Assessment of size-fractionated species of curium-244 via alpha spectrometry in groundwater

S. M. Pike · H. Dulaiova · K. O. Buesseler

Abstract Curium was produced for experimental programs for use as a heat source for isotopic electrical power generators and by 1968 approximately 5 kg had been produced at the Savannah River Site (SRS). Size fractionated groundwater samples were collected near a disposal basin in F-Area at SRS in 1998 and in 2004. Separation of ^{244}Cm via extraction chromatographic methods was followed by alpha spectrometric measurement. In both years a trend of increasing Cm activities downstream of the seepage site was observed. Migration and immobilization resulting from base injection remediation between sampling dates explain large differences in ^{244}Cm concentration.

Keywords Curium · Groundwater · Size-fractionation

Introduction

Curium was produced for experimental programs for use as a heat source for isotopic electrical power generators and by 1968 approximately 5 kg had been produced at the Savannah River Site (SRS) [1]. The waste disposal basin in F-area received liquid waste effluents from the separation facilities, including waste from the nitric acid recovery unit and the evaporators that concentrated the dilute uranium nitrate solutions and plutonium from the SRS heavy

water moderated reactors. Discharges ceased and a low-permeability clay closure cap was placed over the basin in 1998 [2].

In 1998 and 2004 two site visits investigating the migration of plutonium (Pu) in SRS groundwater took place as part of DOE remediation efforts [3, 4]. Ground waters sampled downstream from the F area were elevated in plutonium and had variable ^{240}Pu/^{239}Pu ratios. These ratios were used to interpret the fractionation and speciation of plutonium that affect its mobility in the groundwater aquifer. Pu originating from the SRS heavy water moderated reactors had a characteristic ^{240}Pu/^{239}Pu ratio of 0.062 [5]. However, ^{240}Pu/^{239}Pu ratios in the basin were 13 and 8–9 in the oxidized plutonium fractions [3, 4]. These findings led us to believe that these ratios can not be explained by the speciation and mobility of plutonium and must be influenced by an independent source—the decay of ^{244}Cm ($T_{1/2} = 18.1$ y) into ^{240}Pu ($T_{1/2} = 6563$ y). The rapid transport of ^{244}Cm within the aquifer and subsequent decay to oxidized, non-colloidal ^{240}Pu through the electron stripping Szilard-Chalmers process was hypothesized to be the mechanism for far field occurrence of Pu and extreme ratios. The methods presented in this study are the first to produce size-fractionation data for ^{244}Cm present in SRS groundwater. The results provide evidence of far field migration of Cm and subsequent decay to ^{240}Pu which controls the systematic increase in ^{240}Pu/^{239}Pu ratios with distance from the source.

Experimental

Groundwater wells sampled in 1998 during a comprehensive site visit to SRS investigating colloid facilitated transport of Pu were re-visited in 2004 (Fig. 1). As shown

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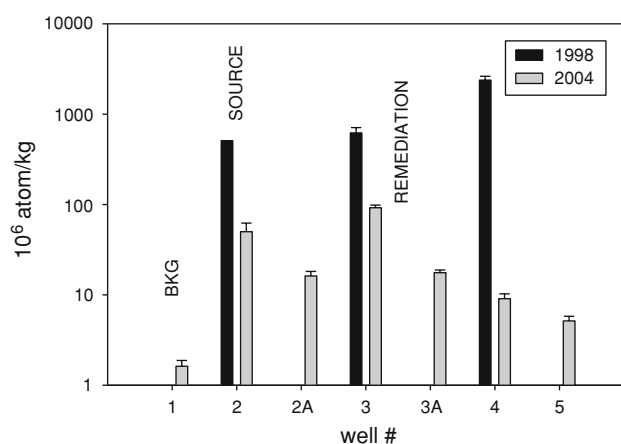Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA
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Fig. 1 Savannah River Site F-area transect of ^{244}Cm in filtered (<0.2 μm) ground water from 1998 (*black*) and 2004 (*gray*). Well 1 is a "background" located upstream of source well 2. Site of 2003 base injection remediation "Funnel and Gate" project is upstream of well 3A. Concentration units of 10^6 atom/kg are presented on a logarithmic scale

in Buesseler et al. (2009), well 1 is a "background" well located upstream of the seepage basins. Target wells formed a transect downstream of the seepage basins with the furthest at a distance of 700 m from the source. For the most part, the direction of flow of groundwater in the upper water table is due south to south-east from the seepage basins towards Fourmile Branch tributary of the Savannah River lying approximately 2,200 feet from the F-area seepage basins.

Using an all-Teflon bladder pump, groundwater was purged and sampled from the wells at a flow rate of ∼ 0.15 L/min through acid cleaned Teflon tubing and fed directly to the CFF system. In a brief review of cross-flow ultrafiltration methods described in Dai et al. (2002), a prefiltered (<0.2 μm) sample solution flows parallel to the CFF membrane. Hydrostatic pressure drives solutes with an effective molecular size less than the cut-off of the membrane, through the membrane (permeate, <1 kDa). The remaining solution (retentate, <0.2 μm–1 kDa) is swept along the membrane surface and recycled through the retentate reservoir. Compounds rejected by the membrane are thus increasingly concentrated in the retentate over time.

