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## Uranium series isotopes in the Avon Valley, Nova Scotia

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### Abstract

An U-series isotopic study was carried out in the waters of the Avon Valley, Nova Scotia. The fresh and acidic recharge waters flow rapidly through the watershed composed of a granitic highland and a sedimentary, largely carbonate, lowland plain, before draining to the sea. There is no significant anthropogenic pollution; but, naturally elevated U levels can be encountered within the bedrock. Nonetheless, the U concentrations of the surface and groundwater are low (generally within the range of several hundredths to several tenths of a  $\mu\text{g l}^{-1}$ ), except in the proximity to weathering of U mineralization. The dissolved U in the surface waters appears to be stabilized by organic rather than inorganic complexes. Both the groundwaters and surface waters have similar  $^{234}\text{U}/^{238}\text{U}$  activity ratios that rarely deviate from secular equilibrium by more than 20% throughout the watershed. The magnitude of the  $^{234}\text{U}/^{238}\text{U}$  activity ratio is not determined by lithology but rather by the weathering mechanism, the high rate of flushing, and the leaching of local U mineralization. Dissolved Ra is consistently absent. The dissolved Rn concentrations, though variable, are measurable even in surface waters. This may be due to a continual degassing from the U-enriched bedrock or release from local sites of U mineralization underlying the surface water sources.

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**Keywords:** Nova Scotia; U series disequilibrium; Rn; Ra; Groundwater; Alpha recoil; U mineralization; Leaching

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## 1. Introduction

The Avon River Valley in central Nova Scotia (Fig. 1) was the site of U exploration in the late 1970s and early 1980s. Despite successful results, public pressure in 1982 forced a complete moratorium in Nova Scotia on all U exploration and further prospecting. Until that time, a number of wells in the study area had been tested and found to contain U concentrations that exceeded the Canadian Health Standards for drinking water. Unfortunately, much of the original data was either inaccurately mapped or was proprietary and not opened to the public domain. This study was planned to investigate the geochemistry of U series isotopes ( $^{238}\text{U}$  and  $^{234}\text{U}$  and its daughters  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$ ) in this catchment basin, as it is known to contain occurrences of U ore. We attempted to use U series disequilibrium as a hydrologic tracer of water flow through the catchment basin, from the granitic highlands through the sedimentary lowlands. U-series disequilibrium has proven itself to be a successful method in geohydrologic investigations (Ivanovich and Harmon, 1992). In hydrogeological studies, U isotopes have been used successfully to delineate specific groundwater bodies, to trace flow paths, and to detect the presence of economic resources in prospecting (Ivanovich and Harmon, 1992). Moreover, the clear division within this watershed of a granitic highland and a sedimentary, largely carbonate low-lying plain, combined with the absence of significant anthropogenic pollution, makes this study area a good model area to study the relative importance of the effects of lithology versus weathering in establishing the magnitude of the  $^{234}\text{U}/^{238}\text{U}$  activity ratios. One school of thought contends that lithology is the important control (for example, Sarin et al., 1990; Riotte and Chabaux, 2001; Chabaux et al., 2001). Others have implied that rock weathering is the important determinant (for example, Kronfeld and Vogel, 1991; Tricca et al., 2001).

The solubility of elemental U is governed by its valence state. Under reducing conditions  $\text{U}^{4+}$  is insoluble. Under oxidizing conditions  $\text{U}^{6+}$  is soluble. It forms various soluble complexes with carbonate, phosphate, sulfate, fluoride and silicate ions, and adsorbs onto organic compounds (Ivanovich and Harmon, 1992). The most often encountered complex in natural waters is the soluble uranyl carbonate complex. There is no significant isotopic fractionation in nature between  $^{238}\text{U}$  and  $^{235}\text{U}$ , each of which heads a decay series, because of the small difference in their atomic masses. In contrast, the isotopes of U in the  $^{238}\text{U}$  series are readily separated in nature by radiogenic processes related to the nuclear transformation from parent to daughter. Fig. 2 presents the relevant isotopes in the  $^{238}\text{U}$  series, from U to Rn, plus their modes of decay and half-lives. Two pathways produce isotopic separation at a water-bedrock interface. One is the result of nuclear transformations that break chemical bonds, cause displacement within the crystal structure, create micro-channels that allow for migration of water molecules into mineral grains, and auto-oxidation of the daughter nuclide through the loss of the two nuclear betas to the more soluble  $6+$  valence. All of these make the daughter nuclide more susceptible to solution than the parent, and allow it to be preferentially leached across rock boundaries. In addition, alpha-recoil enables the

