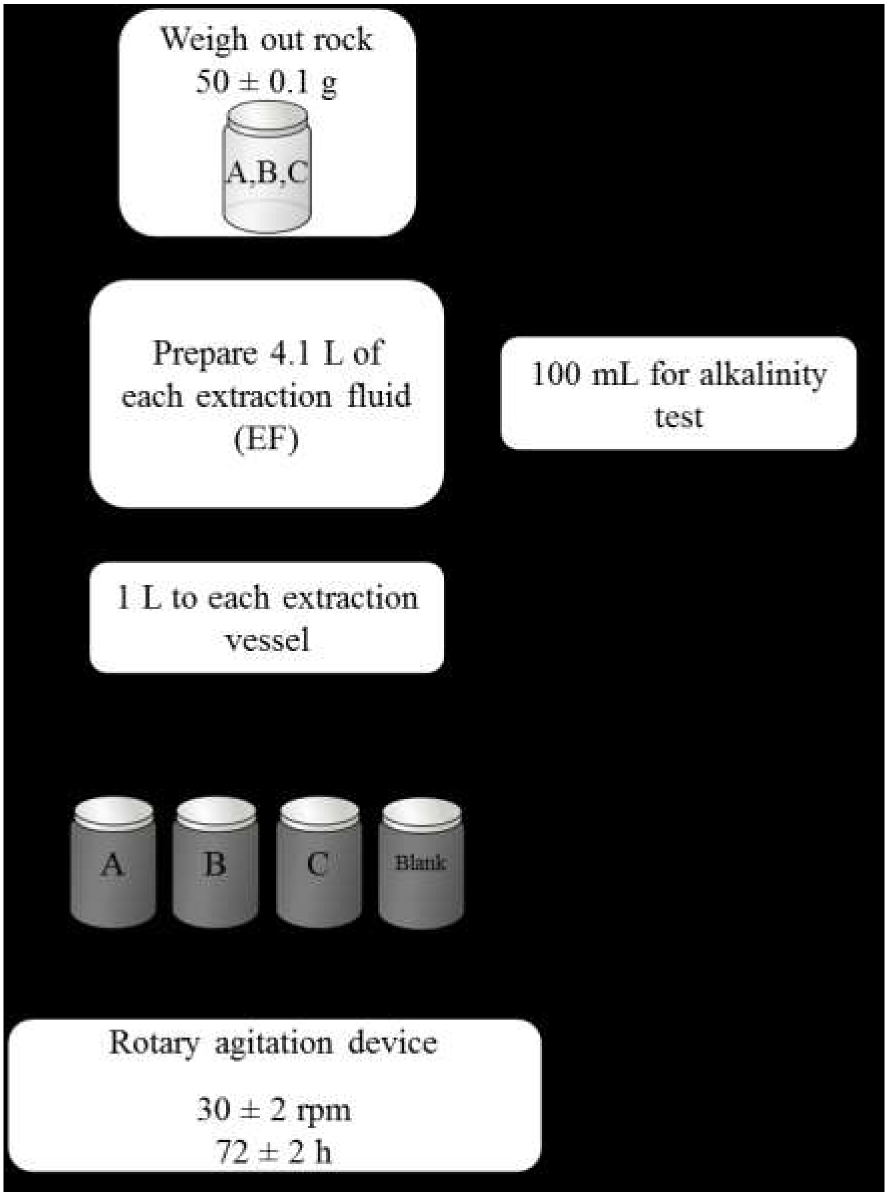

Figure 3-2: Flow chart illustrates preparation of samples and fluids for extraction.

The vessels were removed after the appropriate extraction time and the particulate matter was allowed to settle for 30 to 90 minutes while the final pH and ORP were once again measured and recorded. In the investigation of groundwater uranium concentrations, this project is concerned with dissolved, not total, uranium, so the standard method involves the use of a 0.45 μm filter to isolate the dissolved uranium species. Approximately 200 mL of supernatant from each bottle was filtered first through a glass filter (1.5 μm pore size) and then a mixed cellulose ester 0.45 μm pore size filter. The resulting fluid was called the extract.

50 mL of the extract was placed in a Falcon tube and the pH was reduced to below 2 using nitric acid to prevent further reaction or complexation. This sample was sent to Maxxam Analytics for uranium analysis using inductively coupled plasma collision cell (ICP-CC). 50 mL of the extract was placed in Digi Tubes and acid digested according to Standard Method 3050 (APHA, 2012) in preparation for in-house analysis of 26 metals using inductively coupled plasma mass spectrometry (ICP-MS) in the Center for Water Resources Studies (CWRS) water lab (Thermo Scientific XSeries 2 ICPMS).

3.3.1 Phase 1: The Effect of pH, Extraction Fluid, and Extraction Time

This phase of experiments was performed on St. Croix siltstone (S1) with the goal of determining the duration of extraction in subsequent phases of lab work. The three factors under evaluation in Phase 1 were the extraction time, extraction fluid, and pH. Three extraction fluids were used: reverse osmosis (RO) water, to evaluate the leaching of uranium without the influence of added ions; a low concentration solution, to represent background levels of ions in groundwater; and a high concentration solution, to represent groundwater that has been contaminated with leachate enriched in complexing ions. Typical values for the parameters of concern in Phase 1 are summarized in Table 3-1.

Table 3-1: Summary of pH and concentrations of key ions in Nova Scotian groundwater (Kennedy & Finlayson-Bourque, 2011) and leachate from a construction and demolition debris disposal cell (CRA, 2011).

	pH	**Ion Concentrations, mg/L**			
		Calcium $[Ca^{2+}]$	**Sodium $[Na^{+}]$**	**Bicarbonate $[HCO_3^{-}]$**	**Chloride $[Cl^{-}]$**
Mean in Nova Scotia	7.6	44.6	45.5	94.4	68.9
Median in Nova Scotia	7.7	29	20	86.6	24
C&D Disposal Cell Leachate	6.8 – 7.9	300 – 1200	108 – 446	97 – 2570	83 – 2580

The chemistries of the extraction fluids were based on the values above and can be found in Table 3-2. Initially, the high concentration extraction fluid was to contain concentrations close to the upper range of those found in C&D leachate, but when high concentrations of salts were added to the extraction fluid, precipitate was formed. Therefore, the concentrations were reduced to achieve an extraction fluid that was elevated in calcium, sodium, and bicarbonate, but formed little or no precipitate. The pH was varied between 5.5 and 8.5 for each of these fluids using 1N HCl or NaOH, as needed. Further discussion on the impact of the reagents added for pH adjustment can be found in Appendix F. The experimental design is summarized in Table 3-3.

Table 3-2: Chemistries of the different extraction fluids used in Phase 1.

	Ion Concentrations, mg/L			
	Calcium $[Ca^{2+}]$	**Sodium $[Na^{+}]$**	**Bicarbonate $[HCO_3^{-}]$**	**Chloride $[Cl^{-}]$**
RO Water	-	-	-	-
Low Concentration	62	35	40	140
High Concentration	200	181	400	400

Table 3-3: The three factors evaluated in Phase 1 and their parameters. Note that when water was the extraction fluid, only two pH levels were evaluated: 7.00 and 9.00.

<table>
<tr><th>Factor</th><th colspan="6">Levels</th></tr>
<tr><td>Extraction Time (± 2h)</td><td colspan="3">18</td><td colspan="3">72</td></tr>
<tr><td>Extraction Fluid</td><td colspan="2">RO Water</td><td colspan="2">Low Concentration</td><td colspan="2">High Concentration</td></tr>
<tr><td>pH (± 0.05)</td><td colspan="2">5.50</td><td colspan="2">7.00</td><td colspan="2">8.50</td></tr>
</table>

These extractions were performed between July 26 and August 12, 2015. It was expected that a 72 hour extraction with high concentration and basic pH would produce a greater final concentration of uranium in the extract than any other combination.

As will be discussed later, the results of the low concentration extractions did not follow expectations; it was hypothesized that this was because the low concentration extraction fluid used in Phase 1 did not contain the ideal 1:2 ratio of Ca^{2+} to HCO_3^{-} that would produce the desired zero-valent calcium-uranyl-carbonate species. An additional phase called "Phase L" was added to repeat the low concentration experiments with an extraction fluid composed of 50 mg/L Ca^{2+}, 100 mg/L HCO_3^-, 150 mg/L Cl^-, and 78 mg/L Na^+. This phase was done from October 6 to 23, 2015.

3.3.2 Phase 2: The Effect of Calcium Concentration

The objective of this phase of testing was to examine the relationship between the calcium concentration in the extraction fluid and the uranium concentration in the extract. The results from this phase were used to determine the appropriate calcium concentration in the extraction fluid for the next phase of experiments. This phase was performed on the St. Croix siltstone (S1) and the Millet Brook granite with low uranium content (MBL). Each extraction was 72 ± 2 hours in duration. The concentrations of bicarbonate and chloride ions were held constant at 500 mg/L while the calcium concentrations were varied from 0 to 250 mg/L in increments of 50 mg/L, as shown in Table 3-4. The Phase 2 extractions were performed between September 15 and 25, 2015.

Table 3-4: Extraction fluid composition for Phase 2 extractions, wherein calcium was varied from zero to 250 mg/L and bicarbonate and chloride were held constant at approximately 500 mg/L.

Ion Concentrations, mg/L			
Calcium **[Ca^{2+}]**	**Sodium** **[Na^{2+}]**	**Bicarbonate** **[HCO_3^-]**	**Chloride** **[Cl^-]**
0	513	500	500
50	455	500	500
100	398	500	500
150	341	500	500
200	283	500	500
250	226	500	500

3.3.3 Phase 3: Performance of the ULP on Uranium-bearing Nova Scotian Rocks

The results of the previous phases culminated in the development of the Uranium Leaching Procedure (ULP) for this thesis, which was designed to maximize the concentration of uranium in the extract. Extractions were performed under oxidizing conditions for 72 hours. Based on results from Blume (2016) discussed in Section 2.4.1.5, calcium sulphate was used to obtain the desired calcium concentration in the extraction fluids. Calcium sulphate, sodium chloride, and sodium bicarbonate were used to obtain the desired ion concentrations in the extraction fluid (outlined in Table 3-5). The objective of this phase was to validate the ULP on a variety of uranium-bearing rocks from Nova Scotia and compare it to the general Synthetic Precipitation Leaching Procedure (SPLP). The SPLP was performed according to USEPA method 1312 (1993), but was scaled down to 50 mg of sample and 1 L of extraction fluid. This phase was completed between November 27 and December 15, 2015.

Table 3-5: Composition of the ULP extraction fluid compared to the SPLP extraction fluid. Sulphate concentrations in the SPLP extraction fluid come from the sulphuric acid in the pH adjustment solution and vary each extraction.

		Ion Concentrations, mg/L				
	pH	**Calcium [Ca^{2+}]**	**Sodium [Na^{+}]**	**Bicarbonate [HCO_3^{-}]**	**Chloride [Cl^{-}]**	**Sulphate [SO_4^{2-}]**
ULP	8.00	150	308	300	300	360
SPLP	4.20	-	-	-	-	as required

3.4 Data Interpretation

For the results from Phase 1, an initial two-tailed t-test was performed to determine which extraction time resulted in higher extract concentrations of uranium. Subsequently, an Analysis of Variance (ANOVA) was conducted in Sigma Plot (version 13.0, Systat Software, Inc., San Jose, CA) to assess the significance of extraction time, extraction fluid ion concentration, and pH. When ANOVA determined that there was a difference between treatments, a post-hoc Tukey test was also performed in Sigma Plot.

In Phase 3, t-tests were performed on the uranium concentrations between the SPLP and the ULP extracts for each rock sample. Uranium concentrations in the extracts were plotted to allow for visual comparison of the performance of the SPLP and ULP tests. The extraction fluids that were composed of calcium chloride dihydrate (from

Phase 2) and calcium sulphate (from Phase 3) were compared with respect to the extracted uranium concentrations.

In all three phases, the concentrations of 26 metals were evaluated for each of the extracts. These data were collected in order to facilitate the development of a geochemical model in future works. Like the uranium results, the data for these metals were also analyzed using t-tests to compare the SPLP and ULP extract concentrations to provide insight into their adsorption-desorption behaviour in an environment that promotes uranium mobilization.

The results of the whole rock analysis were used in a mass balance to estimate what percentage of the uranium contained in the rock was mobilized during extraction.

Chapter 4 Results and Discussion

4.1 Rock Sample Descriptions and Composition

The whole rock analysis revealed key differences between the six rock samples evaluated through the course of this work. Maxxam Analytics provided the analysis for 21 metals, which are tabulated with their reportable detection limits in Appendix B, along with photos of the crushed samples. The uranium contents of the rocks are of critical relevance to this project and are displayed in Table 4-1.

Table 4-1: Uranium content of the test rock samples (Maxxam Analytics, 2015).

Label and Lithology	**Location**	**Source**	**Date Collected**	**Uranium Content (mg/kg)**
S1: Siltstone (1)	St. Croix	Field	21 July 2015	20
S2: Siltstone (2)	St. Croix	Field	27 Sept 2015[1]	20
Sa: Sandstone	St. Croix	Field	21 July 2015	16
TMP: Sandstone	Three Mile Plains	DNR Core Library	19 June 2015	13
MBL: Granite	Millet Brook	DNR Core Library	13 May 2015	8.2
MBH: Granite	Millet Brook	DNR Core Library	13 May 2015	34

The uranium concentrations in the rock samples were between 8.2 and 34 ppm, which fall well below the values of 100 ppm or more that were observed by the uranium exploration companies in the 1970s and early 1980s. The companies that reported these concentrations measured radioactivity in counts per second to find an equivalent uranium concentration, whereas the uranium contents in Table 4-1 were obtained using a strong acid digestion of the rock samples, so this could explain the difference in the reported

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[1] Sampled by Anne-Marie Ryan.

rock uranium concentrations. When the Three Mile Plains and Millet Brook samples were taken from the DNR Core Library, the depth intervals that were shown to have high uranium in the drill log had already been extensively sampled. Material may be taken with permission from the Core Library as long as only half of what is there is taken, but if there is only ¼ section of the core left, it may not be further divided and therefore may not be sampled. As a result, some of the high-uranium intervals of the core could not be sampled. The field samples came from the Green Street occurrence in St. Croix, which has been described by Ryan et al. (2009) and Parsons (2007). Parsons used ICP-MS to determine siltstone uranium contents of 109.2 to 212.1 ppm and mixed media uranium contents ranging from 39.7 to 52.3 ppm. Extensive weathering of this outcrop in the intervening years since their work has likely leached away some of the environmentally available uranium at this location, resulting in the disparity between the two rock analyses. Loose material of the outcrop has fallen down from above the horizons containing elevated uranium, which could contribute to a dilution effect on the samples taken. The difference in uranium content between the analyses could also be due to local variations in the rock, particularly with respect to the distribution of redox potential within the sedimentary rocks; Parsons sampled areas with more significantly reduced horizons (2007; O'Beirne-Ryan, personal communication, 2016).

The granites were found to be higher than the sedimentary rocks in the alkaline earth metals barium and strontium, and possess higher copper, cobalt, iron, and zinc contents (Appendix B). The siltstones and sandstone from St. Croix were higher in arsenic, selenium, tin, and vanadium than the other rock types. Most of the rocks contained similar amounts of aluminum, chromium, beryllium, lead, nickel, and thallium. The sandstone from Three Mile Plains tended to have the lowest uranium content of all metals analyzed, except that it had the highest concentration of magnesium. There were no detectable concentrations of antimony or molybdenum in any of the rock samples. Cadmium was detected at low concentrations in the two granite samples, but these were lacking in selenium.

4.1.1 Sample Mineralogy

The rock samples collected for Phase 3 came from well-documented uranium occurrences. Existing data was consulted to understand the mineralogy of the samples, as discussed in the next three sections.

4.1.1.1 Millet Brook Granite

The granite samples from Millet Brook were taken from cores drilled in the spring of 1981. Uranium mineralization at depth is typically pitchblende veinlets in the C2 zone, which is where the samples came from. At the depth of sampling, borehole C2-1 was primarily porphyritic biotite granodiorite with fracture faces showing small pyrite crystals. Calcite veinlets were observed just below the interval sampled for MBL and MBH (Robertson & Duncan, 1981).

4.1.1.2 Three Mile Plains Sandstone

The sandstone from Three Mile Plains came from the 1-306 borehole drilled in 1980. At the depth sampled, the rocks were part of the lower Cheverie Formation, which is dominated by arkosic channel conglomerates. Uranium in this rock formation is associated with uplift of the source granites. The interval sampled contained feldspar discoloured red and smoky quartz (Quarch et al., 1981).

4.1.1.3 St. Croix Sandstone and Siltstones

The field samples from the Green Street occurrence in St. Croix have been examined in the past (Parsons, 2007; Ryan & O'Beirne-Ryan, 2009; Ryan et al., 2009). The outcrop from which the samples were taken is part of the Horton Group, which is a well-documented uranium roll-front occurrence bordered by the metasedimentary rocks of the Meguma Group and overlying the intrusive igneous South Mountain Batholith. The upper part of the Horton Group is the Cheverie Formation, which tends to be an arkosic granite-pebble conglomerate and contains grey to black organic-rich shale, siltstone and quartz-rich sandstone (Ryan & O'Beirne-Ryan, 2009; Ryan et al., 2009).

4.2 Phase 1: The Effect of pH, Extraction Fluid, and Extraction Time

Phase 1 was undertaken to investigate the mobilizing factors discussed in the literature review to further understand the mobility of uranium from siltstone due to influences such as pH, concentrations of key ions in extraction fluids, and extraction times. The primary goal of this phase was to determine the extraction time (18 h or 72 h) that maximizes uranium uptake into water. The parameters under investigation are outlined in Section 3.3.1. Appendix C tabulates the uranium concentrations in the extract from each phase of experiments. The measured pH for each extraction is tabulated in Appendix D. Redox potential was measured in this phase, but calibration of the ORP probe was not performed due to the absence of calibration solution until near the end of the phase. The ORP values that were measured were between 255 and 355 mV. ORP values greater than 200 mV are considered to be oxidizing (Kumar et al., 2011). All ORP data are available in Appendix E, but redox potential in Phase 1 will not be discussed here.

