NATURALLY-OCCURRING RADIONUCLIDES IN GROUNDWATER: RECENT EXPERIENCES IN NOVA SCOTIA

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ABSTRACT
The weathering of soil and rock containing naturally-occurring radionuclides can produce elevated levels of radionuclides in groundwater. In Nova Scotia, naturally-occurring uranium was first identified in groundwater in 1978. In 2002, lead-210 was identified in the well water of a school near Halifax. Lead-210 is a daughter product of the uranium -238 decay series which was not previously tested for in Nova Scotia. As a result, a province-wide radionuclide testing program was initiated. The initial results indicated that lead-210 and uranium can exceed drinking water guidelines in drilled wells in granite and upper Carboniferous sandstone and shale. However, subsequent investigations revealed that the lead-210 testing method did not provide a realistic indication of lead-210 levels because radon gas in the water samples was rapidly decaying to lead-210. The sampling protocol has now been modified to eliminate radon effects and testing is on-going.

RÉSUMÉ
L'altération du sol et des roches contenant naturellement des radio-nucléides peut entraîner des niveaux élevés de radio-nucléides dans les eaux souterraines. En Nouvelle-Écosse, la présence d'uranium de source naturelle a été identifiée pour la première fois en 1978. En 2002, le plomb-210 a été identifié dans le puits d'une école près d'Halifax. Le plomb-210, un produit de dégradation de l'uranium-238, n'était pas testé auparavant. En conséquence, un programme provincial de dépistage des radio-nucléides a été entrepris. Les premiers résultats indiquaient que le plomb-210 et l'uranium excédaient les limites permises dans les puits forés. Cependant, des investigations subséquentes ont révélé que la méthode utilisée pour détecter le plomb-210 était inadéquate étant donné que le gaz radon dans les échantillons se dégradait rapidement en plomb-210. Le protocole d'échantillonnage a donc été modifié de façon à éliminer cet effet et le programme de dépistage se poursuit.

1. INTRODUCTION

The weathering of soil and rock containing naturally-occurring radionuclides can produce elevated levels of radionuclides in groundwater. The Guidelines for Canadian Drinking Water Quality (Health Canada 1996) specify Maximum Acceptable Concentrations for 14 naturally-occurring radionuclides, most of which are daughter products of the uranium and thorium decay series. Although it is common to test water supplies for uranium, most of the other 14 naturally-occurring radionuclides are not commonly tested for and, therefore, there is a lack of information on the occurrence of these radionuclides in Canadian drinking water supplies. This paper presents a summary of results from an on-going province-wide radionuclide testing program in Nova Scotia.

2. BACKGROUND

In Nova Scotia, the presence of elevated levels of naturally-occurring uranium in groundwater was first identified in 1978. In response to this discovery, a Provincial Uranium Task Force was formed and subsequent investigations during the 1980's included the testing of more than 700 water wells for radionuclides (Grantham 1986). The results of these early investigations indicated that uranium commonly occurs in drilled wells at concentrations exceeding 0.02 mg/L, which is the current Canadian Drinking Water Guideline for uranium. It has now become routine in Nova Scotia to test for uranium in drinking water monitoring programs, groundwater monitoring programs and during property transactions.

In 2002, elevated levels of lead-210 were identified in well water at a school in Hubley, Nova Scotia. The discovery occurred during an environmental assessment in which the school's drinking water was tested for gross alpha and beta activity. The gross alpha activity of the water exceeded Health Canada's current screening level of 0.1 Bq/L, indicating that further testing for individual radionuclides should be carried out. Follow-up testing showed that all 14 naturally-occurring radionuclides were below guidelines, except for lead-210. Lead-210 is a daughter product of the uranium-238 decay series which was not previously tested for in Nova Scotia groundwater. As a result of this finding, an inter-governmental Special Well-Water Advisory Group (SWAG) was formed in 2002 and a province-wide radionuclide testing program was initiated.

3. DESCRIPTION OF THE INVESTIGATION

The investigation included a province-wide testing program and an evaluation of radionuclide treatment methods. The objectives of the province-wide testing program were: to determine the levels of radionuclides in public drinking water supplies; to identify the specific individual radionuclides that are most likely to exceed guidelines; and to identify the areas and geological formations in the province where water supplies are more likely to have elevated radionuclide levels.

