Integration of Hydrogeological, Geophysical and Geochemical Methods for the Delineation of Natural Sources of Uranium in Groundwater

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Abstract
Uranium is known to naturally occur in some bedrock lithologies in some locations at higher than average crustal concentrations. Rock formations that contain elevated solid-phase concentrations of uranium can act as a source of uranium and associated radionuclides to groundwater that flows through the bedrock. An integrated approach based upon geophysical, hydrogeological and geochemical methods can be employed to delineate natural subsurface source zones that may contribute uranium to the groundwater. A case study using this approach is presented to demonstrate how the integration of these methods provides a better understanding of the potential influence that bedrock sources of uranium can have on groundwater quality.

Key Words: pegmatite, uraninite, oxidative dissolution, gamma radiation

Introduction
Uranium naturally occurs in soils, sediments and bedrock and is commonly observed to occur at higher concentrations than typical crustal concentrations in special geological environments (Siegel and Bryan 2004; Baborowski *et al*. 2006). Weathering of uranium-rich soils or bedrock can release dissolved uranium into groundwater. The persistence and concentration of uranium in groundwater largely depends on the nature of the source, and the physical, geological, and geochemical characteristics of the groundwater environment. As a result, the occurrence of uranium can vary spatially and temporally, which is evident by large increases or decreases in concentrations over relatively short distances between sampling locations. Because exposure to uranium through consumption of drinking water can be detrimental to human health, an understanding of linkages between regional occurrences and potential sources presents an opportunity to minimize future incidences of uranium exposure.

This paper presents a multidisciplinary approach for evaluating sources of uranium in groundwater. The methods discussed herein include hydrogeological, geophysical and geochemical techniques that can be collectively used to better evaluate processes that control the release and transport of uranium in the subsurface. Results from a case study conducted during 2010 within the Algonquin Highlands in Ontario, Canada are presented to demonstrate the effectiveness of using a multidisciplinary approach for investigating uranium sources in groundwater.

Hydrogeological, Geophysical and Geochemical Methods
Transport of uranium through the subsurface is highly influenced by the physical, geological, and geochemical characteristics of the groundwater environment. The methods described below can be applied using an integrated approach to better understand the physical, geological and geochemical characteristics of the subsurface.

Hydrogeological methods
Hollow-stem auguring through the overburden and diamond drill coring techniques through underlying bedrock are common methods for collection of soil and rock samples, respectively, and were applied at the study site to attain subsurface information. Often hydrogeological drilling programs incorporate packer testing to determine local-scale transmissivity or hydraulic conductivity of bedrock across specific

intervals of a borehole. During the drilling, packer testing was completed at the study site, which involved using inflatable bladders and staged drilling techniques to isolate specific zones or fractures. The isolated zones within the bedrock were then subjected to hydraulic testing, such as falling head tests. The packer testing produced hydraulic conductivity or transmissivity profiles of the bedrock below the casing.

Geophysical methods

To supplement a drilling program and hydraulic testing, borehole geophysical methods were applied at the study site to attain additional physical and radiological information to assist with the evaluation of the subsurface hydrogeological conditions. The borehole geophysical log suite that was applied to the study site consisted of natural gamma, apparent conductivity, mechanical caliper, acoustic televiewer, optical televiewer, fluid temperature, fluid resistivity and heat pulse flow meter. The information collected from the geophysical methods was used along with data attained from rock core and packer testing to assist with further defining the distribution of the rock units at the site, interpreting the bedrock geology and evaluating the structural controls on groundwater flow. In addition, borehole geophysics provided supplementary data (i.e., information in addition to the continuous rock core samples) to assist with the selection of monitoring well screen intervals within the bedrock that contain important features, such as key water-bearing fracture zones (i.e., hydraulic controls) and uraniferous bedrock that emits elevated levels of natural gamma relative to background. As such, the geophysical logs were reviewed in detail along with the borehole logs and the rock core samples before the installation of monitoring wells, in order to select the zones of interest. Figure 1 presents an example of a 1 m interval of a geophysical borehole log showing the results of the acoustic televiewer, optical televiewer and natural gamma. A water-bearing fracture within uraniferous bedrock is identifiable using the acoustic and optical televiewer results within a pegmatite zone (pinkish rock evidenced using the optical televiewer).