The addition of acid (1N HCl) or base (1N NaOH) to achieve the desired pH added sodium or chloride ions to the extraction fluid. Greater volumes of acid and base were required to change the pH of the high concentration extraction fluids compared to the low concentration extraction fluids. As a result, the overall chemical nature of the two extraction fluids remained high and low relative to each other and did not change the overall nature of the system. Approximate masses of the chloride and sodium added through pH adjustment can be found in Appendix F, along with measured concentrations of sodium from the blanks. Chloride was not measured so the concentrations indicated are approximate. The addition of these ions to the extraction fluids could affect uranium speciation through ion exchange or the formation of complexes if the concentrations were different than desired. However, the measured sodium concentrations were similar to the desired concentrations, indicating that the impact of the ions added for pH adjustment was likely insignificant.

4.2.1 Uranium Extracted in the Absence of Complexing Ions

The first extractions were performed using reverse osmosis (RO) water at pH levels of 7 and 9 (the pH was adjusted using 1N NaOH). This was done to assess the potential for uranium mobilization from the St. Croix siltstone in the absence of the ions of interest discussed in Section 2.4.1. The results are presented in Figure 4-1. Uranium concentrations were much lower than the drinking water guideline of 20 μg/L, but were above the detection limit of 0.1 μg/L.

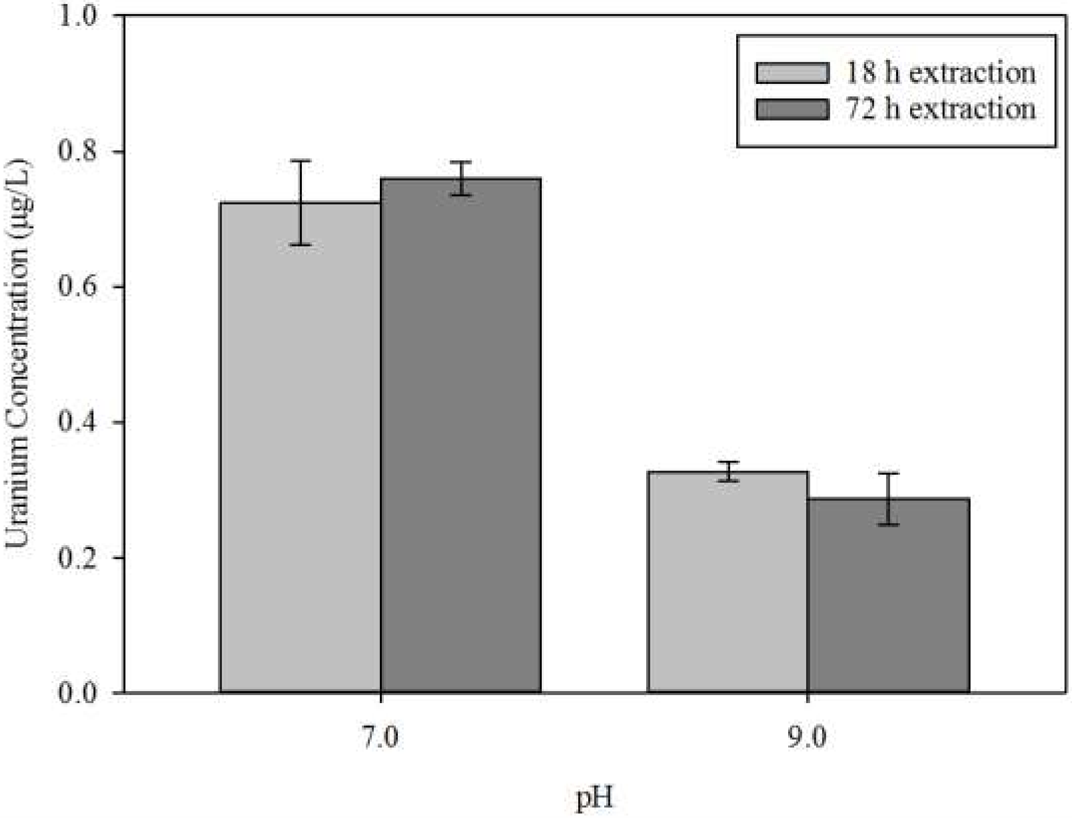

Figure 4-1: Uranium concentrations in extracts from siltstone field samples (S1) extracted with reverse osmosis grade water adjusted to the desired pH using 1N NaOH. Error bars represent 95% confidence intervals.

The extraction of low concentrations of uranium from siltstone using water suggests that the uranium in the St. Croix sample is readily mobilized. A two-tailed t-test (assuming equal variance) indicated a significant difference between the different pH levels for both the 18- and 72-hour extractions (both p-values <0.01); uranium concentrations were higher at pH 7.0 for both extraction times. There was no significant difference found between the two extraction times at pH 7 (p-value = 0.079) but the difference was statistically significant at pH 9 (p-value = 0.01).

The difference in uranium concentration between the two pH levels here may be due to the dependence of inorganic carbon on pH, which in turn influences the complexation of uranyl with carbonate ions (Dong et al., 2004). The lack of difference between the two extraction times at pH 7 and the small difference at pH 9 in these preliminary extractions suggests that uranium equilibrium is achieved within the first 18 hours of extraction. The significant difference between extraction times at pH 9 could be due to the presence of sodium ions added during pH adjustment. Although the volume of 1 N NaOH added to achieve the elevated pH was not measured, the mean concentration of sodium after the extractions were 5 mg/L and 1.5 mg/L for the 18- and 72-hour extractions, respectively. The higher concentration of sodium in the 18-hour extract indicates that there was more sodium added to that extraction fluid, which could result in the mobilization of uranium through ion exchange or speciation.

4.2.2 Uranium Extracted in the Presence of Low and High Ion Concentrations

A primary goal of Phase 1 was to evaluate the effect of different extraction fluids on dissolved uranium concentrations. Figure 4-2 presents the preliminary results of extractions performed using low and high concentrations of key ions in the extraction fluid. The error bars show the 95% confidence interval from the triplicate treatments.

Figure 4-2 demonstrates a range of uranium extract concentrations. Analysis of variance (ANOVA) testing was performed on the results and revealed that there was significant variation between the experimental conditions (results are in Table 4-2). In the results table, DF indicates degrees of freedom, SS indicates sum of squares, and MS indicates mean square. A pairwise t-test compared the 18-hour and 72- hour extractions for each measurement of each treatment and found a p-value of 0.032, indicating significance at the 95% confidence level, so it was decided that Phase 2 would continue with 72-hour extractions. This decision was also made because at the pH level of 8.5, the 72-h extraction released significantly more uranium than the 18-h extraction. That treatment was the highest uranium concentration observed in Phase 1, so in the interest of releasing as much uranium as possible, an extraction time of 72 hours was appropriate.

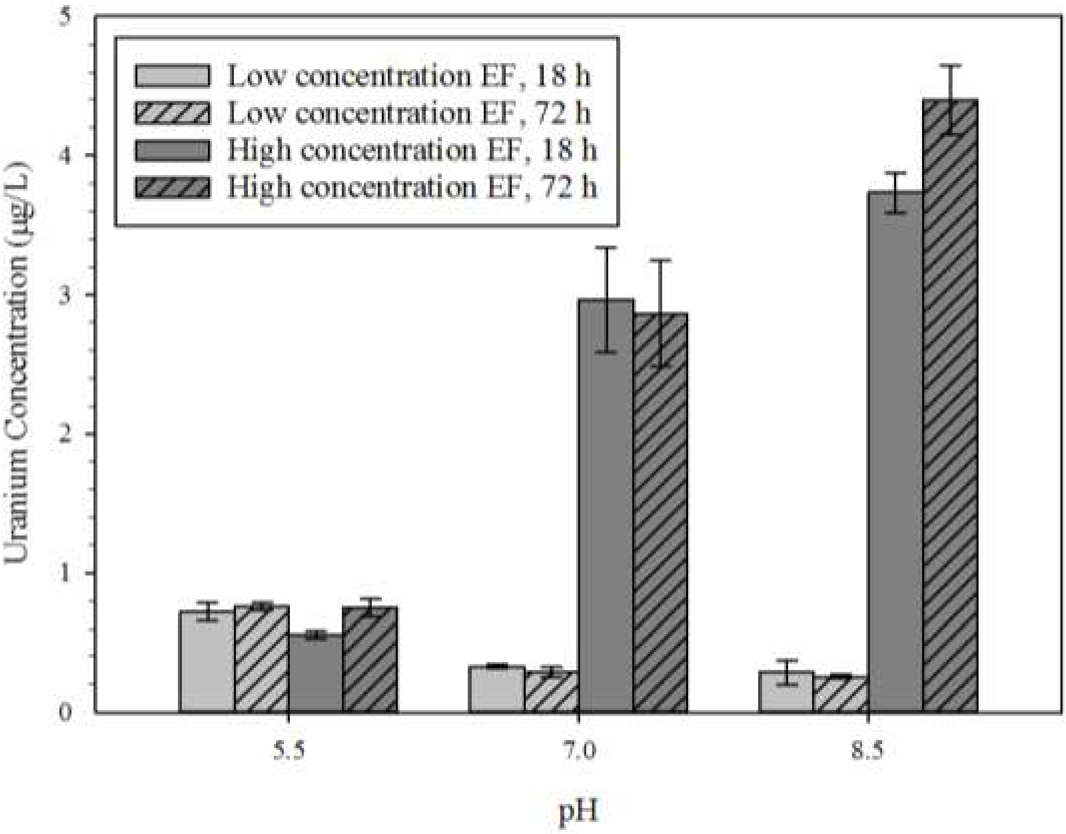

Figure 4-2: 18- and 72-hour extractions of siltstone with extraction fluids containing low and high concentrations of key ions. Low concentration extraction fluid contained 62 mg/L calcium, 35 mg/L sodium, 140 mg/L chloride, and 40 mg/L bicarbonate. High concentration extraction fluid contained the same ions at concentrations of 200, 180, 400, and 400 mg/L, respectively. pH was adjusted using 1N HCl or 1N NaOH as needed. Error bars represent 95% confidence intervals.

Table 4-2: Analysis of variance (ANOVA) results demonstrating the effect of ion concentration, extraction time, and pH on uranium extraction based on Phase 1 results.

Source of Variation	**DF**	**SS**	**MS**	**F**	**P**
Ion Concentration (low/high)	1	13.3	13.3	11.458	**0.012**
Extraction Time (18/72 h)	1	0.044	0.044	0.0379	0.851
pH (5.5/7.0/8.5)	2	4.416	2.208	1.902	0.219
Residual	7	8.126	1.161		
Total	11	25.886	2.353		

The key results from this phase indicate that the low- and high-concentration extraction fluids behave differently. A post-hoc Tukey test showed that the uranium concentrations extracted with low concentrations of key ions in the extraction fluid were statistically different from the high concentration extraction fluid (p-value = 0.012). The extraction time did not have a significant impact on uranium extraction (p-value = 0.771) and pH did not demonstrate a significant difference either (p-value = 0.215). However, Figure 4-2 allows trends in pH to be observed. At low pH, the uranium concentrations extracted with both extraction fluids were similar, but as pH increased, the concentrations of uranium extracted with the high concentration extraction fluid increased, while uranium extracted with the low concentration extraction fluid decreased slightly.

From Nair and Merkel (2011), the uranium concentration in the extract was expected to increase as the pH increased due to the formation of calcium-uranyl-carbonate species at high pH. This was observed for the high concentration extraction fluid; conversely, the low concentration extractions exhibited the opposite trend; an apparent decrease in extracted uranium occurred with each increase in pH, consistent with Bäckström et al. (2004). The response of uranium to the low- and high-concentration extraction fluids could be due to uranyl complexation as ion exchange occurs, particularly in the high concentration fluid. The decrease in uranium concentration from the low concentration extractions as pH increased suggests that the expected calcium-uranyl-carbonate species did not dominate the aqueous uranium concentration. It is also possible that key ions precipitated out of solution under the high pH condition but remained dissolved and available for complexation at low pH.

4.2.3 Uranium Extracted with a 1:1 and a 1:2 Ratio of Calcium to Bicarbonate

As discussed in Section 3.3.1, an additional phase of testing was added to further evaluate the low concentration extraction fluids with respect to the importance of the ratio of calcium to bicarbonate. This second iteration of the low concentration extractions was called Phase L and was done with an approximate 1:2 ratio of Ca^{2+}: HCO_3^- in an attempt to promote the formation of the calcium-uranyl-carbonate species identified by Drage & Kennedy (2013) and Fox et al., (2006). Phase L evaluated the influence of the calcium and bicarbonate species on uranium mobilization. The results are presented along with the original 1:1 ratio results in Figure 4-3.

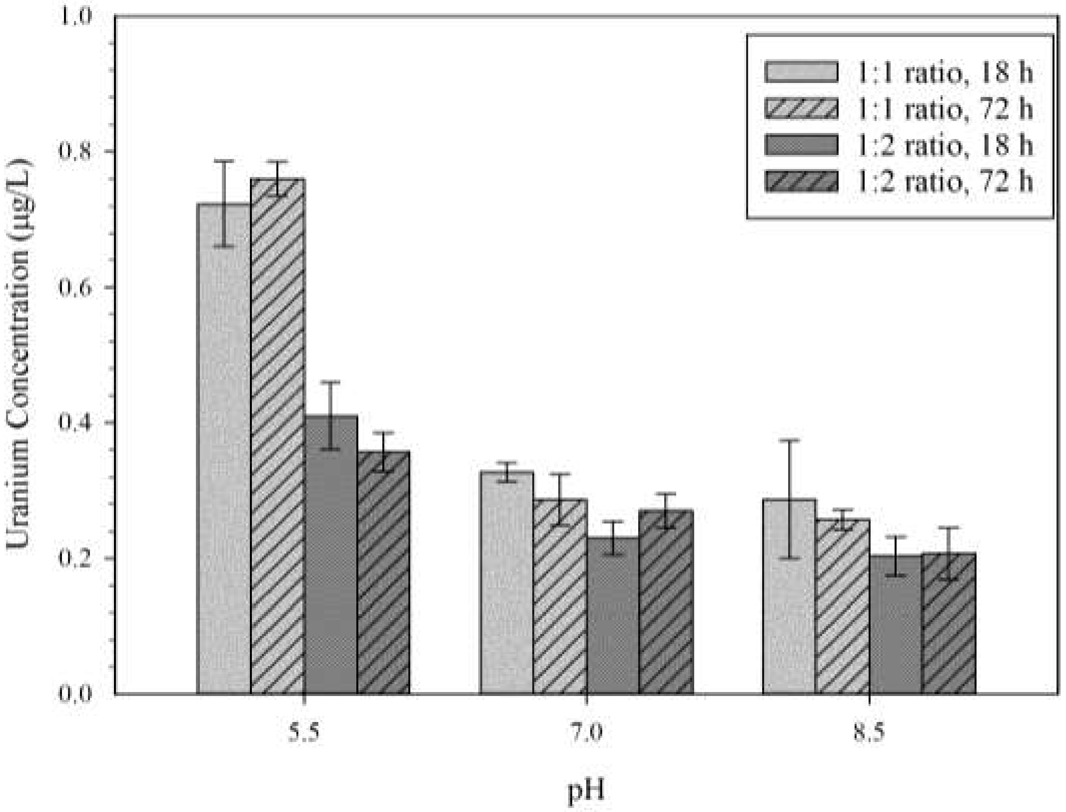

Figure 4-3: Uranium concentrations extracted using low concentration extraction fluids with calcium and bicarbonate in an approximate 1:1 or 1:2 ratio. The 1:1 ratio extraction fluid was the same as in Phase 1; the 1:2 extraction fluid contained calcium, sodium, chloride, and bicarbonate in concentrations of 50, 78, 150, and 100 mg/L, respectively. Error bars represent 95% confidence intervals.

Uranium behaved similarly when extracted with each of the calcium to bicarbonate ratios, indicating that the proportion of calcium and bicarbonate in the extraction fluid is not as important as originally theorized. This supports earlier speculation that the low concentration extraction fluid might form a different dissolved uranium complex than the high concentration extraction fluid does.

It must be noted that although the siltstone samples for the 1:1 and 1:2 ratios were taken from the same place and horizon of the Green Street outcrop in St. Croix and had the same uranium content (20 mg/kg), the extractions that used the 1:2 ratio were performed on S2, which was sampled at a later date. Therefore, no direct comparison can responsibly be made between the two treatments except an observation of the overall trends.

4.3 Phase 2: The Effect of Calcium Concentration

Phase 2 was undertaken to further understand the behaviour of uranium in response to different concentrations of calcium, which has been found to inhibit sorption of uranium to quartz minerals in lab-scale tests due to the formation of $Ca_xUO_2(CO_3)$ species (Fox et al., 2006). From Phase 1, a pairwise t-test determined that 72-hour extractions resulted in small increases in uranium in solution and therefore the longer extraction time was used in the final two phases. ANOVA was performed later and did not reveal a significant difference between extraction times at the 95% confidence level, so the last two phases of extractions used a 72-hour extraction time; however, the 18-hour extraction could have been used and no significant difference in results would be expected. Similarly, Phase 2 determined what the calcium concentration would be in the extraction fluids in Phase 3. This section explores the results of Phase 2 with respect to both of the rock types that were evaluated, siltstone and granite, and discusses the choice of the calcium concentration for the Phase 3 extraction fluid. Note that there was no pH adjustment performed during Phase 2, but the pH was measured for each extraction and these are reported in Appendix D.

