

URANIUM IN HOT WATER TANKS: A SOURCE OF TENORM

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Abstract—Uranium deposits were detected inside hot water tanks using gamma-ray spectroscopic techniques and corroborated by the difference in the uranium concentration of the groundwater entering and leaving the hot water tanks. In-situ gamma-ray spectroscopy was performed using a transportable high-purity germanium (HPGe) gamma-ray spectrometer to estimate the mass of uranium in the hot water tanks. Gamma-ray spectroscopic analyses of hot water tanks in four residences with groundwater uranium concentration between 732 and 7,667 $\mu\text{g L}^{-1}$ revealed an estimated 3.5 to 69 g of uranium in each hot water tank. The uranium deposit within the tanks was indicated by the 143.8, 163.4, and 185.7 keV gamma rays of ^{235}U and confirmed with the 63.3, 92.3, and 92.8 keV gamma rays of ^{234}Th as well as the 1,001 keV peak of $^{234\text{m}}\text{Pa}$. An average decrease in uranium concentration of 23% was observed in the groundwater that passed through the hot water tanks. Additionally, once “uranium free” water entered the hot water tanks, the uranium deposits within the tanks resulted in an increase in the uranium concentration in the effluent water. The groundwater had an alkalinity in the range of 46–96 mg L^{-1} as CaCO_3 , and a pH range of 7.3–8.1. The accumulation of uranium in these hot water tanks results in them being classified as technologically enhanced naturally occurring radioactive materials (TENORM).

Health Phys. 87(6):659–663; 2004

Key words: uranium; naturally occurring radionuclides; groundwater; radioactivity, environmental

INTRODUCTION

TECHNOLOGICALLY ENHANCED naturally occurring radioactive material (TENORM) is defined by the EPA as material that “contains radionuclides that are present naturally in rocks, soils, water, and minerals and that have become concentrated and/or exposed to the accessible environment as a result of human activities such as manufacturing, water treatment, or mining operations” (U.S. EPA 2000). In January 1999, the Committee on Evaluation of EPA Guidelines for Exposure to Naturally

Occurring Radioactive Materials of the National Academy of Sciences (NAS) completed an evaluation of the risks from TENORM (NAS 1999). Although no direct regulations currently exist to monitor TENORM, it is regulated indirectly by application of various regulations and policies.

Uranium is a primordial radionuclide created during the formation of the earth and is ubiquitous in the environment. Uranium can be found in rocks and soils including granite, metamorphic rocks, lignites, monazite sand, and phosphate deposits (Hess et al. 1985) with a typical concentration in materials of a few parts per billion (ATSDR 1999). Uranium(IV) and uranium(VI) are the most common forms of uranium present in minerals. The uranium(IV) minerals are much less soluble than the uranium(VI) minerals. Of the reduced uranium minerals, uraninite (U_3O_8) is the most important mineral in terms of abundance and economic value (Finch and Murakami 1999). Coffinite [$\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$] and uranophane [$\text{Ca}(\text{UO}_2)_2\text{Si}_2\text{O}_7$], both hydrated uranium silicates, are also common uranium minerals. All of these minerals can be oxidized to the U(VI) state, where the dissolution of the uranium from the mineral species is key to the mobility of the uranium in the subsurface as well as the resulting bioavailability. The hexavalent state is most important for drinking water concerns (Cothorn and Lappenbusch 1983) and is typically found as either di- or tri-uranyl carbonate anions (Hess et al. 1985), which are soluble over a wide range of conditions (Hutchinson and Blackwell 1984). According to Hayes et al. (2000), the National Council on Radiation Protection and Measurements (NCRP) in Report 94 (NCRP 1988) identifies numerous factors affecting the solubility of uranyl complexes including pH, temperature, oxidation/reduction potential, concentration and composition of dissolved solids, and flow rate. According to Hess et al. (1985), these factors vary throughout the United States due to rainfall, geology, and groundwater flow patterns, and to anthropogenic factors such as the use rate of groundwater and surface water, which allows for large variations of uranium concentrations in drinking water sources from area to

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(Manuscript received 22 December 2003; revised manuscript received 24 May 2004, accepted 10 August 2004)

