



Development of a leaching procedure to assess the risk of uranium leaching due to construction and demolition waste disposal



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ABSTRACT

Naturally-occurring uranium can be found at elevated concentrations in groundwater throughout the world, with the potential to cause kidney damage in chronically exposed individuals. Empirical evidence shows that uranium mobilization can be enhanced in the presence of ions that are associated with leachate from construction and demolition (C&D) disposal sites. There is need for a simple and effective procedure to evaluate soil and rock formations for uranium mobility prior to the permitting of waste disposal facilities which could alter groundwater chemistry. A series of leachate extractions were performed to represent the impact of C&D leachate on uranium-bearing rocks, focusing on the impact of calcium, sodium, chloride, sulphate, and bicarbonate concentrations on uranium mobilization. Based on these observations a uranium leaching procedure (ULP) was developed and compared to the synthetic precipitation leaching procedure (SPLP). The ULP was capable of mobilizing an order of magnitude more uranium than the SPLP from six rock samples and shows promise as a tool for assessing the risk of groundwater contamination by C&D waste through uranium mobilization.

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1. Introduction

Historically, the disposal of construction and demolition (C&D) waste has not been regulated as strictly as domestic or hazardous waste with respect to containment practices due to the perception that this waste material was relatively inert (USEPA, 1995). However, several studies have revealed that leachate from C&D disposal sites can significantly impact ground and surface water, particularly in terms of metals such as arsenic, cadmium, chromium, copper, iron, and lead (Butera et al., 2014; Melendez, 1996; Weber, 2002; Wang, 2012). Although uranium is not a metal that is typically present in C&D waste, leachate from C&D waste facilities has been identified as a potential cause of uranium release to groundwater from natural rock formations (Drage & Kennedy, 2013). Uranium occurs naturally in certain rock formations throughout the world and can result in elevated uranium concentrations in groundwater under certain geochemical conditions. At the concentrations observed in well water, the chemical toxicity of uranium is more dangerous to human health than its radioactive properties (Health Canada, 2009). The World Health Organization [WHO] provisional guideline for uranium is 15 µg/L due to kidney

damage observed in lab and epidemiological studies and, in turn, Health Canada has set the drinking water guideline at 20 µg/L. (Health Canada, 2009; WHO, 2012). This paper discusses the development of a procedure that simulates the effect of C&D leachate on uranium leaching from rock material, which could be used to evaluate appropriate sites for C&D waste disposal.

The mobilization of naturally-occurring uranium in groundwater has been attributed in the literature to several mechanisms, including weathering of uranium-bearing rocks (O'Beirne-Ryan, 2006; Parsons, 2007; Ryan and O'Beirne-Ryan, 2009; Ryan et al., 2009), ion exchange (Drage and Kennedy, 2013; Kennedy and Finlayson-Bourque, 2011; Riedel and Kübeck, 2018), the formation of soluble complexes between the uranyl ion and other constituents present in groundwater (Bachmaf et al., 2008; Bäckström et al., 2004; Drage and Kennedy, 2013; Nair and Merkel, 2011), and changes in pH and oxidation–reduction potential (ORP; Eh) (Drage and Kennedy, 2013; Nair and Merkel, 2011; Riedel and Kübeck, 2018; Samolczyk et al., 2012). 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, dissolved inorganic carbon (DIC), sulphate, and chloride. The mobile or environmentally

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available form of uranium is generally considered to be the uranyl ion, UO_2^{2+} (Murphy and Shock, 1999), and its complexes (Grantham, 1986; Kumar et al., 2011; Langmuir, 1978; O'Reilly, 1982; Ryan and O'Beirne-Ryan, 2009). 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 and Shock, 1999). Correlations between oxidizing groundwater and elevated uranium have been noted in evaluations of existing groundwater data (Jurgens et al., 2010; Riedel and Kübeck, 2018; Samolczyk et al., 2012). The complexing ions required for the formation of the mobile uranium species can be inherently present in aquifer material or can be added to groundwater from both natural and anthropogenic activity, such as seawater intrusion, road salt application, or, most notably, leachate from C&D waste disposal sites.

