

Investigation of radioactivity in selected drinking water samples from Maryland

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In 2004, levels of radioactivity exceeding federal drinking water standards were found by state laboratories in two separate areas of Maryland through gross alpha and beta screening measurements. It was desired to know which radionuclides were responsible for the activity and what effect water softener systems installed in individual households had on the mitigating problem. Non-destructive gamma-spectrometry and gross alpha-beta liquid scintillation measurements, as well as chemical separations followed by measurements of ²²²Rn, ²²⁶Ra and ²²⁸Ra, uranium and thorium isotopes, ²¹⁰Po, and ²¹⁰Pb were carried out by National Institute of Standards and Technology (NIST). The results of the studies indicated disequilibrium among the decay products in the Th and U decay chains had a major influence on the radionuclide content. Unsupported ²¹⁰Po was found to be the predominant radionuclide in drinking water at one of the locations. Furthermore, the influence of the use of water softeners was found to be much more effective for radium than for uranium.

Introduction

When the bedrock contains considerable amounts of uranium and its daughter nuclides, drinking water taken from drilled wells may contain high concentrations of natural radionuclides. With respect to radiation dose, the most significant radionuclides typically found in drinking water are isotopes of uranium, radium, polonium, lead, and short-lived ²²²Rn. The United States Environmental Protection Agency (EPA) has set standards in drinking water for contaminants that pose a health risk in public water supplies. Presently the maximum contaminant levels for radionuclides are 0.19 Bq/l (5 pCi/l) for radium (²²⁶Ra and ²²⁸Ra combined), and 0.56 Bq/l (15 pCi/l) for gross alpha (including radium but excluding uranium and radon).¹ No standards have been established for ²²²Rn in drinking water.

In 2004 levels of radioactivity exceeding federal drinking water standards were found in separate areas of Maryland by state laboratories charged with the responsibility for overseeing water quality. The drinking water samples with high radioactivity originated from two regions in Maryland: Baltimore County and the Chapel Point Woods community located in Charles County. In the Chapel Point Woods community in Southern Maryland the level determined from gross alpha and beta screening measurements was not accounted for by more specific analyses for uranium and radium concentrations in that water. The gross alpha concentration of 1.6 Bq/l, determined by State Laboratory was three times above the EPA limit for gross alpha. Prior to 2002 the gross alpha content of

water was only 0.3 Bq/l, one fifth of what was found after 2002. It was desired to know which radionuclides were responsible for the elevated radioactivity levels in the water, so that an effective clean-up technology could be chosen to meet the EPA drinking water regulations. This community is small and consists of 95 homes. Drinking water is taken from three wells, the water is combined and then distributed to people. The Patapsco aquifer where the water is taken from is the second deepest in Southern Maryland and its waters are thousands of years old. No other water system in the area has shown elevated radiation levels. The only treatment for the water is chlorination. The sampling procedure was also changed at the same time as these high radioactivity levels were detected. Prior to 2002 all samples were collected from resident homes whereas after 2002 they were taken from the treatment plant where the water enters the distribution system. In addition, prior to 2002 it took about a year before samples were analyzed whereas after 2002 the samples were analyzed within three days of collection.

In the second case, in Baltimore County, elevated levels of radioactivity in the water supply system were likewise observed by gross alpha and beta activity screening. It was desired to know which radionuclides were responsible for the activity, and additionally authorities wanted to know what effect water softener systems installed in individual households had on mitigating the problem. Water softeners are ion-exchangers which are used to treat hard water by removing Ca and Mg. They may also reduce radioactivity in drinking water by removing some of the radionuclides present.

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NIST provided radiochemical analyses that were instrumental in addressing both situations. Non-destructive gamma-spectrometry, ^{222}Rn , gross alpha-beta liquid scintillation measurements, as well as chemical separations followed by measurements of ^{228}Ra , uranium and thorium isotopes, ^{210}Po and ^{210}Pb were carried out.

Experimental

Samples from Charles county, Maryland

Water samples from three wells and from the entry point to the distribution system were received 19 February 2004. Samples were taken from the Chapel Point Woods community in Southern Maryland. The depth of the wells is 210 m. The state laboratories measured that the gross alpha-concentration was 1.6 Bq/l. They analyzed Ra and U concentrations and found that there were only 0.01 Bq/l of ^{226}Ra and no uranium or ^{228}Ra present at all.