0017-9078/04/0

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area. Typical U.S. concentrations of uranium in surface water are 1–10 $\mu\text{g L}^{-1}$ and 1–120 $\mu\text{g L}^{-1}$ for groundwater (Hess et al. 1985). Most drinking water supplies in the U.S. contain natural uranium levels below 1.5 $\mu\text{g L}^{-1}$, although a number of states have an average concentration of uranium in drinking water exceeding 6 $\mu\text{g L}^{-1}$ (Hayes et al. 2000). In a survey of nearly 30,000 public surface and groundwater supplies, 7% contained uranium at or above 30 $\mu\text{g L}^{-1}$ (Cothorn and Lappenbusch 1983). The predominant uranium isotopes, based on radioactivity, in naturally occurring water are ^{238}U and ^{234}U at natural activity ratio ($^{234}\text{U}/^{238}\text{U}$) typically between 1 and 3; however, values as high as 28 have been observed (Hayes et al. 2000). The EPA has set the standard for uranium in drinking water from municipal supplies at 30 $\mu\text{g L}^{-1}$, which became effective 8 December 2003 (Federal Register 2000).

The focus of this research was to investigate if uranium present in groundwater deposits inside the hot water tank, thus resulting in the production of TENORM. The study was conducted on five hot water tanks in private residences near the Simpsonville/Fountain Inn area of South Carolina. Following an early 2001 recognition of the occurrence of anomalously high levels of uranium in groundwater in the area, 778 private wells have been sampled for uranium in the upstate region of South Carolina, of which 80 had uranium concentrations above 30 $\mu\text{g L}^{-1}$. Uranium was detected as high as 10,100 $\mu\text{g L}^{-1}$, with several wells greater than 1,000 $\mu\text{g L}^{-1}$ (Neel 2002).

MATERIAL AND METHODS

Four residences near Simpsonville/Fountain Inn, SC, with elevated levels of uranium in their groundwater were chosen for this investigation. The uranium concentration in the groundwater at these residences had been previously measured between 947 and 5,570 $\mu\text{g L}^{-1}$ (Hughes et al. 2005). Uranium concentration in the “as pumped” groundwater (hence forth referred to as cold water) as well as “as pumped” groundwater that was heated in the hot water tank (hence forth called hot water) was measured. At the initial sampling there were no water treatment systems installed at the residences. Following the initial water sampling, in-situ gamma-ray spectroscopy was conducted on the hot water tank(s) at each residence. Following these initial measurements, residence 2 had a point-of-entry water treatment system installed and residences 3 and 4 were connected to a municipal water supply. Following these remedial actions, a second round of samples of the cold and hot

water was taken and analyzed. After the second sampling, residences 3 and 4 had their hot water tanks removed and then a third round of sampling of the cold and hot water commenced at these two residences.

Aqueous samples were analyzed for total uranium by kinetic phosphorimetric analysis (KPA). Both cold and hot water samples were typically taken from the same faucet within the house. At residence 1, the hot water sample was collected directly from the drain port on the hot water tank. The uranium in water analysis was conducted with a 10–100 μL aliquot of a homogenized sample and analyzed with a KPA-10 (ChemChek Instruments, Inc., Richland, WA 99352-4959) system following manufacturer procedures (Brina and Miller 1992).

In-situ gamma-ray spectroscopy was performed on all hot water tanks immediately following the initial water sampling. The purpose of the spectroscopy was to determine if uranium was deposited in the hot water tanks. A total of five hot water tanks (residence 2 has two hot water tanks in series) were analyzed with a transportable HPGe detector (ORTEC, Oak Ridge, TN 37831-0895) in conjunction with an Inspector 2000 data acquisition system (Canberra, Perkin-Elmer Instruments, Boston, MA 02118-2512). The absolute detection efficiency for ^{235}U (185.7 keV) for the setup was approximated by a 20-gallon plastic tank filled with 7,667 $\mu\text{g L}^{-1}$ uranium (which contained no measurable ^{226}Ra) in groundwater. The set up was such that the detector was placed six inches from the bottom of the tank, with lead bricks below the detector to provide shielding from the ground. The end-cap of the detector was flush with the tank. A representative background spectrum was obtained with the detector approximately 1 m from the tank. The live count time was 2,410 s for both the tank and the background. The absolute detection efficiency for a homogeneous source was calculated to be 0.04% at 185.7 keV. This homogeneous source detection efficiency calculation is a rough estimate for the hot water tank geometry because the uranium deposits in the hot water tank are heterogeneous. Note that for measurement of the hot water tanks, the detector was located within 12 inches (on the circumference) of the heating element panel for all tanks. The ^{235}U activity in each of the hot water tanks was calculated with the measured absolute detection efficiency (ϵ) determined for the 20-gallon homogeneous sample. This calculation provides the estimated activity due solely to ^{235}U . The mass of uranium in the tank was calculated using the specific activity of ^{235}U , 0.07992 Bq μg^{-1} , and the percent mass of ^{235}U in natural uranium, 0.7204%. The total mass of uranium inside the tank is based on the total amount of uranium in the tank at the time of the measurement. In most cases, the uranium in

