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CONTRIBUTION OF SHORT-LIVED RADIONUCLIDES TO ALPHA-PARTICLE RADIOACTIVITY IN DRINKING WATER AND THEIR IMPACT ON THE SAFE DRINKING WATER ACT REGULATIONS

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INTRODUCTION

In 1976, the U. S. Environmental Protection Agency established the National Interim Primary Drinking Water Regulations (NIPDWR) for radioactivity in drinking water.[1,2] These regulations establish the monitoring frequency and set a maximum contaminant level (MCL) for gross alpha-particle activity, excluding radon and uranium, of 15 pCi/L in public drinking water supplies. Radium-226 measurement is required when gross alpha-particle activity exceeds 5 pCi/L and Ra-228 measurement is required when the Ra-226 concentration exceeds 3 pCi/L. Under Section 141.15 of NIPDWR, the MCL for combined Ra-226 and Ra-228 is 5 pCi/L.

During March and April 1996, testing of public water supplies in Dover Township, Ocean County, NJ showed elevated gross α-particle activity levels which were significantly higher than historical values. Wells drilled into the Cohansey aquifer system of the New Jersey Coastal Plain province were identified as having the highest levels. The subsequent Ra-226, Ra-228, Po-210, isotopic uranium and isotopic thorium analyses could not account for the bulk of the elevated alpha radioactivity. Throughout 1996, repeated sample collection from same wells yielded different gross α-particle activity, with samples analyzed within 48 hours of sample collection having the highest value. Moreover, delaying the analysis by re-preparation of the same collected samples at a later date and consequent alpha counting showed much lower values. Such variability can only be attributed to the presence of short-lived alpha-emitting radionuclides. Radium-224 and its 4 α-emitting progenies (Rn-220, Po-216, Bi-212, and Po-212) could be the contributory constituents in raising the alpha acitivity of a sample. In situations where Ra-228 concentrations are high, Ra-224 presence, even if it is in equilibrium with Ra-228, will significantly elevate the alpha-activity levels. However, due to alpha-recoil process, Ra-224/Ra-228 activity ratios of over one are usually expected; similar to U-234/U-238 ratios observed in water samples.[3]

Currently, little is known about the geographic distribution and concentration of Ra-224 in potable waters, especially in private ground water supplies. From the limited data that have been collected, it appears that the activity of Ra-224 is equal to or as much as twice the Ra-228 activity.[4] As the Safe Drinking Water Act (SDWA) regulations do not specify a sample holding time for gross alpha measurements, and, similarly, do not address Ra-224 as a

potential contributor to the radium radioactivity of drinking water, the available data is insufficient regarding the true gross alpha and total radium exposure to the population through ground water supplies. The purpose of this study is to identify the source of the elevated short-lived alpha-particle activity found in samples from the Southern New Jersey area, and evaluate its impact on the SDWA regulations.

EXPERIMENTAL METHODS

Gross Alpha-Particle Determinations: Gross alpha-particle determinations were performed by the evaporation method, US EPA Method 900.0.[5] In addition, in some cases, a fast radium- isolation method was performed in order to separate out the unwanted radioactivity, to shorten the time involved in radiochemical preparation, and to initiate the alpha counting faster than the evaporation method. This was done by adding sodium sulfate and sulfuric acid to the sample, boiling the mixture, and coprecipitating the Ra and Pb radionuclides by adding lead carrier to the solution.[6] The precipitate was collected on a pre-weighed 47-mm diameter Durapore filter, 0.45 micron porosity. The filter paper was then placed on a planchet with retaining ring and counted on a low-background gas-flow proportional counter for consecutive 200-min counting periods. After gross alpha counting was completed, the filter paper containing the $PbSO_4$ precipitate was weighed for chemical yield and detection efficiency determinations.

Ra-224 Determinations: Separate 12-L aliquots of each sample were measured gravimetrically and the lead sulfate coprecipitation procedure described above was carried out. Finally, the filter paper containing the $Pb(Ra)SO_4$ precipitant was analyzed by gamma-ray spectroscopy, using Ge detectors, having about 10% relative efficiencies, for repeated 1000-min counting durations. The 238-keV Pb-212 and 583-keV Tl-208 photopeaks were followed for several days.

The chemical recoveries were 90% or higher, leading to Ra-224 minimum detectable concentrations (MDC) of 0.3 pCi/L, based on the conditions discussed above.