Samples from Baltimore County, Maryland

On 17 November 2004 samples were received from two different wells. These two wells were identified with codes 2103 and 2144. In each case one sample was raw water (2103 RAW, 2144 RAW) and the other sample was taken after the water was passed through water softeners installed in the homes (2103 AT, 2144 AT). Gross alpha-content for the raw water samples (2103RAW and 2144 RAW) was measured by the State Laboratory to be 1.1 Bq/l and 5.5 Bq/l and gross beta content 0.2 Bq/l and 3.0 Bq/l, respectively. Depths of the wells where water samples 2103 and 2144 were collected are 70 m and 120 m, respectively. Both wells are located in the Baltimore gneiss formation.

Gamma-determination by HPGe detector

Water samples were analyzed with a high purity Ge detector for gamma-emitters. 500 ml Marinelli beakers were used for the measurement. Each sample was measured at least three times over a period of 20 to 24 hours. Blanks were also measured in the same manner.

Alpha-measurements

U, Th, Pu and Am were determined from one-liter samples following the Eichrom procedure.² One liter of each water sample was gravimetrically spiked with tracers of ^{232}U , ^{229}Th , ^{242}Pu , and ^{243}Am . Radionuclides were concentrated from solution by phosphate precipitation, then separated from each other and from impurities through extraction chromatography. Sources were made by electrodeposition and samples were

counted by alpha-spectrometers. The counting sources were covered by thin films to prevent possible detector contamination by alpha-recoil ions.

^{210}Po and ^{210}Pb : Polonium was determined from 200 ml samples. ^{209}Po was gravimetrically added as the tracer, and sample was evaporated and dissolved in dilute HCl acid. 1 ml saturated hydrazine hydrochloride was added and then the sample was transferred to 30-ml plastic bottles. Silver discs were placed in the caps of each bottle. The bottles were turned upside down so that silver discs were covered by the sample solutions. The samples were heated in a water bath at 60 °C for 2 to 4 hours. The silver plates were removed, rinsed with alcohol and counted with alpha-spectrometers. Samples were covered with thin films to prevent recoil ion contamination of the detectors.

Measurements of ^{210}Pb and ^{210}Po were made from 500 ml samples. A radiochemical procedure based on extraction chromatography with a crown ether extractant was used to separate the lead and polonium fractions simultaneously.³ Pb carrier (30 mg) and ^{209}Po tracer (ca. 0.15 Bq) were added in order to correct for chemical recoveries after separation and purification. Purified Pb was isolated as PbC_2O_4 , dried and weighed to determine the chemical recovery. It was then dissolved in 1 ml of 6M HNO_3 and mixed with 15 ml of Packard InstaGel XF liquid scintillation cocktail in a 20 ml glass vial and measured in a Canberra Packard TriCarb 2500 TR liquid scintillation analyzer. Purified Po was spontaneously electrodeposited onto Ag disks and measured by alpha-spectrometry for ^{210}Po relative to ^{209}Po with solid-state planar Si alpha-detectors.

^{228}Ra : ^{228}Ra was determined by measuring ^{228}Ac that was separated from its parent using Diphonix ion-exchange resin.⁴ ^{228}Ac was measured by liquid scintillation counters (LSC), and the yields were determined using a tracer of ^{133}Ba (SRM 4251C) that is measured by gamma-spectrometry. ^{228}Ra was preconcentrated (with ^{133}Ba as a yield tracer) by coprecipitation with MnO_2 . ^{228}Ac is the first daughter of ^{228}Ra , and it was separated along with other elements (U, Th, Sr etc) using a Diphonix Resin column. The fraction of ^{228}Ra was held for >30 hours to allow ^{228}Ac ingrowth until secular equilibrium and then was isolated using chromatographic separation of Ac via a second Diphonix column. ^{228}Ac was eluted from the second Diphonix Resin with 5 ml 1M 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) and quantified by LSC counting.

Radon measurement

For the radon measurements 200 ml of test water were placed into the bubbler. The bubbler was purged by nitrogen, and two pulse ionization chambers (PIC) with volume 4 l each were loaded with the gas

sequentially. The activities of gas in both chambers were measured for approximately 60 hours by 2-hour runs. Background, measured before the chambers were filled by gas, was subtracted for each chamber's results individually. The activity in the second chamber was always indistinguishable from background activity and only the results obtained with the first chamber were used. Typically the number of counts acquired in 2 hours was 700 to 800 while the background count was around 300.