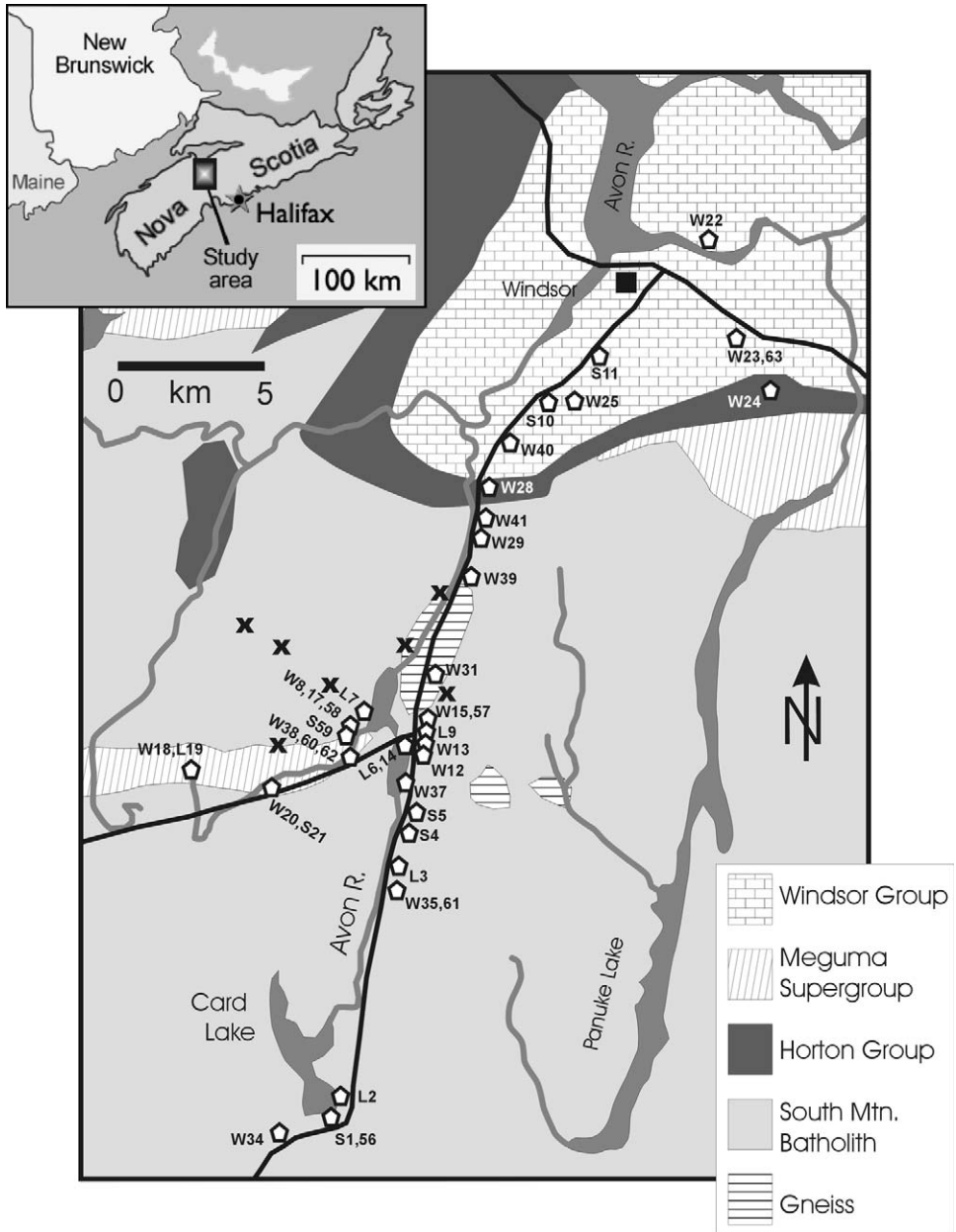


Fig. 1. Geological map of the bedrock of the study area showing sampling sites. The symbol 'X' denotes an area of known U ore.

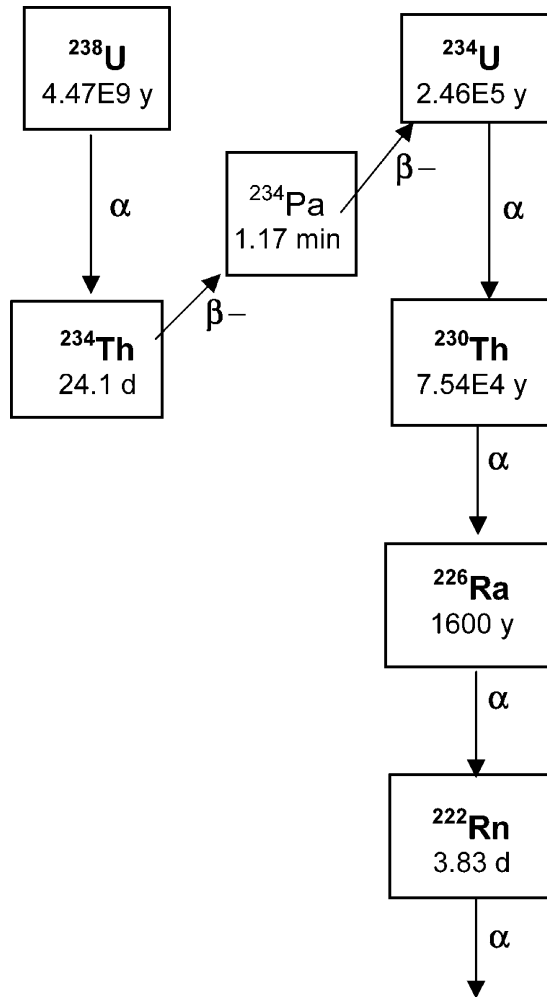


Fig. 2. Partial  $^{238}\text{U}$ -decay series, from U through Rn, showing the modes of decay and approximate half-lives.

ejection of the  $^{234}\text{U}$  across grain boundaries, irrespective of the prevailing redox conditions (Kigoshi, 1971; Kronfeld, 1974).

## 2. Bedrock geology

The bedrock in the study area is dominantly composed of the South Mountain Batholith (SMB) in the south and the Carboniferous sedimentary strata of the Minas Basin in the north (Ham, 1991; MacDonald, 1994). Topographically, the

resistant granites form rolling highlands with a steep, glacially rounded scarp where they contact the Carboniferous strata, which form fairly flat lowlands. The SMB also contains some inliers of metagraywackes and slates of the Meguma Supergroup and an unnamed gneiss. These units are described briefly as follows, from oldest to youngest.

