TESTING AND MONITORING OF RADIOLOGICALS IN DRINKING WATER

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ABSTRACT

The presence of radionuclides in drinking water can be attributed to natural sources or the result of human activities. Environmental levels of natural radionuclides may be increased by industrial processes. The Health Canada drinking water guidelines include maximum acceptable concentrations (MACs) for the seven most commonly detected natural and artificial radionuclides. This presentation will focus on the analytical screening scheme, monitoring programs, sample collection, storage and analysis procedures for gross alpha and beta as well as for the individual regulated radionuclides. Radiological results from a 2006 and 2010 Saskatchewan drinking water study will be discussed.

Introduction

Both groundwater and surface water have the potential to contain radionuclides. Groundwater contamination is most likely to occur due to the presence of low concentrations of natural radionuclides in rock and soil, while surface water contamination is more often caused by human activities.

MACs for the most commonly reported natural and artificial radionuclides have been established. There are MACs for three natural radionuclides, uranium, lead-210 and radium-226 and 4 artificial radionuclides, tritium, strontium-90, iodine-131 and cesium-137. A full discussion on Health Canada's rationale for these MACs is provided in their guideline technical documents (Health Canada, May 2009).

1. Saskatchewan Drinking Water Study 2010

In 2010 SRC Environmental Analytical Laboratories carried out testing of 98 drinking water supplies across Saskatchewan for an extensive list of parameters including radiologicals. This was a repeat of a study carried out in 2006. In 2009 the MAC for gross alpha was increased to 0.5 Bq/L from 0.1 Bq/L and the list of individual radionuclides with MACs was reduced to just seven. However, for consistency, testing was done according to the 2008 Guidelines for Canadian Drinking Water Quality Summary Table, which still referenced the extensive list of radionuclides and the 0.1 Bq/L MAC for gross alpha.

2. Sample Collection and Storage

All sample containers, preservatives and other supplies are provided by the laboratory. The requirement for gross alpha and beta is preservation with nitric acid to a pH of <2. In case either of the gross alpha or beta exceeds the MACs, additional containers and preservatives should be provided for sampling for possible testing of the individual radionuclides. Typically, 4 litres along with nitric acid to be used as a preservative would be sent in order that, if necessary, all the regulated natural and artificial radionuclides could be tested. Tritium requires 100 mL of unpreserved sample. The holding time for acidified water samples is 6 months.

3. Gross Alpha and Beta

The gross alpha and beta test is very useful as a screening method to determine if more extensive radiochemical measurements are required. The Guidelines for Canadian Drinking Water Quality (GCDWQ) Summary Table May 2009 lists MACs for individual radionuclides, but testing for these can be very costly. If the gross alpha results are less than 0.5 Bq/L and the gross beta results are less than 1 Bq/L, then this indicates that concentrations of these radionuclides are less than their individual MAC. Alpha emissions are generally associated with naturally occurring radionuclides, whereas beta emissions are generally associated with artificial radionuclides.

However, if the gross alpha or gross beta activity exceeds these values, it does not necessarily mean that there are radionuclides present in concentrations which exceed the individual MACs. The guidelines values for gross alpha and beta are derived from the radionuclides with the most restrictive MACs. The gross alpha or gross beta activity can be from a different radionuclide. It is not possible to establish which radionuclides are present from the gross alpha and beta test.

In addition, the detection limit for the gross alpha and beta method is highly dependent on the total dissolved solids in the water. As the level of total dissolved solids increases, so does the detection limit for gross alpha and beta, to a point where the detection limit may be higher than the MAC. It then becomes necessary to analyze for the individual isotopes to establish whether or not the sample meets the radiological guidelines.

Testing for individual radionuclides with MACs higher than the gross alpha or beta values is not necessary. This is because even if one such isotope is contributing 100% of the gross alpha or beta it is still within its own MAC.

4. Analytical Method for Gross alpha and beta

Total dissolved solids (TDS) is first determined on the sample, and then an appropriate volume is taken to yield 100 mg of solids. For example, if a sample contains 1000 mg/L TDS, then a 100 mL aliquot is taken to yield 100 mg of solids. For practical reasons the maximum sample size is 1 liter.

The appropriate aliquot is evaporated to dryness in a 5 cm stainless steel planchette and counted on a low background gas-flow proportional counter. The detection limit for gross alpha and beta depends on the background count rate and efficiency of the counting instrumentation as well as sample volume. The reportable detection limit for each sample must be calculated based on the volume used. The best detection limit will be achieved when the maximum volume of sample is used. For a l liter sample the approximate detection limit for both gross alpha and beta is around 0.03 Bq/L.