The province-wide testing program involved several phases, including: 1. Initial testing of 52 school water supplies for 14 naturally-occurring radionuclides listed in the Guidelines for Canadian Drinking Water Quality; 2. expanded testing program to cover all provincial schools on their own water supplies (184 in total); 3. follow-up monitoring at all schools with elevated radionuclides levels; and 4. testing of all municipal water supplies (82 in total) and selected registered public drinking supplies (99 in total). The results presented in this paper focus the first two phases of the testing program.

During the province-wide testing program, water samples were collected at locations representative of water that people were drinking (i.e., sampled at the point of exposure). In the schools, water samples were collected from the highest-use water fountain, after running the fountain for 10 minutes. All radionuclide analyses were completed at SRC Analytical Laboratories in Saskatchewan, except for total uranium which was completed at Philip Analytical Services in Nova Scotia.

The evaluation of radionuclide treatment methods involved an initial literature review to identify the most promising methods. Two main treatment methods were selected for field testing: ion exchange and reverse osmosis. The field testing was carried out at schools that had been identified with elevated radionuclide levels. During the treatment evaluation, schools with elevated radionuclide levels were supplied with bottled water produced from Nova Scotian sources. The bottled water was tested for radionuclides to confirm that it met the guidelines.

4. RESULTS

4.1 Province-Wide Testing Program

The initial sampling program, conducted in June of 2002, involved the testing of drinking water at 52 schools for 14 radionuclides. The results in Table 1 show that drinking water guidelines were exceeded for two parameters: lead-210 and total uranium. All other radionuclide levels were low in comparison to drinking water guidelines, except for polonium-210, which was detected at levels of up to 60% of its guideline value. The results also indicated that lead-210 exceeded guidelines much more frequently than uranium and can be present above guidelines even when uranium is either below guidelines or not detected.

Based on the results in Table 1, it was concluded that the testing program should be expanded to cover all schools in the province with their own drinking water supplies. During this phase of the program, testing was refined to focus on the parameters that exceeded guidelines in Table 1: lead-210 and total uranium. Radium-226 was also included in the analyses because earlier investigations in the 1980's had indicated that radium-226 levels in well water in some areas of the province could exceed guidelines.

Table 1. Radionuclide results for 52 school water wells.

Radionuclide	Canadian Drinking Water Guideline	Maximum Level	Number of Guideline Exceedances
Be-7	4000	<5	-
Bi-210	70	0.44	-
Pb-210	0.1	0.44	12 of 52 (23%)
Po-210	0.2	0.12	-
Ra-224	2	<0.01	-
Ra-226	0.6	0.04	-
Ra-228	0.5	0.14	-
Th-228	2	<0.01	-
Th-230	0.4	0.01	-
Th-232	0.1	<0.01	-
Th-234	20	<4	-
U-234	4	1.0	-
U-235	4	0.05	-
U-238	4	1.0	-
Total U	0.2	0.081	2 of 52 (4%)

Note: All results are in Becquerels per Litre (Bq/L), except Total Uranium, which is expressed in mg/L.

An expanded testing program was initiated in September 2002. The program included 184 schools across the province; 178 of these schools had groundwater supplies and six had surface water supplies. Radionuclides were not detected in any of the surface water supplies. The results for schools with groundwater supplies are presented in Table 2.

As observed in the initial testing program, the results in Table 2 confirm that lead-210 and uranium levels commonly exceeded drinking water guidelines (i.e., 9% of wells tested), although the percentage of lead-210 exceedance was lower than observed in the initial testing program. This was probably because the initial sampling program included a high proportion of wells in granite which, as discussed below, is more likely to have elevated radionuclide levels. The results also confirmed that lead-210 exceeds guidelines more frequently that uranium, with 9% of wells exceeding lead-210 guideline and 2% exceeding the total uranium guideline. No radium-226 exceedances were identified.

Table 2. Radionuclide results for 178 school water wells.