Results and discussion

Charles county

Gamma-ray measurements failed to find the presence of any anthropogenic radionuclides such as ^{60}Co or ^{137}Cs , and any ^{228}Ac . Liquid scintillation measurement confirmed the gross alpha-measurements by the Maryland State Laboratory. No beta-emitting nuclides were detected.

Radiochemical alpha-analysis showed no other alpha-radionuclides of significant amounts to be present in water except ^{210}Po . The ^{210}Po activity was 1700 ± 100 mBq/l and the gross alpha-activity detected is solely due to ^{210}Po present in water. Results for the abbreviated uranium decay chain series are shown in Fig. 1. Other alpha-nuclides were found to be below detection limits: ^{235}U (<0.4 mBq/l), ^{232}Th (<0.4 mBq/l), $^{239,240}\text{Pu}$ (<0.1 mBq/l), and ^{241}Am (<0.1 mBq/l). Based on LSC measurements there were no beta-nuclides present in water, not even ^{210}Pb , the parent nuclide of ^{210}Po . There is a disequilibrium in the uranium series radionuclides as shown in Fig. 1, ^{210}Po being the only radionuclide present in water during the time of the measurement were being conducted. The ^{226}Ra supported ^{222}Rn concentration was less than 0.04 Bq/l. This is consistent with the Maryland State measurements of low levels of ^{226}Ra (0.01 Bq/l) in the water.

The unsupported ^{222}Rn in water determined by the Maryland State in 1998 was 8.5 Bq/l at the water treatment plant.

In the late 1990s hundreds of wells in Anne Arundel County were found to have elevated levels of radium but this is the first discovery of elevated levels of unsupported polonium in Maryland drinking water samples. Several occurrences of unsupported ^{210}Po have been found in Florida groundwater.^{5,6} These studies suggested that polonium is cycled by sulfur bacteria, which reduce polonium to a more soluble species while the ^{210}Pb and uranium remain reactive and sorb to the solid phase of the aquifer. However, future studies are needed to confirm that this explanation is applicable to the Chapel Point Woods water system.

Elevated radioactivity concentrations due to polonium were detected beginning in 2002. Prior to that the activity levels were normal. What has caused this high rise of ^{210}Po in water? The water sampling procedure was changed in 2002. Prior to 2002 samples were collected from homes and it took about a year before the samples were analyzed. After 2002 the samples were collected from the water treatment plant and analyzed within three days of collection. The half-life of ^{210}Po is 103 days and, therefore, after a year the post-2002 concentration observed would have decreased to a level of 0.4 Bq/l, which is statistically the same value as 0.3 Bq/l, the pre-2002 gross alpha-value the Maryland State Laboratory measured. It is likely that the concentration of ^{210}Po in the water had not really changed in 2002; rather, it just was not noticed before because of the sampling procedure used.

The removal of ^{210}Po from drinking water is demanding since polonium in groundwater is bound to various sizes of particles.^{7,8} Ion-exchange or activated carbon units are not the best choice to remove ^{210}Po because they do not completely retain the different size particles in groundwater to which polonium are bound.⁹ The only practical method for the efficient removal of polonium is achieved through reverse osmosis. A pilot study performed later by Watek Engineering Corp. in the entry point to the distribution system showed that 97% of polonium was removed from the drinking water. A reverse osmosis filtration system was installed at the treatment plant to remediate the Po from the drinking water.

Baltimore County

Well water samples with elevated radioactivity levels were received from two different homes (2103 and 2144), before (RAW) and after treatment (AT) with water softeners. Results are shown in Table 1. All freshly measured water samples contained considerable amounts of radon. The two raw waters had very different compositions; 2144 (raw) contained mainly radium isotopes and radon whereas 2103 (raw) contained uranium and radon. After treatment with water softeners the radium concentration was reduced by factor of ten but uranium levels remained the same. Water softeners are known to remove more than 90% of radium from drinking water.¹⁰ The most efficient removal methods for radium from drinking water are ion-exchange using strong acid cation resins and reverse osmosis. The removal efficiencies attained by these methods can be as high as 99%.¹⁰ However, the water softener (cation-exchanger based) did not remove uranium from the drinking water. This is not however unexpected since uranium in drinking water often exists in anionic complexes.⁹