1. The unnamed gneiss is suspected of being the oldest rocks in the study area, due to the intensity of metamorphism. The unit is significant to the study for the largest of the inliers is adjacent to the Avon River and is host to the Hemlock Hill U deposit. Additional U showings are found around the contact between the gneiss and granite (Ham, 1991).
2. The Meguma Supergroup is a thick sequence of siliciclastic rocks ranging in age from late Cambrian or older to Early Ordovician (Schenk, 1975, 1995). The Meguma Supergroup is divided into an underlying Goldenville Group (dominantly massive thick-bedded quartzose to feldspathic metawacke with minor slate and siltstone) and the Halifax Group, made up of slate with minor silt and stone. The Meguma is known to contain sulfide minerals including pyrrhotite, pyrite and arsenopyrite, which can produce acid rock drainage (Pupp and Grove, 1988; Fox et al., 1997; Zentilli and Fox, 1997).
3. The SMB is the largest peraluminous granitoid body in the Appalachian orogen (MacDonald et al., 1992). The pluton is a composite intrusion that can be divided into as many as 49 mappable units (MacDonald et al., 1992; MacDonald, 1994). U mineralization in the study area is strongly associated with the contacts between these intrusions, in addition to mineralization associated with the inliers of the Meguma and the gneiss (Fig. 2). The SMB is on average high in U compared to other granitic bodies in Nova Scotia and to the average of granites worldwide (Barkhouse and Laffin, 1982). The SMB has high average U concentrations. The granodiorites have  $3.9 \text{ mg kg}^{-1}$  U, the monzogranites  $6.1 \text{ mg kg}^{-1}$  U, and the leucogranites  $8.3 \text{ mg kg}^{-1}$  U (Chatterjee and Muecke, 1982). The values are somewhat higher compared to similar rock types elsewhere in Nova Scotia (Gulf Minerals Canada, Ltd., 1980; Barr et al., 1982), and are rather enriched in U compared to worldwide averages for diorites ( $1.8 \text{ mg kg}^{-1}$ ) and granites ( $3.5 \text{ mg kg}^{-1}$ ) (Vinogradov, 1962).
4. The western part of the Minas Basin in the vicinity of the town of Windsor is the type area for two major sedimentary units known as the Horton Group and the Windsor Group. The Horton Group is of Late Devonian–Early Carboniferous age. It is composed dominantly of arkosic sandstone and mudstones with some red and gray-green conglomerates, oil shales and minor non-marine evaporites (van de Poll et al., 1995; Gibling, 1995). There are known to be high concentrations of U in the Horton Group.
5. The Windsor Group of Middle to Late Visean age, consists of marine red beds, carbonates and evaporites, mainly gypsum with minor amounts of anhydrite, halite, and potash (e.g. van de Poll et al., 1995; Gibling, 1995).

### 3. Till geology

The Pleistocene glaciations that flowed over the study area stripped away the soil cover, replacing it in part by a generally thin veneer of glacial drift. In the highlands the bedrock is often exposed or thinly covered by glacial till. In the lowlands the bedrock is covered by a thin layer of till. There are two tills in the study area (Finck and Stea, 1995). The oldest and most extensive is the Lawrencetown Till. Where it is found as a ground moraine its thickness varies from 1 to 10 m. It contains significant amounts of soft carboniferous sediments which have been transported considerable distances southwards. Thus, the till has a moderate to good buffering capacity for acid rains because of the calcareous clasts within. The Beaver River Till, predominantly overlies the granitic and siliciclastic rocks. It contains very few clasts that have been transported from the sedimentary bedrock region in the north.

### 4. Climate

The general climate of Nova Scotia is humid and temperate. Rainfall is high, varying from 1000 mm to over 1500 mm total precipitation per year. Thus, groundwater is young and of good quality. Precipitation in the highlands is significantly higher than in the lowlands, though annual precipitation is highly variable. The average annual temperature is from 5.9 °C to 7.0 °C (Porter, 1982; Trescott, 1969a,b). Nova Scotian precipitation has a low salt concentration and a low pH. Rain collects in the abundant lakes of the granitic highlands where only minor additional contribution to the rainfall chemistry come from water–rock interactions. The lakes persist with low pH and low total dissolved solids (TDSs) of a Na–Cl water type (Gorham, 1957; Johannessen, 2000). The lakes also contain solid and dissolved organic matter, as is indicated by the tea-brown color of the water. The high amount of rainfall coupled with the steep gradients and the low storage capacity of the granites ensures that the recharge waters flow quickly through the watershed.

As rainfall (and lake water) infiltrates into the ground, it changes towards a HCO<sub>3</sub> composition by the dissolution of limestone or limestone clasts in the aquifer, with a concomitant rise in pH and TDS. Stream waters flowing out of the lakes are generally similar to lake water in composition, or may be intermediate between lake and groundwater compositions. In all the samples (except for two groundwater samples W15 and W23) both the surface and ground waters are undersaturated with respect to calcite and even more so with respect to the common evaporite salts (Johannessen, 2000).

The groundwater samples were obtained from shallow wells. Often the depth of the wells was not known; though, where information was available, it was found that both the drilled and dug wells are generally quite shallow, ranging from less than 2 m to 8 m depth. Sample W13 (*ca* 30 m depth) and W35 (*ca* 37 m depth) are the deepest wells in our study for which depths are known.

## 5. Sampling and methods

The sampling was carried out in the Avon River drainage basin, located *ca* 55 km NW of Halifax, and stretching roughly 30 km N–S along Highway No. 14 from Card Lake to Windsor (Fig. 1). This valley was chosen because it straddles two typical Nova Scotian geographic and geologic terrains: the granitic highlands and the sedimentary lowlands. Furthermore, the valley is known to host U deposits (Fig. 1). Samples of lake, stream, and domestic well waters were collected during May 1998 to November 1999. Samples that were collected for Rn and Ra analysis were collected in 250 ml brown glass bottles, whose tops were dipped in liquid paraffin to ensure a gas-tight seal. U samples were collected in 10–20 l polyethylene jerry cans and acidified to pH = 2. Ideally, tap water samples should be collected after the tap has been flowing for 10–20 min, to ensure that the line is fully flushed. However, as the well samples were from private residences and most of the sampling was during a drought (relative to typical Avon Valley conditions), it was not always possible to be entirely sure that the lines had been fully flushed. To offset this, all bottles were rinsed before filling, and where large samples for U analysis were collected, these were collected first, to ensure that the Rn samples were sampled from the longest-running stream of water.