the liquid phase represents a small fraction (<5%) of the total uranium being detected inside the tank.

Qualitative x-ray fluorescence (XRF) analysis was performed on solid deposits obtained from within hot water tanks 1 and 4. XRF analysis was performed on sediment that flowed freely from the bottom of tank 4 and scale obtained from each of the heating elements of tanks 1 and 4. The XRF used for this analysis was the Rigaku X-Ray Spectrometer, model RIX 3000 (Rigaku, The Woodlands, TX 77381-5209). The light elements that were scanned for include: calcium, potassium, chlorine, sodium, phosphorous, silicon, aluminum, magnesium, fluorine, oxygen, nitrogen, carbon, and manganese. Other light elements were left out because they were not expected to be present based on groundwater quality parameters.[†] The heavy element scan was conducted where the entire spectrum is accumulated and then elements were identified based on their characteristic x rays. The samples were prepared by placing the material in an X-Cell container (3565 43 mm X-Cell produced by Spex CertiPrep, Metuchen, NJ 08840) and covered with Mylar (3516 Mylar, 0.12 mL thick, produced by Spex CertiPrep). The samples were not prepared in a standard geometry; therefore, the analyses are only qualitative. A background sample was also analyzed using an empty X-Cell covered with Mylar.

RESULTS AND DISCUSSION

Uranium concentration measurements for samples obtained from the four residences in the Simpsonville/Fountain Inn area are shown in Table 1. In addition to the cold water results, hot water samples were analyzed from

[†] Personal communication, P. Stone, South Carolina Department of Health and Environmental Control, Columbia, SC; April 2002.

residences 1, 2, and 4. The uranium concentration in the hot water was lower than that in the cold water by 15% to 33%. In these samples, the only difference between the cold water sample and the hot water sample is the presence of the hot water tank. No other treatment devices were present; therefore, the loss is attributed to the deposition of uranium in the hot water tank.

Following remedial action at three of the residences, as indicated in the Methods section, a second round of sampling was conducted; the results from which are also shown in Table 1. At all three residences, there was an increase in the uranium concentration for the hot water relative to the cold water entering the hot water tank. In all three cases, there was at least an order of magnitude increase in the uranium concentration, with the largest being 150 times greater. As seen in Table 1, all of the second round cold water samples measured well below $30 \mu\text{g L}^{-1}$. Of the three hot water samples collected, two were above $30 \mu\text{g L}^{-1}$. These results also confirm the presence of uranium in the hot water tank and indicate the dissolution of the uranium deposit back into the "uranium free" water. A third round of sampling at residences 3 and 4 was conducted following the replacement of the hot water tanks. In these cases, both cold and hot water samples were below the detection limit of $0.1 \mu\text{g L}^{-1}$. These results indicate that the amount of uranium that is contained in the hot water pipes is small relative to that in the hot water tank.

With analytical evidence supporting the hot water tank being classified as TENORM, gamma ray spectroscopy was utilized in the field to estimate/quantify the amounts of uranium present in the tanks. The spectrum obtained of hot water tank 2b (the second tank connected in series at residence 2) is presented in Fig. 1. Present in the spectrum is the 185.7 keV peak from ^{235}U , along with

Table 1. Drinking water and hot water tank analysis sample locations. (Except for hot pre-treatment water from location 2, all analyses were conducted with KPA.)