Radionuclide	Canadian Drinking Water Guideline	Maximum Level	Number of Guideline Exceedances
Pb-210	0.1	0.65	16 of 178 (9%)
Ra-226	0.6	0.08	-
Total U	0.02	0.12	3 of 178 (2%)

Note: All results are in Becquerels per Litre (Bq/L), except Total Uranium, which is expressed in mg/L.

As shown in Table 3, when the data are grouped by bedrock geology, it is evident that the majority of radionuclide exceedances occur in two bedrock types: granites and sandstone/shales of the upper Carboniferous sedimentary basin. Of these bedrock types, granites were more likely to be associated with elevated lead-210 levels, with 62% of the wells in granite exceeding the lead-210 guideline.

Table 3. Lead-210 results compared with bedrock type for 178 school water wells.

Bedrock Type	Number of Wells Sampled	Number of Guideline Exceedances
Granite	21	13 of 21 (62%)
Carboniferous Sandstone and Shale	28	2 of 28 (7%)
Other bedrock types	129	1 of 129 (<1%)

Note: All results are in Becquerels per Litre (Bq/L), except Total Uranium, which is expressed in mg/L.

4.2 Evaluation of Radionuclide Treatment Methods

Based on the radionuclide levels observed in the province-wide testing program, it was anticipated that owners of domestic wells and public water supplies would require information on how to treat for lead-210 and uranium. Although there are commonly used and readily available drinking water treatment systems for uranium in Nova Scotia, there are no water supplies that are currently being treated for lead-210 removal. A literature review indicated that reverse osmosis and ion-exchange treatment systems were likely to be the most practical treatment options for treating lead-210 (U.S.EPA. 2000); however, no specific examples were found where these systems were being used for lead-210 and no information was available on lead-210 reduction efficiencies. Therefore, a field testing program was initiated at several of the schools with elevated radionuclide levels to confirm that these systems would adequately treat for lead-210.

As shown in Table 4, the results from the field testing indicated that neither reverse osmosis nor ion-exchange performed well, with average lead-210 removal efficiencies of less than 29%. The lead-210 influent levels in these field tests ranged up to 0.48 Bq/L and, therefore, these treatment methods were not able to consistently reduce lead-210 levels below the drinking water guideline of 0.1 Bq/L. However, once activated carbon or aeration was added, removal efficiencies were greatly improved.

The apparent poor performance of reverse osmosis and ion-exchange alone may have been caused by the presence of radon gas, which was able to pass through the treatment units and decay to lead-210. Dissolved radon levels in water at the field test sites ranged up to 1,400 Bq/L. Once radon removal was added to the treatment systems (i.e., by adding aeration or activated carbon units) lead-210 levels were reduced below guidelines.

Table 4. Field test results for radionuclide treatment units.

Treatment Method	Average Lead-210 Reduction
Reverse Osmosis	29%
Reverse Osmosis with activated carbon	93%
Ion-exchange	11%
Ion-exchange with aeration	94%

Note: Raw water influent levels of lead-210 ranged from 0.09 Bq/L to 0.48 Bq/L.

Subsequent investigations, based on a limited amount of sampling, have indicated that aeration by itself has an apparent lead-210 removal efficiency of 93%. Since aeration removes radon, not lead-210, this finding suggests that radon may play a significant role in the occurrence of lead-210.

4.3 The Significance of Radon

Radon is a gas that is relatively mobile in the subsurface compared to its daughter products, which tend to be bound to the aquifer matrix. It decays rapidly to lead-210, with a half-life of 3.8 days. Previous studies have suggested that radon may play an important role in the fate and transport of lead-210 in the subsurface (Focazio et al. 2001; Upchurch et al. 1991). As discussed below, the results from this study suggest that radon in water samples can also influence the laboratory measurement of lead-210.

Radon was not included in the initial testing program of this study. However, subsequent tests at 16 schools that exceeded the lead-210 guideline indicated that radon levels in the water ranged between 120 Bq/L and 1,400 Bq/L, with an average of approximately 600 Bq/L. These radon levels of are high enough to generate significant levels of lead-210 within a few days and, therefore, the amount of lead-210 measured at the laboratory can be significantly higher than the amount of lead-210 present in the water at the time of sampling.