Major components of C&D waste include wood, cardboard, concrete, and drywall, which can affect leachate quality in terms of pH, conductivity, alkalinity, organic constituents, and ion concentrations (Townsend et al., 1999). There is considerable heterogeneity in C&D waste leachate with wide ranges of key parameters measured in field and lab-scale studies. In general, however, the pH of C&D leachate is basic (6.4–11.9) and total dissolved solids (TDS) tend to be elevated (500–8400 mg/L) (Butera et al., 2014; Melendez, 1996; Townsend et al., 1999). The elevated TDS are usually attributed to calcium and sulphate, which are the major components of drywall and have ranged from 28 to 1150 mg/L and 75 to 1700 mg/L, respectively, in previous studies (Butera et al. 2014; López & Lobo 2014; Melendez, 1996; Townsend et al., 1999). Another major constituent is carbonate, which can be derived from concrete or asphalt, and is measured as alkalinity, ranging from 34 to 6520 mg/L as $CaCO_3$ (Melendez, 1996; Townsend et al., 1999; USEPA, 1995). These ions and others, such as chloride, have been demonstrated to enhance uranium mobility in lab, field, and modeling studies (Bachmaf et al., 2008; Bäckström et al., 2004; CRA, 2011; Dong et al., 2005; Drage and Kennedy, 2013; Fox et al., 2006; Murphy and Shock, 1999; Nair and Merkel, 2011; Riedel and Kübeck, 2018; Samolczyk, et al., 2012). Calcium can inhibit uranium sorption to solid material at circumneutral pH (Fox et al., 2006; Nair and Merkel, 2011) and it is widely believed that this effect is due to the formation of the calcium-uranyl-carbonate complexes $Ca_2UO_2(CO_3)_3^0$ and $CaUO_2(CO_3)_3^{2-}$ (Dong et al., 2005; Drage and Kennedy, 2013; Fox et al., 2006; Nair and

Merkel, 2011; Riedel and Kübeck, 2018). Uranium mobilization is controlled largely by carbonate concentration in geochemical environments (Bachmaf et al., 2008; Dong et al., 2005; Jurgens et al., 2010; Murphy and Shock, 1999; Nair and Merkel, 2011), particularly when uranyl-carbonate complexes dominate the groundwater system at alkaline pH (>7) (Dong et al., 2005; Fox et al., 2006). Sulphate is also 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 (Bachmaf et al., 2008). However, when pH is low (<5), sulphate is capable of forming these aqueous uranyl ionic species. An increase in uranium mobility in the presence of chloride has also been noted in lab and field evaluations (Drage and Kennedy, 2013; Samolczyk et al., 2012), possibly due to ion exchange, the association with other salts, or changes in ionic strength (Bäckström et al., 2004).

1.1. Case study: Nova Scotia, Canada

The impacts of C&D waste leachate on groundwater quality have been documented in Harrietsfield, Nova Scotia, Canada, where a C&D waste disposal facility has come under scrutiny in recent years due to an increase in heavy metal concentrations, including uranium, in residential wells downgradient of the site. The facility stored C&D waste on an unlined pad from 1998 until the construction of a containment cell under new ownership in 2004. In Fig. 1 the continuous increase in uranium concentrations in a domestic water supply well and an on-site monitoring well downgradient of the disposal cell is illustrated; concentrations were well in excess of the Guideline for Canadian Drinking Water Quality of 20 $\mu\text{g/L}$ (3076525 Nova Scotia Ltd. v. Nova Scotia (Environment), 2015; Health Canada, 2009). A background well, located upgradient of the site, consistently possesses uranium concentrations $<15 \mu\text{g/L}$, illustrating the impact of the C&D waste facility. Leachate collected from the on-site containment cell contained elevated concentrations of heavy metals such as aluminum, arsenic, and lead, but the uranium concentrations never exceeded 10 $\mu\text{g/L}$ (Conestoga-Rover and Associates [CRA], 2011). The low concentrations of uranium in the leachate suggest that the C&D site does not act as a source of uranium, but rather as a catalyst for the mobilization of the naturally present uranium in the shallow groundwater in the area (CRA, 2011). Fig. 2 illustrates that