Geochemical methods

A geochemical analytical program was used to evaluate potential impacts on groundwater quality through leaching of uranium from subsurface materials. Static tests were conducted in the laboratory to evaluate the mineralogical and geochemical characteristics of the solid-phase samples (i.e., overburden and bedrock). Mineralogical methodology, such as qualitative X-ray diffraction and bulk modal analysis, was completed to determine the mineralogical composition of overburden and bedrock. In addition, a scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM-EDS) was employed to identify mineral grains in subsurface materials that contain uranium-bearing minerals. Geochemical test work, including solid-phase elemental analysis, short-term leach tests (extractions) and groundwater quality analysis, provided information on the bulk composition of the subsurface materials and geochemical processes (i.e., dissolution/precipitation, adsorption/desorption) that control the release of uranium into the groundwater flow system.

Case Study – Investigation of Uranium Source in Groundwater

Geological Setting

The project site is located within the physiographic region of the Algonquin Highlands, which is characterized by shield terrain (i.e., Canadian Shield geological region) and located in the Grenville Province, where rocks have been subject to metamorphic and intrusive processes (Chapman and Putnam, 1984). Two major rock types are present at the site: 1) Grenville-type metasediments, and 2) plutonic rocks (Satterly and Hewitt, 1955; Goad, 1990). The metasediments are the oldest rocks in the area, which originally consisted of limestone/dolomites, shaly/sandy limestones, limy shales, sandy shales and sandstones that have been metamorphosed into the present form of marble, silicate marble, amphibolites, paragneiss and quartzite, respectively (Satterly and Hewitt, 1955). A series of plutonic rocks, including gabbro, diorite and ultrabasic rocks, cut the Grenville metasediments and were subsequently altered to form an intrusion of metamorphic rocks consisting of metagabbro, metadiorite, amphibolites and hornblende schist. The intrusive body is referred to as the Faraday Metagabbro, which is about 10 km

long and 1 km wide, (Satterly, 1956). A more recent intrusion (subsequent to the intrusion of the basic rocks) consisted of the emplacement of three other groups of plutonic rocks: nepheline syenites, syenites and granites (Satterly and Hewitt, 1955), which are the rock bodies that contain the uranium and other radioactive minerals. Figure 2 shows examples of granitic pegmatite intrusions at the study site.