In order to assess the influence of radon on the laboratory measurement of lead-210, a set of time-series samples was collected from several schools with elevated radon levels. The time-series samples were collected on the same date, but were held in the laboratory and analysed for radon and lead-210 at times of 1, 2, 3 and 4 weeks. One of the time-series samples was analysed immediately upon receipt at the laboratory to provide an initial measurement. The lead-210 analyses for the time series samples were carried out at Becquerel Laboratories in Ontario.

The time-series results for the school with the highest initial radon level (1,400 Bq/L) are presented in Figure 1 and 2. The radon results in Figure 1 indicate virtually all of the radon has decayed after four weeks in the sample bottles. The measured radon levels in Figure 1 closely follow the theoretical radioactive decay curve, which can be calculated using Equation 1.

$$\text{Radon}(t) = \text{Radon}(t_o)\exp(-\ln(2)t/t_{1/2}) \qquad [1]$$

where Radon(t) is the activity of radon at time t, Radon (t_o) is the initial radon activity, t is elapsed time in days, and $t_{1/2}$ is the half life of radon in days (i.e., 3.8 days).

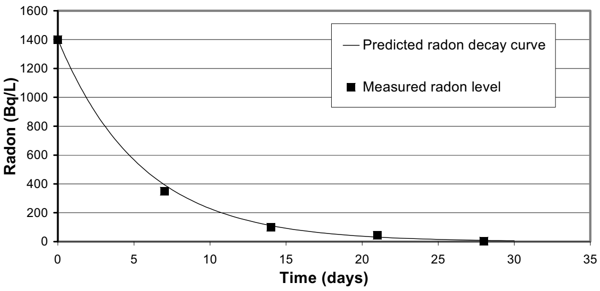

Figure 1. Radon time series for a school water well with an initial radon level of 1,400 Bq/L.

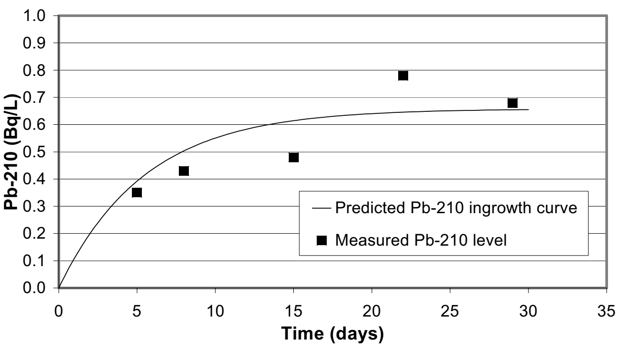

Figure 2. Lead-210 time series for a school water well with an initial radon level of 1,400 Bq/L.

The lead-210 time series results in Figure 2 indicate that the measured lead-210 levels increase with the sample holding time. Furthermore, the measured lead-210 levels generally follow the theoretical curve for lead-210 ingrowth from radon decay, which can be approximated using Equation 2.

$$\text{Lead-210}(t) = 0.00047(\text{Radon}(t_o))(1-\exp(-\ln(2)t/t_{1/2}) \qquad [2]$$

where Lead-210 (t) is the activity in Becquerels per Litre of lead-210 at time t, Radon (t_o) is the initial radon activity in Becquerels per Litre, t is elapsed time in days, and $t_{1/2}$ is the half life of radon in days (i.e., 3.8 days).

An investigation of the geochemistry mechanism that controls lead-210 dissolution in the subsurface was beyond the scope of this study. However, it is suggested here that as radon decays to lead-210 in the subsurface, the lead-210 will adsorb to the aquifer matrix. Therefore, prior to sample collection, dissolved lead-210 levels are likely to be relatively low. Once a sample is collected, however, radon continues to decay to lead-210 in the sample bottle. This process could explain the decreasing radon and increasing lead-210 levels as observed in the time-series measurements in Figure 1 and 2. This would also imply that if groundwater samples have elevated radon levels, then the lead-210 measured in the laboratory can be significantly influenced by the sample holding time. As indicated in Figure 2, for an initial radon level of 1,400 Bq/L, the level of lead-210 ingrowth from radon decay will exceed the drinking water guideline of 0.1 Bq/L within a holding time of approximately one day. It is usually not possible to meet holding times of less than one day because there are only two laboratories in Canada (located in Ontario and Saskatchewan) that routinely analyse drinking water for lead-210.