For this study two 1 kDa regenerated cellulose ultrafiltration membranes by Millipore (0.5 m^2 surface area, Pellicon-2) were stacked in the cassette holder (Millipore Pellicon) for a total surface area of 1.0 m^2. The characteristics of each CFF system must be demonstrated for every application of CFF in environmental sampling [3, 4, 6–9]. Retention characteristics (RC) for the CFF membrane were determined through calibrations using fluorescein marked 10 kDa and 3 kDa Dextran standards (Molecular Probes) a 1.3 kDa Vitamin B12 (SIGMA) and 0.5 kDa rhodamine (Molecular Probes). Using filtered fresh water from a clean pond and under standard operating conditions the retention coefficients were found to be >99%.

Size-fractionated samples from 1998 and 2004 site visits were acidified upon collection with ULTREX HNO$_3$ (J.T. Baker, USA) at 1 mL/L. An initial set of samples without a yield monitor added were prepared and measured by alpha-spectrometry to calculate Am and Cm isotope ratios originally present in the groundwater. No detectable amounts of ^{243}Am ($t_{1/2}$ = 7380 y) were present in any of the samples and this isotope was selected as a chemical yield monitor for this work. The preliminary analysis also helped to estimate the expected Cm activities and the amount of the yield monitor to be added to each sample to closely match the expected Cm activities. ^{243}Am tracer was used with an activity of 0.165 Bq mL^{-1} (9.89 dpm mL^{-1}) from which we added 1 mL/sample for 1998 and 0.1 mL/sample for 2004 sample aliquots of 150–500 mL. The samples were allowed to equilibrate for 12 h after tracer addition. After the equilibration all samples were pre-concentrated by evaporation to near dryness.

To prepare samples for extraction chromatography using TRU resin, precipitates were dissolved in 20 mL 1 M Al(NO$_3$)$_3$–3 M HNO$_3$. Since Fe(III) interferes with Am and Cm uptake on the TRU resin it has to be reduced to Fe(II) which was accomplished by adding 200 mg of ascorbic acid to each sample. Conversion of FeII to FeIII was determined by reacting a drop of the load solution with ammonium thiocyanate crystals. The absence of pink color visible upon addition meant that the conversion was complete and the sample was loaded on to the extraction chromatography TRU resin [10]. The column was washed with 10 mL of 3 M HNO$_3$ to rinse out the common ions present in the sample matrix. The resin was then converted to Cl$^-$ form by adding 2 mL of 9 M HCl and Am/Cm was eluted using 20 mL of 4 M HCl. Both HCl fractions containing Am/Cm were combined. The purified Am and Cm isotopes were co-precipitated with cerium fluoride and filtered onto a 0.1 μm filter. Dried filters were mounted on steel planchets using a glue stick and measured via alpha spectrometry.

Alpha counting was done on an ORTEC based system equipped with AMETEK detectors MN# BR-021-300-100 (Oak Ridge, TN) with efficiencies ranging from 18.9 to 20.9%. Signal processing through a Canberra MCA mixer/router MN#1520 used Canberra Genie 2000 acquisition software version V1.3 for spectrum analysis. Alpha counting of ^{244}Cm (5.805 MeV) and ^{241}Am (5.486 MeV) and ^{243}Am (5.277 MeV) was performed on both spiked and un-spiked samples over a period of 8 h to a few days. Recoveries determined from chemical yields ranged from 64 to 87%.

In some samples with very high ^{241}Am, a partial overlap of ^{241}Am and ^{243}Am peaks occurred and resulted in high ^{243}Am peak uncertainties. For these samples gamma spectrometry of ^{241}Am (59.537 keV) and ^{243}Am (74.670 keV) was used to evaluate ^{243}Am activities which was subsequently used to determine the chemical recovery. Filters were carefully removed from the steel planchets used in alpha counting and placed flat into polycarbonate counting vials with the cerium fluoride precipitate facing up. Gamma counting was performed using a Canberra High Purity Germanium (HPGe) well detector MN# GCW4023S. This is a closed-ended coaxial well with a diameter of 33 mm and a depth of 48 mm. To reduce background levels, the system incorporates cosmic ray anticoincidence shielding using a Bicron MN#BC408 guard consisting of 640 cm^2 plastic scintillation plates equipped with a Bicron PMT MN#PA14. Captured events were processed through a delayed coincidence box ORTEC MN# OB463 and spectrum were analyzed using Aptec MCA V6.31 software.

Results and discussion

Levels of ^{244}Cm measured in Savannah River Site F area groundwater from this study are compared with TIMS results in Table 1 [4]. Up stream of the basin, ^{244}Cm in control well #1 was at or below detection limits for both site visits. In well #2, nearest the basin, Cm levels were >500 × 10^6 atoms/kg in 1998. Significant downstream migration of more than 1,000 m from the seepage basin is evidenced by a factor of 5 increase in ^{244}Cm by well #4. While there were considerable decreases in overall activities between 1998 and 2004, measurable levels were still present in the furthest downstream wells. Base injection remediation processes downstream of well #3 were initiated prior to the 2004 site visit a result of which was a decrease in Cm concentrations of more than two orders of magnitude in well 4.