The pH was measured on site using an Oyster<sup>™</sup> portable pH meter, calibrated with standard solutions before measurement. The temperature was measured on site, using a mercury bulb glass thermometer. The alkalinity and chemical analyses, which are reported here as TDS, were performed in the laboratory.

Initially the Rn was measured in the laboratory by extracting the gas and measuring its alpha particle activity using a Scintrex RDU-2 Rn analyzer. After one month, when all excess Rn had decayed away, the sample was again analyzed for Rn. This latter value should reflect the activity of <sup>222</sup>Rn in equilibrium with its parent <sup>226</sup>Ra. During the second field season, a DurrIDGE RAD7 Rn detector with RAD H<sub>2</sub>O attachment for field measurements of Rn in water samples was employed. The instrument uses an air bubbling process to strip Rn gas from water, and then pump it into a chamber containing a solid-state alpha detector, which resolves the specific energy of the alpha particles.

The U isotopic analyses were performed using alpha spectrometry. The acidified sample was spiked with <sup>232</sup>U. After agitation, iron nitrate was added. The samples were heated to boiling and U was precipitated with the iron at pH = 9. Purified U metal was electroplated on a stainless steel disc following ion exchange and solvent extraction. Counting times for the samples varied between 2 and 10 days.

## 6. Results

The results of the water chemical and the isotopic data for U and Rn are presented in Table 1. The associated statistical counting error is quoted at the 1σ level of confidence. The U concentration varies from 0.024±0.004 μg l<sup>-1</sup> to a high of 41 μg l<sup>-1</sup>, though most of the values fall in the tenths of a μg l<sup>-1</sup>. Thus, the U

Table 1

U-series isotopes and chemical data of the waters of the Avon Valley

Sample	pH	Temperature (°C)	TDS (mg l <sup>-1</sup> )	Alkalinity (mg l <sup>-1</sup> )	<sup>238</sup> U(μg l <sup>-1</sup> )	<sup>234</sup> U/ <sup>238</sup> Uactivity ratio	<sup>222</sup> Rn(Bq l <sup>-1</sup> )
s01 <sup>k</sup>				6	0.24±0.01	1.06±0.08	4.44±0.93
s56 <sup>c</sup>	5.6	9.5	73	6			6.48±2.52
l02 <sup>k</sup>				1.5	0.25±0.02	1.17±0.10	0.63±0.26
l03 <sup>k</sup>				1.8	0.23±0.01	0.98±0.07	0.44±0.30
s04 <sup>k</sup>							2.33±0.78
s05 <sup>k</sup>				2.5	0.26±0.02	1.04±0.08	1.00±0.33
l6 <sup>k</sup>				1.9	0.24±0.01	1.17±0.08	0.70±0.26
l14 <sup>a</sup>	4.6	24.5	12	1.2			0.00±0.10
l07				3.8	0.25±0.01	1.15±0.08	0.67±0.26
w08 <sup>k</sup>							265±8
w17 <sup>a</sup>	7.0	15.5	64	39	2.31±0.08	1.11±0.04	172±5
w58 <sup>c</sup>	6.7	11.5	66	39			282±14
l09 <sup>k</sup>							0.30±0.19
s10 <sup>k</sup>							0.04±0.04
s11 <sup>k</sup>				28	0.15±0.01	1.19±0.09	0.44±0.22
w12 <sup>a</sup>	5.6	14.0	51	31	0.06±0.01	1.24±0.17	5.85±0.81
w13 <sup>a</sup>	6.0	12.5	36	20	0.04±0.01	1.10±0.17	30.7±2.0
w15 <sup>a</sup>	7.8	8.5	263	190	0.34±0.02	1.07±0.08	0.00±0.07
w57 <sup>c</sup>	7.3	11	303	211			0.85±0.22
w18 <sup>a</sup>	6.8	22	233	162	1.62±0.03	0.98±0.02	85.8±4.0
L19 <sup>a</sup>	5.1	25	9	1.8	0.29±0.02	1.15±0.09	1.04±0.37
w20 <sup>a</sup>	6.3	14.5	439	33	0.37±0.02	1.03±0.08	0.00±0.11
s21 <sup>a</sup>	5.5	25.5	10	1.8	0.28±0.01	1.11±0.06	
w22 <sup>b</sup>	7.3	10	242	151	0.29±0.01	1.39±0.10	
w23 <sup>b</sup>	7.5	14.5	396	241	2.59±0.11	1.19±0.06	
w63 <sup>f</sup>							6.67±2.63
w24 <sup>b</sup>	5.8	12	120	41	0.029±0.008	1.33±0.38	
w25 <sup>b</sup>	5.2	18.5	200	17	0.024±0.004	1.27±0.30	
w28 <sup>b</sup>	6.8	17.5	615	169	0.53±0.02	1.13±0.06	
w29 <sup>b</sup>	6.5	17	609	122	0.40±0.02	1.05±0.06	
w31 <sup>b</sup>	6.5	19	256	111	0.21±0.01	1.36±0.08	
w34 <sup>c</sup>	7.0	21	162	99	0.45±0.01	1.10±0.04	
w35 <sup>c</sup>	6.8	14.5	311	181	41.08±0.47	0.99±0.01	
w61 <sup>f</sup>							656±17
w37 <sup>c</sup>	7.3	14	115	72	0.80±0.04	1.10±0.05	
w38 <sup>c</sup>	6.0	20	152	36	0.66±0.04	1.00±0.09	
w60 <sup>e</sup>	5.7	12.5	161	23			321±11
w62 <sup>f</sup>							360±35
w39 <sup>c</sup>	6.4	19	79	50	0.10±0.01	1.25±0.19	
w40 <sup>c</sup>	7.0	17	448	285	0.61±0.04	1.13±0.07	
w41 <sup>c</sup>	5.6	19	77	18	0.079±0.003	1.43±0.08	
s59 <sup>e</sup>	5.9	9.5	15	4.2			22.0±2.8