4.3.1 Uranium Extracted from Siltstone

The uranium concentrations extracted from siltstone (S1) are presented in Figure 4-4. As expected, the dissolved uranium concentration was low when the calcium concentration was low, and more uranium was extracted as the calcium concentration increased. When the calcium concentrations were approximately 100-150 mg/L, the uranium levels in the extract appear to reach a maximum. The pH of the blanks were between 7.44 and 8.14 and the average extract pH levels ranged from 6.66 to 7.04, indicating circumneutral conditions. Measurements of the redox potential after extraction indicate that the conditions of extraction were consistently oxidizing; Eh ranged from 279 mV to 318 mV with an average of 299 mV. It must be noted once again that the concentration of uranium in this evaluation does not exceed the drinking water guideline of 20 µg/L, but of course field conditions related to the mass of contaminant and the volume of fluid must be considered in order to make conclusions as to the mobilization risk from these rock samples.

The similarity in uranium concentrations when calcium exceeds 100 mg/L could indicate that the uranium available for mobilization in the siltstone has been exhausted or that there is a different limiting factor. In the extraction fluids containing higher concentrations of calcium, some precipitation formed in the mixing bottle, even before the addition of the rock samples. The precipitation of calcite at high calcium concentrations could remove calcium and carbonate from solution, reducing the availability of these ions for further uranyl complexation.

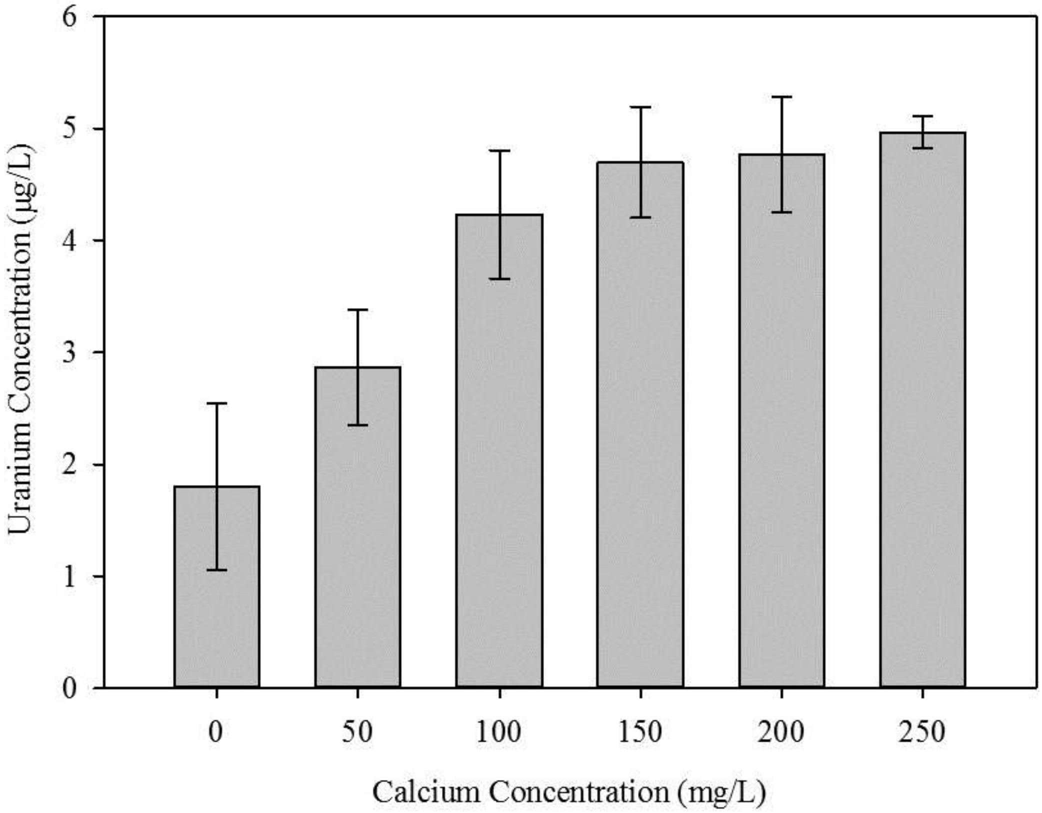

Figure 4-4: Uranium extracted from siltstone in the presence of varying extraction fluid calcium concentrations at circumneutral to alkaline pH. Chloride and bicarbonate concentrations were maintained at approximately 500 mg/L; sodium concentrations varied from approximately 230 to approximately 500 mg/L as the solution chemistry was adjusted for the desired concentrations of calcium. Error bars represent 95% confidence intervals.

4.3.2 Uranium Extracted from Granite

The same extractions were performed on the granite sample from Millet Brook and the results are presented in Figure 4-5. For these rocks, the extract concentration of uranium appeared to generally decrease with an increase in calcium concentration; however, the results were quite variable. The pH of the blanks ranged from 7.20 to 8.11 and the average pH at each calcium level after extraction were between 7.21 and 8.37. The redox potential of the granite extractions were between 158 mV and 286 mV (absolute) with a mean of 234 and a median of 240. The triplicate extractions performed at the 50 mg/L calcium level exhibited a wide range of Eh, from 99 to 206, indicating a fluctuating redox conditions that could be the cause of the greater variation in uranium concentrations for that treatment level. Other possible explanations for the variance in uranium concentrations at this calcium dose could be the presence of small amounts of something in solution causing changes in Eh/pH conditions. Regardless of the reason for the variance, the overall trends of uranium mobilization due to different calcium doses could still be observed.

Once again, a leveling out of uranium concentration occurred when calcium was 150 mg/L or greater, which means that some factor besides calcium limits the reaction at these levels. Note that all of the concentrations from the granite samples exceeded the uranium concentrations extracted from the siltstone, even though this granite sample had the lowest whole-rock uranium content. This suggests that the uranium in the MBL samples is present in easily weatherable minerals. A mass balance was performed to determine the percent of the available uranium that was extracted (see Table 4-3). Approximately 10% of the available uranium was extracted from the granites, compared to less than 1% from the siltstones. One explanation for this phenomenon could be that the granite contains greater concentrations of magnesium and strontium than the sandstones, which have been proven to form dissolved uranyl-carbonate complexes like calcium (Nair and Merkel, 2011).

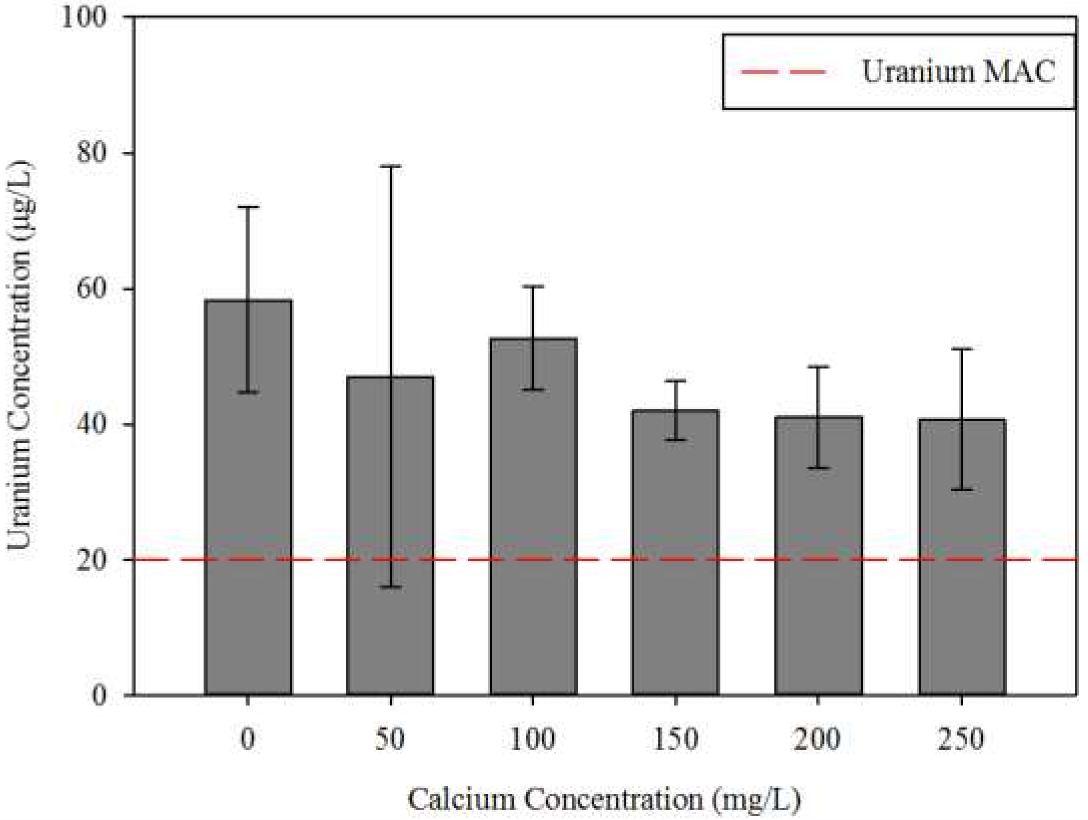

Figure 4-5: Uranium extracted from granite in the presence of varying extraction fluid calcium concentrations. Just like the siltstone extractions, chloride and bicarbonate concentrations were added at 500 mg/L and sodium concentrations were between 230 and 500 mg/L. Error bars represent 95% confidence intervals.

4.3.3 A Comparison of the Mobilization of Uranium from Siltstone and Granite in the Presence of Calcium

Both the siltstone and the granite results are presented together in Figure 4-6.Visual inspection of the results makes it clear that both rocks achieved a more or less constant uranium concentration at calcium concentrations greater than 100 mg/L. Although the uranium concentrations extracted from the granite samples exhibit a decreasing trend until 150 mg/L of calcium, these concentrations were consistently more than five times greater than the ones in the siltstone extract. To improve upon the standard SPLP, the goal is to maximize the uranium concentration being extracted. Therefore, a calcium concentration of 150 mg/L was selected for Phase 3to maximize the uranium from the siltstones. A mass balance used the mass of rock (50 g) and the whole rock uranium content to determine the percent of the input uranium that was found in the dissolved phase in the extract (see Table 4-3).

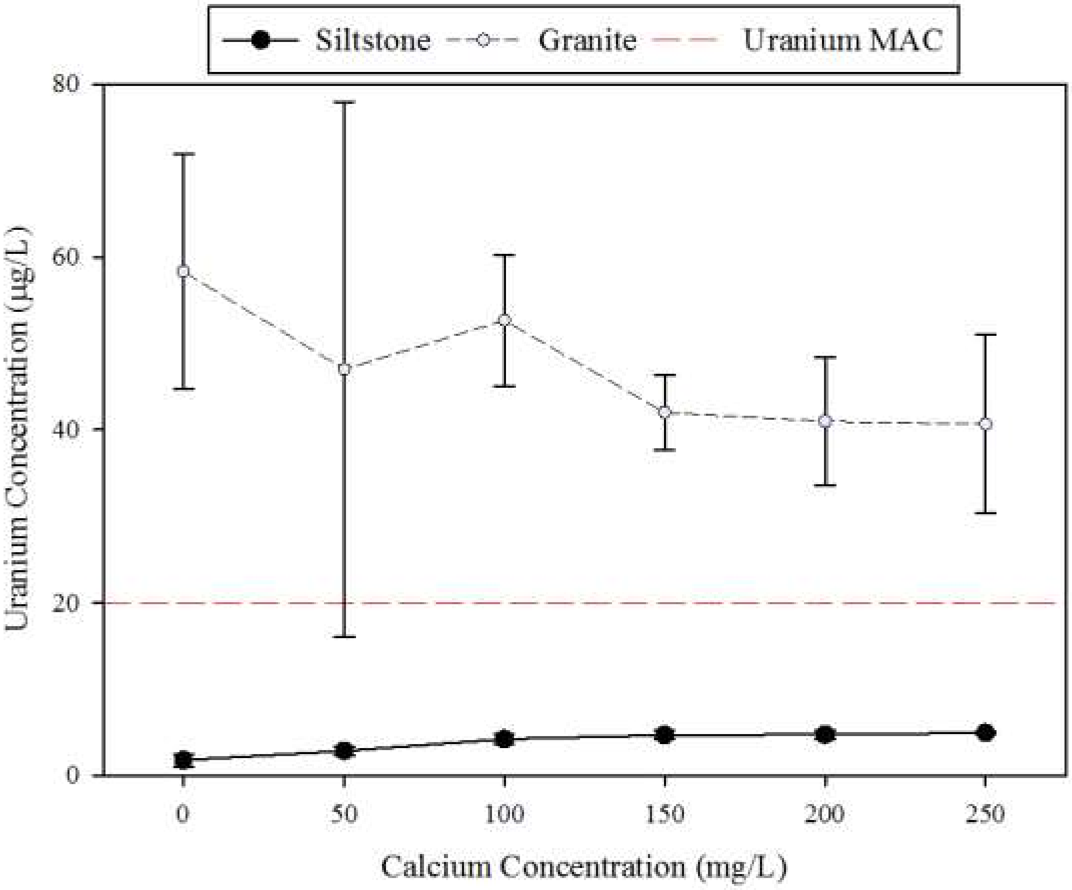

Figure 4-6: A comparison of the behaviour of uranium from siltstone and from granite in the presence of varying levels of calcium and sodium. Error bars represent 95% confidence intervals

The differences in uranium concentrations from the same treatment on different rock types can be attributed to the properties of the crushed rock samples. The Millet Brook granite samples contained the lowest rock concentration of uranium, but the dissolved uranium concentration in the extract from these rocks was greater than from the siltstone. These observations suggest that the uranium present in Millet Brook granites is more easily mobilized than the uranium in the St. Croix siltstones. For example, uranium present in biotite minerals in granites, particularly if partially weathered, is easily mobilized and leached into groundwater (O’Beirne-Ryan, 2006). This is demonstrated in Table 4-3, which reports the mass percent of uranium in the dissolved phase after extraction; the siltstones have released 0.4% of the total uranium on average while the granites released 11.4%. The uranium present in the siltstone samples may be associated with the organic-rich layers in the siltstone and therefore is more strongly held than the uranium from the granites (Ryan & O'Beirne-Ryan, 2009).

Table 4-3: Percent uranium extracted from both rock samples in Phase 2 with varying concentrations of calcium added to the extraction fluid.

Rock Sample	**Calcium Concentration**	**U Content (mg/kg)**	**Total U in extraction (mg)**	**Dissolved U in extract (µg/L)**	**Percent extracted**
Siltstone	0	20	1.0	1.80	0.2
	50	20	1.0	2.87	0.3
	100	20	1.0	4.23	0.4
	150	20	1.0	4.70	0.5
	200	20	1.0	4.77	0.5
	250	20	1.0	4.97	0.5
Granite	0	8.2	0.4	58.3	14.2
	50	8.2	0.4	47.0	11.5
	100	8.2	0.4	52.7	12.8
	150	8.2	0.4	42.0	10.2
	200	8.2	0.4	41.0	10.0
	250	8.2	0.4	40.7	9.9

An additional difference between the two rock samples is particle size; while all rock samples were crushed to less than 2 mm, the siltstones were much finer than the granites. Increased surface area in the finer siltstone samples could provide more surface sites for ion exchange and complexation and could be expected to produce a higher uranium concentration than if the rocks had been crushed to a coarser grain size. Conversely, while the coarse-grained granite sample produced a high extract uranium concentration, it might be expected to produce an even higher uranium concentration if it had been crushed to a finer particle size. However, since the fine-grained siltstones produced a lower uranium concentration than the coarse-grained granites, particle size is likely not responsible for the difference between the two rock samples.

4.4 Phase 3: Performance of the ULP on Uranium-bearing Nova Scotian Rocks

The final phase of experimental testing used the uranium leaching test (ULP), created during this study, to evaluate uranium mobility from the six uranium-bearing rock samples collected in the spring and summer of 2015. The ULP was created based on the results from Phases 1 and 2 and on preliminary results from Blume (2016). The extraction fluid uses a calcium concentration of 150 mg/L as calcium sulphate in a 1:2 ratio to bicarbonate (added as sodium bicarbonate) and to chloride (added as sodium chloride). The pH of the ULP extraction fluid was adjusted to 8.00 ± 0.05 using 1N NaOH. This added some sodium ions to the extraction fluid, but the measured sodium concentrations in the blanks were similar to the desired concentration, so this added sodium likely has little effect on the desired outcome of the test (see Appendix F). The ULP extraction fluid was expected to mobilize greater amounts of uranium from rock samples than the SPLP, which is currently the standard for evaluating the mobility of contaminants from solid samples. Water quality data for the ULP and SPLP extraction fluids are presented in Table 4-4 along with background values throughout Nova Scotia and C&D leachate data. The results of the ULP and the SPLP extractions on Nova Scotian igneous and sedimentary rock from the Windsor area are presented below.

Table 4-4: A comparison of the ULP and SPLP extraction fluids to the mean values in Nova Scotia (median in brackets) and values found in C&D leachate

Parameter	ULP	SPLP	Mean in Nova Scotia	C&D Leachate[a]
pH	8.0	4.2	7.6 (7.7)	6.8 - 7.9
Calcium (mg/L)	150	-	44.6 (29)	300 - 1200
Sodium (mg/L)	308	-	45.5 (20)	108 - 446
Bicarbonate (mg/L)	300	-	94.4 (86.6)	97 - 2570
Chloride (mg/L)	300	-	68.9 (24)	83 - 2580
Sulphate (mg/L)	360	15.4[b]	41.6 (12)	890 - 1950

[a] Values from the environmental assessment for the case study C&D site (CRA, 2013)

[b] Approximate concentration based on the average volume of acid required to adjust pH.

4.4.1 Uranium Concentrations in the Extract from Different Rocks

Figure 4-7 illustrates the results from the SPLP and ULP extractions performed on the six rock types discussed in Sections 3.1 and 4.1. The uranium content of each whole-rock sample is presented on the figure as well. In order to determine the extent of uranium extraction from the rocks, a mass balance was performed (see Table 4-5).

The release of uranium using the SPLP can be largely attributed to the pH conditions and mineralogy of the rock. Both the SPLP and ULP are performed under oxidizing conditions, confirmed by the positive Eh measurements (reported as 194 mV or greater in Appendix E), which means that the uranium is likely present as the hexavalent ion, U(VI), and is therefore available for mobilization. At low pH, uranium has been shown to be more mobile in the presence of sulphate due to competition between the sulphate and uranyl ions for surface sites and due to the formation of uranyl-sulphate complexes (Bachmaf et al., 2008); this could be the mechanism that releases uranium using the SPLP.