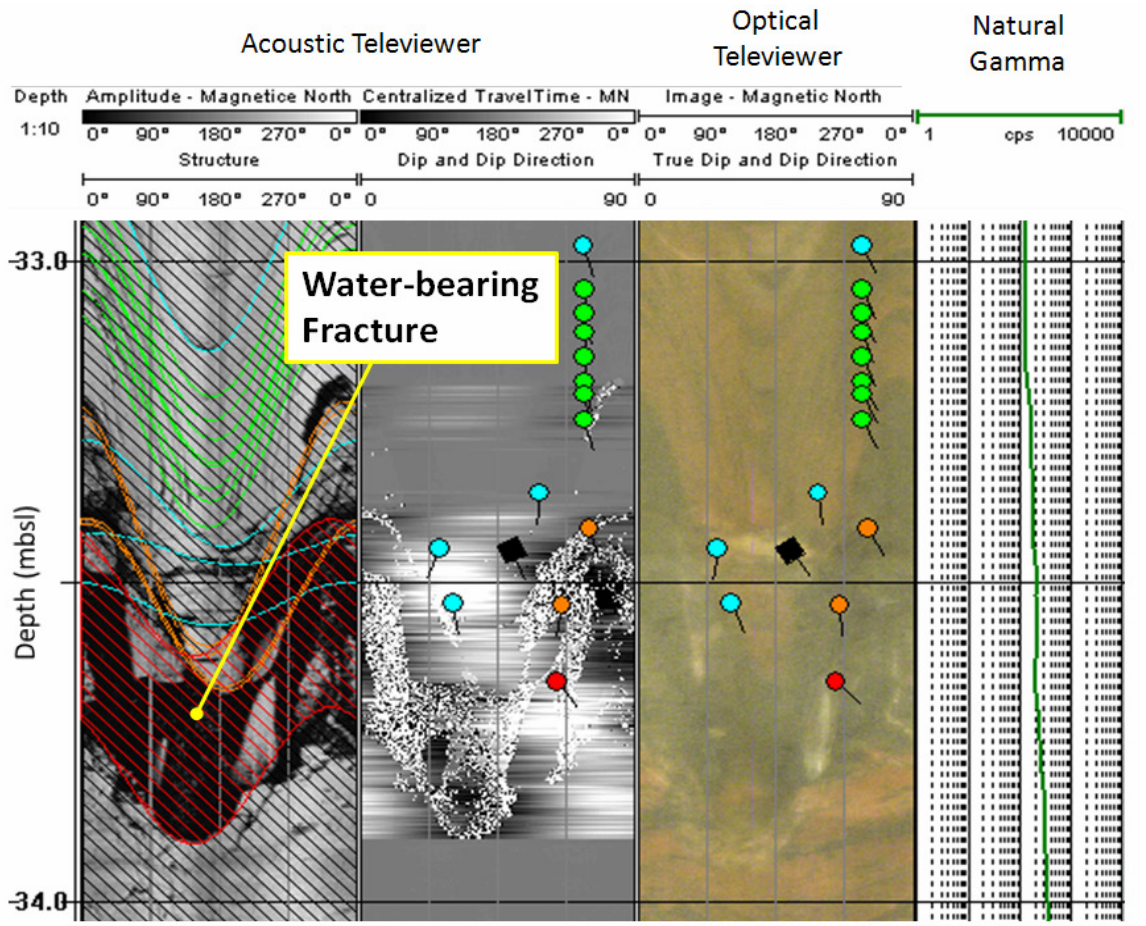

Figure 1. Geophysical borehole log completed at BH10-02, from 33 metres below surface level (mbsl) to 34 mbsl, showing the results of acoustic televiewer, optical televiewer and natural gamma. A water bearing fracture within uraniferous bedrock is identifiable using the acoustic and optical televiewer results.

The principal uranium-related mineralogical components of the pegmatite bodies include (Satterly, 1956) uraninite [UO_2], uranothorite [$(Th,U)SiO_4$], thorite [$ThSiO_4$], allanite [$(Ca,Ce,La, Y)_2(Al, Fe)_3(SiO4)_3(OH)$], secondary uranophane [$Ca(UO_2)_2SiO_3(OH)_2•5(H_2O)$] and beta-uranophane [$Ca((UO_2)SiO_3(OH))_2•H_2O$]. The mineralization of uranium exists as discrete particles that occur as pods, lenses and bodies within the pegmatite. Hematite and calcite commonly occur as secondary minerals in zones where chemical weathering has affected the uraniferous zones (Satterly, 1956). Secondary uranium minerals, such as uranophane, which are characteristically yellow, are often present as coatings on fracture surfaces (Satterly and Hewitt, 1955).