Residence	pH ^a	Alk. ^b	Initial sampling U concentration ($\mu\text{g/L}$)			Second sampling U concentration ($\mu\text{g/L}$) ^c			Est. U in hot water tank (g)
			Cold	Hot	Hot/Cold ratio	Cold	Hot	Hot/Cold ratio	
1	7.3	50	7,667	6,491 ^d	0.85	NA	NA	NA	3.5
2	7.5	46	1,754	1,183 ^e	0.67	7.2 ^f	170	23.6	12 ^g 69 ^h
3	8.1	96	1,900	NA	NA	0.4 ⁱ	25.2	63	4.5
4	8.1	78	732	568	0.76	0.4 ⁱ	60	150	29

^a Stone (2002).[†]

^b Alkalinity quantifies as mg/L CaCO_3 (Stone 2002).[†]

^c Hot water tanks still in use.

^d Sample taken directly from hot water tank drain port. Suspended solids were filtered.

^e Value based on % removal from alpha spectroscopy analysis.

^f Culligan treatment unit consisting of aeration, ion exchange, carbon filter, and UV used for point of entry treatment.

^g Hot water tank a (referred to as tank 2a).

^h Hot water tank b (referred to as tank 2b).

ⁱ Greenville Water System water.

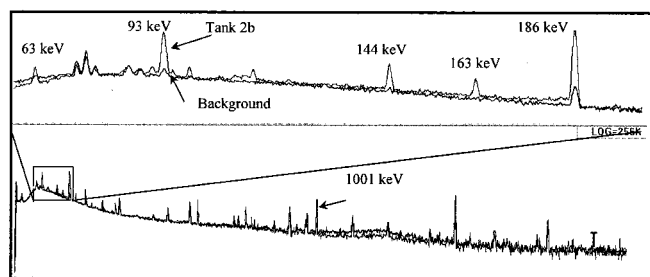


Fig. 1. In-situ high-resolution gamma-ray spectra for tank 2b and background.

the 144 and 163 keV peaks. Additionally, the 63 and 93 keV peaks from ^{234}Th (progeny of ^{238}U) are present as well as the 1,001 keV peak of $^{234\text{m}}\text{Pa}$ (progeny of ^{234}Th). Each of these peaks is indicated with the background spectrum underlaid. The total amount of uranium in the hot water tanks was estimated to be between 3.5 g and 69 g, as summarized in Table 1. Calculation of the ^{235}U activity with the 144 and 163 keV gamma-rays verified the absence of ^{226}Ra . Of the five hot water tanks that were measured, tank 2b has the highest estimated mass of uranium, 69 g. A vertical and radial gamma-ray emission scan of tank 4 indicated that uranium was concentrated at the bottom of the tank and on the heating element (Woodruff 2002).

Sediment from hot water tank 4, and scale from the heating elements of tanks 1 and 4 were analyzed by XRF to corroborate the presence of uranium and to identify other precipitated elements. Only qualitative determinations of the elements present in the samples were made because of the lack of an appropriate standard. There are a few conclusions that can be drawn from the data. The silicon concentration in the sediment is approximately an order of magnitude higher than in the scale, which agrees with the observation of the sandy composition of the sediment. The calcium concentration in the sediment was higher than that of the scale by a factor of at least three, while the uranium concentration in the sediment was lower than that in the scale by a factor of two to four. These results indicate the possibility of either a uranium-calcium or a uranium-silicon mineral being present in the tanks. These findings are consistent with preliminary findings using equilibrium modeling (Woodruff 2002), but further evaluation is necessary.

SUMMARY AND CONCLUSION

The objective of this research was to determine if uranium would deposit inside the hot water tanks, resulting in the hot water tank being classified as TENORM. Private wells of several of the residences in the Simpsonville/Fountain Inn area, where the uranium concentration exceeded $30 \mu\text{g L}^{-1}$, some by more than 200

times, were tested to determine if the uranium deposits were possible. Gamma-ray spectroscopy has shown that uranium concentrates in the hot water tank. XRF analyses confirm the presence of other elements in the deposit material, most notably calcium and silicon. Although not a direct radiation dose exposure hazard due to its presence in the tank, uranium in the hot water tank has been shown in these cases to dissolve back into the "uranium-free" water, sometimes creating a situation where the hot water exceeds $30 \mu\text{g L}^{-1}$.

Acknowledgments—Capt. R.L. Woodruff would like to thank the United States Air Force for academic funding during the time that this work was completed. The authors wish to also acknowledge the support received from B. Ayaz-Maierhafer and L. Hughes for their assistance with the XRF, P. Suwanathada for her help with the XRF, and P. Stone for providing the water quality data on the wells.

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