Ra-226 and Ra-228 Determinations: Ra-226 and Ra-228 analyses were performed according to the procedures described by B. Parsa.[7]

RESULTS AND DISCUSSIONS

The activities of Ra-224 and its progenies are obtained from appropriate Bateman equations, and following relationships can be derived:

$$A_1 = A^o_1 e^{-\lambda_1 t} \quad (1)$$

$$A_2 = A^o_1 e^{-\lambda_1 t} \quad (2)$$

$$A_3 = A^o_1 e^{-\lambda_1 t} \quad (3)$$

$$A_4 = 1.14\, A^o_1 (e^{-\lambda_1 t} - e^{-\lambda_4 t}) \quad (4)$$

$$A_5 = 1.14\, A^o_1 e^{-\lambda_1 t} - 1.26\, A^o_1 e^{-\lambda_4 t} + 0.104\, A^o_1 e^{-\lambda_5 t} \quad (5)$$

where: A°_1 = Initial Ra-224 activity,
A_1 = Activity of Ra-224 at any time t,
A_2 = Activity of Rn-220 at any time t,
A_3 = Activity of Po-216 at any time t,
A_4 = Activity of Pb-212 at any time t,
A_5 = Activity of Bi-212 at any time t,
λ_1, λ_4, and λ_5 are decay constants for Ra-224, Pb-212 and Bi-212, respectively.

Gross Alpha-Particle Activity Measurements: The α-particle activity from the samples varied with time because of essentially immediate in growth of Ra-224 daughter products and their subsequent decay, and from the in growth of Ra-226 progenies. The dependence of those alpha-particle grow-in/decay factors on time for three radionuclides, Ra-224, Ra-226, and Pb-212 are shown in Table 1. For Ra-224, contributions from Eqs (1), (2), (3), and (5) have been taken into account, which includes Pb-212 and its progenies, as well. However, if Pb-212 is not supported by Ra-224, it will follow a decay pattern indicative of its 10.64-hour half-life.

Gross alpha-particle activity measurement of public water supplies and private wells in Southern New Jersey, collected through routine monitoring program by the New Jersey Department of Environmental Protection (NJDEP), display the presence of Ra-224 in addition to the usual Ra-226 and Ra-228 activities. Table 2 presents gross alpha-particle activity of some of these samples counted at various times after radiochemical preparation. They all display a transient alpha activity with about a 4-day half-life.

In situations where the concentrations of uranium, thorium, and other α-emitting radionuclides, except radium, are very low, a rough estimation of Ra-224 concentration can be achieved from the gross α-particle activity data. The total alpha activity is due to the sum of Ra-224 (and its progenies) and Ra-226 (and its progenies). By measuring this activity in two different times, one can use the appropriate in-growth/decay factors presented in Table 1, and estimate the initial concentrations of Ra-224 and Ra-226. However, if Th-230 (E_α = 4.7 MeV) is the calibration standard for the detectors, Ra-224 determinations will be biased high. This is due to the higher alpha energies associated with the decay of Ra-224 and its progenies.

Radium-224 Measurements: These samples became available through a joint project of NJDEP and U.S. Geological Survey(USGS). In addition to Ra-224, gross α-particle activity (measured at different times), Ra-226 and Ra-228 were also determined. As described in the Experimental Section, for Ra-224 analysis, the 238-keV Pb-212 and 583-keV Tl-208 photopeaks were analyzed and followed for a period of one week, starting from the day of sample collection. The half-life for decay of these peaks signifies whether the Pb-212 is supported by Ra-224 or not. For Ra-224 determinations, the data from spectra taken between 36 to 48 hours after sample collection (the time for maximum Ra-224 supported Pb-212 activity, refer to Eq. 4) was generally selected for calculations. One should note that Pb-214, a Ra-226 progeny, has a 242-keV gamma ray (7.5% abundance), and if not resolved correctly

in the gamma spectrum, it could cause interference with the 238-ke-V peak and bias Ra-224 determinations high. Results for a few of the samples analyzed are presented in Table 3.

In conclusion, analysis of ground water samples taken from public water supply wells drilled into the Cohansey aquifer in Southern New Jersey have demonstrated that the time interval between sample collection and analysis will have a direct impact on the gross α-particle activity, if Ra-224 is present. In these samples, the gross α-particle activity and Ra-224 measurements revealed that the contribution of Ra-224 and its progenies to alpha-activity levels were significant. In order to estimate the magnitude of this contribution, the gross α-particle activity assay should be performed close to the time of sample collection. When this is done, a substantial number of Cohansey aquifer wells in the Southern New Jersey will exceed US EPA criterion for gross α-particle contaminant level, under the present SDWA protocol. The same wells, however, would be within the criterion, if their samples were analyzed after a period of 2 weeks or more.