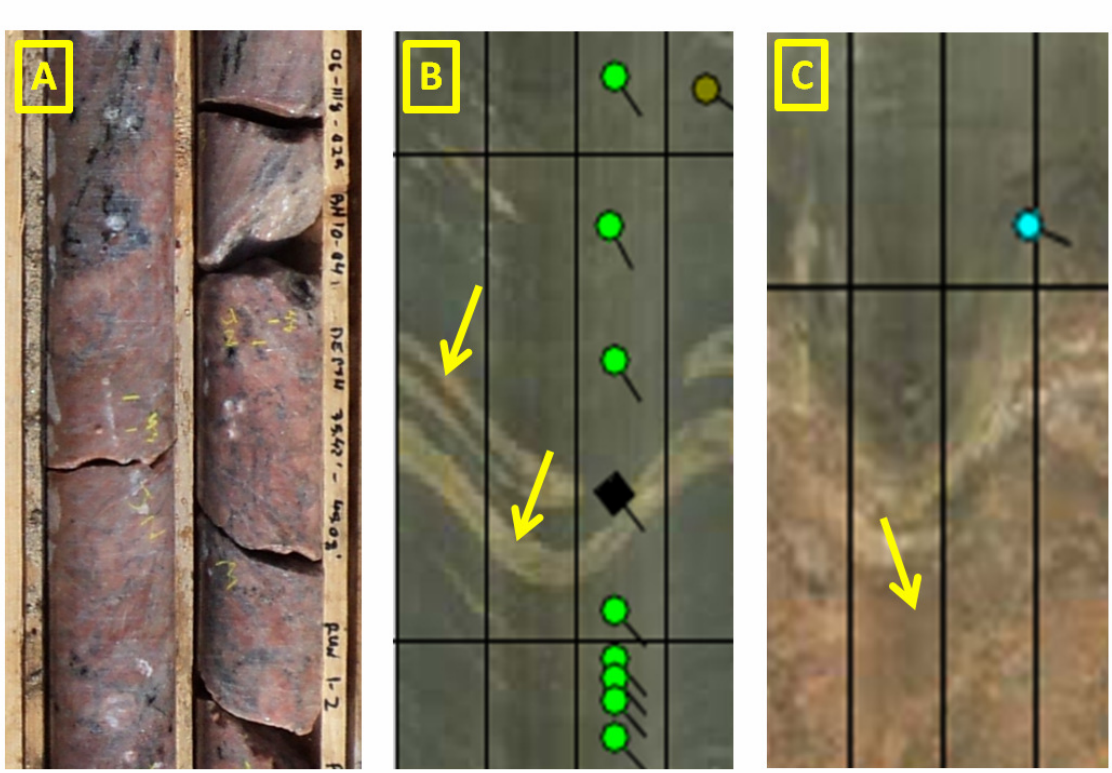

Figure 2. Pegmatite intrusions at BH10-04. Rock core sample of pegmatite is shown in photo (A), and photos via optical televiewer (B and C) show thinner veins of pegmatite within feldspathic gneiss.

Hydrogeochemistry

To illustrate the depth intervals of bedrock that contain elevated concentrations of uranium, Figure 3 shows profiles of natural gamma measurements for the three borehole locations (BH10-02, BH10-03 and BH10-04). Each of the boreholes were drilled through cross-cutting pegmatite intrusive bodies (e.g., Figure 2). To show correlations between high gamma zones, solid-phase, soluble and dissolved concentrations of uranium, the following data were plotted alongside the natural gamma data:

- Uranium concentrations in solid-phase (whole rock; blue bars);
- Uranium concentration in the leachate from de-ionized (DI) water static test work (green bars); and
- Uranium concentration in dissolved groundwater (orange lines).

The hydrogeological, geophysical and geochemical results at BH10-02, BH10-03 and BH10-04 are discussed below.

Uranium in Bedrock

Some bedrock zones at the borehole locations were determined to have elevated concentrations of uranium in the solid phase. In particular, bedrock at BH10-02, BH10-03 and BH10-04 contained concentrations of uranium up to 390 µg/g. The elevated solid-phase concentrations of uranium are due to the presence of uranium-bearing minerals within granitic pegmatite and gneiss. The presence of uranium minerals in bedrock at concentrations higher than typically observed in the crustal environment are expected, as the area is known to host uranium mineralization from similar bedrock formations (i.e., study site is located within former uranium mining region).