Agreement between calculated Cm from Dai et al. (2002) TIMS results and from this method are encouraging. Size-fractionation results show more than 90% of the ^{244}Cm was found in the dissolved or non-colloidal phase during both years despite large differences in concentration (Table 2). Good agreement is seen for the CFF mass balance from 1998 samples for wells 3 and 4 (100 ± 2–8%) and from 2004 well 3 (100 ± 5%). Successful mass balance of the size fractions indicates there is no significant loss to the system and that no contamination has been introduced 6. The fact that SRS groundwaters had pH values ranging from 3 to 4 at which Cm K_d values are low

Table 2 SRS F-area cross-flow filtration results from May 1998 and October, 2004. Presented are concentrations of ^{244}Cm (10^6 atoms/kg) found in filtered (<0.2 μm), colloidal (1 kDa to <0.2 μm to 1 kDa>) and permeate (<1 kDa) fractions and mass balance for the experiment

Well	FSB #	Filtered (<0.2 μm)	Permeate (<1 kDa)	Retentate (1 kDa to 0.2 μm)	Mass balance (%)
May 1998					
3	78	620 ± 102	629 ± 100	1 ± 1	102
4	79	2380 ± 390	2125 ± 350	66 ± 10	92
October 2004					
3	78	92 ± 14	84 ± 9	3 ± 3	95

Table 1 Concentrations of ^{244}Cm (10^6 atoms/kg) and ^{240}Pu/^{239}Pu ratios found in filtered (<0.2 μm) SRS F-area ground water. Well water samples were collected in May 1998 and October, 2004 and results from this study are compared to TIMS [4] and values calculated from in-growth calculations [3]. Pu isotopes were analyzed using a three-stage TIMS instrument at the Pacific Northwest National Laboratory ([3] and references therein). Ratios of ^{240}Pu/^{239}Pu have been in-growth/decay-corrected to the date of collection

Well	FSB #	pH	Alpha	TIMS	In-growth calculated	^{240}Pu/^{239}Pu
May 1998						
1	108D	6.80	bd	<3		0.055 ± 0.009
2	92D	4.03	508 ± 130	560 ± 30	470	0.27 ± 0.01
3	78	3.85	620 ± 90	1,520 ± 120	800	3.4 ± 0.4
4	79	4.11	2,380 ± 240	2,320 ± 170	2,750	13 ± 2
October 2004						
1	108D	5.6	1.6 ± 1			
2	92D	3.5	50 ± 12			0.138 ± 0.005
2A	119D	3.5	92 ± 6			0.924 ± 0.030
3	78	3.8	16 ± 2			0.052 ± 0.001
3A	117D	3.7	18 ± 2			0.640 ± 0.028
4	79	6.0	9 ± 5			6.119 ± 0.113
5	104D	5.5	5 ± 1			

explains the high dissolved fraction. Studies of SRS sediment and groundwater and the impact pH had on Cm behavior determined that K_d values increased from 40 mL g^{-1} at pH 4 to 15,000 mL g^{-1} at pH 6.7 (unpublished work by Kaplan, SRNL). Our results are in accordance with these findings and confirm high mobility of Cm in this environment.

Based on the observed ^{240}Pu/^{239}Pu ratios measured in wells downstream of SRS F-Area seepage basin which were 200 times greater than productions ratios, Dai et al. (2002) hypothesized that this was the result of rapid transport and subsequent decay of ^{244}Cm to ^{240}Pu. They calculated the amount of ^{244}Cm expected in these wells to produce the appropriate amount of ^{240}Pu. Size fractionated experiments found more than >90% of ^{244}Cm found in the permeate fraction (<1 kDa) in all wells during both site visits. Our results confirm earlier predictions as we found increases in ^{244}Cm downstream of the F area that correspond with increases in ^{240}Pu, especially in the oxidized forms, and can thus explain the elevated ^{240}Pu/^{239}Pu ratios.

Conclusions

The findings of this work are the combined results of careful field sampling protocols and CFF operations with proven analytical and extraction methods. This is the first study to examine changes in ^{244}Cm activity over time and to present size-fractionation of these isotopes within and downstream of the SRS seepage field. While detection of ^{244}Cm in SRS groundwater is not new, we have developed new methods in collection and quantification of Cm in ground water. The results show that ^{244}Cm moves readily through the aquifer compared with Pu and then decays to ^{240}Pu further downstream. The resulting oxidized, non-colloidal form of ^{240}Pu further enhances mobility downstream. Evidence of Cm as a source for ^{240}Pu is additionally confirmed by the elevated. ^{240}Pu/^{239}Pu ratios particularly in oxidized fractions.

These findings are one more piece of the fundamental scientific puzzle regarding the transport and/or transformation of transuranic waste found in subsurface environments. This study suggests that effective subsurface remediation at nuclear production facilities will need to consider the influences of progenitor radionuclides in groundwater reactive transport models.

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