The uranium liberated by the ULP could be released due to a number of mechanisms. The uranium present in the rock samples, under oxidizing conditions created in the end-over-end rotation, may be present as a number of ions, including uranyl (UO_2^{2+}) and uranyl-carbonate species ($UO_2(CO_3)_x^-$). The dissolution of calcium sulphate, sodium chloride, and sodium bicarbonate in the extraction fluid allows for ion exchange to occur with the solid media. The addition of cations such as calcium and sodium may allow the positively charged uranyl ion to be released from the solid phase and go on to form aqueous complexes with carbonate and other ions noted in Section 2.4.1. Similarly, the addition of the anions in the ULP extraction fluid can participate in ion exchange to release negatively charged uranyl-carbonate complexes from the soil. Uranyl-carbonate species may be exchanged for chloride in the soil due to preference of many solid media for holding chloride. Uranium may also be mobilized due to the formation of soluble complexes between the uranyl ion and the ions present in the extraction fluid or released from the media through ion exchange. In particular, since the extraction is performed at a pH of 8.0, uranyl is likely present as a uranyl-carbonate complex ($UO_2(CO_3)_x$) or as a ternary calcium-uranyl-carbonate complex ($Ca_xUO_2(CO_3)_3$).

The extractions performed on the siltstones from St. Croix suggest that while there are appreciable concentrations of uranium in the rocks themselves, the uranium is not easily mobilized at concentrations close to the drinking water MAC. This is contrary to what was found by Parsons (2007), who obtained uranium concentrations of 16 and 24 µg/L from the same rocks when they were equilibrated with rainwater. As discussed previously, it is possible that the available uranium has been leached from the outcrop since Parsons collected her samples. This suggests that the strong affinity of uranium for the organics that are likely in the clay and silt layers of the St. Croix siltstones can inhibit uranium mobilization from these rocks. This is in keeping with Bäckström et al. (2004), who concluded that metals that have a strong association with organic matter tend to counteract mobilizing factors by sorbing or coagulating with the organic matter.

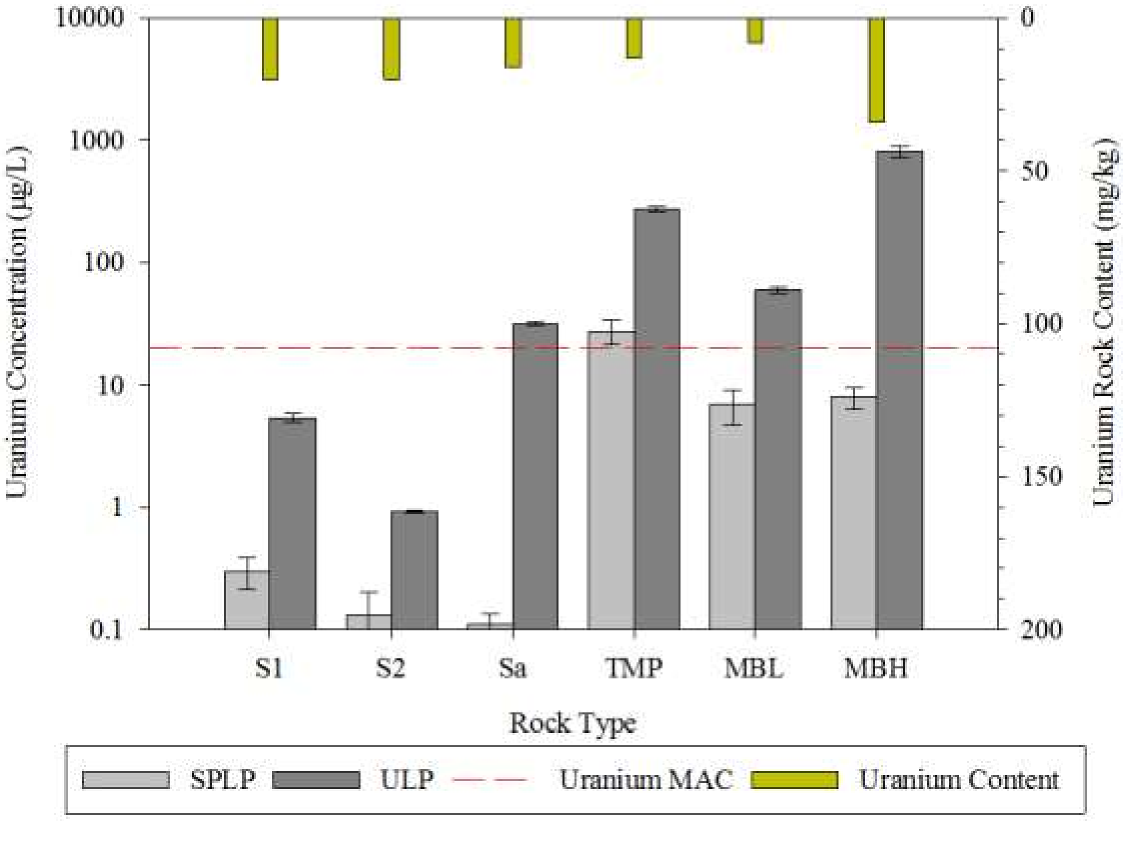

Figure 4-7: Uranium concentrations in the extract from the synthetic precipitation leaching procedure (SPLP) and uranium leaching procedure (ULP) performed on six rock types. The SPLP uses an extraction fluid of water adjusted to a pH of 4.20 in a 20:1 mass ratio to solid material. The ULP uses an extraction fluid with a pH of 8 containing 150 mg/L calcium, 308 mg/L sodium, 300 mg/L chloride, 300 mg/L bicarbonate, and 360 mg/L sulphate. The uranium content of the rocks is presented as well for comparison. Error bars represent 95% confidence intervals.

Table 4-5: Percent uranium extracted from each rock sample using SPLP and ULP.

Label	Test	U Content (mg/kg)	Total U in extraction (mg)	Dissolved U in extract (µg/L)	Dissolved U in extract (mg)	Percent extracted
S1	SPLP	20	1.0	0.30	0.00030	< 0.1
	ULP	20	1.0	5.4	0.0054	0.5
S2	SPLP	20	1.0	0.15	0.00015	< 0.1
	ULP	20	1.0	0.93	0.00093	0.1
Sa	SPLP	16	0.80	0.12	0.00012	< 0.1
	ULP	16	0.80	32	0.032	4.0
TMP	SPLP	13	0.65	27	0.027	4.2
	ULP	13	0.65	270	0.27	42.0
MBL	SPLP	8.2	0.41	7.0	0.0070	1.7
	ULP	8.2	0.41	59	0.0590	14.5
MBH	SPLP	34	1.7	8.0	0.0080	0.5
	ULP	34	1.7	810	0.810	47.6

Compared to the siltstone extractions, uranium in the St. Croix sandstone appears to be more easily mobilized by the ULP and less easily mobilized by the SPLP. While there is less uranium in the sandstone (16 mg/kg compared to 20 mg/kg in the siltstones), the ULP was able to extract uranium at 31.7 µg/L from the sandstone and only 5.4 µg/L and 0.93 µg/L from siltstones 1 and 2, respectively (these concentrations in the extract represent 4.0, 0.5, and 0.1% of the total uranium in the rock samples, respectively). The difference in the uranium extract concentrations between the siltstone and sandstone samples indicates that the uranium in the sandstone may be more easily mobilized than from the siltstones. This could be attributed to mineralogy; as previously discussed, certain minerals readily release uranium to the aquatic environment while others bind it tightly.

The uranium in the Three Mile Plains sandstone was extracted at concentrations exceeding the drinking water guideline with both the SPLP and the ULP. This rock was the only test sample that produced uranium levels exceeding 20 µg/L from the SPLP (27.3 µg/L, 4.2% extracted). The uranium present in the TMP sandstone therefore appears to be easily mobilized under both the acidic conditions of the SPLP and the alkaline, high ionic strength conditions of the ULP. This indicates that the uranium in the TMP sandstone is distributed in minerals that are easily weathered or oxidized to release the uranium. Under oxidizing conditions, the uranium is likely present as the uranyl ion, which complexes with carbonate at high pH levels. The whole rock analysis revealed that TMP was low in most metals but was high in magnesium. Nair and Merkel (2011) reported uranium mobilization through the formation of both calcium-uranyl-carbonate and magnesium-uranyl-carbonate species. Although magnesium is not a focus of this thesis, this could explain why the TMP samples had the second-highest uranium concentration extracted with the ULP. Geochemical modeling could explain this phenomenon further.

The granite samples from Millet Brook were separated into low concentration material (8.2 mg/kg) and high concentration material (34 mg/kg) when the uranium content was measured after sampling, but both samples behaved similarly with the SPLP (7.0 and 8.03 µg/L for MBL and MBH, respectively). The uranium concentration extracted by the SPLP was below the drinking water guideline and approximately the same for both samples. The ULP extracted uranium in concentrations greater than the drinking water guideline and reflected the difference in the uranium content of the two samples; the high concentration rock was extracted at 810 µg/L (47.6% of the total uranium in the rock) and the low concentration rock was extracted at 59.3 µg/L (14.5% extracted).

The Phase 3 results show that the ULP can consistently extract more uranium than the SPLP across all of the rock types used in this study. Two-tailed t-tests assuming equal variance were performed to compare the SPLP and the ULP for each rock type and all were significant ($p<0.05$). For the St. Croix sandstone and the two Millet Brook granites, the extract uranium concentrations were below the 20 µg/L guideline when evaluated with the SPLP but above the guideline when the ULP was used. These three rock samples demonstrate the effectiveness of the ULP and the need for such a test to properly characterize the risk of uranium mobilization from aquifer material.

4.4.2 The Effect of Calcium Sulphate versus Calcium Chloride

Preliminary results from Blume (2016) suggested that sulphate is an important mobilizing factor for uranium. In Phases 1 and 2, the desired calcium concentrations were achieved through the addition of calcium chloride. After Blume found that the amount of uranium extracted from a sample was nearly doubled when calcium sulphate was used instead of calcium chloride in the extraction fluid, it was determined that calcium sulphate would be used for Phase 3. To justify this change, the results from Phase 3 for the Siltstone 1 and Millet Brook (low) were compared to the similar treatments on the same rock in Phase 2 (Figure 4-8).

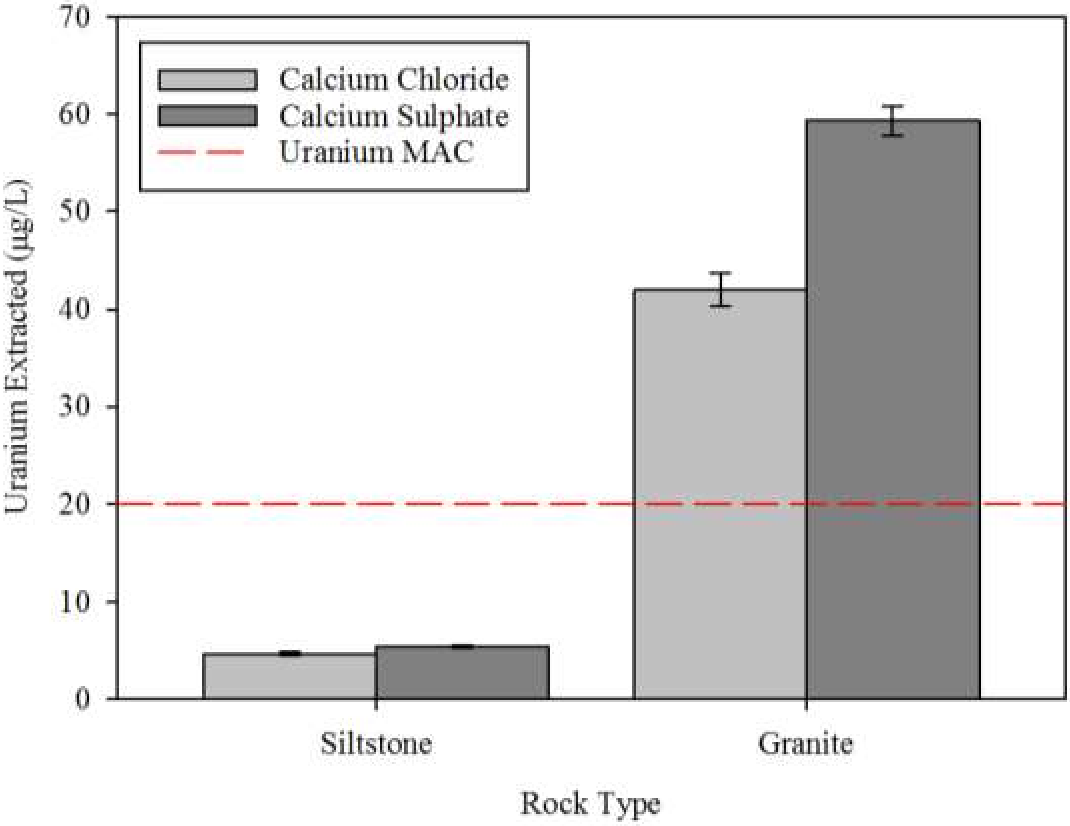

Figure 4-8: A comparison between similar treatments of St. Croix siltstone 1 and Millet Brook granite (low) between Phases 2 and 3. The Phase 2 extraction fluid used calcium chloride and had concentrations of calcium, sodium, chloride, and bicarbonate of 150, 340, 500, and 500 mg/L, respectively, and was not pH-adjusted. The Phase 3 extraction fluids used calcium sulphate and contained the same ions at concentrations of 150, 308, 300, and 300 mg/L, respectively with an additional 360 mg/L of sulphate. Error bars represent 95% confidence intervals.

It is clear from Figure 4-8 that the method of calcium addition has some effect on uranium concentration in the extract for the siltstone and granite samples. T-tests revealed that the extraction fluids containing calcium chloride and calcium sulphate had a significant effect on the siltstone samples (p-value = 0.01) and on the granite samples (p-value <0.01). The formation of uranyl-sulphate complexes could enhance uranium mobilization and the competition between uranyl and sulphate for sorption sites on rock surfaces could inhibit uranium sorption. It must be mentioned that these treatments in Phases 2 and 3 used different reagents to obtain a calcium concentration of 150 mg/L, but the treatments were also different in the concentrations of other ions and in pH, so a direct comparison with respect to the effect of calcium sulphate could not be made. Additional extractions could be performed where the concentrations of other ions are held constant and the extractions are performed at the same pH; then the extract uranium concentrations could be compared directly to evaluate the impact of sulphate and chloride on uranium mobilization. For the purposes of this thesis, it is sufficient to note that the ULP, which used calcium sulphate, had a significantly different uranium concentration in the extract than the Phase 2 extractions, which used calcium chloride.

4.4.3 The Effectiveness of the SPLP and ULP on Other Metals

The statistical differences between the ULP and SPLP tests for 25 metals were evaluated using two-tailed two sample t-tests performed in Excel at the 95% confidence level (assuming equal variances). The results of the t-tests are represented in Table 4-6 as significant (s) or non-significant (ns). Many of the analyzed metals exhibited no significant difference for any of the rock types and are not included in Table 4-6, including phosphorus, chromium, cobalt, zinc, selenium, silver, cadmium, antimony, cerium, and lead. Many elements were present at levels below the ICP-MS reportable detection limit, so it was difficult to quantify the effect of the SPLP and the ULP. For the metals that were significantly different, the concentrations in the extract from each rock for the SPLP and the ULP were plotted. These are discussed in the next several sections.

Table 4-6: A comparison of the ULP to the standard SPLP for each rock type and metal that was evaluated. The significant differences are indicated by 's' and the non-significant differences are indicated by 'ns'.

Element	**St. Croix Siltstone (1)**	**St. Croix Siltstone (2)**	**St. Croix Sandstone**	**Three Mile Plains Sandstone**	**Millet Brook Granite (low)**	**Millet Brook Granite (high)**
Lithium	s	s	s	ns	ns	s
Sodium	ns	s	s	s	s	s
Magnesium	s	s	s	s	s	s
Aluminum	s	s	ns	s	s	s
Potassium	ns	ns	ns	s	s	s
Calcium	s	s	s	s	s	s
Titanium	s	ns	ns	ns	ns	s
Vanadium	ns	ns	ns	ns	s	ns
Manganese	s	s	s	s	s	s
Iron	s	ns	ns	ns	ns	s
Nickel	ns	ns	s	ns	ns	ns
Copper	ns	ns	ns	s	ns	s
Arsenic	ns	ns	ns	ns	s	s
Barium	s	s	s	s	s	s
Uranium	s	ns	s	s	s	s

4.4.3.1 Alkali and Alkaline Earth Metals

Alkali metals (such as lithium, sodium, and potassium) and alkaline earth metals (such as beryllium, magnesium, calcium, strontium, and barium) appeared to have an important role in the mobilization of uranium during SPLP and ULP extractions, which is supported by the literature (Nair and Merkel, 2011; Nair et al., 2014). The ULP extraction fluid involves the addition of calcium (an alkaline earth metal) and sodium (an alkali metal) to promote uranium leaching. These results are presented in Figure 4-9 below. The significant difference between the SPLP and ULP is intuitive because sodium and calcium have been added to the matrix in the ULP, whereas in the SPLP extract, no calcium or sodium has been added, so these concentrations must have been extracted from the rock samples.

More interesting are the extracted concentrations of ions that were not added through the extraction fluid. Below are the results for barium, magnesium, sodium, and lithium (Figure 4-10). Barium and magnesium, like calcium, are capable of forming $M_xUO_2(CO_3)_3$ species, where M is an alkaline earth metal (Fox et al., 2006; Nair & Merkel, 2011). Strontium, another alkaline earth metal, was not analyzed during this project. The figures demonstrate that the ULP extracted significantly more barium and magnesium than the SPLP at a 95% confidence level for each rock type analyzed (all p-values < 0.01). This could occur due to the formation of uranyl-carbonate complexes with magnesium (Nair & Merkel, 2011) or due to ion exchange between the complexing ions in the extraction fluids and the rocks. The sodium in the extraction fluid, for example, is easily exchanged with the magnesium, calcium, and barium present in solid media.