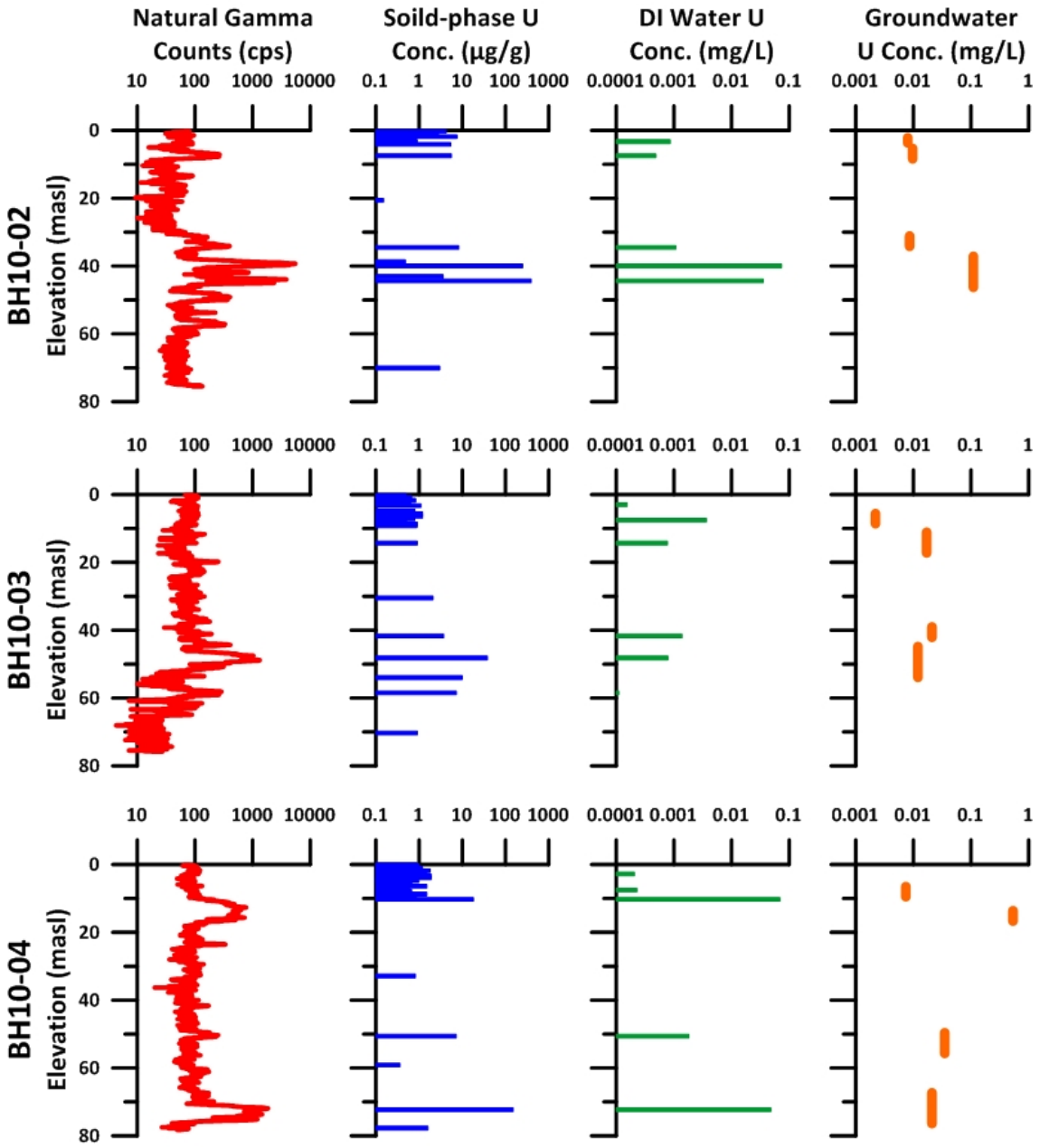

Figure 3. Profiles of natural gamma and uranium concentrations in bedrock, DI water leachate test effluent and groundwater at BH10-02, BH10-03 and BH10-04.