Note: the prefix of the sample code refers to sample type with L for lake sample; S for a stream sample and W for a well water sample. <sup>k, a-f</sup> collection dates: k = 28 May 1998; a = 24 July 1998; b = 6 Aug. 1998; c = 13 Aug. 1998; e = 22 Oct. 1999; f = 2 Nov. 1999.

concentration in all of the samples in this study fall within the current guidelines of  $<154 \mu\text{g l}^{-1}$  for Canadian drinking water (Federal-Provincial Subcommittee on Drinking Water, 1998). The  $^{234}\text{U}/^{238}\text{U}$  activity ratios range from  $0.98 \pm 0.07$  to  $1.43 \pm 0.08$ . Neither the U concentration nor the  $^{234}\text{U}/^{238}\text{U}$  activity ratio shows any correlation to geographical location, or to bedrock type, or to water chemistry. Therefore, it was not possible to discern a consistent evolutionary change along the water flow path within the river basin from the granitic highlands seawards. Nor was it possible to distinguish water from the igneous province from that of the sedimentary bedrock in the lowlands.

The Rn activities were highly variable geographically, ranging from zero to  $656 \pm 17 \text{ Bq l}^{-1}$ . There are no current Canadian guidelines for maximum permissible Rn in drinking water. No Ra was detected above the limit of detection, which is  $0.1 \text{ Bq l}^{-1}$ . Thus, the Rn activities should be considered as excess Rn, that is, above the amount that can be generated by the parent in solution at secular equilibrium with its daughter. Ra must be removed from solution as soon as it is formed, since the waters of the study area contain both a parent (U) of Ra and its immediate daughter of short half-life (Rn). Previous studies have also found very little Ra in the Nova Scotia waters (Grantham, 1986; Page, 1999). As the waters in the area are undersaturated with respect to carbonate and sulfate species, it is unlikely that either precipitation with calcium carbonate/sulfate or formation of Ra carbonate/sulfate of low solubility is the reason for the low levels of Ra. Ra is highly soluble as a chloride, but levels of chloride in the Avon Valley are very low. In the present study area, adsorption (Krishnaswami et al., 1982) or cation exchange (Sturchio et al., 1989) are thus the most likely processes causing low Ra concentrations.

## 7. Discussion

On a watershed-wide scale, the U concentration is affected by the high rate of flushing. More locally, the weathering of ores may augment significantly the soluble U. It has been put forth that the U concentration in surface waters should correlate with water alkalinity; for, it affects the stability of the soluble uranyl carbonate complex (Mangini et al., 1979). Fig. 3 shows the U concentration versus the alkalinity. The waters are divided into two groups, surface (lake and stream water) and shallow groundwater. Though the six groundwater samples with the least U content have the lowest alkalinity, there is no statistical correlation between these two parameters ( $r = 0.15$ ). The concentration of U in the groundwater is not dependent upon the extent of its formation of carbonate complexes. It is interesting to note that all of the waters, which are in general of Ca-HCO<sub>3</sub> type, are undersaturated with respect to the common carbonate minerals (Johannessen, 2000). It appears that the dissolved U concentration is controlled by the rate of flushing, which should be a function of the aquifer transmissivity at each site and the high precipitation regime, as well as the presence of labile U in the vicinity.

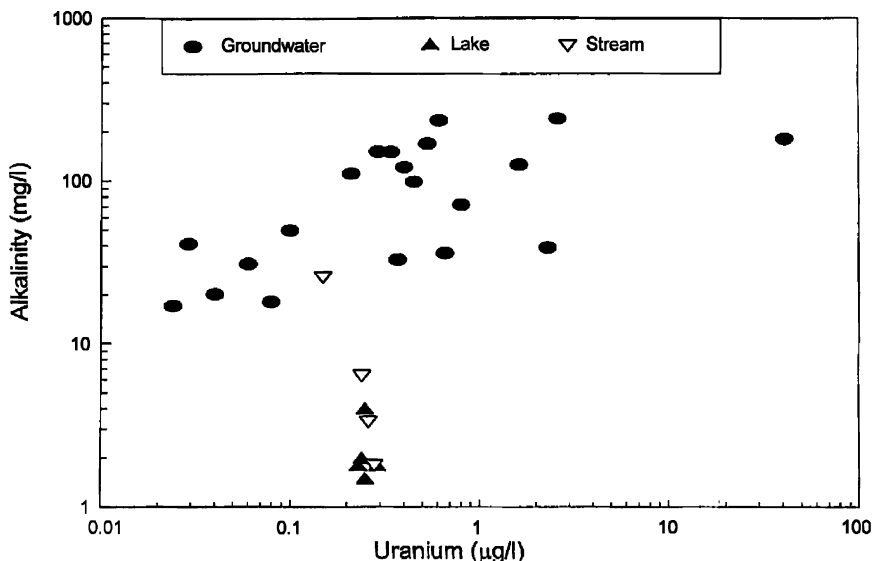


Fig. 3. U concentration versus alkalinity in the waters of the Avon River valley.

The U concentrations of the surface waters

1. fall in a relatively restricted range of  $0.1\text{--}0.3 \mu\text{g l}^{-1}$ ; and
2. when contrasted with the groundwaters would appear to be too high for their alkalinity.