Similarly, the alkali metals lithium and potassium (Figure 4-11) could interact with the sodium ions in solution through ion exchange. For lithium, all of the St. Croix samples demonstrated a significant difference between the two procedures, with a higher lithium concentration in the SPLP extract than the ULP extract. The Millet Brook sample (high concentration) also exhibited a significant difference, but it was the ULP that extracted more lithium. Potassium was extracted significantly more by the ULP than by the SPLP for the Three Mile Plains and Millet Brook samples.

4.4.3.2 Manganese and Iron

Samolczyk et al. (2012) reported correlations between uranium, manganese, and iron in the Grand Pré region of Nova Scotia. In that study, iron was used to indicate the redox state of the groundwater; elevated iron indicated a reducing environment and low iron indicated an oxidizing environment. They concluded that uranium tends to be elevated in groundwater that is low in manganese and iron, while groundwater that exceeds aesthetic objectives for iron and manganese tend to be low in uranium. The concentrations of manganese and iron extracted by the SPLP and ULP are presented in Figure 4-12 (both use a log scale).

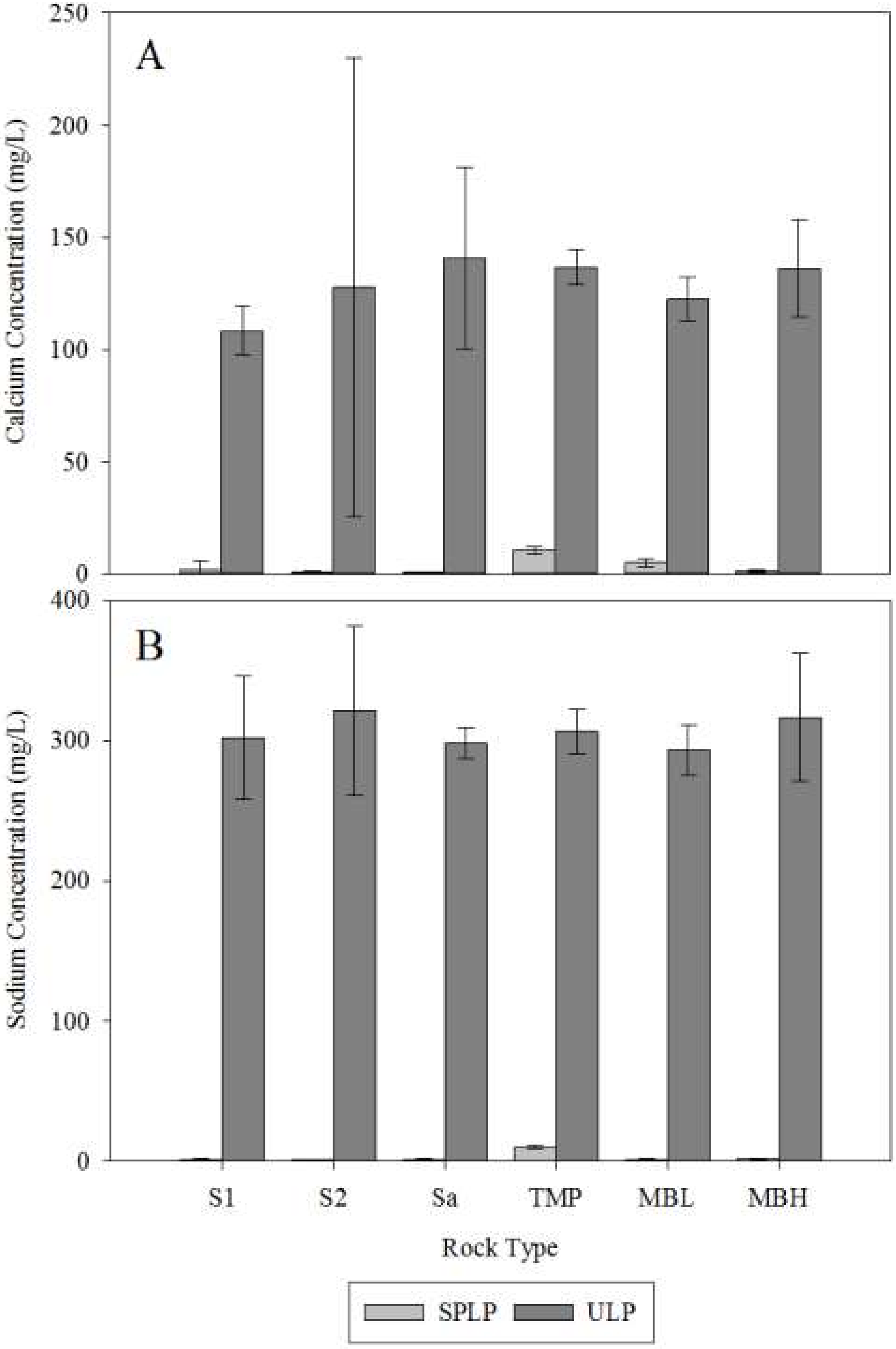

Figure 4-9: Extracted concentrations of (A) calcium and (B) sodium from SPLP and ULP. Error bars represent 95% confidence intervals.

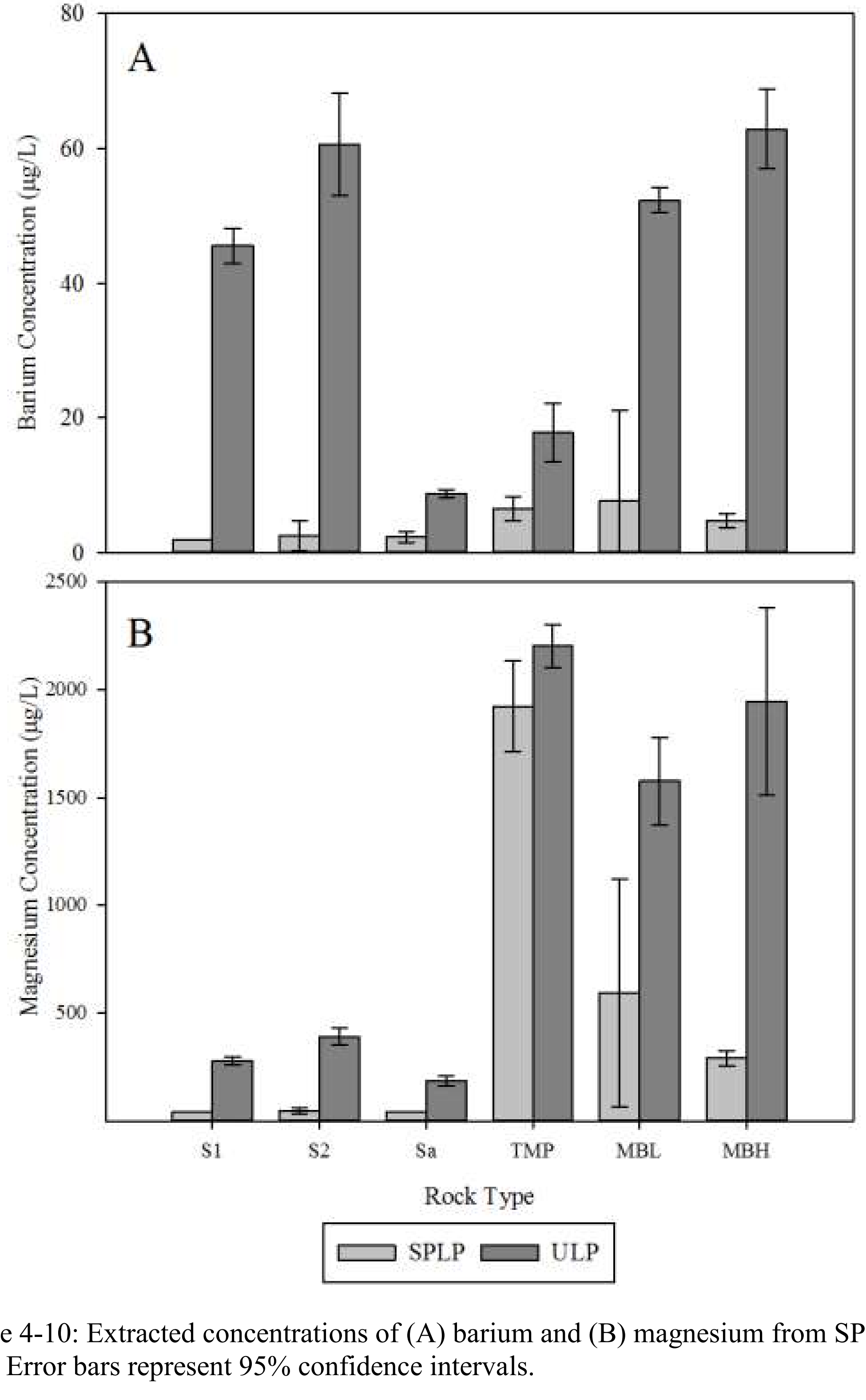

Figure 4-10: Extracted concentrations of (A) barium and (B) magnesium from SPLP and ULP. Error bars represent 95% confidence intervals.

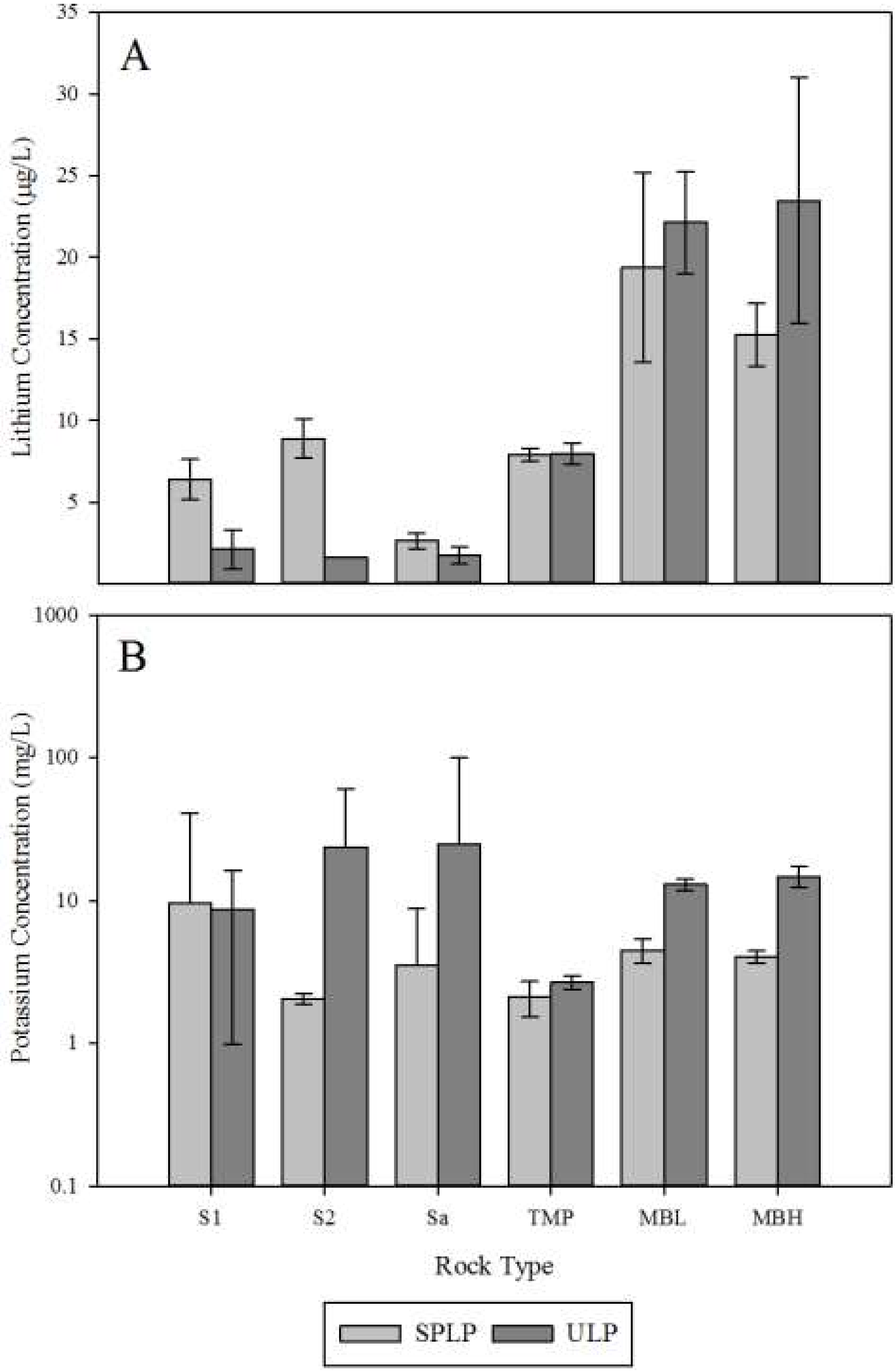

Figure 4-11: Extract concentrations of (A) lithium and (B) potassium from SPLP and ULP. Error bars represent 95% confidence intervals.

4.4.3.3 Manganese and Iron

Samolczyk et al. (2012) reported correlations between uranium, manganese, and iron in the Grand Pré region of Nova Scotia. In that study, iron was used to indicate the redox state of the groundwater; elevated iron indicated a reducing environment and low iron indicated an oxidizing environment. They concluded that uranium tends to be elevated in groundwater that is low in manganese and iron, while groundwater that exceeds aesthetic objectives for iron and manganese tend to be low in uranium. The concentrations of manganese and iron extracted by the SPLP and ULP are presented in Figure 4-12 (both use a log scale).

The iron concentrations were below the detection limits for all extractions done with the ULP, and some of the rocks extracted using SPLP were low as well. The oxidizing conditions of extraction for both of these tests likely caused iron to precipitate out of solution. The iron concentrations extracted by the SPLP and the ULP were significantly different at the 95% confidence level for S1 and MBH. Conversely, the ULP extracted significantly more manganese than the SPLP for all rock samples. The manganese extractions with ULP were above the aesthetic objective for all rock samples. Samolczyk et al. reported that iron and manganese dissolve in reducing environments as Fe^{2+} and Mn^{2+} and precipitate out of solution in oxidizing environments as $Fe(OH)_3$ and $Mn(OH)_2$. This behaviour also depends on pH, so the differences in iron and manganese concentrations between the two leaching procedures could be attributed to the low pH of the SPLP and the high pH of the ULP. The dissolved manganese ion is stable under oxidizing conditions for a wider range of pH than the iron ion, which precipitates out of solution as goethite in oxidizing environments around pH 7 (Samolczyk et al., 2012).

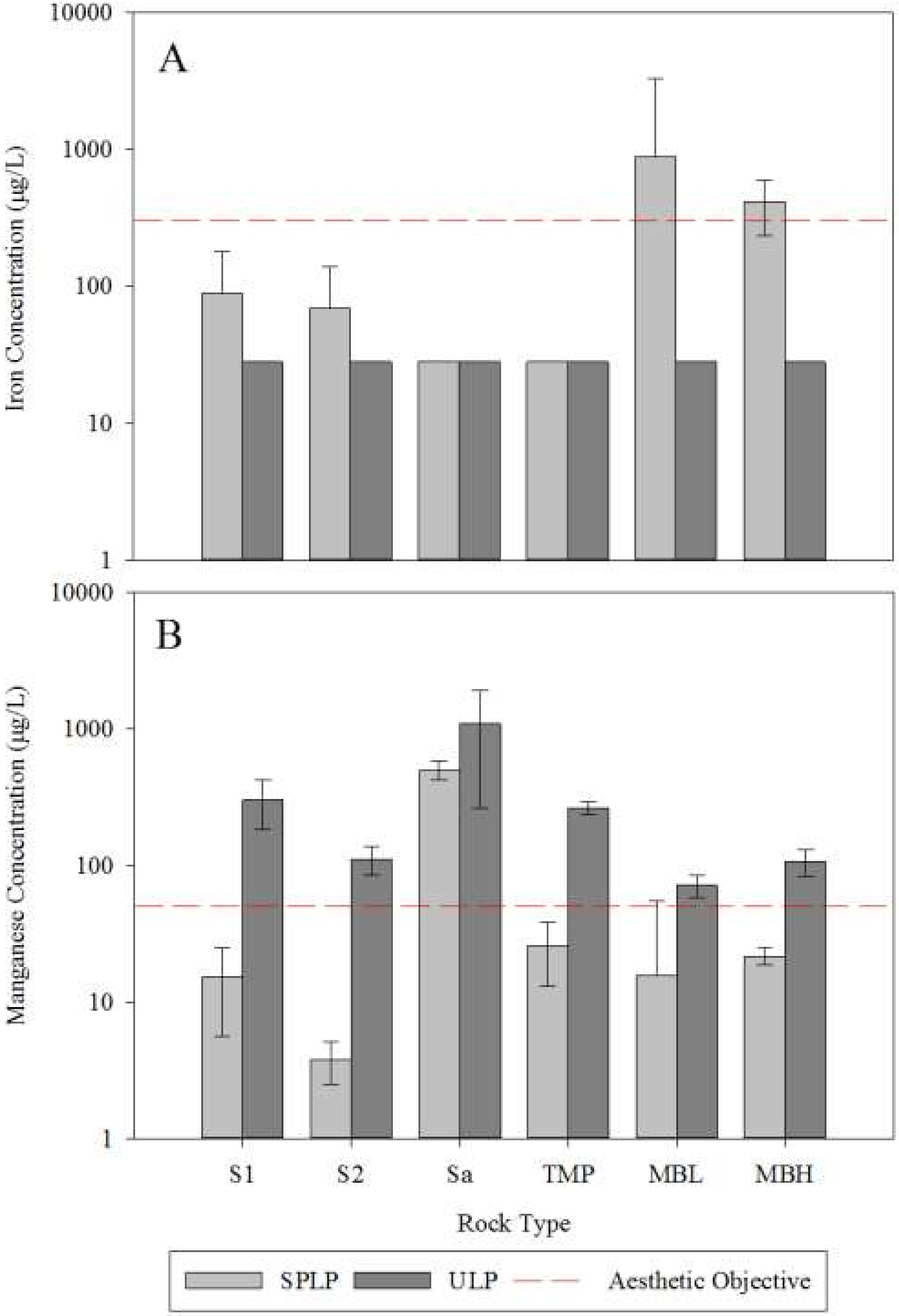

Figure 4-12: Extract concentrations of (A) iron and (B) manganese from SPLP and ULP. Note that many of the iron concentrations were below the detection limit of 28 µg/L. Error bars represent 95% confidence intervals.