To achieve a detection limit equivalent to the gross alpha MAC of 0.5 Bq/L the minimum sample size that could be used is 60 mL. If the TDS is such that 60 mL would yield more than 100 mg of solids, then the gross alpha test will not provide useful information about the alpha radioactivity present and the sample will have to be analyzed for the individual alpha-emitting radionuclides. Correspondingly, the minimum sample size that could be used for gross beta to yield a detection limit equivalent to the MAC of 1 Bq/L is 30 mL. Again, if the TDS in the sample is such that 30 mL would yield more than 100 mg of solids, then the sample will need to be analyzed for the individual beta-emitting radionuclides.

Table 1 tabulates the gross alpha and beta results for the 98 sites in the Saskatchewan Drinking Water Study. In 2006, 38 of the sites exceeded the MAC for gross alpha and in 2010 if the same MAC had been applicable 17 sites would have exceeded. Based on the new MAC of 0.5 Bq/L, 9 sites exceeded the gross alpha MAC. All 9 sites were ground water sites. None of the 98 sites exceeded the MAC for gross beta.

5. Total Uranium

The MAC for drinking water is set at 0.02 mg/L and is based on its chemical toxicity, rather than is radiological toxicity. The half-lives for the isotopes of uranium are very long and therefore their activities are very low. A total uranium concentration of 0.02 mg/L would correspond to 0.25 Bq/L of uranium-238, 0.01 Bq/L of uranium-235 and 0.25 Bq/L of uranium-234. Note that uranium-234 and uranium-235 are beta-emitters, while uranium-238 is an alpha emitter.

Table 1 tabulates the uranium results for the Saskatchewan drinking water study. Although Regina is known to have high levels of natural uranium in soil, none of the 98 sites tested exceeded the MAC.

5.1 Analytical Method for Uranium

Uranium, along with many other elements may be determined quickly and easily using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The plasma is a stream of argon gas that is ionized by an applied radio frequency field. Sample aerosols are injected into the plasma which subjects the atoms to temperatures of 6000 to 10000°K. The plasma disassociates the sample into its constituent atoms or ions. The ions are extracted from the central channel of the plasma and pass into the mass spectrometer, where they are separated based on their atomic mass-to-charge ratio by a quadruple analyzer. The high number of ions produced, combined with very low backgrounds, provides the best detection limits available for many of the elements, normally in the parts per trillion range. The routine detection limit for Uranium is 0.0001 mg/L.

6. Radium-226

The MAC for radium-226 in drinking water is set at 0.5 Bq/L. Radium is an alpha emitter and is a bone-seeking radionuclide. Table 1 tabulates the radium-226 results from the drinking water study. All of the samples tested (24 sites out of the 98) showed very low radium-226 levels, the highest being 0.01 Bq/L, well below the MAC of 0.5 Bq/L.

6.1 Analytical Method for Radium-226

All radium isotopes and other actinide and lanthanide elements in the sample are separated by co-precipitation with lead sulfate. The precipitate is redissolved and radium isotopes are separated by co-precipitation with barium sulfate. The precipitate is filtered and mounted on a stainless steel disk. It is then counted on an alpha spectrometer. The detection limit is 0.005 Bq/L.

7. Thorium Isotopes

Until 2009, the GCDWQ Summary Table listed four MACs for thorium isotopes (thorium-228, 230, 232 and 234). Thorium-228, 230 and 232 are alpha-emitters, while thorium-234 is a beta-emitter.

Some of the samples in the water quality study were tested for thorium-230 and 232 because the gross alpha levels were greater than the individual MACs of 0.4 Bq/L and 0.1 Bq/L. None of the samples tested exceeded the MACs. See Table 1 for a summary of the results.

Currently, there are no MACs set for the thorium isotopes in drinking water.

7.1 Analytical Method for Thorium- 230 and 232

Thorium is isolated by precipitation with barium sulfate, several cleanup steps and subsequent precipitation with ceric hydroxide. It is collected on a filter paper and individual isotopes are determined by alpha spectrometry. The prepared planchet must be counted immediately when thorium-227 is required, otherwise the thorium-228 progeny will interfere. The detection limit is 0.01 Bq/L for both isotopes.

8. Lead -210

Lead-210 is a bone-seeking radionuclide, with a MAC set at 0.2 Bq/L. It is a beta-emitter, and since none of the water samples in the study exceeded the MAC for gross beta, it was not necessary to test any of the samples for lead-210.