Thus, it would appear that the high amounts of dissolved organics present in the waters play an important role in stabilizing U in solution. Halbach et al. (1980) noted that in the Harz Mountains, a region of similar climatic and bedrock type, the surface (bog) water which was rich in dissolved organic matter removed U from the granite as uranyl fulvate. Additionally, they noted that the U concentration in the water was maintained in a restricted range ( $0.1\text{--}0.6 \mu\text{g l}^{-1}$ ) by the high steady dilution by rainwater, which prevented the U concentration from attaining very high values. It is interesting to note that the uptake of U by organic acids attains a maximum at a pH of *ca* 4.5. The acid groups are easily dissociated near this pH. The pH values which are available for four of the eight surface water samples of the Avon valley fall within the range of 4.5–5.6. It is expected that the four waters of this study for which pH was not obtained should fall in the same range, since other surface waters from the same granitic bedrock from the Avon Valley had exhibited pH in this range (Johannessen, 2000). Lake water on granitic basement in Halifax County, within 50 km of the study area, exhibited pH values even closer to 4.5 (Gorham, 1957). Zielinski et al. (1988) similarly reported the strong association of U with high dissolved organic carbon and low pH in water from the Lake Tahoe area. Moreover, the high rate of flushing, while keeping the U concentration low, also keeps the TDS of surface water very low.

The extent of the  $^{234}\text{U}/^{238}\text{U}$  fractionation exhibited here (excluding the ore deposits) appears to be climate dependent. The Avon Valley is a humid area, subject to plentiful precipitation year round. Such a climatic regime will lead to low  $^{234}\text{U}/^{238}\text{U}$  activity ratios. The  $^{234}\text{U}/^{238}\text{U}$  activity ratio in the water is affected mainly by the U residing on the outer rim of mineral grains. It is here that the  $\alpha$ -recoil across phase boundaries is effective. It is here too that water can reach and dissolve the preferentially vulnerable  $^{234}\text{U}$  nuclide. U atoms residing deep within mineral grains do not contribute much to the disequilibrium in the water. However, if aggressive water is constantly removing  $^{234}\text{U}$  preferentially faster than the  $^{234}\text{U}$  can be regenerated, or faster than  $^{238}\text{U}$  can be brought toward the surface by the sloughing off of the grain's now U-depleted outer rim, both  $\alpha$ -recoil to the water and preferential leaching will transfer only minor amounts of  $^{234}\text{U}$  to the water. As secular equilibrium is activity and not mass related, the activity ratios of parent to daughter will tend to be similar under such conditions. This is unlike desert areas, where rainfall is seasonal and the amount of water sporadic, while high mechanical weathering causes new crystal surfaces to form. This prevents the buildup of U-depleted crystal rims. Under these conditions, much higher amounts of  $^{234}\text{U}$  would be preferentially available. At the same time the volume of water would be smaller, though the rate of U dissolution would be faster, so that the U concentration should be higher in solution for the same bedrock type.

Fig. 4 plots the  $^{234}\text{U}/^{238}\text{U}$  of the water against the concentration of U for the humid Avon Valley, as well as for that of water sources from non-mineralized granitic bedrock from the hot and hyperarid southern Sinai desert (Kronfeld et al., 1992). For similar bedrock type, the effect of 1300–1500 mm year<sup>-1</sup> precipitation is compared to a region where the average annual precipitation which is <50 mm. Two distinct groups are readily apparent, based upon their U and  $^{234}\text{U}/^{238}\text{U}$  activity ratio. The Avon Valley forms a group of significantly lower normal U concentration with small  $^{234}\text{U}$  excess ( $^{234}\text{U}$  excess is defined as the  $^{234}\text{U}/^{238}\text{U}$  activity ratio minus 1, times the concentration of U), compared to the grouping composed of larger  $^{234}\text{U}/^{238}\text{U}$  activity ratios and higher  $^{238}\text{U}$  concentrations in Sinai. Also presented in this figure is the U concentration and  $^{234}\text{U}/^{238}\text{U}$  from humid regions of variable bedrock type, represented by the (A) Amazon River (Moore, 1967); (B) the world average river discharge, which is based upon major rivers that are obviously discharging from humid regions (Borole et al., 1982); and (C) the values from a semi-arid zone, as represented by southern Africa (Kronfeld and Vogel, 1991). Notably, A and B fall within the cluster of values represented by the Avon Valley waters, on the low to mid-range of U concentration. The semi-arid region falls midway between the clusters of the hyper-arid and humid zone  $^{234}\text{U}$  excess groups. This indicates that the primary process that continually removes the  $^{234}\text{U}$  excess in the Avon River drainage is under climatic control.

The thick sedimentary rock sequence in the lowlands, having a greater reservoir capacity, should contribute groundwater to stream flow. Riotte and Chabaux (1999) have noted that where groundwater contributes to stream flow the  $^{234}\text{U}/^{238}\text{U}$  activity ratio should rise, as groundwaters generally have higher  $^{234}\text{U}/^{238}\text{U}$  activity ratios than surface water. This is usually because groundwater