4.4.3.4 Other metals of concern in Nova Scotia

As discussed in Section 2.1, arsenic is a major concern as a naturally occurring contaminant in Nova Scotia, in both groundwater and in soils. Nair et al. (2014) found evidence of competitive sorption between uranium and arsenic on various media in a laboratory experiment. Figure 4-13 shows that the SPLP extracted significantly more arsenic than the ULP for both of the granites, but otherwise all concentrations were below the detection limit of 1.6 μg/L. The greater mobilization of arsenic from the SPLP can be attributed to the low pH.

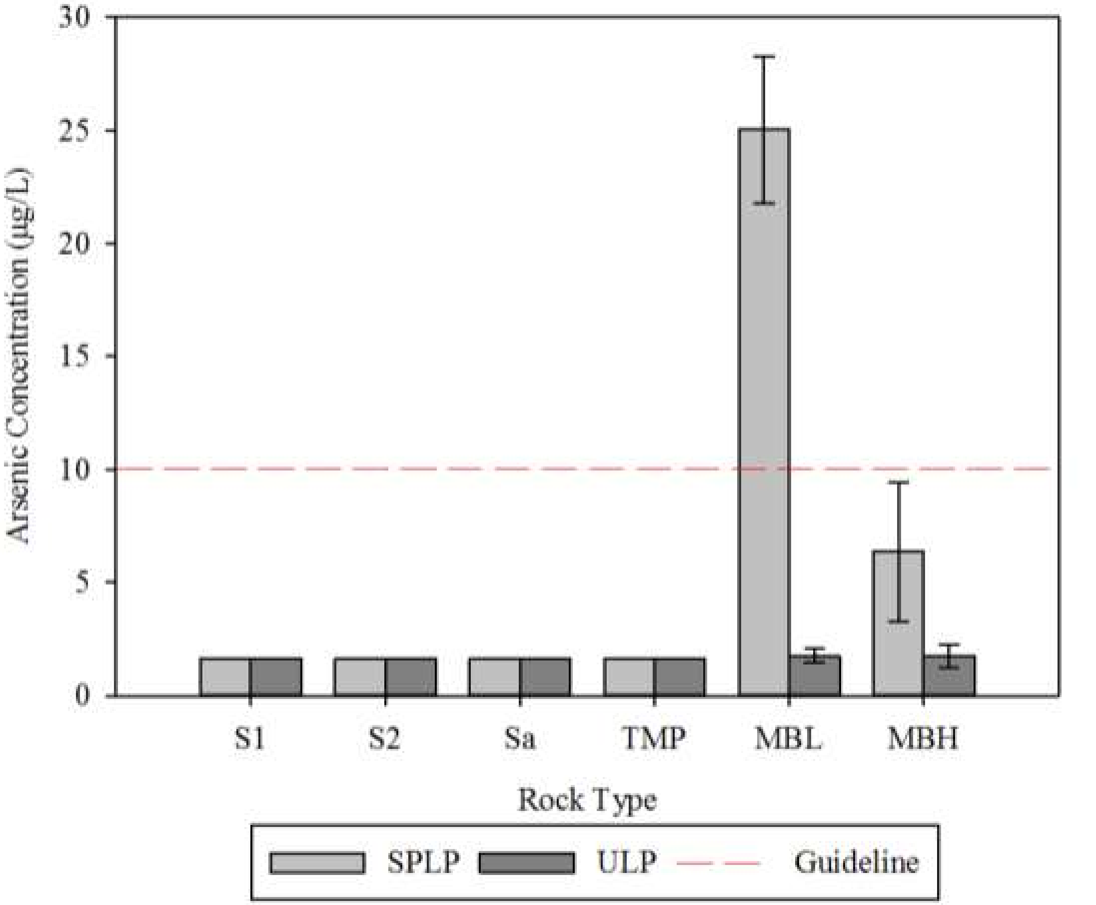

Figure 4-13: Arsenic concentrations in the extract from SPLP and ULP. Error bars represent 95% confidence intervals.

The other five metals that were found to be significantly different between the two procedures are aluminum, copper, nickel, titanium, and vanadium. Most of the extracted concentrations were close to the detection limits, allowing few conclusions to be drawn. These figures can be found in Appendix G.

4.5 Limitations

The discussion of redox potential was prevalent throughout the literature related to the mobilization of uranium (Murphy & Shock, 1999; Dong et al., 2005; Samolczyk et al., 2012; Wu et al., 2014). This study was limiting in that the end-over-end extraction procedure only considered oxidizing environments and the resultant mobility of hexavalent uranium. It could be argued that this test may not reflect actual groundwater conditions in the areas of Nova Scotia where reducing groundwater dominates. However, since the oxidized form of uranium is considered the most mobile in the environment, the development of a leaching test that simulates oxidizing conditions leads to an acceptable conservative estimate of the potential for uranium mobility from subsurface material.

Another potentially significant bias of this study was the exclusive analysis of the dissolved portion of uranium in the extracts. Analysis of total uranium in the extracts could lead to a greater understanding of the behaviour of uranium associated with colloids in the environment. However, Parsons (2007) noticed a similarity between total and dissolved uranium concentrations leached from Horton Group sandstones, suggesting that much of the uranium is dissolved, not associated with suspended particulate matter or large colloids. Furthermore, only the aqueous phase was analyzed for uranium. A more robust analysis of uranium mobilization might measure total, in addition to dissolved, uranium in the aqueous phase of extracts and the solid phase in the extracted rock samples.

The rock samples used in this study came from the same area of the South Mountain Batholith and its overlying sedimentary layers. This area is the subject of many studies related to uranium mobilization or sorption in Nova Scotia (O'Beirne-Ryan, 2006; Parsons, 2007; Ryan et al., 2009; Samolczyk et al., 2012, Drage & Kennedy, 2013). Cores drilled in River John during the uranium exploration period were considered but not sampled for this project. Extraction of rock samples from other areas of the province, such as the volcanic or black shale deposits in northern mainland Nova Scotia and Cape

Breton, would further validate the effectiveness of the ULP on a spectrum of material from across Nova Scotia.

While the influence of calcium on uranium concentrations in test extracts was explored in depth, anion impacts were not considered to the same extent. The primary purpose of this study has been to develop an effective uranium leaching procedure; building a complete understanding of uranium geochemistry with respect to every ion of interest was beyond the scope of this project, which is why a parallel analysis of potential anion influence on uranium mobilization was undertaken by Blume (2016, unpublished results) as a companion to this study.

Temperature was not controlled in the extractions performed in this study. The temperature of the room in which the extractions were performed ranged from approximately 17 °C to 30 °C. From a thermodynamics perspective, 25°C is considered "low temperature" for many uranium reactions and differences of 5-10 degrees have little influence on the reaction kinetics of uranium mobilization (Langmuir, 1978). For most of the reactions listed by Langmuir (1978), there is less than a 10% difference in log K between 17°C and 30°C.

Microbial geochemistry is an interesting concept and has been explored in more depth with respect to uranium than for any other actinide. The redox reactions that influence uranium mobility can act as an energy source to microorganisms, which can contribute to the weathering of uranium-rich minerals (Murphy & Shock, 1999) and can influence the dissolved inorganic carbon concentration (Jurgens et al., 2009). The impacts of microbial geochemistry were not evaluated in the development of the ULP, but it must be noted that the activity of microorganisms could have a significant effect on uranium mobilization in the environment.

Many important anions have been identified in the literature review; the influence of the presence of chloride, bicarbonate, and sulphate has been prevalent in this discussion section. However, these parameters were not measured except for bicarbonate, which was measured as alkalinity of the extraction fluid prior to extraction. A more complete understanding of the mobilizing factors could be facilitated in future studies by measuring these anions prior to and after extraction.

Finally, many other complexing ions, including fluoride, phosphate, other alkaline earth metals, and transition metals have been identified in the literature as enhancing or inhibiting uranium mobilization in groundwater (Bachmaf et al., 2008; Kumar et al., 2011; Nair & Merkel, 2011; Samolczyk et al., 2010; Nair et al., 2013). An attempt was made in Section 4.4.3.4 to consider the effect of the ULP on various metals that were analyzed in this study, but a comprehensive evaluation of the impact of these groundwater constituents was not undertaken.

Chapter 5 Conclusions and Recommendations

Four sedimentary and two igneous rock samples with known or suspected elevated uranium content were collected and a whole rock analysis revealed that they contained uranium contents ranging from 8.2 to 32 mg/kg. While these uranium values would not be considered particularly high from a mineral resource exploration point of view, this study confirmed that the uranium present in these rocks can be mobilized and therefore can have a potentially significant impact on human and environmental health. It was observed that the uranium content from the whole rock analysis did not predict the concentration of uranium in the extract due to differences in uranium distribution within the minerals of each rock type.

Appreciable concentrations of uranium were mobilized from the St. Croix siltstones in the absence of complexing ions at pH levels of 7 and 9. This confirms similar studies on this rock type (Parsons, 2007) and indicates that uranium may be leached from rocks to nearby surface water and groundwater even in areas that are not influenced by known uranium mobilizing factors.

When the complexing ions calcium, sodium, chloride, and bicarbonate were added to the extraction fluid in Phase 1, they had a significant impact. The high concentration extraction fluid was chosen to represent groundwater conditions in areas influenced by seawater intrusion, road salt application, or leachate from a construction and demolition site. Extractions performed under high concentration conditions mobilized more uranium than the low concentration extraction fluid, which represented typical background concentrations in Nova Scotian groundwater.

Calcium and bicarbonate are considered key ions in this project. It was originally thought that a 1:2 mass ratio of calcium to bicarbonate would maximize the formation of calcium-uranyl-carbonate complexes. The influence of the ratio between these two ions was evaluated in two suites of extractions representing calcium to bicarbonate mass ratios of approximately 1:1 and 1:2 in the extraction fluids. The extract uranium concentrations for both of the calcium to bicarbonate ratios were similar; it can therefore be concluded that the proportion of calcium relative to bicarbonate in the extraction fluid is not as important as originally believed.

An evaluation of how calcium concentration in the extraction fluid affected uranium mobilization from the St. Croix siltstone and Millet Brook granite revealed that varying calcium levels influence the two rocks differently. The siltstone showed an increasing trend of uranium in the extract but remained well below the drinking water MAC of 20 μg/L while the granite exhibited a decreasing trend and was consistently greater than 20 μg/L. The differences can be attributed to mineralogy and the affinity of uranium for organic matter in the siltstone, while it is easily mobilized from granitic minerals such as biotite. Both rock types produced consistent uranium concentrations when calcium was greater than 100 mg/L, thus a calcium concentration of 150 mg/L was chosen for the uranium leaching procedure.

A comparison of extractions performed with calcium chloride and calcium sulphate in the presence of high concentrations of all complexing ions suggests that sulphate is a more significant mobilizing agent for uranium from granites. No significant difference was noted when the siltstone extractions were compared.

Finally, the most significant contribution of this study to the body of knowledge on uranium mobilization in the environment is the development of the ULP. This test uses an alkaline pH and oxidizing conditions along with higher than background concentrations of calcium, sodium, chloride, carbonate/bicarbonate, and sulphate to extract uranium at concentrations an order of magnitude greater than the current standard SPLP. This optimization of uranium extraction from rock samples emphasizes the importance of an alkaline environment and the presence of the complexing ions calcium, sodium, chloride, bicarbonate, and sulphate.

The ULP is capable of extracting uranium at concentrations greater than the drinking water MAC of 20 μg/L on some rocks that have extract concentrations below the MAC when evaluated with the SPLP. This indicates that the ULP is a more conservative test that could effectively evaluate subsurface material in Nova Scotia to identify areas of high risk for uranium mobilization. This knowledge can inform decisions on the safety of groundwater as a local drinking water resource in a particular location and enable the safe siting of construction and demolition processing or disposal sites.

5.1 Recommendations for Future Work

This study evaluated the mobility of uranium in Nova Scotian groundwater through laboratory testing and developed a conservative, effective leaching procedure for assessing the potential of uranium mobilization from a crushed rock sample. As discussed in Section 4.5, there were certain limitations to this study that could be evaluated in future work to produce a more robust understanding of the behaviour of uranium in Nova Scotian groundwater. Some suggestions for future work are discussed below.

A key focus of this study was the influence of calcium on uranium mobilization through the formation of calcium-uranyl-carbonate complexes. Phase 2 was an in-depth evaluation of varying calcium concentrations on the liberation of uranium from siltstone and granite. There were anions of interest present in these extractions, but they were not a focus of the evaluation. Blume (2016) extracted the same rocks with a focus on understanding the impact of anions such as chloride, bicarbonate, and sulphate at high and low concentrations. This has been a valuable companion study and has informed the development of the ULP. A more in-depth evaluation of these anions and their performance on the extraction of uranium in the presence of other ions might better represent complex groundwater conditions and the interactions between these ions.

This study focused on extractions performed in the laboratory. A modeling study that attempts to replicate the results from the extractions performed in all phases of this project would allow the mechanisms driving uranium mineralization to be better understood.

The rocks that were extracted in this project represented different rock types (siltstones, sandstones, and granites), but they all came from the same geographic area of the South Mountain Batholith granitic rocks and Horton Group sandstones near Windsor, Nova Scotia. Expanding the validation of the ULP to rocks from other known uranium occurrences across the province would reinforce the applicability of this test to a wider variety of geologic environments.

The rock samples used in all phases had a particle size of less than 2 mm, but some samples were much finer than others. The crushed siltstone contained much finer particles than the sandstones, which were finer than the granites. It could be expected for finer samples to produce higher uranium extract concentrations due to increased surface area and therefore contact with uranium-bearing minerals, but the extracts from the coarser-grained granites were consistently greater in uranium than the fine-grained siltstones. This is of course due to the mineralogy of those distinct rock types, but future undertakings could evaluate the impact of particle size of a single rock type on uranium mobilization, which would lead to an increased understanding of the distribution of leachable uranium within rocks.

All extractions performed in this project were performed under oxidizing conditions (Eh values were greater than zero and in most cases were greater than 200 mV) because of the known mobility of the oxidized hexavalent uranium ion, U(VI). This allowed for the development of a conservative leaching test by maximizing the formation of aqueous uranium species, but may not be representative of actual groundwater conditions. The performance of a similar test in anoxic or reducing conditions could be an interesting complement to this study by representing a broader range of environmental groundwater conditions in Nova Scotia.

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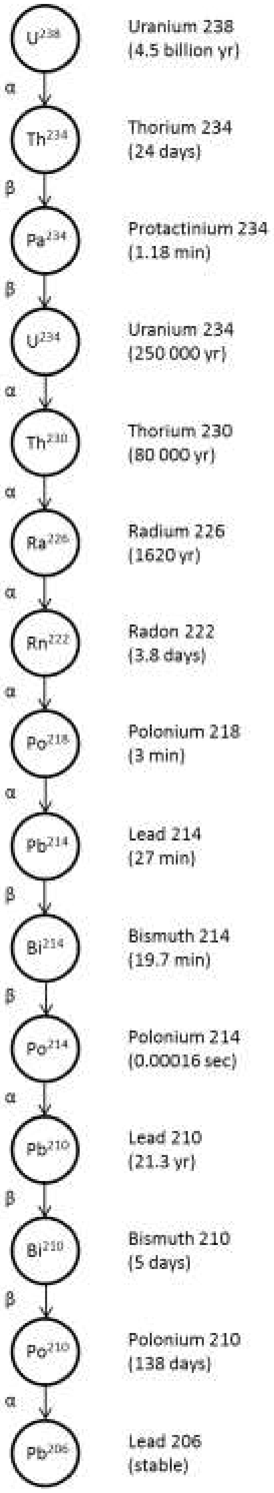
Appendix A Uranium-238 Decay Series



Adapted from O'Reilly, 1982

Appendix B Rock Sample Analysis – Metals and Pictures

	RDL	St. Croix Siltstone (1)	St. Croix Siltstone (2)	St. Croix Sandstone	Three Mile Plains Sandstone	Millet Brook Granite (low)	Millet Brook Granite (high)
Metals (mg/kg)		S1	S2	Sa	TMP	MBL	MBH
Total Aluminum (Al)	10	78000	98000	75000	40000	66000	62000
Total Antimony (Sb)	2.0	ND	ND	ND	ND	ND	ND
Total Arsenic (As)	2.0	17	22	22	ND	5.6	14
Total Barium (Ba)	5.0	170	190	180	120	590	760
Total Beryllium (Be)	2.0	3.0	4.4	3.0	ND	2.2	2.4
Total Cadmium (Cd)	0.15	ND	ND	ND	ND	0.23	0.39
Total Chromium (Cr)	2.0	23	37	22	4.8	25	24
Total Cobalt (Co)	1.0	3.5	2.3	5.4	1.9	7.1	9.2
Total Copper (Cu)	2.0	45	39	45	7.2	74	95
Total Iron (Fe)	50	11000	14000	14000	5300	26000	32000
Total Lead (Pb)	0.50	21	25	29	33	37	29
Total Manganese (Mn)	2.0	140	120	450	680	500	620
Total Molybdenum (Mo)	2.0	ND	ND	ND	ND	ND	ND
Total Nickel (Ni)	2.0	6.7	7.1	8.8	6.2	8.3	9.3
Total Selenium (Se)	2.0	4.1	4.7	5.4	ND	ND	ND
Total Strontium (Sr)	5.0	45	76	52	26	120	100
Total Thallium (Tl)	0.10	1.1	1.2	1.2	0.30	0.98	1.1
Total Tin (Sn)	2.0	8.9	12	8.2	4.3	3.1	3.5
Total Uranium (U)	0.10	20	20	16	13	8.2	34
Total Vanadium (V)	2.0	60	78	68	15	41	54
Total Zinc (Zn)	5.0	21	27	17	ND	120	130

Figure B-1: St. Croix sedimentary rocks. Sampled from the field (Green Street, St. Croix, NS).