The radioactive decay of both the uranium and thorium decay series' results in the emission of gamma radiation as a result of the daughter nuclei being in an excited state after alpha decay (e.g., uranium-238→thorium-234) or beta decay (e.g., lead-210→bismuth-210→polonium-210). As gamma radiation is a by-product of radioactive decay of naturally occurring radionuclides (i.e., uranium-238, uranium-235 and thorium-232), the down borehole natural gamma measurements are effective means for delineating the bedrock intervals that contain uranium-bearing minerals.

The notable bedrock intervals at the two borehole locations where there are high zones or spikes (i.e., greater than 'background', which locally is about 100 counts per second [cps]) in natural gamma measurements are summarized in Table 1. The bedrock at borehole location BH10-02 was observed to have numerous intrusive pegmatite dykes (some on the order of metres thick), and exhibited the highest natural gamma counts down the borehole profile (max. 5818 cps). Similarly, the bedrock at BH10-03 and BH10-04 contained relatively massive granitic pegmatite dykes that range in thickness from metres to centimetres, with associated gamma counts that reach maximums of 1364 cps and 1852 cps, respectively.

Depth intervals within the bedrock where natural gamma show marked increases in radioactivity levels (cpm) correlate well with the presence of granitic pegmatite intrusions, and within some zones of host rock, such as granitic gneiss (Figure 3). Furthermore, samples of bedrock that were analyzed for solid-phase uranium show that these zones contain concentrations of uranium that are up to one to two orders of magnitude greater than the typical crustal abundance concentration.

Uranium in Groundwater

Monitoring wells were screened in the bedrock to evaluate the potential effects of the uranium-bearing bedrock zones on groundwater quality. For comparison, monitoring wells were also screens within the overlying bedrock. Hydrogeological and geophysical methods, as described above, were used to select depth intervals to screen monitoring wells. Four monitoring wells were installed at each borehole location, one within the saturated zone of the overburden and three within the bedrock. The depth profile of the monitoring well screens (i.e., intervals of subsurface sampled) with the concentrations of uranium measured in each of the monitoring wells is illustrated in Figure 3.

Groundwater concentrations of uranium in the overburden ranged from 0.0022 mg/L to 0.0080 mg/L. Within the bedrock, groundwater concentrations of uranium were greater than those observed in the overburden and ranged from 0.0056 mg/L to 0.54 mg/L. The highest uranium concentrations in the groundwater were observed within granitic gneiss at BH10-02 (0.11 mg/L) and pegmatite at BH10-04 (0.54 mg/L) and correlate well with high natural gamma levels and elevated solid-phase concentrations of uranium in the bedrock.

Within the bedrock aquifer, it is postulated that the elevated concentrations of uranium and associated daughter products occur due to leaching of uraniferous bedrock (oxidative dissolution/desorption reactions) as aerobic groundwater moves through fractures. De-ionized (DI) water leach test work was completed on select samples to qualitatively evaluate the potential for solubilization of uranium from the bedrock zones that contain elevated concentrations of uranium in the solid-phase under aerobic conditions. This static leach test consists of adding DI water to the subsample of solids (either overburden or bedrock) at a ratio of liquid to solid of 3:1. Generally, the samples from the high gamma zones exhibited elevated concentrations of uranium in the leachates. The elevated uranium in the DI water leachates also correlated well with the elevated solid-phase concentrations (Figure 3). Thus, the DI water leachate results show that uranium is leachable from the uraniferous bedrock under laboratory conditions.

The leaching or solubilization of uranium from bedrock has shown to be enhanced in waters that are alkaline and carbonate-rich, whereby aqueous carbonate species bind with the uranyl ion (Noubactep *et al*. 2006; Jurgens *et al*. 2010). For example, the following reaction shows aqueous carbonate species reacting with reduced uranium to form an aqueous uranyl-carbonate species (Buck *et al*. 1996):

$$UO_{2(s)} + 1/2O_{2(aq)} + 3CO_3^{2-}{}_{(aq)} + H_2O_{(aq)} \leftrightharpoons [UO_2(CO_3)_3]^{4-}{}_{(aq)} + 2OH^-{}_{(aq)} \qquad (1)$$

Because the DI leach test uses de-ionized water (which contains very low concentrations of carbonate species), the it likely underestimates the concentrations of uranium that could possibly be solubilised from the uranium-rich bedrock zones under actual field conditions where concentrations of alkalinity within the bedrock groundwater are moderate to high (66–394 mg/L as $CaCO_3$).