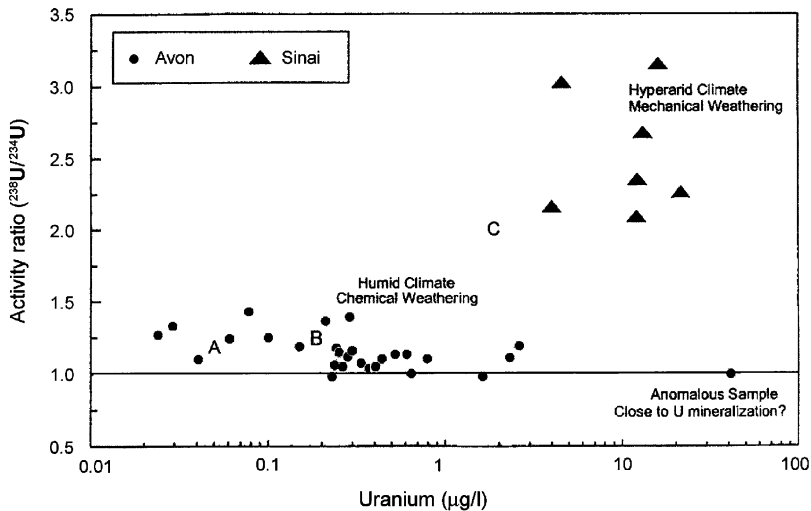


Fig. 4. A comparison between the U concentrations and  $^{234}\text{U}/^{238}\text{U}$  activity ratios in the waters from the non-mineralized granitic area of the hyperarid Sinai region and the waters of the Avon Valley. To the scatterplot are added the letters, A, B, C, which correspond to the values of U and  $^{234}\text{U}/^{238}\text{U}$  activity ratio for: A, the Amazon River (Moore, 1967); B, the average discharge of the world's rivers (Borole et al., 1982); C, the average surface water from semi-arid southern Africa (Kronfeld and Vogel, 1991). The two groupings reflect the relative importance of mechanical versus chemical weathering. The anomalous Avon sample, combining high U concentration with a  $^{234}\text{U}/^{238}\text{U}$  activity ratio close to unity, suggests proximal U mineralization.

flows generally much more slowly, and in deep aquifers U may encounter reducing conditions and precipitate. Under such conditions the  $\alpha$ -recoil contribution of  $^{234}\text{U}$  to the  $^{234}\text{U}/^{238}\text{U}$  activity ratio of the groundwater may become very appreciable. The amount of  $^{234}\text{U}$  injected into the water by this process from the aquifer's host rock is dependent on the residence time of the groundwater (Kronfeld et al., 1975). Even in shallow, well oxygenated groundwater  $\alpha$ -recoil inputs have been shown to raise the  $^{234}\text{U}/^{238}\text{U}$  activity ratio directly as a function of residence time (Rogojin et al., 1998). However, no such increase is noted as the stream water traverses the sedimentary sections, though groundwater contributions to the stream flow are likely. This is again assumed to be related to the high rate of flushing, which does not allow the groundwater to reside long enough in the aquifer for the  $\alpha$ -recoil mechanism to alter the  $^{234}\text{U}/^{238}\text{U}$  activity ratio. Superimposed upon this signature of low dissolved U concentration combined with low  $^{234}\text{U}/^{238}\text{U}$  activity ratio, is one generated by the leaching of U anomalies in the region. Leaching of U ores should naturally lead to raising the U concentrations with respect to the background values. At the same time, it will lead to dissolved  $^{234}\text{U}/^{238}\text{U}$  activity ratios similar to that of the source, for at such high absolute U concentrations in ore, leaching removes both parent and daughter readily from the ore (Cherdyntsev, 1971). If the ore is over a million years old, it would be near secular equilibrium, and its  $^{234}\text{U}/^{238}\text{U}$  activity ratio = 1.

In desert areas, where both normal background U concentrations and the  $^{234}\text{U}/^{238}\text{U}$  activity ratios are high, the presence of U leached from an ore deposit is readily identifiable by its low  $^{234}\text{U}/^{238}\text{U}$  activity ratio near secular equilibrium, in contrast to the high natural  $^{234}\text{U}/^{238}\text{U}$  activity ratios generated by mechanical weathering. In a humid region, the climate controls result in all waters exhibiting isotopic fractionation near secular equilibrium. Therefore, the difference in  $^{234}\text{U}/^{238}\text{U}$  activity ratio between background and ore should not be as striking. In the Avon Valley, the dilution factor of any signal is great, and only a very high U concentration coupled with a  $^{234}\text{U}/^{238}\text{U}$  activity ratio very close to 1 suggests an unambiguous anomaly. This was clearly observed in the present study in one sample (W35, Fig. 4). The case for other anomalies would be strengthened by corroborating isotopic data from other daughters in the  $^{238}\text{U}$  decay series, notably  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$ .

## 8. Radon

In the present study,  $^{226}\text{Ra}$  is not detected; however,  $^{222}\text{Rn}$  is plentiful and may be a useful isotope for the purpose of reconnaissance prospecting in the region, used in conjunction with the U isotopes. Though the Rn concentration in surface water is generally low, at least in comparison to several of the groundwater values, it should be remembered that this is all excess Rn, unsupported by a parent. Having a very short half-life of 3.8 days, it should decay away if there was not a Ra parent present in the very near vicinity to continuously regenerate it. Moreover, in surface water, were it not for a continuous and rather large supply of Rn being introduced by Ra, it is ordinarily expected to be close to zero. The partition coefficient of Rn between water and gas is 0.23 at 25 °C (Washington and Rose, 1990). Therefore, because the concentrations of Rn in air are very low, water in contact with air rapidly degasses. This phenomenon makes Rn useful as a tracer in hydrological studies: the presence of Rn in surface water would generally be indicative of recent groundwater inputs, or imply the presence of a source at the lake bottom that is continually emitting Rn. In streams, the input must be local, due to the short half-life of Rn (Kraemer and Genereux, 1998). Since it is so mobile in groundwaters and so easily scavenged into air, Rn is often observed to correlate poorly with its ultimate U parent. Conversely, when a correlation does exist, it should suggest proximity to a U source.