8.1 Analytical Method for Lead- 210

Lead-210 is determined indirectly by the precipitation and counting of its high energy beta emitting progeny, bismuth-210. Bismuth is isolated by solvent extraction and subsequently precipitated as bismuth oxychloride. The precipitate is collected on a filter paper/disk assembly and beta counted in a low background counting system.

Groundwater samples should be aerated as soon as possible after collection to purge radon from the sample. Radon concentrations of greater than 50 Bq/L will decay into a detectable quantity of bismuth-210 if allowed to remain in the sample. The detection limit is 0.02 Bq/L.

9. Cesium-137 and Iodine-131

Cesium-137 undergoes radioactive decay with the emission of beta particles and gamma radiation. Cesium-137 in the environment comes from a variety of sources. The largest single source was fallout from atmospheric nuclear weapons tests in the 1950s and 1960s, which dispersed and deposited cesium-137 world-wide. However, since the half-life is 30 years much of the cesium-137 from testing has now decayed. Nuclear reactor waste and accidental releases such as the Chernobyl accident in the Ukraine released some cesium-137 to the environment.

9.1 Analytical Method for Cs-137 and Iodine-131

Both of these radioisotopes are easily detected and measured by gamma spectrometry. The detection limit for both cesium and iodine is 0.2 Bq/L.

10. Strontium-90

Strontium-90 is a bone-seeker and undergoes beta decay. It is a product of nuclear fission and is present in significant amounts in spent nuclear fuel, wastes from nuclear reactors and in nuclear fallout from nuclear testing. It is found almost everywhere in small amounts due to past nuclear testing and nuclear accidents. The MAC for strontium-90 is set at 5 Bq/L. The samples in the study were not tested for strontium-90 as the gross beta MAC was not exceeded.

10.1 Analytical Method for Strontium 90

Strontium-90 is determined using solid phase extraction to allow selective adsorption of strontium. The disks are placed in steel planchettes and then counted on a low background gas-flow proportional counter. The detection limit is 0.1 Bq/L.

11. Tritium

Tritium is a beta emitter which forms in the upper atmosphere through interactions between cosmic rays and the gases that make up the atmosphere. Tritium can be deposited from the atmosphere onto surface water via rain or snow and can accumulate in ground water via seepage. Tritium is also formed from human activities including electricity production, and the production of nuclear weapons, nuclear medicines, etc. Natural tritium tends not to occur at levels of concern but contamination from human activities can result in relatively high levels.

The MAC for tritium is 7000 Bq/L. Since none of the samples exceeded the MAC for gross beta, it was not necessary to test for tritium.

11.1 Analytical Method for Tritium

Tritium is measured using liquid scintillation counting, with a detection limit of 15 Bq/L.

Table 1. Saskatchewan Drinking water sources

Parameter	MAC Bq/L	# of sites Exceeding MAC	Highest level Bq/L
Gross alpha	0.5	9	1.6
Gross beta	1	0	0.81
Uranium	0.02	0	0.019
Ra 226	0.5	0	0.01
Th 230	0.4	0	<0.01
Th 232	0.1	0	0.02
Pb 210	0.2	0	N/A
Sr 90	5	0	N/A
Iodine 131	6	0	N/A
Cs 127	10	0	N/A
Tritium	7000	0	N/A

12. Monitoring for Radiologicals

The radionuclides most frequently reported in Canadian groundwater sources are radium-226, radon-22, and lead-210 from the uranium series. In surface waters the most commonly detected radionuclides are radium-226, tritium, strontium-90 and cesium-137.

Sampling should be carried out often enough to accurately characterize the annual exposure. If the source of the activity is known to be changing with time, then the sampling frequency should be carried out to reflect this. If there is no reason to think that the source varies over time, then the sampling can be done annually. If measured concentrations are consistently well below the MACs, then the sampling frequency can be reduced.

When a private well is constructed in bedrock, the water should be tested. The concentration of radioactive minerals in well water can vary substantially based on rainfall and other factors. Therefore, at least two samples (taken a month or two apart, if possible) should be taken before conclusions are reached regarding the average concentration of any radionuclide. The first test should be for gross alpha; then if it is necessary, test for radium-226, radium-228 or uranium.

13. Conclusions

Health Canada sets guidelines for the most commonly detected natural and artificial radionuclides in Canadian drinking water. When routine monitoring indicates that the levels or any of these radionuclides are above the MAC, the water supplier must take steps to reduce the amount of radionuclides to below the acceptable level. Private well owners have the responsibility of ensuring adequate monitoring and removal of these regulated radionuclides if required.

14. References

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