Borehole ID	**Elevated Natural Gamma (γ) Zones**		
	Depth (m)	**Lithological Description**	**Maximum Gamma (γ) Measurement (γ; cps)**
BH10-02	6–8	Granitic pegmatite veins within amphibolite gneiss.	274
	31–34	Granitic pegmatite dyke.	425
	38–40	Granitic gneiss.	5818
	42	Granitic gneiss.	867
	43–45	Granitic gneiss.	3980
	48–50	Granitic pegmatite dyke.	422
	56–58	Granitic pegmatite dyke.	329
BH10-03	20	Granitic pegmatite vein within amphibolite gneiss.	300
	44	Granitic pegmatite veins within biotite-amphibolite gneiss.	397
	47–50	Granitic pegmatite dyke.	1364
	58, 59	Granitic pegmatite veins within marble.	272
BH10-04	11–16	Granitic pegmatite dyke.	768
	50	Granitic pegmatite vein within feldspathic-calcareous-biotite gneiss.	252
	71–76	Granitic pegmatite dyke.	1852

Table 1. Bedrock zones where elevated natural gamma activity was measured at BH10-02, BH10-03 and BH10-04. Elevated Natural Gamma (γ) Zones refers to bedrock depth intervals where gamma counts are notably greater than local 'background' (which for the purposes of discussion is defined to be ≤100 cps).