Figure B-2: Three Mile Plains sandstone. Sampled from the DNR Core Library (drill hole 1-306, 262 to 267 m depth, Saarberg Interplan Canada, Ltd.).

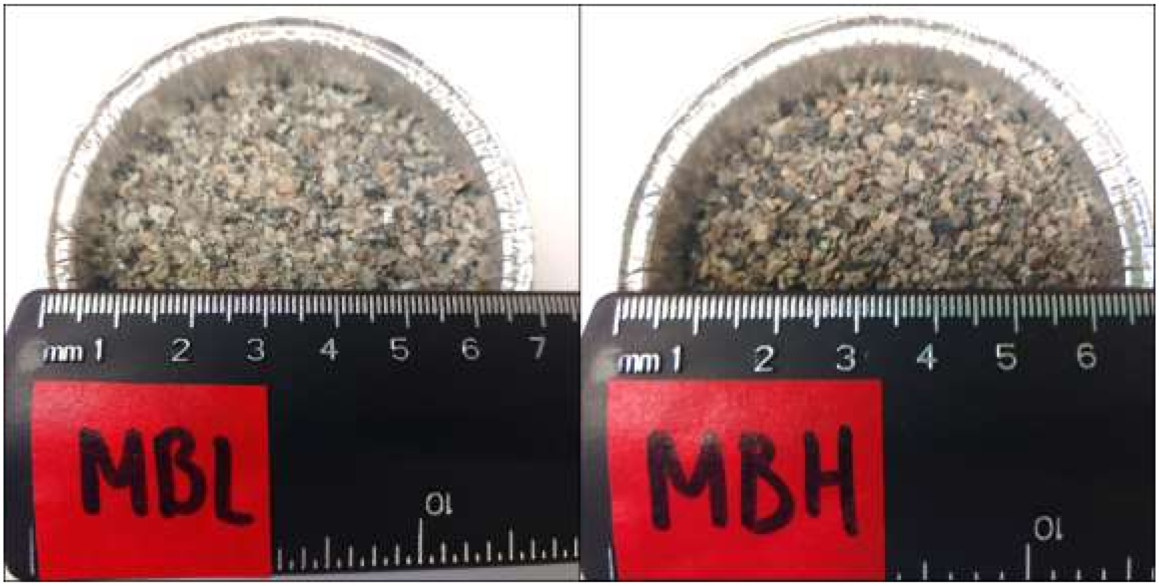


Figure B-3: Millet Brook granite. Sampled from the DNR Core Library (drill hole MB 80 C2-1, 37.7 to 41.8 m depth, Aquitaine Company of Canada, Ltd.).

Appendix C Uranium Concentrations for All Phases

Phase	Treatment Description	Uranium Concentration (µg/L)			Mean Uranium Concentration (µg/L)
1: water	pH 7, 1 d	0.72	0.75	0.70	0.72
	pH 7, 3 d	0.75	0.76	0.77	0.76
	pH 9, 1 d	0.33	0.32	0.33	0.33
	pH 9, 3 d	0.29	0.27	0.30	0.29
1: low concentration	pH 5.5, 1 d	0.72	0.75	0.70	0.72
	pH 5.5, 3 d	0.75	0.76	0.77	0.76
	pH 7, 1 d	0.33	0.32	0.33	0.33
	pH 7, 3 d	0.29	0.27	0.30	0.29
	pH 8.5, 1 d	0.29	0.32	0.25	0.29
	pH 8.5, 3 d	0.26	0.25	0.26	0.26
1: high concentration	pH 5.5, 1 d	0.55	0.57	0.55	0.56
	pH 5.5, 3 d	0.73	0.78	0.74	0.75
	pH 7, 1 d	2.80	3.00	3.10	2.97
	pH7, 3 d	3.00	2.70	2.90	2.87
	pH 8.5, 1 d	3.70	3.70	3.80	3.73
	pH 8.5, 3 d	4.50	4.40	4.30	4.40
L	low, pH 5.5, 1 d	0.39	0.43	0.41	0.41
	low, pH 5.5, 3 d	0.35	0.37	0.35	0.36
	low, pH 7, 3 d	0.28	0.26	0.27	0.27
	low, pH 8.5, 3 d	0.21	0.22	0.19	0.21
	low, pH 7, 1 d	0.22	0.24	0.23	0.23
	low, pH 8.5, 1 d	0.21	0.21	0.19	0.20
2: siltstone	0 mg/L calcium	1.5	1.8	2.1	1.80
	50 mg/L calcium	2.8	2.7	3.1	2.87
	100 mg/L calcium	4.5	4.1	4.1	4.23
	150 mg/L calcium	4.9	4.5	4.7	4.70
	200 mg/L calcium	4.6	4.7	5.0	4.77
	250 mg/L calcium	5.0	4.9	5.0	4.97
2: granite	0 mg/L calcium	52	61	62	58.33
	50 mg/L calcium	57	33	51	47.00
	100 mg/L calcium	50	52	56	52.67
	150 mg/L calcium	43	40	43	42.00
	200 mg/L calcium	44	41	38	41.00

	250 mg/L calcium	42	36	44	40.67
3	SPLP, Siltstone 1	0.31	0.26	0.33	0.30
	ULP, Siltstone 1	5.30	5.60	5.30	5.40
	SPLP, Siltstone 2	0.16	0.10	0.13	0.13
	ULP, Siltstone 2	0.94	0.92	0.93	0.93
	SPLP, Sandstone	0.12	0.11	0.10	0.11
	ULP, Sandstone	32	32	31	31.67
	SPLP, TMP sandstone	27	25	30	27.33
	ULP, TMP sandstone	280	270	270	273.33
	SPLP, Millet Brook granite (low)	6.7	8.0	6.3	7.0
	ULP, Millet Brook granite, low	61	59	58	59.33
	SPLP, Millet Brook granite (high)	7.4	8.7	8.0	8.03
	ULP, Millet Brook granite, high	770	840	820	810

Appendix D pH Measurements for All Phases

pH was measured in the extraction fluid prior to extraction and in the blank and triplicate extracts after extraction.

Phase	Treatment Description	Initial pH of blank	Final pH of blank	Final pH (extractions)			Mean Final pH
1: water	pH 7, 1 d	7.26	6.95	5.42	5.31	5.24	5.32
	pH 7, 3 d	6.90	7.40	6.00	6.01	6.07	6.03
	pH 9, 1 d	8.93	9.22	5.63	5.70	5.54	5.62
	pH 9, 3 d	8.67	8.08	6.12	6.02	6.09	6.08
1: low concentration	pH 5.5, 1 d	5.49	5.71	4.43	4.44	4.47	4.45
	pH 5.5, 3 d	5.17	5.15	4.46	4.45	4.47	4.46
	pH 7, 1 d	7.05	7.08	4.85	4.83	4.85	4.84
	pH 7, 3 d	7.05	7.09	4.76	4.77	4.78	4.77
	pH 8.5, 1 d	8.52	8.06	4.90	4.92	4.92	4.91
	pH 8.5, 3 d	8.51	8.24	4.90	4.91	4.90	4.90
1: high concentration	pH 5.5, 1 d	5.55	5.63	4.87	4.85	4.88	4.87
	pH 5.5, 3 d	5.83	5.47	4.66	4.68	4.70	4.68
	pH 7, 1 d	7.04	7.01	6.55	6.58	6.57	6.57
	pH7, 3 d	7.05	7.15	6.49	6.45	6.47	6.47
	pH 8.5, 1 d	8.08	7.12	6.80	6.80	6.81	6.80
	pH 8.5, 3 d	8.16	7.19	6.73	6.71	6.70	6.71
L	low, pH 5.5, 1 d	5.49	6.83	4.28	4.31	4.34	4.31
	low, pH 5.5, 3 d	5.55	6.50	4.34	4.36	4.37	4.36
	low, pH 7, 3 d	7.00	6.86	4.57	4.47	4.42	4.49
	low, pH 8.5, 3 d	8.52	8.20	4.55	4.60	4.57	4.57
	low, pH 7, 1 d	7.01	7.39	4.39	4.40	4.40	4.40
	low, pH 8.5, 1 d	8.52	8.55	4.43	4.47	4.50	4.47
2: siltstone	0 mg/L calcium	8.14	8.27	7.07	7.02	7.03	7.04
	50 mg/L calcium	7.69	7.77	6.75	6.81	6.84	6.80
	100 mg/L calcium	7.69	7.15	6.80	6.78	6.80	6.79
	150 mg/L calcium	7.55	7.03	6.75	6.72	6.75	6.74
	200 mg/L calcium	7.44	6.82	6.66	6.67	6.67	6.67
	250 mg/L calcium	7.36	6.84	6.63	6.66	6.69	6.66
2: granite	0 mg/L calcium	7.95	8.20	8.38	8.36	8.37	8.37
	50 mg/L calcium	8.11	7.40	7.82	7.80	7.81	7.81
	100 mg/L calcium	7.95	7.17	7.55	7.49	7.50	7.51
	150 mg/L calcium	7.75	7.07	7.48	7.52	7.39	7.46

Phase	Treatment Description	Initial pH of blank	Final pH of blank	Final pH (extractions)			Mean Final pH
	200 mg/L calcium	7.28	6.95	7.42	7.42	7.41	7.42
	250 mg/L calcium	7.20	6.79	7.22	7.21	7.19	7.21
3	SPLP, Siltstone 1	4.22	4.32	5.52	5.51	5.65	5.56
	ULP, Siltstone 1	7.97	7.29	6.66	6.66	6.67	6.66
	SPLP, Siltstone 2	4.20	4.17	4.92	4.85	4.88	4.88
	ULP, Siltstone 2	7.94	7.19	6.19	6.24	6.25	6.23
	SPLP, Sandstone	4.20	3.90	6.09	6.23	6.57	6.30
	ULP, Sandstone	8.16	7.31	6.96	7.01	7.05	7.01
	SPLP, TMP sandstone	4.23	3.96	8.69	8.64	8.73	8.69
	ULP, TMP sandstone	8.03	7.75	7.55	7.56	7.61	7.57
	SPLP, Millet Brook granite (low)	4.13	3.87	9.07	9.08	9.16	9.10
	ULP, Millet Brook granite, low	7.97	7.34	7.72	7.74	7.72	7.73
	SPLP, Millet Brook granite (high)	4.19	3.79	8.64	8.46	8.36	8.49
	ULP, Millet Brook granite, high	7.99	7.29	7.70	7.71	7.67	7.69

Appendix E Oxidation-Reduction Potential Measurements for all Phases

Measurements of oxidation-reduction potential as Eh in all extractions. Eh was measured in the extraction fluid prior to extraction and in the blank and triplicate extracts after extraction. All measurements in mV. Note that Eh was measured for all extractions, but the proper calibration solution was not available until partway through the extractions with low concentrations of ions in Phase 1.

Phase	Treatment Description	Initial Eh of blank	Final Eh of blank	Final Eh (extractions)			Mean Final Eh
1: water	pH 7, 1 d[b]	[a]	-80.1	-51.2	-38.6	-46.8	**-45.5**
	pH 7, 3 d[b]	-100.6	-74.6	-27.0	-19.4	-15.4	**-20.6**
	pH 9, 1 d[b]	[a]	-114.9	-57.7	-56.2	-46.2	**-53.4**
	pH 9, 3 d[b]	-96.9	-93.4	-21.2	-14.6	-9.6	**-15.1**
1: low concentration	pH 5.5, 1 d	303.5	484.9	355.9	351.9	350.1	**352.6**
	pH 5.5, 3 d	306.2	275.4	323.1	331.8	331.6	**328.8**
	pH 7, 1 [b]	-54.4	-67.7	-18.0	-17.0	-17.4	**-17.5**
	pH 7, 3 [b]	-102.1	-51.5	5.3	4.1	3.6	**4.3**
	pH 8.5, 1 [b]	-78.1	-95.2	-17.8	-15.9	-10.8	**-14.8**
	pH 8.5, 3 [b]	-121.7	-83.3	-3.9	-6.9	-11.5	**-7.4**
1: high concentration	pH 5.5, 1 d	306.2	336.1	328.9	321.0	320.0	**323.3**
	pH 5.5, 3 d	311.1	298.8	310.9	314.2	312.9	**312.7**
	pH 7, 1 d	296.6	307.8	305.5	303.9	303.5	**304.3**
	pH7, 3 d	244.6	240.2	256.9	256.8	258.3	**257.3**
	pH 8.5, 1 d	279.1	301.8	297.3	292.6	293.7	**294.5**
	pH 8.5, 3 d	231.5	246.3	254.3	255.7	256.5	**255.5**
L	low, pH 5.5, 1 d	319.9	293.2	395.0	397.9	386.4	**393.1**
	low, pH 5.5, 3 d	321.3	297.3	372.9	377.8	375.9	**375.5**
	low, pH 7, 3 d	286.7	484.4	411.8	397.1	418.1	**409.0**
	low, pH 8.5, 3 d	271.7	412.1	410.7	411.8	396.6	**406.4**
	low, pH 7, 1	[a]	363.9	397.6	390.7	395.3	**394.5**
	low, pH 8.5, 1 d	[a]	302.8	395.3	400.7	398.0	**398.0**
2: siltstone	0 mg/L calcium	238.7	228.0	274.1	279.1	282.7	**278.6**
	50 mg/L calcium	275.8	264.9	299.3	302.0	296.6	**299.3**
	100 mg/L calcium	268.2	271.6	290.5	292.4	291.8	**291.6**
	150 mg/L calcium	283.4	282.4	290.1	293.5	293.8	**292.5**
	200 mg/L calcium	382.7	305.2	314.6	316.6	318.1	**316.4**
	250 mg/L calcium	412.2	315.1	317.6	319.0	316.4	**317.7**

Phase	**Treatment Description**	**Initial Eh of blank**	**Final Eh of blank**	**Final Eh (extractions)**			**Mean Final Eh**
2: granite	0 mg/L calcium	391.7	270.2	217.9	219.7	247.0	**228.2**
	50 mg/L calcium	264.0	250.9	205.9	98.9	171.5	**158.8**
	100 mg/L calcium	277.6	263.3	224.5	211.4		**218.0**
	150 mg/L calcium	204.0	423.6	253.1	281.0	240.1	**258.1**
	200 mg/L calcium	230.9	382.4	247.9	245.4	267.1	**253.5**
	250 mg/L calcium	333.4	307.6	277.9	290.0	289.5	**285.8**
3	SPLP, Siltstone 1	398.7	398.2	378.7	375.0	365.9	**373.2**
	ULP, Siltstone 1	305.6	320.1	338.6	339.2	341.5	**339.8**
	SPLP, Siltstone 2	378.3	415.8	377.5	385.1	385.5	**382.7**
	ULP, Siltstone 2	317.2	338.7	377.8	370.5	370.0	**372.8**
	SPLP, Sandstone	429.0	402.9	332.9	320.1	340.7	**331.2**
	ULP, Sandstone	321.4	319.9	317.3	318.4	315.6	**317.1**
	SPLP, TMP sandstone	511.4	416.3	248.6	247.4	237.7	**244.6**
	ULP, TMP sandstone	385.9	317.2	278.1	267.7	273.5	**273.1**
	SPLP, Millet Brook granite (low)	421.0	418.7	244.9	243.4	241.9	**243.4**
	ULP, Millet Brook granite, low	308.0	320.9	278.1	297.2	277.4	**284.2**
	SPLP, Millet Brook granite (high)	451.3	432.7	134.7	219.7	227.2	**193.9**
	ULP, Millet Brook granite, high	321.1	316.4	292.5	260.3	243.2	**265.3**

[a] Eh not measured.

[b] Eh measured before calibration solution was available

Appendix F Ions Added as a Result of pH Adjustment

Phase 1

Chloride was not measured in any of the phases, but it was approximated based on the dissolution of sodium chloride. In addition to this salt, the adjustment of the pH using 1N HCl added several milligrams of chloride to the extraction fluid that were not originally accounted for. This addition may have led to chloride concentrations that were significantly greater than the desired concentration, but the impact cannot be confirmed without measured chloride data. The table below lists the approximate masses of chloride added in each extraction of Phase 1. The volume of acid used was not recorded for the extractions performed at pH 7. The extraction fluids with pH 8.5 were adjusted using 1N NaOH.

	Chloride added as 1N HCl (mg)	
pH	**Low Concentration EF**	**High Concentration EF**
5.5	34.4	130
	24.1	216
7	nm	25.9
	nm	34.4
8.5	0	0
	0	0
Desired Concentration (mg/L)	**140**	**400**

Unlike chloride, the impact of pH adjustment on sodium concentrations in the extraction fluids can be evaluated. Although the volume of 1N NaOH used to adjust the pH to 8.5 was only recorded for the high concentration extraction fluid, sodium concentrations were measured for all of the extractions. The following table shows the measured concentrations of sodium for each extraction fluid in Phase 1. All measurements were close to the desired sodium concentration.

	Measured Sodium Concentrations (mg/L)	
pH	Low Concentration EF	High Concentration EF
5.5	34	157
	26	231
7	34	173
	35	163
8.5	35	194[a]
	35	179[b]
Desired Concentration (mg/L)	**35**	**181**

[a]28 and [b]14 mg of sodium were added as 1N NaOH.