Current US EPA drinking water regulations do not specifically address the presence of Ra-224. If Ra-224 is to be regulated as radium hazard, the sample holding time for the gross α-particle activity assay must be addressed, a suitable protocol established for the confirmation and quantitation of Ra-224, and an aprropriate MCL promulgated for Ra-224.

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TABLE 1

TIME DEPENDENCE OF ALPHA-PARTICLE IN-GROWTH/DECAY FACTORS FOR Ra-224, Ra-226 and Pb-212

Time	Ra-224	Ra-226	Pb-212
2 hours	2.99	1.05	0.69
4 hours	3.05	1.09	0.78
6 hours	3.10	1.13	0.73
12 hours	3.19	1.26	0.51
24 hours	3.16	1.50	0.23
36 hours	2.99	1.71	0.11
2 days	2.77	1.91	0.05
3 days	2.32	2.26	0.01
4 days	1.93	2.55	0
6 days	1.32	2.99	0
8 days	0.90	3.30	0
16 days	0.19	3.84	0
24 days	0.04	3.96	0

TABLE 2

GROSS ALPHA-PARTICLE ACTIVITIES FOR SELECTED PUBLIC AND PRIVATE WATER SUPPLIES FROM SOUTHERN NEW JERSEY

LC#	Collection Date	Gross alpha (pCi/L)	LC#	Collection Date	Grosalpha (pCi/L)
75466	12/5/96	18 ± 2 (12/6/96) 6 ± 1 (12/7/96) 3 ± 1 (12/9/96)	9702165	5/6/97	38 ± 2 (5/7/96) 12 ± 1 (5/20/97)
75499	1/13/97	28 ± 2 (1/14/97) 20 ± 2 (1/18/97) 13 ± 2 (1/24/97)	9704064	7/30/97	39 ± 2 (7/31/97) 23 ± 1 (8/4/97) 14 ± 1 (8/12/97)
9700682	2/13/97	61 ± 3 (2/14/97) 14 ± 1 (3/1/97)	9704195	8/4/97	121 ± 3 (8/6/97) 109 ± 3 (8/8/97) 78 ± 3 (8/11/97) 55 ± 2 (8/20/97)
9701031	3/10/97	82 ± 3 (3/11/97) 11 ± 1 (4/11/97)	9704196	8/4/97	111 ± 3 (8/6/97) 94 ± 3 (8/8/97) 82 ± 3 (8/11/97) 69 ± 3 (8/20/97)

* The counting date is in parenthesis.

TABLE 3

RADIOANALYTICAL RESULTS FOR SELECTED SAMPLES FROM SOUTHERN NEW JERSEY NJDEP/USGS GROUND WATER MONITORING PROJECT

LC#	Collection Date	Gross α-Particle Activity	Ra-224	Ra-226	Ra-228
9702800	6/2/97	22.8 ± 1.5 (6/3/97) 14.5 ± 1.2 (6/9/97) 10.2 ± 1.1 (6/13/97) 9.9 ± 1.0 (6/23/97)	2.4 ± 0.3	1.4 ±0.2	1.7 ± 0.4
9703596	7/8/97	38.8 ± 1.4 (7/9/97) 33.0 ± 1.1 (7/11/97) 3.6 ± 1.0 (7/15/97) 20.4 ± 1.0 (7/18/97) 18.0 ± 1.0 (7/21/97) 16.0 ± 0.8 (7/26/97) 14.2 ± 0.7 (8/2/97) 12.0 ± 0.7 (8/10/97)	4.5 ± 0.4	3.8 ± 0.5	2.5 ± 0.5
9703654	7/14/97	49.7 ± 3.1 (7/15/97) 38.2 ± 2.7 (7/18/97) 27.0 ± 2.0 (7/21/97) 23.7 ± 2.1 (7/25/97) 16.3 ± 1.7 (8/2/97) 12.3 ± 1.5 (8/9/97)	3.4 ± 0.3		2.4 ±0.3

esults are in pCi/L. Associated uncertainties are counting statistics at 95% level of confidence.

** The counting date is in parenthesis.