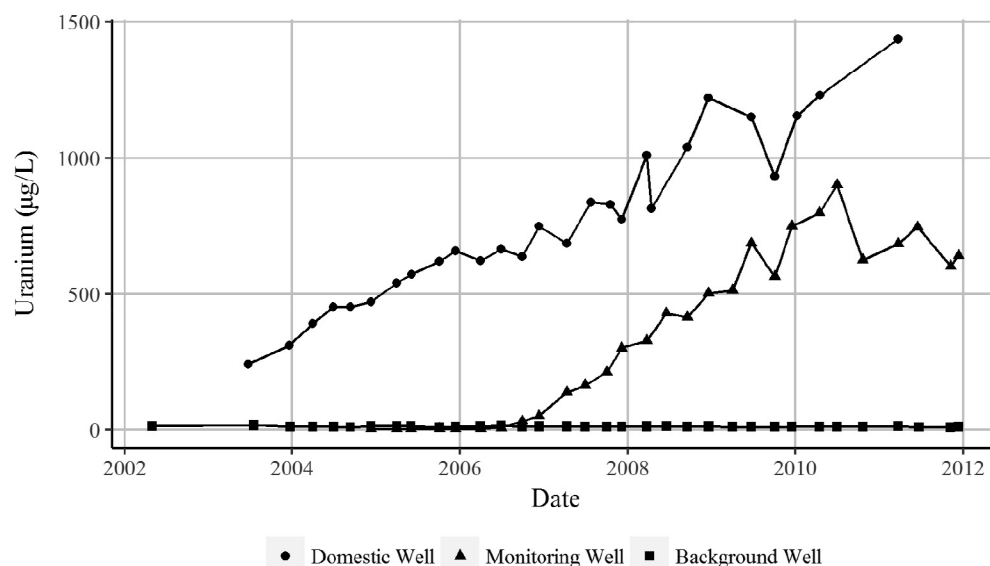


Fig. 1. Uranium concentrations in wells downgradient of the C&D disposal site in Harrietsfield, NS from 2003 to 2012 (CRA, 2011).

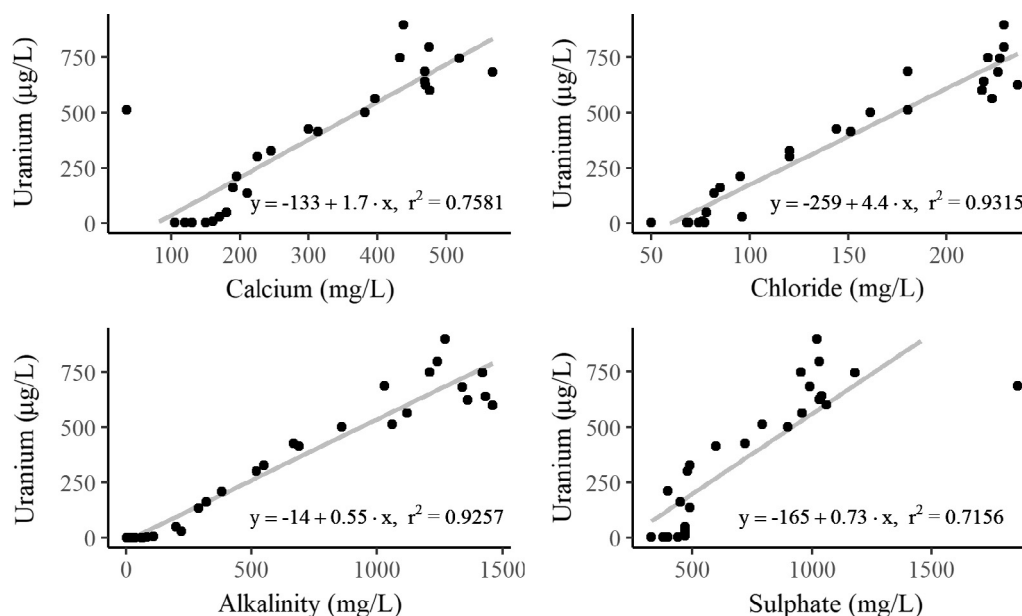


Fig. 2. Correlations between uranium concentration and the concentrations of key ions in an on-site monitoring well in Harrietsfield, Nova Scotia, Canada (CRA, 2011).