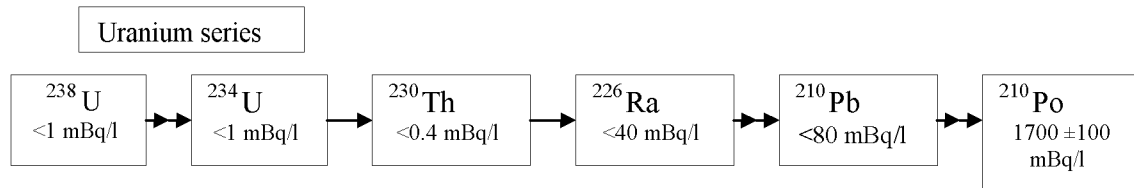


Fig. 1. Results from Charles County water samples are shown as abbreviated uranium decay chain series. Activities are calculated for March 4, 2004. An expanded uncertainty ($k = 2$) is given for the concentration of ^{210}Po . All other values were below detection

Table 1. Activity concentration in drinking water samples from Baltimore County

Nuclide	Half-life	2103 RAW, Bq/l	2103 AT, Bq/l	2144 RAW, Bq/l	2144 AT, Bq/l
U-238	$4.5 \cdot 10^9$ y	0.29 ± 0.04	0.31 ± 0.01	<0.003	<0.003
U-235	$7.13 \cdot 10^8$ y	0.014 ± 0.002	0.017 ± 0.001	<0.003	<0.003
U-234	$2.46 \cdot 10^5$ y	0.41 ± 0.02	0.43 ± 0.02	<0.003	<0.003
Th-228	1.9 y	<0.001	<0.001	<0.001	<0.001
Th-230	$7.54 \cdot 10^4$ y	<0.001	<0.001	<0.001	<0.001
Th-232	$1.4 \cdot 10^{10}$ y	<0.001	<0.001	<0.001	<0.001
Ra-224*	3.66 d	<0.2	<0.2	5.66 ± 0.05	0.4 ± 0.2
Ra-226	1600 y	NA	0.07 ± 0.02	0.12 ± 0.01	NA
Ra-228	5.7 y	<0.2	<0.2	4.3 ± 0.6	0.4 ± 0.5
Rn-222	3.82 d	251 ± 1	$28 \pm 1^{**}$	21 ± 1	19 ± 1
Bi-214***	19.8 min	256 ± 16	232 ± 18	18 ± 4	15 ± 4
Pb-210	22.3 y	0.18 ± 0.04	0.09 ± 0.03	<0.04	<0.04
Po-210	138 d	0.017 ± 0.002	0.005 ± 0.0002	0.003 ± 0.002	0.002 ± 0.002

RAW – raw water, AT – after treatment with water softener. Expanded uncertainty values, U ($k = 2$), are indicated next to the activity values. Activities are calculated for 11/17/2004. When measured values were below detection, minimum detectable activity has been given.

* Activity includes both ^{224}Ra and short living daughters.

** This value is substantially lower than the measured activity of ^{214}Bi (which is in equilibrium with ^{222}Rn). Most probably this lower result is due to the gas leakage in the process of radon transfer from the sample to the pulse ionization chamber.

*** ^{214}Bi is a short lived daughter of ^{222}Rn .

NA: Not analyzed.

The most efficient and frequently used method in private homes for uranium removal is anion-exchange. Anion-exchange resins have a high capacity for uranium, where thousands of bed volumes of natural water can be treated without breakthrough. In most cases the removal efficiency is over 95% and independent of water quality.⁹

These discoveries helped to formulate policy regarding required radionuclide sampling from drinking water in Baltimore County. For instance, follow-up testing for uranium in addition to radium may be required to verify the cause of elevated gross alpha results before prescribing treatment.

Conclusions

High polonium concentration (1.5 Bq/l) was recently discovered from drinking water samples in Maryland for the first time. Polonium was found to be unsupported and virtually the only radionuclide present in the water

(with the exception of Rn, which had already decayed by the time of measurement). To reduce the radiation level below the EPA limit for gross alpha (0.56 Bq/l), a reverse osmosis plant was installed to remove polonium from drinking water.

In other places where elevated levels of gross alpha and beta were measured from well waters, the effect of residential water softeners on radioactivity levels was studied. It was found that the effectiveness of water softeners to reduce elevated gross alpha and beta levels depended on what radionuclides were present. Cationic water softeners removed 90% of radium, but uranium levels were unaffected because it probably existed in anionic complexes. The radionuclide equilibrium in uranium and thorium decay series is not a likely condition in the complex environmental crucible. Detailed radionuclide evaluations are needed to appropriately select remediation technologies for well waters with elevated levels of natural radioactivity to meet the EPA drinking water regulations.

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Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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