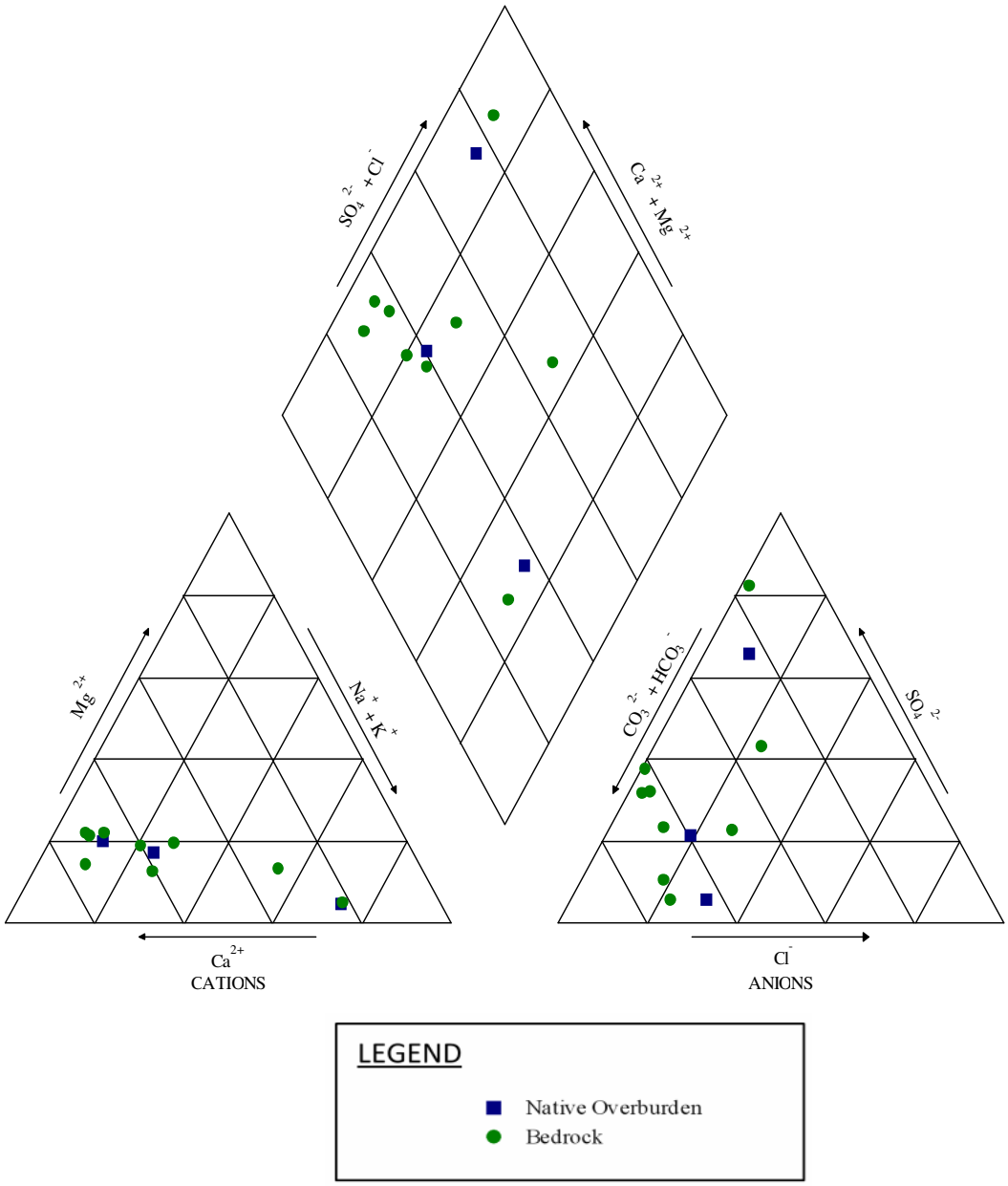

Figure 4. Piper plot showing the major ion composition of groundwater samples collected at BH10-02, BH10-03 and BH10-04.

To show the carbonate-dominated water chemistry within the local groundwater, Figure 4 shows a Piper plot that presents the major ion composition of the overburden and bedrock groundwater samples collected from twelve monitoring wells installed at BH10-02, BH10-03 and BH10-04. Three of the twelve monitoring wells were screened within the sandy overburden (plotted as blue squares), whereas the

remaining samples were collected from wells screened within the bedrock (plotted as green circles). The groundwater sampled from the monitoring wells at these locations is characterized by near-neutral pH (7.4–8.5) with moderate to high concentrations of alkalinity (54–1080 mg/L). Based on the results presented on the Piper plot for BH10-02, BH10-03 and BH10-04, it is clear that the groundwater is dominated by calcium and carbonate with minor sulphate.

The calcium- and carbonate-rich nature of the groundwater within the bedrock well reflects the local geology that is known to contain an abundance of carbonate minerals, particularly in the marble and amphibolite units. Based on the groundwater quality results, enhanced dissolution of uraniferous bedrock (i.e., greater than depicted by the DI water leach test work – see Equation 1) may be occurring due to the presence of aqueous carbonate species in the groundwater.

Conclusion

The methods described above have proved effective in providing several lines of evidence to effectively determine the presence, source and potential mobility of uranium in groundwater, as demonstrated through the case study presented. These methods are effective for delineating naturally occurring source zones that are contributing uranium to groundwater, and would be expected to be similarly useful in other instances where the source of uranium in well waters is unknown.

The results of the hydrogeological, geophysical and geochemical testing for the case study provide an enhanced understanding of the presence of uranium in specific pegmatite units and its mobilization into groundwater, measured in wells screened in intervals within the uraniferous pegmatites and gneiss formations. It is hoped that this study will lead to an increased awareness of the conditions that can lead to natural uranium mobilization and elevated concentrations of uranium within groundwater in certain geological environments. Of particular importance are the uraniferious pegmatite dykes and gneisses within the Grenville-type metasediments, which were observed to have thicknesses ranging on the order of centimetres to metres at the studied project site. It is recommended that wells, particularly drinking water wells that are drilled within these geological units, or that are to be drilled through these geological units be analyzed for uranium prior to use.

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