uranium concentrations in groundwater can increase concurrently with increases in calcium, chloride, alkalinity and sulphate, which are associated with C&D leachate.

1.2. Study objectives

Uranium is naturally present in granitic rocks and their sedimentary derivatives across Nova Scotia, other areas of Canada, and the world. An evaluation of the relative mobility of uranium from aquifer material could identify regions that are vulnerable to uranium mobilization into groundwater and inform the siting and design of C&D waste disposal facilities. The United States Environmental Protection Agency (USEPA) Synthetic Precipitation Leaching Procedure (SPLP) was developed to evaluate the transport of contaminants from solid waste and soils (USEPA, 1994). The SPLP simulates acidic rainfall to determine whether a contaminant would represent an “unacceptable leaching threat” if disposed on land (New Jersey Department of Environmental Protection [NJDEP], 2013). However, the SPLP may underestimate uranium leachability because uranium tends to be mobilized in alkaline, oxidizing conditions in the presence of specific complexing ions. Therefore, there is a need for a more appropriate leaching procedure that employs the potential groundwater conditions that are conducive to the mobilization of uranium. To the authors’ knowledge, this type of procedure does not currently exist. A uranium-specific leaching procedure would have value for risk analysis and making management decisions about the siting of C&D waste disposal sites for groundwater protection. By choosing experimental factors that maximize the uranium concentration in the extract, it is possible to create a “worst-case scenario” of uranium mobilization in the environment.

The area of focus for experimental testing in this study is the province of Nova Scotia, Canada, where approximately 4% of wells exceed the uranium Health Canada Maximum Acceptable Concentration (MAC) for drinking water of 20 µg/L (Drage and Kennedy, 2013; Health Canada, 2009), making uranium the second most common naturally occurring contaminant to exceed its guideline in the province, after arsenic (Drage and Kennedy, 2013). 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 leachate from C&D processing or disposal sites. The redox potential was maintained approximately constant for each extraction performed to simulate the oxidizing conditions conducive to uranium mobilization. The complexing ions under examination in this study were calcium, sodium, bicarbonate, chloride, and sulphate, which are known or suspected to influence the dissolution or desorption of uranium. Particular emphasis is placed on calcium, based on strong correlations between uranium and calcium observed in several uranium-contaminated wells associated with the C&D debris disposal and processing site in Harrietsfield (see Fig. 2) (CRA, 2011; Drage and Kennedy, 2013). This paper discusses the creation of the Uranium Leaching Procedure (ULP) through two distinct evaluations. First, two rock types were extracted with varying concentrations of calcium in the extraction fluid to determine the appropriate calcium dose for the ULP. Second, a total of six rock types were extracted using both the ULP and the SPLP for comparison purposes.

2. Materials and methods

2.1. Sample collection and preparation

Uranium-enriched rock materials came from the Nova Scotia Department of Natural Resources (NSDNR) Core Library, where two granite samples and one sedimentary rock sample were taken, and from an outcrop of sedimentary rock in St. Croix, Nova Scotia, where three samples were taken. All samples were oven dried and the particle sizes were reduced to less than 2 mm. The particle size of less than 2 mm was modified from the SPLP requirement (that material must fit through a 9.5 mm sieve) in order to maximize exposed surface area. Each bag of crushed sample was well mixed and a subsample of each 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.