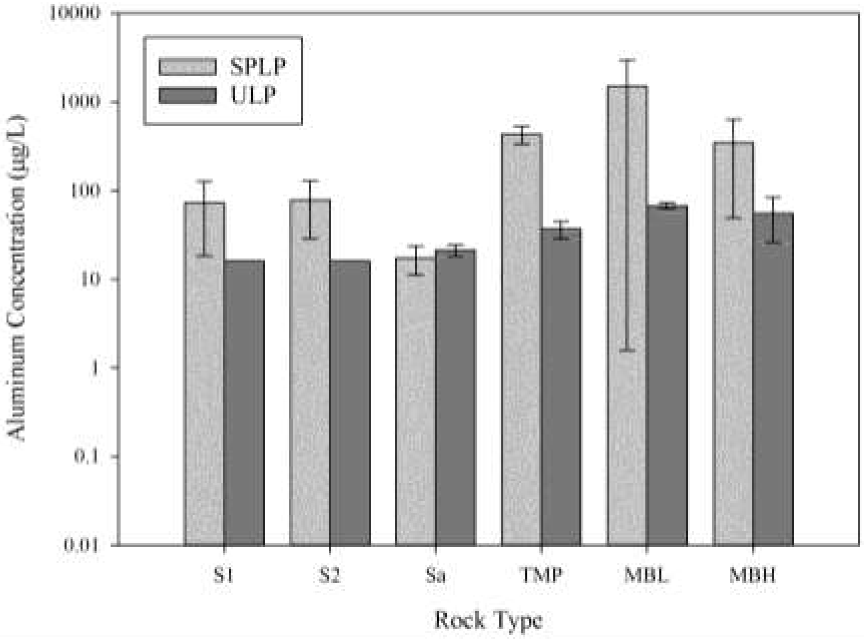
Phase 3

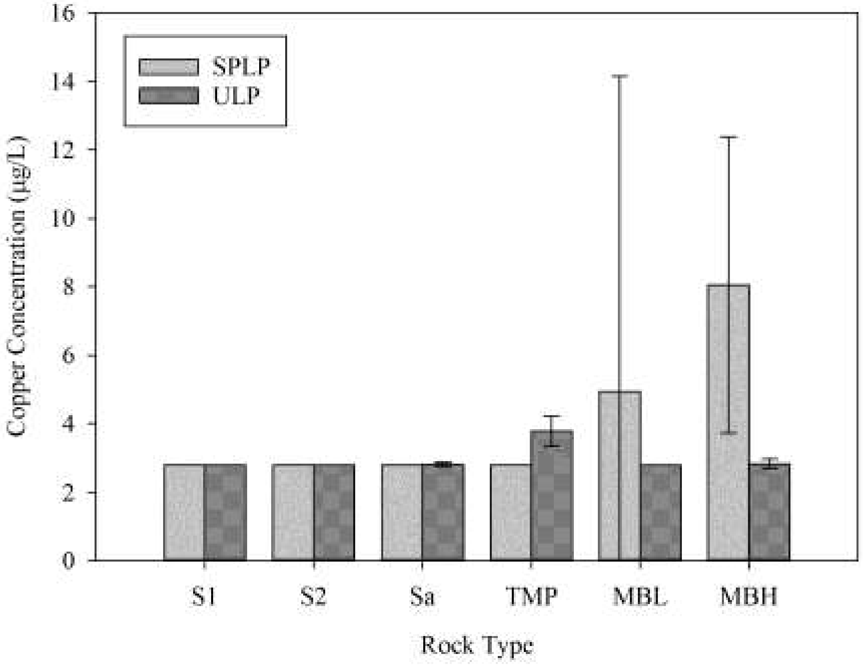
The pH was adjusted in both the SPLP and the ULP extraction fluids. The SPLP used a 60:40 mass ratio of nitric to sulphuric acids to adjust the pH of the extraction fluid to 4.20 and the ULP used 1N NaOH to adjust the pH to 8.0. If the pH was greater than 8 when measured, no pH adjustment was performed.

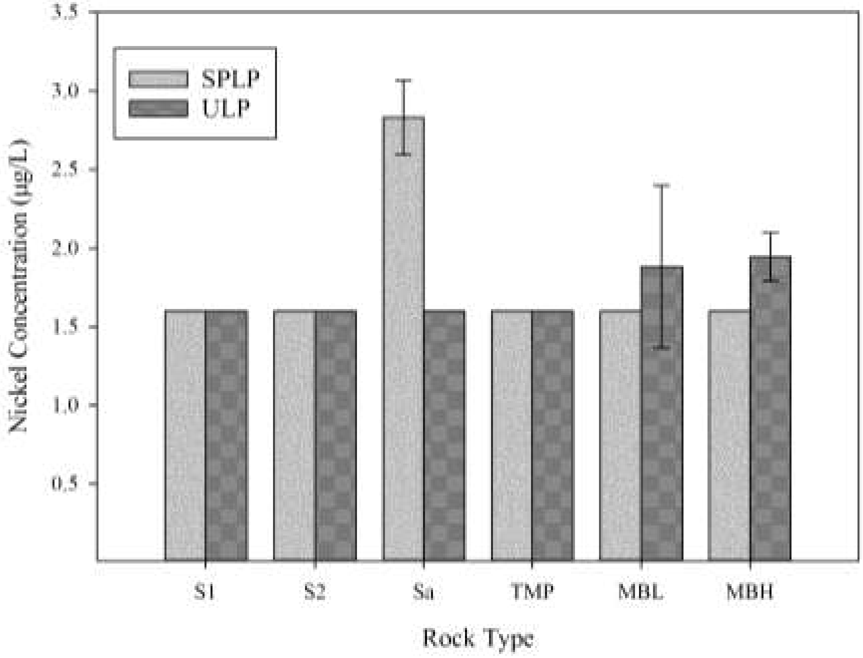
	Sodium (mg/L)		Sulphate (approximate mg/L)	
Rock Sample	SPLP	ULP	SPLP	ULP
Siltstone 1	<1	295.3[a]	8	360
Siltstone 2	1.1	297.2	8.5	360
Sandstone	31.3	288	39	360
TMP	1.6	297.6	17	360
MBL	<1	307.8[b]	11	360
MBH	1.6	295.3[c]	9	360
Desired Concentration (mg/L)	**0**	**308**	**As necessary**	**360**

[a]62, [b]28, and [c]34 mg of sodium were added as 1N NaOH.

Appendix G Metals Extracted using SPLP and ULP






3.5
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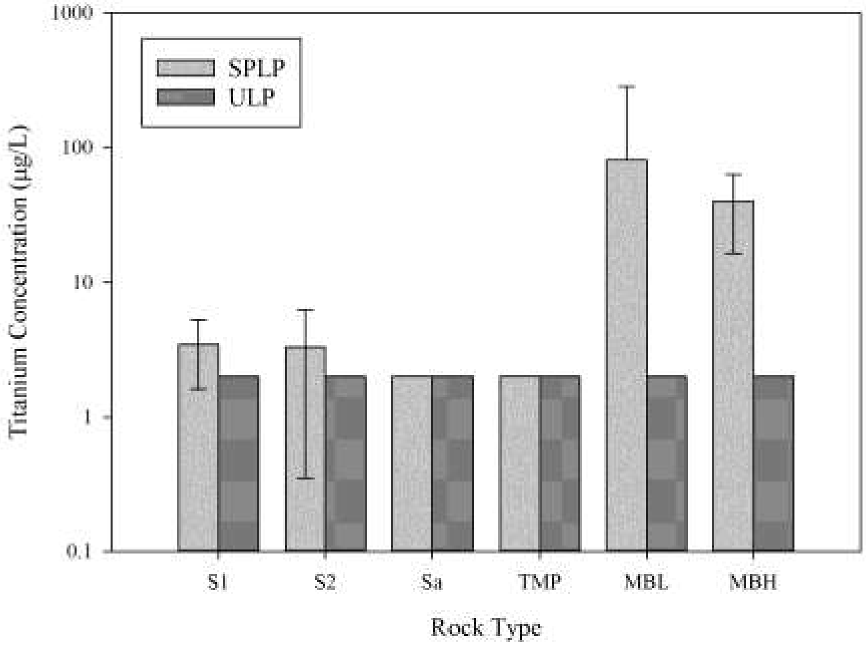
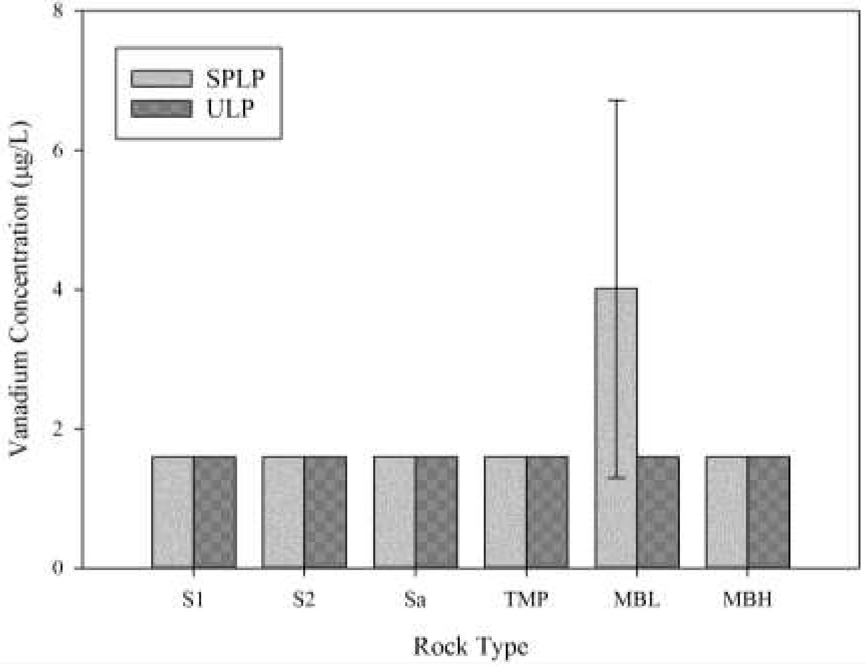
2.5
2.0
1.5
1.0
0.5
SPLP
ULP
Nickel Concentration (µg/L)
S1
S2
Sa
TMP
MBL
MBH
Rock Type


1000
100
10
1
0.1
SPLP
ULP
Titanium Concentration (µg/L)
S1
S2
Sa
TMP
MBL
MBH
Rock Type


8
6
4
2
0
SPLP
ULP
Vanadium Concentration (µg/L)
S1
S2
Sa
TMP
MBL
MBH
Rock Type

Appendix H Uranium Leaching Procedure

1. SCOPE AND APPLICATION
    1.1. The ULP is designed to characterize the mobility of uranium from subsurface material to groundwater.
2. SUMMARY OF METHOD
    2.1. The materials to be evaluated are rock samples that have been dried before undergoing particle size reduction. The material is extracted with an amount of extraction fluid equal to 20 times the weight of the material. The extraction fluid employed is a mixture of calcium sulphate, sodium chloride, and sodium bicarbonate adjusted to a pH of 8.00 or greater. Following extraction, the liquid extract is separated from the solid phase by filtration first through a 1.5 µm filter, to remove the majority of solids, then through a 0.45 µm filter to isolate the dissolved species. This method was modified from the Synthetic Precipitation Leaching Procedure (SPLP) which is Method 1312 from the United States Environmental Protection Agency (USEPA, 1994)
3. INTERFERENCES
    3.1. The extraction fluids used in this procedure contain high concentrations of salts. Care should be taken during ICP-MS analysis to provide appropriate dilutions to avoid matrix interference during analysis.
4. APPARATUS AND MATERIALS
    4.1. Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 ± 2 rpm. Any device that rotates the extraction vessel at 30 ± 2 rpm is acceptable.
    4.2. Bottle extraction vessels: A jar or bottle with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel. The extraction vessels may be constructed from various materials, including plastic and glass. It is recommended that borosilicate glass bottles be used instead of other types of glass. Bottles are available from a number of laboratory suppliers.
    4.3. Filtration Devices

4.3.1. Filter Holder: A filter holder capable of supporting a filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting high pressures. The type of filter holder used depends on the properties of the material to be filtered (see Step 4.3.2). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended).

4.3.2. Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb sample components of interest. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used. Devices made of high-density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles.

4.3.3. Filters:

4.3.3.1. Pre-filter: The initial filter should have a pore size greater than 0.45 µm. Pre-filtration is usually required to speed up overall filtration time due to the solids content of the extract.

4.3.3.2. The secondary filters should have a pore size of 0.45 µm.

4.3.3.3. Filter material can be borosilicate glass fiber or mixed cellulose ester.

NOTE: When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with reagent water (a minimum of 1-L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.4. pH Meters: The meter should be accurate to ± 0.05 units at 25°C.

4.5. Laboratory balance: Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

5. REAGENTS

5.1. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2. Reagent Water: Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest. ASTM Type II water or equivalent meets the definition of reagent water.

5.3. Extraction Fluid

5.3.1. Calcium sulphate, $CaSO_4$

5.3.2. Sodium bicarbonate, $NaHCO_3$

5.3.3. Sodium chloride, NaCl

5.3.4. Sodium hydroxide, 1N NaOH

5.3.5. The extraction fluid is prepared by adding reagents 5.3.1-5.3.3 in the quantities outlined in Table 1 to obtain the desired aqueous concentrations of calcium, sodium, bicarbonate, chloride, and sulphate. The pH is measured and recorded after 20 minutes of equilibrium time.

5.3.6. If the pH is less than 8.00, 1N NaOH is added until the pH reaches 8.00 ± 0.05. The fluid may then be stored for later use.

5.3.7. If the pH is 8.00 or greater, no further action is required and the extraction fluid may be stored for later use.

Table 1: Masses of each reagent required to prepare one liter of extraction fluid.

Reagent	**Mass required per liter of extraction fluid (mg)**	**Approximate resulting concentrations**
$CaSO_4$	510	150 mg/L Ca^{2+}; 360 mg/L SO_4^{2-}
$NaHCO_3$	413	113 mg/L Na^{+}; 300 mg/L HCO^{-}

Reagent	Mass required per liter of extraction fluid (mg)	Approximate resulting concentrations
NaCl	495	195 mg/L Na^+; 300 mg/L Cl^-
1N NaOH	as required	pH 8.0

Analytical standards shall be prepared according to the appropriate analytical method.

6. SAMPLE COLLECTION, PRESERVATION, AND HANDLING
   - 6.1. All samples shall be collected using an appropriate sampling plan.
   - 6.2. The minimum mass of sample required for ULP evaluation is 50 g. It is recommended that extractions be performed in duplicate or triplicate, so allowances must be made for the use of double or triple the sample mass. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.
   - 6.3. Preservatives shall not be added to samples before extraction.
   - 6.4. Samples may be stored at room temperature in a cool, dry location.
   - 6.5. ULP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see Step 7.2.5 if precipitation occurs).
7. PROCEDURE
   - 7.1. Determination of whether the sample requires particle-size reduction (particle-size is reduced during this step):
     - 7.1.1. Evaluate the sample for particle size. Particle size reduction is required, unless the solid is smaller than 2 mm in its narrowest dimension. If the particle size is larger than described above, prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a particle size of less than 2 mm.
   - 7.2. Extraction Procedure

A minimum sample size of 50 grams dry solid is recommended. Enough solids should be generated for extraction such that the volume of ULP extract will be sufficient to support all of the analyses required.

7.2.1. If particle-size reduction of the sample was needed in Step 7.1.1, proceed to Step 7.2.2. If the sample as received passes a 2 mm sieve, quantitatively transfer the sample into the extractor bottle, and proceed to Step 7.2.3.

7.2.2. Prepare the sample for extraction by crushing, cutting, or grinding the sample to a surface area or particle size as described in Step 7.1.1. When the particle size has been appropriately altered, quantitatively transfer the material into an extractor bottle.

NOTE: Sieving of the sample is not normally required; sand-size particles or smaller are desired to expose mineral surfaces for extraction. If sieving is necessary, a clean and dry sieve should be used to avoid contamination of the sample.

7.2.3. Determine the mass of extraction fluid to add to the extraction vessel by multiplying the mass of the sample by 20. A 50 g sample therefore requires approximately 1 L of extraction fluid. Slowly add this amount of extraction fluid to the extraction vessel. Close the extraction vessel tightly (it is recommended that Parafilm be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 6°C during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of sample (e.g., limed or calcium carbonate-containing sample may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

NOTE: During the development of the ULP, extractions were performed for 72 hours, but when compared to the same treatment extracted for 18 hours, there was no significant difference at the 95% confidence interval , so an 18-hour extraction time is sufficient.

7.2.4. Following the 18 ± 2 hour extraction, isolate the extract by allowing the solids to settle in the extraction vessel for 20 minutes or more, then filtering approximately 200 mL of supernatant through first a 1.5 μm pore size filter, then a 0.45 μm pore size filter. Filters may be changed to facilitate filtration. Filter(s) shall be acid-washed (see note after Step 4.3.3) if evaluating the mobility of metals. The filtered liquid material obtained is defined as the ULP extract.

7.2.5. Following collection of the ULP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH < 2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4°C) until analyzed. The ULP extract shall be prepared and analyzed according to appropriate analytical methods. ULP extracts shall be acid digested except in those instances where digestion causes loss of metallic analytes. Compare the uranium concentrations in the ULP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

8. QUALITY CONTROL

8.1. A minimum of one blank (using the same extraction fluid as used for the samples) for every 20 extractions that have been conducted in an extraction vessel.

8.2. Samples must undergo ULP extraction within the following time periods:

From:	Field collection	ULP Extraction	Total Elapsed Time
To:	ULP Extraction	Uranium Analysis	
Maximum holding time (days)	180	180	360

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a sample does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the sample exceeds the regulatory level.

9. METHOD PERFORMANCE

9.1. An analysis was done to compare ULP performance to SPLP performance. Six uranium-bearing rock samples from Nova Scotia were evaluated. Two of the samples were igneous from the South Mountain Batholith and the other four were from the overlying sedimentary formations of the same geographical area. The uranium concentrations in the ULP extract were consistently greater than the concentrations in the SPLP extract by approximately an order of magnitude.

	Mean U Concentration (µg/L)	
	SPLP Analysis	**ULP Analysis**
Siltstone (1)	0.30	5.4
Siltstone (2)	0.15	0.93
Sandstone (1)	0.11	32
Sandstone (2)	27	270
Granite (1)	7.0	59
Granite (2)	8.0	810

10. REFERENCES

10.1. United States Environmental Protection Agency. (1994, September). Synthetic Precipitation Leaching Procedure. Method 1312.