No correlation was found between dissolved U and Rn in other areas of Nova Scotia (Grantham, 1986). However, based on previous studies nearby, a correlation might be expected in the Avon Valley. Page (1999) has tabulated U and Rn concentrations from 631 wells in the Windsor and Rawdon Hills area, immediately adjacent to the present study area. Using this data (Fig. 5) a direct correlation ( $r = 0.98$ ) is found between soluble Rn and U. At first glance, the present Avon Valley data does not show a good correlation (Fig. 6). However, inspection of each sample indicates that degassing may have affected several of them to variable extents prior to sampling. Two groundwater samples (W20, W15) lacked measur-

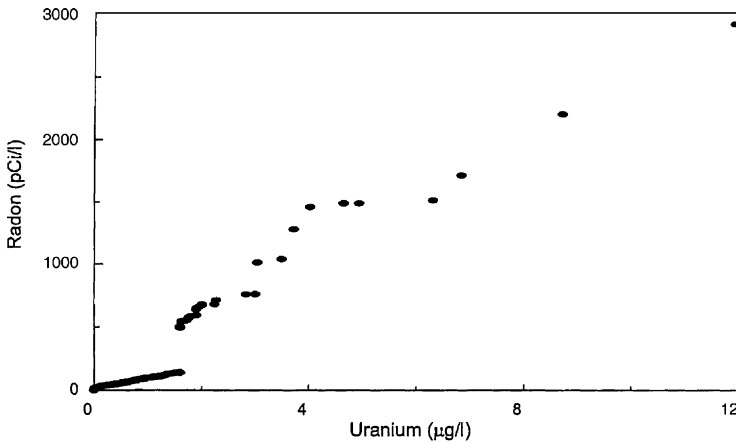


Fig. 5. Scatterplot of the soluble U versus Rn for well water in the Windsor and Rawdon Hills area, immediately adjacent to the present study area (data from Page, 1999).

able Rn and a third (W23) plots between the Rn-free wells and the other well data points. The Rn-free well, W20, is well ventilated, having screens that allow air in the well to exchange with the atmosphere. Well 15 is a Provincial Park pump that is not frequently used. Information concerning its construction and maintenance was not obtained; but, here too Rn degassing is suspected to be occurring in the pump. A re-measurement of this well yielded a higher Rn content, but this value also falls below its expected position on the correlation line, likely due to partial degassing. Well 23 is likely a partially degassed sample. This well was also noted to be rarely used, as its owner used bottled water for all potable water needs. The sur-

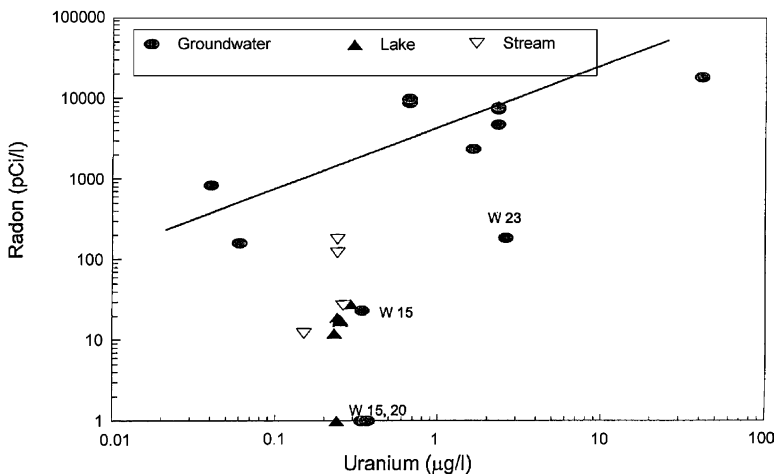


Fig. 6. Scatterplot of the soluble U versus Rn in the groundwater of the present study of the Avon Valley.

face water data points in Fig. 6 show a trend away from the correlation line, which can also be explained by Rn degassing. Thus, if we remove those samples for which a case can be made for significant degassing, the remaining seven groundwater samples do show a good correlation ( $r = 0.84$ ). It is important to note that for this correlation to exist, the source of the Rn must be nearby, due to the short half-life of Rn.

The U anomaly at W35 is likewise strengthened as being related to a U enrichment by the concomitantly high Rn concentration of  $656 \pm 17 \text{ Bq l}^{-1}$ . The values of Rn in our study area would suggest several more groundwater samples could potentially be added to a list of sites to be examined in greater detail in future U-mineralization exploration. Such a follow-up should include samples that exhibit  $^{234}\text{U}/^{238}\text{U}$  activity ratios near unity, relatively high U concentrations relative to the average of the region, and a high Rn activity. In our study area, samples W38, W08, which are within 1–2 km of known U anomalies (Fig. 2), and W18, show such elevated values. In addition, stream sample S59, located in the same vicinity, should be included solely on the basis of its excessively high Rn value for a surface water, of  $22 \text{ Bq l}^{-1}$ .

## 9. Conclusion

There are no observable geographic trends to the U and Rn concentrations nor  $^{234}\text{U}/^{238}\text{U}$  activity ratios across the watershed. Thus, employing the U-disequilibrium technique in this area as a hydrologic tool to trace water flow or delineate areas where water bodies mingle, is not efficacious. The data demonstrate that the  $^{234}\text{U}/^{238}\text{U}$  activity ratios in the waters of the Avon Valley are predominantly influenced by the weathering conditions rather than lithology. In addition, on a more local scale, the dissolved U and Rn are responsive to inputs from leaching of nearby U mineralization. The U anomalies are within the bedrock and not within the thin cover of glacial till. Where it is present, the till serves to absorb the radiation signal from shallowly covered bedrock anomalies, hindering rapid prospecting based upon gamma-ray detection. However, in these areas it seems apparent that future U exploration could be well served by employing hydrogeochemical surveys, emphasizing U-series disequilibrium (U and Rn), as a prospecting technique. The regional climate results in low background  $^{234}\text{U}/^{238}\text{U}$  activity ratios, while the high rate of dilution keeps U concentrations low. The U signal from the leaching of U ores should also yield low  $^{234}\text{U}/^{238}\text{U}$  activity ratios near unity, coupled with higher than average U concentrations coupled to high Rn values, which may rise in the direction of the U source. As an additional benefit, this method will alert the public to locations in which drinking water wells should not be placed.

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