2.1.1. Characterization of rock samples

The sedimentary rock samples from St. Croix, Nova Scotia (44.956, -64.072) (Silt-1, Silt-2, and Sand-1) come from the Horton

Group, which overlies the South Mountain Batholith and is known to contain some layers and lenses of elevated uranium (Ryan and O'Beirne-Ryan, 2009; Ryan et al., 2009). Silt-1 and Silt-2 are siltstones taken from the same outcrop in St. Croix on different days and differ from Sand-1, the sandstone, in grain size. An additional sedimentary rock (Sand-2) was sampled from a borehole that was drilled in Three Mile Plains, Nova Scotia (44.967, –65.076) in 1980 and kept at the DNR Core Library. Finally, granite from a borehole drilled in 1981 in Millet Brook, Nova Scotia was sampled (44.859, –64.271). The Millet Brook samples were separated into two subsamples after initial spectrophotometer screening revealed that one of the sample bags emitted higher levels of radiation than the rest. These were labeled Gran-1 (low uranium content) and Gran-2 (high uranium content). The whole rock analysis revealed key differences between the six rock samples, with uranium contents of the rocks ranging between 8.2 and 34 mg/kg (Table 3).

2.2. Extraction procedure

The general extraction procedure is based on the SPLP, which can be explored in more detail in USEPA Method 1312 (USEPA, 1994). The procedure developed in this project is a scaled-down version of the SPLP. The SPLP uses 100 g of sample and 2 L of extraction fluid; however, the ULP uses 50 g of rock sample with 1 L of extraction fluid. The smaller quantities were used in the ULP due to limited availability of material for testing.

The extraction fluids were prepared in amber jugs filled with reverse osmosis treated water (RO). Calcium chloride or sulphate, sodium chloride, and sodium bicarbonate were added to obtain the desired ion concentrations according to Sections 2.2.1 and 2.2.2. After the reagents were mixed, 20 min of equilibrium time was allowed before reading the pH and Eh of each jug. If necessary, the pH was adjusted using sodium hydroxide (NaOH). All extractions were performed in triplicate with a blank. 50.0 ± 0.1 g of the appropriate crushed, mixed rock sample, according to Sections 2.2.1 and 2.2.2, was measured into each extraction vessel before the extraction fluids were added and the vessels were closed and wrapped in Parafilm to prevent leaks. The extraction vessels were secured in a rotary agitation device at room temperature 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. The vessels were removed after 72 ± 2 h and the particulate matter was allowed to settle for 30 to 90 min while the final pH and Eh were once again measured and recorded. Approximately 200 mL of supernatant from each bottle was filtered first through a glass filter (1.5 μ m pore size) and then a mixed cellulose ester filter (0.45 μ m pore size). 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 trace metal grade 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).

2.2.1. Determination of calcium dose

Preliminary method development involved several extractions to determine the appropriate extraction time (18 vs 72 hr) and pH (low vs neutral vs high) and confirmed that the concentration of key ions is an important factor in uranium mobilization (Letman, 2016). Preliminary tests also revealed that when there were high concentrations of ions in the extraction fluid, more uranium was released from the rocks when the pH was high (pH \approx 8.50) as compared to neutral and low pH conditions. Due to strong correlations between calcium and uranium in the literature (Dong et al., 2005; Drage and Kennedy, 2013; Fox et al., 2006; Nair and Merkel, 2011; Riedel and Kübeck, 2018) and in samples from the Harrietsfield site (CRA, 2011), more detailed testing was then conducted to determine the appropriate calcium concentration in the extraction fluid for the ULP. Extractions were performed on the St. Croix siltstone (Silt-1) and the Millet Brook granite with low uranium content (Gran-1). Calcium concentrations were achieved using calcium chloride. 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 1.

2.2.2. ULP validation

The results of previous extractions culminated in the development of the Uranium Leaching Procedure (ULP). The ULP was then

Table 1

Extraction fluid composition for detailed extraction fluid testing, wherein calcium was varied from 0 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

Table 2

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

Parameter	ULP	SPLP	Mean groundwater in Nova Scotia ^a	C&D leachate ^b
pH	8.0	4.2	7.6 (7.7)	6.8–7.9
Calcium (mg/L)	150	–	44.6 (29)	300–200
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 ^c	41.6 (12)	890–1950

^a Values reported for groundwater across Nova Scotia. Median values in brackets (Kennedy and Finlayson-Bourque, 2011).