The method used to analyse lead-210 in the province-wide testing program determines lead-210 indirectly through its daughter bismuth-210 and involves holding the sample for 30 days prior to analysis to ensure that there is greater than 98.5% equilibrium between lead-210 and bismuth-210 (CANMET 1978). The 30 day equilibration time is equal to approximately eight half-lives of radon and, therefore, this allows sufficient time for ingrowth of lead-210 if elevated levels of radon are present. Because of the long holding times involved with this method, the lead-210 levels presented in Section 4.1 are not expected to be a realistic indication of dissolved lead-210 levels in the aquifer. They are likely to represent the level of lead-210 that would be in water after letting it sit for 30 days, rather than the level present when water is first drawn from a water well.

Once the influence of holding time on lead-210 measurements was recognized, an inter-laboratory comparison was initiated to compare results from laboratories that used analytical protocols that did not require 30 day holding times as part of the testing method. Duplicate samples were collected from one school and sent to three difference laboratories: SRC Analytical Laboratories in Saskatchewan, Becquerel Laboratories in

Ontario and Eberline Services Laboratory in New Mexico. SRC uses the CANMET (1978) method and requires a 30 day holding time before analysing the sample. Both of the other two laboratories use a lead-210 separation and extraction process that eliminates the need to hold the sample for 30 days. The separation process, which usually is carried out within 2 days of sample collection, prevents further lead-210 ingrowth from radon.

The lead-210 results from the inter-laboratory comparison for the duplicate sample were 0.19 Bq/L, 0.04 Bq/L, 0.03 Bq/L from SRC, Becquerel and Eberline, respectively. Using Becquerel Laboratories lead-210 method, subsequent re-testing of water from the 16 schools that originally exceeded the lead-210 guideline indicated that only five of these schools exceeded guidelines. These results suggest that the analytical method can have a significant influence on lead-210 measurements. However, as discussed above, if samples have high levels of radon, lead-210 ingrowth may exceed the drinking water guideline after holding times of less than one day. Therefore, even laboratory methods that eliminate the effects of radon within two days may not provide realistic measurements of the lead-210 level when water is first drawn from a well.

Based on the findings in this study, it is recommended that radon be removed from lead-210 water samples at the time of sample collection. In future sampling programs in Nova Scotia, all water samples collected for lead-210 will likely be boiled at the time of sample collection to remove radon. This is approach is expected to provide a more realistic measurement of lead-210 levels at the time when water is withdrawn from a water well. Therefore, it should give a more realistic indication of lead-210 levels in drinking water at the time of exposure, except in cases where water is withdrawn and stored for long periods before being used (e.g., water systems with long water retention times associated with large cisterns or pressure tanks).

Additional sampling will need to be carried out in Nova Scotia using the modified lead-210 sampling protocol discussed above to determine more realistic lead-210 levels in groundwater. It is expected that lead-210 levels based on the modified sampling protocol will be lower than indicated by the data collected during the earlier province-wide testing program.

5. CONCLUSIONS AND RECOMMENDATIONS

The results of the province-wide radionuclide testing program confirmed that uranium can occur above drinking water guidelines in groundwater in Nova Scotia. The results also confirmed that water wells located in granites and upper Carboniferous sandstones and shales are more likely to contain elevated uranium levels than other rock types.

Radon appears to be important in understanding the subsurface mobility, treatment and laboratory analysis for lead-210. Furthermore, radon has the potential to significantly influence the measurement of lead-210 by causing lead-210 ingrowth in the sample bottle after sample collection. It is recommended that radon be removed from lead-210 water samples at the time of sampling to eliminate lead-210 ingrowth during the laboratory analysis. Additional sampling using this approach is needed to determine the occurrence of lead-210 levels in groundwater in Nova Scotia.

6. REFERENCES

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