^b Values reported for leachate from the Harrietsfield, NS C&D site (CRA, 2011).

^c Approximate concentration based on the average volume of acid required to adjust pH.

Table 3

Uranium content of the test rock samples. All samples were from Nova Scotia, Canada.

Label and lithology	Location	Source	Uranium content (mg/kg)
Silt-1: Siltstone	St. Croix	Field	20
Silt-2: Siltstone	St. Croix	Field	20
Sand-1: Sandstone	St. Croix	Field	16
Sand-2: Sandstone	Three Mile Plains	DNR Core Library	13
Gran-1: Granite	Millet Brook	DNR Core Library	8.2
Gran-2: Granite	Millet Brook	DNR Core Library	34

validated on a variety of uranium-bearing rocks from Nova Scotia and the results were compared to the SPLP results. The SPLP was performed according to USEPA method 1312 (USEPA, 1994), but was scaled down to 50 mg of sample and 1 L of extraction fluid. The desired calcium concentrations in the extraction fluids were achieved using calcium sulphate, based on results of a companion study, in which extractions performed with gypsum (calcium sulphate dihydrate) were capable of leaching nearly twice as much uranium from sedimentary rock samples than when calcium chloride was used in the extraction fluid (Blume, 2016). Table 2 compares the water quality parameters of the ULP and SPLP extraction fluids to mean and median levels in Nova Scotian groundwater (Kennedy and Finlayson-Bourque, 2011) and concentrations reported for leachate from the C&D waste disposal cell in Harrietsfield, Nova Scotia (CRA, 2011).

3. Results and discussion

3.1. Determination of calcium dose

The uranium concentrations in the extracts from both siltstone and granite in the presence of different doses of calcium are presented together in Fig. 3. The measured Eh ranged from 158 to 318 mV, verifying that all of the extractions were performed under oxidizing conditions.

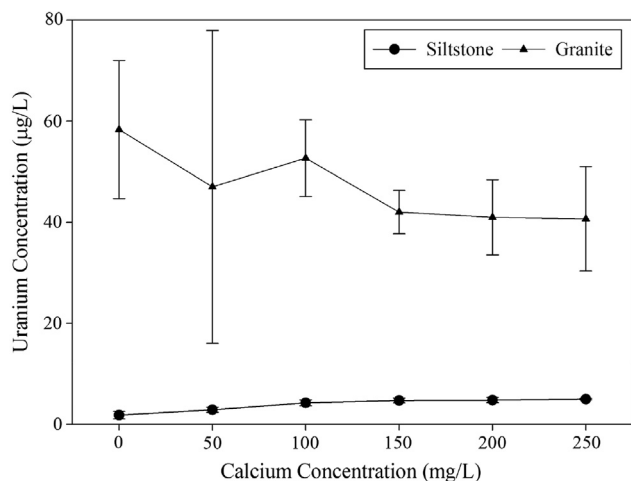


Fig. 3. A comparison of uranium leachate concentrations from siltstone (Silt-1) and from granite (Gran-1) in the presence of varying levels of calcium. Error bars represent 95% confidence intervals.

Uranium concentrations in the extracts from the siltstone (Silt-1) were low when the calcium dose was low, and increased as the calcium concentration increased. This indicates a relationship between calcium concentration and uranium mobilization. The uranium concentration appears to have reached a maximum at the 150 mg/L calcium dose, with little change in uranium concentration corresponding to any further increases in calcium concentration. This could indicate that there were other factors limiting uranium mobilization when calcium concentrations were high, or that the leachable portion of the total uranium in these rocks had been exhausted.

Granite (Gran-1) extractions produced the opposite trend to the siltstone results; uranium concentrations were high when the calcium dose was low and decreased as the calcium dose increased, indicating that uranium was mobilized from the two rock types by different mechanisms. It is interesting to note that uranium concentrations in the extracts from the granite reached a consistent level around a calcium dose of 100–150 mg/L.

Visual inspection of the results suggests that both rocks produced consistent uranium concentrations at calcium concentrations greater than 100 mg/L. Although the uranium concentrations extracted from the granite samples exhibited a decreasing trend until 150 mg/L of calcium, these concentrations were consistently more than five times greater than those in the siltstone extract. The goal was to maximize the uranium concentration being extracted. Therefore, a calcium concentration of 150 mg/L was selected for the ULP to maximize the uranium from the siltstones. A mass balance comparing the whole rock uranium content to the mass extracted into the dissolved phase was also computed (Table 4).

The differences in uranium leachate concentrations from different rock samples can be attributed to the properties of the rock. The granite samples contained the lowest rock concentration of uranium, but the dissolved uranium concentrations in the extract from these rocks were greater than from the siltstone. These observations are in agreement with Ryan & O'Beirne-Ryan (2009), and suggest that the uranium present in Millet Brook granites is more easily mobilized than the uranium in the St. Croix siltstones and emphasize that total uranium content in the rock may not be an effective tool for predicting the mobility of uranium from a given rock type, which is in agreement with O'Beirne-Ryan (2006). This is demonstrated in the mass balance analysis (Table 4), which provides the mass percent of uranium in the dissolved phase after extraction; the siltstones 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 in the granites, which may be present in minerals that are more resistant to weathering.

Table 4

Percent uranium extracted from granite (Gran-1) and siltstone (Silt-1) samples with varying concentrations of calcium added to the extraction fluid.

Rock sample	U Content (mg/kg)	Total U in extraction (mg)	Calcium concentration	Dissolved U in extract (µg/L)	Percent extracted
Silt-1	20	1.0	0	1.80	0.2
			50	2.87	0.3
			100	4.23	0.4
			150	4.70	0.5
			200	4.77	0.5
			250	4.97	0.5
Gran-1	8.2	0.4	0	58.3	14.2
			50	47.0	11.5
			100	52.7	12.8
			150	42.0	10.2
			200	41.0	10.0
			250	40.7	9.9

3.2. ULP validation

The results of the ULP and the SPLP extractions on Nova Scotian igneous and sedimentary rock from the Windsor area are presented in Fig. 4. For all six rock samples evaluated, the ULP extracted approximately an order of magnitude more uranium than the SPLP (Table 5 and Fig. 4).

The St. Croix sedimentary samples (Silt-1, Silt-2, and Sand-1) had the lowest extract uranium concentrations when extracted with the SPLP. While there was less uranium in Sand-1 (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 Sand-1 and only 5.4 µg/L and 0.93 µg/L from Silt-1 and Silt-2, respectively (these concentrations in the extract represent 4.0, 0.5, and 0.1% of the total uranium in the rock samples, respectively). Sand-2 was extracted at greater concentrations than the rest of the sedimentary samples, although the ULP extracted much more uranium; 270 µg/L was extracted using ULP, compared to 27 µg/L from the SPLP, representing 42 and 4.2% of the total available uranium, respectively. The uranium present in Sand-2 therefore appears to be easily mobilized under both the acidic conditions of the SPLP and the alkaline, high ionic strength conditions of the ULP. The SPLP extracted similar uranium concentrations from both Gran-1 and Gran-2. When the ULP was

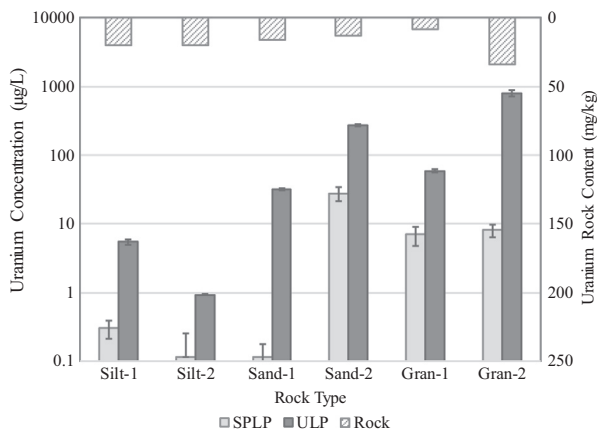


Fig. 4. Uranium concentrations in the extract from the synthetic precipitation leaching procedure (SPLP) and uranium leaching procedure (ULP) performed on six rock types. The SPLP uses an extraction fluid of water adjusted to a pH of 4.20 in a 20:1 mass ratio to solid material. The ULP uses an extraction 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 rock types that correspond to the x-axis labels are: siltstone (Silt-1, Silt-2), sandstone (Sand-1, Sand-2), and granite (Gran-1, Gran-2). Error bars represent 95% confidence intervals.

used, Gran-1, which had a total uranium content of 8.2 mg/kg, produced 59 µg/L uranium, while Gran-2, which had a total uranium content of 34 mg/kg, had an extract uranium concentration of 810 µg/L.

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 (all were reported as 194 mV or greater), 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 ions such as carbonate and sulphate. Similarly, the anions introduced in the ULP extraction fluid can cause ion exchange reactions to release negatively charged uranyl-carbonate complexes that are adsorbed onto mineral surfaces. Uranium may also be mobilized due to the formation of soluble complexes between the uranyl ion and the ions present in the extraction fluid. In particular, since the extraction is performed at a pH of 8.0, uranyl is likely present as a mobile species: a uranyl-carbonate complex ($UO_2(CO_3)_x$) or as a ternary calcium-uranyl-carbonate complex ($Ca_xUO_2(CO_3)_3$).

These 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 ($p < 0.05$). The SPLP is the standard test for contaminant transport from materials, but it does not simulate the conditions favourable to uranium mobilization that could exist in an environment influenced by C&D waste. The ULP incorporates known uranium mobilizing factors and is therefore a more appropriate tool for risk assessment of uranium mobilization. The ULP could be used to identify regions of high uranium mobilization risk to help in land use planning decisions, including siting of construction and demolition disposal and storage sites, to prevent the creation of a mobilizing environment and protect groundwater quality in the vicinity.

Table 5

Percent uranium extracted from each rock sample using SPLP and ULP.

Label	U concentration in rock (mg/kg)	Mass U in extraction (mg)	Test	Dissolved U concentration in extract (µg/L)	Dissolved U mass in extract (mg)	Percent U extracted (%)
Silt-1	20	1.0	SPLP	0.30	0.00030	< 0.1
			ULP	5.4	0.0054	0.5
Silt-2	20	1.0	SPLP	0.15	0.00015	< 0.1
			ULP	0.93	0.00093	0.1
Sand-1	16	0.80	SPLP	0.12	0.00012	< 0.1
			ULP	32	0.032	4.0
Sand-2	13	0.65	SPLP	27	0.027	4.2
			ULP	270	0.27	42.0
Gran-1	8.2	0.41	SPLP	7.0	0.0070	1.7
			ULP	59	0.0590	14.5
Gran-2	34	1.7	SPLP	8.0	0.0080	0.5
			ULP	810	0.810	47.6

4. Conclusions

In areas where uranium is naturally present in groundwater geology, an assessment tool for the risk of uranium mobilization could help prevent the harmful health effects of long-term uranium exposure through drinking water. The new Uranium Leaching Procedure 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 commonly used SPLP. This optimization of uranium extraction from rock samples emphasizes the importance of an alkaline environment and the presence of complexing ions on uranium mobility. The ULP is a conservative test that can be used to evaluate the uranium leaching potential in geologic environments that could be influenced by anthropogenic activities that in turn alter groundwater chemistry. Ion concentrations in the ULP extraction fluid are consistent with those found in leachate from C&D disposal areas; thus this procedure could be used in the assessment and siting of construction and demolition waste disposal sites for optimal groundwater protection.

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